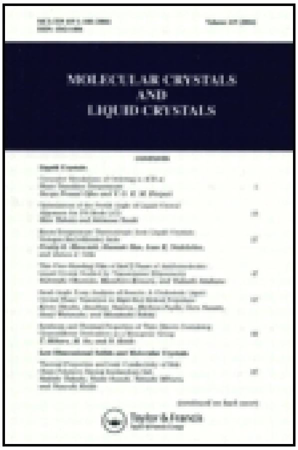

Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

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

Droplets Formation in UV Cured Polymer Dispersed Liquid Crystals

S. Di Bella [a] , L. Lucchetti [a] & F. Simoni [a]

[a] Dipartimento di Scienze dei Materiali and Istituto Nazionale per la Fisica della Materia (INFM), Università di Ancona, via Brecce Bianche, 60131, Ancona, Italy

Version of record first published: 24 Sep 2006

To cite this article: S. Di Bella, L. Lucchetti & F. Simoni (1998): Droplets Formation in UV Cured Polymer Dispersed Liquid Crystals, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 320:1, 139-148

To link to this article: http://dx.doi.org/10.1080/10587259808024390

Mol. Cryst. Liq. Cryst., Vol. 320, pp. 139–148
Reprints available directly from the publisher
Photocopying permitted by license only

DROPLETS FORMATION IN UV CURED POLYMER DISPERSED LIQUID CRYSTALS

S. Di Bella, L. Lucchetti and F. Simoni
Dipartimento di Scienze dei Materiali and Istituto Nazionale per la Fisica della Materia (INFM). Università di Ancona, via Brecce Bianche, 60131 Ancona, Italy.

Abstract

Film morphology and electro-optical behaviour of Polymer Dispersed Liquid Crystals (PDLC) made by the standard mixture NOA 65/E7 have been studied for different exposure times and intensities of UV curing light. Special attention has been devoted to the study of the effects of curing parameters on film morphology, which were analysed by means of scanning electron microscopy (SEM). UV intensity has been proved to play an important role in the phase separation process. It affects not only liquid crystal droplets size, but also the morphological uniformity of PDLC samples and the extent to which phase separation is complete. A simple interpretation based on the temperature dependence of the free energies involved in the curing process is proposed. As we expected electro-optical responses show to be strictly related to film morphology.

INTRODUCTION

In Polymer Dispersed Liquid Crystals (PDLC) nematic liquid crystals are dispersed as micro size droplets in a polymer matrix[1]. They can be switched from an opaque to a transparent state by means of application of an external electric field. In fact, in absence of an applied field the symmetry axis of the droplets (i.e. the droplet's director) is randomly oriented. In this case, the refractive index mismatch between droplets and polymeric matrix produces a strong light scattering and the sample looks opaque. When an electric field of sufficient intensity is applied, droplet directors are collectively aligned parallel to the field. When, as usual the value of the ordinary refractive index of the droplet is close to the one of the matrix this reorientation reduces the refractive index mismatch and the sample becomes transparent[2]. The switching field of a PDLC depends on a variety of factors among which film morphology plays a crucial role[3]. In particular, the threshold voltage for the transition to the transparent state is inversely related to liquid crystal droplets size[2]. Nevertheless, to date there has been little effort to find out the parameters which determine sample morphology and to relate them to the electro-optical behaviour.

In this paper we report a study performed on samples prepared by phase separation of the initial pre-polymer liquid crystal mixture. Phase separation is induced by polymerisation of the matrix under UV light curing. In this situation samples morphology should be mainly determined by UV intensity and curing time. As a matter of fact, our SEM investigation shows that not only droplet's size and distribution, but also film homogeneity is strongly affected by the curing parameters. Moreover, the relationship between droplets size and distribution and the resulting electro-optical properties of the samples has been analysed. These results are discussed in the frame of a model describing the phase separation process as nucleation and growth of the liquid crystal droplets from the polymeric matrix.

EXPERIMENTAL

PDLC samples have been prepared using 50% nematic liquid crystal (E7) and 50% UV curable Norland photopolymer (NOA 65). The E7 and pre-polymer mixture has been sandwiched between two ITO glass plates and 23μm mylar spacer has been used to control the film thickness.

