Extreme Swelling of a Lyotropic Lamellar Liquid Crystal

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The angular distribution of light scattered by an extremely dilute birefringent lyotropic phase shows two well-defined Bragg peaks providing strong evidence of a true lamellar order (lamellae ~ 40 Å thick and 6500 Å apart in the diluent). The steric origin of the stabilization of this stacking is discussed.

It is now well established that the lyotropic lamellar liquid crystal in a number of ternary systems containing an ionic surfactant, a long-chain alcohol, and water can be swollen by water (or brine)[1,2] or by an aliphatic hydrocarbon.[3-5] The initial lamellar crystal has essentially symmetric water and aliphatic regions [Fig. 1(a)] while the swollen crystal can be described in terms of lamellae separated by the diluent, either water [Fig. 1(b)] or aliphatic hydrocarbon [Fig. 1(c)]. It is noteworthy that even at high dilutions, the phase obtained shows an important birefringence indicative of a long-range orientational order.

The lamellar spacing has been followed up in a number cases by small-angle x-ray scattering. The spacings thus measured increased with dilution up to several times the spacing in the initial lamellar crystal (e.g., 90 Å for 35-Å lamella[5] or 200 Å for 25-Å lamella[2]). This provided experimental evidence that a translational order is also preserved at least up to an interlamellar spacing of ca. 10 times the lamella thickness.

It was then tempting to attempt higher dilutions up to the domain where the lamellar spacing would be on the scale of visible-light scattering in order to test whether the translational order persists as does the orientational order. We report here such an attempt—the first successful one, to our knowledge. We have prepared a "hyper"swollen lamellar crystal
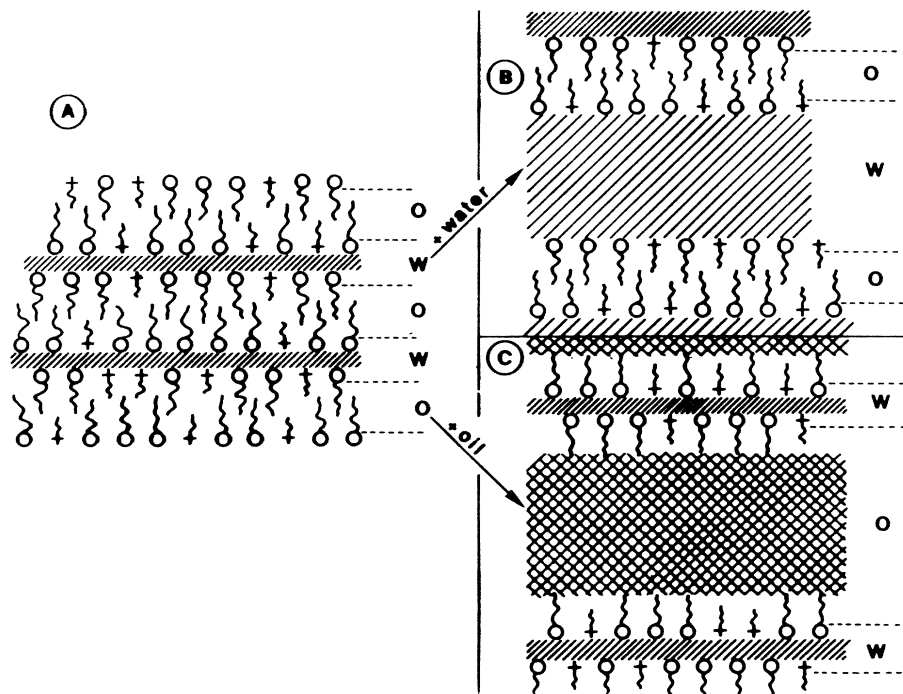

FIG. 1. (a) The ternary lamellar liquid crystal. (b) A lamellar liquid crystal swollen by water. (c) A lamellar liquid crystal swollen by an aliphatic hydrocarbon. Crossed heads denote alcohol; circular heads, ionic surfactant. Simple cross hatch denotes water; double cross hatch, oil.

and obtained, from light scattering, the lamellar spacing which is hundreds of times larger than the spacing of the initial lamellar liquid crystal.

