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# Observation of a Change from Splay to Bend Orientation at a Phase Transition in a Langmuir Monolayer

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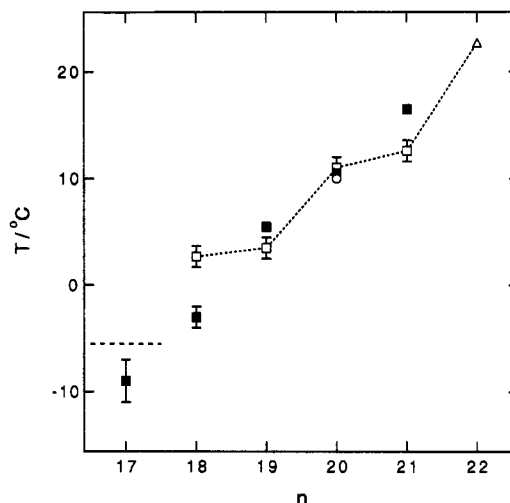
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The behavior of Langmuir monolayers of methyl octadecanoate, methyl nonadecanoate, and methyl eicosanoate has been studied by polarized fluorescence microscopy and Brewster angle microscopy in the neighborhood of a transition between two liquid-condensed (LC) phases. As the monolayer is cooled through the transition, the molecular tilt azimuth in six-arm star defects of the LC phase changes by 90° (from a splay to a bend texture), a process that we call "blooming". In other domains the transition is seen as a change from textured distorted hexagons to rectangular domains in which the tilt direction is uniform. The changes in texture and morphology are consistent with a transition from a hexatic phase to a crystalline phase with herringbone order.

Phase diagrams of monolayers of long-chain fatty acids and their esters at the air/water interface (Langmuir monolayers) have been studied for more than 50 years. While much of the knowledge about transitions between monolayer phases has been derived from surface pressure-area ( $\pi$ - $A$ ) isotherms, direct visualization of phase transitions is becoming increasingly important. Transitions between the gas (G) and liquid expanded (LE) phases and between the LE phases and liquid condensed (LC)<sup>1</sup> phases are readily observed by fluorescence microscopy.<sup>2,3</sup> Recently, techniques such as polarized fluorescence microscopy (PFM)<sup>4</sup> and Brewster angle microscopy (BAM),<sup>5,6</sup> which are sensitive to differences in molecular tilt, have allowed transitions between several condensed monolayer phases to be detected.<sup>7,8</sup>

PFM and BAM have also revealed that Langmuir monolayers often self-organize into structures in which the molecular tilt azimuth is ordered over mesoscopic (and even macroscopic) distances.<sup>9,10</sup> This organization produces an optical "texture" similar to those characteristic of liquid crystals. The textures are sometimes associated with metastable defects,<sup>9</sup> but they may also correspond to equilibrium states.<sup>11,12</sup> As in liquid crystals, they reflect the underlying microscopic order in each phase, which, for monolayers of fatty acids, has been determined from diffraction studies.<sup>13-15</sup> While no molecular theory of the textures exists, a phenomenological model that incorporates the structural information is capable of describing many of the observed textures.<sup>12,16</sup>

Qiu et al.<sup>9</sup> examined the textures in LC domains of the C<sub>14</sub>-C<sub>19</sub> methyl esters in coexistence with the isotropic LE phase. At high temperatures, the domains have a uniform texture consistent with a phase in which the molecules are normal to the surface. When the temperature is lowered, the domains undergo a sharp transition to a tilted phase, one in which the molecules are uniformly inclined with respect to the surface normal. The transition is accompanied by the formation of defects. Some domains organize into "star defects" that contain six wedge-shaped regions in which the tilt azimuth is uniform; the azimuthal angle changes sharply by 60° at walls that separate the wedges. Others form defects in which there are three arms that meet at the vertex of the hexagon. Qiu et al. reported that there is a second transition at lower temperature but gave no details; in this paper we consider this low-temperature transition more fully and describe the behavior of the textures in domains of methyl octadecanoate (C18-M), methyl nonadecanoate (C19-M), and methyl eicosanoate (C20-M) in its vicinity.



