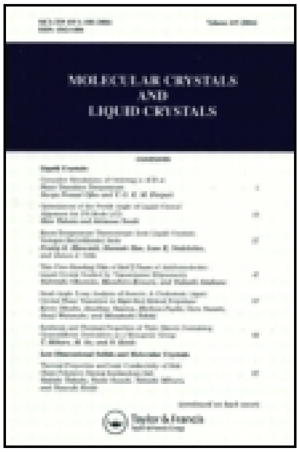

Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

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

High Transmission Polymer Dispersed Liquid Crystals

Ziqiang Huang [a c] , Giuseppe Chidichimo [a] , Giovanni De Filpo [a] , Attilio Golemme [a] , Hassan-Ali' Hakemi [a b] & Michele Santangelo [a b]

[a] Dipartimento di Chimica, Università della Calabria, 87030, Rende, Italy

[b] SNIA Ricerche, via Pomarico, Pisticci Scalo, Italy

[c] Dept. of Opto-Electronic Technology, University of Electronic Science and Technology of China, 610054, Chengdu, China

To cite this article: Ziqiang Huang, Giuseppe Chidichimo, Giovanni De Filpo, Attilio Golemme, Hassan-Ali' Hakemi & Michele Santangelo (1997): High Transmission Polymer Dispersed Liquid Crystals, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 307:1, 135-144

To link to this article: http://dx.doi.org/10.1080/10587259708047092

Mol. Cryst. Liq. Cryst., 1997, Vol. 307, pp. 135–144
Reprints available directly from the publisher
Photocopying permitted by license only

High Transmission Polymer Dispersed Liquid Crystals

ZIQIANG HUANG[a,*], GIUSEPPE CHIDICHIMO[a],
GIOVANNI DE FILPO[a], ATTILIO GOLEMME[a],
HASSAN-ALI' HAKEMI[a,b] and MICHELE SANTANGELO[a,b]

[a]*Dipartimento di Chimica, Università della Calabria, 87030 Rende, Italy;*
[b]*SNIA Ricerche, via Pomarico, Pisticci Scalo, Italy*

(Received 18 February 1997; In final form 19 March 1997)

We present evidence that polymer dispersed liquid crystals (PDLC) with high on state transparency can be obtained following two conditions: the solubility of the liquid crystal within the pre-polymerized resin should be low and the resin itself should not be a mixture but a single chemical species. We prepared PDLC's according to such provisions and measured high on state transparencies. Experimental data have also been interpreted in terms of existing light transmission theories. Results indicate that the high transparency is associated with a high degree of homogeneity of the polymer matrix.

Keywords: Liquid crystals; polymers; PDLC

INTRODUCTION

Polymer Dispersed Liquid Crystals started to attract the attention of researchers more than ten years ago [1–3], also because of their potential applications in optoelectronic devices and their simple preparation procedures. In principle, PDLC's can be used for displays, switchable windows, and light control devices. Nevertheless, their performance is strictly tied to the properties of the constituent materials and to the method of preparation, and for many applications PDLC with the appropriate features are

---

*On leave from: Dept. of Opto-Electronic Technology, University of Electronic Science and Technology of China, 610054 Chengdu, China.

not yet available. In the last years many efforts have been devoted towards the aim of linking PDLC performance with the nature of the materials used and/or the preparation methods [4–8]. However, the mechanisms of both methods used to obtain PDLC's phase separation and encapsulation, are relatively complex and their understanding far from complete.

One of the most important features of PDLC's is their on state transmission, which was studied in good detail in several works [9–13]. Nontheless, a transmission figure of 85%, for a reasonably small collection angle like 2.5°, is considered good [11]. With this work we intend to give a contribution to the understanding of the conditions which can improve PDLC transmission. It has recently been found that, when dispersions are prepared from mixtures of different resins, there can be a higher concentration of one of them near the interface after phase separation [14, 15] and this could be one of the most important reason for extra-scattering [16]. In addition, the interface itself can be relatively large [17] and contribute to the decrease of transparency. In the following we will present data that confirm that both such inhomogeneities at the droplet boundary contribute to scattering and we will also show how this scattering can be decreased.

LIGHT TRANSMISSION IN PDLC

In PDLC's transmission in the on state is lowered by different scattering mechanisms including those associated with multiple scattering, refractive index mismatching between the polymer and the liquid crystal, incomplete alignment of the mesophase director near the droplet boundaries, even in high fields, due to strong anchoring at the surface [18], droplet size and shape distributions and, finally, inhomogeneities of the composition of both the solid matrix and the droplets.

