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## Liquid Crystals

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Ulrich Maschke; Nicolas Gogibus; Andre Traisnel; Xavier Coqueret

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## Preliminary communication

# Electron beam cured liquid crystal-polymer composite materials: electro-optical enhancement effect

by ULRICH MASCHKE\*, NICOLAS GOGIBUS,  
ANDRE TRAISNEL and XAVIER COQUERET

Laboratoire de Chimie Macromoléculaire, CNRS (URA No 351), Bâtiment C6,  
Université des Sciences et Technologies de Lille, F-59655 Villeneuve d'Ascq Cedex,  
France

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Polymerization induced phase separation initiated by electron beam radiation has been used as a powerful method to obtain well defined PDLC films. Mixtures of different amounts of an aromatic polyester acrylate, an oligoether triacrylate and nematic liquid crystal material E7 were exposed to the electron beam radiation. The electro-optical properties strongly depend on the liquid crystal concentration and on the amount of the oligoether triacrylate in the prepolymer mixture, and are highly reproducible. An unusual enhancement effect of the electro-optical sensitivity was found for samples containing 28 weight per cent and 34 weight per cent of the oligoether triacrylate.

Polymer dispersed liquid crystal (PDLC) films consist commonly of micron-sized droplets of low molecular mass liquid crystal (LC) dispersed in a solid polymer matrix [1]. The starting materials are chosen so that an external electric field applied on the PDLC film aligns the LC in the droplets and switches the film from a cloudy light scattering off-state to a highly transparent on-state. These new materials are of considerable interest for display applications and light control devices like optical shutters. Polymerization induced phase separation (PIPS) initiated by electron beam (EB) radiation has been used to obtain well defined PDLC films [2-4]. The use of EB processing offers various advantages: precise control of the curing conditions, fast cure rate without thermal activation, possibility of high conversion of monomers, initiation of the polymerization at a desired temperature. Compared with the PIPS process by ultraviolet light, EB curing has the unique advantage of not requiring the presence of a photoinitiator that itself may be detrimental to the PDLC film performances and to long term ageing.

The electro-optical properties of PDLC films are controlled by several factors including the type of LC and polymer precursor of the initial reactive mixture, film thickness and droplet morphology. The present work was focused on the scattering efficiency and the

electro-optical behaviour of PDLC films depending on the sample composition. The transmission properties of selected films of approximately equal thickness were investigated as a function of driving a.c. voltage, LC concentration and dependence on the weight fraction of the oligoether triacrylate in the prepolymer mixture.

A eutectic nematic mixture of cyanoparaphenylene derivatives (E7, Merck Ltd, U.K.) was employed as the LC material during this work. The prepolymer chosen consisted of blends of an aromatic polyester acrylate (Genomer 7151, called hereafter PE-A, Rahn AG, Switzerland) and propoxylated glyceryl triacrylate (GPTA, Cray Valley, France). These materials were reagent grade chemicals and have been used without further purification.

(100- $x$ ) weight per cent (wt %) of blends of PE-A and GPTA ( $x=50, 60, 70$ ) and  $x$  wt % of the LC material were mixed together at room temperature for several hours. Different weight fractions of GPTA in the prepolymer mixture were employed, and for each composition several samples were prepared. The details of each composition of selected samples are given in the table.

Samples for electro-optical studies were prepared by sandwiching the initial reactive mixture between a glass plate (Balzers, Liechtenstein) and a 100  $\mu\text{m}$  thick poly(ethyleneterephthalate) sheet (Renker, Germany), both coated with a thin transparent layer of conducting indium/tin oxide. The thickness of the composite films

\*Author for correspondence.

Composition of liquid crystal/prepolymer mixtures before electron beam curing.

Sample	Liquid Crystal		Prepolymer	
	E7/wt %	PE-A/wt %	GPTA/wt %	Weight fraction of GPTA in the prepolymer
A	50	15	35	0.7
B	60	6	34	0.85
C	60	12	28	0.7
D	60	18	22	0.55
E	70	9	21	0.7

was controlled by using 25  $\mu\text{m}$  thick spacers (double face adhesive strips, 3M, France).

