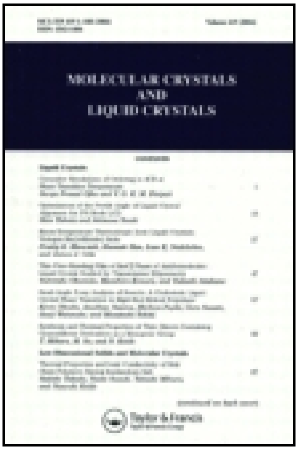

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A BOUNDARY INDUCED SMECTIC A-LIKE STRUCTURE

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Abstract A smectic A-like state induced by the boundary forces is investigated. Two different methods are used for the identification of this state: the textural method and the depolarized scattered light intensity thermal analysis. We found that the S_A-like state can be induced as an intermediate one, close to the nematic-smectic C phase transition temperature. It is also demonstrated that at some orientations a S_A-like state (presumably generated in the frame of the cybotactic groups, close to the orienting substrates) can be induced still in the nematic phase preceding the smectic C.

INTRODUCTION

We have demonstrated[1,2,3,4,5] that smectic A(S_A)-like structure can be induced by the boundary conditions as an intermediate between nematic (N) and smectic C(S_C) phases. The used liquid crystals were seventh, eighth, nineth, tenth and twelfth homologues of the p-n-alkyloxybenzoic acid - HOBA, OOBA, NOBA, DOBA, DDOBA with hyfrogen bonds as well as 4,4'-di-n-heptyloxyazoxybenzene and 4,4'-di-n-octyloxyazoxybenzene-OOAB - without hydrogen bonds. These substances are of C_1 type[6] and possess a tilt angle ω constant with the temperature variation.

The purpose of this work is on the base of our recent investigations, concerning the smectic A-like state induction by the boundaries at different geometries, to discuss the phenomenon in a broader aspect.

As it is known[7], the S_A phase manifests itself by the different textures at different geometries of the initial orientation. Commonly, the formed S_A layers can be oblique or vertical (with a small longitude) or parallel to the orienting substrates (with a large longitude). The oblique and vertical layers can be easily deformed under external forces in simple confocals, keeping constant the interlayer distance where the molecular director is normal toward whichever element from the plane of the bent layers. Consequently, the simple confocals can be accepted as a direct indication of a S_A structure at oblique and vertical layers. The growing of S_A layers with a large longitude and parallel to the orienting substrates can be directly identified in the ideal homeotropic case only (the angle θ between the normal to the substrates and the molecular director is approximately zero) - pseudoisotropic S_A texture. In our experiment we work with quasihomeotropic orientation where bend or twist can be easily obtained and consequently the S_A-like state identification is an indirect one. The stripe-like texture[8] is an indication for the coexistence of the S_A and the N phase in this case. In parallel with the texture identification of the S_A-like state, we have used the thermal analysis of the depolarized light scattering. At S_A formation, the depolarized scattered light intensity (I^s) falls down to a definite minimum reflecting the molecular director depressing fluctuation. We also used a broken confocal and a thermomechanical undulation instability texture always accompanying the S_C formation after S_A cooling for identification of the S_A-like state. The corrsponding changes in the depolarized light scattering thermal analysis, at appearing of these textures, express in nonlinear intensity increasing (to saturation), reflecting the ω angle fluctuation at second order S_A-S_C phase transition.

Using different initial orientations,we found in our experiment that the induced S_A-like state is an intermediate one and can be obtained similarly as in the N-S_C phase transition, as well as in the nematic phase preceding S_C. We shall consider the most typical geometries for the two cases leading to the S_A-like state induction.

i. S_A-like state induction in the N-S_C phase transition

The induction of the S_A-like state at N-S_C phase transition is more pronounced than the one induced in the nematic phase. More suitable for the purpose is the tilted orientation on angle θ different from angle ω . At a such orientation, approximately 1 - 1,5 degrees below the N-S_C phase transition at a very slow cooling for OOBA, we have observed a simple confocal texture, Fig. 1, which passes at further cooling into a broken confocal one[1], Fig. 2.

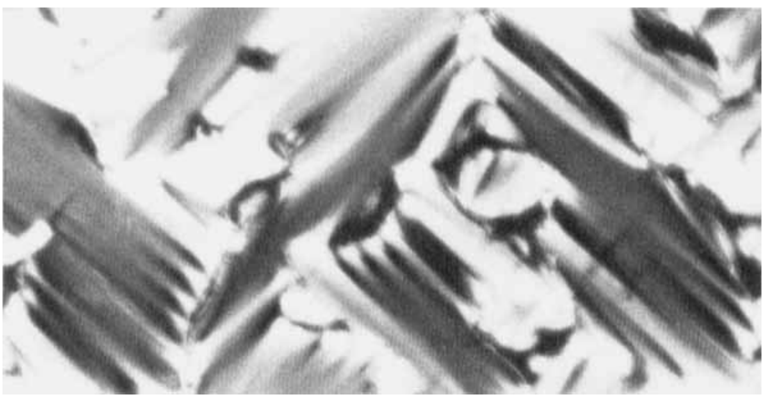

FIGURE 1. The induced S_A-like simple confocal texture of OOBA at tilted orientation. Magnification 250X.

