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Vincent Allouchery [a] , Frederick Roussel [a] & Jean-Marc Buisine [a]

[a] Laboratoire de Thermophysique de la Matière Condensée, Equipe de l' UPRES A CNRS 8024 Université du Littoral, MREID, F-59140, Dunkerque, France

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Thermodynamic and Electro-Optic Characteristics of UV-Cured Monofunctional Acrylate/Nematic Liquid Crystal Mixtures

VINCENT ALLOUCHERY, FREDERICK ROUSSEL* and JEAN-MARC BUISINE

Laboratoire de Thermophysique de la Matière Condensée, Equipe de l'UPRES A CNRS 8024 Université du Littoral, MREID, F-59140 Dunkerque, France

Polymer Dispersed Liquid Crystals (PDLC) were prepared via a Polymerization Induced Phase Separation (PIPS) mechanism using U.V. radiation. The samples were obtained from the liquid crystalline mixture E7 and a monofunctional monomer (Ethylene Glycol Phenyl Ether Acrylate). The thermodynamic properties of cured samples were studied by Differential Scanning Calorimetry (DSC). The LC solubility limit in the polymer matrix, A, and the fractional amount of LC contained in the droplets, α, were determined (A=20 wt-%; α=0.76 for 50 wt-% LC). The electro-optic characteristics of the PDLC films were investigated as a function of the LC composition and of the amplitude of the applied voltage. For a series of PDLC films with different thicknesses, the droplet distributions and the droplets densities were found nearly identical.

Keywords: polymer dispersed liquid crystals; nematic liquid crystal; phase separation; solubility limit; electro-optical properties

INTRODUCTION

Polymer Dispersed Liquid Crystals (PDLCs) form a new class of promising materials for electro-optical applications such as flexible information displays

* Author for correspondence

or light shutter devices[1-3]. In their most common form, they consist of a low molecular weight liquid crystal dispersed as microsized droplets in a solid polymer matrix. PDLC films can be electrically switched between a light scattering 'OFF' state and a transparent 'ON' state. Typically, as the electric field aligns the liquid crystal in the droplets, the scattering power of the film decreases substantially, bringing the film from a highly scattering state to transparency. One way to prepare PDLCs is polymerization-induced phase separation (PIPS), which occurs when a homogeneous mixture of monomers and liquid crystals is polymerized. UV-induced polymerization is a preferred method because the curing parameters can be chosen independently[4,5].

This work is part of an extensive study of the relationship between the phase separation processes and the electro-optical properties upon changing the polymer architecture (linear, crosslinked,...) and the polymer nature through the use of various monomers/LC blends. Previous studies[6] have shown that for crosslinked PDLC systems-based on multifunctional acrylate/LC mixtures, the higher the amount of phase separated LC in droplets, the better are the electro-optical properties. The purpose of this paper is to extent this study to a linear polymer/LC system. The thermodynamic properties and the electro-optical features of UV-cured blends of a monofunctional acrylate monomer and a nematic liquid crystal are then presented and discussed.

EXPERIMENTAL

Materials

The liquid crystalline mixture E7 (Merck, Nogent, France) was used during this work. E7 exhibits a nematic phase at room temperature. The nematic- isotropic

transition occurs at T_{NI} = 58°C with $\Delta H_{NI}(LC)$=4.4J/g. The precursor of the matrix consists of a monofunctional acrylate monomer: Ethylene Glycol Phenyl Ether Acrylate (EGPEA ; Aldrich, Saint-Quentin Fallavier, France). The UV-polymerization was induced by 2 wt-% of Darocur 1173 (Ciba, Rueil Malmaison, France) with respect to the amount of monomer used.

Preparation of PDLC samples

The monomer and the liquid crystal were mixed together at room temperature until a homogeneous mixture was obtained. Samples for the calorimetric measurements were prepared by introducing the PDLC precursors into the aluminium DSC pan. Thin films for electro-optical measurements were realized by placing a small amount of the reactive mixture between two glass plates coated with a thin transparent layer of conducting Indium Tin Oxide ITO (Balzers, Zaventem, Belgium). PolyEthyleneTerephtalate film spacers (Goodfellow, Lille, France) were placed between the plates in order to keep uniform film thicknesses. The UV-curing was performed using a SEIKO UV-1Unit. The wavelength of the UV radiation was set at λ = 365nm with a beam intensity of 17.5mW/cm^2. The UV exposure time was fixed at three minutes[5,7].

Characterization methods

The DSC measurements were performed on a SEIKO DSC 220C. The DSC cell was purged with 50 ml/min of nitrogen. Rates of 10°C/min (heating) and 30°C/min (cooling) were used on the temperature range -100 to +100°C. The program consists, first in cooling the sample followed by several heating and cooling cycles. Data analysis have been carried out on the second heating ramp.