The electron beam generator used to prepare the PDLC samples by a PIPS process was an Electrocurtain Model CB 150 (Energy Sciences Inc.) with an operating high voltage of 175 kV. This value was increased to 190 kV to allow a uniform penetration of the applied dose in the depth of the sample. The sandwiched composite materials were placed in a sample tray, which was passed in an inert atmosphere under the accelerated electron curtain on a conveyor belt. The applied dose of 60 kGy was achieved by using a beam current of 4 mA and a conveyor speed of 0.22  $\text{m s}^{-1}$ . These values have not been changed during the experiments in order to apply each time the same curing conditions. No temperature control during the irradiation process was applied.

The electro-optical experiments were performed at room temperature by measuring the transmission of unpolarized He/Ne laser light at a wavelength  $\lambda = 632.8 \text{ nm}$ . The sample cells with the PDLC films were oriented normal to the laser beam. The distance between the sample holder and the detector (silicon photodiode) was approximately 30 cm. The collection angle of the transmitted intensity was about  $\pm 2^\circ$ , so that principally forward scattering was detected. The intensity of transmitted light was recorded on a micro-computer using an interface card (DAS 1602). The transmission values were corrected for the loss of transparency which results from the reversible darkening of the glass plates upon EB irradiation.

For electro-optical measurements, an external electric field was applied across the cured sandwiched PDLC film. The output of a frequency generator was amplified and used to drive the shutter device. Starting from the electrical off-state, the applied sinusoidal voltage of frequency 145 Hz was increased continuously up to a desired maximum value  $V_{\text{max}}$ . Subsequently it was decreased in the same way. The whole scan up and down ramp was usually performed during 120 s, an additional measuring time of 60 s allowed the relaxation behaviour of the transmittance in the off-state to be

followed. The same procedure was repeated several times using appropriate voltage maximum values.

The electro-optical properties of sample B as a function of applied voltage are presented in figures 1 and 2. The voltage maximum applied on the sample cell during the different runs was  $V_{\text{max}} = 20 \text{ V}$  (ramps 1 and 3, figure 1). The transmission values changed only from approximately 12% ( $T_0$ , transmission value at zero volt) to 38% ( $T_{100}$ , transmission value at voltage maximum) upon application of the first voltage ramp. Figure 2 illustrates the electro-optical characteristics for the second voltage application of  $V_{\text{max}} = 120 \text{ V}$  (ramp 2). At first, the transmission increases with increasing voltage until a maximum is reached at about  $V = 94 \text{ V}$ ; a further increase of the voltage leads to slightly decreasing transmission values. An unusual behavior is observed in the decreasing electric field (ramp 2 (down)): after passing a minimum at  $V = 94 \text{ V}$ , the transmission increases with decreasing voltage until a horizontal plateau is reached between 30 and 10 V. The transmitted intensity decreases drastically if the voltage is further reduced. A strong light scattering was observed for the final off-state (ramp 2 (down)): the transmission was substantially lower as compared with the initial off-state. The following third voltage application (ramp 3 in figure 1) of  $V_{\text{max}} = 20 \text{ V}$  exhibits low threshold and saturation voltages. The particular values corresponding to the voltages required for obtaining 10 and 90% of the maximum transmission were 4.6 and 7.8 V, respectively. A highly transparent on-state and thus a high contrast ratio (by calculating  $T_{100}/T_0$ ) was observed. Upon further voltage applications of  $V_{\text{max}} = 20 \text{ V}$ , the PDLC film recovers the scattering properties of the third voltage application. The electro-optical characteristics obtained were highly reproducible and have also been found for several other sample compositions. To our knowledge, such a 'wake-up' effect of the electro-optical sensitivity has not been reported in the literature so far. Further studies are in progress to understand the observed electro-optical response.