In order to study the effects of the curing parameters on film morphology, three sets of samples have been prepared at different UV curing intensity: I_1=45.0 mW/cm^2; I_2=24.0 mW/cm^2; I_3=12.5 mW/cm^2 . For each set, the exposure time has been varied from 5 to 30 minutes with 5 minutes step.

Measurements of the electro-optical response have been performed on each sample. Transmission versus voltage and threshold voltage for the transition to the transparent state have been measured at a frequency of 10 Hz using a 633nm He-Ne laser. After passing through the sample, the transmitted light has been detected by a photodiode and measured with a digital oscilloscope.

The morphology of the same samples has been investigated by Scanning Electron Microscope (SEM). Analyses have been performed on both the sample surfaces and in cross section. After removing one of the two glasses, samples have been placed under vacuum for some hours. Then, they were coated by a thin film of gold (thickness about 10 nm) using a sputter coater. Samples cross sections have been obtained fracturing the samples in liquid nitrogen.

Sample temperature during the curing process has been measured as a function of the curing time, by means of a thermocouple. During the measurement, the thermocouple was kept in contact with the UV irradiated glass surface (i.e. the surface directly exposed to UV light). The same measurement performed directly on PDLC mixture has given the same temperature values within experimental errors.

RESULTS

Electro-optical properties

Figure 1 shows the transmittance vs. voltage curve for the second set of samples (I_2 = 24.0 mW/cm^2). The value of the threshold voltage for the transition to transparent state is defined as the voltage necessary to reach a transmittance correspondent to 50% of the saturation value. As can be observed, it decreases by increasing the curing time. The maximum transmittance values are quite high (80-90%) and seem to be not strongly affected by curing time. Similar results have been obtained for the other sets of samples.

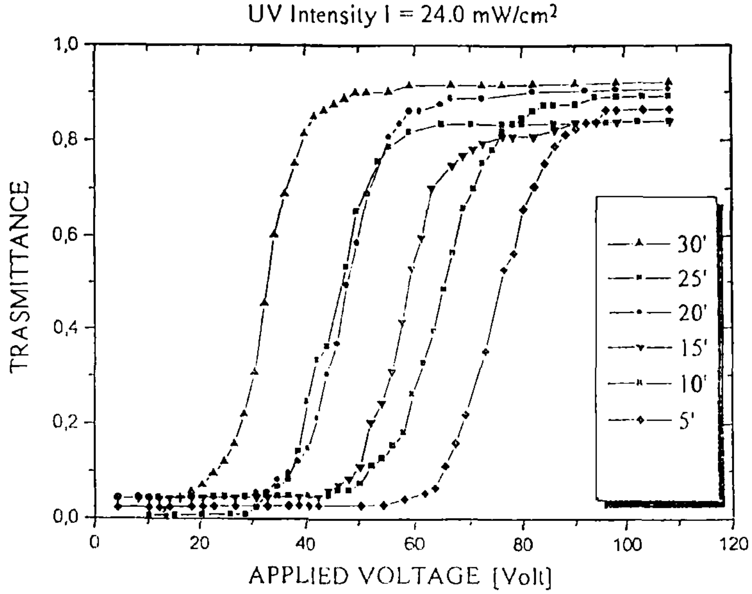

FIGURE 1 Transmittance vs. voltage curve for samples of the second set.

In figure 2 the electro-optical response is reported using the UV intensity as a parameter. Here the curing time has been fixed at 30 minutes and the transmittance vs. voltage curve has been reported for one sample of each set. As it is evident, threshold voltage decreases with UV intensity while maximum transmittance is only weakly affected by this parameter.

