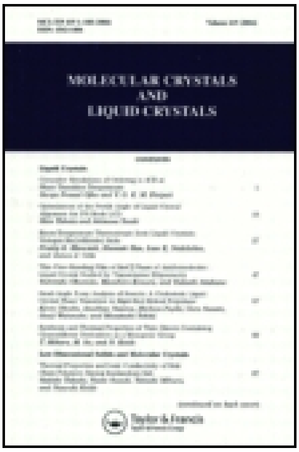

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Phase Transitions in Freely Suspended Smectic Droplets. Cotton-Mouton Technique, Architecture of Droplets and Formation of Nematoids†

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Phase transitions of aqueous suspensions of droplets of smectogens have been studied using the collective Cotton-Mouton (CM) technique. Two compounds were examined: NPOOB and 8OCB. A statistical model (previously developed for suspensions of nematogens) has been adapted to describe the collective CM effect in these systems. It was found that both the phase transitions and the changes of architecture within the droplets cause distinct changes in the CM effect.

An attempt was made to investigate suspensions of theliquid crystalline germs created in the isotropic melts of nematic and smectic mesogens mixed with a chiral additive. In such mixtures, nematoids (the liquid crystal analogues of the whiskers of crystalline solids) are formed. It is usually found that nematoids arise as an extension of the tail of a monopole droplet or grow from a focal conic multipole droplet but "free" nematoids (without droplets at their ends) can also occur. The aspect ratio of nematoids varies with the composition, ranging from about 3 to 3,000. When cooled, nematoids rapidly condense to droplets with the formation of a spiral or double spiral often occurring at an intermediate stage. The architecture of germs in N–S-chiral melts is discussed.

Keywords: liquid crystals, suspensions, Cotton-Mouton effect, saturation, statistical model

I. INTRODUCTION

It is now well-established that most of the physical properties of dispersed phases (especially those in an ultra-dispersed state) differ significantly from those of the bulk samples.[1,2] These new properties, caused by the so-called size effects, arise as a result of appreciable influence of the surface energy and of the energy associated with defects. If we consider a small particle (a grain) inside a fluid at equilibrium, then its free energy density F can be regarded as being made up of two contributions. One part, F_b, is the bulk free energy density. Its magnitude depends on the undisturbed bulk structure and it is always positive. The second contribution, F_s, is due to the time-average of the interactions between molecules on the surface itself

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within and from interactions across the surface between molecules on either side. We then write $F = F_b + F_s$. The contribution F_s is a very complicated function depending on various inter-phase interactions including those at the electric double layers. For an isolated particle, $F = \sigma S/V$, where σ is the surface tension and S and V are the surface area and volume, respectively. In multicomponent systems, the composition of the boundary layer must be also taken into account. This composition will, in general, differ from that in the bulk of the sample as the concentration of each individual component in the boundary layer depends on its influence on the surface energy.[3]

It is well established that the size effect is common for ultra-dispersed metals, e.g., Fe, Co, Ni, Mn, and rare-earth metals and for inorganic compounds, e.g., AgI and Al_2O_3.[4] In particles of a diameter between 10 and 10^2 nm, very distinct changes of the phase temperatures are found and some new phases, not shown by the bulk sample, are observed.

For liquid crystal droplets in suspension, structural defects within the droplets are a consequence of the spheroidal shape, the liquid crystal ordering and the boundary conditions.[5-10] Since these defects involve changes of the elastic energies of the liquid crystalline material, the defect component of the free energy density, F_d must be taken into account. Hence, the total free energy density is due to the bulk, the surface interactions and the defect and we can write $F = F_b + F_s + F_d$. It would be expected that the size effect in liquid crystals will be especially noticeable for weak first-order phase transitions.

If we have two neighboring phases 1 and 2, the stable state should be that for which the total free energy density F is lower. For example, phase 2 will be stable if

$$F_{b2} + F_{s2} + F_{d2} \leq F_{b1} + F_{s1} + F_{d1} \tag{1}$$

The equality sign denotes the conditions for the transition between the phases 1 and 2. The temperature shift of the phase transition due to the size effect, $\Delta T = T_{12}^b - T_{12}$, where T_{12}^b and T_{12} are the temperatures of the phase transition for the bulk sample and for a droplet, respectively, can be estimated taking into account that

$$F_{b2} - F_{b1} = H \frac{\Delta T}{T_{12}^b} \tag{2}$$

where H is the latent heat of the phase transition. Substituting Equation (2) into Equation (1) we obtain

$$\Delta T = \frac{T_{12}^b}{H} [(F_{s1} - F_{s2}) + (F_{d1} - F_{d2})] \tag{3}$$

In liquid crystal suspensions, the relationships between the bulk, surface and defect energies are very complicated and the temperature shift can be positive as well as negative. Moreover, under the influence of the surface interactions, some liquid crystal phases can disappear as well as arise. For example, liquid crystal ordering can be seen in thin layers of non-mesogenic nitrobenzene or of monosubstituted derivatives of benzoic acid on a glass surface.[4,11]

In the present paper we discuss phase transitions in micron-size droplets of smectogens. These phase transitions were studied experimentally using both the Cotton-Mouton (CM) technique and by initial microscopy. Two types of systems were investigated:

1. droplets of pure smectogens freely suspended in water;
2. liquid crystal germs immersed in the isotropic melts of the multicomponent mixtures below the phase-separation temperature.

The organization of the paper is as follows: In Section II the Kr–A, A–N and N–Iso phase transitions of aqueous suspensions of one-component smectogens are investigated by examination of the collective C-M effect as a function of temperature. In Section *III* the creation of the liquid crystal germs in multicomponent melts below the critical temperature when the phase separation occurs is investigated microscopically. The architecture of droplets in the melts and formation of the new structures, which we have called nematoids, are described.

