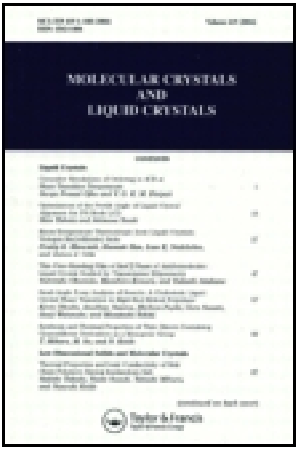

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# Polymer Dispersed Liquid Crystals for Large Area Switchable Windows: Effect of Liquid Crystal Loading

Fiore Pasquale Nicoletta [a] , Martino Caporusso [b] , Hassan-Ali Hakemi [b] & Giuseppe Chidichimo [a]

[a] Dipartimento di Chimica, Università degli Studi della Calabria, 87036, Rende, ITALY

[b] Snia-Ricerche, Via Pomarico 14, 75010 Pisticci Scalo, ITALY

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# Polymer Dispersed Liquid Crystals for Large Area Switchable Windows: Effect of Liquid Crystal Loading

FIORE PASQUALE NICOLETTA[a], MARTINO CAPORUSSO[b], HASSAN-ALI HAKEMI[b] and GIUSEPPE CHIDICHIMO[a]

[a]*Dipartimento di Chimica, Università degli Studi della Calabria, 87036 Rende, ITALY and* [b]*Snia-Ricerche, Via Pomarico 14, 75010 Pisticci Scalo, ITALY*

Polymer dispersed liquid crystals are composite materials which have been proposed in the last years as large area electrically switchable windows. Their electro-optical performance is strictly related to the morphology of liquid crystal droplets. We have investigated the morphological and electro-optical properties of droplets of nematic liquid crystals dispersed in NOA65 polymer matrix. We found that droplets size and dispersion become larger and larger as the liquid crystal loading is increased. At higher concentrations of liquid crystal two different distribution of droplet size are recognised. Switching fields and haze in the ON state show a minimum value when the liquid polymer/crystal weight ratio is around 55:45 for which the best performance is achieved.

*Keywords:* PDLC; phase separation; liquid crystals; polymer films

## INTRODUCTION

Polymer Dispersed Liquid Crystals (PDLC) appear to be extremely promising materials for their use as large area display, light valves and switchable windows[1-3], also because of their simple preparation procedures. PDLCs are composite materials consisting of liquid crystal microdomains dispersed within a polymer matrix and can be switched from a translucent state (OFF state) to a transparent state (ON state) by application of an electric field. Their performance is strictly related to the properties of constituent materials and the method of preparation (micro-encapsulation or phase separation) which determine the film morphological properties such as droplet size, number density and polydispersity. Consequently switching fields, contrast ratio, response time, haze, adhesion of a PDLC can be quite different as a function of liquid crystal loading in the mixture which will form the films. Generally PDLCs with an ON transmittance of 80%, an OFF transmittance less than 2% and a normal haze less than 5% (high transparency over wide angles) are considered good industrial standards for a reasonably small collection angle like 2.5°.

In the last years many efforts have been devoted towards the aim of linking PDLC performance and preparation procedure but a complete understanding has not still achieved[4-6]. In this paper we intend to give a contribution in order to understand the role played by liquid crystal content in the performance of a set of UV-cured PDLC prepared with a well known photomer and commercially available liquid crystals. Several electro-optical properties have been determined and related to film morphology according to some theoretical models present in literature. We found that a size monodispersed PDLC with a good performance can be achieved in well defined range of liquid crystal-polymer weight ratio.

## EXPERIMENTAL METHODS

PDLC films were prepared by mixing the appropriate amounts in weight of NOA65 prepolymer (Norland) and TN0403 or TN0623 liquid crystal (Rolic). The liquid crystal concentration was varied between 0 and 80 weight %. NOA65 has a refractive index value of 1.504 in the prepolymer state and 1.524 after polymerisation. Some physical properties of the used liquid crystals are reported in Table I.

