Optica Applicata, Vol. XXXII, No. 4, 2002

Electro-optical properties of polymer-dispersed liquid crystals in antiferroelectric SmC_A^* phase

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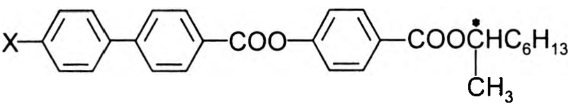
Static and dynamic electro-optical properties of polymer-dispersed liquid crystals (PDLC) composites containing antiferroelectric liquid crystal phase SmC_A^*, have been measured. The effect of PDLC morphology on tristable switching has been studied. Differences between electro-optical behaviour of the same liquid crystal in PDLC and classical thin layer are discussed.

1. Introduction

Polymer-dispersed liquid crystals (PDLC) are heterogeneous composites in which liquid crystal droplets of micrometer size are embedded in a solid polymer matrix. They are very interesting due to the curvilinear geometry of the confined liquid crystal and the pronounced effect of its interaction with the surface of polymer cavity as well as possible size effects [1], [2]. Such structures containing nematic and chiral nematic liquid crystals are well known and used due to their simple technology, low cost and good electro-optical performance. The main electro-optical effect observed in those composites is so-called electrically-induced light transmission [2]. PDLC containing ferroelectric smectics SmC* have also been carefully studied [3]–[5]. In this case bistable effects of helix unwinding, similar to the surface stabilised ferroelectric liquid crystal and deformed helix ferrfoelectric effects known for thin layers [6], are observed. On the other hand, PDLC containing antiferroelectric SmC_A^* have been studied only recently [7], [8]. One could expect that such composites should present behaviour analogous to PDLCs containing SmC* phase, *i.e.*, that electro-optical effects should be similar to those observed for this phase in thin layer geometry. In particular, field-induced transition from the antiferrolectric to ferroelectric state, *i.e.*, effect resembling tristable switching of thin SmC_A^* layer should be observed. This suggestion has been confirmed in earlier works [7], [8]. In this paper we present electro-optical properties of a few new antiferroelectric liquid crystal mixtures embedded in a polymercaptoester matrix.

2. Experimental

Three antiferroelectric mixtures with codenames W-101, W-101A and W-104, obtained at the Institute of Chemistry, Military University of Technology, Warsaw, Poland, have been chosen as liquid crystal materials. The composition and the essential properties of those mixtures are described in detail elsewhere [9], [10]. The general formula of their components is as follows:



where X stands for different alkyl, alkoxy, alkoxyesther substituents, including fluorinated ones.

PDLC composites have been prepared by photopolymerisation-induced phase separation [4], [11] between glass plates of 0.7 mm in thickness with deposited conducting ITO thin layer. Photocurable polymerkaptoesters NOA-65 (mainly) and NOA-68 (Norland Optical Adhesives) have been selected as the prepolymers. Glass spacers of 6, 9 or 14 μm in thickness have been introduced into the prepolymer – liquid crystal mixture to secure desired PDLC film thickness. The mixture has been deposited on a glass plate, covered by the other plate and weighted to reach the spacer's thickness. Such a sample has been heated up to the temperature of smectic phase appearance and then irradiated by UV lamp Bondwand (electrolite). Liquid crystal droplets in the PDLC obtained in a phase separation process have had nearly spherical shape and a random orientation of optical axes, which effects in an optically isotropic structure.

In order to obtain an optically anisotropic structure a laminar flow of liquid crystal-prepolymer mixture and a bias electric field ($E \sim 8$ V/μm, $f \sim 10$ Hz) have been applied during the curing of the composite binder. The anisotropic shape of LC droplets has been obtained due to a movement of the upper glass plate with a speed of approximately 1 mm/s which caused a flow of a prepolymer. The application of an electric field has improved an optical axis uniformity, which affected the optical contrast of the electro-optical switching. Irradiation conditions have been chosen experimentally to obtain such an elongation of droplets which yields the sharpest optical contrast of the given sample (UV flux intensity of 5 – 20 mW/cm^2). Optical axes in droplets obtained in this way have been oriented approximately along the flow direction, hence long axes of LC droplets. Such a preparation method has been used for all materials with similar results.