The polymer matrix may not have a homogeneous composition if it is obtained from a mixture of several components which have different curing rates and solubilities in the liquid crystal. We showed evidence [16] that the components which cure faster and/or have poorer solubility in the liquid crystal, tend to separate first. The other components separate later, when the droplet structure is already formed or being formed, and in doing so they concentrate around the droplet boundary. Such concentration gradients and the relative refractive index variations induce additional scattering. Concentration gradients may also exist within the liquid crystalline droplet. In fact, the slower reacting and more soluble components of the initial mixture which polymerize at later stages, may carry with them a consistent amount of liquid crystalline molecules. In other words it may be possible to have an interface of a certain thickness, with its own composition and refractive index, which will induce additional scattering. Both kinds of contributions to scattering may be then minimized by using a single component resin with low solubility in the liquid crystal, as we will show in the following.

Light transmission in PDLC's in the on state can be calculated according to [9]:

$$\frac{I}{I_0} = \frac{1}{2}\{\exp[-\beta\sigma_{sv}d] + \exp[-\beta\sigma_{sh}d]\} \tag{1}$$

where I and I_0 are the transmitted and incident intensities, respectively, β is the droplet density, d the sample thickness and σ_{sv} and σ_{sh} are the total diffraction cross sections of a uniformly oriented spherical nematic droplet for V and H polarized light. Equation 1 of course does not take into account all the effects which derive from a non-uniform director orientation and from composition disomogeneities. We can obtain, using Equation 1, information on the transmission expected in the absence of such effects. To do so, we calculated the transmission assuming a sample thickness $d = 40$ μm, a droplet density β corresponding to equal volumes if liquid crystal and polymer and total cross sections obtained assuming an anomalous diffraction regime [10] for a liquid crystal like E7 with $n_0 = 1.525$ and $n_e = 1.745$. Figure 1 shows the results for different incident angles, droplet sizes and polymer refractive index. The incident angle is the angle between the incident light and the sample normal. From these calculations it is clear that a requirement for high on state transmission is that the refractive index of the polymer should be equal or slightly higher than the liquid crystal ordinary refractive index.

EXPERIMENTAL

Resin

We synthesized oligomers of simple preparation and capable of further polymerization. We choose polyesters with some acrylic moieties which can react when exposed to UV radiation. The obtained compound is:

$$[\text{—OOC—R—COO—}(\text{CH}_2)_m\text{—}]_n.$$

Here R can be either CH═CH or a phenyl ring and their molar ratio M_p/M_a has been varied between 1 and 5. A higher ratio gives a higher

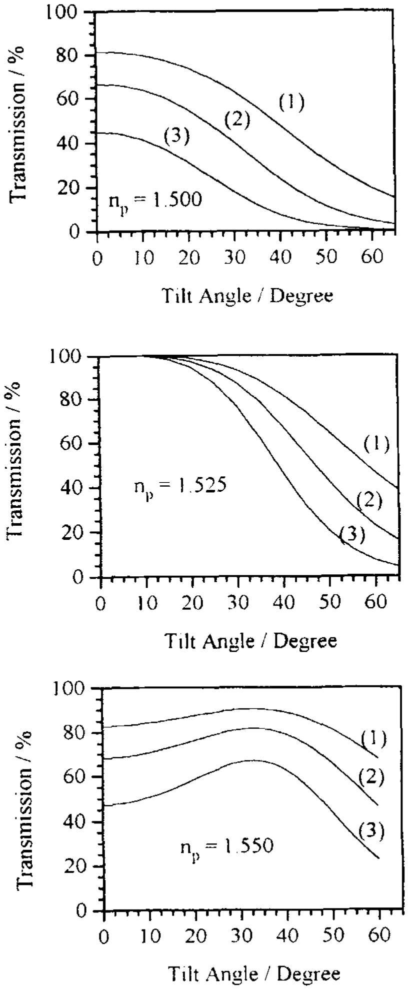

FIGURE 1 Theoretical transmissions calculated according to Equation 1 as a function of tilt angle for different droplet diameters: $\phi = 2$ µm (curve 1), $\phi = 4$ µm (curve 2), $\phi = 8$ µm (curve 3). n_p is the polymer refractive index.

refractive index in the final oligomer, as shown in Figure 2. The index of refraction was measured using an Abbe refractometer.

