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EFFECT OF UV-CURING CONDITIONS ON THE FERROELECTRIC BEHAVIOUR IN FLC NETWORKS

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Abstract : Liquid crystal micro-composites based on ferroelectric liquid crystal and a chiral photocrosslinkable liquid crystal polymer are studied. Their ferroelectric properties are closely connected to their polymerization process. The effect of the UV curing conditions on the ferroelectric behavior is discussed. Low UV intensity applied for a long time treatment leads to a polymer network that introduces little variations on the pure FLC behaviors.

Keywords : smectic, ferroelectric, polarization, tilt angle, polymer, network, gel, photocrosslinking.

INTRODUCTION

Anisotropic gels, also called liquid crystal dispersed polymers (LCDP), are created by the polymerization of mesomorphic (or non-mesomorphic) molecules in the presence of conventional LC molecules without reactive groups [1]. Contrary to polymer dispersed liquid crystal (PDLC) systems [2], anisotropic gels contain only small amounts of polymer in a continuous LC matrix which, therefore, acts as an anisotropic solvent. These new materials present some challenging aspects such as behavior of LC molecules confined in a three-dimensional anisotropic network, which involves a strong influence on the anisotropic properties of LC.

In the case of FLC gels, it has been shown that a volume mechanical

stabilization of the cell has been reached [1][3]. The possibility of a technology involving thicker cells, compared to Surface-Stabilized FLC (SSFLC) systems, gray scales performances [2] or the influence of the polymer concentration on switching speed and tilt angle [4] have also been investigated.

The purpose of this article is to study the role played by different UV curing conditions on the field-induced polarization and the tilt angle variations. Focus is made on two different polymerization processes : a high intensity applied for a short time and a lower UV intensity for a longer irradiation time.

EXPERIMENTAL SECTION

Preparation

The ferroelectric liquid crystal materials used in the experiments are either a lab synthesized compound (here called G1) made by one of us or a commercial mixture (called RD) purchased from HOESCHT. Tables I and II resume the different phases of liquid crystal compounds.

TABLE I. Polymorphism data for G1.

<i>Kr</i>	-14	<i>SmC*</i>	64	<i>SmA</i>	83	<i>N*</i>	108	<i>I</i>
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TABLE II. Polymorphism data for RD.

<i>Kr</i>	6	<i>SmC*</i>	54	<i>SmA</i>	59	<i>N*</i>	68	<i>I</i>
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The polymer network is obtained by adding to the liquid crystal, 3wt% of reactive chiral monomers. A small amount of Irgacure 907 (Ciba-Geigy) is added for photocrosslinking purposes at 2wt% - calculated from the photocrosslinkable component weight. Mixtures are brought by capillarity between two glass plates coated with rubbed polyimide and separated by about 4 μ m. The surface of ITO electrodes is about 0.25cm². The rubbing directions on the two glass surfaces are parallel. Before UV curing and in order to obtain the most uniform bookshelf geometry, samples are brought up to the isotropic point and then slowly cooled at 0.2°C/min down to 40°C. Then, they are irradiated by a UV light mercury lamp. Both the irradiation time and the intensity depend on the polymerization process which are considered in the following. Cross-linking is carried out at 40°C in the chiral smectic phase.

The measuring setup

We study the following ferroelectric characteristics : polarization vs the voltage applied, polarization vs the temperature and the tilt angle vs the

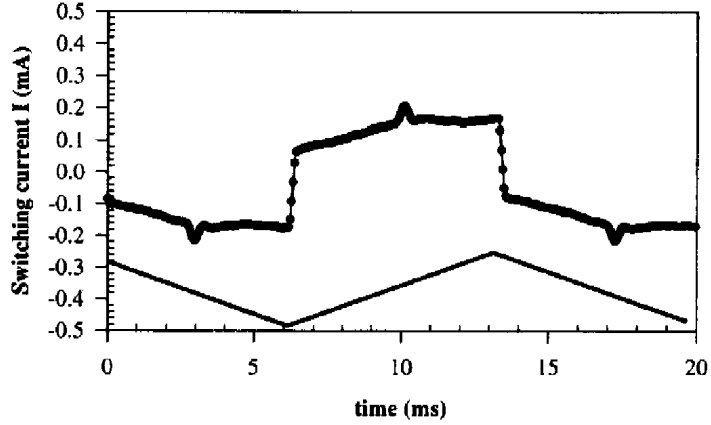


FIGURE 1. Typical recorded signal. The applied field is shown at the bottom.

temperature.