**Figure 1.** Low-temperature transition in esters. The open squares represent values for the pure methyl esters determined in this work by BAM. The other points have been obtained from isotherm studies. They represent the extrapolation to zero pressure of the L<sub>2</sub>'/L<sub>2</sub> phase boundary: (Δ) methyl docosanoate, Stenhagen;<sup>20</sup> (O) ethyl eicosanoate, Bibo et al.<sup>19</sup> (■) ethyl esters, Lundquist.<sup>18</sup> The error bars in the literature data represent uncertainties in the extrapolation. The horizontal dashed line at  $n = 17$  is the lowest temperature at which we were able to obtain measurements. The transition was not observed; hence, the line represents an upper bound. The line connecting the points for the methyl esters is simply a guide to the eye.

## Experimental Section

Details of the measurements by PFM have been described previously.<sup>7</sup> The Brewster angle microscope, which is of our own construction, is similar in concept to that described by Hönig and Möbius.<sup>5</sup> An Ar<sup>+</sup> laser (wavelength 514 nm) is used as a light source, however, and the higher intensity allows us to work with a smaller aperture, thereby increasing the depth of field. The laser was operated at a power level of 500 mW, but after the beam has passed through the optics and the trough cover glass, it has been attenuated to 280 mW. Noticeable convection is induced only when the nominal laser power exceeds 1 W. In the experiments described here, the polarization of the incident beam was tilted very slightly out of the plane of incidence, and the analyzer (extinction ratio 10<sup>-5</sup>) was set at 85° from the plane of incidence, conditions that gave the greatest contrast. The trough is constructed of Teflon and has an area of 100 cm<sup>2</sup>. Its temperature is controlled by water from a thermostat that circulates through the base plate. Bead thermistors immersed in the subphase are used to measure the temperature. There is a

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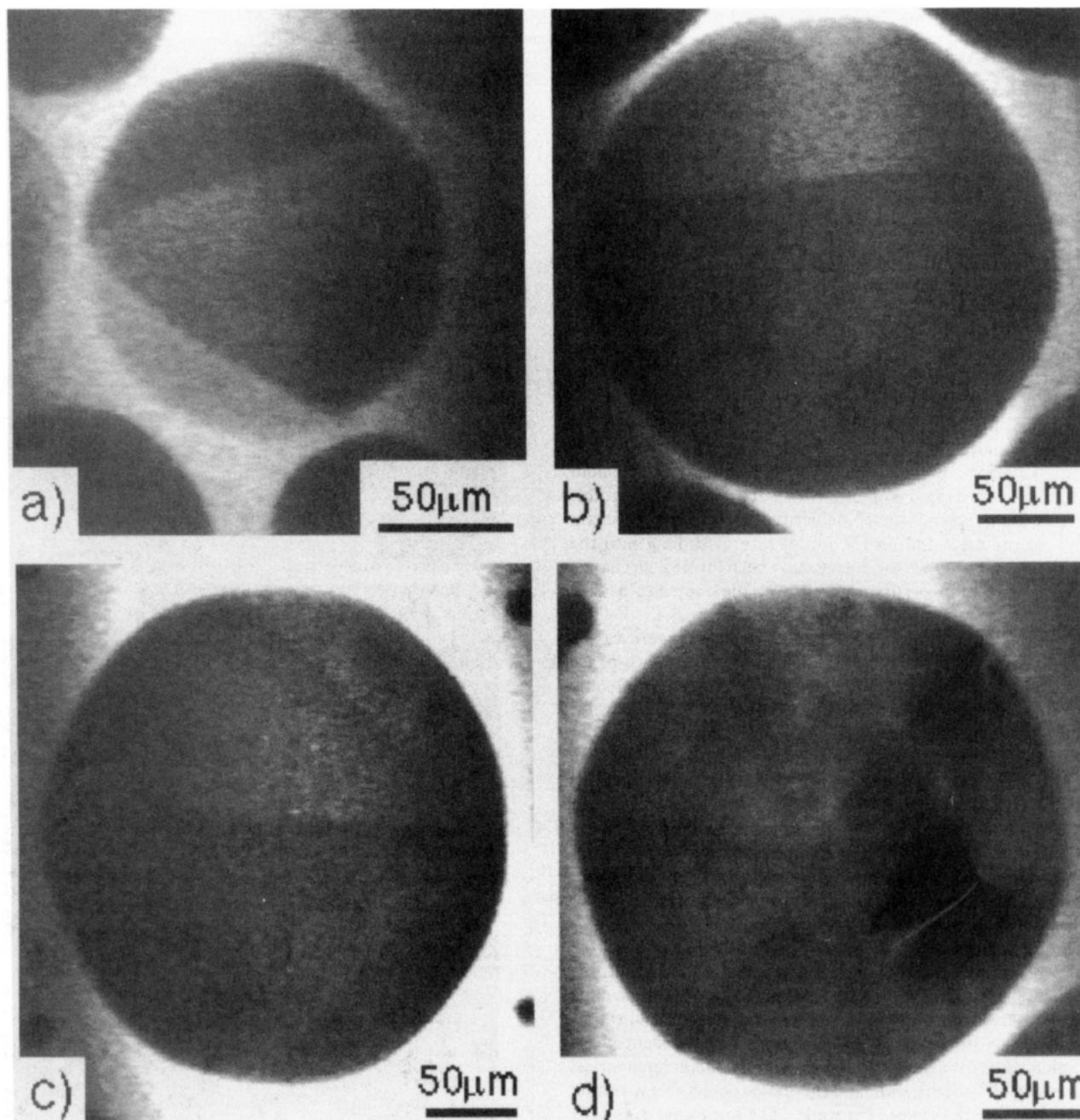


