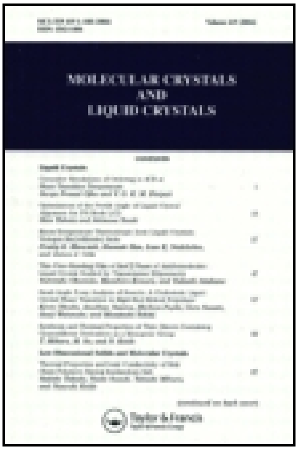

Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

Equilibrium Shape of a Smectic-A Phase in an Isotropic Phase Formed on Substrate Surface

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Version of record first published: 24 Sep 2006

Mol. Cryst. and Liq. Cryst., 2000, Vol. 347, pp. 137-146
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Equilibrium Shape of a Smectic-A Phase in an Isotropic Phase Formed on Substrate Surface

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Equilibrium shapes of smectic-A domains in an isotropic phase formed on a substrate surface have been observed using a polarizing microscope. Polarizing-microscope images of some possible structures are simulated to determine the shape of the smectic-A domains. It is found from a comparison between experimental and simulated images that the shape formed on the substrate surface is a hemisphere. The hemispherical smectic-A domains are shown to be equilibrium shapes in terms of a theory proposed earlier (H. Naito, M. Okuda and Z. Ou-Yang, *Phys. Rev. Lett.* **70**, 2912 (1993)) by taking account of the change in the transition temperature from an isotropic phase to a coexisting phase during the growth of a smectic-A phase.

Keywords: smectic-A liquid crystal; isotropic phase; simulated polarizing-microscope images; equilibrium shape

INTRODUCTION

Geometrically interesting shapes have often been observed in smectic liquid crystals grown from an isotropic phase [1]. One of the interesting shapes is equilibrium spherical domains of a smectic-A phase in an isotropic phase. The understanding of formation processes of the equilibrium shapes is important for the development of new display technologies as well as for the basic understanding of pattern formation of soft matter. However, the shapes of smectic-A domains formed on a substrate surface have not been examined yet.

We have observed equilibrium smectic-A domains formed on the substrate surface using a polarizing microscope by cooling the sample gradually and keeping at a temperature in the coexisting region of the smectic-A and isotropic phases. In some cases, it is difficult to determine the

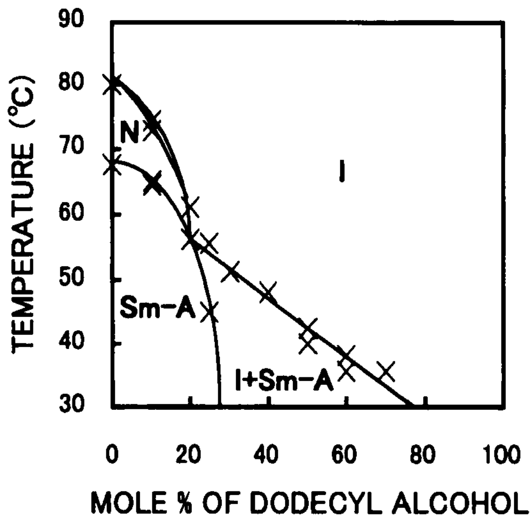


FIGURE 1 Phase diagram for a mixture of 8OCB and DODA [1].

3-dimensional structures of smectic-A domains from microscope images of smectic-A domains.

In this paper, we simulate the polarizing-microscope images of smectic-A domains to determine the 3-dimensional smectic-A structures. The simulated images are compared with the observation of smectic-A domains under crossed polarizers. We find that the equibrium smecctic-A domains formed on a substrate surface have a hemispherical geometry. The hemispherical smectic-A domains are shown theoretically to be an equilibrium shape in terms of a theory that we have proposed earlier [3] by taking account of the change in the transition temperature from an isotropic phase to a coexisting phase (T_c) due to the segregating of a smectic-A phase.

EXPERIMENT

Dodecyl alcohol (DODA) was mixed with octyloxycyanobiphenyl (8OCB) (a mole ratio of 8OCB to DODA is 4 to 6) to suppress the nematic phase and to observe a smectic-A phase in an isotropic phase. The liquid crystal material filled into the cell with dimensions of 10 mm×10 mm×50 μm. Figure 1 shows the phase diagram of a mixture of 8OCB and DODA. There appears a coexisting region of the smectic-A and the isotropic phases. The cells were cooled from the isotropic phase at -0.1 ℃/min and the cooling was stopped in the coexisting region of the smectic-A and isotropic phases for the observation of the equilibrium smectic-A domains formed on the glass plates. The sample temperature was controlled using a hot stage (Instec HS1-i) with an accuracy of ±0.002 ℃. The pattern formation of smectic-A phase was observed with a polarizing microscope (Nikon X2TP-11) equipped with a color video camera (Sony DXC-107A) using a monochromatic light whose wavelength was 546 nm.

