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OPTO-ELECTRONICS REVIEW 14(4), 319–322

DOI: 10.2478/s11772-006-0043-8

Electrooptic study of antiferroelectric mixtures for display application

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The aim of this paper is to study the influence of electric field on alignment of para-, ferro- and antiferroelectric phases in the vicinity of SmA – SmC* or SmC* – SmC_A^* phase transitions as to obtain mono-domain cells. Four mixtures studied (W-193B, W-193B-1, W-201, W-204D) show the SmC_A^* phase in a wide room temperature range. Measurements of the spontaneous polarization versus temperature by using reversal current method give an answer to the question, what kind of the transitions take place between para-, ferro- or antiferroelectric phases using the Landau mean field theory. Optimal electrooptic parameters for different compositions of the mixtures such as tilt angle, spontaneous polarization and saturation voltage have been measured to compare parameters of the mixtures studied.*

Keywords: antiferroelectric mixtures, tilt angle, spontaneous polarization.

1. Introduction

Antiferroelectric liquid crystals (AFLCs) have become a very interesting field of research due to their practical applications in science and technology. It seems to be very important to study electrooptic properties of such systems. There is a close relation between the anisotropy of physical properties, molecular structures and the phase diagrams of chiral compounds [1–4].

In the scope of this paper, four liquid crystalline mixtures, namely W-193B-1, W-193B, W-204D, and W-201, have been studied to find optimal electrooptic parameters, such as tilt angle, spontaneous polarization, and saturation voltage. Measurements of the spontaneous polarization and tilt angle versus temperature could give an answer to the question, what kind of the transition takes place between para- and ferroelectric phases. One can determine the order of the transition based on temperature dependence of the tilt angle and spontaneous polarization by using the Landau mean field theory. According to the extended mean-field theory [4] the spontaneous polarization P_S and the tilt angle θ should obey the square root law of Eqs. (1a) and (1b) with the critical exponent $\beta = 0.5$.

$$P_s(T) = P_o(T - T_c)^{\beta}, \tag{1a}$$

$$\theta(T) = \theta_o(T - T_c)^{\beta}. \tag{1b}$$

Very fast development of liquid crystal display (LCD) technology has focused scientific research on finding new antiferroelectric liquid crystal (AFLC) materials with short switching time and high optical tilt angle in the room temperature range. AFLC having tilt angle equal to 45 degree, the so-called orthoconic antiferroelectric liquid crystal (OAFLC), could give a perfect dark state between crossed polarizers [5–7]. From this point of view, the liquid crystalline mixtures fulfil such requirements. Using electrooptic cell one can study influence of electric field on physical properties of liquid crystalline phases [8–13].

2. Experimental

The properties of four different mixtures, namely W-193B, W-193B-1, W-201, and W-204D have been studied. Each mixture exhibits antiferroelectric phase in a wide temperature range around room temperature. During heating, the ferroelectric SmC* and then paraelectric SmA* phases appear before transition to the isotropic phase.

The differential scanning calorimetry (DSC) method (using Perkin Elmer Pyris 1 DSC calorimeter) has been applied to find the transition temperatures and to study stability of the mixtures examined. The polarizing microscope Jenapol with Mettler Toledo hot stage, Agilent 33120A wave form generator, FLC Electronics F20ADI amplifier, and digital oscilloscope DSO6102A have been used to perform the tilt angle and spontaneous polarization measurements as well as texture observation of the mixtures studied. Temperature dependences of spontaneous polarization, tilt angle and threshold voltage have been determined at a frequency of 50 Hz using ITO cell (made by AWAT Company) having thickness equal to 1.7 μm. The measurements of P_S have been done by reversal current method and optical tilt angle double has been measured between two extinction positions [14].

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3. Results and discussion

DSC measurements have been done on the samples of ca. 8 mg at heating/cooling rate equal to 10 K/min between –60°C and 120°C. DSC curves taken for W-201 mixture are presented, as an example in Fig. 1. As one can see, the anomalies connected with transitions Cr. – SmC_A^*, SmC_A^* – SmC^*, SmC^* – SmA^*, SmA^*- I are well visible. For other three mixtures, the anomalies at the phase transitions are weaker. Additionally, any melting point during heating and also any crystallization upon cooling were not observed on the DSC curves.

Using polarizing microscope textures observation, one can determine the nature of the liquid crystalline phases. The characteristic textures taken in antiferroelectric phase for each mixture: W-204D, W-193B, W-193B-1, and W-201 are presented in Figs. 2(a), 2(b), 2(c), and 2(d), respectively. The horizontal contour in the middle of the photos is a border line of the ITO electrode. Above this line, there is a mono-domain obtained by applying electric field (sinusoidal, ca. $V_{p\text{-}p}$ = 100 V, ν = 10 Hz) in the paraelectric SmA^* phase during cooling down. It is quite easy to obtain very well aligned antiferroelectric SmC^*_A phase under these conditions for all mixtures studied.