The resulting homogeneous solutions were placed between two indium tin oxide conducting substrates and thickness was controlled at 15 μm by glass spheres.

Table I. Some physical properties of the liquid crystals: nematic-isotropic temperature, $T_{NI}$, parallel dielectric susceptibility, $\varepsilon_{||}$, dielectric anisotropy $\Delta\varepsilon$, ordinary refractive index, $n_o$, birifringence, $\Delta n$, and viscosity, $\eta$.

| L.C. | $T_{NI}$/°C | $\varepsilon_{\|\|}$ | $\Delta\varepsilon$ | $n_O$ | $\Delta n$ | $\eta$/mPa s@25°C |
|---|---|---|---|---|---|---|
| TN0403 | 82 | 24.8 | 19.2 | 1.524 | 0.258 | 66 |
| TN0623 | 102 | 22.4 | 17.2 | 1.507 | 0.198 | 66 |

Samples were kept at a constant temperature (50 °C for TN0403, 80 °C for TN0623) for ten minutes and, finally, exposed to 20 mW/cm$^2$ UV source (total energy supplied 2 J/cm$^2$). The haze of PDLC films was measured with a Macam LSO-4514 haze meter instrument (a square wave electric signal with $\nu$=50 Hz and V=100 V was applied) and calculated according to the relation:

$$\text{Haze}(\%) = 100 * \frac{I_s}{I_s + I_r}$$

where $I_S$ and $I_r$ are the intensities of light transmitted, respectively, outside and inside a collection angle equal to 2.5°.

The opacity of films was determined with a customised photometer by measuring the field off transmittance at the collection angles less than 2.5° from the axis of incident light and according to the following relation:

$$\text{Transmittance}(\%) = 100 * \frac{I_r}{I_i}$$

where $I_i$ is the intensity of incident light measured with empty substrates.

SEM analysis was performed on cross sections of PDLC films, cutted after immersion in liquid nitrogen, left under vacuum for several hours at a pressure of $10^{-6}$ atm in order to remove liquid crystal from droplets, gold coated and, finally, examined in a Jeol JSM 6300 scanning electron microscope. The average diameter, D, the number density, β, and the areal fraction (i.e. the percentage of liquid crystal coverage on SEM image), $\alpha=\frac{\pi}{4}D^2\beta$, were determined from the SEM images.

## RESULTS

### SEM analysis

Figure 1 reports the SEM microphotographs of some examined PDLC samples for different values of liquid crystal concentration.

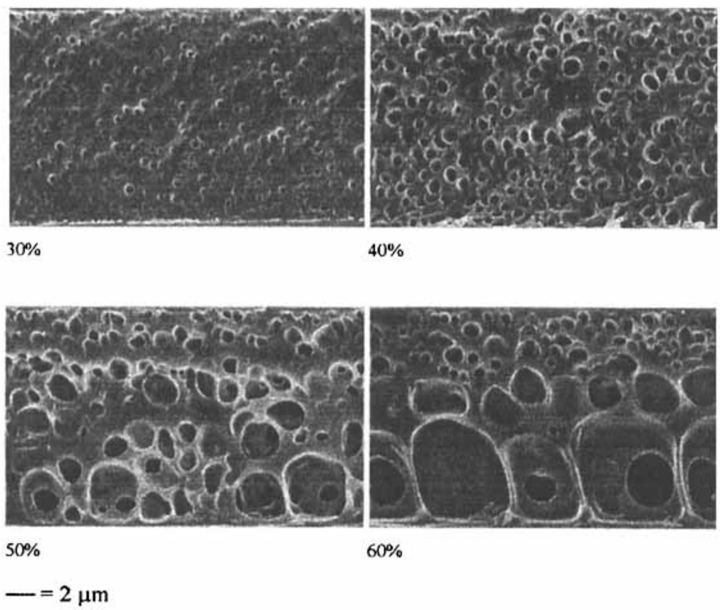


FIGURE 1. SEM microphotographs of PDLC films for different liquid crystal content (system NOA65+TN0403).