The sample was prepared along the lines developed in Ref. 5. Namely, starting from a lamellar liquid crystal of the ternary system [octylbenzene sulfonate (OBS), water, pentanol] it was then shown that it could swell upon addition of a mixture of decane and pentanol. The composition of this diluent was estimated on the basis of the pseudophase model initially developed by Biais et al.[6] to describe microemulsions. The initial lamellar liquid crystal contains, by weight, 39.5% OBS, 18% pentanol, and 42.5% water; its spacing, measured by Marignan, Delichere, and Larche[7] is 35 Å. The diluent is, by weight, 92% decane and 8% pentanol. The resulting hyperswollen phase contained 0.7% volume fraction of the initial liquid crystal.

This phase showed a remarkable birefringence considering the extremely low content of active matter. When filled into a cylindrical tube (sample container for the light scattering, diameter $\sim$ 10 mm) it showed a strong tendency to orient under the influence of the glass walls. The same orientation as viewed by birefringence persists over distances of the order of 1 cm.

The angular distribution of scattered light was measured on a commercial laser spectrophotometer (AM-TEC Inc.) by use of the $\lambda = 4880$ Å polarized beam of an argon-ion laser. The sample was thermostatted at $25 \pm 0.1\,°C$. The obtained distribution is depicted in Fig. 2. Two well-defined peaks are observed. Their spacing (1:2) corresponds to the first- and second-order Bragg maxima characteristic of a lamellar structure. We thus have clear-cut evidence that this hyperswollen birefringent phase is lamellar and corresponds to a stacking of lamellae as depicted in Fig. 1(c).

The measured interlamellar distance is $d = 6500 \pm 300$ Å. This is of the same order of magnitude as but significantly larger than expected from the dilution procedure[5] if we assume the conservation of the volume of each constituent[7] ($d \sim 5000$ Å). This discrepancy is, however, not so surprising when one considers the actual degree of dilution. Neglecting an even very low solubility in the diluent of any of the species of the lamella can lead to a strong underestimation of the expected d. Neglecting the thermally induced undulations of the lamallae can further alter the prediction of d.

This work provides direct experimental evidence for the very remarkable persistence of both orientational and translational orders in the lamellar phase at extreme dilution. Then the question arises, what long-ranged interlamellar repulsion is responsible for the regularity of the stacking at such a large d?

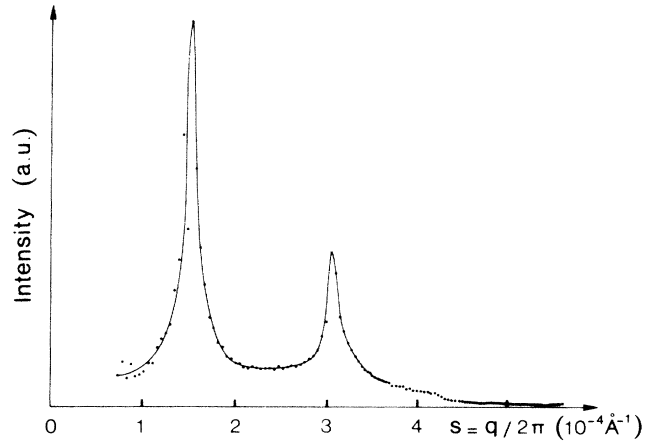The measured d is very large compared to the ex-

FIG. 2. The angular distribution of intensity scattered by the hyperswollen lamellar liquid crystal (OBS/water/pentanol/decane).

pected range of the interactions usually involved in such an oil-rich system, namely (attractive) van der Waals interactions and correlation effects in the swelling fluid. The only interaction which is likely to be responsible for the stability of the structure must then be the repulsive "steric interaction."[8,9] It arises from the fact that the spontaneous undulation modes of one given lamella are strongly hindered by the presence of the two adjacent, also undulating, lamellae. This purely entropic interaction is long ranged; Helfrich[10] has evaluated the corresponding free energy per unit area of membrane in the system, which decreases like d^{-2}.

