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O. A. Aphonin<sup>a</sup> & V. F. Nazvanov<sup>a</sup>

<sup>a</sup> Department of Physics, University of Saratov, Astrakhanskaya 83,  
Saratov, 410071, Russia

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## ANOMALOUS ELECTRO-OPTICAL RESPONSE OF NCAP-TYPE NEMATIC / POLYMER DISPERSIONS

O. A. APHONIN, and V. F. NAZVANOV

Department of Physics, University of Saratov, Astrakhanskaya 83,  
Saratov 410071, Russia.

**Abstract** We have experimentally investigated the mechanism of switching a composite film consisted of a dispersion of micron-sized nematic droplets in a polyvinyl alcohol matrix. Principal transmittances of the film and the phase shift between principal components were measured ellipsometrically as functions of applied electric field and incidence angle. It is found that in the region of low fields the transmission curves often exhibit a pronounced local minimum, while the phase shift curves have a local maximum. With increasing the incidence angle, the transmittance for light polarized in the incidence plane starts to oscillate, whereas the transmission curve for orthogonal component becomes monotone. The obtained results are discussed in terms of the phenomenological model which takes into account the non-uniform realignment of the local director in the bulk of nematic droplets and the surface orientation effects at LC/polymer interface.

### INTRODUCTION

Dispersions of nematic liquid crystals in polymer matrices form a class of composite materials with a high potential for a variety of optoelectronic applications.<sup>1</sup> It is of great scientific and practical interest to understand the relationship between the light scattering properties of these materials and the orientation of liquid crystal in the droplets. Typically, the light transmission through the nematic composite film and the phase shift between light components polarized parallel and perpendicular to the incidence plane are monotonically increasing functions of applied electric field,<sup>2,3</sup> except a small decrease in transmission at high fields when the refractive index (RI) of the polymer is larger than RI of liquid crystal.<sup>2</sup> In some cases one can observe an anomalous minimum in the transmission curve at low fields.<sup>4,5,6</sup> The reason of such a behavior was attributed to a partial orientation of liquid crystal at the droplets which causes the more intensive scattering. However, this phenomenon was not studied in detail.

In this paper, we investigate the angular and polarization dependence of the anomalous electro-optical response in nematic composite films with NCAP-type<sup>4</sup> morphology. The particular emphasis is placed upon the consideration of the role of strong surface anchoring at the nematic/polymer interface in controlling the non-uniform realignment of director field in the droplets at low fields. A simple phenomenological model

is proposed which interpret the optical characteristics of the studied films in terms of light scattering by the spatially dependent refractive index gradients within the droplets.

## EXPERIMENTAL

The NCAP films examined in this study were made by an emulsification method,<sup>4</sup> using polyvinyl alcohol (PVA) as the matrix material and nematic mixture SZK-1 (NIOPIK, Moscow). The starting emulsion with a LC/PVA ratio 3/2 was diluted with additional PVA solution to create emulsions with LC/PVA ratios down to 1/15. The droplet size distribution, measured by optical microscopy, covered the droplet diameter range from approximately 0.5  $\mu\text{m}$  to 8  $\mu\text{m}$  with an average diameter of 3  $\mu\text{m}$ . The film thickness ranged from 20 to 50  $\mu\text{m}$ . Films substrates were ITO-coated glass plates.

The angle-dependent light transmission, phase shift and scattering measurements were performed with the linearly polarized monochromatic light from a 5 mW He-Ne laser ( $\lambda = 632.8\mu\text{m}$ ) on an optical bench system described previously.<sup>7</sup> The samples were electrically switched with a 1 kHz sine wave applied normal to the film surfaces. We have examined the four polarized principal transmittances,  $T_{\parallel\parallel}$ ,  $T_{\perp\parallel}$ ,  $T_{\perp\perp}$ , and  $T_{\parallel\perp}$ , where the pair of indices  $\parallel$  and  $\perp$  denote the polarized-analyzer combinations with respect to the incidence plane. Phase shift between  $\parallel$  - and  $\perp$  - polarized components was measured by a conventional ellipsometric technique.<sup>3</sup>

