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Analysis of the Phase Separation Process in UV Cured Polymer Dispersed Liquid Crystals for Optical Applications

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We have examined the morphology of UV cured PDLCs made by the standard mixture NOA65/E7, for different liquid crystal content, UV dose and intensity and exposure time. The distribution function for the liquid crystal droplets size has been determined in order to provide much understanding in the UV light-induced phase separation process.

Keywords: PDLC; Phase separation; Particle Size Distribution

INTRODUCTION

Polymer Dispersed Liquid Crystals (PDLCs) films are very useful in electro-optic applications because they can be switched electrically between opaque and transparent state. They are composite materials in which nematic liquid crystals are dispersed, generally in form of micro size droplets, in a polymer matrix[1]. The used liquid crystals have a positive dielectric anisotropy and therefore align with their director parallel to an external electric field. Thus the film, which is normally scattering because of the random orientation of n_0 in the absence of an electric field, becomes transparent when such a field is applied. The switching field of a PDLC depends on a variety of factors among which film morphology plays a crucial role[2,3]. This is determined primarily by composition, cure rate and extent (which in turn are functions of UV intensity and temperature) and by the mutual solubility of liquid crystal and pre-polymer. It is thus obvious that PDLCs are very complex systems that require precise morphological and processing control.

As it is well known, the scattering properties of a PDLC in the opaque state represent another aspect connected to the film morphology[4]. In particular, the geometric cross section of the liquid crystal droplets depends on the volume fraction of the liquid crystal in the matrix and on the average droplet radius. Moreover, all the theories about light scattering from PDLCs

assume a very narrow distribution of droplet size and shape. For all these reasons, a detailed analysis of PDLCs morphology as a function of the curing parameters together with a deeper understanding of the process of liquid crystal droplets formation, can be very important in the frame of the optical application of PDLCs.

In this work, we report a morphological study of UV cured PDLCs in order to figure out the role of the liquid crystal content, UV dose and intensity and exposure time. Moreover, the distribution function for the liquid crystal droplet size has been determined to get a deeper understanding about the UV light-induced phase separation process and thus about liquid crystal droplets formation.

EXPERIMENTAL

PDLC samples have been prepared by UV curing the standard mixture NOA65/E7 .

Several samples have been prepared by varying the liquid crystal weight concentration, the UV intensity and the exposure time. The experimental conditions are summarised in the following scheme:

- E7 weight concentration (C): 20%, 30%, 40%, 50%
- UV intensity (I): 12.5 mW/cm^2
- Exposure time (t): 30 minutes

For samples with C = 50%, both UV intensity and exposure time have been varied among the following values:

- UV intensity (I): 12.5 mW/cm^2, 24.0 mW/cm^2, 45.0 mW/cm^2
- Exposure time (t): 5 minutes-30 minutes with 5 minutes step

PDLCs were prepared by room temperature irradiation of the predetermined mixture using a 100 W UV lamp, which provides UV radiation with a peak at 365 nm. The blended samples have been sandwiched between conductive glass substrates and confined to 23 μm using mylar spacers.

Samples morphology was characterised by optical microscopy and scanning electron microscopy (SEM) investigations.

RESULTS AND DISCUSSION

The typical PDLC morphology consists of liquid crystal-rich droplets distributed within a polymer-rich matrix and, since the droplet size is comparable with the visible wavelength, PDLC samples usually show a scattering appearance. However when the liquid crystal weight concentration is small (i.e. C = 20% and C = 30% in our case), we observe a radically different morphology in which very large liquid crystals spherical domains (up to 1 mm diameter) are dispersed in a birefringent matrix (fig. 1a and 1b). These kind of samples appear transparent even after 30 minutes of UV

exposure. The observed morphology, which resembles the spherulitic one, is generally attributed to PDLCs cured at high temperature or containing less than 25% liquid crystal[5]. Our observation of the spherulitic-like morphology in samples cured at room temperature and for values of C up to 30%, points out that the final film morphology is strongly affected not only by liquid crystal concentration and curing temperature but also by all the other curing parameters.

As can be seen in fig. 2 by increasing C the typical droplet dispersion is obtained. For these samples the liquid crystal droplet size has been measured directly from the SEM micrographs using an image-analysing system.