RESULTS

As the cells were cooled from the isotropic phase at -0.1 ℃/min, the smectic-A initially appears in the form of a number of spherical droplets which grow in size and then start elongating into cylindrical structures (Fig. 2(a)). The cylinders grow rapidly, and become long and entangled threads. The observed area was filled with threads at about 39 ℃ (Fig. 2(b)). These threads suddenly collapse forming domains on the glass plates (Fig. 2(c)). The domains were equilibrium shapes in the sense that the shapes of the domains were essentially unchanged at a constant temperature for a few hours. Figure 3 shows the equilibrium smectic-A domain observed experimentally with the polarizer only (a), and with the analyzer and polarizer crossed (b).

DISCUSSION

Identification of the shape

To determine both the shape of the smectic-A domain and the orientation of 8OCB molecules in the domain simultaneously, we simulated polarizing-microscope images of some possible structures for the equilibrium domain by means of a method described as follows [2]: the intensity of light (I), that passes through the polarizer, the smectic-A domain and finally the analyzer, is expressed as:

$$I = \|\mathbf{e}_A \mathbf{P} \mathbf{e}_P\|^2, \tag{1}$$

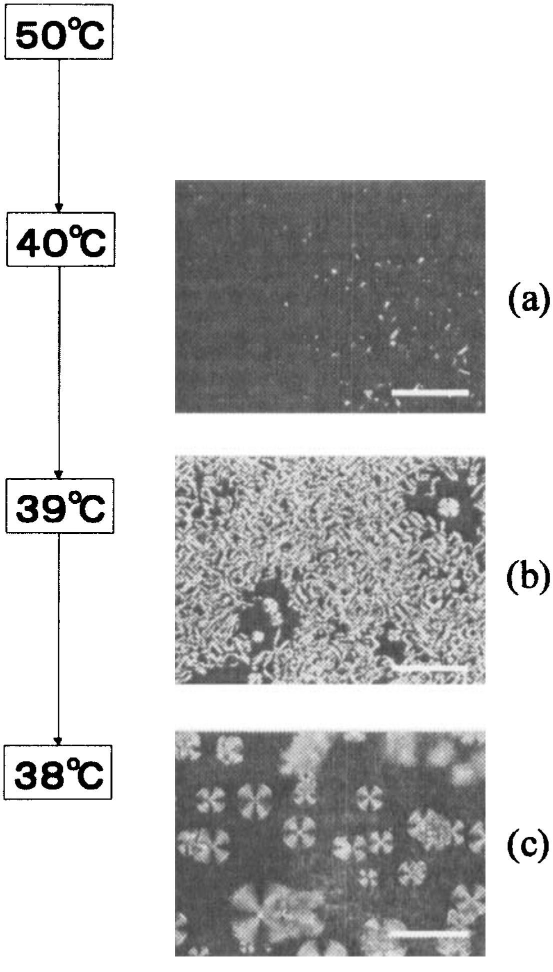
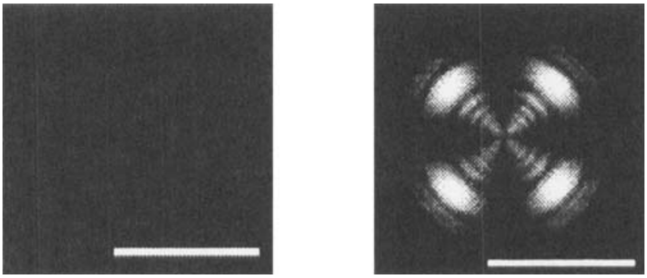


FIGURE 2 Growth sequence of smectic-A domains from an isotropic phase in the mixture of 8OCB and DODA (the molar concentration of 8OCB is 40%) observed with the analyzer and polarizer crossed. The wavelength of a light source of a polarizing microscope was 546 nm. The cooling rate from the isotropic phase was -0.1 ℃/min. The bars indicate 100 μm.



