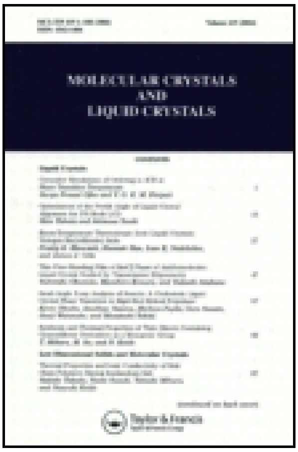

Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

Nematoid Filaments: New Mixtures, Cluster Morphology and Comparative Microinterferometry

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Version of record first published: 23 Sep 2006.

Mol. Cryst. Liq. Cryst. 1995, Vol. 261, pp. 271–282
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NEMATOID FILAMENTS: NEW MIXTURES, CLUSTER MORPHOLOGY AND COMPARATIVE MICROINTERFEROMETRY

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Abstract New three-component liquid crystal systems creating spontaneously nematoid-type filaments at the transition from the isotropic melt and formation of the nematoid-type filaments at the nematic - smectic A transition in dilute solutions of smectogen in silicon oil are reported. We have observed over 50 new three-component systems, composed of smectogen, nematogen and chiral dopant, in which the formation of the nematoids occurs. The plate-type nucleation of the mesomorphic phases has been observed at the transition from the isotropic melt for pure smectogens and also for three-component systems. In addition, creation of the nematoid-type filaments in dilute solutions of mesogen (NPOOB) in silicon oil has been observed here. Early stages of the plate-type nucleation have been examined using Nomarski contrast. The refractive profiles of the filaments have been examined using double-refracting microinterferometers.

INTRODUCTION

Liquid crystal substances, mainly nematics and ferroelectric smectics, develop outstanding usefulness for applications in electrooptic devices such as alphanumeric displays, high-definition TV displays, projection systems and optical computing. The new active-matrix systems in connection with the STN ordering within layers cause the liquid crystal substances to be matchless for such applications. On the other hand, in pure science, processes studied in liquid-crystalline systems can be employed directly in the evaluation of the fundamental ideas concerning the intermolecular interactions and, in general, the thermodynamics of condensed phases. In this field, the self assembling and self organizing processes seem to be the most intriguing and beautiful. The resulting supramolecular structures can adopt very complex topology and survive a rich variety of thermo-temporal evolutions. These phenomena are especially frequent in multiphase liquid crystal systems.

The spontaneous formation of the liquid-crystal filament structures and their thermo-temporal evolutions can serve as the examples of such processes.

Several types of liquid crystal filaments are observed. They are created spontaneously in some processes, e.g.:

1. in lyotropic liquid crystals, especially at the front of diffusion of an amphiphilic substance into isotropic liquid;

2. in thermotropic liquid crystals at the front of diffusion of a chiral substance into nematic or smectic A homeotropic layer;

3. in solutions of thermotropic liquid crystals in some liquids, e.g., silicon oil, after the phase separation and below the point of the nematic-to-smectic transition;

4. in thermotropic liquid crystals at the phase transition from the isotropic phase in some multicomponent and/or multiphase systems. In the cases 3. and 4., the filaments are very similar and are named here nematoids. The typical nematoid filaments are presented in Figure 1.

