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Dynamic Scattering with Storage in Smectics C and Nematics with Smectic C Ordering†

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Stored dynamic scattering and stored domain structure were observed in smectic C and in nematic phases of p-n-heptyloxybenzoic acid (HOBA). The stored texture can easily be erased with a high frequency electric field. The smallest frequency for erasure decreases with the decreasing temperature. Stored scattering centers and stored domain structure in S_1 solid phase of HOBA were also observed.

There are mainly two types of external effects on the liquid crystals and after their removal a typical light scattering texture is preserved, namely electrooptical and thermooptical.

The electrooptical effect consists usually in creating a dynamic scattering in nematic-cholesteric mixtures with a negative dielectric anisotropy ($\epsilon_a < 0$)¹ or of smectics A^2 ; after switching off the electric field a residual scattering texture is preserved. The thermooptical effect is also applied on cholesteric-nematic mixtures³ or smectics A.⁴ The preserving of the scattering texture in this effect is achieved by rapid cooling the disordered isotropic phase at which the disorder (expressed in scattering centers) is preserved in the liquid crystal phase too. These effects are often referred to as storage by the liquid crystal.

The preserved scattering state is usually metastable but the period of natural relaxation toward the initial state of the liquid crystal reaches several months for some substances (mostly smectics). A shorter relaxation time toward the initial state or erasing the preserved texture can be provoked by external effects. In the electrooptical stored scattering texture, the erasing is

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achieved by applying a high frequency electric field. The thermooptical storage is erased by heating up to the isotropic phase and a subsequent slow cooling at which the molecule's adopt the typical liquid crystalline order. As a result scattering centers cannot be formed. This process can be aided also by the electric field.

In ordinary nematic liquid crystals neither electrooptical nor thermooptical effect of preserving the scattering texture is observed.

The purpose of the present paper is to show that there exists an electrooptical storage effect of scattering texture in the nematic phase, close to the transition smectic C—nematic (Sc—N), as well as in the smectic C phase.

Objects of our investigations are the seventh, the eighth and the ninth homologues of the p-n-alkyloxybenzoic acids (p-n-heptyloxybenzoic acid—HOBA, p-n-octyloxybenzoic acid—OOBA and p-n-nonyloxybenzoic acid—NOBA). They possess smectic C and nematic phases. Only the seventh homologue (HOBA) will be discussed here. It possesses smectic C phase (Sc) from

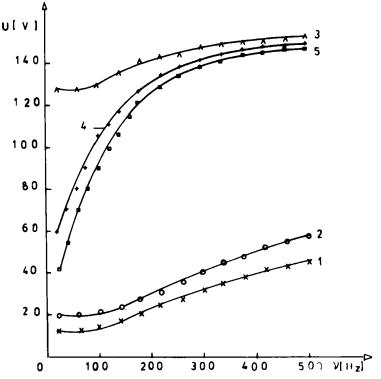


FIGURE 1 The threshold voltages versus frequency for cell-like domains (curve 1), initial dynamic scattering (curve 2), secondary dynamic scattering (curve 3), storage of dynamic scattering (curve 4) and storage of cell-like domains (curve 5) in nematic phase (p-n-heptyloxybenzoic acid—HOBA). The cell thickness is $L = 10 \ \mu m$ and the temperature $-115^{\circ}C$.

92-98°C, nematic (N) between 98° and 146°C and isotropic—above 146°C. Liquid crystal cells of different thickness L are used. The electrodes are rubbed only in one direction.

Preserving the scattering texture in the nematic phase realized only in the temperature range 98-118°C, as follows:

At threshold voltages for a given frequency (curve 1 in Figure 1) the known⁵ cell domains appear (Figure 2). Curve 2 from Figure 1 represents the threshold voltages at which the initial dynamic scattering begins. It is characterized by clearly expressed turbulence which destroys the domains. The scattering centers of this texture are comparatively big. At higher threshold voltages (curve 3 in Figure 1) a secondary dynamic scattering appears⁶ at which a small particle size dynamic scattering texture is observed (Figure 3). At abrupt switching off of the applied electric field, with voltage values given in curve 3, the scattering texture is preserved (Figure 4). For voltages between curve (3) and curve (4) the scattering texture is also preserved but the sizes of the scattering centers are bigger. Curve (4) has a threshold character and reflects the smallest voltage for a given frequency and after its switching off the scattering texture is preserved. After abrupt switching off of the voltages between curve (4) and (5), great parts of the destroyed domains are preserved. At lower temperature (105°C) a slightly destroyed preserved domain structure is observed (Figure 5). Curve

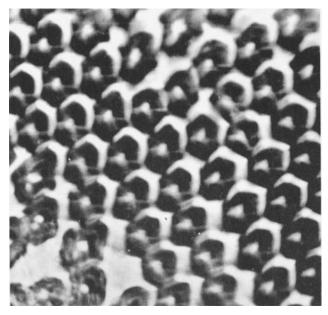


FIGURE 2 The cell-like domains in nematics phase of HOBA, ×200.