The microscopical studies were performed on an optical polarizing microscope LEICA DMRXP at room temperature.

The electro-optical properties of the PDLC films were investigated by using an experimental setup described as follows. The incident light source (HeNe laser, λ = 632.8nm) was passed through the cells normal to the film surface. The collection angle for the forward transmitted light was set to about ±2° by an iris. The transmitted light was then focussed by a lens onto the photodetector (silicon photodiode) ; the intensity of the transmitted light was recorded on a digital oscilloscope (HP 54520A). In order to drive the electro-optic system, the output of a function generator was amplified. Starting from the electrical OFF-state, the applied sinusoidal voltage (v=1kHz) was increased continuously up to 160V, then decreased in the same way. The whole scan up and down was performed during 90s; 30s time delay was set between two scans. Each cycle was repeated at least three times. In order to get reproducible measurements, several samples were prepared. All the electro-optical experiments were carried out at room temperature.

RESULTS AND DISCUSSION

Thermophysical studies

One of the major parameters governing the properties of PDLC materials is the phase separation process. Smith[8,9] has shown that the LC solubility limit, A, in the polymer matrix can be related to the nematic-isotropic enthalpy:

$$P(x) = \left(\frac{x - A}{100 - A} \right), \text{ with } P(x) = \frac{\Delta H_{NI}(x)}{\Delta H_{NI}(LC)} \qquad (1)$$

$P(x)$ represents the ratio of the nematic-isotropic transition enthalpy for a LC/polymer composite material, $\Delta H_{NI}(x)$, to the equivalent value for pure LC, $\Delta H_{NI}(LC)$.

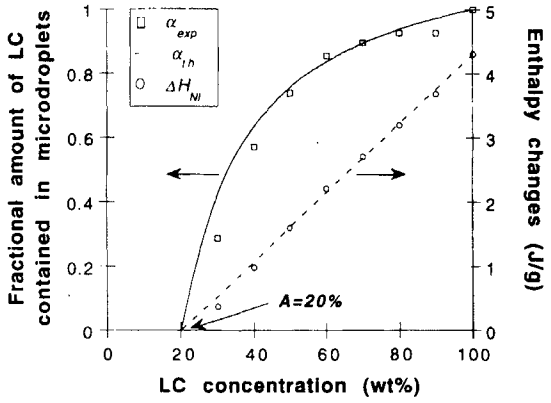

FIGURE 1 Enthalpy changes at the nematic-isotropic transition and fractional amount of liquid crystal contained in the PDLC droplets *vs* LC concentration.

It can be seen on Figure 1(right y-axis) that $\Delta H_{NI}(x)$ increases linearly with x, validating the model given in Eq. (1). The LC solubility limit A was determined by linear regression of the experimental data set in Figure 1, followed by calculating the x-axis intercept. The value of A was 20 wt-% which is quite low compared to other thermoplastic polymer/LC blends (A~40%)[10-12]. The ethylene glycol phenyl ether group in the polymer backbone is suspected to reduce the polymer/LC miscibility and to improve the phase separation process.

ΔH_{NI} can be used to calculate α_{exp}, the LC fraction contained in the droplets:

$$\alpha_{exp} = \frac{m_{LC}^{D}}{m_{LC}} = \left(1 + \frac{m_P}{m_{LC}}\right) P(x) = \left(\frac{100}{x}\right) P(x), \quad (2)$$

where m_{LC}^{D} represents the mass of LC included in the droplets, while m_P and m_{LC} are the masses of the polymer matrix and of the LC in the sample, respectively. Combining Eqs (1) and (2) yields:

$$\alpha_{calc} = \left(\frac{100}{x}\right)\left(\frac{x - A}{100 - A}\right). \quad (3)$$

Figure 1 (left *y*-axis) illustrates the dependence of α on the LC concentration. The points represent α_{exp} values determined for each composition by applying Eq. (2), whereas the curves were calculated by using the previously-mentioned *A* values. The experimental values and calculated curves are in good agreement. Equations (2) and (3) are strictly valid only in the LC concentration range where the LC is entrapped in the droplets. Within these limits, the value of α_{calc} was 0.76, observed for 50 wt-% E7, which is rather high compared to other acrylate systems[8,13]. Therefore EGPEA/E7 mixtures show a high ability to phase separation upon UV-polymerization, probably due to the ethylene glycol phenyl ether group in the polymer backbone which reduce the misciblity between the polymer and the liquid crystal.

Optical microscopical analysis of the texture of the PDLC samples ($30<x<80$) revealed a great number of very small birefringent microdomains, which are thought to represent the LC microdroplets. Although the magnification was as high as possible (x320), the droplet size could not be accurately determined and was estimated to be less than 1μm.