(a) (b)

FIGURE 3 A smectic-A domain observed with the polarizer only (a) and with the analyzer and polarizer crossed (b). The wavelength of a light source of a polarizing microscope was 546 nm. The bars indicate 50 μm.

where $\mathbf{e}_A$ is the orientation of the analyzer, and $\mathbf{e}_P$ is the incident polarization. $\mathbf{P}$ is a transformation matrix written as:

$$\mathbf{P} = \mathbf{R}_{N+1}\mathbf{S}_N\mathbf{R}_N ... \mathbf{S}_2\mathbf{R}_2\mathbf{S}_1\mathbf{R}_1 \tag{2}$$

$$\mathbf{R}_i = \begin{bmatrix} \cos(\alpha_i - \alpha_{i-1}) & -\sin(\alpha_i - \alpha_{i-1}) \\ \sin(\alpha_i - \alpha_{i-1}) & \cos(\alpha_i - \alpha_{i-1}) \end{bmatrix} \tag{3}$$

$$\mathbf{S}_i = \begin{bmatrix} e^{in_o 2\pi\Delta/\lambda_o} & 0 \\ 0 & e^{in_e(\gamma_i)2\pi\Delta/\lambda_o} \end{bmatrix} \tag{4}$$

$$n_e(\gamma_i) = \frac{n_o n_e}{\sqrt{n_o^2 \sin^2\gamma_i + n_e^2 \cos^2\gamma_i}} \tag{5}$$

where $i(= 1, 2, ..., N)$ is the index ranging from 1 to N corresponding to the intervals in the domain (Fig. 4), $\mathbf{n}_i$ is the local smectic-A director at the ith interval, $\mathbf{n}_D$ is the domain director (Fig. 4), n_e is the extraordinary index of refraction, n_o is the ordinary index of refraction, γ_i is the angle between the vectors $\mathbf{k}_o$ (direction of incident light) and $\mathbf{n}_i$ (local optical axis), and λ_o is the wavelength of the incoming light.

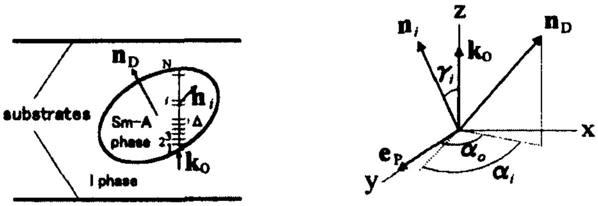


FIGURE 4 Definition of symbols used in the caluculation.

Since the domains observed experimentally are formed on the substrate surface, we simulated polarizing-microscope images of some of the possible structures under the assumption that smectics are layered structures whose interlayer distance is constant. We find from the simulation that the simulated image (Fig. 5) for the shape and director distribution shown in Fig. 6 is in excellent agreement with the experimentally obtained image (Fig. 3(b)). We therefore conclude that the shape of the smectic-A domain formed on substrate surface (Fig. 3) is a hemisphere and hence the director of the smectic-A phase is aligned radially as shown in Fig. 6.

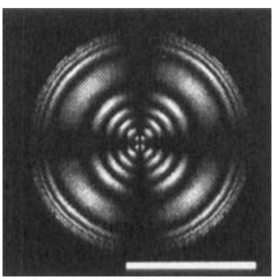


FIGURE 5 Simulated texture for a hemispherical smectic-A domain under crossed polarizers at 546 nm. The bar indicates 50 μm.

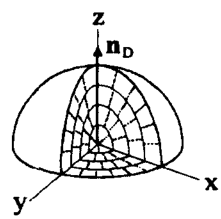


FIGURE 6 The orientation of 8OCB molecules in a hemispherical smectic-A domain.

Stability

Smectic-A domains grown from an isotropic phase can be described as layers whose inner and outer surfaces are parallel surfaces [4]. In order to examine the stability of smectic-A domains in an isotropic phase, the shape equation has been derived by taking account of the net difference in the energy between the smectic-A and isotropic phases that is the sum of the three terms [4]; (1) the volume free energy change due to isotropic–smectic-A transition

$$F_V = -g_o V = -g_o \int \mathrm{d}V, \tag{6}$$

where g_o is the difference in the Gibbs free energy density between the smectic-A and isotropic phases, and V is the volume of the smectic-A domain, (2) the surface energy of the smectic-A/isotropic interface

$$F_A = \gamma A = \gamma \oint \mathrm{d}A, \tag{7}$$

where A is the smectic-A–isotropic interfacial area, and γ is the smectic-A – isotropic interfacial tension, (3) the total curvature elastic energy of the smectic-A layers

$$F_C = \sum_i [\frac{k_{11} d}{2} \oint (2H)^2 \mathrm{d}A_i + k_5 d \oint K \mathrm{d}A_i], \tag{8}$$

