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Memory Effect in Polymer-Liquid Crystal Composites

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The experimental study reveals a connection between topological defects and the memory effect in polymer-dispersed liquid crystal (PDLC) films. By examining the influence of temperature during film fabrication, it was found that pre-heated samples develop a large number of large-scale disclinations. The distortion of the director field caused by these disclinations leads to the formation of degenerate orientations for liquid crystal molecule relaxation. This, in turn, reduces the anchoring energy and gives rise to the memory effect.

Keywords: nematic, polyvinyl acetate, memory effect, topological defects, disclinations, anchoring energy.

Liquid crystal composites combining the electro-optical properties of liquid crystals (LCs) and the mechanical qualities of polymers are currently being used widely. Polymer-dispersed liquid crystals (PDLCs), wherein LCs are dispersed in a polymer matrix in micrometer- and submicrometer-sized domains, are an example of such composites [1]. It is known that certain PDLC types with a specific morphology exhibit the so-called memory effect [2]: their characteristics, such as transparency and capacitance, do not revert to their initial values after the application of an external field. One of the possible causes of this effect is the formation of topological defects (disclinations) in the bulk of an LC with the translational order disrupted in their vicinity [3]. Topological defects in LCs have various formation mechanisms. Specifically, they may be induced by the heating/cooling process with accompanying phase transitions or when the conditions of surface anchoring are violated [4]. The defects in LCs themselves are often regarded as nucleation points of the phase transition to an isotropic state [5]. It should be noted that the influence of disclinations on the physical properties of PDLC films currently remains understudied; therefore, such research is indeed relevant. One of the goals of the present study is to examine experimentally the influence of disclinations formed as a result of heating of PDLC samples on the memory effect.

A nematic LC (4-cyano-4′-pentylbiphenyl, 5CB) and a vinyl acetate polymer (PVA) taken in mass ratio LC : PVA = 2 : 1 were the materials used for synthesis of PDLC samples. PVA and 5CB have similar refraction indices. The nematic phase of 5CB is found within the temperature range of $22-34\,°\text{C}$; all experimental data in the present study were obtained at $23\,°\text{C}$. The PDLC samples were manufactured using the SIPS (solvent-induced phase separation) process in which phase separation occurs due to the solvent (benzene and acetone) evaporation from the polymer–LC solution [6]. The PDLC film thickness was $20\,\mu\text{m}$. The fabrication procedure involves short-term heating of films in an oven at $120-125\,°\text{C}$ at the final stage. As noted by the authors of this technology, heating of films (the so-called thermal shock) is used to relieve fatigue stress. Since heating, as was mentioned earlier, may induce the emergence of disclinations, we prepared two batches of samples: one batch with preheating (thermal shock; see above) and another batch without heating. Typical samples from these batches are considered below.

Figure 1 shows micrographs of the PDLC structures for samples prepared with preheating in a furnace (according to the technology detailed above) and without it. These images were obtained using a polarizing optical microscope (POM). Anisotropic structures corresponding to LCs are seen against the dark background of an optically isotropic polymer. In the heated sample (Fig. 1, *b*), these structures take the form of large „four-leaf clovers" with transverse dimensions reaching $300\,\mu\text{m}$. The cores of topological defects (disclinations) are at the centers of „clovers." The presence of four dark stripes in „clovers" implies that the LC director rotates by 2π while completing a single circuit around the disclination core. The concept of a topological charge is introduced in order to define the disclination strength [3]:

$$k = \frac{1}{2\pi} \oint d\theta, \qquad (1)$$

where the integration of angle θ of the LC director with the chosen direction is carried out along any closed contour around the defect core. Thus, the topological charge for all existing disclinations is $k = 1$. When polarizers rotate, all defects rotate in the direction set by the positive sign of the topological charge. This configuration of „clovers" provides indirect evidence of tangential orientation of 5CB molecules.