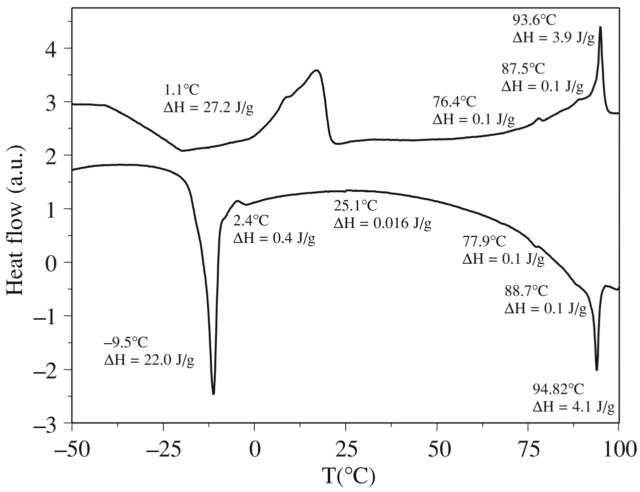

Fig. 1. DSC curves taken for W-201 mixture at heating/cooling rates equal to 10 K/min.

Based on DSC results and texture observation under electric field, it is seen that three mixtures studied (W-193B-1, W-193B, and W-204D) are very stable and easily aligned. Therefore one can conclude that they could be applied in LCD technology. The phase transition Cr. –