Electro-optical properties of PDLC composites have been measured using the set-up presented in Fig. 1. It consisted of the driving PC, the heating stage (Linkam), the HP54501A oscilloscope and the HP33122a function generator (Hewlett –Packard), the polarising microscope Biolar PI (PZO), the photodetecting system PIN 20 (FLC Electronics Inc.) equipped with silicon photodiode BPW 34 (Siemens) with amplifying module (detector responsivity factor $R^D > 300$ mA/W at 600 nm, frequency range 0 – 5 MHz, linearity better than 3% at a full output). Measuring cell has acted as an active element in a birefractive system. A halogen light bulb powered by stabilised DC current supply has been used as a light source.

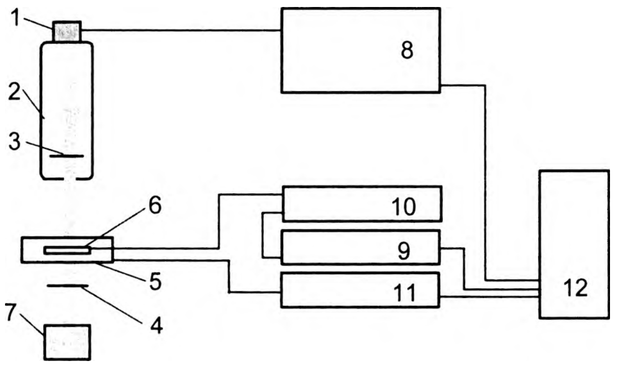


Fig. 1. Block scheme of the electro-optic measuring set-up: 1 – silicone diode photodetector, 2 – polarizing microscope, 3 – analyzer, 4 – polarizer, 5 – hot stage, 6 – PDLC sample, 7 – halogen lamp, 8 – oscilloscope, 9 – signal generator, 10 – voltage amplifier, 11 – hot-stage driver, 12 – driving PC.

Measuring cell has been placed into the thermostatic chamber THMSE 600 driven by the temperature controller TMS 90 (Linkam) securing temperature stability of 0.1 °C. The temperature changed at a rate of 0.01 °C/min.

The sample has been driven by HP 33120A function generator with FLC F20AD voltage amplifier (FLC Electronics Inc.). Photodetector output signal and driving pulses have been monitored by the oscilloscope. The system has been equipped with HP VEE 3.2 software for an automatic data acquisition.

The signal pulses with an arbitrary amplitude and filling factor of 30% have been used for cell driving.

3. Results and discussion

The application of an arbitrary rectangular electric signal to the PDLC sample has caused a tristable switching of SmC_A^* phase. In the case of the W-104 mixture also bistable switching in ferroelectric phase SmC* has been observed. Those effects, compared in Fig. 2, have been fully reversible. Modulation amplitude of light beam by the rectangular signal linearly increased with an amplitude of applied voltage up to its saturation (see Fig. 3).

The optical contrast measured between off-state and on-state (see Fig. 4) has been by 50 – 70% lower compared to the same mixture measured in thin layer of the same thickness. This has been caused by the fact that only part of the whole layer (liquid crystal droplets) can be switched by electric field, moreover some droplets do not contribute to the modulation due to the lack of distinguishable optical

