

# Texture Change Separate from the Transition between Two Tilted Phases in Langmuir Monolayers

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Palmityl acetate monolayers are studied by grazing-incidence X-ray diffraction (GID). The monolayers are found to undergo a transition from a phase with alkyl chains tilted toward nearest neighbors (NN) to a phase with chains tilted toward next-nearest neighbors (NNN) upon monolayer compression. This transition gives rise to a sudden reorientation of the molecules that is determined by Brewster angle microscopy (BAM). At  $T > 15\text{ }^{\circ}\text{C}$ , palmityl acetate monolayers undergo a first-order transition from a fluid phase to a condensed phase indicated by a plateau region in the  $\pi$ - $A$  isotherm. The transition pressure increases with increasing temperature. At low temperatures a phase with alkyl chains tilted toward nearest neighbors is formed from the fluid phase. The critical pressure for the transition between the tilted phases changes only slightly with temperature. Consequently, a phase with chains tilted toward next-nearest neighbors is formed directly from the fluid phase at high temperatures. Then no reorientation of molecules is observed by BAM. The textures of the condensed-phase domains formed during the transition from a fluid phase to a condensed phase are temperature-dependent. Some domains are subdivided into six segments of different orientation. In such domains the molecular chains are tilted along the bisector of the segments at  $T < 22\text{ }^{\circ}\text{C}$ , whereas the tilt azimuth is perpendicular to the bisector at  $T > 24\text{ }^{\circ}\text{C}$ . The crossover from one texture to the other is separate from the transition between the tilted phases. At  $T \leq 26\text{ }^{\circ}\text{C}$ , the sudden reorientation of molecules corresponding to the NN–NNN phase transition is still observed.

## Introduction

Textures in Langmuir monolayers have been the object of interest in many recent publications.<sup>1–7</sup> They have been widely used to study the phase behavior of Langmuir monolayers and also to get information about the line tension<sup>1,2</sup> and elastic properties<sup>1</sup> of the monolayers. Brewster angle microscopy (BAM) and polarized fluorescence microscopy revealed that Langmuir monolayers of many amphiphiles show long-range orientational order.<sup>1–7</sup> The domains of the condensed phases are found to exhibit characteristic textures. One of them is a subdivision of a circular domain into six or seven segments of different molecular orientation. Two types of such textures occur: one with alkyl chains tilted along the bisector of the segment and another in which the tilt azimuth of alkyl chains is perpendicular to the bisector of the segment. The first type is found for 1-monoglycerides<sup>4</sup> and fatty acid methyl esters.<sup>5,7</sup> The second type occurs in monolayers of fatty acid ethyl esters.<sup>6</sup> In a previous paper the crossover from one texture to another has been associated with a transition between tilted monolayer phases.<sup>7</sup>

Until now much work has been done concerning fatty alcohols, fatty acids, and their methyl and ethyl esters. Another class of simple amphiphiles are the fatty alcohol acetates. Monolayers of palmityl acetate show a transition between the two textures mentioned above. In the present paper we study the correlation between this transition and the transition between the tilted monolayer phases. The structures of the phases of palmityl acetate monolayers were investigated by grazing-incidence X-ray diffraction (GID), whereas the temperature

dependence of phase transitions was examined by BAM. Both methods were combined to construct a phase diagram.

## Experimental Section

**Grazing-Incidence Diffraction.** Grazing-incidence X-ray diffraction was performed using the liquid-surface diffractometer on the undulator beamline BW1 at HASYLAB, DESY, Hamburg, Germany.<sup>10</sup> A monochromatic beam with a wavelength of  $1.481\text{ }\text{\AA}$  was adjusted to strike the surface with an angle of incidence  $\alpha_i \approx 0.85\alpha_c$  ( $\alpha_c \approx 0.14^{\circ}$  is the critical angle for total reflection). A linear position-sensitive detector (PSD) (OED-100-M, Braun Garching, Germany) was used to monitor the diffracted intensity as a function of the vertical scattering angle  $\alpha_f$ . A Soller collimator in front of the PSD provides a resolution of  $0.09^{\circ}$  for the in-plane scattering angle  $2\theta$ . According to the geometry of diffraction,<sup>10</sup> the scattering vector  $\mathbf{Q}$  can be written in terms of an in-plane component  $Q_{xy}$  and an out-of plane component  $Q_z$ , where

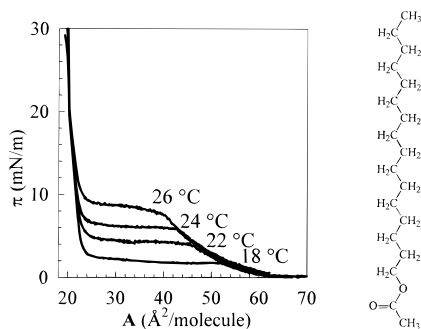
$$Q_{xy} = \frac{2\pi}{\lambda} \sqrt{\cos^2 \alpha_i + \cos^2 \alpha_f - 2 \cos \alpha_i \cos \alpha_f \cos 2\theta} \quad (1)$$