## RESULTS AND DISCUSSION

Figure 1 shows the light transmission curves for NCAP films of ordinary and anomalous types for the case of normal incidence ( $T_{\parallel\parallel} = T_{\perp\perp}$ ,  $T_{\perp\parallel} = T_{\parallel\perp}$ ). For the ordinary-type films, the co-polarized transmittance,  $T_{\parallel\parallel}$ , is a monotonically increasing function of the applied field strength, while the cross-polarized transmission curve,  $T_{\perp\parallel}(E)$ , is nonmonotone with the pronounced maximum at the region of most steepness of the  $T_{\parallel\parallel}(E)$  dependence. It is reasonably safe to suggest that the hump in the  $T_{\perp\parallel}(E)$  curve is an indicator of the intensive reorientation of bipolar nematic structures in the droplets under the action of the field. (In particular, this is correct for the transmission of NCAP films oriented by the uniaxial stretching of the polymer matrix.<sup>7</sup>) For the anomalous-type NCAP films, the co-polarized transmittance exhibits a deep local minimum which can be a 10 times smaller than zero field transmittance. The position of the minimum is substantially shifted from the maximum of the  $T_{\perp\parallel}(E)$  curve towards the region of low fields. It should be stressed that practically no hysteresis effect was observed; the shape of transmission curves was independent of whether the applied field is increasing or de-

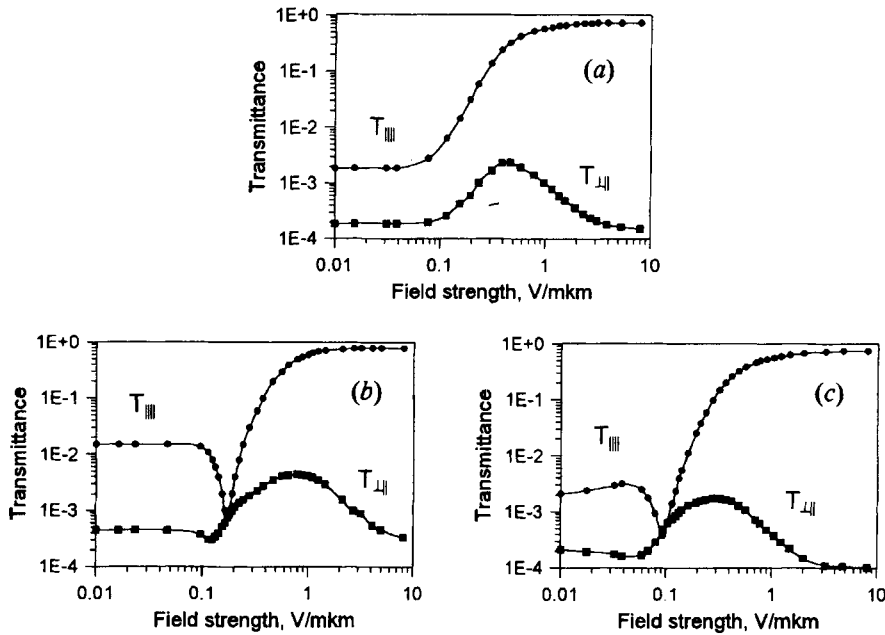


FIGURE 1 Principal polarized transmittances of NCAP films of ordinary (a) and anomalous (b), (c) types as functions of applied field strength at normal incidence. Film thicknesses are 32  $\mu\text{m}$  (a), 45  $\mu\text{m}$  (b), and 34  $\mu\text{m}$  (c). Liquid crystal volume fractions are 0.6 (a), (c), and 0.06 (b).

creasing. Comparison of Figures 1(a) and 1(b) also indicates that the occurrence of the transmission anomaly in NCAP samples does not depend on the volume fraction of liquid crystal in the film as opposed to the network-type composite films.<sup>6</sup> Figure 2 illustrates the energy redistribution between the transmitted and scattered light at zero field and at the minimum of the co-polarized transmission curve. As can be seen, the decrease in transmission at  $E = 0.1 \text{ V}/\mu\text{m}$  is followed by the increase in off-forward scattering.

These results can be explained on the basis of the model for bipolar droplet reorientation in NCAP films proposed by Drzaic.<sup>4</sup> At zero field, the symmetry axis of each bipolar droplet lies in the film plane due to the oblate spheroidal shape of the droplet cavity resulting from anisotropic shrinkage of the polymer during the film formation. This state is shown schematically in Figure 3(a). The different droplets are therewith aligned randomly within the film plane. The mechanism of scattering at zero field is related to the refractive index gradients between the droplet and polymer matrix or between the neighboring droplets with different azimuthal orientation of their symmetry axes.<sup>8,9</sup> At low applied field, only the nematic in the center of the droplet reorients, while the bipolar defects and the surface nematic layer are still placed near they were in