It is evident from figure 2 that the number density shows a maximum value at about 40 weight % of liquid crystal while the average droplet size increases with liquid crystal content. At liquid crystal concentration greater than 50 weight % a polydispersity is observed due, probably, to the absorption of the liquid crystal at the cure wavelenghts which causes different cure intensities along the film thickness. In fact smaller droplets are present on the upper part of samples which is directly exposed to UV radiation, larger ones are on the opposite side where a lower UV dose is supplied (see figure 1). The areal fraction is almost linear with liquid crystal loading (figure 3). It is evident that morphology properties are quite similar for both liquid crystal used.

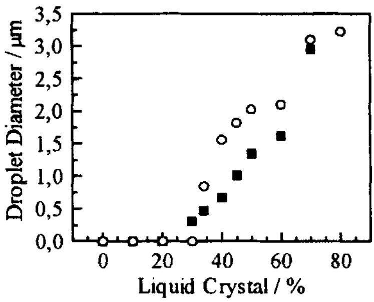


FIGURE 2 Average droplet diameter as a function of liquid crystal loading: NOA65+TN0403 (full square), NOA65+TN0623 (open circle).

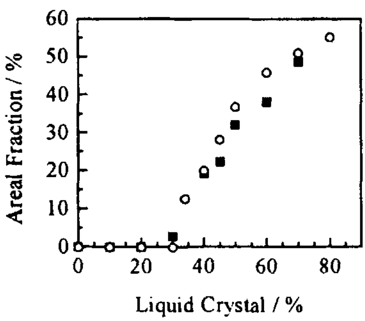


FIGURE 3 Areal fraction as a function of liquid crystal loading: NOA65+TN0403 (full square), NOA65+TN0623 (open circle).

The average droplet diameter and areal fraction graphics allow one to determine the solubility limits of TN0403 and TN0623 in NOA65 polymer matrix. Such values are around, respectively, 25 weight % for TN0403 and 30 weight % for TN0623 and are in the range of solubility limits determined with several different techniques by Smith and Vaz[7].

**Electro-optical measurements**

As both series of samples do not show any important morphology difference we expect that they will behave in a similar way from the electro-optical point of view. Experiments confirmed such previsions. Therefore, we will restrict our analysis to NOA65+TN0403 system and outline the differences of NOA65+TN0623 system, if they exist. In figures 4 and 5 we report the ON and OFF state transmittances and the switching electric fields to reach 10% and 90% of the maximum value of transmittance, respectively. Acceptable values of opacity are achieved for liquid crystal contents higher than 40 weight. ON transmittances in NOA65+TN0623 are some per cent lower. 90% switching field, $E_{90\%}$, shows lower values in the range 40-60 weight % of liquid crystal. 10% switching field, $E_{10\%}$, presents a monotonic decrease.

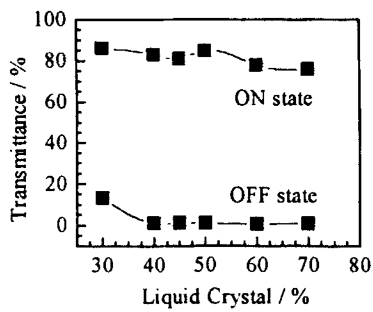


FIGURE 4 ON and OFF state transmittances of NOA65+TN0403.

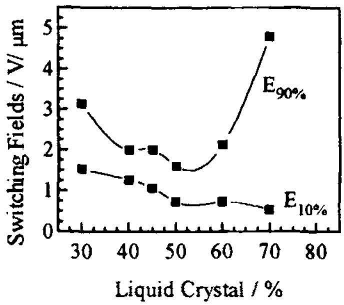


FIGURE 5 10% and 90% switching fields of NOA65+TN0403.

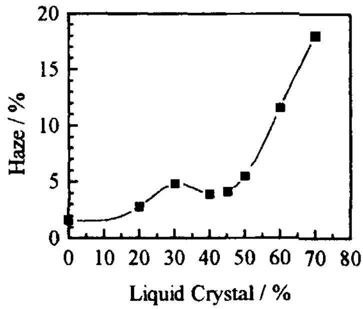


FIGURE 6 Normal haze of NOA65+TN0403.