Electro-optical response

The electro-optical properties of PDLC films were investigated as a function of applied voltage and LC concentration for several film thicknesses. Figure 2 shows the effects of the LC concentration on the electro-optical response for the first application voltage (film thickness 21±2μm); the electro-optical characteristics are gathered in Table I.

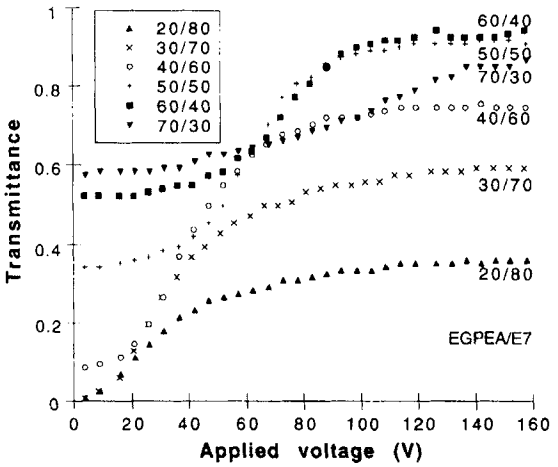

FIGURE 2 Effect of the LC content on the electro-optical response for the first application voltage (film thickness 21±2μm, λ=632.8nm, ν=1kHz).

In the LC weight percentage range from $0<x\leq20$, the transmitted intensity remains nearly unchanged. In this concentration range, the LC molecules are randomly dispersed in the matrix[6,9,14]. The corresponding data were therefore omitted from Fig. 2. The electro-optical properties changed when the LC concentration was varied from 30 to 80 wt-%: increasing the LC content in this range increased the OFF-state scattering, and the threshold and saturation

voltages (V_{10}, V_{90}, voltages required for 10% and 90% of the maximum transmittance value, respectively) were reduced linearly (Table I). Simultaneously, the transmission in the ON-state decreased (except for x=30% for which the plateau in ON-state was not reached upon application of ±160V). This behavior was not observed for PDLCs prepared with crosslinked polymer matrices[6], and remains unclear. In order to decipher this complex behavior, morphological (SEM) and dielectric studies are currently in progress. Samples containing $x \geq 90$ wt-% LC exhibited LC macrodomains and were not used for eletro-optical measurements. Therefore, in the LC concentration 30 to 80 wt-%, the phase separation LC/polymer matrix gives rise to scattering of the light.

LC (wt%)	*Th.* (μm)	T_0 (%)	T_{10} (%)	T_{90} (%)	T_{100} (%)	ΔT	V_{10} (V)	V_{90} (V)	*CR*
30	13	82.2	83.7	96.1	97.6	15.4	30	82	1.19
	23	58.2	61.1*	85*	87.3*	29.1*	44*	146*	1.5*
40	12	75.3	85.2	89.7	99.7	24.4	26	67	1.32
	21	53.9	57.5	86.3	89.9	36	37	107	1.66
50	12	53	57.4	92.3	96.7	43.7	19.4	52.5	1.82
	22	31.7	37.5	84.1	89.9	58.2	30	97	2.84
60	13	20.5	26.7	76.7	83	62.5	11	42	4.05
	20	8.6	15.2	68.7	75.3	66.7	20	78	8.8
70	14	9.4	14.8	57.1	62.5	53.1	5	41	6.64
	20	0.8	6.7	54	59.9	59.1	16	70	74.8
80	11	7.7	12.1	47.8	52.2	44.5	6.5	38	6.8
	21	0.8	4.2	31.7	35.1	34.3	14	63	43.8

Table I Electro-optic characteristics of EGPEA/E7 PDLC films (first application voltage); *LC*: LC concentration; *Th.*: film thickness; T_0: transmittance in the OFF-state; T_{10}, T_{90}: 10%, 90% of the maximum transmittance value; T_{100}: transmittance in the ON-state; $\Delta T = T_{100} - T_0$; V_{10}, V_{90}: voltages required for 10% and 90% of the maximum transmittance value, respectively; $CR = T_{100}/T_0$: contrast ratio; *: estimated value (plateau in the ON-state not reached).

These results confirm the thermodynamic studies, where a value of the LC solubility limit A=20 wt-% was found. PDLC films (13μm) including 60 wt-% LC presented a high transmittance (ΔT~65%) and low threshold and saturation voltages (V_{10}=11V, V_{90}=42V).

