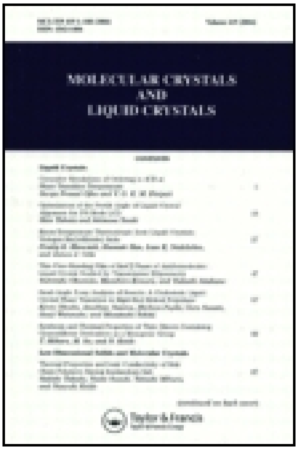

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Phase Transitions in Liquid Crystal Filamentary Structures

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Phase Transitions in Liquid Crystal Filamentary Structures

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Instability of liquid crystal membranes with respect to spontaneous rolling up into cylinders or double cylinders and their subsequent very complicated evolution and also phase transition within cores are reported in the present paper. We have investigated here the formation and spontaneous evolution of liquid crystal membranes and filamentary structures in nematosmectogen 4-nitrophenyl-4′-octyloxybenzoate (NPOOB) dissolved in hydrophobic silicone oil H (SO). The first-type phase transitions are observed here within the filaments produced in system composed of 4-acetyl-4′-dodecylbiphenyl (B8) and 4,4″-pentylcyclohexyl(4′-pentylcyclohexyl) benzoate (B10) dissolved in SO. We discuss crude continuum model ofthe instability of liquid crystal membranes with asymmetric surface tension and the influence of the pressure exerted by such a tension on the phase behavior within the filaments. The fringe-field microinterferometric analysis has provided decisive evidence ofthe homeotropic organization ofthe membranes, planar ordering within the cylinders and of bifilar model of the filaments.

Keywords: liquid crystals; filamentary structures; membranes; phase transitions

INTRODUCTION

Very rich and fascinating self-organization phenomena in liquid crystals, especially in multiphase and/or multicomponent systems, play a crucial role in every biological systems and modern smart materials. These phenomena remain quite mysterious but their scientific meaning is competitive in many instances with the optoelectronic applications of liquid crystals. The most interesting self-organization phenomena, such as formation of filamentary structures and their spontaneous evolution, are observed at the phase transitions from the isotropic melt to the mesomorphic phase in liquid crystal multicomponent systems.

The liquid crystal filamentary structures were observed for the first time in lyotropic systems by R. Virchow [1] and O. Lehmann [2]. Some related structures have been observed later in thermotropic liquid crystals [3-9], in lyotropic system [10], in mixtures of nematosmectogen and inert liquids [11], and in lipid membranes [12-14].

In this work, the instability of liquid crystal membranes are investigated in nematosmectogen A 4-nitrophenyl-4'-octyloxybenzoate (NPOOB) ($C_8H_{17}O$-C_6H_4-COO-C_6H_4-NO_2) in silicone oil (SO) as an inert liquid. If a stiff smectogen is present in the mixture, the phase transition within the core of a nematoid is observed instead of vesicles [15]. Such a transition has discovered in two-component smectogen 4-acetyl-4'-dodecylbiphenyl (B8)($C_{12}H_{25}$-C_6H_4-C_6H_4-CO-CH_3) and 4,4"-pentylcyclohexyl(4'-pentylcyclohexyl) benzoate (B10) (C_5H_{11}-C_6H_{10}-C_6H_4-COO-C_6H_{10}-C_5H_{11}) mixtures in SO.

EXPERIMENTAL

Two types of liquid crystal systems have been investigated: pure NPOOB and mixture B8/B10 both initially dissolved in silicone oil H (Carl Roth OHG) at temperatures slightly above the clearing points. Observations were performed on cooling saturated solutions at various rates, preferentially at 1 deg/min, and registered on magnetic tape. The microscope Biolar PI was used in three regimes: an ordinary polarizing microscope, Nomarski contrast and fringe-field microinterferometer.

The microinterferometric fringe method with two Wollaston prisms used here gives a filament to be separate into two images in which the displacements of the interference fringes are [16]: $c_l = d(n_m - n_l)b/\lambda$ and $c_\perp = d(n_m - n_\perp)b/\lambda$, respectively, where d is the diameter of a filament and b - inter-fringe spacing as measured for the optical system used (calibration constant). The n_l and $n_\perp$ are the refractive indices for vector **E** of the transmitted light parallel and perpendicular to the axis of the filament, respectively, and n_m is the refractive index of surrounding isotropic melt.

RESULTS

The liquid crystal membranes are created and evolve spontaneously during cooling an isotropic melt. These processes include the rolling up the membrane to a double cylinder, its growth to a long filament (nematoid) with the aspect ratio as high as 1:3000, longitudinal splitting of the nematoid and creation of the framed membrane and its collapse to a vesicle, growth the secondary filament from inside the vesicle and formation of the secondary vesicle as the final stage. The stages of spontaneous transformation of the isolated nematoid filament from the initial plate-like germ to the final double-vesicle in NPOOB dissolved in SO are presented in FIGURE 1. The full process lasts for about 2 min.

The first-type phase transition within nematoid filaments in B8/B10 mixture dissolved SO is presented in FIGURE 2. The nucleation of the new phase is initialized at one point (or several distant points) then the front of transition propagates slowly along the filament. The process looks like the forcing of a stiff rod into a soft rubber hose. As the result, the initially flexible filament (1 in FIGURE 2) undergoes partition into stiff segments connected with flexible elbows (2 and 3 in FIGURE 2).

The deflections of the interference fringes, that are proportional to the local optical density for two mutually perpendicular polarizations of light, within the twin images of the nematoid filaments before and after the splitting to form the framed membrane is presented in FIGURE 3.

