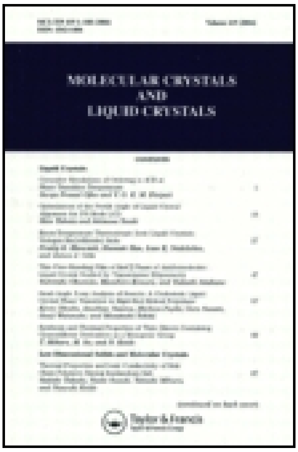

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Electroclinic Effect in a Polymer-Dispersed Ferroelectric Liquid Crystal

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We report on the electo-optic behaviour of a chiral smectic A material dispersed in a uv-cured polymer adhesive. Shearing during the polymerization-induced phase separation resulted in an alignment of the liquid crystal. The ease of preparation suggests applications as flexible displays or shutters. The results are compared to those of the pure liquid crystal.

Keywords: polymer-dispersed liquid crystals, ferroelectricity, electroclinic effect

1. INTRODUCTION

The smectic A phase can be described as a weakly defined layer structure consisting of molecules with their director orthogonal to the layer. If the smectic A phase is formed by chiral molecules a coupling between the tilt angle Θ and the electric polarization P occurs ($P = k\Theta$). Thus an external electric field being applied perpendicular to the layer normal causes the director to tilt thereby inducing a polarization. These electroclinic, or soft-mode properties have been discovered by Garoff and Meyer in 1977.[1,2] Generally, the field-induced tilt angle Θ is a linear function of the applied field E ($\Theta = e_cE$) with e_c, the electroclinic coefficient. If an A − C phase transition is exhibited by the compound the electroclinic coefficient diverges on approaching the transition temperature T_c; in the simplest case: $e_c = k/\alpha(T - T_c)$ where α denotes the coefficient of the Θ^2-term in the Landau free energy expansion. A characteristic feature of the electroclinic effect is its field-independent switching time τ, which is expected also to diverge at T_c according to $\tau = \gamma_0/\alpha(T - T_c)$ where γ_0 corresponds to the tilt viscosity.

The early investigations were all carried out on “DOBAMBC” where the tilt-polarization-coupling is comparably small. It was not until 1987 the effect was considered applicable for electro-optic components.[3–5] When new liquid crystals with high spontaneous polarization in the chiral smectic C phase were discovered and a new cell geometry with the layers aligned uniformly perpendicular to the glass plates (upright bookshelf geometry) was established, the large electrically induced director tilt in combination with the submicrosecond speed spurs the design of fast optical modulators etc.[6]

On the other hand, polymer-dispersed liquid crystals (PDLC) have attracted great interest in the past few years[7] promising use as large area flexible displays. So far, studies mainly focused on droplets of nematic[7] or cholesteric phases[8–10] embedded in a polymer. The nematic PDLC display provides switching between an opaque and a transparent state. Polymer-dispersed cholesteric systems become coloured under the influence of an electric field due to selective reflection. Both effects do not require any prealignment of the molecular director in the field-off state.

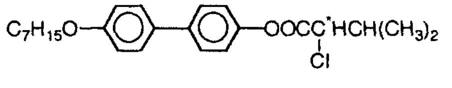
The precondition of uniform alignment seems contradictory to the use of smectic polymer-dispersed systems. However, Lackner *et al.* claimed that nematic liquid crystals can be partially prealigned using either mechanical flow, or electric, or magnetic fields during polymerization-induced phase separation.[11] In our own experiments we could demonstrate that polymer-dispersed chiral smectic C phases are also alignable. The electro-optical effect was attributed to helical unwinding.[12] Recently, Zyryanov *et al.* presented an alignment technique for polymer-dispersed ferroelectric liquid crystals (PDFLC) and studied the electro-optic behaviour of a polymer-dispersed smectic C* system.[13] Ferroelectric polymers have been embedded in an epoxy adhesive together with polychroic dyes to achieve flexible, optically bistable ferroelectric LCDs.[14]

In the present paper we demonstrate that a polymer-dispersed chiral smectic A phase can be used for electro-optic applications. It is shown that the layer normal can be aligned by shearing the sample. The alignment provides reasonable contrast between crossed polarizers when d.c. fields are applied to the sample.