Figure 2. Polarized fluorescence microscopy images of the textures in the high-temperature phase of methyl octadecanoate.

conductive coating on the cover glass so that it can be electrically heated to prevent condensation when experiments are carried out at temperatures below ambient and fogging at high temperatures.

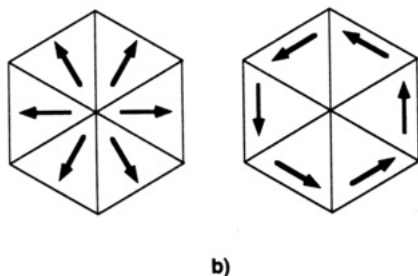
The esters were obtained from Nu-Chek Prep; the supplier claimed them to be 99% pure, and they were used without further purification. Chloroform (Fisher spectranalyzed) was the spreading solvent. The fluorescent probe 4-(hexadecylamino)-7-nitrobenz-2-oxa-1,3-diazole (NBD-HDA) was obtained from Molecular Probes and was used at a concentration of 1 mol % in the PFM studies. The BAM experiments were carried out with both pure samples and those containing probe; unless otherwise noted, they gave the same results. Unbuffered water purified in a Milli-Q system was used as the subphase.

## Results

**Phase Behavior.** Figure 1 shows the temperatures at which the low-temperature transition takes place as a function of chain length  $n$  for the  $C_{17}$ – $C_{21}$  methyl esters. The points represent the temperatures at which there is a sharp change in texture observed

by BAM when LC domains surrounded by the LE phase are cooled. Under these conditions, the surface pressures are immeasurably low, but from a detailed isotherm and optical study of the  $\pi$ - $T$  phase diagram of  $C_{18}$ -M,<sup>17</sup> it is evident that the changes in texture correspond with a phase boundary that rises steeply with pressure.

**Isolated Domains in Coexistence with the LE Phase.** The textures in isolated domains of the LC phase surrounded by the LE phase were followed from 3 to 35 °C. Measurements of isolated domains could be carried out to temperatures below the LE/LC/G triple points because regions of LE phase remain metastable for long times. With PFM there is sufficient contrast between the LC and G phases to allow single LC domains surrounded by the gas to be studied, but under these circumstances the LC domains are very mobile and it is difficult to follow the evolution of the texture in a single domain. In a typical experiment the monolayer was prepared at high temperature in the LE phase at an area of about 25 Å<sup>2</sup> molecule<sup>-1</sup> and then cooled into the two-phase region.



**Figure 3.** Molecular tilt organization in LC domains: (a) splay texture, (b) bend texture. Equal numbers of clockwise and counterclockwise splay textures are observed.