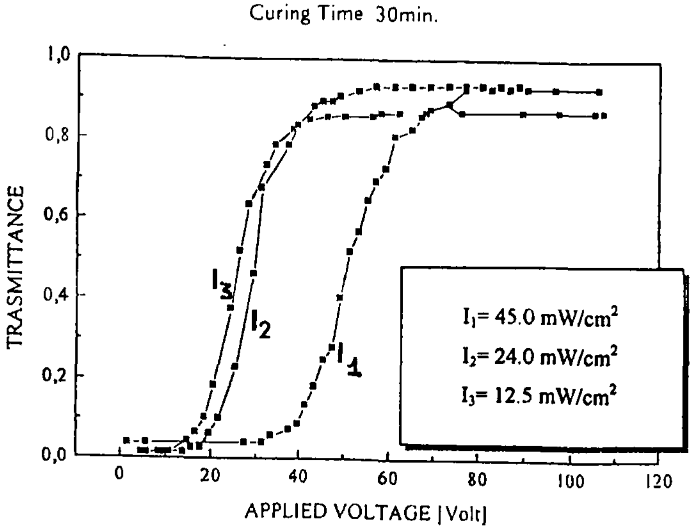

FIGURE 2 Transmittance vs. voltage curve for different UV intensities.

Film morphology

After electro-optical characterisation PDLC samples have been analysed by scanning electron microscopy. Figure 3 shows SEM micrographs of the upper surface and the cross section of three PDLC samples from the three different sets. The curing time has been fixed at 30 minutes for all of them. As can be seen from the micrograph, PDLC cured at I_1 (maximum intensity) presents not uniformly-dispersed and not well phase-separated droplets. Droplets mean dimensions range from 200 to 650 nm. A few droplet of about 1.5 μm can be observed along the volume (fig. 3 a.b). The morphology of sample cured at I_2 is reported in fig. 3 c,d. Liquid crystal droplets are observable along the whole volume, but appear to be interconnected suggesting that phase separation process is not yet complete. Droplet mean dimensions range from 500 nm up to 2μm. The sample cured at the lowest intensity I_3 (fig. 3 e,f) presents nearly spherical droplets, not interconnected and well distributed along the whole volume. The mean dimensions range from 750 nm up to 6μm. A gradient of droplet dimension is clearly visible in figure 3e. Droplets dimension increases passing from the upper (irradiated) surface to the lower one. The different morphological appearance of the two surfaces is a common feature of all the analysed samples. In particular, droplets mean dimensions are always smaller near the surface directly exposed to UV light than near the other surface. As an example, figure 4 shows the lower surface of the same sample in figures 3c and 3d. Droplets size is clearly larger than in figure 3d.