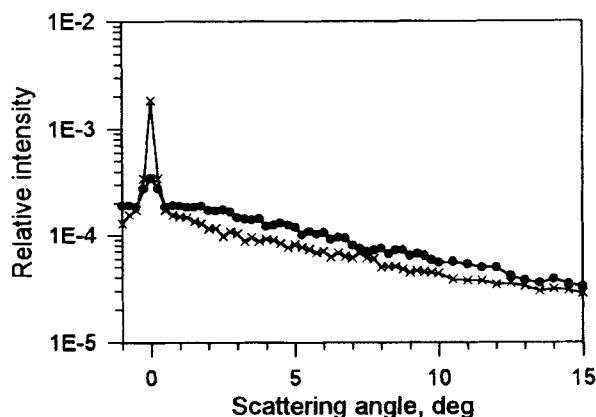


FIGURE 2 Scattered intensity of the anomalous-type NCAP film versus scattering angle at zero field ( $\times$ ) and at the minimum of the transmission curve ( $\bullet$ );  $E = 0.1 \text{ V}/\mu\text{m}$ .

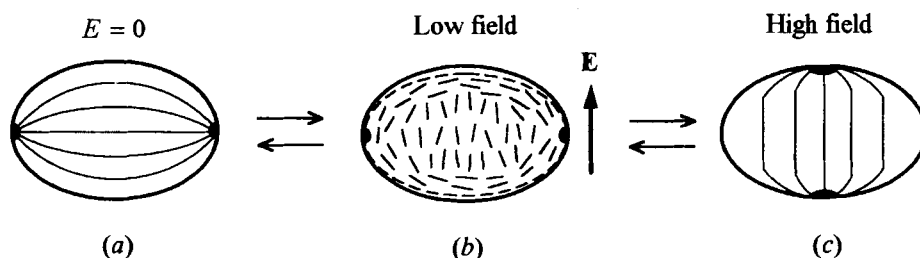


FIGURE 3 Model for the three stage process of reorientation of the bipolar nematic droplet in an external electric field for the anomalous-type NCAP film.

the unpowered film. This leads to droplets existing predominantly in the state shown in Figure 3(b). Since in this state there is a significant spatial change in the director orientation in moving from the wall of the droplet to the droplet center, the intradroplet RI gradients arise which make an additional contribution in light scattering by the film, manifested as a minimum in the co-polarized transmission curve. The origin of the 'freezing on' of the surface nematic layer we attribute with the anisotropic surface interactions arising from the ordered organization of polymer molecules at the droplet/matrix interface,<sup>10</sup> rather than droplet shape anisotropy effect postulated previously.<sup>4</sup> As the film is powered to high field, the elastic torque due to the nematic director field curvature overcomes the anisotropic anchoring force at the droplet surface and the bipolar structure aligns along the field direction as shown in Figure 5(c). The interdroplet and intradroplet RI gradients disappear and the film becomes transparent. Apart from the