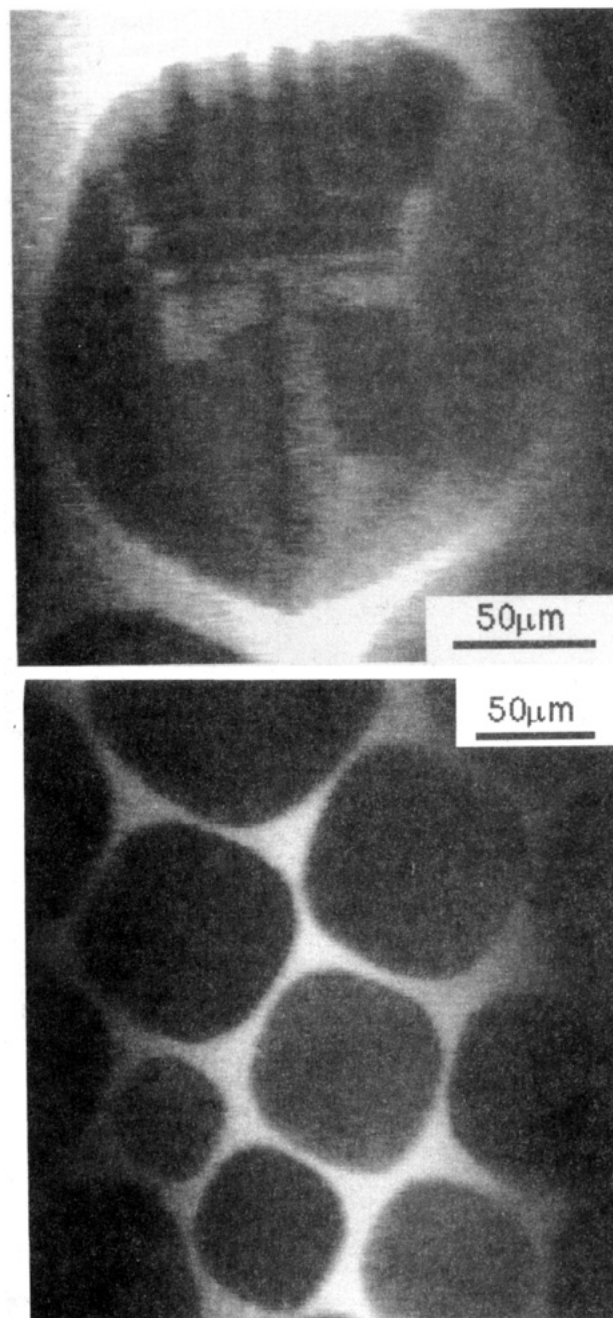
Three types of defects are observed: six-arm stars (Figure 2d) and defects in which there are either three or four tilt regions separated by walls that come together at the domain boundary (Figure 2a,c). The side of the hexagon at which the walls meet is rounded and elongated, and the angle between the walls is typically 50–55°. Some of the two-wall domains contain small triangular-shaped regions of uniform tilt at one edge (Figure 2b). The relative numbers of each defect type depend on the chain length of the ester and on the initial rate of cooling into the two-phase region. Once the defects have been formed, no change in the relative numbers is observed over the course of a 12-h experiment.

The rates of cooling into the two-phase region were varied from 10 K min<sup>-1</sup> to 4 K h<sup>-1</sup>. Rapid cooling into the two-phase region favors six-arm defects, which typically represent 50–60% of the total at high cooling rates. At the slowest cooling rates, about 90% of the domains in C18-M contain two walls (about half of these domains are of the type shown in Figure 2d); the three-wall domains predominant in C19-M, and only three-wall domains are observed in C20-M. If a monolayer is driven out of the two-phase region by heating and then quenched into the two-phase region a second time, the number of six-arm stars formed is fewer even though the cooling rate is unchanged. There is, as well, some day-to-day variation in the relative numbers of each defect.

The domains have also been studied by BAM. Analysis of the images of star defects shows that they are consistent with the tilt organization shown in Figure 3a. This defect structure accounts for the observed variation in the intensities within domains that have different orientations with respect to the incident beam direction. The tilt azimuth is normal to the domain boundaries; it jumps by 60° at each wall, and there is no detectable variation of the tilt azimuth between the walls. The same analysis shows that there are also 60° jumps in tilt azimuth at the walls in the other domains and evidence of a variation of the tilt azimuth within the central wedge-shaped region.

**The Low-Temperature Transition.** There is a sharp change in the domains at the low-temperature transition, but the behavior depends on the cooling rate and on the structure of the defect in the high-temperature phase. If the cooling rate is fast, the domains become irregular in shape and their textures break up into small regions of stripes, often oriented at 90° with respect to each other (Figure 4a). On slow cooling through the transition (~1 K h<sup>-1</sup>), domains that contain three or four tilt regions become square or rectangular in shape and uniformly tilted (Figure 4b). (It is clear that the molecules are tilted because molecules with different orientations with respect to the laser beam fluoresce with different intensities and the intensities change when the direction of the beam is varied.) The transition in shape and texture is fully reversible.