As for the non-heated sample (Fig. 1, *a*), it is clear that the „clovers" are significantly (at least an order of magnitude) smaller in average size than those in the sample prepared
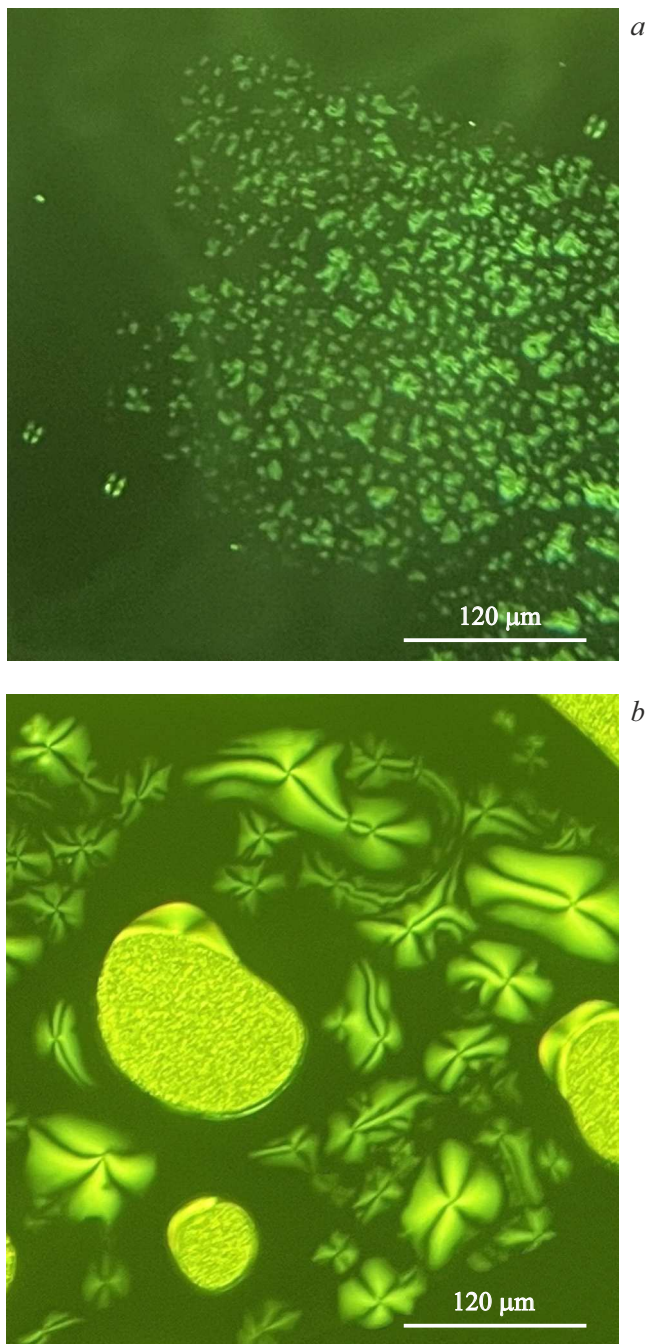
Figure 1. POM images of PDLC samples obtained (*a*) without and (*b*) with preheating.

with heating. Certain regions are completely free from „clovers.“ Thus, heating of PDLC samples unsurprisingly leads to a change in the orientational structure in LC droplets.

A measurement system of our own design [7] was used to determine experimentally the dielectric characteristics of the obtained PDLC samples. All measurements were carried out at an AC generator frequency of 30 kHz. Figure 2, *a* shows the dependences of the absolute capacitance values

on the bias voltage for samples with and without preheating. Hysteresis is seen clearly in both cases, but the capacitance does not revert to its original values. Thus, both samples exhibit a capacitance memory effect. In addition, it should be noted that the capacitance of the heated sample is initially lower than that of the non-heated sample. This is apparently attributable to the fact that heated samples contain a greater number of large-scale disclinations. Indeed, if disclination cores are regarded as nucleation points of a phase transition, order parameter S should tend to zero in the vicinity of these points (as in an isotropic liquid); therefore, with an increase in size of disclinations, the overall value of the order parameter of the entire LC volume should also decrease. Consequently, the initial capacitance, which is proportional to the order parameter, of samples with large disclination regions also tends to decrease.