The cell is thermostated in a Mettler hot stage. The driving voltage is either a triangular or a square wave form generated by the HP33120A function generator and amplified by the TREK 50/750. Variations of both the polarization and the tilt angle are made under a voltage of 90V.

The switching current is measured via a serial resistance [5-7] and stored on a HP54610B oscilloscope. The polarization is determined by integrating the current peak after subtracting both the capacitance and the conductive part (Figure 1) [5-7].

Light intensity is detected by a photomultiplier mounted on a Olympus BH-2 microscope with a small collection angle. A Jobin Yvon HV10 monochromator selects only signals with a 589 nm wavelength. Responses are recorded by either a HP34401A multimeter or the oscilloscope. The whole setup apparatus is computer driven under HPVEE environment.

For determining the electric-field induced apparent tilt angle θ , the cell is first placed between crossed polarizers. Ferroelectric domains are observed in the sample. The transmitted light intensity I through the cell of thickness d can be written as [8] :

$$I(\phi) = I_0 \sin^2(2\phi) \int d\lambda \sin^2\left(\pi \frac{\Delta n d}{\lambda}\right) \quad (1)$$

I_0 is a constant depending on the impinging light and the nature of the polarizers, ϕ is the angle between the optical axis of the material and the analyzer. Δn is the optical birefringence of the medium considered as uniaxial. From (1), the maximum intensity occurs at $\phi = 45^\circ$ and the maximum modulation of the transmitted light intensity at $\phi = 22.5^\circ$. We measure the deviation of the optic axis ϕ from this value for one particular domain when the cell is submitted to an electric field. A 70Hz sinusoidal signal is applied.

The induced tilt angle values θ is approximately given by formula (2) [9]:

$$\theta \approx \frac{1}{4} \left(\frac{\Delta I_{pp}}{I(\phi = 45^\circ) - I(\phi = 0^\circ)} \right) \times \left(\frac{180}{\pi} \right) \quad (2)$$

ΔI_{pp} is a peak-to-peak value of the photomultiplier output modulated by the applied field. $I(\phi = 45^\circ)$ and $I(\phi = 0^\circ)$ are respectively the maximum and the minimum transmitted intensity values at zero field. (2) is particularly well suited to small θ values and assumes that Δn is field independent. For every θ values and especially for the largest one, we can directly determine the field induced tilt angle by applying a 1Hz square wave to the sample. At this frequency, it is easy to follow the switching of a given domain placed in a "black" state. When the field polarity is reversed, the sample is turned in a way to get again a "black" state. The angle associated to this rotation is connected to 2θ .

RESULTS

Before polymerization : effect of dilution

We investigated effects of the addition of 3%wt of reactive chiral monomers on the ferroelectric behavior of the G1 FLC compound which has a high spontaneous polarization (Figure 2). Results are summarized in figure 2 to figure 4.

It comes out that a large decrease of the total polarization happens when adding monomers. Values are lowered by a factor of 8. On the other hand, only slight variations are observed for the tilt angle (figure 4).

After polymerization : the cross-linking effect

Previously, we pointed out changes introduced by the chiral monomer. Now, we study effects of the cross-linked material on the total polarization and the tilt angle, for two different UV curing scenarii. While keeping constant the UV rate received by the sample, we choose two different polymerization processes : a high UV intensity for a short delay - 20mW/cm² for 10 min - and a low UV intensity for a longer delay - 2mW/cm² for 100 min.

As shown in figures 2 and 3, the last curing process leads towards greater polarization values when approaching room temperature. On the other hand, for every polymerization process, the same results are found for the tilt angle (figure 4).

In these micro-composite systems, phase separation is governed by both the chemical reaction initiated by the UV irradiation and the diffusion of the different compounds involved in the mixture.