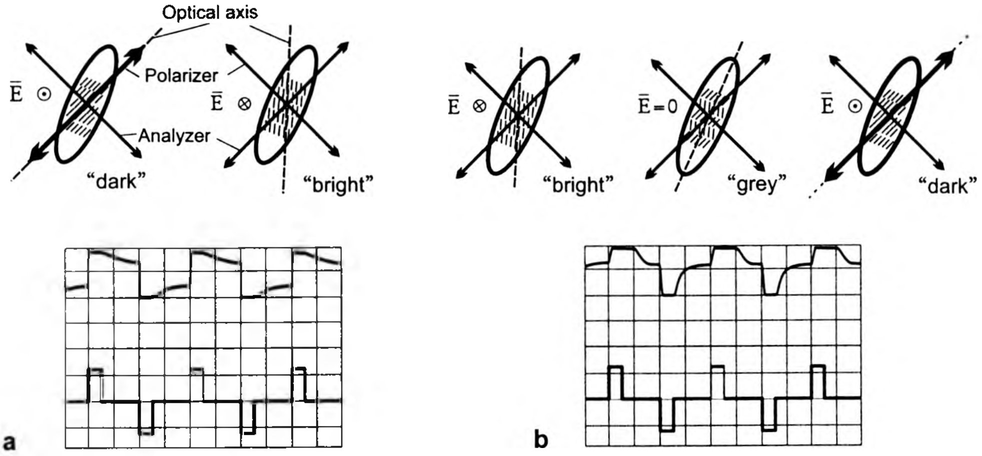


Fig. 2. Schematic oscilloscope view of saturated electro-optical switching of PDLC containing W-104 mixture by 100 Hz signal. Bistable switching of SmC* phase at 85.5 °C (a), tristable switching of SmC_A^* phase at 75 °C (b), mean droplet volume ~15 μm^3, mean droplet aspect ratio ~10.

axes. There has also been observed a significant effect of the surface of polymeric cavity on the alignment of mesogenic molecules, especially at points of ellipsoidal droplets where the curvilinear geometry introduced by an anchoring is the most pronounced.

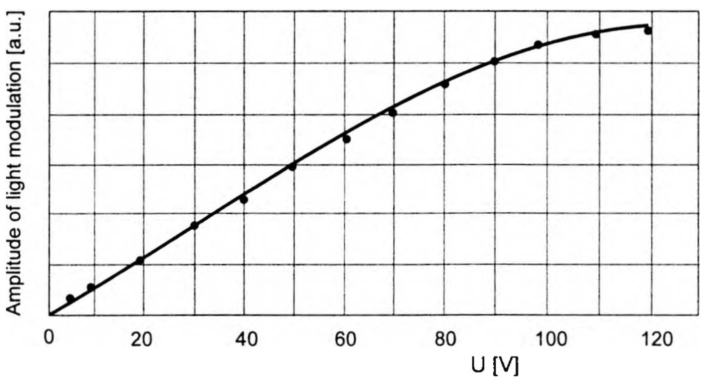


Fig. 3. Amplitude of light modulation *vs.* applied voltage for PDLC containing SmC_A^* phase of W-104 at 30 °C, mean droplet volume ~15 μm^3, mean droplet aspect ratio ~8.

The analogous behaviour has been observed in the case of PDLC containing SmC* phase. As a result, a significant part of the liquid crystal volume is not reoriented by the driving electric field even for its large intensity.

Another reason for the relatively low optical contrast is the presence of very small droplets of liquid crystal which arise due to fast curing and too large amount of liquid crystal in samples under study (relatively low solubility of liquid crystal mixtures in the prepolymer). This effect can probably be avoided by a careful choice

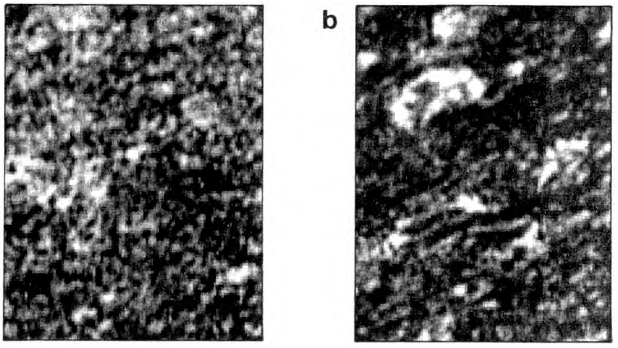


Fig. 4. Microscopic view of the PDLC film containing SmC_A^* phase of W-104 at 75 °C. **a** – off-state, **b** – on state; film thickness 8 μm, mean droplet volume ~15 μm^3 mean droplet aspect ratio 8.

of the properties of system components and preparation parameters for a given system, leading to the highest possible concentration of sufficiently large liquid crystal droplets.