where k_{11} is the splay elastic constant of the smectic-A, k_5 is defined as $2k_{13} - k_{22} - k_{24}$, k_{mn} are the Oseen-Frank elastic constants, i is the index figure of the smectic-A layers, and d is the thickness of each smectic-A layer. We can derive the shape equation and the stability condition from the first variation and the second variation of F $(= F_V + F_A + F_C)$, respectively. We have already demonstrated that some of the observation can successfully be explained by the theory [3]. However, hemispherical as well as spherical smectic-A domains are not stable solutions, indicating that these spherical shapes are not equilibrium ones [3]. We consider that the discrepancy between the experimental result and the theoretical prediction is due to a following reason: the liquid crystal material used here was the binary mixture of 8OCB and DODA. In previous papers [3], the mole ratio of 8OCB and DODA was assumed to be constant during the growth of a smectic-A phase. It is obvious that the molar concentration of 8OCB in the isotropic phase decreases as the smectic-A phase of 8OCB grows in the isotropic phase (Fig. 7). The transition temperature from the isotropic phase to the coexisting phase of smectic-A and isotropic phases (T_c) thereby decreases as the smectic-A phase of 8OCB grows in the isotropic phase (Fig. 1).

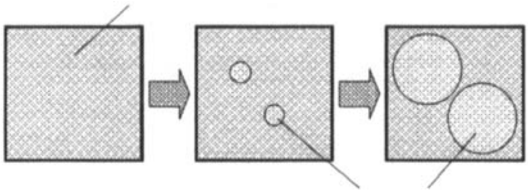


FIGURE 7 Schematic illustration of the growth process of smectic-A domains in an isotropic phase.

We reexamine the stability of the hemispherical smectic-A domain by taking into account of the change in T_c during the growth of the smectic-A phase. The change in T_c can be considered through the difference in the Gibbs free energy densities between the isotropic and the smectic-A phases,

$$g_0 = \frac{\Delta H(T_c - T)}{T_c v_{8OCB}}, \tag{9}$$

where ΔH is the enthalpy of fusion, T is the sample temperature, v_{8OCB} is a molar volume of 8OCB. Let the volume of liquid crystal mixture be V_0, and the initial ratio of mole % of 8OCB to DODA be $a_0 : b_0$. When the smectic-A phase grows to the volume of $V_S = (2/3)\pi r^3$ in the isotropic phase, T_c is changed as

$$T_c = p - q\frac{b}{a+b}, \tag{10}$$

where

$$a = \frac{a_0 V_0}{a_0 v_{8OCB} + b_0 v_{DODA}} - \frac{V_S}{v_{8OCB}}, \tag{11}$$

$$b = \frac{b_0 V_0}{a_0 v_{8OCB} + b_0 v_{DODA}}, \tag{12}$$

v_{DODA} is a molar volume of DODA, and p, q can be determined from the phase diagram (Fig. 1). We show in Fig. 8 the total free energy as a function of the radius of the hemispherical domains using Eqs. (6)-(12). We find the minimum of F at $r = 52.0\ \mu$m and hence that the hemispherical smectic-A domains are equilibrium shapes, which is consistent with the experiment.

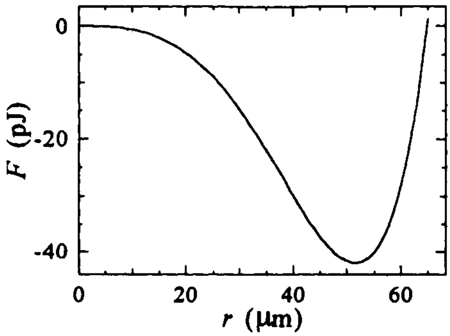


FIGURE 8 The dependence of the total free energy (F) on a radius of a hemishperical smectic-A domain (r).

CONCLUSIONS

We have observed equilibrium smectic-A domains on the substrate surface grown from an isotropic phase using a polarizing microscope. The results obtained in this paper are itemized as follows:

- We have shown from comparison between experimental polarizing-microscope images and simulated one that the equilibrium smectic-A domains in an isotropic phase are hemispheres formed on substrate surface. In addition, we have demonstrated that the simulation of polarizing-microscope images is a useful tool for the determination of the 3-dimensional smectic-A shapes and the orientation of the smectic-A molecules in the domains.
- Experimentally observed equilibrium hemispherical smectic-A domains are shown theoretically to be equilibrium shapes by considering the change in the transition temperature from the isotropic phase to the coexisting phase during the growth of the smectic-A phase.

Acknowledgement

We would like to thank financial support by the Seki Memorial Foundation for the Promotion of Science and Technology and by the Sasakawa Scientific Research Grant from The Japan Science Society.

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