DISCUSSION

The formation and growing of liquid crystal platelets within the melt of mixtures containing one at least smectogen or nematosmectogen and the instability of these membranes with respect to rolling up into cylinders or double cylinders seems to be a common initial stage in formation of the liquid crystal filamentary structures. The fringe-field microinterferometric analysis has provided decisive evidence of the homeotropic organization of the membranes, planar (parallel to the axis of the filament) ordering within the cylinders and of bifilar model of the filaments. Two processes by which the filaments evolve seem to the most important: instability of the

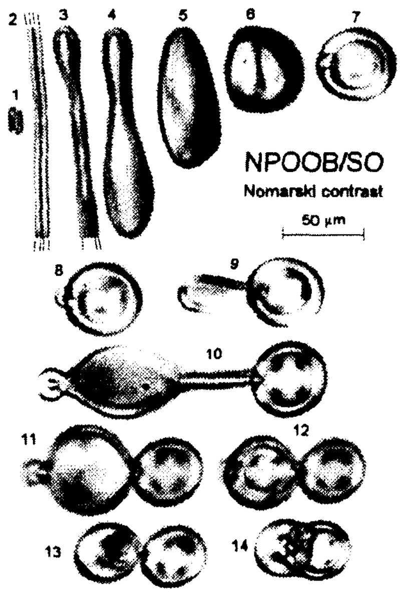

FIGURE 1. Spontaneous evolution from the initial plate-like germ to the final double-vesicle in NPOOB/SO system. 1- phase separation giving thin liquid-crystalline platelets in the bulk or on the surface of the silicone oil and subsequent rolling-up the platelets into initial polygons or bifilar droplets, 2- growing up of highly elongated liquid-crystalline filaments from the rolled-up polygons or droplets, 3-4- crosswise splitting and shortening the filaments to form framed membranes, 5, 6, 7- encapsulation of the framed membranes to form the spheroidal vesicles, 8,9- budding and growth of secondary filaments from inside the vesicle, 10, 11- splitting of the secondary filaments, 12, 13, 14- formation of secondary vesicle connected with the primary vesicle.

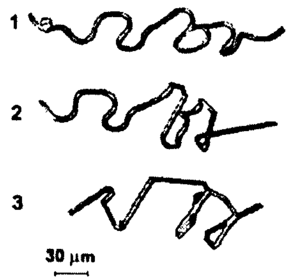

FIGURE 2. Phase transition within nematoid in B8/B10/SO system. 1- initial filament; 2- early stage of the transition; 3- final stage.

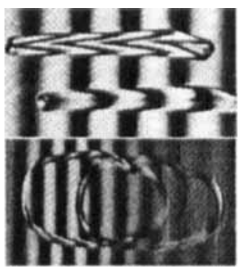

FIGURE 3. Fringe-field patterns of the nematoid filament (upper) and the developed from it framed membrane (lower).

membranes with asymmetric surface tension with respect to spontaneous rolling up into cylinders (FIGURE 4) and the influence of the pressure exerted by such a tension on the phase behavior within the filaments (e.g., phase separation at the core) analogous to the capillary condensation.

To estimate the temperature shift in phase transitions we use the geometry as in FIGURE 4 and from the continuum free energy $\mathscr{F}$

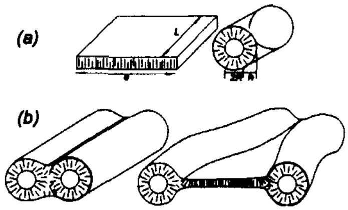

FIGURE 4. The supposed geometry for rolling up the liquid crystal membrane and the splitting of the bifilar nematoid filament.

$$F = \frac{1}{2}\left[K_1 (\nabla \cdot \boldsymbol{n})^2 + K_2 (\boldsymbol{n} \cdot \nabla \times \boldsymbol{n})^2 + K_3 (\boldsymbol{n} \times \nabla \times \boldsymbol{n})^2\right]; \quad \mathcal{F} = \int_V F dV$$

we have for the splay $\mathcal{F} = \pi K_1 L \ln(R + h)/R$. This energy should equal to the difference in the surface energies $\mathcal{F}_S$ before and after the rolling up the membrane: $\Delta \mathcal{F}_S = \mathcal{F}_{S0} - \mathcal{F}_S = \pi L h \Delta\sigma$, where $\Delta\sigma = \sigma_i - \sigma_o$ and σ_i and σ_o denote the surface tensions on internal and external surfaces of a cylinder, respectively. Thus, we obtain $\Delta\sigma = (K_1/h) \ln((R+h)/R)$.

Microinterferometric data suggest that $R \gg h$ so we can use the approximation $\ln(1+x) \approx x$ and we obtain $R \approx K_1/\Delta\sigma$.

The shift in the temperature of the phase transition from the nematic to smectic phase within a filament exerted by the curvature pressure can be obtained using Clausius-Clapeyron equation in the form

$$\frac{dT}{dP} = \frac{T(V_2 - V_1)}{q}$$

By integration between points (P_1, T_1) and (P_2, T_2) and using the approximation $\ln(1+x) \approx x$, we obtain for lowering the temperature

$\Delta T \approx T_1 \Delta P(V_2 - V_1)/q$ where $\Delta T = T_2 - T_1$, $\Delta P = P_2 - P_1$, V_i are molar volumes of smectic and nematic phases, respectively, and q is molar enthalpy of the transition. ΔP is the Laplace curvature pressure $\Delta P = \sigma(1/R_1 - 1/R_2)$ where R_1 and R_2 are the main curvatures. Since usually $V_2 < V_1$, the temperature of the transition from nematic to smectic will be lowered within the cylinder.

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