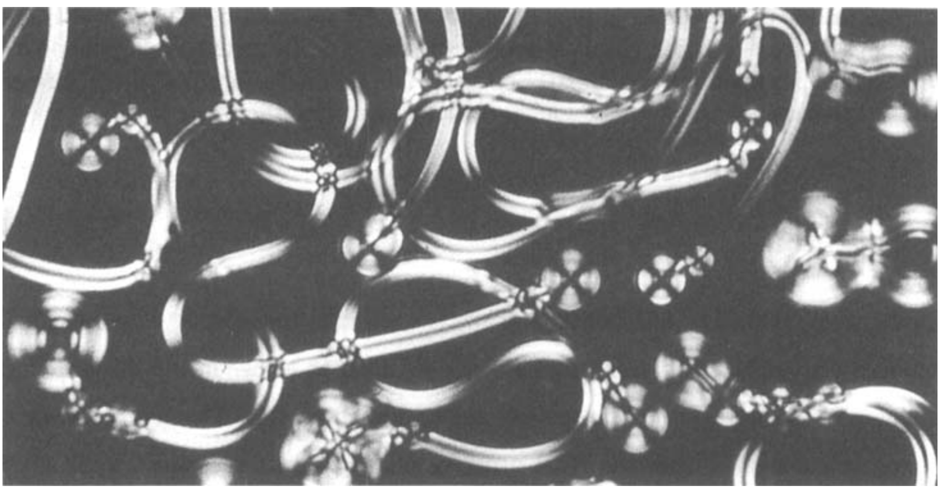


FIGURE 1. Typical nematoid filaments (mixture A1:B6:C2). Magnification 920 x.

Liquid-crystalline filament patterns were initially observed as the axially-symmetric myelins in lyotropic phases. Long time before Reinitzer, R. Virchow reported such filaments in organic material.[1] O. Lehmann observed the myelin filaments in lyotropic phases and stressed their importance in biological structures.[2] Later, the myelin forms have been observed by many authors in several multiphase systems. Unusual filament structures, called nematoids, have been observed in three-component thermotropic system at the phase transition from the isotropic melt.[3] Several types of temporal and thermal evolution are observed [4] in which the nematoids undergo: (a) immediate fast shrinkage to droplet, (b) segmentation, (c) splitting along the longitudinal axis, and (d) double-spiralling. Similar filament structures that reveal some above behavior have been observed in one-component thermotropic mesogen, [5] in two-component system [6] and in lyotropic system composed of diacetylenic phospholipid and ethanol/water.[7] Theoretical model presented by O.-Y. Zhong-can and W. Helfrich predicts liquid-crystal filament structures from a discussion of the Gauss-curvature elastic modulus.[8]

FORMATION OF NEMATOID FILAMENTS IN THREE-COMPONENT MIXTURES

The first nematoid filaments have been observed at the transition from the isotropic melt to the mesomorphic state in three-component mixtures of nematogen, smectogen and chiral dopant.[3] In some cases, the mesogenic nature of the component is only virtual and the substance does not exhibit any liquid-crystal phase in one-component system. The nematoids obtained in such mixtures exhibit very rich set of thermo-temporal evolutions including the immediate fast retraction to droplets, the splitting along the long axis, several types of segmentation, and several kinds of double-spiralling. The final stages of the evolution are focal-conic grain, multiphase lake-type (framed membrane) or monopole-type composed droplet. The shape and behavior of the nematoid filaments depend strongly on composition of the three-component mixtures. The nematoids presented in Figure 2 (left and right) have been obtained in two A1:B6:C2 (see below) mixtures having different relative concentrations.

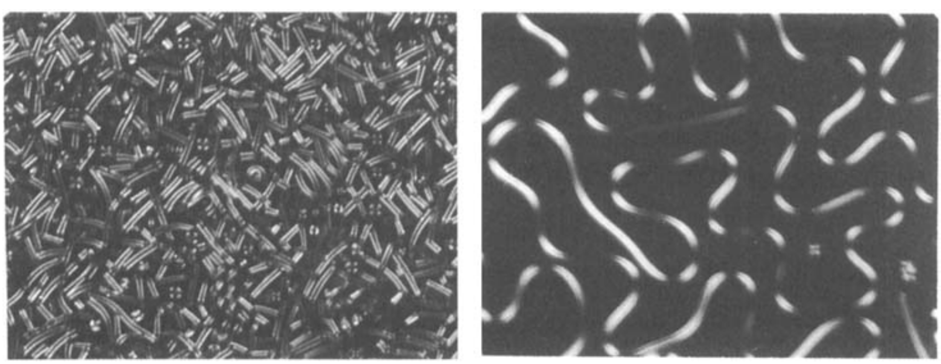


FIGURE 2. The nematoids obtained in two mixtures A1:B6:C2 of different relative concentrations. Magnifications 280 x (left) and 500 x (right).