The same effect can be obtained by decreasing m. In our oligomers n varies between 2 and 5. To reduce the solubility of cyanobiphenyls, about 30% of the $(CH_2)_m$ was replaced with $(CH_2CH_2{-}O{-})_3$ groups. The synthesis consisted of an esterification involving (bis)-pthalic anhydride, fumaric or maleic acid, pentanediol and triethylenglycol. A small amount of photo-

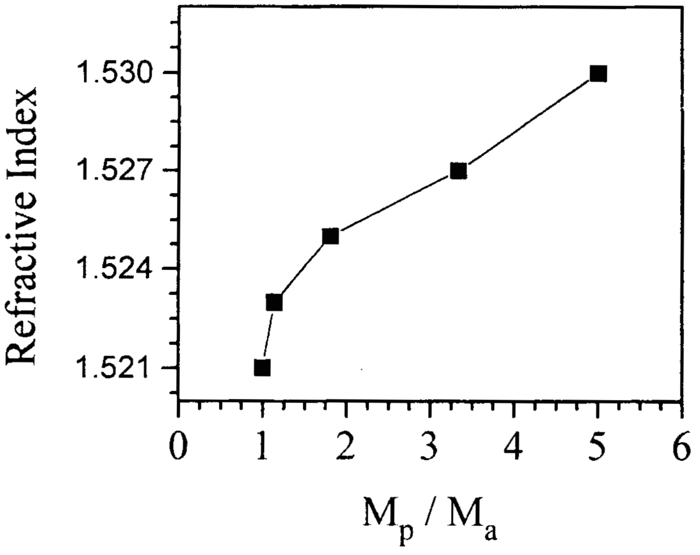

FIGURE 2 Dependence of refractive index of the oligomer on the molar ratio between phenyl and acrylic groups (M_p/M_a).

initiators and acrylic compounds (methylmethacrylate, styrene, acrylic acid) were added to the final product for further UV curing of the oligomers.

The final product was a transparent viscous liquid. It mixed with E7 (Merck) at 90°C at all concentrations and no phase separation was observed after the mixtures were totally cured at this temperature and then cooled to room temperature. At 20°C about 10–20% of E7 can be dissolved depending on the chemical composition of the polymer matrix.

PDLC

PDLC were obtained from the oligomer described above following a three step process. A mixture of the oligomer with the eutectic nematic mixture E7 was first prepolymerized at high temperature. The resulting homogeneous solution was then cooled to room temperature and in this stage phase separation took place. We found that the dimensions of the droplets decrease upon increasing the pre-polymerization time. The third final step is a post curing at room temperature.

In particular, pre-polymerization was carried out by mixing equal weights of oligomer and E7 with photoinitiators (2% Benzoyn ethyl ether, 2% Benzophenone) and 1–4% acrylic acid at 80–90°C. The resulting mixture was placed between two indium-tin oxide coated conducting glasses, controlling the thickness at 40 ± 2 μm by glass spacers, and exposed to a 80 W UV source at 90°C for about 20 minutes of pre-polymerization. The distance between the source and the sample was 10 cm.

Light transmission was measured using the experimental set up shown in Figure 3. A He–Ne laser beam was chopped, expanded and attenuated to properly match the linear range of a photodiode detector. The diameter of the beam impinging on the sample was 0.8 mm, the detector acceptance angle was 2.5° and lock-in amplification was used. The sample was placed on a computer controlled stage where it could be rotated along an axis normal to the incidence plane. All measurements were performed at 30°C, where $n_0 = 1.525$ for E7, and on state intensities were measured at 100 V and 1 kHz.

Since we are interested in the light transmission properties of the PDLC films, we corrected for reflections due to the glass support. To do so, we chose to set the 100% value of transmission as the intensity transmitted through a sample containing pure polymer between two glass slides. The attenuation of the laser beam due to this reference sample was about 9%, and the same value of attenuation was measured using just a single glass slide. In our data we show the transmission relative to the sample containing pure polymer so that the absolute value of transmission, including the effects due to the PDLC and to reflections at the glass surface, is roughly 10% less than the relative values we report.