II. WATER SUSPENSIONS OF MESOGENS

A. Principles of the Cotton-Mouton technique

The basic principle of the method is the analysis of the birefringence induced by an external magnetic field acting on the suspension of liquid crystal droplets. Since the magnetic field interacts with a droplet as a whole, this interaction can be regarded as collective. The degree of orientation of the optical (magnetic) axis of a droplet along the field strongly depends on the molecular organization within it. As a quantitative measure of this orientation, the magnitude of the collective C-M effect can be used. The magnetically-induced birefringence in this effect, Δn is

$$\Delta n = C_c B^2 \lambda \tag{4}$$

where C_c is the collective C-M constant, B is the magnetic field and λ is the wavelength of the light. The statistical description of the collective C-M effect in the liquid crystal suspensions has been proposed recently by the author.[12] In the monodisperse approximation, the expression for the collective C-M constant C_c has been obtained in the form

$$C_c = C(1 + N_g S_g) \tag{5}$$

where C is the "molecular" C-M constant, N_g is the number of molecules in an individual droplet in the suspension and S_g is the orientational order parameter for long molecular axes (averaging is performed over all the volume of a droplet). The value of S_g depends on the type of liquid crystal ordering and on the number and type of the structural defects within a droplet and can be expressed as

$$S_g = \frac{1}{V_g} \int_{V_g} f(\mathbf{r}) dV \tag{6}$$

For a spheroidal droplet, S_g can be expressed in the spherical coordinate system (r, θ, φ) as

$$S_g = \frac{1}{V_g} \int_{V_g} f_g(r, \theta, \varphi) \sin\theta \, d\theta \, d\varphi \, dr \tag{7}$$

where $f(\mathbf{r})$ and $f(r, \theta, \varphi)$ are the distribution functions describing the local projection of the director on the optical (magnetic) axis of a droplet, $\mathbf{r}$ is the radius-vector and V_g is the volume of a droplet. For every magnetic field (including the saturation region), the value of the birefringence Δn in the collective C-M effect is described by the 2nd order Langevin function $L_2(q)$:

$$\Delta n = \frac{(\Delta n)_\infty}{2} (3L_2(q) - 1) \tag{8}$$

where $(\Delta n)_\infty$ is the maximum value of the birefringence at saturation. The parameter q is the ratio of the magnetic and thermal energies

$$q = \frac{\Delta\chi V_g B^2}{2\mu_o kT} \tag{9}$$

with the effective anisotropy of the magnetic susceptibility

$$\Delta\chi = \mu_o N \Delta\alpha^m S_g \tag{10}$$

where $\Delta\alpha^m$ is the anisotropy of the magnetic polarizability of an individual molecule and N is the number of molecules in the unit volume.

In practice, the influence of the external magnetic field B on the functions $f(\mathbf{r})$ and $f(r,\theta,\varphi)$ can play a significant role, especially in the case of nematic droplets.

B. Experimental

The experimental setup used is shown in Figure 1. The nonpolarized He-Ne laser beam 1 propagates horizontally through the system which consists of polarizer 2, cuvette 4 filled with the suspension and placed in a perpendicular magnetic field B, quarter-wave plate 6, oriented as in the de Sénarmonte compensator, analyzer 8, and photomultiplier tube 9. The polarizer and analyzer are crossed and their axes are oriented at 45° to B. The cuvette is located in the thermostatted chamber 3 (between the poles of the magnet), whose temperature is controlled to within 0.1 K. With the automatic controller 7, the field B can be scanned in a linear

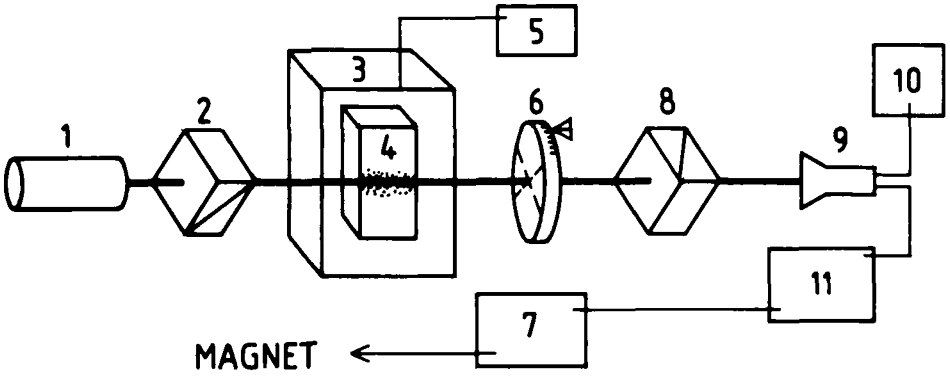


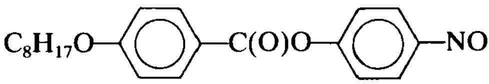
FIGURE 1 Schematic arrangement of the experimental setup. 1, He-Ne laser; 2, polarizer; 3, thermostatized chamber; 4, cuvette; 5, thermostat; 6, quarter-wave plate; 7, supplier of the magnet; 8, analyzer; 9, photomultiplier tube; 10, HV supplier; 11, *X*-*Y* recorder.

fashion from 0 to 1.25 T during the rise and decay times from 1 to 30 minutes. Signals proportional to the field B and the light intensity are applied to the X and Y inputs of the X-Y recorder, respectively.

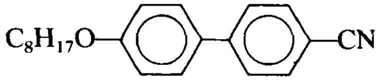
The induced birefringence Δn produces the phase shift $\delta = 2\pi\Delta nl/\lambda$ in the laser beam. Here l denotes the thickness of the effective liquid crystal layer in the sample. In the de Sénarmonte compensator, this phase shift is transformed to the measured rotation of the plane of polarization by an angle $\phi = \delta/2$.

C. Materials

The temperature-dependence of the collective C-M effect has been investigated for the quasi-stable water suspensions of 4-nitrophenyl-4-octyloxybenzoate (NPOOB) (Kr 49 A 61 N 68 Iso)



and 4-*n*-octyloxy-4′-cyanobiphenyl (8OCB)
(Kr 54.5 A 67 N 80 Iso)



The suspensions of NPOOB and 8OCB were obtained using the condensation method by mixing a concentrated ethanol solution of the mesogen with distilled water. The suspension produced was then aged over 48 hours at room temperature. After the aging, the suspension becomes almost mono-disperse with droplets of diameter ranging from 1 to 1.5 micron and was practically stable over several days. The volume ratio of ethanol to water was about 1:100 in the suspension.