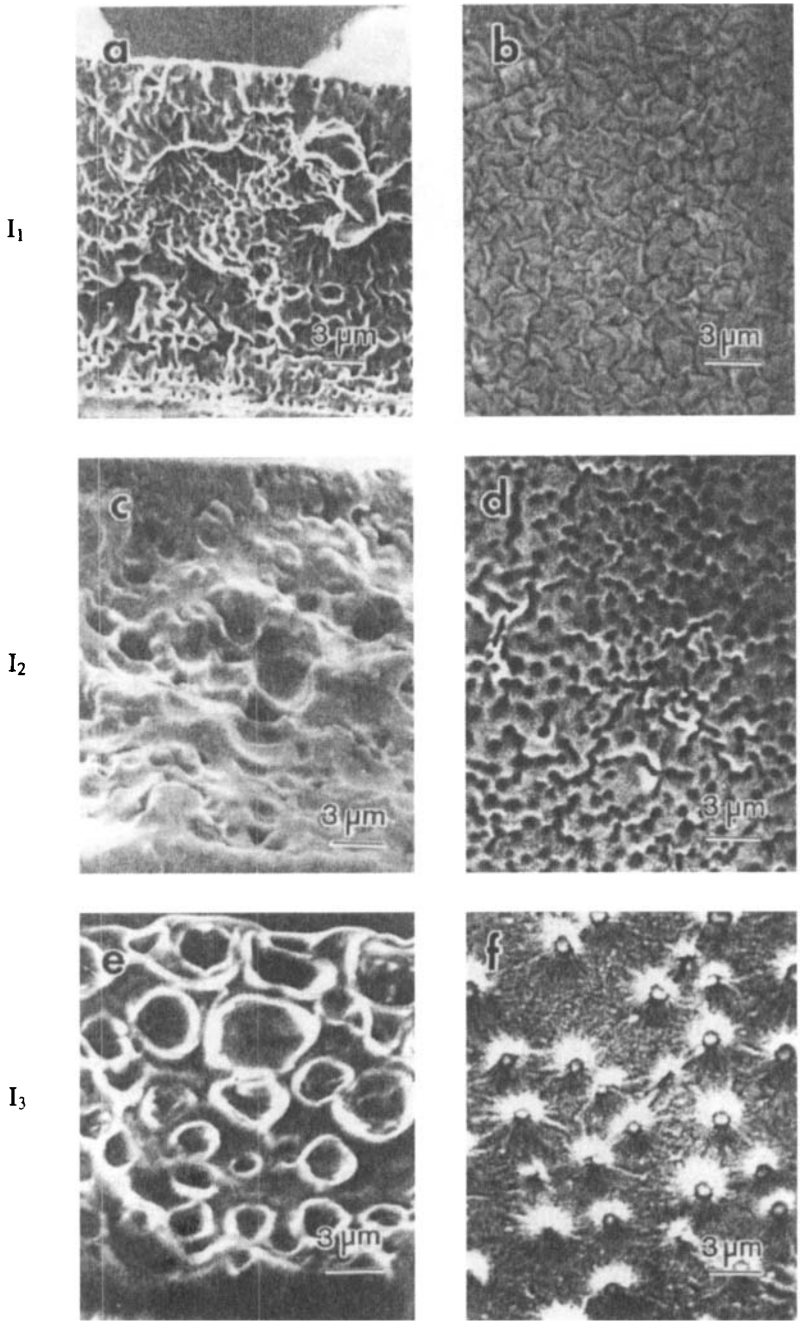

FIGURE 3 SEM micrographs of PDLC samples of the three different sets. a, c, e: cross sections and b, d, f,: upper surfaces.

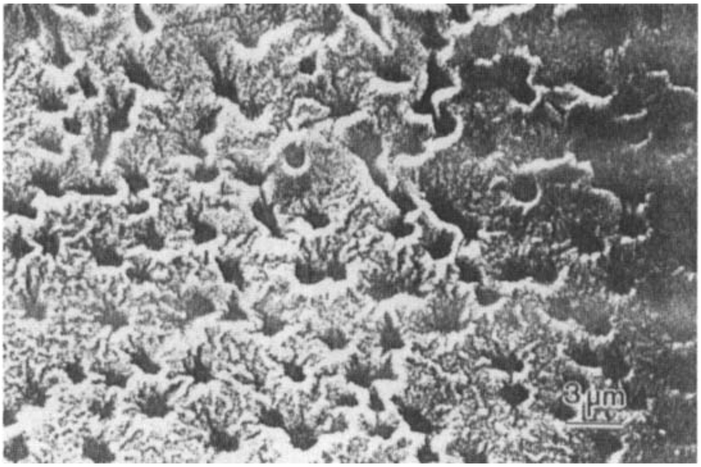

FIGURE 4 SEM micrograph showing the lower surface of the sample in figures 3c and 3d.

SEM analyses performed on many other PDLC samples reveal that liquid crystal droplets formation begins near the glass surfaces. A critical time for droplets formation in bulk has been found. The critical time depends on UV intensity and it is 20 minutes for the first and the second sets of samples (I_1=45.0 mW/cm^2; I_2=24.0 mW/cm^2) and 10 minutes for the third set (I_3=12.5 mW/cm^2).

The main results of morphological characterisation can be summarised as follows:

1. Liquid crystal droplets mean dimension increases by increasing curing time and by lowering UV intensity;
2. Liquid crystal droplets appear uniformly dispersed and well phase-separated from polymer matrix only in samples cured at the lowest intensity;
3. Liquid crystal droplets result always smaller near the irradiated surface than near the other one;
4. Liquid crystal droplet formation begins near the two glasses surfaces. In particular, a UV intensity dependent critical time for droplets formation in bulk has been found.

Measurements of the temperature reached by PDLC samples during the curing process are reported in figure 5 for the three sets of samples as a function of the curing time. As can be seen from the graph, temperature rise is faster and maximum temperature value is higher for samples cured at the maximum intensity.