The textural transition resembles the second order S_A-S_C phase transition at substances possessing smectic C type C_2[6], where the angle ω is comparatively small and depends on the tempera-

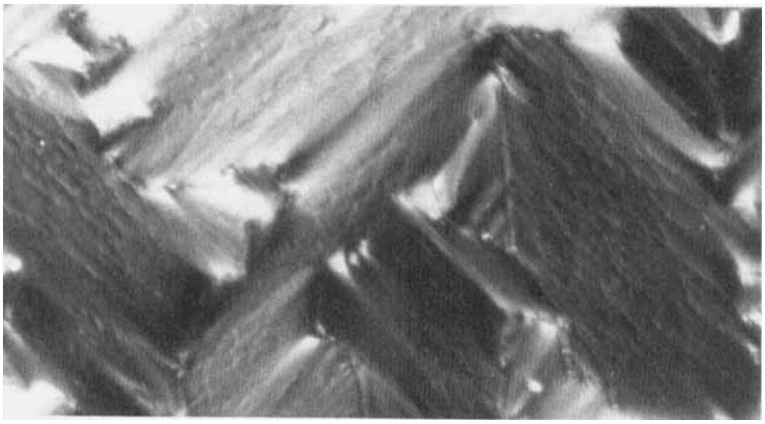

FIGURE 2. The broken confocal texture of OOBA at tilted orientation. Magnification 250X.

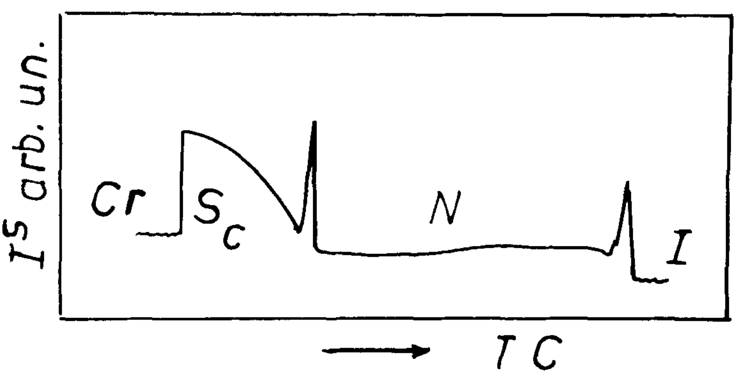

FIGURE 3. The temperature dependence of the depolarized light scattering intensity I^s of OOBA at tilted orientation.

ture. This resemblance is well expressed and in the depolarized scattered light thermal analysis, Fig. 3, from where it is seen that immediately below T_{N-S_C} a minimum is obtained and after this minimum, at further cooling, a nonlinear increasing of the I^s is achieved. We interpret the structure corresponding to this minimum as a S_A-like. The nematic phase of the tilted orientation with an azimuth φ approximately zero is without changes in the texture and the temperature dependence of the intensity I^s, Fig. 3. Presumably, at a such azimuth in the nematic phase, the pseudolayers formation in the frame of the cybotactic groups and the coordination between the groups are more easy. It is reasonable to assume that in the nematic phase the pseudosmectic layer generation starts without noticeable changes in the molecular tilting. The necessary tilting for the stable S_C is accomplished in this geometry in the temperature interval of the S_C phase. This tilting is indicated by the I^s increasing or brokening of the simple confocal texture between T_{N-S_C} and T_{S_C-Cr}.

Our experiments demonstrated that the S_A-like state can be also induced close to the $N-S_C$ transition temperature using quasihomeotropic orientation[4]. This orientation also favours the layer generation in the frame of the nematic cybotactic groups as well as their coordination in larger pseudolayers without a significant molecular director tilting. In a very short temperature interval (some tens of degree) above the $N-S_C$ phase transition[4], these pseudolayers (growing close to the substrates where the energy is minimum[8] in this geometry) start to penetrate in the cell's volume compressing the deformed nematic as it follows from the mechanism presented by Cladis and Torza[8]. In our opinion the texture which is an indication of this process, where the smectic formed close to the boundaries is S_A-like (there is no tilting in the N phase as seen from the dependence $I^s=f(T)$, Fig. 4), is the known pretransition texture-stripe-like domains, Fig. 5. The second texture which is an in-