D. Results and discussion

If the magnetic field B is increased linearly at constant temperature, the birefringence in the collective C-M effect increases monotonically up to saturation in all the ordered phases of NPOOB and 8OCB—crystalline solid, smectic and nematic mesophases. In the suspensions investigated, the collective C-M constants for the Kr, S_A and N phases of both of the compounds remain in the approximate ratio 1:2:3 and for the nematic phases are $3.6 \times 10^6\ m^{-1}T^{-2}$ and $4.2 \times 10^6\ m^{-1}T^{-2}$ for NPOOB and 8OCB, respectively. For comparison, the "molecular" C-M constant for nitrobenzene is about 250 $m^{-1}T^{-2}$. The field at which the saturation occurs is the largest for the crystalline solid phases of both compounds and for crystalline NPOOB the saturation begins at $B = 1$ T.

The temperature variation of the magnetically-induced birefringence for water suspension of NPOOB at $B = 1.2$ T (well above the saturation for the hardest solid phase), is shown in Figure 2. The diagrams show clearly the existence of four phases. As in the bulk, there are the crystalline solid phase, two liquid crystal phases (S_A and N) and the isotropic liquid phase, in which the collective C-M effect diminishes to its "molecular" level. This value is not registered here because of the very small amount of liquid crystal substance (about 10^{-5} g) in the sample. When the temperature increases, the light intensity curve reaches two local maxima in the vicinities of the phase transitions from the crystalline solid to the smectic A and from the smectic A to the nematic mesophase. The nematic–isotropic phase transition is marked as a discontinuity in the slope of the light intensity curve. In the temperature limits of a definite phase, the collective C-M effect decreases

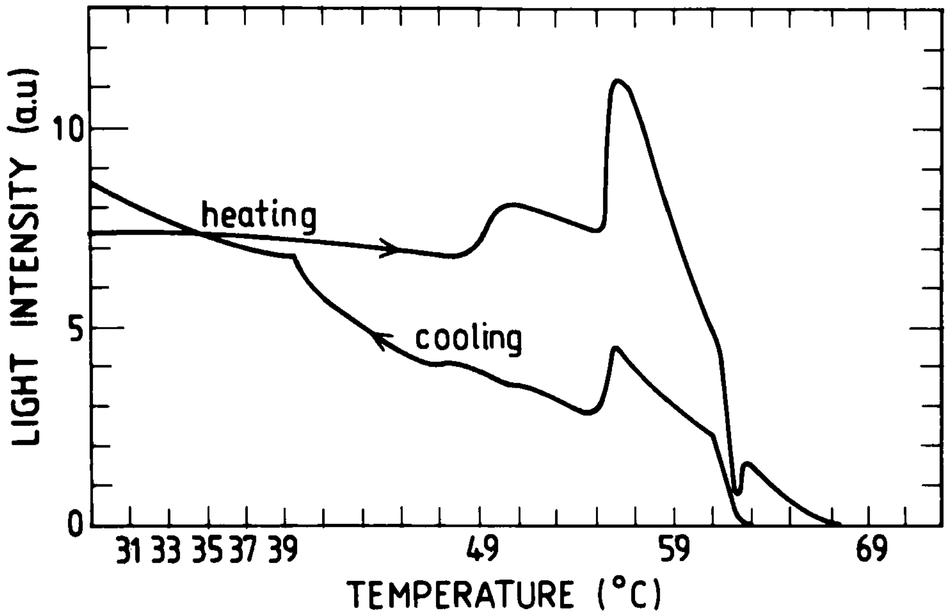


FIGURE 2 Light intensity as a measure of the collective C-M effect in NPOOB/water suspension plotted against the temperature at constant magnetic field $B = 1.2$ T.

monotonically as the temperature increases. The rate of this decrease (shown as the slope of the light intensity curve) is highly dependent on the type of ordered phase. In the crystalline solid, the decrease is mainly due to the excitation of the thermal motion of grains as a whole. In this case, the change in the internal molecular organization has no practical meaning. In the smectic phase, there is only small temperature destruction of the molecular orientation within droplets, whilst in the nematic phase this process is pronounced and is the main cause of the sharp decrease in the C-M effect.

The strong increase in the collective C-M effect observed at the phase transition from the smectic A to the nematic phase can be explained as a result of the change in the internal structure of the droplets. Most of the micron-size S_A droplets have the smectic radial hedgehog structure. Such structures are rather resistent to deformation. At the transition to the nematic phase, they change into the soft nematic radial or hyperbolic hedghogs or into an axially symmetric bipolar structure with boojums at two opposite surface points.[14] Since the transformation occurs at strong magnetic fields, the last process can be regarded as the most probable.

The temperature shifts, i.e., $T_l - T_l^b$ the difference between the temperatures of the phase transitions in the suspension and in the bulk, respectively, are negative for both NPOOB and 8OCB. For NPOOB, these shifts are as follows:

$$T_{Kr-A} - T^b_{Kr-A} \approx 0, \quad T_{A-N} - T^b_{A-N} \approx -4°C, \quad \text{and } T_{N-Iso} - T^b_{N-Iso} \approx -6°C$$

and are comparable with those for 8OCB.

III. SUSPENSIONS OF THE LIQUID CRYSTAL GERMS IN THE MELT

To investigate the formation of liquid crystal droplets and variations in their structure during their growth and at phase transitions, an attempt was made to study the liquid crystal germs growing from the melt. The suspensions of the germs in the melt were obtained in multicomponent systems composed of a low-temperature nematogen and high-temperature smectogen, *B*. In systems of this type, the phase separation occurs below some critical temperature[13] and a suspension of the germs arises as its initial stage. It is very interesting that when a chiral compound is added to the mixture as the third component, the liquid crystal phase separates from the melt, forming thread-like whiskers of various types depending on the relative concentrations of the components. The results presented here were obtained for mixtures of the two mesogens: 4,4′-bis-*n*-pentyl-azoxybenzene (Kr 22 N 65 Iso) and 4-*n*-pentyl-4′-butyloyl-biphenyl (Kr 106 B 110.5 Iso) denoted by *X* and *Y*, respectively.