When star defects are cooled slowly through the low-temperature transition, there is a sudden appearance of six new regions of different tilt orientation at the center of each domain (Figure 5a). The regions grow (Figure 5b,c) and spread out over the entire domain, a process that we call "blooming". When it

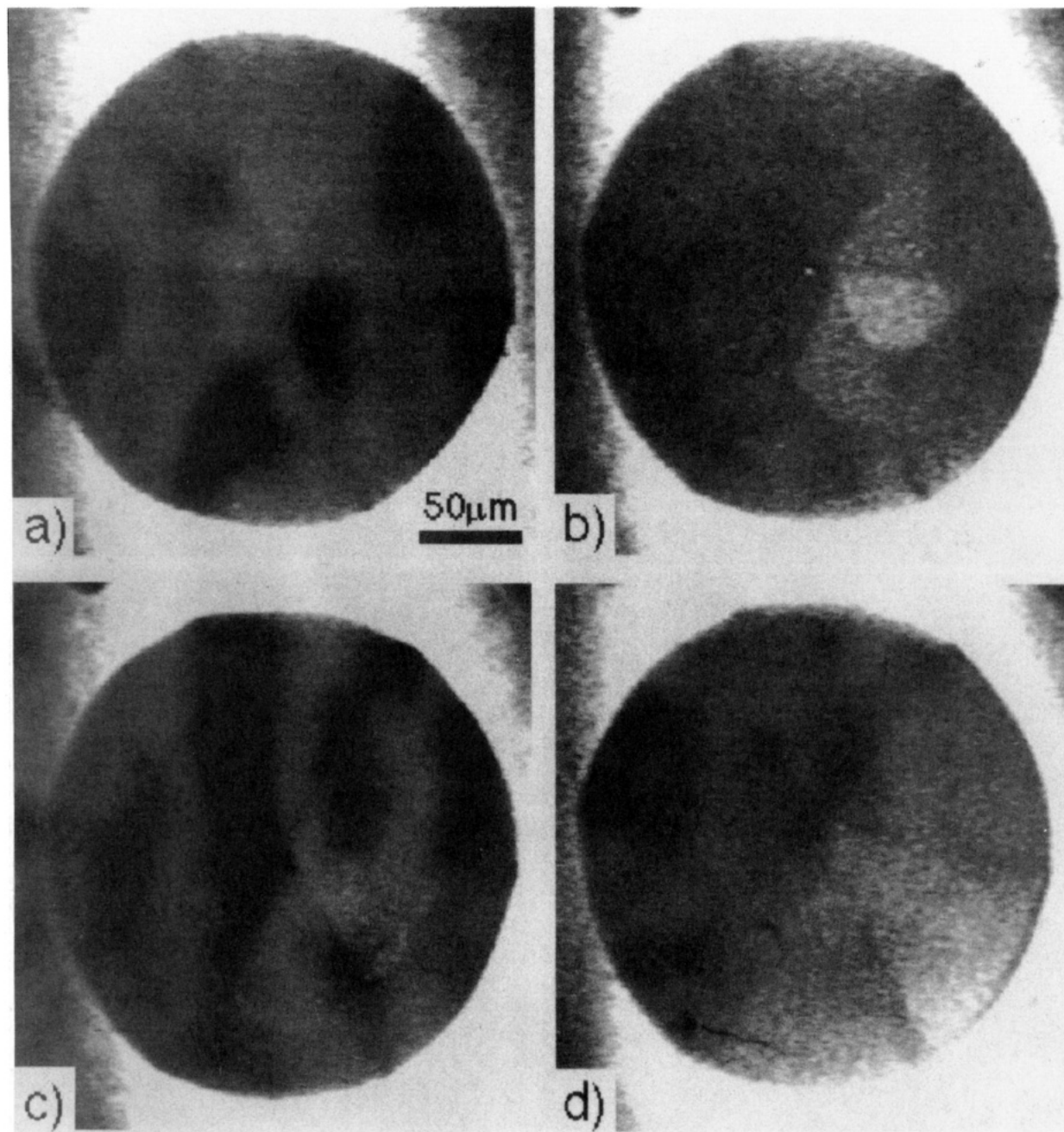


**Figure 4.** Polarized fluorescence microscopy images in the low-temperature phase of methyl octadecanoate: (a) rapid cooling; (b) slow cooling of two- or three-wall domains. The bars represent 100 μm.

is complete, the domain retains its hexagonal shape and has been transformed into a star defect with an organization of the tilt azimuth different from that in the higher-temperature phase (Figure 5d). When the monolayer is heated, the higher-temperature phase reappears at the periphery of a domain and spreads inward (Figure 6a–d). The transition is not completely reversible. After the cooling/heating cycle is repeated two or three times, the regular structure breaks up into small domains that do not heal in several hours.