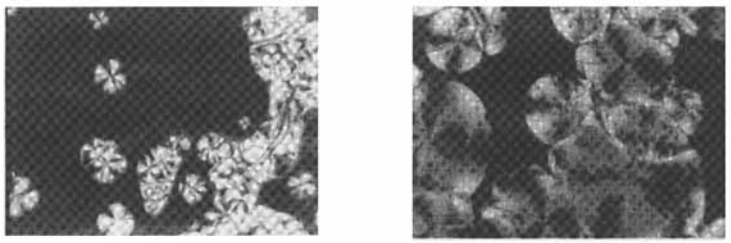


FIGURE 1 Polarising optical microscope view of two PDLCs samples. C is 20% in (a) and 30% in (b)

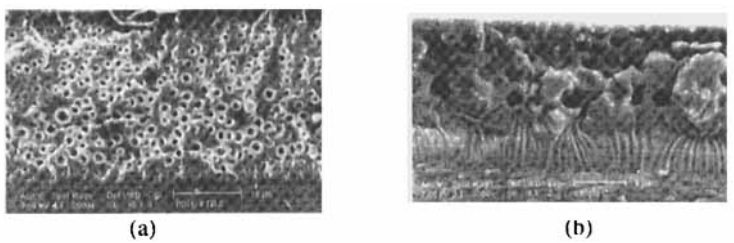


FIGURE 2 SEM micrographs of samples with C = 40% (a) and C = 50% (b).

The Particle Size Distribution (PSD) was built up by taking a number of micrographs and collecting all the measurements. The PSDs of the two

samples in fig. 2 are shown in fig. 3. It is worth noting that the reported histograms represent the area of the droplets cross sections and not of the droplets themselves, for this reason we will call them "planar histograms".

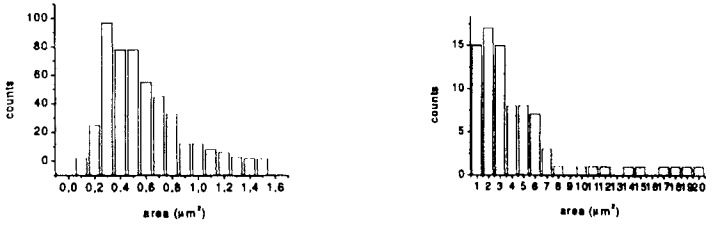
True histograms, representing the distribution of the droplets diameters in the bulk of the sample can be determined from the planar ones. A more detailed analysis of the droplets size distribution including the determination of true histograms will be published elsewhere. In the present paper we will assume that the shape of the PSD can be considered well represented by the planar histograms reported in fig. 3 and we will use these data for a better understanding of the phase separation process in UV cured PDLCs.

In order to analyse the process of droplet formation, we looked for the best fit to the experimental data. We found that all the PSDs can be satisfactory fitted by a lognormal distribution function characterised by a mean value x_c and a distribution width w:

$$p(x) = A \exp\left[- \ln^2 \left(\frac{x}{x_c}\right) / 2w^2 \right]$$

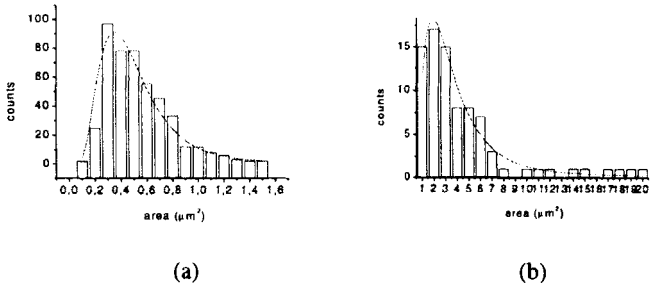
where A is a normalisation factor.

This kind of distribution is skewed and represents naturally occurred populations better than the usual normal distribution, which is symmetrical. Figure 4 shows the two PSDs of fig.3 fitted with the lognormal distribution function.



(a) (b)

FIGURE 3 Planar histograms representing the droplet area distributions for samples reported in fig. 2. C = 40% in (a) and 50% in (b).



(a) (b)

FIGURE 4 Fit of the planar histograms reported in fig. 3.

The lognormal distribution function is usually exploited to describe the distribution of particle precipitates in Al-alloys[6,7,8], in which the formation of precipitates follows the Oswalt ripening coarsening process[9]. The coarsening process describes the change in the average particle size with increasing time while the number of dispersed particles decreases in order to keep constant the volume fraction. Observations show that during the coarsening process the larger particles grow at the expense of the smaller ones and the PSD follows some kind of pattern regardless its initial shape. The driving force for the coarsening process is the reduction in the interfacial free energy associated with the decrease in surface area of the particles during growth.