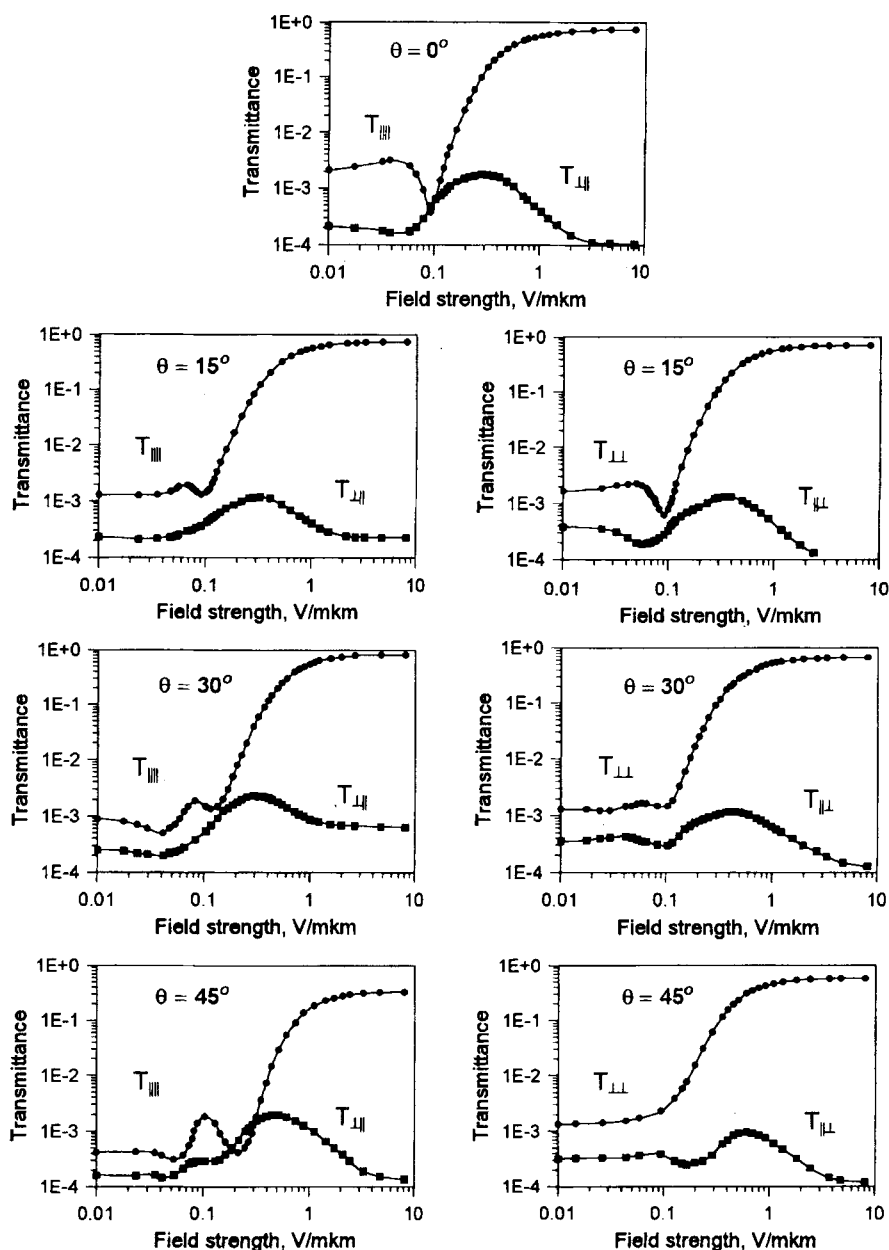


FIGURE 4 Principal polarized transmittances of the NCAP film with anomalous electro-optical response as functions of applied field strength at various angles of incidence. Film thickness and liquid crystal volume fraction are 34  $\mu\text{m}$  and 0.6, respectively.

model of Drzaic, which assumes the direct transition from the droplet state (c) to the state (a) after decreasing of the field, we propose that the orientation process sketched in Figure 3 is completely reversible without the hysteresis effect. This difference is due to that the droplet shape anisotropy, supposed as a primary reason for restoring force in the model of Drzaic, acts on the whole volume of the droplet, while the surface interactions postulated here influence predominantly the nematic near the droplet boundary and thus not strongly affect the field induced orientation in the bulk of the droplet upon decreasing the field from high strength.

To study the transmission anomaly in more detail, we examined the polarized transmission curves for the sample shown in Figure 1(c) versus the incidence angle. These results are presented in Figure 4. With increasing the incidence angle, the co-polarized transmission curve for the component polarized in the plane of incidence,  $T_{||}(E)$ , becomes more complicated acquiring the local maximum at low fields, whereas the initial minimum decreases in amplitude with respect to the zero field transmittance and is shifted towards the higher fields. On the contrary, the transmission curve for the component polarized perpendicular to the incidence plane,  $T_{\perp}(E)$ , goes monotone obtaining the usual S-shape. The modifications in cross-polarized transmittances are less pronounced, although one can observe some peculiarities in the region of the threshold of electro-optical response. The main features of transmission curves shown in Figure 4 were common for a set of NCAP films with thickness varied from 20  $\mu\text{m}$  to 50  $\mu\text{m}$  and LC volume fraction ranged from 0.06 to 0.6.

Figure 5 shows the phase shift in the same NCAP sample versus the applied field strength and incidence angle. It is clearly seen that the phase shift curves are characterized by the local maximum, the position of which well correlates with the minimum in the transmission curve. It is remarkable to note the non-zero phase shifts for  $E = 0$  at non-zero incidence angles. This is the result of confinement of the symmetry axes of bipolar droplets to the film plane; the film is not azimuthally isotropic at  $\theta > 0^\circ$ .

We attempt to interpret the angular dependence of anomalous electro-optical response of NCAP films by considering the nonuniform spatial distribution of refractive index gradients within the distorted bipolar droplet. The relevant simplified model is sketched in Figure 6. Two extreme azimuthal orientations of a droplet - parallel to the incidence plane ( $\varphi = 0^\circ$ ) and perpendicular to it ( $\varphi = 90^\circ$ ) - are shown. It is assumed that near the droplet boundaries faced to the film surfaces and in the vicinity of bipolar defects there are strong splay deformations of the nematic director field  $\hat{n}(\mathbf{r})$ , which cause largest RI gradients within the droplet. On the other hand, near the droplet boundaries which are parallel to the films normal in the distance from the bipolar defects the director deformations are presumed to be of twist type that leads to less abrupt