The transmittance $T=I_T/I_0$ can be expressed as a function of thickness of the film by[15-17]:

$$log(T) = log\left(\frac{I_T}{I_0}\right) \approx -\eta.d \tag{4}$$

where I_T is the transmitted intensity, I_0 the incident intensity, η the scattering coefficient and d the thickness of the scattering film. Figure 3 shows the effect of the PDLC film thickness on the transmission properties (T_0, T_{10}, T_{90}, T_{100}) for composite materials including 50 wt-% LC.

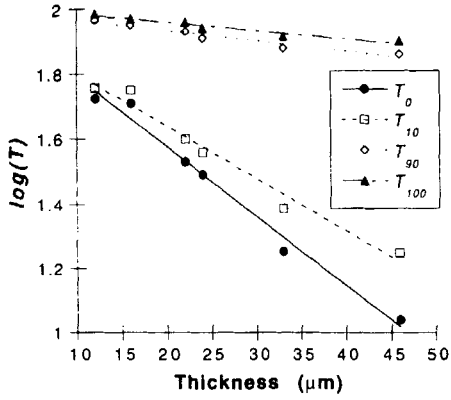

Figure 3 Effect of PDLC film thickness on the transmission properties for composites materials containing 50 wt-% LC (λ=632.8 nm, ν=1kHz).

The logarithm of the transmission varies linearly with d, meaning that the droplet distributions and the droplets densities are nearly identical for a series of PDLC films with different thicknesses[15,17]. The higher values for the slope of the regression curves corresponding to the OFF-states are due to the larger refractive index mismatch[15,17]. The ON-state is characterized by transmission values above 82%.

CONCLUSION

The relationship, between phase separation processes and the electro-optical properties of UV-cured monofunctional acrylate/nematic liquid crystal blends has been studied. The reactive mixtures included monofunctional acrylate monomer (EGPEA) and a nematic liquid crystal (E7). Phase separation induced by UV-polymerization was observed by DSC at low LC concentration; the value of the LC solubility limit was A=20%. High fractional amounts of liquid crystal contained in the droplets were found (α~0.76 for mixtures including 50 wt-% LC). The electro-optical properties of the composite films obtained were strongly related to LC concentration; the values found for the LC solubility limit A agree well with those determined by means of calorimetric measurements. The droplet distributions and the droplets densities were found nearly identical for a series of PDLC films with different thicknesses. The samples prepared with 50 and 60 wt-% LC exhibited the best electro-optical performance (high transmittance and low threshold and saturation voltages).

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References

[1] J.W. Doane in *Liquid Crystals-Applications and Uses*, ed. B. Bahadur (World Scientific, Singapore), **1**, chap. 14, p. 361, (1990).

[2] H.S. Kitzerow, *Liq. Cryst.*, **16,** p. 1, (1994).
[3] P.S. Drzaic, *Liquid Crystal Dispersions* (World Scientific, Singapore), (1995).
[4] C. Serbutoviez, J.G. Kloosterboer, H.M.J. Boots, F.J. Touwslager, *Macromolecules.* **29,** p. 7690, (1996).
[5] F. Roussel, J.M. Buisine, U. Maschke, X. Coqueret, *Liq. Cryst.*, **24,** p. 555, (1998).
[6] F. Roussel, U. Maschke, X. Coqueret, J.M. Buisine, *C.R. Acad Sci. Paris,* **326,** IIb. p. 449, (1998).
[7] P. Nolan, E. Jolliffe, D. Coates, *Proc. SPIE,* **2408,** p. 2, (1995).
[8] G.W. Smith, N.A. Vaz, *Liq. Cryst.*, **3,** p. 543, (1988).
[9] G.W. Smith, *Mol. Cryst. Liq. Cryst.*, **180B,** p. 201, (1990).
[10] M. Ballauf, *Ber. Bunsenges. Phys. Chem.*, **90,** 1053, (1986).
[11] W. Ahn, C.Y. Kim, H. Kim, S.C. Kim, *Macromolecules,* **25,** p. 5002, (1992).
[12] L. Carpaneto, A. Ristagno, P. Stagnaro, B. Valenti, *Mol. Cryst. Liq. Cryst.*, **290,** p. 213, (1996).
[13] F. Roussel, J.M. Buisine, U. Maschke, X. Coqueret, *Mol. Cryst. Liq. Cryst.*, **299,** p. 321, (1997).
[14] J.L. West, ACS Symposium, **32,** 475 (1990).
[15] P.S. Drzaic, *Mol. Cryst. Liq. Cryst.*, **198,** p. 61, (1991).
[16] N. Kinugasa, Y. Yano. A. Takigawa, H. Kawahara, *Proc. SPIE,* **1665,** p. 57, (1992).
[17] U. Maschke, X. Coqueret, C. Loucheux, *J. Appl. Polym. Sci.*, **56,** p. 1547 (1995).