FIGURE 3 The high contrast secondary dynamic scattering in nematic phase of HOBA—the black part of the picture. The white part corresponds to the unexcited state of the nematic phase.

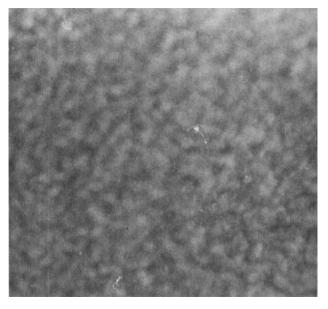


FIGURE 4 The stored scattering texture in nematic phase of HOBA after removing the voltage with value more than that of curve 3.

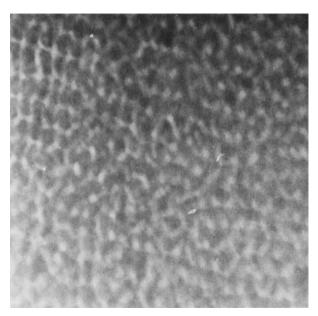


FIGURE 5 The stored cell-like domain structure, ×125.

(5) indicates the smallest voltage for a given frequency at which the domain structure is preserved.

For temperatures from 118° to 145°C in the nematic phase, in spite of the fact that the threshold curves (1), (2) and (3) exist, no preservation of the scattering texture is observed. Thus, the temperature $T^* = 118$ °C can be considered as a point below which the electrooptical effect of storage can be realized. If the voltage with magnitude equal to the threshold of the initial or secondary dynamic scattering is switched off at temperatures a little higher than T^* , a slow relaxation of the disturbed structure toward the initial state is observed. It is accompanied by a change in the color caused by relaxation of the director. However, it does not reach storage.

As is seen from curves (4) and (5) in Figure 1, for low frequencies (from 20 to 100 Hz for 115°C), the threshold voltages for storage increase almost linearly with the frequency. At higher frequencies there is a tendency toward saturation. At lower temperatures of the nematic phase the character of curves (1), (2), (3), (4) and (5) changes; they become steeper, as it is seen from Figure 6.

In Figure 7 is shown the dependence of the threshold voltages for storage of the scattering texture and domains (curves (4) and (5)) on the temperature. On decreasing the temperature from T^* to 110° C the thresholds increase linearly and on further decreasing a saturation is reached.

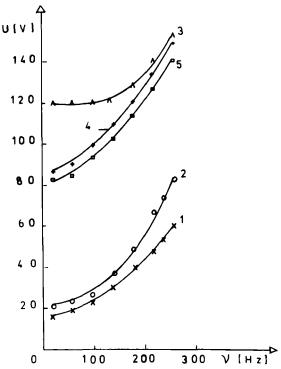


FIGURE 6 The threshold voltages versus frequency for cell-like domains (curve 1), initial dynamic scattering (curve 2), secondary dynamic scattering (curve 3), storage of dynamic scattering (curve 4) and storage of cell-like domains (curve 5) in HOBA at $L=10~\mu m$ and $T=105^{\circ}C$.

The comparison of Figure 1 and Figure 7 shows that the increasing of the frequency and the decreasing of the temperature influence almost equally on the storage thresholds. Probably, this is connected with the relaxation rate of the volume charge, i.e. at higher frequencies equivalent to the lower temperatures its relaxation is inhibited ("freezing" of the charge) and the electric field has an effect mainly on the director through the dielectric anisotropy ϵ_a .

It is difficult to bring back the system to its initial state alone without application of additional external effects since the charge has accumulated in such a way ("frozen") that it is difficult to be set in motion.