The variation in the fluorescence intensity within each of the low-temperature domains suggested that the transition was accompanied by a change of 90° in the tilt azimuth. This was verified by BAM measurements. For the most part, they were performed on monolayers containing probe because there is significantly more coalescence in undoped monolayers at low temperatures, making it difficult to find isolated domains.<sup>18</sup> The BAM studies (Figure 6) confirmed our interpretation of the PFM





**Figure 5.** The "blooming" transition in methyl octadecanoate. PFM images of a domain as it undergoes the transition on cooling.

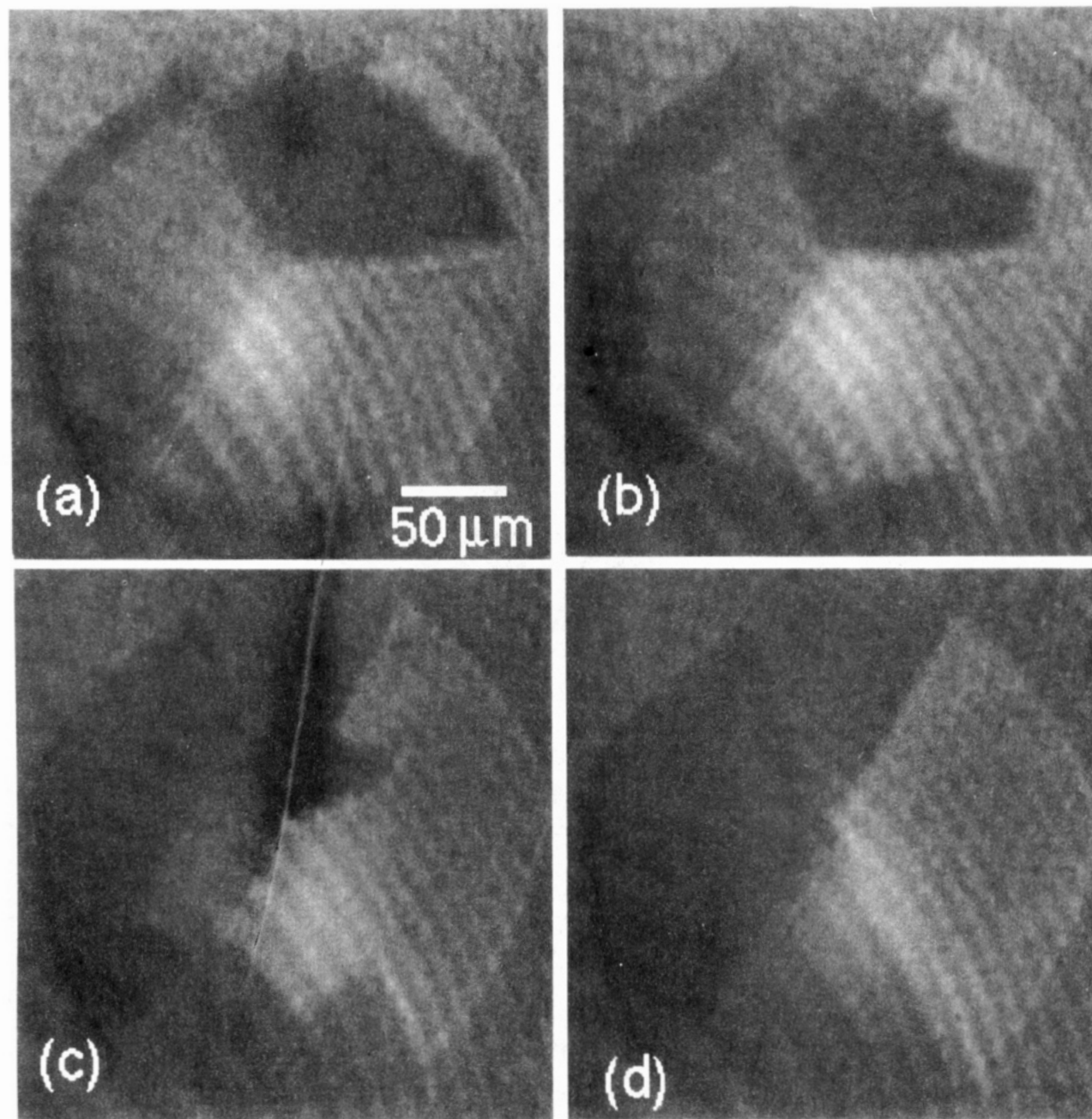
images: the low-temperature transition results in a change of the texture from splay to bend (Figure 3b).