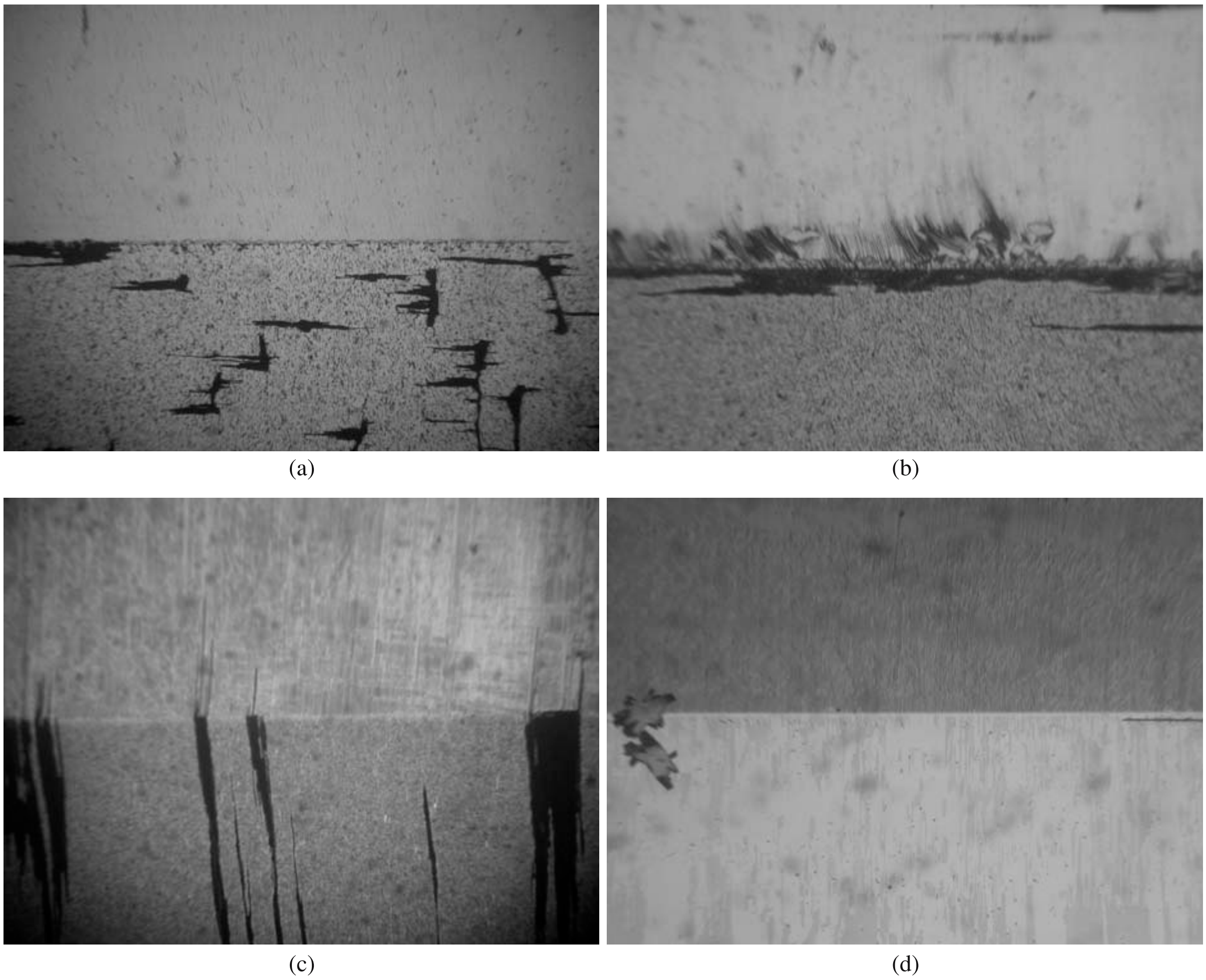

Fig. 2. Textures of antiferroelectric phase taken for (a) W-204D, (b) W-193B, (c) W-193B-1, and (d) W-201.

SmC_A^* for W-201 mixture occurs at room temperature during heating and cooling what is visible on DSC curves as well as under polarizing microscope. However, there are other different parameters such as spontaneous polarization, tilt angle and threshold voltage which are very important from the point of view of applications.

Measurements of spontaneous polarization and tilt angle versus temperature have been done in the ferro- and antiferroelectric phases on the mono-domain cells (see Fig. 3). Based on the temperature dependence of the tilt angle and spontaneous polarization, it is possible to determine the order of the transition by fitting Eq. (1) to experimental data. Fitting parameters are gathered in Table 1. For three of four mixtures studied (W-204D, W-193B, and W-193B--1), the β parameter obtained from temperature dependence of spontaneous polarization is ca. 0.4 and is smaller than the theoretical value 0.5 predicted for the second order transition. Moreover, these transitions are not continuous ones. Additionally, all β parameters obtained from the temperature dependence of tilt angle are equal to ca. 0.2. Based on the results for all mixtures studied, the presented above transition to paraelectric SmA* phase cannot be interpreted as the second order one. On the other hand, because of applying strong electric field (100 V) there is no evidence of the SmC* – SmC_A^* transition on temperature dependence of spontaneous polarization and tilt angle even this transition is of the first order type.

Table 1. The parameter β obtained by fitting Eq. (1) to experimental data.

	W-204D	W-193B	W-193B-1	W-201
$P_S(T) \rightarrow \beta$	0.41	0.40	0.42	0.21
$\theta(T) \rightarrow \beta$	0.21	0.21	0.17	0.23

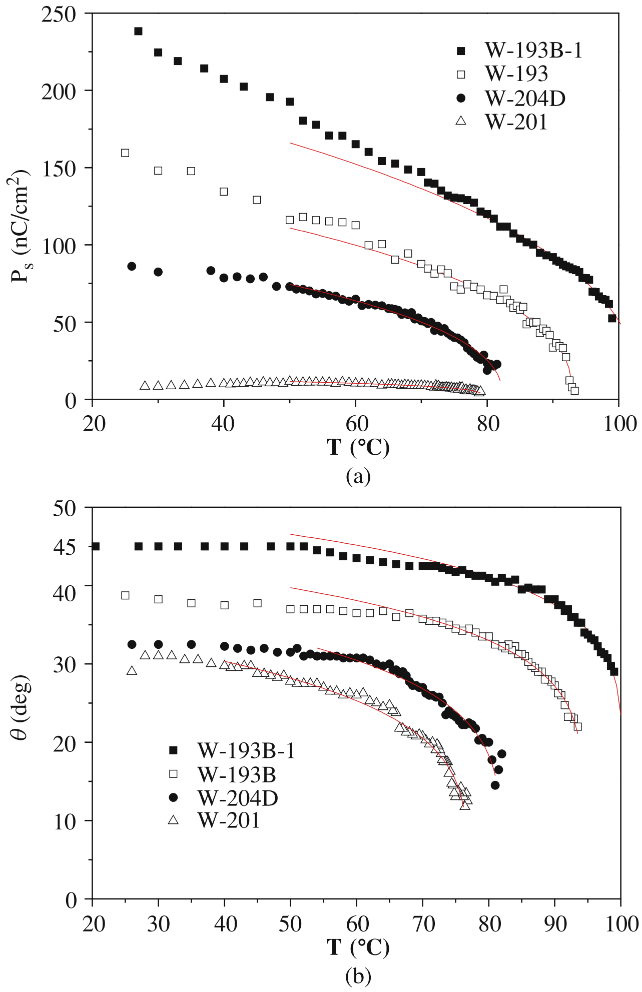

Fig. 3. Temperature dependence of spontaneous polarization (a) and tilt angle (b) for all mixtures studied.