Erasing the preserved scattering texture can be done by applying an electric field of a given frequency $\nu \ge \nu_e$. For 115°C ν_e is 500 Hz (Figure 1). After applying voltages higher than that of curve (4) in Figure 1 and abrupt switching off, the preserved texture is erased. The frequency ν_e decreases with the temperature decreasing (Figure 8) and from 600 Hz at T^* it reaches 200 Hz near the transition N—Sc. At low temperatures the erasing occurs at lower frequencies since the charge relaxes more slowly and the effect of the field acts

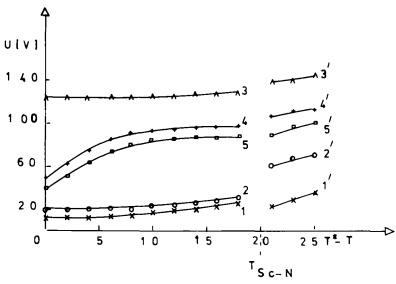


FIGURE 7 The characteristic threshold voltages—curves 1, 2, 3, 4, 5 in nematic phase of HOBA versus temperature. The curves 1', 2', 3', 4', 5' represent the typical threshold voltages in smectic C phase of HOBA. $T_{\text{Sc-N}}$ is the temperature of the phase transition between nematic and smectic C phases. $T^* = 118^{\circ}\text{C}$ is the initial temperature point below which the storage exists. T is the measured temperature in the temperature region $T^* - T_{\text{Sc-S}}$.

again on the molecular director, i.e. the system comes back to the initial state only under the action of the dielectric rotating moment. At higher temperatures the charge is more mobile and a higher frequency ν_e is necessary to prevent charge relaxation and permit action on the dielectric order only.

The storage itself represents a preserved excited state of the system as a result of a deformation of the ordered structure. Such a liquid crystal system could be a layered smectic structure. Above a definite value of the exciting dielectric rotating moment the layer deformation can become irreversible. As we have seen, above T^* it is not possible to preserve an excited state of the system. When a mesogene possessing smectic C and the nematic state is cooled down from the isotropic liquid a new type of nematic phase with some smectic ordering is formed. It differs from the classical nematics (MBBA, PAA, etc.) and consists of prolonged molecular complexes with length about 400 A°. A molecular tilt towards the layers exists in these complexes. The effects of this smectic ordering are also observed in EPR studies. 8 The amount of smectic C ordering decreases with increasing temperature. Our results indicate that below $T = 118^{\circ}$ C for HOBA, because of sharply changing short range order of the system, a change takes place in the elastic, electrooptical and threshold characteristics. Therefore, by a suitable value of the electric field below T^* , we provoke a plastic deformation of the pseudo-layer structure which cannot

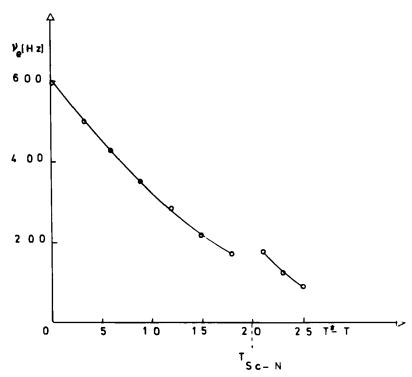


FIGURE 8 The erase frequency ν_e versus temperature for nematic and smectic C of HOBA.

come back to its initial state without an active external interference. Above T^* the nematic structure is classical and no molecular complexes are formed with a consistent tilt of the molecules in the layer. Obviously, the external effect cannot provoke an elastic deformation which should be transformed into plastic at such a molecular level.

As is seen from Figure 1, storage and erasing of the scattering texture are connected with the thresholds for appearance of a domain structure in which the volume charge induced by the conductivity anisotropy σ_a has a significant role. That is why the storage control can be looked for in the mechanism of charge distribution of Carr-Helfrich. ¹⁰ This is confirmed also by the approximately equal frequency dependence of the threshold curves for storage (curves 4, 5) and that of the electrohydrodynamical instability (curve 1, 2) controlled by this mechanism.

Erasing of the storage texture can be done in another way—only by the temperature. For example, after heating from $T^* = 118^{\circ}\text{C}$ to 125°C , the preserved texture is already erased. On heating, the mobility of the molecules in the pseudo-layers increases as the latter are destroyed and the system passes into a classical nematic in which no residual deformation can be preserved.

As described, this electrooptical effect of storage of scattering texture in the nematic phase of HOBA is similar to the electrooptical effect of storage in cholesteric-nematic mixtures. Preserving the scattering texture in nematics of S_c ordering can be considered as a process of a long time storage of information.

