Vol. A55 (1979) ACTA PHYSICA POLONICA No 2

BIREFRINGENCE ANOMALY NEAR THE CLEARING POINT OF NEMATICS*

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(Received March 23, 1978)

The investigations of the nematic–isotropic phase transition in MBBA and EBBA have shown that this transition has a complex nature. At temperature T_0, which is very close to the clearing temperature T_c, a sudden change of the director orientation from planar to homeotropic is observed. The latter is preserved only in small range of temperature (approximately 0.1 K). At slightly higher temperature the coexistence of the nematic and isotropic phases takes place up to the clearing temperature.

1. Introduction

The transition from the nematic to the isotropic phase is of the 1-st kind, involving a discontinuity in the ordering parameter as well as anisotropic properties, like optical birefringence, magnetic and electric anisotropy, and others [1]. At temperatures close to the clearing point, no well perceptible anomalies of these properties are observed in nematics. Thus, we were all the more astonished to observe phenomena of orientation, occuring in the nematic phase in the immediate vicinity of the clearing point [2] and consisting in a one- or twofold drastic change in orientation of the director i. e. local optical axis. We observed the changes in orientation in initially planar-oriented thin layers of the nematic (1–100 μm), situated between two platelets of glass. Orientation of the molecules of the nematic was achieved by the method of Chatelain [3].

The most convenient method of observation of these orientational effects consisted in the use of polarized light. The MPI-5 polarization-interference microscope applied by us was equipped with an electric heater, supplied from a thermoregulator permitting temperature stabilization with an accuracy of ±0.03 deg. Temperature inhomogeneities in the field of vision did not exceed 0.01 deg. In addition to visual observation, the micro-

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* This work was sponsored by the Polish Academy of Sciences within the Project MR-I.5. Presented at the Second Liquid Crystal Conference of Socialist Countries, Sunny Beach, Bulgaria, September 27–30, 1977.

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scope permitted the intensity recording of the light transmitted by the sample as well as the determination of birefringence in the direction perpendicular to the layer. Birefringence was determined interferometrically, recording the changes in intensity of transmitted light as a function of temperature.

2. Results of observations

At slow heating of the planar-oriented sample in a temperature T_0 by about 0.2 deg lower than that of clearing the field of vision suddenly becomes dark. When the temperature is further raised by about 0.02 deg, the field of vision brightens (Fig. 1). We refer to the temperature interval in which the field of vision is dark as the pseudo-isotropic (PI) phase. A convenient physical property for the quantitative description of the effect is to be found in the optical birefringence, understood to mean the difference in refractive indices of the ordinary and extraordinary beams in the direction perpendicular to the surface of the sample. Fig. 2 shows the temperature-dependent changes in birefringence for a sample of EBBA. At T_0, near the clearing point, the birefringence falls to zero. At temperatures slightly higher, it increases again, attains a maximum and decreases, at first as a linear function of increasing temperature.

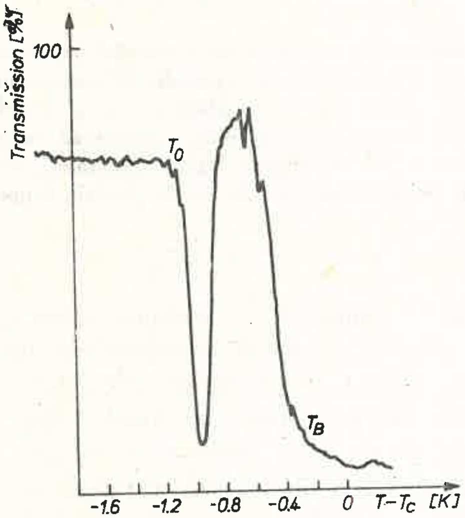

Fig. 1. Transmission of MBBA sample for white light, versus temperaure

At the temperature T_B the birefringence falls jump-wise to zero corresponding to the emergence of first regions of the isotropic phase. In a certain interval of temperature, the nematic and isotropic phases coexist at equilibrium up to the temperature T_c, when the last nematic regions vanish.

The above described process of changes in birefringence near the clearing point can be explained as due to a change in orientation of the director. Observations of texture and conoscopic figures, as well as of changes in orientation on application of an electric field show that, in the PI phase, the director is perpendicular to the walls of the vessel, whereas at higher temperatures it is oriented obliquely. The angle subtended by the optical axis and the glass plate surface varies with temperature. It should be stressed, however, that under certain conditions defined essentially by the state of the surface of the vessel, the orientation can change without becoming perpendicular i.e. it can go over directly from planar to oblique. It is even possible for the oblique orientation to occur at temperatures remote from T_c.

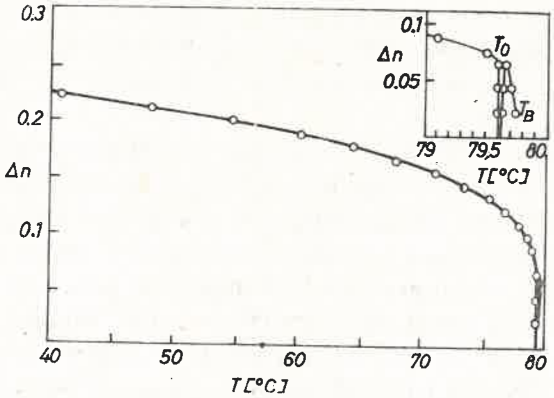

Fig. 2. Birefringence of EBBA vs. temperature

The above described changes in orientation are observed in a variety of nematics (p-methoxy-benzylidene, p-butylo-aniline, p-ethoxy-benzylidene-p-butylo-aniline, p-pentyl-p-cyano-biphenyl, p-nitrophenyl p-octyloxybenzoate).