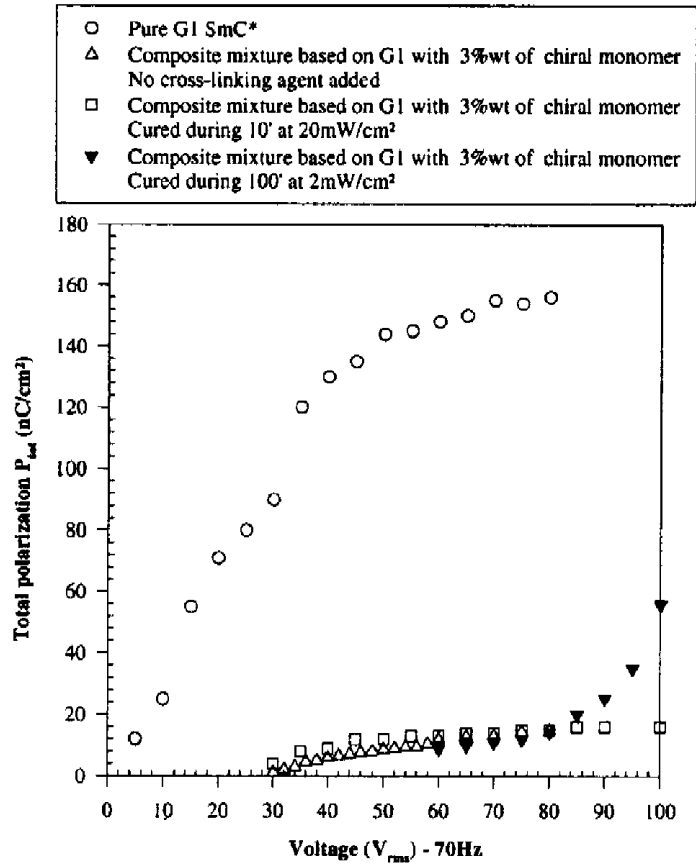


FIGURE 2. Variations of the induced polarization as a function of the applied voltage for various UV curing processes.

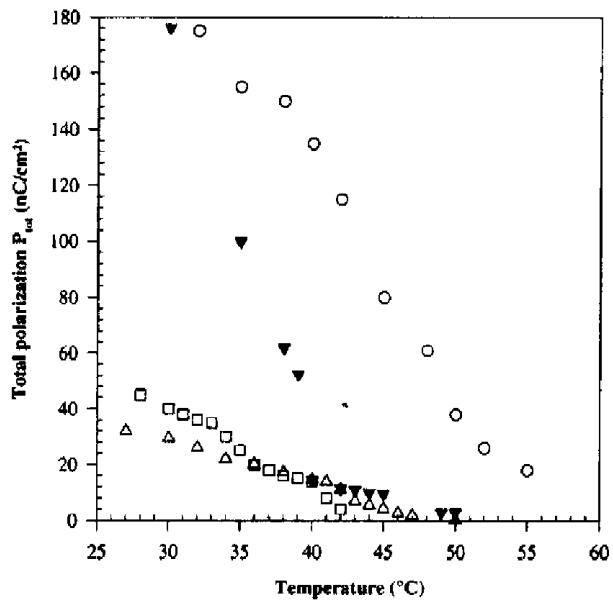


FIGURE 3. Variations of the induced polarization as a function of the temperature for various UV curing processes.

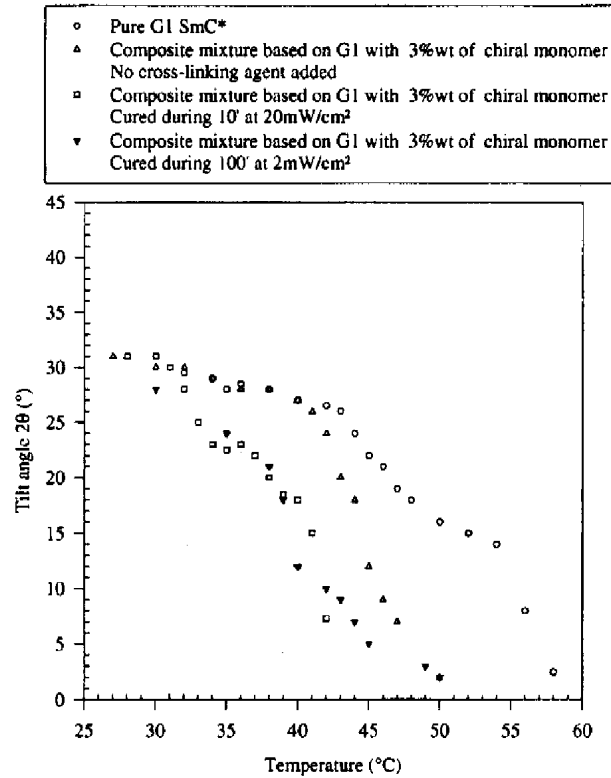


FIGURE 4. Variations of the tilt angle as a function of the temperature for various UV curing processes.

In fact, for the shortest irradiation delay and highest intensity, the first process prevails. As a result, the network may be expected thinner and its density higher [10]. Consequently, the smectic C* layers are strongly influenced by the network proximity. Then, the total ferroelectric polarization measured is lower than for the pure ferroelectric compound. Moreover, as the mesh of the network is thinner, it hinders the switching of the liquid crystal molecules [11]. For a lower UV intensity and a longer irradiation time, the resulting polymer network has a higher molecular weight since fewer radicals are produced. The formed network is less dense and perturbations due to the confinement are smaller. Hence, values closer to those of the pure FLC compound are observed for the induced polarization and the tilt angle.