Let's now turn our attention to storage scattering effect observed in smectic C. The dependence of the threshold voltages on the frequency typical for this phase is shown in Figure 9. "Fundamental" smectic C domains 11 appear at threshold voltages presented by curve 1' for a given thickness of the liquid crystal cell (10 m). Curve 2' from Figure 9 represents the threshold voltages for the initial dynamic scattering in this phase. Curve 3' represents the voltages for small particle size dynamic scattering corresponding to the secondary scattering at nematics with fully destroyed domain structure. After sharp switching off of the electric voltage with values higher than those shown at curve 3', a homogeneous scattering texture (Figure 10) is stored. A scattering texture with greater scattering centers is also preserved at sharp switching off of the

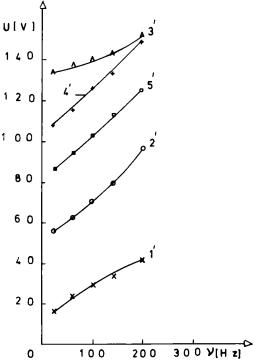


FIGURE 9 The threshold voltages versus frequency for fundamental domains (curve 1'), initial dynamic scattering (curve 2'), secondary dynamic scattering (curve 3'), storage of dynamic scattering (curve 4') and storage of rebuilt fundamental domains (curve 5') in smectic C of HOBA. $L = 10 \mu m$, T = 96.5°C.

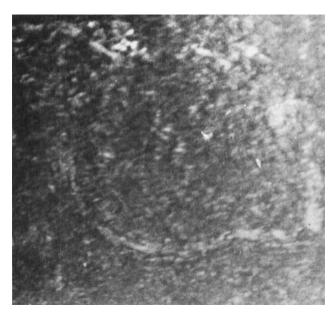


FIGURE 10 The stored scattering texture in smectic C phase of HOBA, ×125.

voltage with values falling between 3' and 4'. Curve 4' is a storage threshold of such a scattering texture. After sharp switching off of voltages with values between those of curves 4' and 5', the rebuilt fundamental domains are stored, cut by domain bands¹² perpendicular to them. The sharp switching off of voltages with values below 5' leads neither to storage of scattering nor to domain structure. Therefore, the "initial" and "fundamental" domains with threshold U_{th} , shown by us¹¹ cannot be stored electrooptically.

In the smectic C phase the erasing of the preserved domain or scattering texture can be done by frequencies higher than ν_e , which are lower than those in the nematic phase. The frequency ν_e in the smectic C phase also decreases with decreasing temperature (Figure 8).

As is seen from Figure 9, the threshold voltages for storage of domain and scattering texture in smectic C increase more rapidly and almost linearly with the frequency and, besides, with the temperature (Figure 7) but without reaching saturation. Probably, in this phase the role of the accumulated volume charge in the storage effect is smaller than the corresponding one in the nematic phase. That is why the erasing takes place also at lower frequencies.

Storage of domain structure and dynamic scattering can be done only after applying an abrupt switching off the strong fields at which the smectic layers are disturbed (plastic deformation). Voltages below the threshold curve 5'

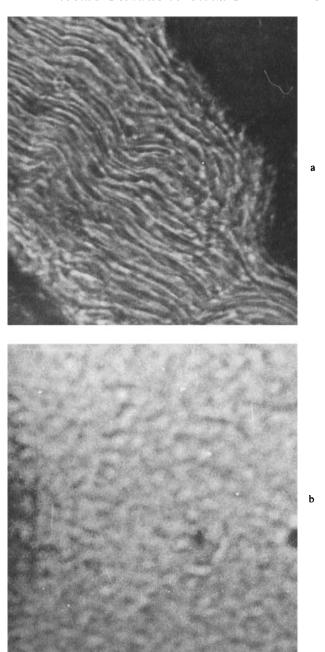


FIGURE 11 The stored domain structure (11*) and scattering centers (11*) in S_1 solid phase of HOBA, $\times 125$.

cannot deform the layer irreversibly. Therefore, at smectic C domains, observed by us¹¹ and other authors, ¹³ the layer is not deformed but is preserved during the time of electrohydrodynamic instability. The rebuilt "fundamental" domains¹¹ after their cutting by domain bands perpendicular to them, a picture which is stored after switching off the field, are obviously connected with a plastic deformation of the layers. In dynamic scattering the layers are already completely destroyed.

The domain picture as well as dynamic scattering can be stored by rapid cooling in the solid phase—S_I (from 64-92°C) (Figure 11). Of course, the short range order of this phase destroys to a great extent the stored structure in Sc phase.

Therefore all electrooptical effects of storage in nematic-cholesterics mixtures and smectic A reported in the literature so far are also observable in smectic C and nematic phases of HOBA. Besides, linear domain structure 12 can be also preserved. In the cholesteric-nematic mixtures the storage is possible only when the dynamic scattering produces scattering centers with sizes no less than the cholesteric pitch. For the nematic phase of substances investigated it is necessary also to apply the deformation below temperature T^* where the layer molecular complexes are already formed. Deformations at temperatures above T^* where the mesophase has molecular level structure cannot be preserved.

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