Experimental

To investigate the nucleation processes and creation of the nematoid filaments the polarizing microscope with hot stage has been used. For studying the internal structure of the filaments, as evidenced by the distribution of the refractive profiles within cross-section perpendicular to their long axes, we have used the double-refracting microinterferometer Biolar PI. This microinterferometer is based on the Pluta bireferacting microinterferometry (PBM) technique with two Wollaston prisms. [9] Using this technique, one can obtain the values of $n_{\parallel} - n_{\perp}$ as well as $n_{\parallel}$ and $n_{\perp}$,separately, for different mutual configurations of the Wollaston prisms. Here $n_{\parallel}$ and $n_{\perp}$ denote the refractive indices for the light with vector **E** parallel and perpendicular to the long axis of the filament, respectively. The displacement c of the interference fringes within the image of the filament of diameter d is immediately related to the phase shift between the beam of wavelength λ transmitted through the filament and the reference beam:

$$c = \frac{d(n_s - n_m)b}{\lambda}$$

where n_s is the mean refractive index along the geometrical path of the beam, n_m - the refractive index of the liquid surrounding the filament and b - the inter-fringe spacing (constant for the optical system). To calculate the value of n_s along the geometrical path h (Figure 3A),

$$n_s = n_m + \frac{1}{h}\int_0^h n_l(y)\,dy - n_m h$$

we need to calculate first the local refractive index $n_l(y)$

$$n_l = \frac{n_e n_o}{\sqrt{n_e^2 \sin^2\beta(y) + n_o^2\cos^2\beta(y)}}$$

where n_e and n_0 are the extraordinary and ordinary refractive indexes, respectively, and β is the angle between the local director **n** and light vector **E** and depends on the model assumed for the molecular organization within a filament. In rather general case of the chiral cylinder in which the screw axis is oriented radially with respect to the long axis of a filament, angle β is determined by three angles (Figure 3B): α - the angle between the axis of the filament and the direction of the vector **E**, φ - the angle of the local helical twist, and θ - the local direction of the screw axis. When the law of cosines of spherical trigonometry is applied to the triangle KMN on unit sphere, Figure 3C, we obtain

$$\cos\beta = \cos\alpha\cos\varphi + \sin\alpha\sin\varphi\cos\Gamma = \cos\alpha\cos\varphi - \sin\alpha\sin\varphi\cos\theta$$

The formula obtained for the angle β in a chiral cylinder can be easy adopted for simpler molecular configurations.

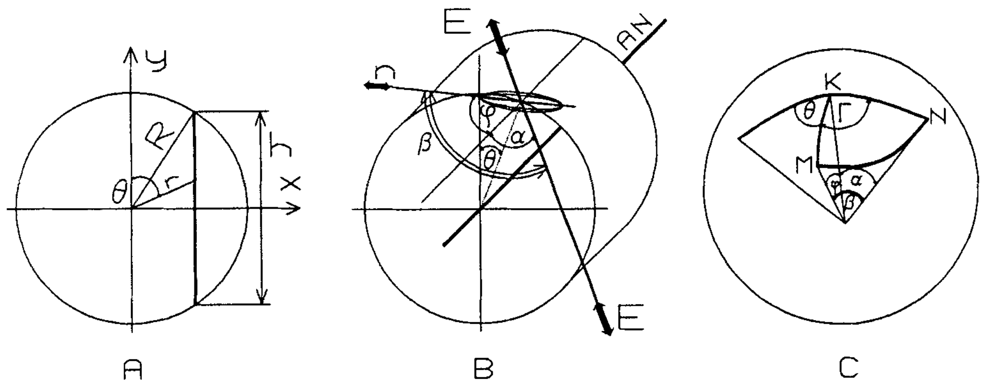
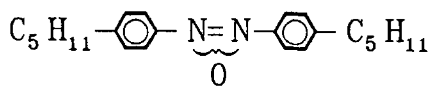