The voltage, at which the dechiralization lines appear under the polarizing microscope, one can call a threshold voltage. Temperature dependence of the threshold voltage $V_C(T)$ has also been measured (see Fig. 4). These dependences are almost linear and threshold voltage is growing up with decreasing temperature for all mixtures studied since the viscosity is increasing.

Measurements of spontaneous polarization versus electric field have been done for the antiferroelectric SmC_A^* phase at room temperature. The results are shown in Fig. 5. It is seen that there is a critical value of voltage applied, the so-called saturation voltage V_{SAT} ($V_{SAT} = E_{SAT}d$, d is the thickness of the cell), different for different mixtures, at which the spontaneous polarization rapidly grows up to the saturated value.

The characteristic parameters such as the spontaneous polarization P_S, the tilt angle θ, the threshold field E_C, and the saturation field E_{SAT}, taken at room temperature, are gathered in Table 2. W-193B-1 mixture exhibits the highest value of spontaneous polarization (238.4 nC/cm^2) as well as tilt angle (45 deg) contradictory to W-201 mixture (P_S =10.5 nC/cm^2 and θ = 31 deg). On the other hand, the saturation field E_{SAT} is the highest for W-201 and the smallest for W-193B-1. There is no visible correlation between threshold field and spontaneous polarization or tilt angle for the mixtures studied.

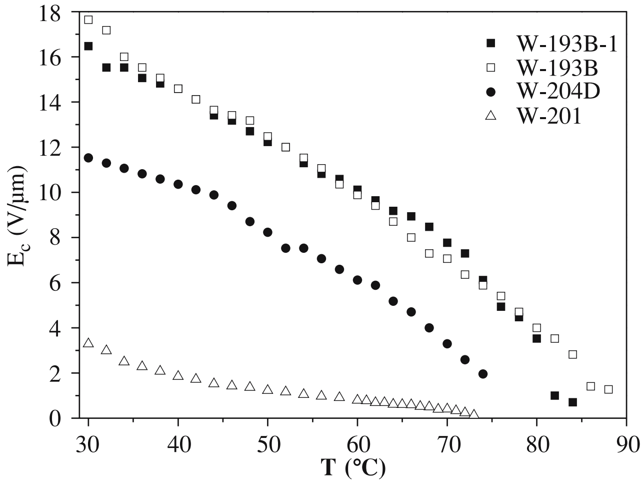

Fig. 4. Temperature dependence of threshold voltage for all mixtures studied.

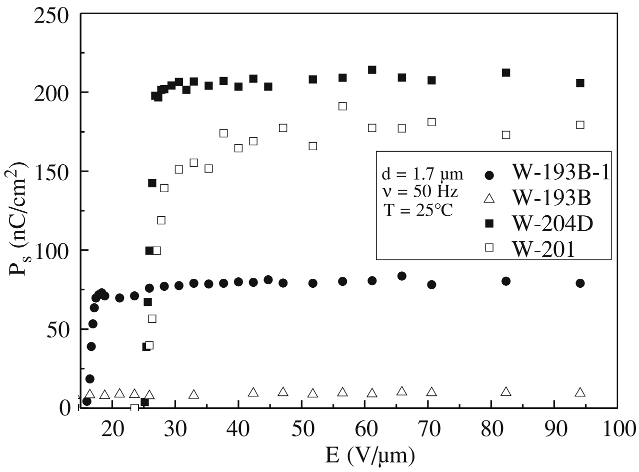

Fig. 5. Spontaneous polarization versus electric field taken at room temperature for all mixtures studied.

Table 2. Electrooptical parameters measured at room temperature for mixtures studied.

	W-204D	W-193B	W-193B-1	W-201
P_S (nC/cm^2)	86.2	159.6	238.4	10.5
θ (deg)	32.5	39.3	45	31
E_C (V/µm)	12	18.4	16.5	2.5
E_{SAT} (V/µm)	32.9	37.6	30.6	42.4

4. Conclusions

This contribution is devoted to our preliminary research on room temperature mixtures. Four mixtures with very broad antifferroelectric phase around room temperature have been studied to find characteristic electrooptical parameters. As shown, it is very easy to obtain mono-domain cell in antiferroelectric phase for all mixtures studied, but the crystallization appearing for W-201 at room temperature and the alignment is lost. This property and small value of spontaneous polarization as well as very high saturation voltage cause that W-201 mixture seems to be not proper for display applications. Conversely, W-193B-1 mixture with tilt angle 45 deg and small value of saturation voltage as well as W-193B with similar properties seem to be attractive for applications. Investigations of other parameters like switching time and contrast are under development.

Acknowledgements

A.M. is a scholar of the project which is co-financed from the European Social Fund and national budget in the frame of the Integrated Regional Operational Programme. A.M., M.M., and S.W. acknowledge financial support the State Committee for Scientific Research under grant No. 1P03B05628.

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