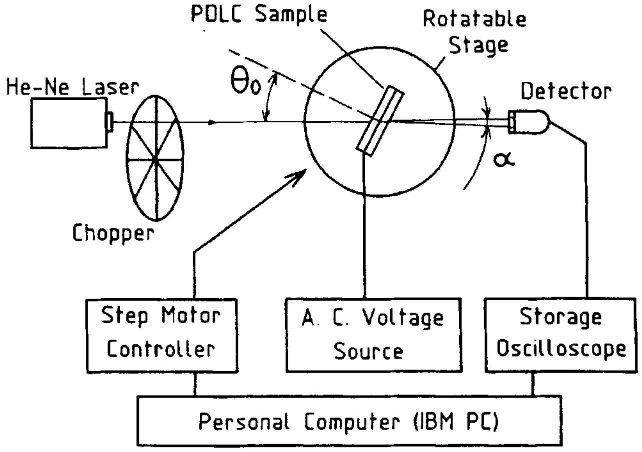

FIGURE 3 Experimental set-up for light transmission measurements. θ_0 and α are the tilt and acceptance angles, respectively.

RESULTS

We report here data obtained using two different oligomers. The refractive index of the resulting polymers were 1.527 and 1.550. The tilt angle dependence of the on state transmission for these samples is shown in Figures 4 and 5, respectively.

In Figure 4 we can see the experimental transmission of two different films, both with nearly matched refractive index, corresponding to two different pre-polymerization times. It should be underlined that both samples exhibit high transmission at normal incidence, higher than 95%, as expected, and this is the main result of our study. The dashed lines are the calculated transmissions obtained using Equation 1. The upper dashed curve has been obtained for a droplet diameter of 0.7 μm and the lower one for diameter of 1.4 μm. Theoretical and experimental curves show good agreement. They are shifted by a constant factor on the vertical scale due to extra scattering factors not included in Equation 1. The experimental and theoretical transmissions of three films with unmatched refractive index are shown in Figure 5. The agreement is good and, as expected, a transmission peak is obtained but it decreases for longer pre-polymerization times, i.e. for smaller droplets.

We also noticed a higher transmission after post-curing. In Figure 6a we show the results for an index matched film. We believe that post curing decreases the size of the interfacial region between the mesophase and the matrix and consequently also the light scattering is decreased. Figure 6b

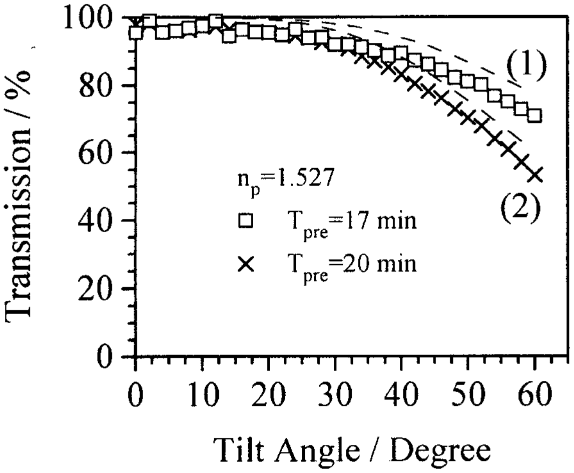

FIGURE 4 Measured transmissions versus tilt angle. n_p is the polymer refractive index, T_{pre} is pre-polymerization time. The dashed lines are the best fit, according to Equation 1, obtained for droplet diameter, ϕ, set to 0.7 μm (curve 1) and 1.4 μm (curve 2).

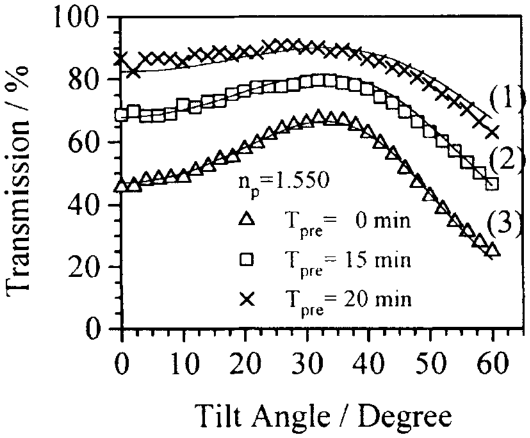

FIGURE 5 Experimental transmissions at different pre-polymerization time, T_{pre}. n_p is the polymer refractive index. The dashed lines represent the calculating results with the droplet diameter set to 2 μm (curve 1), 4 μm (curve 2) and 8 μm (curve 3).