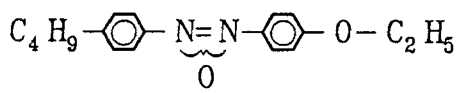
FIGURE 3. A- Definitions of the optical path h and the local direction of the helix axis; B - Relations between the angles α, φ, θ, and β in the chiral cylinder, AN - denotes long axis of the filament; C - Construction for calculation of the angle β.

Materials

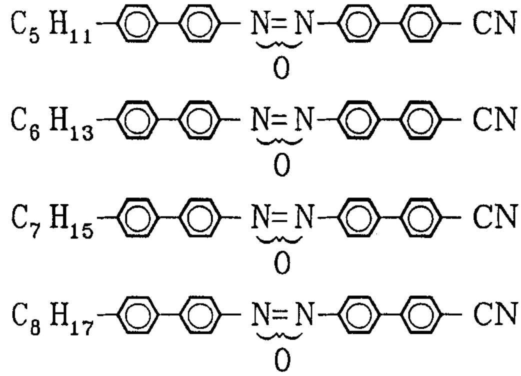
In the present work we find some new three-component systems containing nematogens, smectogens and chiral dopants in which the nematoid filaments can be produced below the transition from the isotropic melt to the mesomorphic state. The new components, nematogen, smectogen and chiral dopants, are listed below.

Nematogen components A_i:

A1:


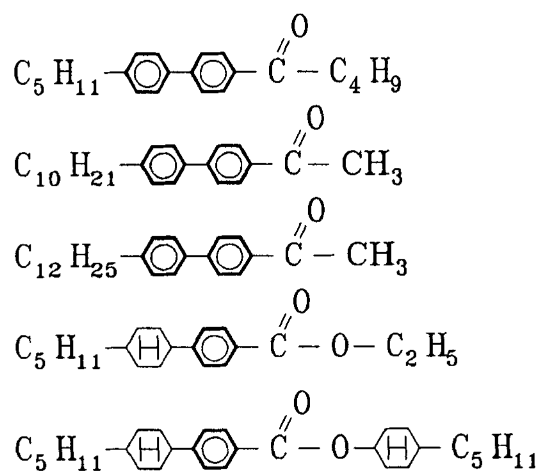
A2:


A3:
A4:
A5:
A6:

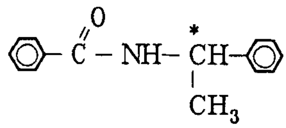


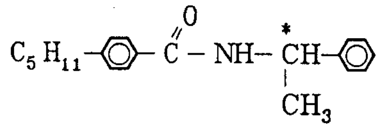
Smectogen components B_j:

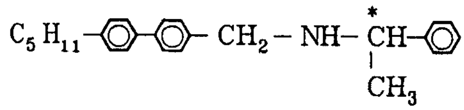
B1:
B2:
B3:
B4:
B5:
B6:
B7:
B8:
B9:
B10:

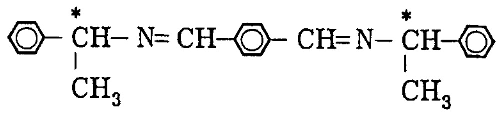


Chiral components C_k:

C1: 

C2: 

C3: 

C4: 

Among the $A_i + B_j + C_k$ mixtures investigated we have found over 50 systems in which the nematoid filaments are produced. However, in some mixtures the nematoids were not observed. It is interesting that in systems in which the nematoid filaments are produced, they are not created when the chiral dopant is removed.