Figure 2, *b* shows the plot of reduced capacitance $\Delta C/C_0 = (C - C_0)/C_0$, where C and C_0 are the current
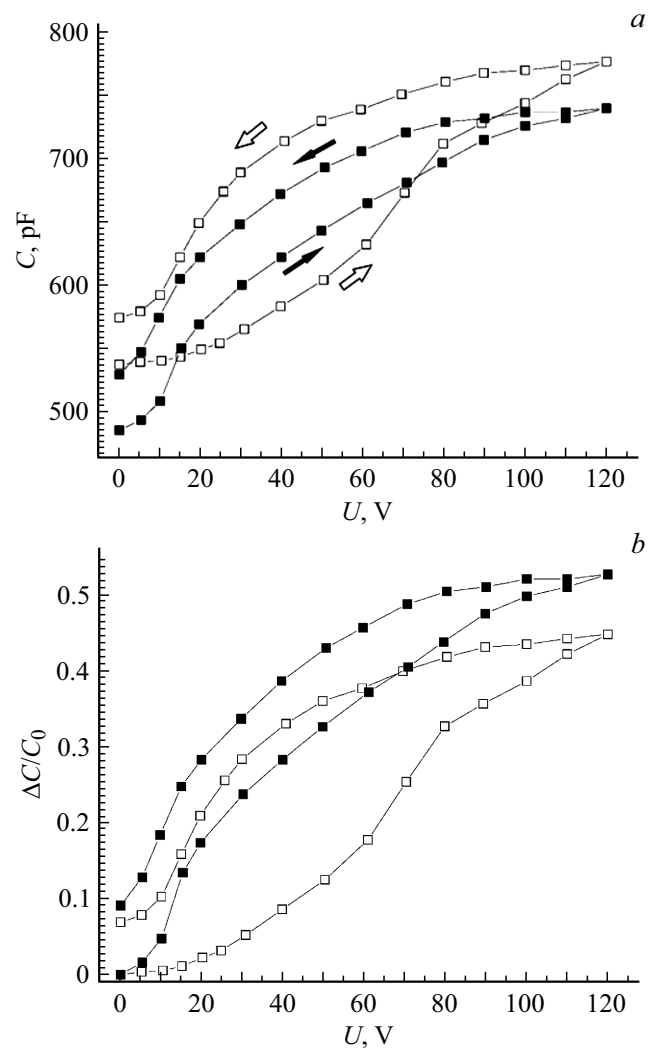

Figure 2. Dependences of (*a*) absolute and (*b*) reduced capacitance values of PDLC samples on the bias voltage. Open and solid squares correspond to the samples without and with preheating, respectively.

capacitance and the capacitance at $U = 0$ V, respectively. This plot illustrates the rate of capacitance growth observed when voltage is applied. It is evident that, in contrast to the absolute capacitance, the reduced capacitance of heated samples remains higher within the entire measured voltage range (Fig. 2, b). In other words, the permittivity of such samples responds more prominently to an external field. This, in turn, is associated with the specifics of interaction of the LC with the polymer surface. Indeed, the LC–polymer surface anchoring energy (f_a) has two components:

$$f_a = \frac{1}{2} W_1 \sin^2 \varphi + \frac{1}{2} W_2 \sin^2 \theta, \qquad (2)$$

where φ and θ are the polar and azimuthal angles of director deviation from the easy axis and W_1, W_2 are the anchoring energies at planar (tangential) and homeotropic orientations of molecules relative to the polymer surface, respectively. Thus, the contribution of each energy component depends on the arrangement of LC molecules. According to [8], the 5CB−PVA interaction is characterized by $W_1 = 1.5 \cdot 10^{-5}$ J/m² and $W_2 = 2.8 \cdot 10^{-3}$ J/m². It can be seen that these two energy contributions differ by two orders of magnitude. Since the emergence of topological defects is accompanied by a distortion of the director field, it is evident that the orientation conditions of molecules at the polymer surface also change. This, in turn, may lead to a redistribution of the contributions of each anchoring energy component and a reduction in surface energy f_a as a whole. The response of the system to an external field naturally intensifies with a reduction in anchoring energy.