A. Running droplets

In the presence of a chiral compound, *Z*, typical cholesteric droplets arise in the mixtures at low concentrations of the smectic compound, *Y*. The structure of the cholesteric droplets depends on the ratio D/P, where D is the diameter of a droplet and P is the cholesteric pitch. For low values of D/P, droplets have layered structures, whereas for high D/P defects of a double helix type, screw dislocations and $\chi(+1)$ or $\chi(+2)$ disclinations appear, Figure 3 and Figure 4. In all the photographs shown in this paper, the black background is the isotropic liquid melt. Small droplets of chiral and tilted smectic liquid crystals can adopt either the monopole structure or the focal conic structure. In the mixtures investigated, the monopole droplets arise when the molar compositions X:Y:Z are in a broad composition range around 1:1:1. For some compositions, a very fast translatory motion of the growing monopole droplets is observed, Figure 5. The "running droplet" moves in the direction opposite to the direction of its monopole tail. The velocity of this motion is inversely proportional to the size of the droplets and becomes zero when the monopole droplet reaches its final diameter. For droplets of diameter about 1 micron, the velocity is of the range 10^2 micron/s. Probably, the "running droplet" phenomenon arises when the growth of the monopole droplet produces a local change in the composition of the melt. As a result, the gradients in the surface tension appear, causing the motion.

B. Architecture of the droplets

At constant temperature, the monopole droplets float freely in the isotropic melt or cluster together in groups of 3 to 5 monopoles connected by the ends of their

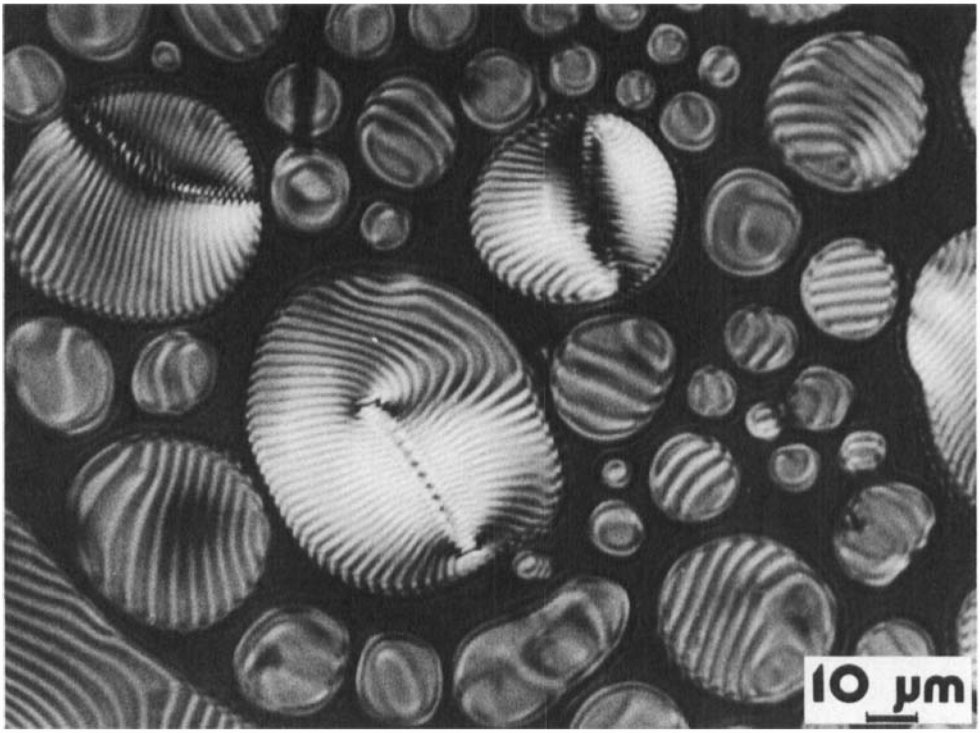


FIGURE 3 Layered cholesteric droplets with the ratio D/P from 2 to 12 and defect droplets for D/P > 20.

