

MOLECULAR ARRANGEMENT IN THE NEMATIC DROPLET

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Optical studies were made of the molecular arrangement in the nematic droplet which was allowed to remain stable over the temperature range of the nematic mesophase. A new model of the molecular arrangement was proposed to explain the observed changes of the microscopic pattern.

It has been well established by use of a polarizing microscope that the nematic mesophase separates from the isotropic liquid as spherical droplets which exist only in a short range of temperature and coalesce to give the threaded texture or the centered texture.^{1),2),3)}

The molecular arrangement in such a nematic droplet has so far been considered either to radiate from the center of the drop or to be arranged in concentric circles about the center of the droplet on the basis of microscopic observation. However, no detailed arguments have been made on the molecular alignment in the nematic droplet because of the rapid movement and coalescence of the nematic droplet itself.

In this letter, we wish to report a new model concerning the molecular orientation in the nematic droplet which is fixed in the matrix of a very viscous polymer (Araldite AN-100 cement) and remains stable as the spherical body over the temperature range of the nematic mesophase. The liquid crystal used for this study was n,p-octyloxybenzoic acid which was purified by successive recrystallization with both benzene and ethanol. A mixture of the liquid crystal and the polymer matrix was heated to give the isotropic state between the glass slide and the cover slip on the microscope stage with a heating block and then cooled slowly to the nematic state. In such a matrix the nematic droplets are not free to move and to coalesce with each other over the temperature range of the nematic mesophase. The uniaxial character of the nematic droplet was determined using a polarizing microscope. A sensitive color plate ($R=550m\mu$) was used

as the test plate to determine the sign of uniaxial crystals.

Two typical patterns observed with crossed polaroids by removing the Bertrand lens and the condenser are illustrated in Fig. 1. In these patterns, the first and third quadrants were yellow while the second and fourth quadrants were blue. Furthermore, the isogyre of the pattern B was invariant on rotating the stage of the polarizing microscope while that of the pattern A varied successively with the rotation of the stage as indicated in Fig. 2 and the rotation of the angle 180° gave the same pattern as the original.