Figure 6 shows that the haze in NOA65+TN0403 films is larger than 5% at liquid crystal loading higher than 50 weight %. NOA65+TN0623 samples present always haze values larger than 6 %.

## DISCUSSION

The relationships between morphology and electro-optical properties are theoretically expressed by the following equations[8,9]:

$$\mathrm{Transmittance}(\%) = 100 * e^{-\beta\sigma d}$$

$$E_{switching} = \frac{A}{D}\frac{2\varepsilon_{pol} + \varepsilon_{lc}}{3\varepsilon_{pol}}\sqrt{\frac{K}{\varepsilon_o \Delta\varepsilon}}$$

$$\sigma = 2\sigma_0\left(\frac{\pi D}{\lambda}\right)^2\left[\frac{n(\vartheta)}{n_{pol}} - 1\right]^2$$

where $\sigma$ is the scattering cross section, d is the sample thickness and K is the liquid crystal elastic constant in the one constant approximation. $\varepsilon_{pol}$ and $\varepsilon_0$ are, respectively, the dielectric susceptibilities of polymer matrix and vacuum; $\varepsilon_{lc}$ and $\Delta\varepsilon$ are the average dielectric susceptibility and dielectric anisotropy of liquid crystal. A is a geometrical factor, $\sigma_0=\pi/4D^2$, $n_{pol}$ and $n(\theta)$ are the refractive indices of polymer matrix and liquid crystal at a viewing angle $\theta$, respectively.

Experimental behaviours of electro-optical properties can be easily explained in terms of the previously reported equations and electro-optical properties of liquid crystals ($\Delta\varepsilon$, $n_o$ and $\Delta n$). In fact opacity shows a maximum value, i.e. light scattering is higher, when the morphology presents a larger droplet density (at around 40 weight % of liquid crystal). The ON state transparency is related to the refractive indices of liquid crystal and polymer matrix. In the ON state TN0403 liquid crystal droplets present an index mismatch with polymer matrix lower than TN0623 ($\Delta n_{mismatch}$(TN0403)=0.021 and $\Delta n_{mismatch}$(TN0623)=0.031, calculations have been done including the liquid crystal entrapped in polymer matrix) and, therefore, we can justify the few per cents of difference in the ON transmittances. The 10% switching fields, which are able to turn the larger droplet in the ON state, decrease as the average diameter of such droplets increases with liquid crystal content. The $E_{90\%}$ behavior, i.e. the behavior of the fields which are able to turn the smaller droplets in the ON state, is justified because the smaller droplets diameters have slightly higher values in the range 40-60 wt % of liquid crystal due, probably, to a different mutual solubility of liquid crystal and polymer in that concentration range.

Morphology dispersion affects drastically the haze values for liquid crystal concentrations higher than 45%. In facts it is theoretically known[8] that in mismatch conditions the ON state transmittance are lowered at every viewing angle if the droplet size is increased. In addition, the higher haze values of NOA65+TN0623 films are due to the higher refractive indices mismatch shown by such series[6]. Consequently, only the samples of NOA65+TN0403 within the range of 40-50 weight % of liquid crystal, which have an haze lower than 5% and an ON state transmittance higher than 80%, can be accepted by industrial quality controls.

## CONCLUSIONS

We showed that polymer dispersed liquid crystals must present a well defined range of liquid crystal content in order to obtain an acceptable performance. Such range is due to the fact that there is no phase separation at lower liquid crystal loading and droplet size and its dispersion increase at higher liquid crystal content. We found that NOA65+TN0403 and NOA65+TN0623 systems present a maximum value of number density at 40 weight % of liquid crystal. Around such value the film morphology of NOA65+TN0403 presents an average diameter, a polydispersity and an optical refractive index mismatch which allow to get the best acceptable electro-optical characteristics.


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