Figure 3 illustrates the influence of LC concentration

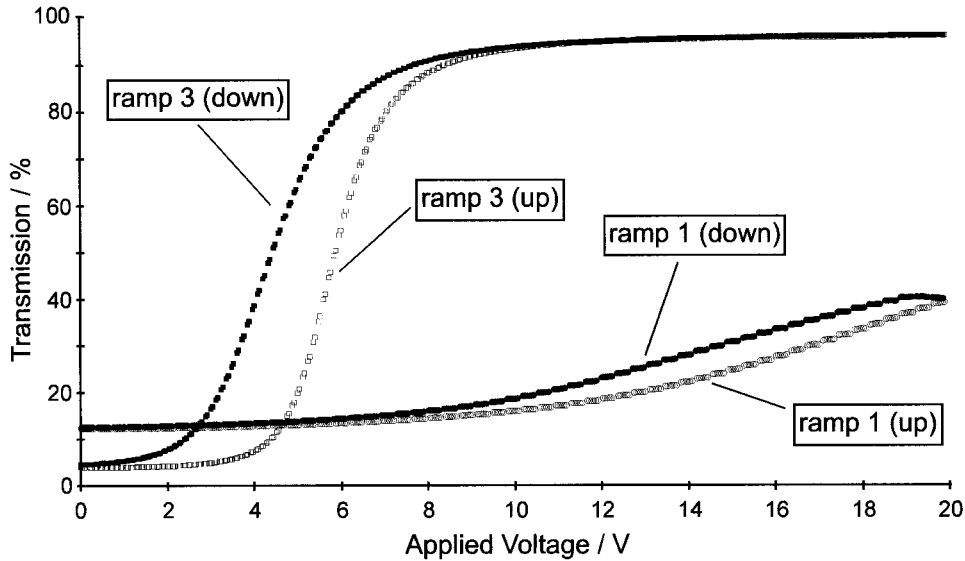


Figure 1. Electro-optical response of a PDLC film (sample B, initial composition: 6 wt % PE-A, 34 wt % GPTA, 60 wt % E7) taken in repeated increasing and decreasing voltage scans ( $\lambda=632.8$  nm,  $\nu=145$  Hz). The voltage maximum applied on the sample cell during ramps 1 and 3 was  $V_{\max}=20$  V (ramp 2 is given in figure 2).

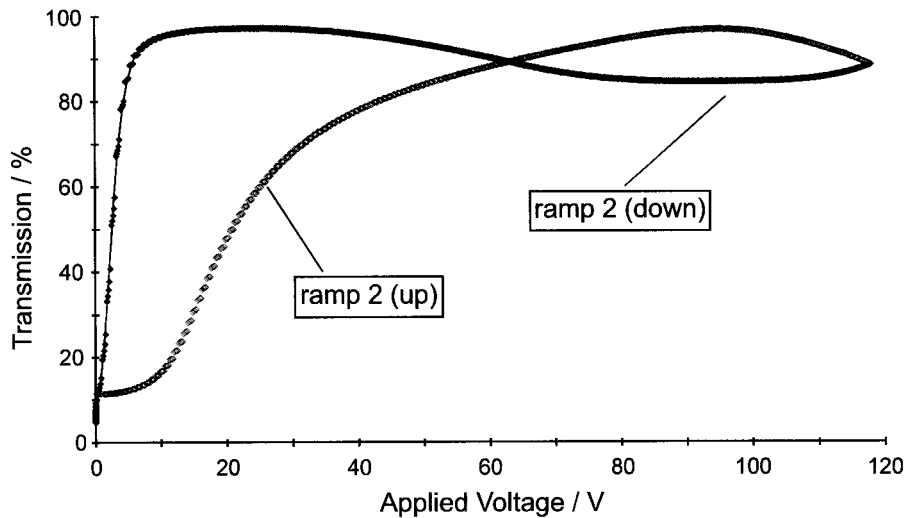


Figure 2. Transmission properties of sample B (initial composition: 6 wt % PE-A, 34 wt % GPTA, 60 wt % E7) for the second voltage application (ramp 2,  $\lambda=632.8$  nm,  $\nu=145$  Hz). The voltage maximum was  $V_{\max}=120$  V (ramps 1 and 3 are given in figure 1).

on the electro-optical behaviour for the first voltage application (ramp 1 (up)). The polymer matrix composition remained constant during these experiments (weight fraction of GPTA in the prepolymer=0.7). A voltage ramp with a maximum of 60 V was applied on samples A, C, and E containing 50, 60 and 70 wt % of LC. At the LC concentration of 50 wt % (sample A), the transmission values change only a few per cent. Starting from an off-state transmission of 8%,  $V_{10}$  was estimated as high as 60 V. This finding has been confirmed in a subsequent experiment (not shown) using a voltage

maximum of  $V_{\max}=135$  V. Optical saturation with high and constant transmittance characterizing the on-state ( $T_{100}$ ) could not be obtained.