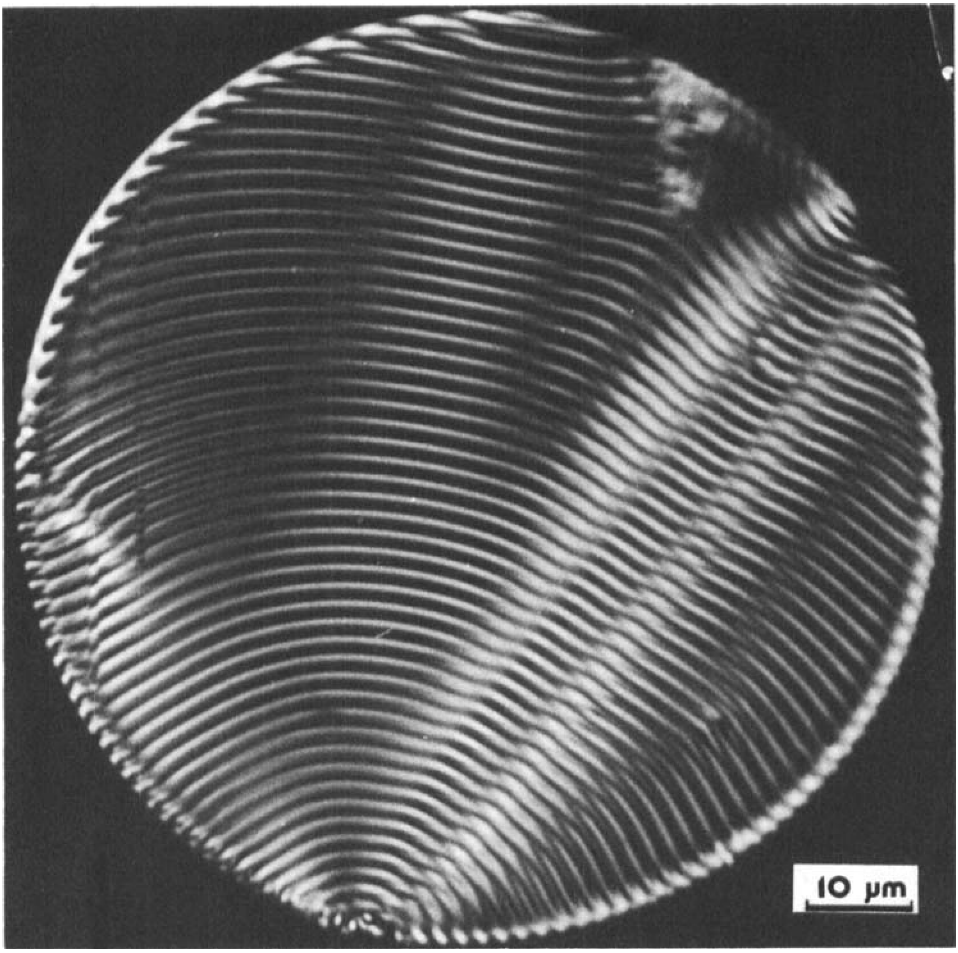


FIGURE 4 Defect cholesteric droplet with D/P = 50.

tails. Multipolar droplets containing several focal-conic domains, Figure 6, or conical segments, Plate 1, also frequently appear. The number of segments in the conical droplets varies with the temperature. If the temperature is lowered, an individual segment in the conical droplet can divide into two new segments and conversely the fusion of two segments into one is observed at higher temperature.

For high concentrations of the nematic component, *X*, very interesting freely suspended droplets shaped like clowns' hats arise, Figure 7. Probably, the axis of the "clown hat" can be identified with the line of flare typical of cholesteric structures.

C. Formation of the nematoids

The most interesting phenomenon observed in the mixtures of the *X*, *Y* and *Z* components is the creation of long liquid crystalline threads freely floating in the

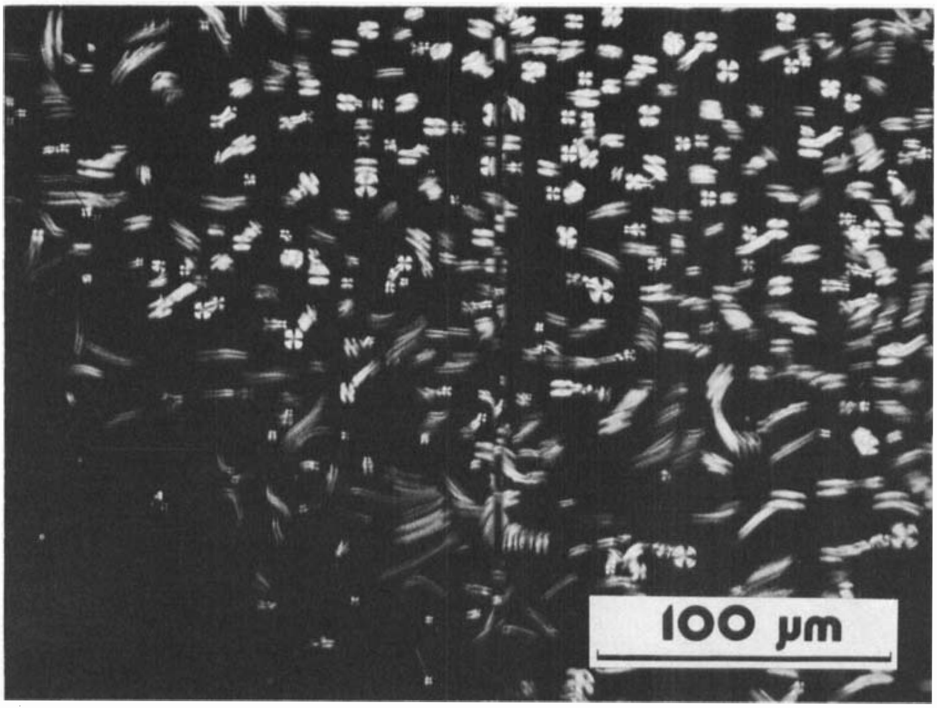


FIGURE 5 "Running droplets." The segmentation of the traces arises as a result of the pulsed illumination (100 Hz). Mixture with X:Y:Z = 2:1:2.

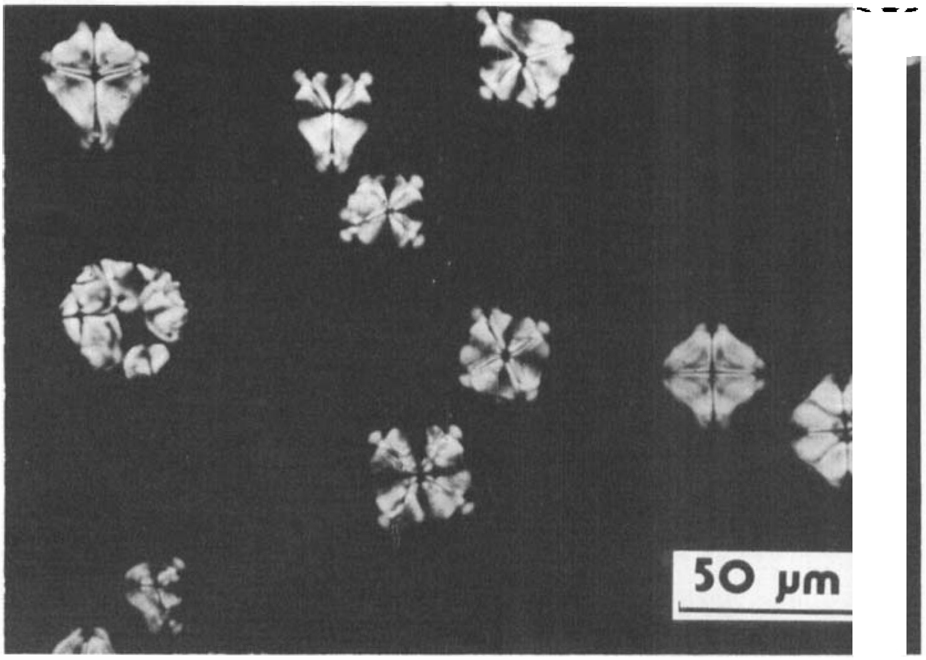


FIGURE 6 Multipole droplets, X:Y:Z = 2:2:1.