The permanent memory effect (PME) coefficient, which characterizes its strength, was calculated based on the initial and final capacitance values:

$$\text{PME} = \frac{C_{off} - C_0}{C_{on} - C_0} \cdot 100\,\%, \qquad (3)$$

where C_0, C_{on}, and C_{off} are the initial capacitance, the maximum capacitance of the PDLC sample under voltage, and the residual capacitance after removal of voltage, respectively. The PME values for the heated and non-heated samples are 17.3 and 15.4 %, respectively. It is known that the weaker the interaction of LC molecules with the polymer surface is, the higher is the PME value [9]. This verifies our earlier conclusion regarding the reduction in LC–polymer anchoring energy in samples with a large number of defects.

Thus, it can be concluded that the memory effect in PDLCs is closely related to the formation of topological defects in the bulk of an LC. As is known, the memory effect is induced by violation of the conditions of LC anchoring on the polymer surface and the formation of additional degenerate directions near this surface [10]. When the field is turned off, nematic molecules relax along these directions without reverting to their original state. The research results reported above revealed that topological defects are what gives rise to this violation of anchoring

conditions and the emergence of degenerate axes at the surface. Therefore, samples with a great number of large-scale topological defects do exhibit, on the one hand, a more pronounced response of dielectric parameters to an external field and, on the other hand, a more pronounced memory effect.

Conflict of interest

The authors declare that they have no conflict of interest.

References

[1] H. Zhang, Z. Miao, W. Shen, Composites A, **163**, 107234 (2022). DOI: 10.1016/j.compositesa.2022.107234

[2] R. Yamaguchi, S. Sato, Jpn. J. Appl. Phys., **30** (4A), L616 (1991). DOI: 10.1143/JJAP.30.L616

[3] S. Fumeron, B. Berche, Eur. Phys. J. Spec. Top., **232** (11), 1813 (2023). DOI: 10.1140/epjs/s11734-023-00803-x

[4] J. Angelo, C. Culbreath, H. Yokoyama, Mol. Cryst. Liq. Cryst., **646** (1), 214 (2017). DOI: 10.1080/15421406.2017.1287486

[5] Y. Han, J. Lagerwall, A. Majumdar, Phys. Rev. E, **109** (6), 064702 (2024). DOI: 10.1103/PhysRevE.109.064702

[6] G.M. Zharkova, V.P. Fomichev, Sib. Fiz. Zh., **13** (3), 47 (2018). DOI: 10.25205/2541-9447-2018-13-3-47-54

[7] S.V. Kalashnikov, N.A. Romanov, A.V. Nomoev, IOP Conf. Ser. Mater. Sci. Eng., **1198** (1), 012006 (2021). DOI: 10.1088/1757-899X/1198/1/012006

[8] Y. Iimura, N. Kobayashi, S. Kobayashi, Jpn. J. Appl. Phys., **33** (3B), 434 (1994). DOI: 10.1143/JJAP.33.L434

[9] M.C.C.V. da Silva, J.L.M. Figueirinhas, J.C. da Silva Barbosa Sotomayor, Liq. Cryst., **43** (1), 124 (2016). DOI: 10.1080/02678292.2015.1061713

[10] J. Han, Korean Phys. Soc., **43** (1), 45 (2003). DOI: 10.1016/S0022-3697(03)00042-8

Translated by D.Safin