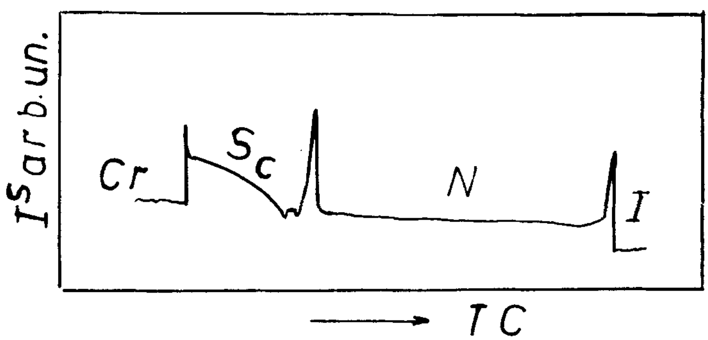

FIGURE 4. The temperature dependence of the depolarized light scattering intensity of OOBA at quasihomeotropic orientation.

dication of the further tilting of the molecules at cooling in order to achieve the necessary tilt for S_C at coordinated layers, is the undulation domain instability[9], Fig. 6. Consequently, in the N phase of the quasihomeotropic geometry, there are conditions for easy molecular coordin-

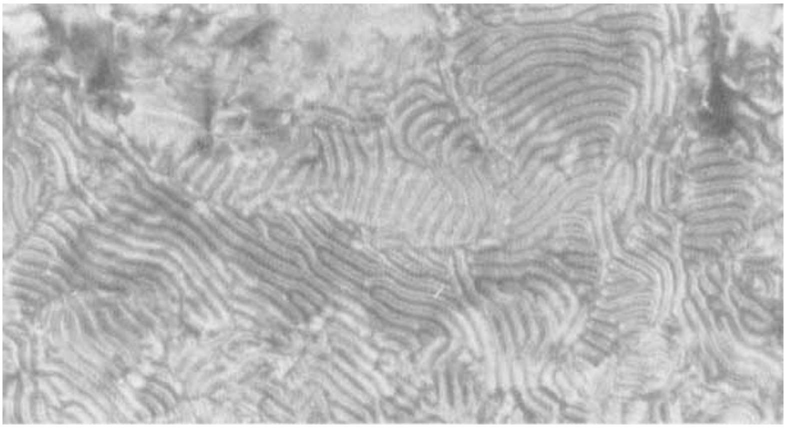

FIGURE 5. The pretransition striped texture at quasihomeotropic orientation. Magnification 125X.

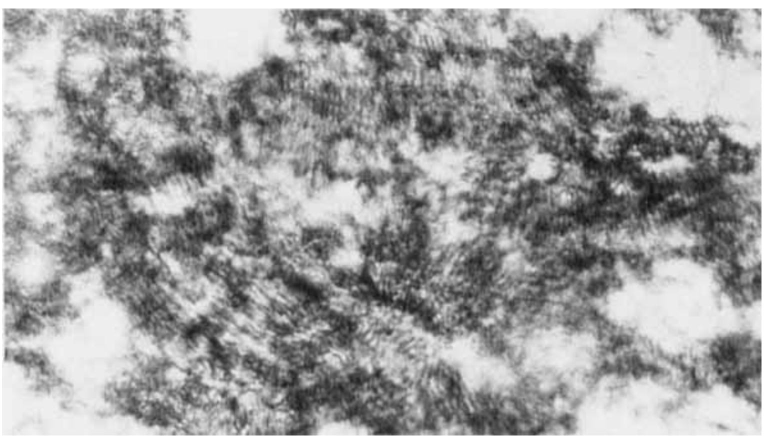

FIGURE 6. The thermomecanical undulation instability at quasihomeotropic orientation. Magnification 125X.

ation in pseudolayers without molecular tilting. The molecular tilting whose fluctuation is reflected in the dependence $I^s=f(T)$ starts closely below T_{N-S_c} after the minimum corresponding to the S_A-like state, Fig. 4, and continues through the whole S_c phase temperature region resembling the S_A-S_C second order phase transition.

ii. Induction by the boundaries of the S_A-like state in the nematic region.

We shall consider here the most typical geometry for this induction - the planar one.