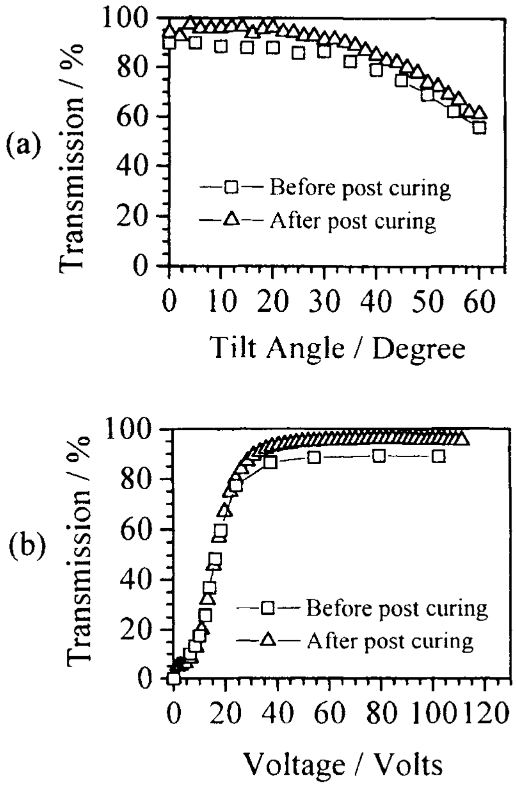

FIGURE 6 Effect of post curing on transmission, (a), and switching voltages, (b). The post curing allows a better phase separation and does not effect the switching voltages.

shows the voltage dependent transmission before and after post-curing. It is evident that the switching voltage is unaffected, which indicates that the concentration of E7 (which acts as a plasticizer) in the matrix is not influenced by post-curing [19].

CONCLUSIONS

We showed that polymer dispersed liquid crystal films can have high on state transparency if they are prepared following two simple rules: a single component for the polymer and a low solubility of the liquid crystal in the polymer. We synthesized two oligomers with different refractive index and obtained high on state transparency for the index matched films. The dimensions of the droplets were regulated by controlling the time of prepolymerization. Post curing was used to complete the phase separation and improve the on state transmission without increasing the switching voltage. In addition, experimental transparencies showed good agreement with scattering theories due to the absence of extra scattering factors connected to the chemical heterogeneities of the polimer matrix.

Acknowledgment

The authors wish to acknowledge A. I. Mashin for computer calculations.

References

[1] J. L. Fergason, *SID Int. Symp. Digest Tech. Papers*, **16**, 68 (1985).
[2] J. L. Fergason, *U. S. Patent 4435047* (1984).
[3] J. W. Doane, N. A. Vaz, B. G. Wu and S. Zumer, *Appl. Phys. Lett.*, **48**, 269 (1986).
[4] P. S. Drzaic, *Appl. Phys.*, **60**, 2142 (1986).
[5] N. A. Vaz, G. W. Smith and G. P. Montgomery, *Mol. Cryst. Liq. Cryst.*, **146**, 1 (1987).
[6] A. Fuh and O. Caporaletti, *Appl. Phys.*, **66**, 5278 (1989).
[7] S. Tahama, T. Mazumi, S. Kaho and M. Mizunuma, *Mol. Cryst. Liq. Cryst.*, **8**, 99 (1992).
[8] P. S. Drzaic and A. Muller, *Liq. Crystal*, **5**, 1467 (1989).
[9] B. G. Wu, J. L. West and J. W. Doane, *Appl. Phys.*, **62**, 3925 (1987).
[10] S. Zumer, *Phys. Rev.*, **A37**, 4006 (1988).
[11] P. Nolan, M. Tillin and D. Coates, *Liq. Crystals*, **14**, 339 (1993).
[12] R. S. Stein and M. Srinivasarao, *Proc. SPIE-Int. Soc. Opt. Eng.*, **1911**, 132 (1993).
[13] S. C. Jain, D. K. Rout and S. Chandra, *Mol. Cryst. Liq. Cryst.*, **188**, 251 (1990).
[14] N. Kawatsuki and H. Ono, *Chem. Lett.*, **5**, 333 (1995).
[15] H. Ono and N. Kawatsuki, *Jpn. J. Appl. Phys.*, **33**, 6268 (1994).
[16] Z. Huang, G. Chidichimo, A. Golemme, H. A. Hakemi, M. Santangelo and F. P. Nicoletta, *Submitted to Liq. Crystals.*

[17] Y. C. Kim, S. H. Lee, J. L. West and E. Gelerinter, *Appl. Phys.*, **77**, 1914 (1995).
[18] K. Naoki, Y. Yuichi, T. Akio and K. Hideo, *Proc. SPIE-Int. Soc. Opt. Eng.*, **1665**, 57 (1992).
[19] P. Adomenas, M. Buivydas, A. Vareikis and V. Pamedityte, *Mol. Cryst. Liq. Cryst.*, **215**, 153 (1992).