As it has been expected, the optical contrast, *i.e.*, the ratio of intensity of transmitted light I_{on}/I_{out} in on-state and off-state, respectively, decreased with temperature (see Fig. 5) due to the decrease of the tilt angle.

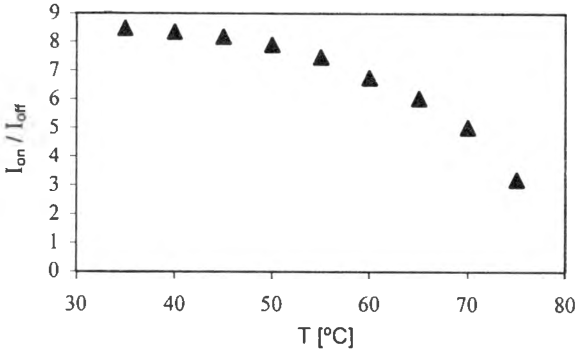
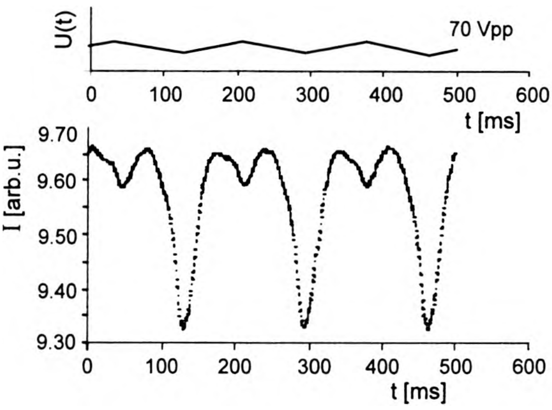


Fig. 5. Optical contrast *vs.* temperature for PDLC film containing 20% by weight of W-101A mixture; film thickness 8 μm, mean droplet volume ~15 μm^3, mean droplet aspect ratio 10.

The elongation of liquid crystal droplets improves the uniformity of layer switching, however, it reduces optical contrast due to a decrease of the reoriented liquid crystal volume and also the equivalent thickness of liquid crystal inside the sample. For example, if spherical droplet diameter of 3 μm is elongated up to the aspect ratio of 10, the shorter axis of an ellipsoid is about 0.67 μm, while the droplet thickness in the vicinity of its tops is remarkably smaller. It means that nearly all liquid crystal volume has strongly curvilinear geometry, different from thin-layer one, and the significant part of the droplet cannot undergo antiferroelectric –ferroelectric transition.



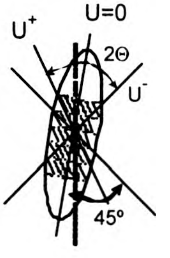


Fig. 6. Electro-optical response to triangle signal of PDLC film containing 20% bw. of W-101 mixture measured at room temperature; film thickness 8 μm, mean droplet volume ~15 μm^3, mean droplet aspect ratio 10.

The possibility of obtaining a greyscale in samples under study has been investigated using triangle driving signals. An example of the electro-optical response of a sample to the applied triangle electric signal is presented in Fig 6. This particular example has been chosen to show the complexity of phenomena observed in PDLC containing SmC_A^* phase. The orientation of the optical axis at the negative polarisation (negative potential at the top electrode) has been chosen to match the orientation of the polarizer in order to obtain the lowest light transmittance. The reorientation of the optical axes of droplets with an increase voltage has caused a rapid rise of the light intensity reaching its maximum at the orientation of 45 deg regarding to the initial position. Further voltage rise has caused partial transmittance to decrease as a result of due to moving the director beyond its most favourable orientation of 45 deg. The saturation has taken place at an angle of 2θ which is about 60 deg at room temperature for mixtures under study. This orientation (being less favourable for a transmission) has been a reason for the partial decrease of transmission at the maximum positive polarisation. This behaviour suggests that materials with tilt angle close to 22.5 deg at the operation temperature should be used for applications. Nevertheless the results show that it is possible to obtain grayscale in SmC_A^* containing PDLC.