3. Discussion

With the aim of elucidating the reason of the orientational effects, we studied the influence thereon of various factors, such as: impurities, admixtures, the properties of the vessel surface, and the initial structure of the nematic.

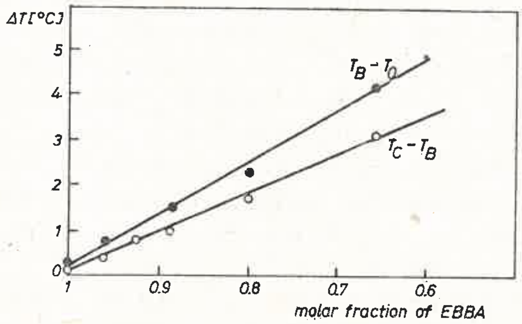

Fig. 3. Difference between the temperature of clearing and that of orientation effects in EBBA, as a function of temperature

A. Influence of impurities

The relationship between the changes in birefringence and the presence of impurities was studied admixturing the carefully purified initial preparations.

On initial, careful purification, samples of MBBA and EBBA were admixtured with butyl alcohol, or benzene. In these cases the nature of the orientational effects remained unchanged. However, the temperature interval in which the anomalies occurred increased proportionally to the concentration of the admixture (Fig. 3). Also, in Fig. 3, the temperature interval ($T_c - T_B$) of phase equilibrium increased linearly with the admixture concentration.

This would suggest that the effects of orientation and phase equlibrium are related with the presence of admixtures or impurities. However, the orientation effects are present in even very pure MBBA and EBBA samples ($T_c = 48°C$ and 80°C, respectively).

The only explanation of these apparently contradictory results of observation is to be found in the assumption that even traces of impurities, present in even the purest of our samples, suffice to bring about the effects of orientation. Presumably, a decisive role is played by adsorption of these traces of impurities on the walls of the vessel. An adsorbed film of this kind can affect the type and energy of anchoring thus affecting the process of orientation.

B. Influence of surface properties

Most observations of orientation effects were performed on samples the initial (low-temperature) orientation of which was planar, induced by the special processing applied to the glass platelets destined as boundaries for the layer of liquid crystal. However, differences in processing subsequently lead to different anchoring energies of the nematic molecules on the glass surface, and this obviously can affect the orientation process. In order to find whether the anchoring energy is somehow related with the nature of the transition to the isotropic phase, we attempted to vary the energy in accordance with a pre-established program by varying the process applied to the glass surface. To obtain strong anchoring we applied rubbing of glass surfaces, initially purified on blotting-paper, cerium oxide, or by means of fine, hard polishing powder. In such cases, the planar orientation went over into an oblique one without passing through the perpendicular orientation.

We obtained weak anchoring by coating the glass surfaces with a film of amorphous material, such as decay products of cellulose (Ryschenkow's method [4]), or polystyrene. When applying the method of Ryschenkow one observes the perpendicular orientation; however, this is due to diffusion of the impurities from the amorphous film into the layer of liquid crystal and the resulting concentration gradient rather than to weak anchoring.

The situation is less equivocal when having recourse to polystyrene, which does not dissolve in the liquid crystal. The orientation is oblique already at room temperature and remains unchanged up to the clearing point.

The preceding experiments lead to the conclusion that the anchoring energy is not the sole parameter decisive for the occurrence of orientation effects prior to the phase transition.

C. Influence of molecular structure

In the effects under consideration. a decisive role has to be attributed to interactions between the molecules of the liquid crystal and the material of the vessel at the surface. We accordingly proceeded to observations of the effects in nematics differing as to the direction of their dipole moment and their molecular symmetry. The following molecules were studied: two nematics of the p-alcoxy benzylidene-p-butylo-aniline series (EBBA and MBBA) and p-nitrophenyl p-octyloxy-benzoate, with molecules unsymmetric and dipole moments not parallel to the long axis of the molecule; pentylbiphenyl (PCB), with dipole moment parallel to the long axis; and p-azoxyanisol (PAA), with the dipole moment of its symmetric molecule more or less perpendicular to the long axis of the latter. The glass surface used were all prepared in the same way. Our attempt to determine an influence of the direction and magnitude of the dipole moment of the molecule as well as the symmetry of its end groups failed to permit a correlation of the nature of the pre-transitional effects and the structure of the molecule. This suggests that the nematic-surface interaction is more highly complex and by no means reduces to e.g. dipole interaction.

5. *Conclusions*

Our results point to the presence of competitive interactions at the glass-nematic interface, i.e. leading to planar order primarily due to the elastic properties of the nematic. Other interactions tend to produce a perpendicular configuration of the director; these may be electrostatic or dispersional, or anisotropic interactions between the molecules of the nematic themselves responsible for surface tension anisotropy. It is also highly plausible that the molecules of the nematic interact with the ions and molecules adsorbed on the glass surface.

With increasing temperature, as the elasticity coefficients decrease, the forces causing planar orientation weaken. At sufficiently high temperatures, those leading to perpendicular or oblique orientation of the director become predominant and changes in orientation, apparent as drastic variations in birefringence, are observed. It is less easy to explain the presence of another change in orientation immediately preceding the transition to the isotropic phase. In our experiments, this was not due to the presence of isotropic films on the glass surface, as was the case in those of Ryschenkow [4].

Maybe some role herein is played by structural defects and perturbations in director orientation related thereto which, under the conditions of very weak anchoring prevalent immediately before the phase transition, can become apparent even at a considerable distance from their source.

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