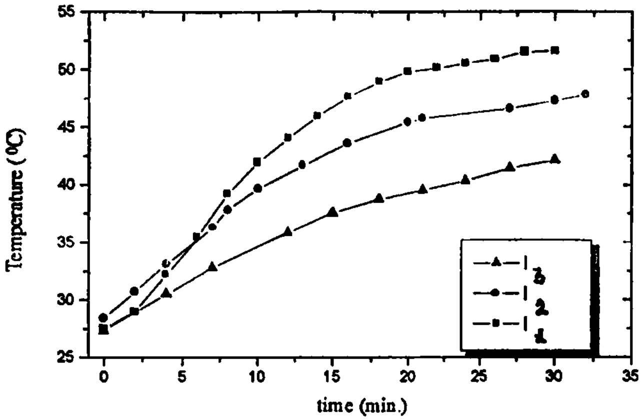

FIGURE 5 PDLC temperature vs. curing time for the three different UV intensities.

DISCUSSION

Transmittance vs. voltage measurements clearly show the close relationship between PDLC electro-optical response and morphology. In particular the threshold voltage is strictly connected to liquid crystal droplets dimension. The comparison between electro-optic and SEM characterisation shows that the threshold voltage lowering is always linked to the increase of droplets dimension, as it is already known from literature [3].

It is well known that liquid crystal droplets size in PDLC is determined by the rate of droplets formation[6], i.e. by the polymerisation rate of the polymer matrix. In PDLC formed by a UV curable polymer the matrix cure rate is determined by UV intensity [7,8]. In particular, an increase of UV intensity produces shorter cure times leading to a decrease of droplets size, in agreement with our results.

As we observed, UV intensity also greatly influences cure kinetics and the extent to which the cross-linking reaction is complete (i.e. the degree of cure).

Liquid crystal droplets are uniformly dispersed only in samples cured at the lowest intensity. This fact together with results reported in fig.3 suggests that morphological uniformity of PDLC samples increases by lowering UV intensity. Moreover, phase separation appears to be complete only in samples cured at the lowest intensity. Liquid crystal droplet formation is a result of the phase separation process due to polymerisation of the matrix. In this respect, the whole process can be regarded as strictly linked to the liquid-solid phase transition of the matrix and droplets formation can be treated as the nucleation of a solid from a liquid phase. As a matter of fact, liquid crystal itself does not undergo any phase transformation, nevertheless we could image that droplets nucleate from the liquid crystal-polymer mixture which is in the liquid phase at the beginning of the process. The two main steps of phase transformation are nucleation and growth[9]. For nucleation to occur the free energy Δg^* must be furnished to the system. Δg^* is the activation energy and increases with temperature. The free energy Δg_D, i.e. the activation energy for diffusion, is associated to the second step. Δg_D increases by lowering temperature. The rate of formation of the new phase measured in nuclei per second, can be expressed as :

$$\frac{dN}{dt} \propto e^{\frac{(\Delta g^*+\Delta g_D)}{KT}}$$

where N can be regarded as the number of formed liquid crystal droplets. By increasing temperature Δg_D decreases and droplets formation rate increases until Δg_D becomes comparable to Δg^*, which on the other hand is increasing with temperature. After that, the activation energy for nucleation drives the process and dN/dt decreases. This model can explain the lowering of morphological uniformity of PDLC films connected to the increase of UV intensity. Temperature measurements reported in fig.5 show that temperature increases with UV intensity and, more important, that temperature rise becomes steeper. Our data can be qualitatively explained assuming that at low intensity the correspondent temperature makes Δg^* lower than Δg_D so that nucleation rate is higher than growth rate. In this situation, diffusion is quenched and the system keeps the degree of uniformity present before the curing process. On the contrary, if UV intensity increses temperature increases as well and Δg^* becomes higher than Δg_D. Now the growth rate is higher than nucleation rate and diffusion prevails on nucleation. Under these conditions, liquid crystal droplets result not uniformly dispersed in polymer matrix. The viscosity of PDLC increases as the polymerisation goes on, so that morphological disuniformity remains freezed. If the curing process is stopped before the end of phase separation, diffusion can occur because of the low viscosity and the droplets distribution tends to become uniform. This last consideration would explain why the sample of the first set cured for 5 minutes appears almost uniform after three days from the curing process. Actually, it is well known that photo-cured polymers show substantial "post cure" effects and that polymerisation continues even after the end of the curing process.