The switching characteristics of samples under study slightly depend on the conditions of sample preparation. This effect is connected with an imperfect alignment of liquid crystal inside droplets in the specific sample. First, as already mentioned, part of liquid crystal volume at points of ellipsoidal droplets has different alignment from that of the central part of the droplet. Second, microscopic observations of switching have shown that in some droplets optical axes are aligned in random directions. It has been considered to be a source of a noise decreasing electro-optical contrast. This effect is less pronounced at temperatures higher than the room one, nevertheless it shows the essential influence of composite preparation parameters on its electro-optical properties.

The rising time T_{on} has been measured as a period of time during an increase of light intensity from 10% up to 90% of the maximum value (T_{10-90}). The falling time has been taken as a time change of light intensity from 90% to 10% during cell relaxation.

The total switching time τ of samples studied varied from 0.1 to 0.5 ms, while the rising time T_{10-90} varied from 2 to 60 μs depending on the mixture used and the voltage applied. In Figs. 7 and 8 the dependences of total switching time on temperature and voltage are presented for different PDLC samples.

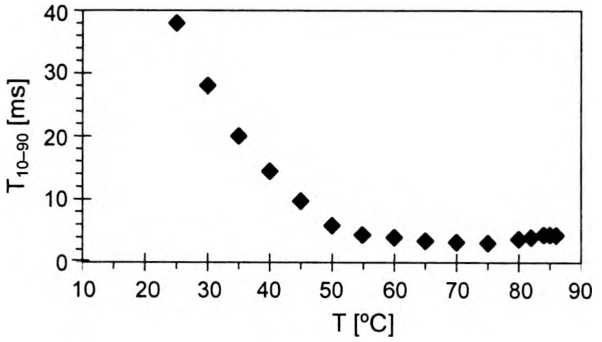


Fig. 7. Response time of PDLC film containing 20% b.w. of W-101A mixture *vs.* temperature; film thickness 8 μm, mean droplet volume ~15 μm^3, mean droplet aspect ratio 10.

As one can see, the response time in SmC_A^* phase decreases with temperature, while after the transition to SmA phase it slightly increases because there appear another electro-optical effects. This behaviour is analogous to that one observed in the case of a thin layer of the same mixture [9]. The response time of the PDLC sample is shorter, however, due to the more pronounced effect of surface interactions (greater stiffness of the liquid crystal), and in the case of W-101A mixture it is about 2 μs at temperatures higher than 60 °C, while for thin (1.9 μm) layer of the same mixture it is about 3 μs in the same temperature range.

An example of the static electro-optical characteristics for the mixtures under study is presented in Fig. 9. This result confirms that relatively high voltages are required to drive PDLC samples containing SmC_A^* phase.

Electro-optical parameters of the PDLC samples slightly depended on the size of liquid crystal droplets. The switching voltage decreased, while the response time increased with an increase of the size of droplets by about 20% in the range being studied, *i.e.*, mean droplet volume from ~10 to 200 μm^3, mean aspect ratio ~10. There are no changes of electro-optical parameters of samples obtained during the period of 9 months.

The results obtained for composites containing W-101 and W-101A mixtures exhibited slightly less homogeneous alignment of liquid crystal in droplets than in the case of W-104 mixture.