<u>Plate-Type Nucleation in Pure Smectogen Components</u>

At the transition from the isotropic melt, all the smectogen members B_j of three-component mixtures, analyzed separately as one-component system, exhibit plate-type nucleation giving usually twofold symmetric clusters. At later stages, the plates become unstable with respect to the rolling-up or self-crushing processes initiated at their peripheral regions. The final stages of smectic layers are polydomain mosaic or ordinary focal-conic textures. The Nomarski interference contrast has been used to examine the initial stages of the plate-type nucleation. The schematic diagrams and photographs of the rolling-up or self-crushing processes are presented in Figure 4.

<u>Plate-Type Nucleation in Three-Component Systems and Plate-to-Nematoid Transition</u>

In several three-component mixtures, the plate-type nucleation has been observed as the initial stage of the formation of the nematoid filaments at the transition from the isotropic melt. In this case, elliptical clusters are formed. At later stages, the plates undergo the rolling-up process to form very original framed membrane from which the nematoid

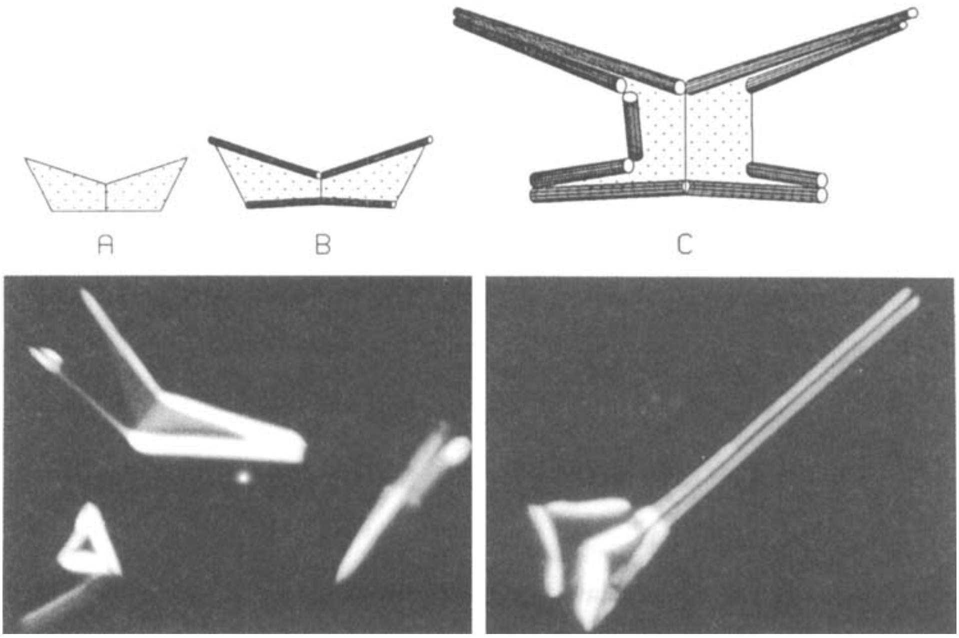


FIGURE 4. Schematic diagram and photographs of the plate-type nucleation in pure smectogen (B1) component and the rolling-up process. Magnification 640 x.

filaments are growing. The nematoid filaments are initiated at the contact of two ends of tubes surrounding the rolled-up plate and are growing from inside the tubes (not on their tips). In such an "in-container" production, up to 4 filaments can grow from one rolled-up plate. Schematic diagram and photographs of the plate-type nucleation in three-component systems and "in-container" growth of the nematoids are presented in Figure 5.