Comparison with another FLC mixture

To check if these results are also valid for another ferroelectric liquid crystal, we carry out experiments on the commercial RD compound (Table II). Its spontaneous polarization is far smaller than that of G1. Figures 5 and 6 compare variations of the polarization versus the tilt angle which is nearly unaffected by the curing process. For the micro-composite based on G1 FLC,

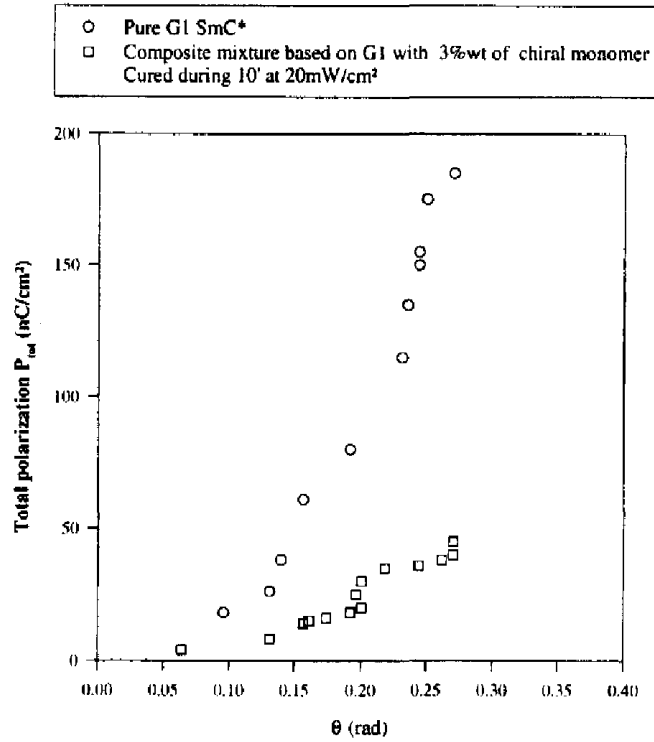


FIGURE 5. Variations of the total polarization as a function of the tilt angle for G1 FLC and for various UV curing processes.

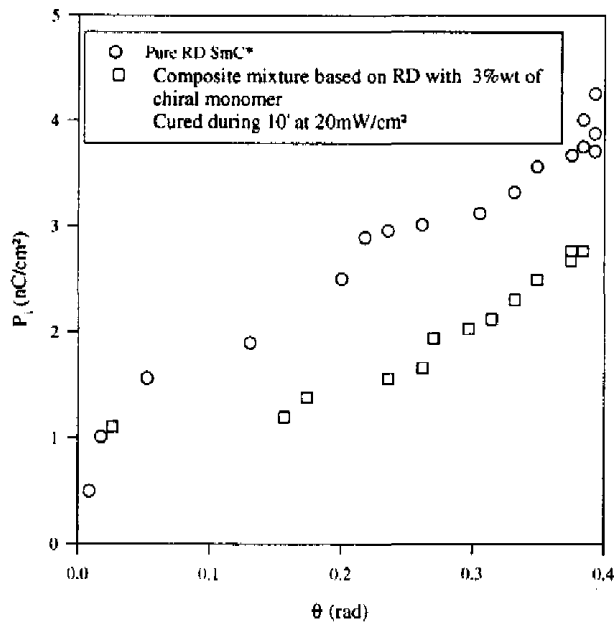


FIGURE 6. Variations of the induced polarization as a function of the tilt angle for RD FLC and for various UV curing processes.

the polarization is a power law of the tilt angle whereas it is rather linear for the RD FLC compound. It seems that the behavior previously described is dependent on the ferroelectric liquid crystal studied.

CONCLUSION

The effect of the UV curing conditions on the total polarization and the tilt angle has been investigated in a mixture made of a chiral photocrosslinkable LC and a FLC. Two different scenarii have been considered for the photo-cross-linking step : (a) a "high" light intensity applied for a "short" time and (b) a lower intensity applied for a longer time. It has been shown that while the admixture of photocrosslinkable liquid crystal involves a strong decrease in the total polarization with regard to the pure FLC, the polarization performance may be almost recovered or improved by using the (b) curing process, and the benefit of the polymer network for mechanical shock stability being present.

Further investigations will be devoted to electron microscopy studies of the network morphology (size, density) for the different cross-linked systems and to modifications of the anisotropy degree by applying an electric field during the UV-curing process.

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