An indication for an induced S_A-like state in the nematic phase is more difficult to be found mainly because the pseudolayers are limited in the cybotactic group frames and the formation of textures typical for the S_A state is strongly hampered. Some textural changes, however, in the nematic phase start at a definite temperature point T_p[10], but it is difficult to be interpreted. More convenient for the structural indication or the changes in it for this case is the depolarized scattered light thermal analysis. It is seen from this analysis, Fig. 7, that in the nematic phase of OOBA the intensity increases nonlinearly below T_p (in an interval of 4-5 degrees) and then starts to saturate. The I^s increasing again resembles a S_A-S_C second order phase transition. Presumably, in the temperature interval T_p-T_{N-S_c}, the pseudolayer coordination and the molecular tilting occur in the cybotactic groups. As seen from Fig. 7, after

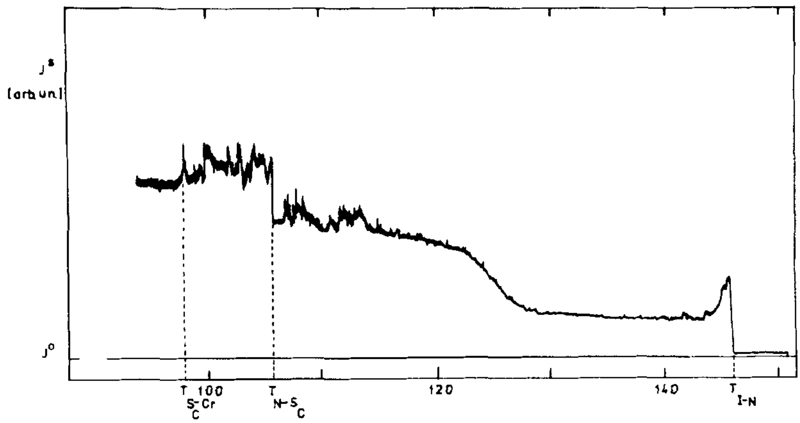

FIGURE 7. The temperature dependence of the depolarized light scattering intensity at planar orientation. T_p is the temperature of the N phase where I^s starts to increase nonlinearly.

the transition in the S_C phase I^s=const in the whole temperature region implying that the necessary tilt (ω) for a stable S_C state is accomplished still in the nematic phase. Consequently, we can assume that a S_A-like state is possible to be induced during the molecular tilting and the pseudolayer coordination.

An other geometry for OOBA in support to the assumption that the necessary for the stable S_C tilt is accomplished still in the N phase is the one at which $\theta \approx \omega$. This geometry assumes very easily the S_C tilt angle formation in the nematic phase and we have not found an indication (by texture or depolarized light scattering) for an induced S_A-like state.

The S_A-like state as an intermediate one, between the S_C and the N phases, is well pronounced at slow heating of the S_C phase. The N, S_A-like and S_C phases from left to right are simultaneously seen in Fig. 8.

FIGURE 8. The induced S_A-like state at heating of OOBA (middle part of the picture). The left part - N phase, the right part - S_C phase.

The strength of the anchoring plays a significant role in the balance between the bulk and the boundary forces in the smectic layer formation process. If the boundary forces are big enough in this balance, as for example at planar orientation, the S_A-like state induction in the frame of the cybotactic groups is possible in the nematic phase. This obviously indicates that for S_A-like state it is energetically more advantageous to generate in the region close to the orienting substrates, i.e. the S_A-like state growing as an intermediate one between the classical nematic (above T_p) and the S_C phase starts from the boundaries and with the cooling penetrates into the cell's volume. The role of the boundaries in the S_A-like state induction is also seen from the following example. At inhomogeneously distributed forces (different strength of the anchoring) on the orienting substrates, due to imperfection in their treating, a spontaneous passing from one geometry into another is possible thus provoking different corresponding textures for the S_A-like state induction. For example, in the same cell (at a hybrid orientation[4]), the pretransition stripe lines used for S_A-like state identification spontaneously relax in simple confocals. This implies that a geometry provoking layer formation with a large longitude and parallel to the substrates passes into a geometry provoking a layer formation with a small longitude - vertical or oblique to the substrates.

For some of the liquid crystals possessing N and S_C phases investigated by us as HOBA and DDOBA we had not the possibilities to observe a S_A-like state. As it is known[5], these substances possess a comparatively big N-S_C phase transition energy H. For example, a transition striped texture (indicating S_A-like state) cannot appear at $H/K_BT_c > 1$, where K_B - the Boltzman's constant, T_c - the clearing point. In order to overcome this strong factor in the balance between the boundary and the bulk forces at the S_A-like state induction for HOBA and DDOBA, a very strong anchoring is necessary which is difficult to be done by our treatment.

As shown above, by treating the substrates accomplished by us, we had possibilities only to registrate the S_A-like state in the substances OOAB, HOAB, OOBA, NOBA, DOBA with factor H/K_BT_c approximately 0,26, 0,30, 0,30, 0,4, 0,4, respectively as follows from the mechanism presented by Cladis and Torza[8].

Our experiments[1-5] with differently oriented samples give us a reason to accept that the S_A phase does not exist really in the substances possessing N and S_C but can be induced only at suitable boundary conditions; and that if there is any weak S_A fluctuation of the smectic order, it is not in a state to give any noticeable changes which can be registered without special preparation.

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