As can be deduced from results reported in fig.3, liquid crystal droplets appear well phase-separated from polymer matrix only in samples of the third set. This suggests that the extent to which the cross-linking reaction is complete depends on UV intensity being higher for lower intensity. This situation can be easily accounted for referring to the increase of PDLC temperature connected to the increase of UV intensity. Samples temperature affects liquid crystal solubility in the matrix. If temperature is too high a large amount of liquid crystal remains dissolved in the matrix thus slowing down the curing process.

SEM characterisation shows that liquid crystal droplets begin to nucleate near the glass surfaces indicating that in these regions the free energy required for phase separation is lower than in bulk. This is a typical feature of the nucleation of a solid from liquid phase[9].

The observed critical time for droplets formation in PDLC bulk can also be discussed considering that the degree of cure is higher at lower UV intensity. As reported in last section, the critical time decreases by lowering UV intensity, i.e. droplets nucleation in bulk begins earlier in PDLC of the third set than in PDLC of the first and second sets indicating that, for the same the curing time, the extent to which phase separation is complete is higher for lower intensity.

In figure 3e a gradient of droplets dimensions is evident from one glass surface to the other. This is a common feature of all the analysed samples: droplets dimensions are always smaller near the irradiated surface than near the other one. This result can be easily explained taking into account the absorption of UV light by the mixture. The E7 absorption spectrum reported in figure 6 clearly shows that the liquid crystal itself contributes to strong UV absorption. In this way an intensity gradient is established along the sample thickness which in turn gives rise to a gradient of droplets dimension.

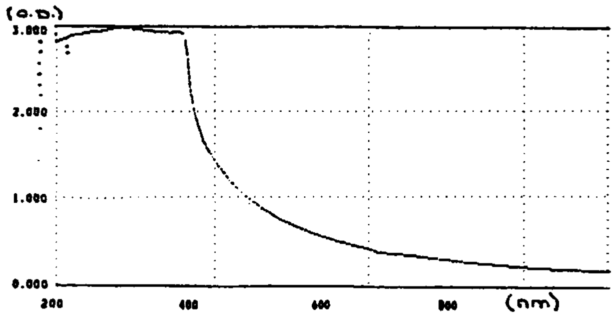

FIGURE 6 Absorption spectrum of E7

CONCLUSION

A detailed investigation of the droplets formation has been performed in UV cured PDLC. Both SEM and electro-optical measurements have been carried out. As already known, PDLC with liquid crystal droplets of submicron dimensions can be easily obtained by a proper choice of curing parameters, i.e. using high UV intensity and low curing times. However, our results show that low curing time and high UV intensity lead to PDLC with droplets which are not well phase-separated from polymer matrix and not uniformly dispersed.

An interpretation based on the temperature dependence of the droplets formation process, has been proposed.

Acknowledgments

This work has been supported by European Community through the european fund of regional development, under the frame of Progetto Sud - INFM subproject FESR-UME.

REFERENCES

[1] J.W. Doane, N.A. Vaz, B.G. Wu, S. Zumer, *Appl. Phys. Lett.* **48**, 269 (1986).

[2] F. Simoni, *Non linear Optical Properties of Liquid Crystals and Polymer Dispersed Liquid Crystals,* World Scientific, Singapore (1997).

[3] H. Liu, H. Ding, J.R. Kelly, *Mol. Cryst. Liq. Cryst.* **26,** 99 (1995).

[4] N.A. Vaz, G.W. Smith, G.P. Montgom ery, *Mol. Cryst. Liq. Cryst.* **146,** 17 (1987).

[5] N.A. Vaz, G.W. Smith, G.P. Montgomery, *Mol. Cryst. Liq. Cryst.* **146,** 1 (1987).

[6] G.W. Smith, *Mol. Cryst. Liq. Cryst* **196,** 89 (1991).

[7] G.R. Tryson, A.R. Shultz, *J. Polymer Science* **17,** 2059 (1979).

[8] G. Oster, N. Yang, *Chem. Revs.* **68,**125 (1968).

[9] J.H. Brophy, R.M. Rose, J. Wulff, *Struttura e proprietà dei materiali,* edited by Casa Editrice Ambrosiana (Milano, 1975).