The electro-optical characteristics change drastically if the LC content is changed from 50 to 60 wt % (sample C): increasing the LC concentration in this range considerably increases the off-state scattering. Simultaneously, threshold and saturation voltages are reduced substantially.

The limit of miscibility of the initial reactive mixture before curing was reached at 62 wt % of LC. In spite of

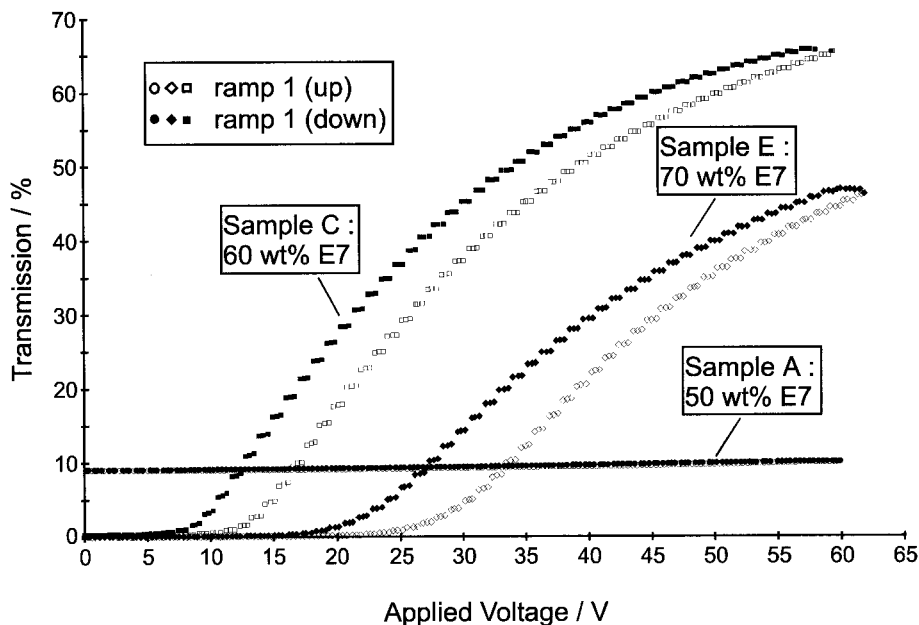


Figure 3. Effect of the liquid crystal concentration on the electro-optical response for the first voltage application (ramp 1 (up),  $V_{\max}=60$  V,  $\lambda=632.8$  nm,  $\nu=145$  Hz). The weight fraction of GPTA in the prepolymer has been kept constant at 0.7 (samples A, C, E).

