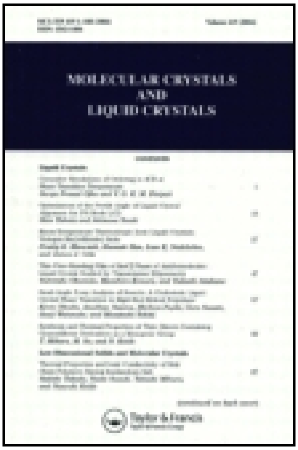

Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

The Fluctuation Layered Structure of Induced Cholesterics

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The Fluctuation Layered Structure of Induced Cholesterics

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This work is dedicated to nematic liquid crystals structure studies and its correlation with an induced cholesterics supermolecular spiral organiztion fixing. The cholesteric-nematic mixtures on the base of polar and non-polar nematics with the dopants of cholesterine esters are studied. The layered structure period temperature dependencies, correlation length and small-angle X-ray scattering intensity in nematic-cholesteric mixtures show, that the nematic matrix structural perfection is slightly disturbed when the cholesterine esters molecules are introduced into the matrix.

Keywords: nematic liquid crystals; cholesterics structure

INTRODUCTION

The structures of nematic matrices and induced cholesterics on their base were studied by means of small-angle X-ray chamber KPM-1 with a chink beam collimation. The CuKa radiation filtered by nickel filter was used. The rectangular profile of X-ray radiation forming was realized by means of three chinks with a width of 5×10^{-5}; 1×10^{-4}; 5×10^{-5} m. The origin beam height was equal to 0.01m. The acute-focal X-ray tube working conditions were: feeding voltage - 40 V; feeding current - 20...25 mA. The small-angle X-ray scattering experimental profiles were fixed at intervals of 2" by the number of pulses collection method in 100 s. For liquid crystal substances alignment magnetic field with induction value of 0.1 T was used. The experimental scattering profiles processing was carried out by the technique described in[1,2,3,]

Let us go to the experimental studies results considering. At the references[3,4,5] the studies of 5CB and GK-440 nematic liquid crystals by small-angle X-ray scattering method were described. The mixture of this nematic substances we have used as a matrix of induced cholesterics for our studies. The mesophase existence temperature intervals for 5CB and GK-440 are 293...308 K and 268...347 K correspondingly. Two incommensurable periods d and d' were observed simultaneously for pure 5CB. The d period corresponds to a monomeric density wave, d' period - to a dimeric density wave. As a result, d period is in correlation with a characteristic dimensions of 5CB monomer, and d' period is connected with a characteristic dimer dimensions.

The mixture of asoxycompounds GK-440 (4-butil-4'-methoxyasoxybenzole (BMAOB) and 4-butil -4'-pentanoil-oxyasoxybenzole (BGAOB) in weight ratio 2:1) is used as a weak polar matrix component. The results of this substance X- ray studies[6] show, that X- ray beams scattering localizes close by a high q (|q| =0. 26 A), the layered structure period d=24.2 A at the temperature of 300 K.

In the process of X -ray experiment the mixtures with a strong polar component content from 0 to 100 weight % were studied. For all this mixtures the scattering close by the one inversed space vector q is observed. The dependence of layered structure period on strong polar component concentration is shown on the Fig. 1.

Taking into account the linear character of physical properties on components concetration dependence, it can be assumed, that there are no associated states between the asoxycompounds and cianoderivatives molecules. That is why the properties must be defined by the concentrational balance between asoxycompounds molecules and cianoderivatives dimers and monomers[7]. Where as the fluctuation layered structure period will depends on the relationship between the structural units of all three types. It should be noted, that asoxycompounds molecule can be the ensemble of two different types molecules, which are characterized by the certain "effective" length. The results of asoxycompounds (GK-440) X-ray studies allow to affirm that such the supermolecular formation is enough stable and can be the structural unit. Let us assume, that the layered structure period is created at the expence of additive contribution of structural units, that form the layer: cianoderivative dimers and asoxycompounds structural units. In this case the formula for the layered structure period can be written as [5]:

$$d = x\, l_{2d} + (1-x)\, l_{lef} \qquad (1)$$

where l_{2d} and l_{lef} - cianoderivatives dimers length and the "effective" asoxycompounds molecules length, X- strong polar component concentration.

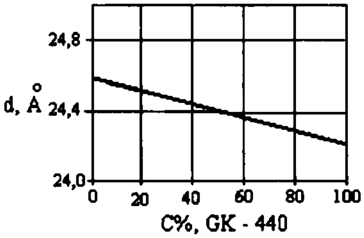

Fig. 1. Dependence of fluctuation layered structure period on component concentration in the mixture 5CB+GK-440 (at the T = 300 K).