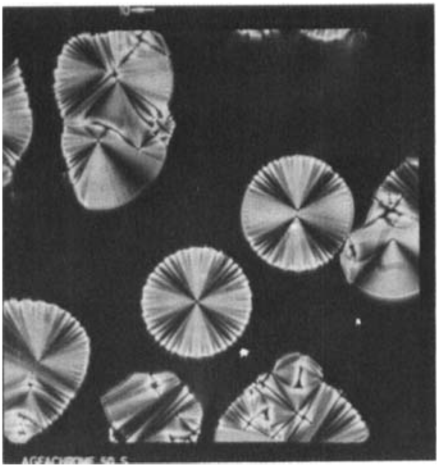


PLATE 1 Segmented droplets. X:Y:Z = 2:2:1.

isotropic melt. When the temperature of the melt is decreased, they arise spontaneously below the point of the phase separation. These threads can be regarded as the liquid crystal analogues of the whiskers frequently observed in the crystalline solid phases. In this work, the liquid crystal threads are called nematoids.

For low concentration of the Z component, the nematoids grow as an extension of the tail of the monopole droplets, Plate 2. For some compositions, the nematoids

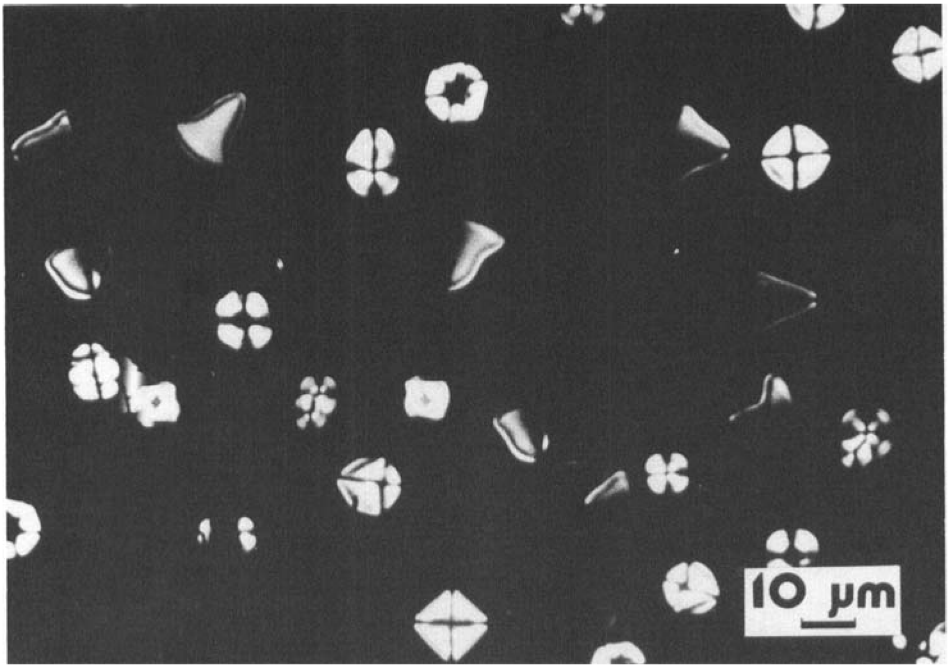


FIGURE 7 Free droplets with a line of flare (the "clown hats"). X:Y:Z = 2:1:1.

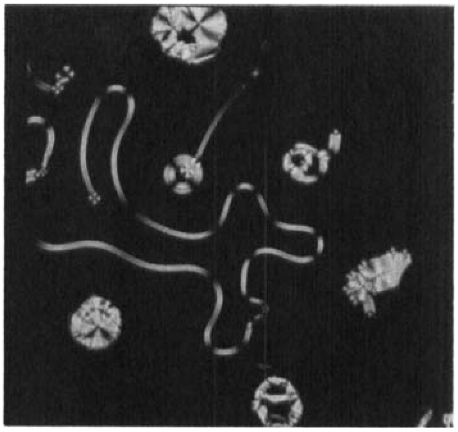


PLATE 2 A nematoid as an extension of the monopole. X:Y:Z = 2:2:1.

form a very dense, disordered set of long threads, Plate 3. Nematoids can also grow from the segmented droplets (Figure 8), and from the multipole droplets, (Plate 4). When the concentration of the Z component is high, the nematoid grows directly from the melt without the monopole droplet as its initial stage (the "free" nematoids). If in this case the relative amount of the smectic component Y is also increased, the "free" nematoids progressively enlarge and the length-to-diameter ratio becomes as high as 3000, Figure 9. Low concentrations of the Y component result in a decrease in the length of the "free" nematoids, Figure 10.

At lower temperatures the nematoids become unstable and contract to form droplets. The speed of this contraction depends on the molar composition of the mixture and on the length of the nematoid. The duration of the contraction varies

PLATE 3 A developed system of highly elongated nematoids with the monopole droplets on their ends. X:Y:Z = 3:2:2.