We now investigate the effect of the steric interaction upon the smectic orders. We align the layers parallel to the x-y plane denoting the positions in the plane by the coordinate $\rho(=x,y)$. The positional fluctuations in the z direction are denoted by the displacement $u_n(\rho)$ of the nth layer. Within the classical harmonic approximation for the elastic free energy of the lamellar stacking, the mean square amplitudes of the q modes are

$$\langle |u_q|^2 \rangle = k_B T (\bar{B}_{st} q_z^2 + K q_\perp^4)^{-1}.$$

Here K is related to the rigidity modulus k_c of the lamellae by $K = k_c/d$, and B_{st} accounts for the steric interaction.[9] According to Helfrich[10]

$$B_{st} \simeq 5 (k_B T)^2 k_c^{-1} d^{-3}.$$

Introducing

$$\Lambda = d^{-1}(K/B_{st})^{1/2} = 0.45(k_c/k_B T),$$

we calculate the following average values,[11-14] where

$$\langle |\Delta u_n(\rho)|^2 \rangle = \langle |u_n(\rho) - u_0(0)|^2 \rangle,$$

and where $\theta(\mathbf{r})$ is the angle between the normals to

the layers at point r and point 0:

$$\lim_{r \to \infty} \langle |\theta^2(\mathbf{r})| \rangle = (k_B T/\pi k_c)\{\tfrac{1}{2} + \ln[(d/a)(\pi\Lambda)^{1/2}]\}, \tag{1}$$

$$\langle |u^2| \rangle / d^2 = (4\pi)^{-1}0.45 \ln[L/d(\pi\Lambda)^{1/2}], \tag{2}$$

$$\frac{\langle |\Delta u_n(\rho)|^2 \rangle}{d^2} = (2\pi)^{-1}0.45\left\{\ln\frac{(\pi n)^{1/2}}{-\Omega + (\Omega^2+1)^{1/2}} + c_1(\Omega)\right\}. \tag{3}$$

Here a^2 is the area per surfactant molecule in a layer, L is the size of the sample, $|c_1(\Omega)| < 1$, and Ω is related to n and ρ by $\Omega = \rho/2d(\Lambda n)^{1/2}$. Note that Eqs. (2) and (3) differ from the results in Refs. 12 and 13: They do not involve[14] a because of the very large value of d (here $\Lambda d^2/\pi a^2 \sim 10^6$).[15]

The orientational fluctuations are bounded above by 1; the orientational order is truly long-range. $\langle |\theta^2(\mathbf{r})| \rangle$, however, diverges logarithmically with d. The calculation is valid for small orientation fluctuations only [$\langle \cos\theta(r) \rangle > 0.9$]. This condition introduces a maximum value $(d/a)_{\max}$ which increases exponentially with $k_c/k_B T$.[16] Clearly, if k_c is large enough ($> 10 k_B T$), *the phase can be swollen enormously while keeping a strong orientational order.*

Using (3) and following Refs. 12–14, we can derive the intensity pattern $I(\mathbf{q})$ of the scattered light. Around the nominal Bragg reflection of the mth order we have

$$I(q_\perp = 0, q_z) \propto [q_z - (2m\pi/d)]^{2-0.7m^2}. \tag{4}$$

$I(q)$ thus exhibits a true singularity at the nominal first Bragg reflection, and *the steric interaction alone actually stabilizes the positional order* for any degree of swelling (in the limit $d < d_{\max}$ at least).

On the other hand, no singularity is predicted for higher-order Bragg reflections, which seems in contradiction with the experimental evidence in Fig. 2. However, note the following:

(i) The finite-size effect discussed in Ref. 14 alters strongly the predicted $I(q)$. Expressions (3) and (4) are for an infinite medium sampled by an infinite plane wave. In the present experimental conditions the size of the sample is $L \simeq 1$ cm and the scattering subvolume is 1 mm wide. Using (2) and (3) we get $\langle u^2 \rangle / d^2 \lesssim 0.3 (< 1)$ over the entire sample and $\langle \Delta u_n(\rho)^2 \rangle / d^2 \lesssim 0.3 (< 1)$ over the scattering subvolume. Over these finite although macroscopic scale lengths, the smectic stacking shows an effective long-range ordering[14] which could restore a moderate ratio between the two first Bragg maxima.

(ii) We have used the harmonic approximation. A more rigorous approach should consider the nonlinear character of the steric interaction and involve a q-dependent effective k_c because of the scale-dependent softening effect discussed by Helfrich and by Peliti and Leibler.[17] Such nonlinear couplings between modes should[18] increase the range and magnitude of the steric interaction and stiffen the positional order.

In summary, we have obtained clear-cut experimental evidence for a new class of smectic liquid crystal with extremely large periodicity ($d \sim 6000$ Å) which is obtained by enormous swelling of an initial classical lyotropic lamellar phase. We have also shown that the stability of both observed long-range orientational and quasi long-range positional orders could be interpreted in terms of Helfrich's steric interactions alone as long as the layer rigidity is high enough.

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