<u>Microinterferometric Results</u>

It has been observed that all the deflections of the interference fringes within the images of nematoid filaments in PBM technique have predominantly one sign (plus or minus) over entire transverse cross section of a filament except central region thin compared to the filament diameter.[10] The inequalities $n_{\parallel} > n_{\perp}$, $n_{\parallel} > n_m$, and $n_{\perp} < n_m$, which obey in both lateral parts of a nematoid, indicate that the long axes of the molecules in these parts are oriented parallel to the longitudinal axis of the nematoid (planar orientation). Since $n_{\parallel} - n_m$ is almost equal to $n_{\perp} - n_m$ at the central part of a nematoid, this region should be interpreted as to have the homeotropic orientation. These results and the character of the temporal and thermal evolutions [4] provide experimental evidence that the nematoid filaments have bifilar internal organization. The calculations of the interference shifts and distributions of the refractive indexes performed for radial and chiral cylinders and for bifilar set of cylinders are presented in Figure 6 and are in good qualitative agreement with the experimental data. Dynamic processes associated with the formation of plates and evolution of the nematoids have been demonstrated as video presentation (41 min.) at the 15th International Liquid Crystal Conference, Budapest, 3 -8 July, 1994.

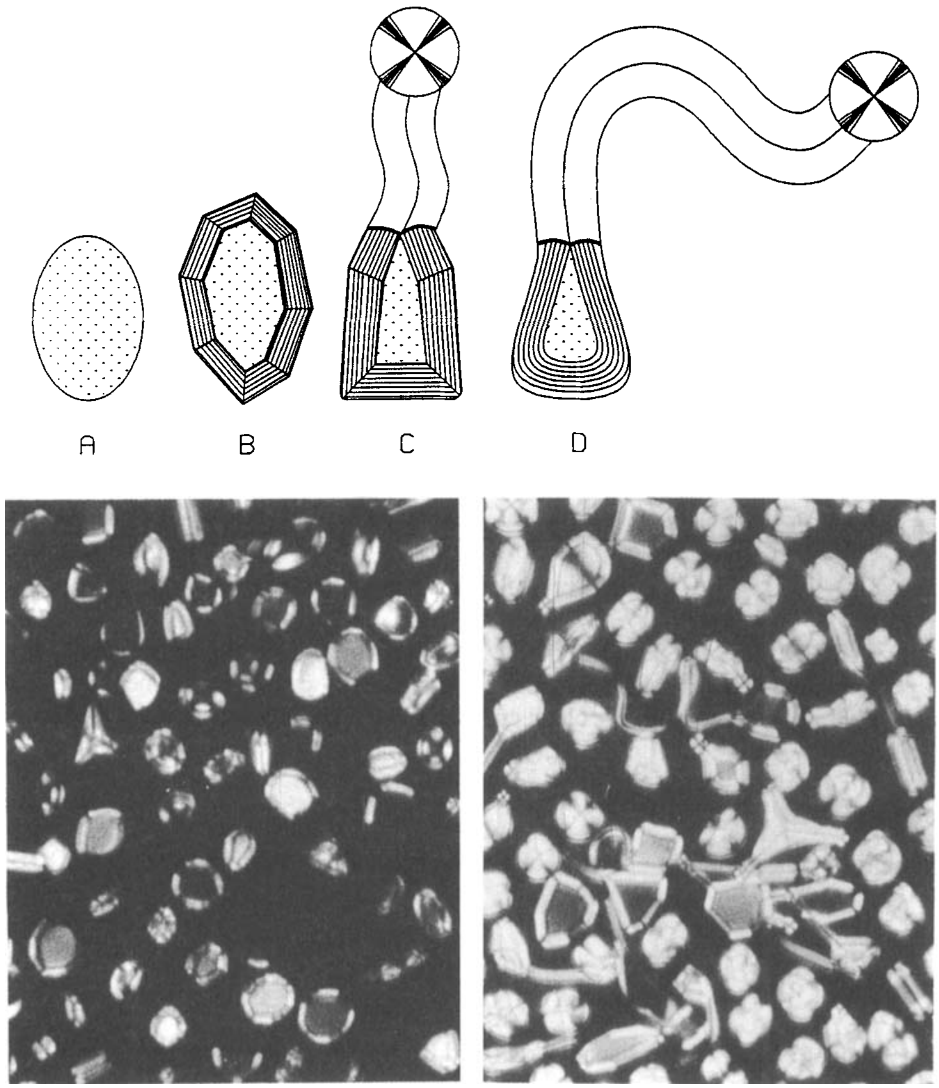