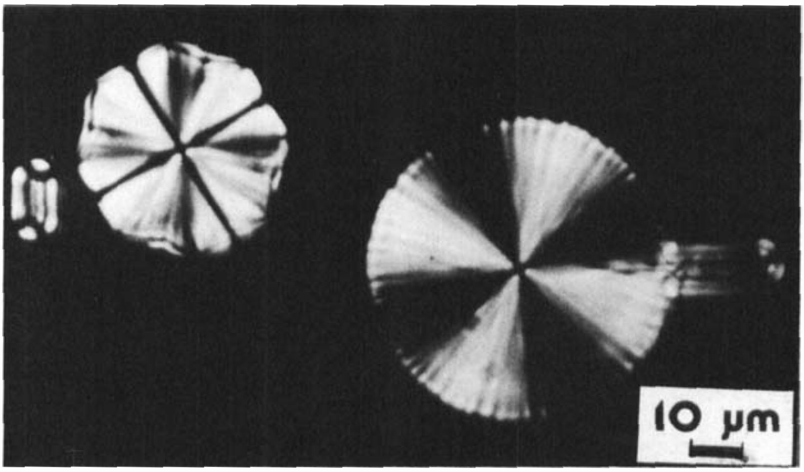


FIGURE 8 A nematoid growing from a segmented droplet. X:Y:Z = 2:2:1.

from about 0.1 s to 1 s. Nematoids, which have grown on a monopole, are drawn back into it and after this process the droplets do not then change their form. A "free" nematoid is drawn into a droplet created on one of its ends. Before the transformation to droplets, the large-diameter nematoids often form spirals or double-spirals (Figure 11), and they can form various segmented structures. A nematoid of this type can also split at one end forming a homeotropically aligned smectic plate surrounded by a chiral edge. The plate enlarges as the nematoid shortens. In this case, the final droplet is in the form of a round smectic plate with a focal-conic or planar edge (Figure 12). As the temperature is raised again, only the melting of the final droplets is observed. Thus, the formation of nematoids can be considered to be an irreversible process.

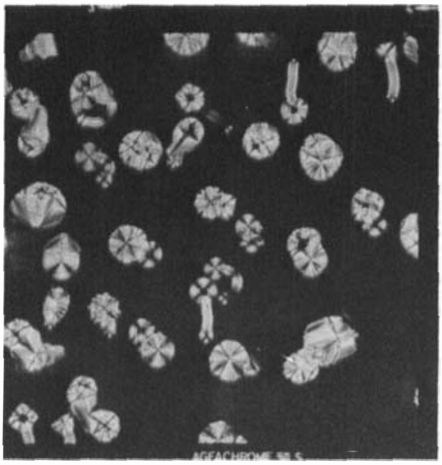


PLATE 4 Nematoids growing from multipole droplets. X:Y:Z = 2:2:1

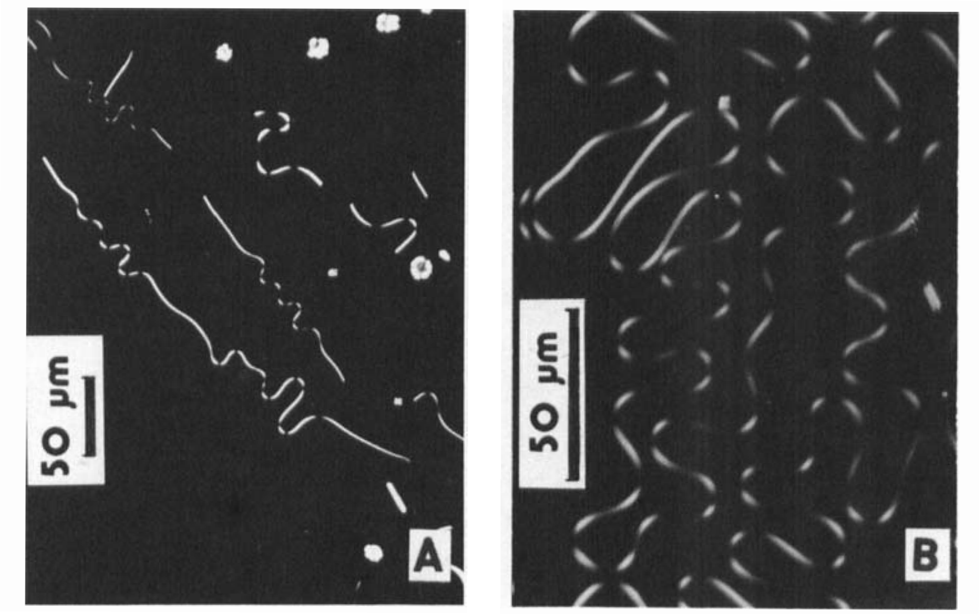


FIGURE 9 A) Developing "free" nematoids (without monopole droplets). $X:Y:Z = 2:2:3$. B) The essential part of one only highly-elongated "free" nematoid. $X:Y:Z = 2:2:3$.

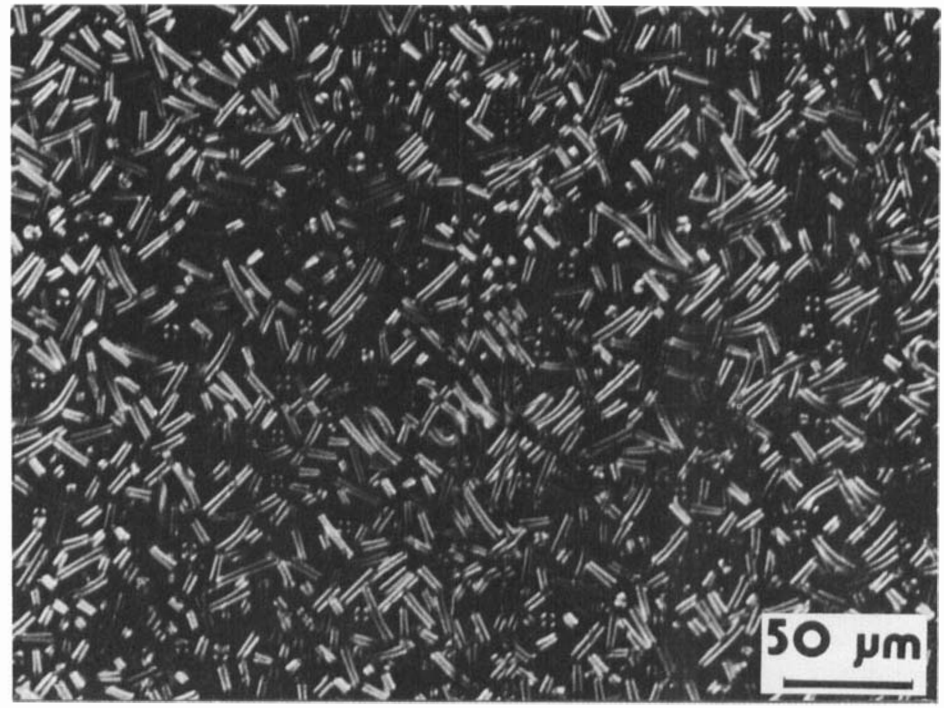


FIGURE 10 Very short "free" nematoids. $X:Y:Z = 3:1:3$.