### Discussion

**Identity of Phases.** No diffraction studies of the esters have been performed so the structures of the high- and low-temperature phases cannot be specified unequivocally. Lundquist<sup>19</sup> determined the phase diagrams of several ethyl esters from isotherm measurements. She ascribes a feature in the isotherms at low temperatures and pressures to a transition between the  $L_2'$  and  $L_2''$  phases. The open square symbols in Figure 1 are the temperatures of this transition extrapolated to zero pressure. Bibo et al.<sup>20</sup> reported a phase diagram for ethyl eicosanoate in which they identified the higher-temperature phase as  $L_2$  rather than  $L_2'$ . Stenhagen performed isotherm studies of ethyl eicosanoate and methyl docosanoate.<sup>21</sup> He also believed the phases at high temperature to be  $L_2$  but claimed that low-temperature phases were CS. Points representing the zero-pressure values of the phase boundaries taken from Bibo et al. and Stenhagen are also plotted in Figure 1.

The  $L_2$  and  $L_2'$  phases are hexatics that differ primarily in the direction of the molecular tilt. In  $L_2$  the molecules tilt toward nearest neighbors, while in  $L_2'$  the tilt is toward next-nearest neighbors. Lundquist gives no reason for the identification of the high-temperature phase as  $L_2'$ . On the other hand, Bibo et al. performed a miscibility study that allowed them to connect the ethyl eicosanoate phases to those of docosanoic acid. Diffraction studies of acids show that the tilt in low-pressure, high-temperature phase is toward the nearest neighbor. Hence, it appears likely that the tilt is toward nearest neighbors in the higher-temperature phase of the esters. The fact that we are able to observe different tilt orientations in the low-temperature phase demonstrates that it cannot be CS, as proposed by Stenhagen, because in the CS phase the molecules are untilted.

**High-Temperature-Phase Textures.** Fischer et al.<sup>16</sup> have examined theoretically the formation of various defect structures in domains of tilted hexatic phases of Langmuir monolayers. They showed that the theory could account for the structures of many defects, including those of a variety of six-arm stars and of boojums, textures in which the tilt azimuth changes continuously



**Figure 6.** The "blooming" transition in methyl octadecanoate. BAM images of a domain as it is heated through the transition. The transition has already begun in (a), where the new phase can be seen around the periphery.

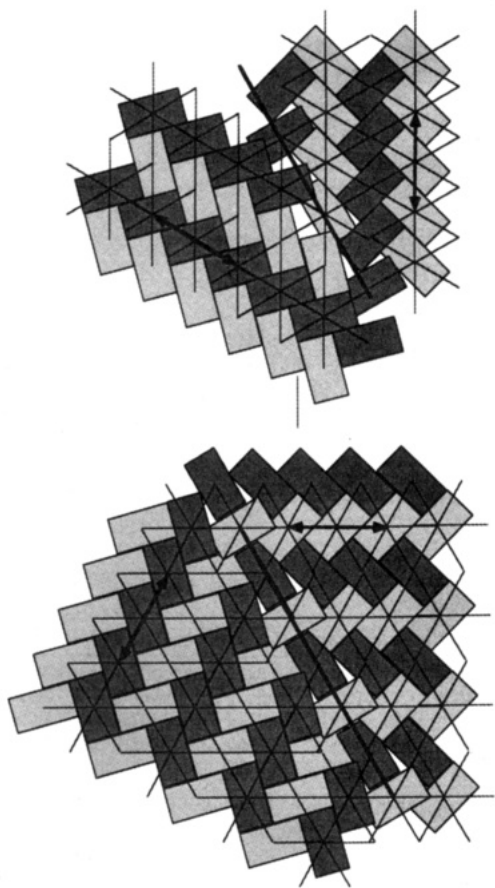
and the core defect lies at the edge of a domain or is a virtual defect located outside the domain. The stability of each type of defect is determined by a variety of factors, including the identity of the phase, the values of elastic constants, the strength of the coupling between the bond-order and tilt-azimuth fields, the energy of the core, and the boundary conditions at the interface between the domain and the surrounding isotropic medium.