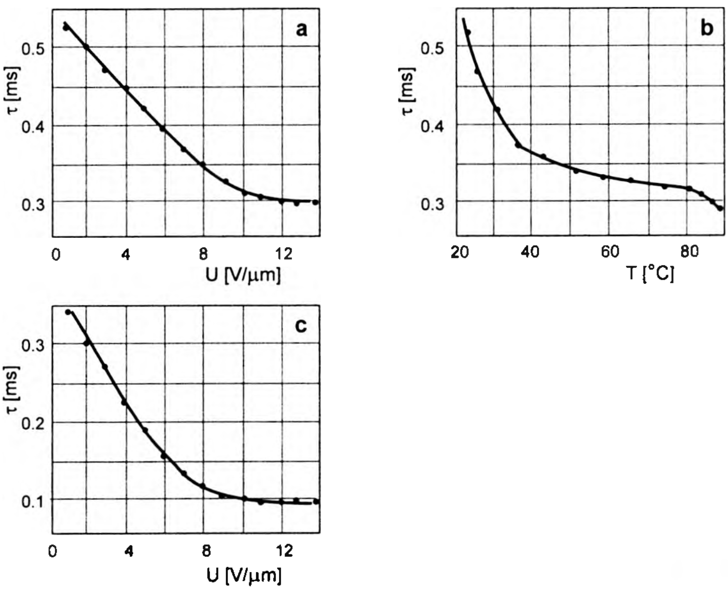


Fig. 8. Dependence of total switching time PDLC containing: SmC_A^* phase of W-104 mixture on: a — applied voltage (at $T = 30$ °C), b — temperature (at $U = 4$ V), c — SmC* of the same mixture on applied voltage, $T = 85.5$ °C; film thickness 8 μm, mean droplet volume ~15 μm³, mean apect ratio ~10.

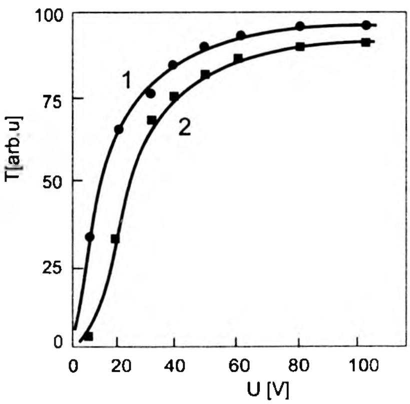


Fig. 9. Static electro-optical characteristics of PDLC containing: 1 — W-104 and 2 — W-101 mixtures; $T = 40$ °C; film thickness 8 μm, mean droplet volume ~15 μm³, mean aspect ratio ~10.

However, W-101 and W-101A mixtures are also interesting for applications due to comparable electro-optical characteristics. Homogeneity of the alignment should probably be much better for mixtures having also nematic phase N as it is in the case of PDLC containing SmC* phase [4].

From the point of view of application [6], it is purposeful to use mixtures with 45° tilt, which is possible using compounds analogous to thoes studied in the present work. This should result in a better optical contrast and allow us to use simpler driving schemes for black and white, and also greyscale modes. It appears necessary to prepare antiferroelectric liquid crystal mixtures better adjusted to PDLC systems.

4. Conclusions

The following conclusions can be derived from conducted studies:

1. The polymer-dispersed antiferroelectric smectic liquid crystals under study exhibit electro-optical behaviour similar to that of the same materials in the form of a thin layer, *e.g.*, tristable switching.

2. Driving voltages are higher, while switching times are slightly shorter than in the case of thin-layer geometry due to the more pronounced anchoring effects inside polymer cavity.

3. Optical contrast is much lower than in the case of thin-layer geometry because only part of the volume of liquid crystal droplets in PDLC film can be reoriented by electric field.

4. Results obtained depend on temperature and the morphology of PDLC layer.

Acknowledgment – This work has been supported by the Polish State Committee for Scientific Research (KBN) (grant No. 3 T0 9A 13517 and MUT Statutory Task PBS171) and INCO-COPERNICUS grant IC15-CT98-0806.

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Received May 16, 2001
in revised form May 6, 2002