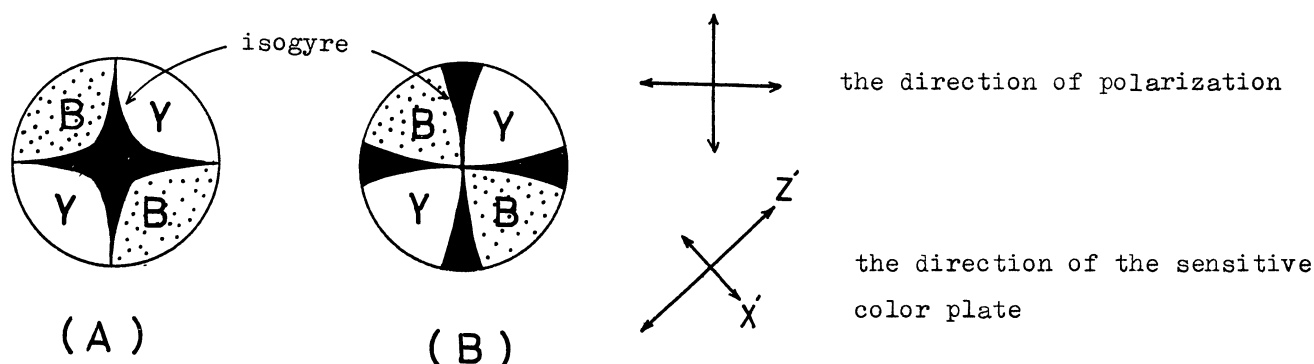


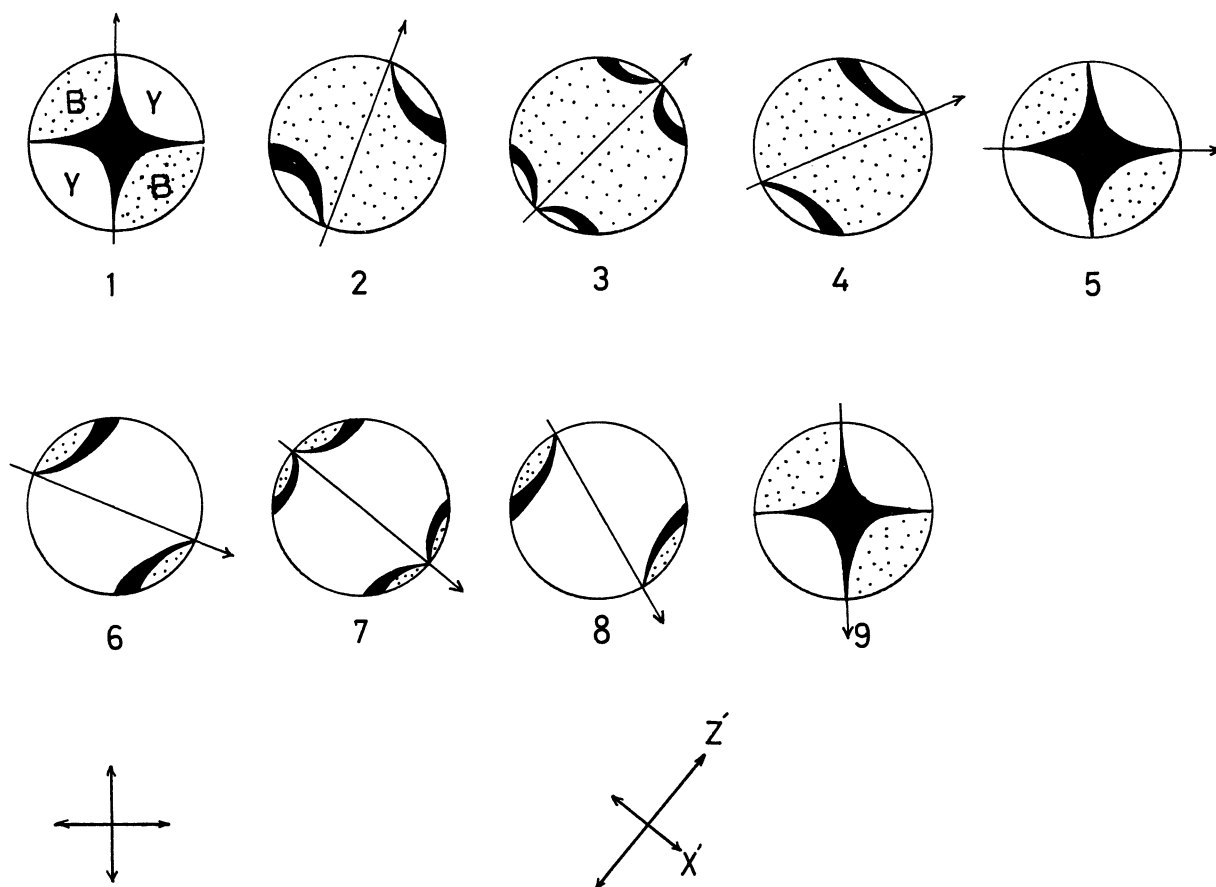
Fig. 1. Two typical patterns of the nematic droplet
Y ; yellow, B ; blue

We propose the following new model of the molecular arrangement in the nematic droplets to explain reasonably all the results of the observation. In the following discussions it is reasonably assumed that the maximum dipole moment lies parallel to the long axis of the molecule. The model is shown in Fig. 3, where the optic axis of the microscope lies perpendicular to paper and rod-like molecules are arranged in layers with their long axes lying tangential to the perimeters of concentric circles about the optic axis. Moreover, the layers spread convex to the perpendicular bisector of the optic axis.

Pattern B is attributed to a nematic droplet with the optic axis perpendicular to the plane of the stage of the polarizing microscope as shown in Fig. 3(c), where the molecules are arranged symmetrically in the concentric circles, and the pattern remains unchanged with respect to the rotation of the stage.