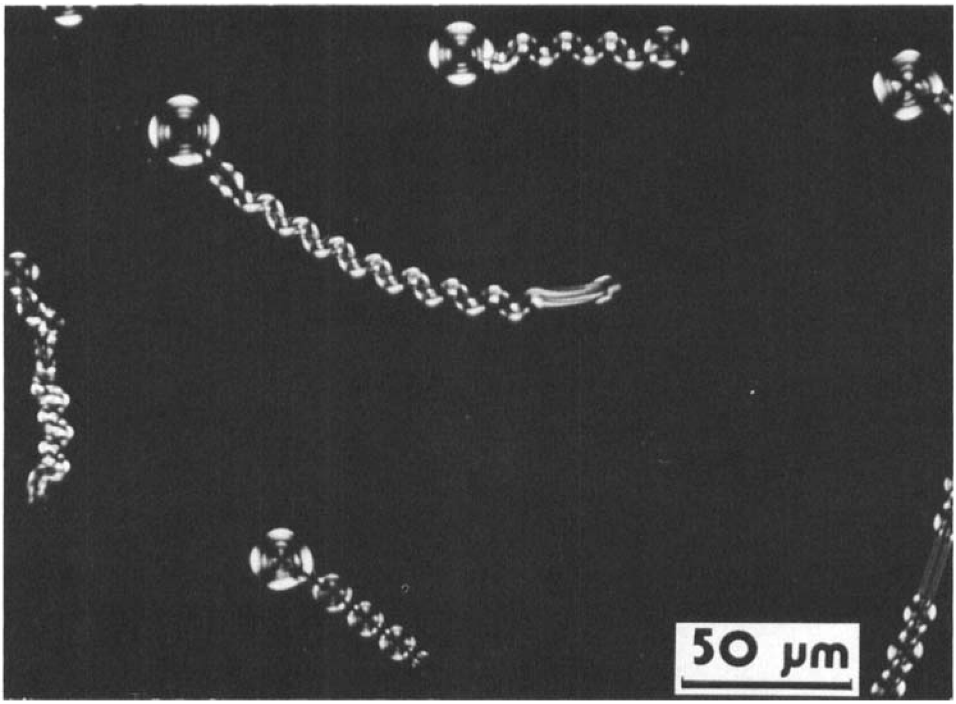


FIGURE 11 Spiralized nematoids in the vicinity of the transition to the final droplet. $X:Y:Z = 3:2:2$.

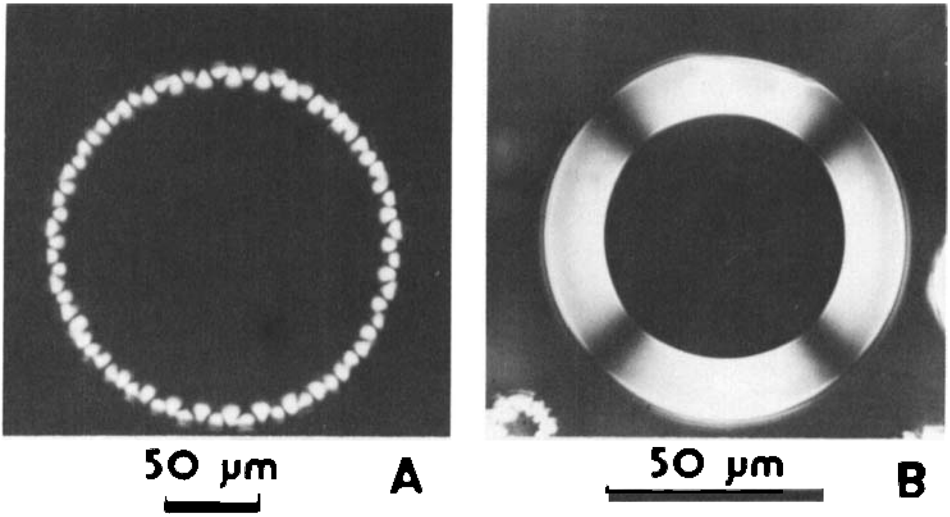


FIGURE 12 Final droplets. A) With focal-conic edge. $X:Y:Z = 2:2:1$; B) with planar edge. $X:Y:Z = 2:1:2$.

Many details of the internal structure of nematoids are not yet clear. The microscopic observations show that the optical axis of the non-spiralized nematoid is parallel to its geometrical axis. Thus, it is possible to regard a nematoid as the system composed of a long core with the nematic or smectic ordering surrounded by a chiral coating. In other words, the nematoid can be regarded as a peculiar variety of the monopole structure highly elongated by the growth of the achiral core. To some extent, nematoids, freely suspended in the isotropic melt, correspond to the striped domains of the chiral phase freely floating in the nematic liquid.[15] The simple model of the striped domains[16] should be modified for the nematoids by addition of the "escaped" core of various thicknesses at the center. The contraction of the nematoid to the droplet is probably connected with the phase transition within the core.

IV. CONCLUSIONS

The analysis of the temperature dependence of the collective C-M effect can be used as an important and simple method for investigating the phase transitions within suspended grains with ordered internal structure. In addition, the changes in the molecular organization resulting from the transformation of defects can be revealed. This approach should pave the way toward further investigations of the size effect in liquid crystalline systems, especially those of biophysical significance.

SUMMARY

We have described for the first time a study of the thread-like liquid crystal forms, which we have called nematoids, freely suspended in the isotropic multicomponent melts of the nematic and smectic mesogens doped with some chiral compounds, e.g., cholesteryl benzoate. These nematoids arise spontaneously below the phase-separation temperature and, to some extent, can be regarded as the liquid crystal analogues of whiskers of crystalline solids. It seems that the creation of the nematoids can be directly related to various features of the morphogenesis and self-organizing processes which occur in living systems.

Acknowlegment

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