FIGURE 5. Schematic diagram and photographs of the plate-type nucleation in three-component system (A1:B1:C2) and "in-container" growth of the nematoids. The time interval between pictures (from left to right) is 20s.Magnification 650x.

FORMATION OF THE NEMATOID FILAMENTS FROM SOLUTIONS OF NPOOB IN SILICON OIL

Besides the case of three-component mixtures, creations of the nematoid-type filaments in solutions of mesogens in silicon oil have been observed here. In the case when the mesogen can exhibit both the nematic and smectic phases, the process is realized on cooling from the isotropic phase in three steps: (i) phase separation giving isotropic plates of the mesogen immersed or floating on the silicon oil, (ii) formation of separated nematic droplets and (iii) transformation of nematic droplets into elongated bifilar nematoids.

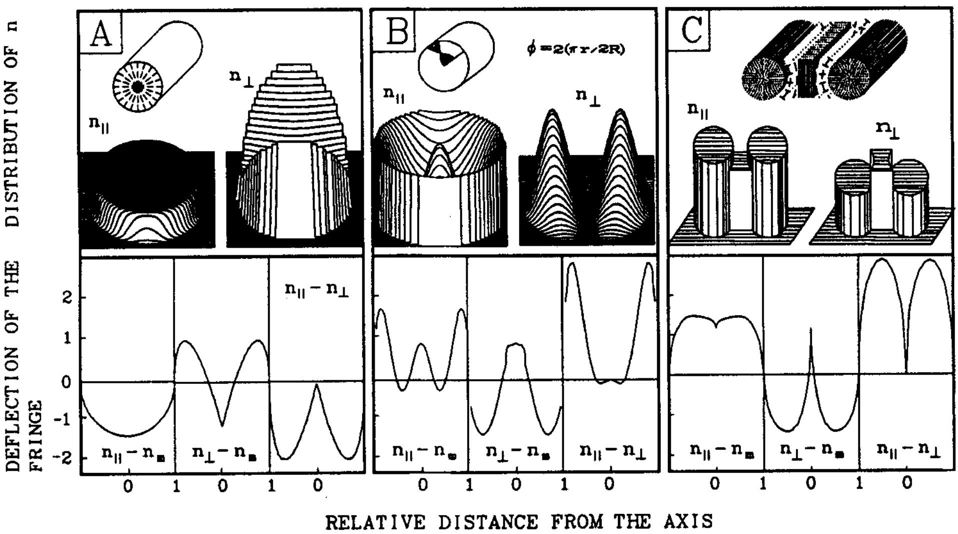
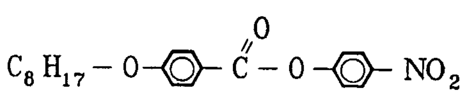


FIGURE 6. Deflections of the interference fringes and distributions of the refractive indexes calculated from the models: A - cylindrical filament with radial field of the director **n**; B- chiral cylinder and C - bifilar set of planar cylinders.

Materials

Solutions of concentrations ~ 2 wt.% of 4-nitrophenyl 4'-n-octyloxybenzoate (NPOOB)



(Kr 49 SmA 61 N 68 Iso) in silicon oil H (Carl Roth OHG) were used. Isotropic NPOOB was dissolved in the silicon oil at about 100° C. Observations were performed on cooling with the use of both ordinary polarizing microscope and Nomarski interference contrast.