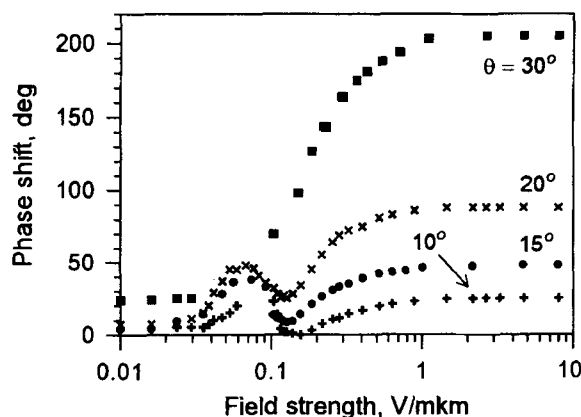


FIGURE 5 Phase shift between  $\parallel$ - and  $\perp$ -polarized components of probing light for the NCAP film characterized in Figure 4 as a function of field strength at various angles of incidence.

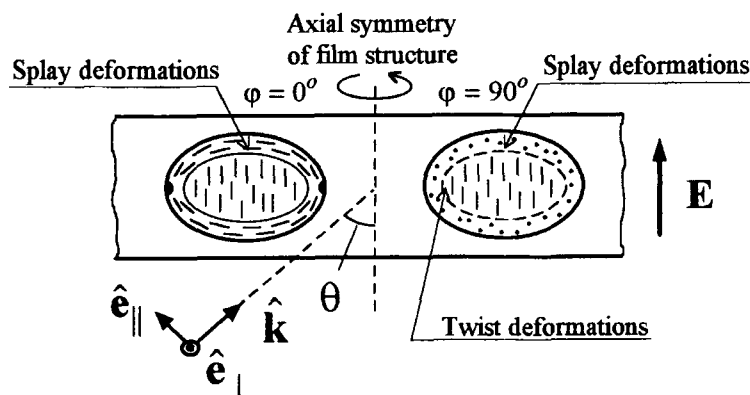


FIGURE 6 Schematic presentation of orientation of the distorted bipolar nematic droplets with respect to the applied field,  $E$ , and the polarization of incident light in the anomalous-type NCAP film.

changes in RI on passing from the droplet's boundary to the bulk (see Figure 6). For light polarized perpendicular to the incidence plane ( $\hat{e}_\perp$ ), the droplet with  $\varphi = 0^\circ$  is weakly scattering since  $\hat{e}_\perp \perp \hat{n}$  practically everywhere in its volume, while the droplet with  $\varphi = 90^\circ$  scatters strongly due to  $\hat{e}_\perp \parallel \hat{n}$  in the surface nematic layer and  $\hat{e}_\perp \perp \hat{n}$  near the droplet center. In the latter case the intradroplet refractive index gradient is a maximum at normal incidence and decreases with increasing the incidence angle because the splay deformations in the pass of light are replaced by twist deformations. Therefore, the intradroplet scattering decays with increasing  $\theta$  that manifests in vanishing of anomalous minimum in the transmission curve. For light polarized in the incidence plane



( $\hat{e}_{\parallel}$ ), the droplet with  $\varphi = 0^\circ$  possesses the strong RI gradients at all angles of incidence, whereas the RI gradients in the droplet with  $\varphi = 90^\circ$  increase from zero at  $\theta = 0^\circ$  to non-zero values at oblique incidence when  $\hat{e}_{\parallel}$  is no longer perpendicular to  $\hat{n}$  in the center of the droplet. The associated scattering processes are more complex than for the case of  $\hat{e}_{\perp}$  polarization, giving rise to nonmonotone behavior of the transmission curve. Averaging over all possible azimuthal orientations of bipolar droplets does not change the qualitative picture outlined above. Interpretation of local maximum in the phase shift curves in terms of RI gradients is much less clear and necessitates a better characterization of nematic orientation within droplets together with application of a more adequate optical model.

## CONCLUSIONS

We have studied in detail the anomalous electro-optical response in NCAP-type nematic/polymer films with the PVA as film forming material. The observed anomaly, emerging in the nonmonotone behavior of light transmission and phase shift curves, is found to strongly depend on the angle of incidence and polarization of probing light. We explain these results by the presence of spatially dependent refractive index gradients within the droplets, arising from the distortion of bipolar nematic director field due to interplay between the strong surface anchoring at droplet boundaries and the orienting action of the external electric field. It is inferred that the influence of these gradients on light scattering substantially depends on the beam direction and its polarization. Unfortunately, we do not completely understand why one can observe ordinary or anomalous response in NCAP films made from the same LC/polymer combination. This requires a further study.

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