Although we have not examined the two- and three-wall textures theoretically, we can make some informed guesses about their nature. In essence, they lie between the star defects and the boojum textures, which have no walls. In boojums, the molecular tilt azimuth is everywhere locked to the hexatic order parameter. The texture arises from the balance of the tendency to have a uniform splay (or bend) structure within the domain and the preference for a specific boundary condition (usually normal) at the LE/LC interface. Textures in which there are walls arise when the hexatic stiffness is high, which favors uniform domains. The boundary conditions for the tilt azimuth can then be maintained only if the tilt azimuth is no longer locked to the hexatic order. Such deviations are energetically costly and are

therefore localized in narrow regions (walls) where the tilt azimuth changes sharply, usually by  $60^\circ$ . The progression of dominant textures from C18-M to C20-M can then be seen as the result of increasing stiffness in the hexatic order with increasing chain length of the aliphatic tail. Such a progression is evident in the fatty acids as well, where spiral textures are common in tetradecanoic acid and much rarer in hexadecanoic acid.<sup>10</sup>

The presence of both two-wall defects and star defects in domains of C18-M demonstrates that the stabilities of the two textures are not very much different; the decrease in the number of stars when the cooling rate is lowered suggests that they are the less stable texture. In some cases the relative stabilities of the textures can be computed from the theory, as has been done, for example, in determining the optimal numbers of arms in a star defect.<sup>9</sup> But we do not know the values of the core energies, so it is impossible to determine the relative stabilities of textures with different core defects.

**Low-Temperature Phase.** Although the structures of the high- and low-temperature phases are unknown, much about the nature of the low-temperature phase can be deduced from the changes



**Figure 7.** The 60° walls in a phase with herringbone order: (a) splay orientation of the tilt azimuth; (b) bend orientation of the tilt azimuth. The rectangles represent the orientations of the molecules.

in the domains that accompany the phase transition. There are two striking results: the blooming, in which the ordering of the tilt azimuth in hexagonal domains changes from splay to bend, and the change in the morphology of domains from hexagonal to rectangular.

The blooming is consistent with the onset of herringbone order. Figure 7 shows the structure of walls at which the molecular tilt azimuth jumps by 60° in a phase in which there is herringbone order. The shading of the rectangles distinguishes the two types of molecules in such a structure, and the arrows indicate the direction of the tilt azimuth, which is also the direction of elongation in the distorted hexagonal structure. If the tilt is radial, as in a splay defect, the herringbone order is largely disturbed at the wall; i.e., there is a disruption of the alternation of molecules of different types (Figure 7a). If, on the other hand, the tilt is changed by 90°, as in a bend defect, the herringbone structure at the wall is maintained (Figure 7b). Thus, when there is herringbone order, bend defects are favored over splay defects in six-arm stars.

The observation of rectangular domains only in the low-temperature phase suggests that this phase is crystalline and not hexatic. The morphology of a crystalline domain can be related to its interfacial free energy by the Wulff construction.<sup>22</sup> If we take the rectangular shape of the low-temperature domains and their uniform tilt direction to be equilibrium features, then the interfacial free energy must have rectangular symmetry, which is consistent with a rectangular unit cell. We know from diffraction studies of the fatty acids that in the  $L_2$  and  $L_2'$  phases, which are hexatics, the hexagonal symmetry is broken by the molecular tilt. As in the  $L_2''$  phase, there is an elongation in the tilt direction so the structures are rectangular, and one might therefore ask why the domains of the high-temperature phase are not rectangular as well.

Domains of the tilted hexatic phases surrounded by an isotropic medium are hexagonal or circular, not rectangular. A calculation with a simple model,<sup>23</sup> applicable only in the zero-temperature limit, indicates that the shape of a small domain of an *untilted* hexatic phase is hexagonal but becomes circular as the domain size increases. In tilted hexatic phases, the departure from hexagonal symmetry can be accommodated by very small variations of the bond orientation between the walls (much as there is a variation between the walls in the five-arm star defects that are observed in freely suspended liquid-crystalline films<sup>24</sup>). The morphology of the domains appears to be determined by the boundary condition at the interface with the surrounding medium.<sup>16</sup> When the molecular head-tail asymmetry is sufficiently large, there is a preference for the molecular tilt to be normal to the interface, which can be achieved in six-wall stars by an hexagonal shape.

In summary, the blooming transition and the rectangular morphology of the domains are consistent with the identification of the low-temperature phase as  $L_2''$ . It is a crystalline phase with herringbone order. The walls between regions of different tilt azimuth can therefore be described as twinning boundaries between crystalline regions of different orientation.<sup>25</sup> Although we feel confident about this interpretation, it can be confirmed only by diffraction studies.

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