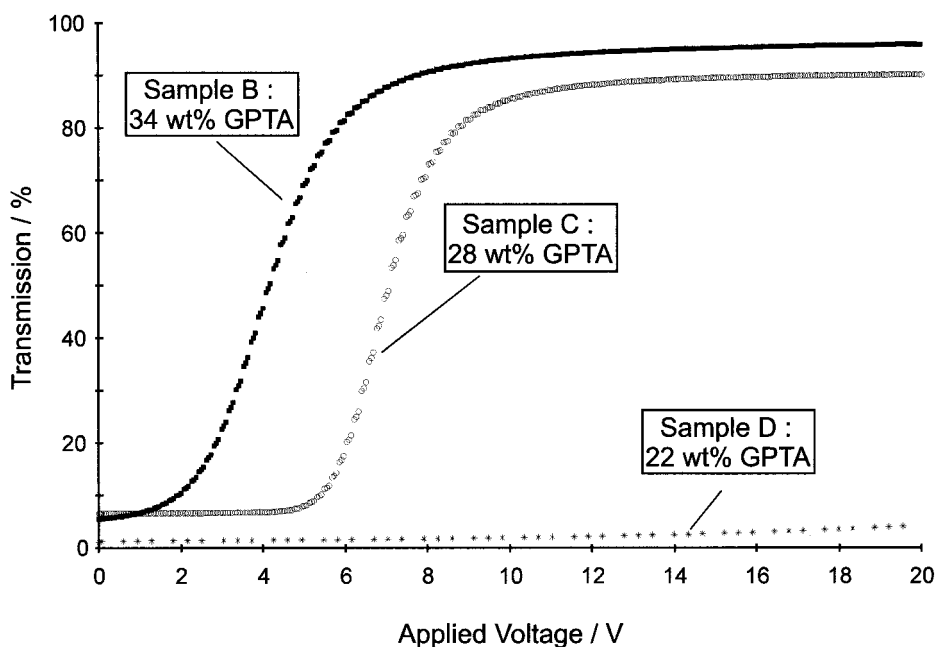


Figure 4. Influence of GPTA-concentration on the electro-optical curves for the third voltage application (ramp 3 (down),  $V_{\max}=20$  V,  $\lambda=632.8$  nm,  $\nu=145$  Hz); the liquid crystal concentration remains constant at 60 wt % E7 (samples B, C, D).

the fact that blends including more than 62 wt % of LC did not form homogeneous solutions at room temperature, an attempt was made to study the electro-optical behaviour of a sample containing 70 wt % of LC (sample E). Compared with sample C, this film exhibited the same strong scattering in the off-state, but is characterized by higher threshold and saturation voltages. The phase separation between LC and polymer precursor prior to curing might be partially responsible for the limited performance. Furthermore, a volume fraction of the LC will not be under kinetic or thermodynamic

control of the PIPS process. This will, therefore, change the optical properties of the polymer matrix.

Figure 4 illustrates the electro-optical response for the third voltage application (ramp 3 (down)), when the weight fraction of GPTA in the prepolymer was varied (samples B, C and D). The LC concentration was kept constant at 60 wt %. It has been shown before (figure 3), that composite films containing 60 wt % of E7 were characterized by improved electro-optical performance. As in experiments mentioned above (see figures 1 and 2), two previous voltage scans (ramp 1:  $V_{\max}=20$  V,

ramp 2:  $V_{\max}=135\text{ V}$ ) have already been applied on the samples. Composite films containing 18 wt % PE-A and 22 wt % GPTA (sample D) do not show the 'wake-up' effect. Increasing the GPTA content from 22 to 34 wt % leads to high on-state transmission and low threshold and saturation voltages. The best electro-optical performance was found for films composed of 6 wt % PE-A, 34 wt % GPTA and 60 wt % E7 ( $T_0=4\%$ ;  $T_{100}=96\%$ ;  $V_{10}=4.6\text{ V}$ ;  $V_{90}=7.8\text{ V}$ ). Further analysis of these PDLC materials is in progress.

In conclusion, various mixtures made of LC E7 and of reactive blends of PE-A and GPTA were efficiently cured by EB radiation using a PIPS process. The electro-optical properties of the composite films obtained were strongly related to the LC concentration and to the weight fraction of GPTA in the prepolymer mixture. An unusual enhancement effect of the electro-optical sensitivity was found for samples containing 28 and 34 wt % GPTA. An optimum weight fraction of the LC mixture E7 (60 wt %) has to be added to the polymer precursor for good performance of the PDLC films. The finite solubility of LC mixture in the polymer affects the properties of the polymer matrix and hence the electro-optical characteristics significantly. The best electro-optical performance was found for films composed of 6 wt % PE-A, 34 wt % GPTA and 60 wt % E7. The electro-optical curves are characterized by low threshold and saturation voltages, strong off-state scattering and highly transparent on-states. Scanning electron microscopy investigations are currently in progress to correlate

the morphology of the samples with the observed electro-optical behaviour.

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