The obtained results for the PSDs of our PDLCs suggest that the formation of liquid crystal droplets can occur following a similar process. In order to analyse this point, three sets of samples with C = 50% have been prepared by varying the curing intensity, using the values 12.5 mW/cm^2, 24.0 mW/cm^2 and 45.0 mW/cm^2 and by varying the exposure time from 5 to 30 minutes, for each set. For each sample the PSD has been built up and the histograms have been fitted by means of a lognormal distribution function. Moreover, the UV dose, which represents the energy density totally received by the sample during the curing process, and the droplet density have been measured. The average radius R has also been derived from the average area in the hypothesis of spherical droplets. The experimental data obtained are reported in the following tables:

$I = 12.5\ mW/cm^2$

Exposure time (min)	UV dose (J/cm^2)	x_c (μm^2)	w (μm^2)	R (μm)	Density (droplets/μm^2)
5	3.7	-	-	-	-
10	7.5	0.5	0.3	0.40±0.08	0.32
15	11.2	1.2	0.4	0.62±0,02	0.29
20	15.0	1.5	0.7	0.69±0.03	0.27
25	18.7	1.9	0.7	0.78±0.03	0.23
30	22.5	1.9	0.7	0.78±0.03	0.23

$I = 24.0\ mW/cm^2$

Exposure time (min)	UV dose (J/cm^2)	x_c (μm^2)	w (μm^2)	R (μm)	Density (droplets/μm^2)
5	7.2	-	-	-	-
10	14.4	-	-	-	-
15	21.6	-	-	-	-
20	28.8	0.3	0.5	0.31±0.06	0.33
25	36.0	0.45	0.6	0.38±0.05	0.3
30	43.2	0.5	0.6	0.40±0.05	0.3

$I = 45.0\ mW/cm^2$

Exposure time (min)	UV dose (J/cm^2)	x_c (μm^2)	w (μm^2)	R (μm)	Density (droplets/μm^2)
5	13.5	-	-	-	-
10	27.0	-	-	-	-
15	40.5	-	-	-	-
20	54.0	0.15	0.35	0.22±0.06	0.55
25	67.5	0.15	0.39	0.22±0.05	0.55
30	81.0	0.17	0.39	0.23±0.05	0.55

Errors on R have been derived from the mean standard deviation ($w/N^{1/2}$) of the distribution.

It is important to note that the lackage of data corresponds to the observed critical time for the formation of liquid crystal droplets in some of the investigated samples[3].

By analysing the three tables, it is possible to obtain some important information about the process of droplet formation. First of all, the UV dose does not seem to play an important role in determining the final PDLC morphology, which is on the contrary strongly affected by the curing intensity. In fact comparable UV dose values lead to different droplet size and, in some case, to completely different morphologies (see for instance the second sample of the first set and the first sample of the second set). UV intensity is thus the important parameter in the formation of PDLCs, since it directly affects the speed of polymerisation and the consequent increasing of viscosity.

Looking at each single table it is possible to note that, once fixed the curing intensity, liquid crystal droplets dimension increases with time while droplets density tends to decrease. This trend, which is in agreement with the Ostwald ripening kinetic, is less evident when the curing intensity increases. Moreover, for each value of the exposure time, droplets density increases with UV intensity and the average dimension decreases. This behaviour is probably due to the increase of viscosity connected to the polymerisation of the matrix, which is faster at higher intensity. In this case, all the diffusion-driven effects, such as the growth of larger droplets at the expense of the smaller ones, should tend to be quenched and thus less evident. Following these ideas, liquid crystal droplets formation in UV cured PDLCs can be interpreted as a coarsening process keeping in mind that the interpretation works well if the UV intensity is low enough to avoid a too fast increase of viscosity. At this regard, it is worth noting that the fit of the PSDs of samples of the second and third sets is not as good as in the low intensity case. Anyway, the increase of viscosity with time, is an additional parameter which is not present in the Al-alloys case for which the coarsening model is usually exploited.

CONCLUSIONS

We have presented some result that can provide a deeper understanding about the phase separation process in UV cured PDLCs. Our results point out that UV intensity instead of UV dose has to be regarded as one of the crucial parameters in determining the final sample morphology. Moreover, we have found that the droplet size distribution is fairly well described by a lognormal distribution function, which indicate that the formation of liquid crystal droplets can be interpreted as a coarsening process. Further work is in progress in order to get much deeper insight on the similarity between the Ostwald ripening kinetic and the formation of PDLCs.

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