Let us consider the scattering intensity maximum and correlation length dependencies on component concetration at the certain reducted temperatures, that are shown at the Fig. 2,3. As we can see from the experimental dependencies, the scattering intensity and correlation length values are observed at the concentration region of 70...80 % of cianoderivative. Such an increasing can be caused by a system tendency to an induced smectic phase creation, though it is not experimentally observed. Such a great potential "smectogenety " of the mixture would be shown by its physical properties. It should be noted, that the scattering intensity and correlation length values retain almost a constant at the cianobiphenile concentrations up to 70 %. Let us consider the main regularities of layered structure forming when the cholesterine esters are added to the mixture of asoxycompounds and cianobipheniles for spiral structure creation. This regularities are the most pronounced in the induced cholesterics on the base of nematic matrix, that maintains a 80 % of strong polar component. Let us consider the dependence of layered structure period d dependencies are shown for the induced cholesterics on the base of a different content matrices with a dopant of cholesterylmiristate. The period d value a somewhat differs from the matrix period value. So, the layered structure period for the nematic matrix with a 80 % of strong polar component is d=24.4 A, and for the induced cholesteric - d=25.8 A (at the T=293 K).

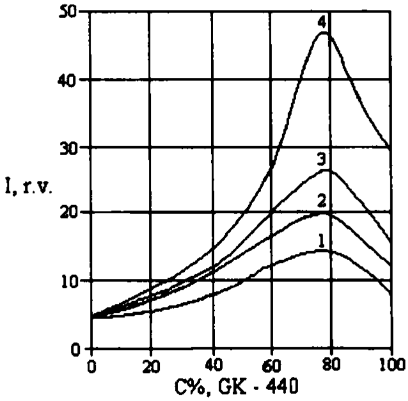

Fig. 2. Concentrational dependencies of scattering for the mixtures 5CB and GK-440 at the reducted temperatures : 1-3; 2-5; 3-10; 4-13 K .

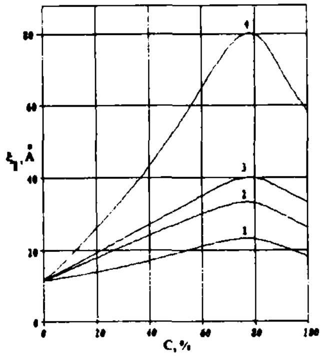

Fig. 3. Concentrational dependencies of correlation length for the mixtures of 5CB and GK-440 at the reducted temperatures: 1-3; 2-5; 3-10; 4-13 K .

So, the cholesterylmiristate molecules a somewhat "stabilize" the matrix structural units. The scattering intensity and correlation length concentrational dependencies at a fixed cholesterine ester content repeat the basic regularities, that are inherent in the nematic matrix. An essential correlation length growth is observed exactly for the induced cholesteric on the base of the nematic matrix with 80 % of cianobiphenile. Jast in this mixtures the most " smectogenety " exists. The induced smectic phase is not created, but the fluctuational layered structure is of a high regulating degree. Such a structure regularity is shown by its physical properties, in particular, the elasticity constants a sharp increasing.

One of this method is an infra-red absorption spectrums in polarized light studies. The molecular interaction changes the characteristics oscillations spectrum of different molecular groups. This changes will be the more stronger, the more strongly the given molecular group interacts with its surroundings. Such a changes display in a displacement, widening or origin of new stripes in absorption spectrum. Thus the total analysis of X-ray data and IR- spectroscopy results gives a possibility to estimate not only the scattering objects shape and dimensions, and even their inner structure features: the structural units, that form the scattering object, type. We have obtained the

IR-absorption spectrums for individual nematic substances (asoxycompounds and cianobipheniles) and for their mixtures with 40 and 80 % of strong polar component content. The individual substances and their mixtures spectrums were fixed in liquid crystal state at the temperature of 293 K and wavelength range from 400 to 4000 cm^{-1} by means of "SpecordM-40" spectrometer. The samples are overflowed into KBr cuvettes. Liquid crystal layer thickness was of 15 μm KBr plates inner surfaces were not treated for the alignment obtaining. Let us analyze the individual substances spectrums, the mixture with 80 % of strong polar component content spectrum, and the same mixture with 1 % cholesterylmiristate content spectrum. The strong polar nitril group C=N in cianobiphenile corresponds to the clear-cut absorption stripe in IR spectrum range (wave number 2235 cm^{-1}) which oscillator coincides with a long molecular axis direction. Probably that just this polar group defines the molecular interaction effects [8]. This stripe can be used as a spectrum mark for molecular associate creation studies. The asoxycompounds, that maintain besides BMAOB and BGOAOB molecules also have the clear-cut absorption stripe in IR-region of spectrum (wave number 1760 cm^{-1}). This stripe corresponds to the carbonil group C=O of one of the matrix component, and also can be used as a spectral mark. The all individual substances stripes are kept for the spectrum of the mixture, that maintains 80 % of strong polar component. There were not new stripes, but the integral stripes intensity increasing was observed for the nitril and carbonil groups. The absorption stripes integral intensity growth is observed when the cholesterylmiristate is added to the nematic matrix with 80 % of strong polar component in concentration from 0.4 to 1.5 weight %. On the base of our results it is possible to make the conclusion, that the main structural units of the matrix with 80 % of strong polar component are: cianoderivative dimers (molecular interaction character not changes), single asoxycompounds molecules or a pair of molecules, which are "put" into the cianoderivative origin layered structure. The new type associates (of strong and weak polar components molecules, for example) are not created. The molecules packing density increases when the cholesterine esters are added to the mixture. There are no essential changes in the molecular interaction character.

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