2. EXPERIMENT

The system studied consists of a chiral monomer liquid crystal dispersed in a non-mesogenic polymer matrix. The pure ferroelectric liquid crystal (1) exhibits strong coupling between induced polarization and tilt angle.[3] The phase sequence is: Cryst 72°C (S_H 64°C S_G 71°C)S_C^* 73°C S_A 81.5°C Iso.

(1)



Polymer-dispersed samples were produced by polymerization-induced phase separation[15] at elevated temperature using the uv-curable material NOA65 (Norland). The liquid crystal, heated above its clearing temperature, was mixed with the uv-curable monomer in a 1:2 ratio and sandwiched between two ITO-coated glasses. Glass cylinders of 4 μm in diameter were used to control the sample thickness. The sample was exposed to type A uv-light with an irradiance of approx. 30 mW/cm^2 for a few seconds. During the exposure the glasses were sheared in order to elongate the droplets dispersed in the uv-cured polymer film.

To study the optical properties the sample placed in a hot stage (Mettler FP2) was mounted in a macroscope between crossed polarizers and illuminated with white light. The transmitted light intensity was detected by a photomultiplier tube (PMT) connected to the macroscope. The crossed polarizers were adjusted at 22.5° and 112.5° with respect to the optical axis of the sample. Voltages up to 200 V_{PP} were applied to the 4 μm thick film. For dynamic investigations a square wave was applied to the sample and both the applied voltage and the PMT signal were recorded with a 100 MHz storage oscilloscope. The induced tilt angle Θ was determined by computer-controlled simultaneous rotation of the crossed polarizers until minimum transmittance was found for each positive and negative d.c. bias applied to the sample. By changing the bias voltage and the temperature we measured Θ as a function of voltage and temperature.[16]

3. RESULTS

A. General properties

By sliding the cover glass of the sample during polymerization cylindrical droplets with an average diameter of 2.5 μm were obtained. The transmitted light intensity on a macroscopic scale as a function of the azimuthal angle φ between the shear direction and the orientation of the polarizers exhibits the periodicity of $\pi/2$. This indicates that the sample behaves uniaxially birefringent with their layer normal presumably parallel to the shear direction.

The SmA phase is found between 68.6 and 74.4°C, i.e. in a considerably smaller temperature range and at lower temperatures than observed for the pure material. This change is attributed to the heterogeneity of the polymer-dispersed systems and found to be dependent on droplet size.

B. Electrooptics

The coupling between tilt angle and the applied voltage is illustrated in Figure 1. From the slopes in Figure 1 we obtain values of $e_c = 0.5 \cdot 10^{-3}$ and $2.1 \cdot 10^{-3}$

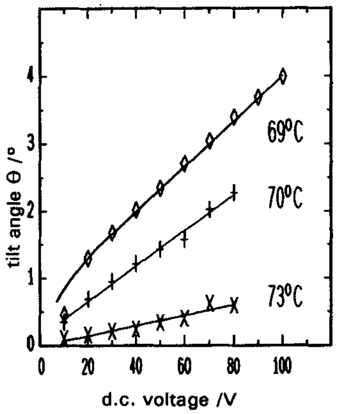


FIGURE 1 Induced tilt angle versus applied d.c. voltage at various temperatures before the heating procedure.

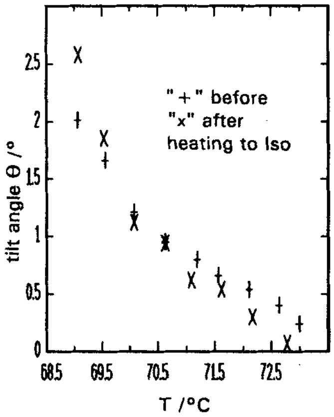


FIGURE 2 Induced tilt angle versus temperature at an applied d.c. field of 40 V/4 μm.