Considering the correlation between the orientational arrangement of the molecule and the direction of the sensitive color plate, the retardation decreases in the first and third quadrants, while increases in the second and fourth quadrants.⁴⁾ Accordingly, interference color shows the lower order, i.e. yellow in the first and third quadrants,

on the other hand, blue in the second and fourth quadrants.



the direction of polarization

the direction of the sensitive color plate

Fig. 2. The changes of the pattern A on rotating the stage of the microscope

In the case of the pattern A where the isogyre varies successively with the rotation of the stage, the optic axis lies parallel to the plane of the stage as illustrated in Fig. 3(b). If the molecules in the droplet are arranged in convex layers as shown in Fig. 3(b), the retardation should decrease in the first and third quadrants and then interference color should be yellow. With this model of the molecular arrangement, the changes of the interference color and the pattern on rotating the stage would be identical with those obtained experimentally, which are shown in Fig. 2.

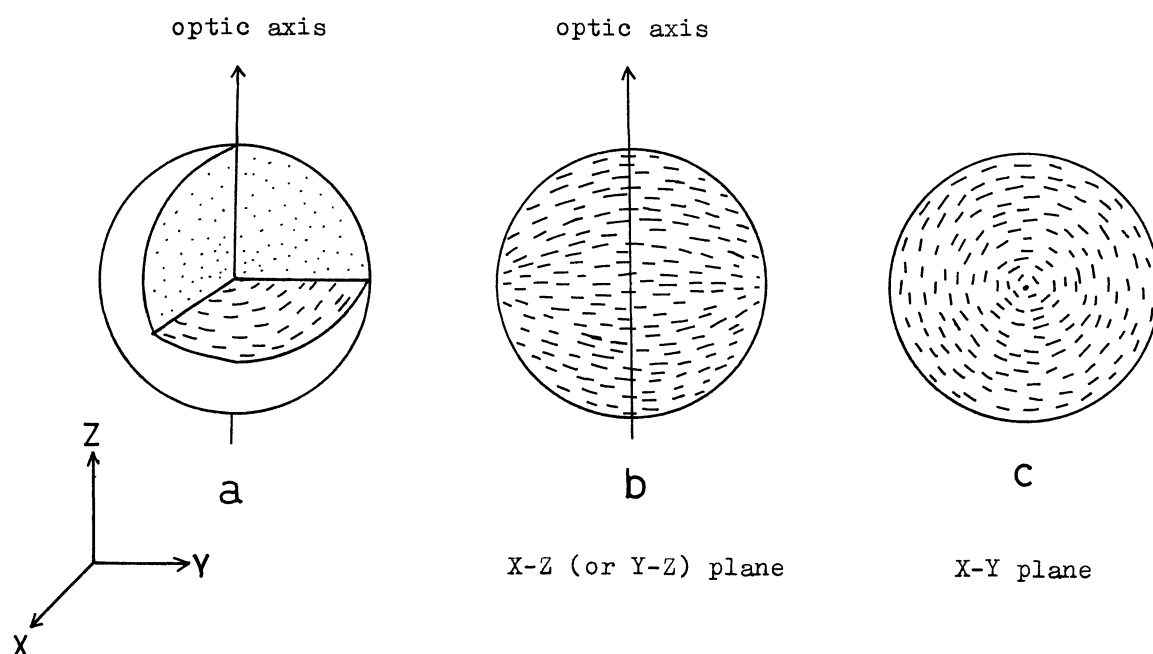


Fig. 3. The model of the molecular arrangement in the nematic droplet

These results obtained in this study might be apparently contradictory with the conventional idea that the nematic mesophase behaves optically in the same way as uniaxial crystals with positive birefringence.^{1),5)} It should be borne in mind, however, that in the proposed model of the molecular arrangement in the nematic droplet the small part of the spherulite has held the parallel molecular orientation. At present, it could not be concluded that the reason of the conflict is attributed to either the characteristic properties of the nematic droplet of *n,p*-octyloxybenzoic acid or the environmental effect of the matrices.

Further detailed study will be published shortly.

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