Production and Evolution of the Nematoid-Type Filaments in NPOOB/Silicon Oil System

The creation of the nematoid filaments in the NPOOB/silicon oil systems can be divided into three steps observed upon cooling of the solution:

1. phase separation observed at about 80°C, resulting in a production of isotropic NPOOB regions of the form of rounded platelets on the surface and droplets in the bulk of the silicon oil;

2. isotropic-to-nematic transition in NPOOB producing small nematic droplets on the surface and in the bulk;

3. transformation of the droplets (on the surface and in the bulk) into bifilar filaments originated as elongation of the droplets in two opposite directions. The maximum observed aspect ratio was in matured filaments of 100:1. The droplets coupled to the bottom of the glass container were not transformed into the filaments. Such a growth of a nematoid from nematic droplet is also observed in some three-component mixtures.

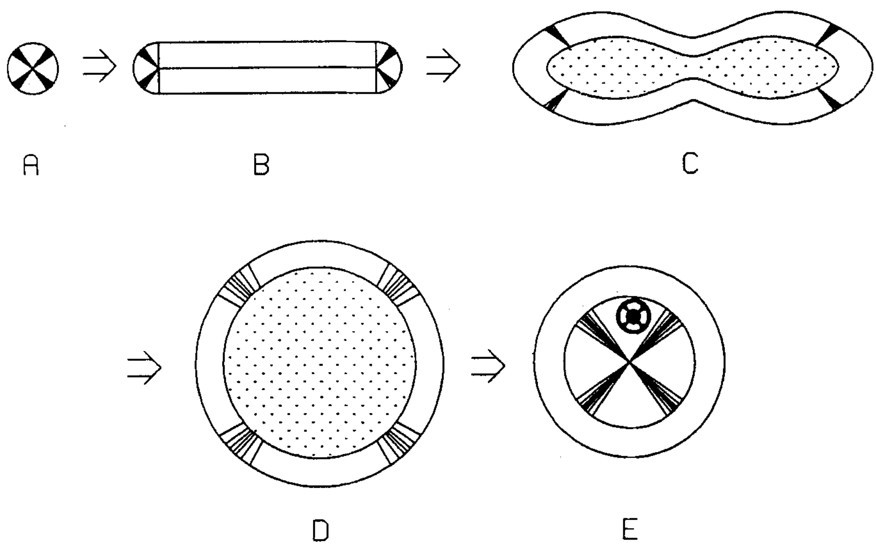


FIGURE 7. Schematic diagram of the production and evolution of the nematoid filaments in NPOOB/silicone oil systems. A - nematic droplet; B - elongation of the droplet into filament; C - splitting of the filament; D - the state of "framed membrane"; D - droplet as the result of the encapsulation of the framed membrane (the round crater is visible at the upper part of the droplet)

The thermo-temporal evolution of the filaments in the NPOOB/silicon oil systems is reduced to splitting and segmentation. The splitting process is ended when the bifilar filament reaches the form of the framed membrane, i.e., almost circular membrane fastened inside the toroidal frame. The next step is the encapsulation of the framed membrane. This very beautiful process is initiated with shortening of the toroidal frame causing the membrane to be deformed into spheroidal bubble having toroidal neck. The toroidal neck is shrinking continuously to form a crater on the surface of the created droplet. This crater is often the source from which the secondary nematoid is ejected. The creation and evolution of the nematoid filaments in the NPOOB/silicon oil systems are presented on the schematic diagram in Figure 7.

CONCLUSIONS

Two types of production of the nematoid filaments have been observed in both the three-component mixtures and smectogen solution in silicon oil: (i) growth from the nematic droplet and (ii) growth from the rolled-up plate or from the bulk of the primary droplet ("in-container" production of the nematoids or secondary nematoids).

Both detailed observations of the evolution and extensive analyses of the microinterferometric data suggest that the nematoid filaments represent composed multiphase structures and have, as a rule, bifilar internal organization.[10]

Acknowledgment

This work was supported by the KBN grant No. DNS - P/04/166/90-2.

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