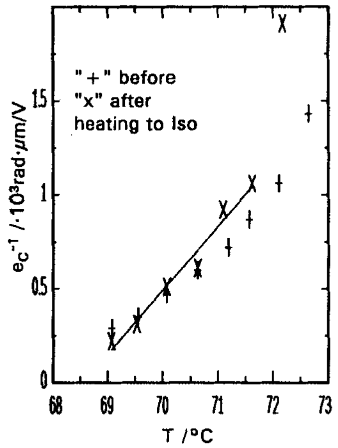


FIGURE 3 Reciprocal electroclinic coefficient versus temperature at an applied field of 40 V/4 μm.

rad · μm/V for the electroclinic coefficient at 73°C and 70°C, respectively. For lower temperatures the polymer-dispersed system shows a non-linear response which is observed in some monomer systems, too.[6] Furthermore, we have to consider an electric field-induced shift of the S_A-S_C^* transition temperature into a two-phase region to be responsible for the nonlinearity.

As in pure SmA materials the induced tilt angle rises with decreasing temperature for the polymer-dispersed system (Figure 2). This behaviour becomes even more distinct when the sample has been repeatedly heated close to the S_A-Iso transition temperature. This change might be controlled by diffusion.

In Figure 3 we show the temperature dependence of the reciprocal electroclinic coefficient before and after the heating near to the S_A-Iso transition. We calculated the slope for tempered sample to $3.4 \cdot 10^2$ rad · μm/(V · K). This value is about one order of the magnitude higher than measured for the pure monomer.[3] The increase can be due to a diminished coupling constant k and/or an increased coefficient of

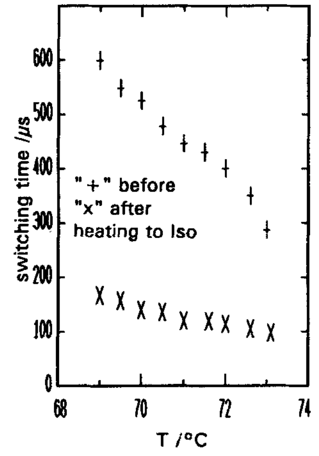


FIGURE 4 Switching time versus temperature on a voltage step of 80 V/4 μm.

the Θ^2-term in the Landau free energy expansion α. Moreover, the electric field acting on the liquid crystal droplet might be smaller than the external one: on approaching the phase transition from above the dielectric constant of the LC material is increasing whereas the value of the polymer remains constant, therefore the effective field should decrease.[7]

The optical switching time was measured as a function of temperature on a voltage step from -40 V to $+40$ V (Figure 4). In our polymer-dispersed sample the optical switching time, defined as a 90% change of the optical transmission, ranges from 100 μs to 170 μs, i.e. is 1–2 orders of magnitude longer than that of the pure bulk material. This might be due to the increased tilt viscosity γ_Θ: when the polymer-dispersed droplets are understood as microscopic cells of extreme small cell gaps, the switching time becomes dependent on the cell thickness. Decreasing the cell gap results in an increased switching time as reported in Reference 6. Furthermore, an incomplete phase separation results in impure liquid crystal droplets with a changed behaviour. In the progress of our investigation we found that the switching time can be decreased by repeated heating the cell near to the S_A-Iso phase transition (Figure 4). We suspect a diffusion-controlled transport to be responsible for this finding. It is interesting to note that no clear divergence of the switching time is observed in our sample.

4. CONCLUSION

We have shown that electroclinic switching is obtained when the chiral smectic A phase material is embedded in a polymer matrix. The transition temperatures are considerably depressed and the phase width decreased. The alignment of the liquid crystal was achieved by mechanical shear during polymerization-induced phase separation which, consequently, produced a macroscopic birefringence. The different electro-optical behaviour of pure and polymer-dispersed samples could

not be explained on the base of the performed experiments. The results presented suggest applications as submillisecond shutters or flexible displays.

Acknowledgment

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