and

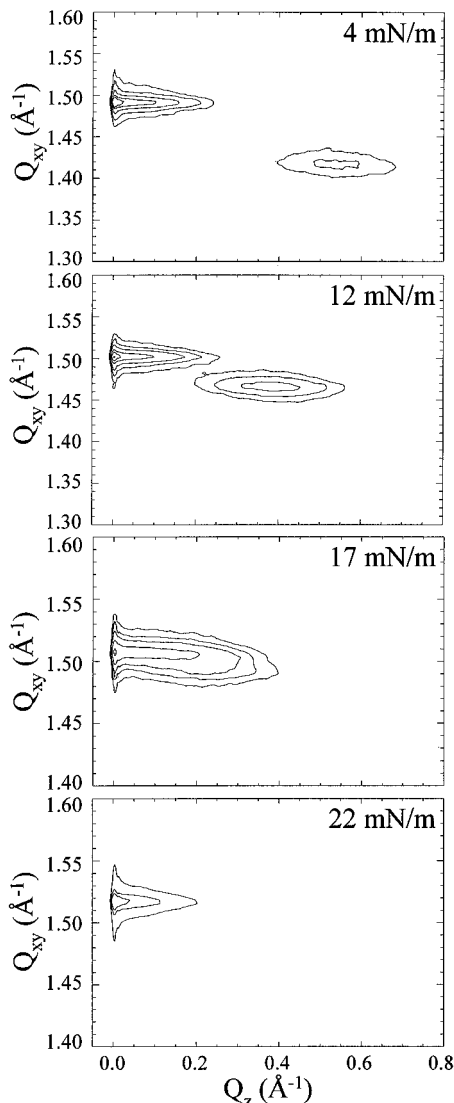
$$Q_z = \frac{2\pi}{\lambda} (\sin \alpha_i + \sin \alpha_f) \quad (2)$$

From the in-plane reflex positions the lattice spacings can be

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**Figure 1.**  $\pi$ - $A$  isotherms at different temperatures and chemical formula of palmityl acetate.



**Figure 2.** Contour plots of the diffracted intensity versus in-plane ( $Q_{xy}$ ) and out-of-plane component ( $Q_z$ ) of the scattering vector at 18 °C and different surface pressures indicated.

obtained:

$$Q_{xy} = \frac{2\pi}{d_{hk}} \quad (3)$$

The out-of-plane scattering component can provide information about the polar tilt angle  $t$  and the tilt azimuth  $\Psi$  of the alkyl chains. These two parameters can be obtained from the scattering-vector components according to the cylinder model.<sup>10</sup>

$$Q_z^{hk} = Q_{xy}^{hk} \cos \Psi \tan t \quad (4)$$

The positional correlation length  $\xi$  can be estimated from the full width at half-maximum (fwhm). For an exponential decay of positional correlation as observed in liquid crystals (corresponding to a Lorentzian as a reflex profile), it is

$$\xi = \frac{2}{\text{fwhm}(Q_{xy})} \quad (5)$$

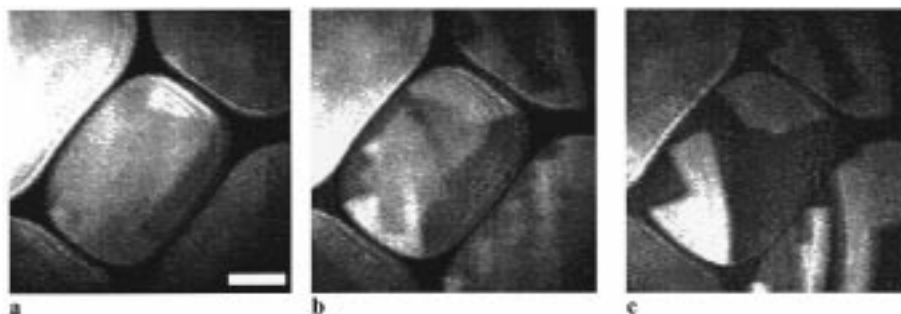
**Brewster Angle Microscopy.** For the observation of the monolayers a Brewster angle microscope (BAM1 from NFT, Göttingen) was mounted on a Langmuir film balance (FW2 from Lauda) with a Teflon trough and an area of 1000 cm<sup>2</sup>. The BAM images presented here are mirror images of the monolayer, since in the BAM1 the reflected beam is directed into the CCD camera by a mirror. The lateral resolution of the BAM1 is about 4  $\mu$ m. An image-processing software was used to correct the BAM images for the distortion due to the observation at the Brewster angle. In the present work only the well-illuminated part (500  $\mu$ m  $\times$  500  $\mu$ m) of the original images was used.

**Materials.** Palmityl acetate from Sigma, Deisenhofen (approximately 99%) was used without further purification. The spreading solvent was heptane from Merck, Darmstadt (UVA-SOL). The subphase water was purified by a Millipore desktop (Millipore, Eschborn). The substances were spread from a 10<sup>-3</sup> M heptane solution and compressed at a rate of 3 Å<sup>2</sup> molecule<sup>-1</sup> min<sup>-1</sup>.

## Results and Discussion

Palmityl acetate monolayers undergo a first-order phase transition from a fluid phase to a condensed phase corresponding to a plateau region in the  $\pi$ - $A$  isotherms at temperatures  $T > 15$  °C (Figure 1). The condensed phases of palmityl acetate monolayers have been studied by GID at 18 °C. At 4 mN/m two reflexes of a rectangular lattice with chains tilted toward nearest neighbors (NN) are observed (Figure 2 and Table 1). Consequently, a condensed phase with NN-tilted chains is formed in the phase coexistence region from the fluid phase at 18 °C. Upon further compression the reflexes shift to lower  $Q_z$  values, indicating a decrease of the polar tilt angle from  $t = 25^\circ$  at 4 mN/m to  $t = 18^\circ$  at 12 mN/m (Table 2). At 17 mN/m both reflexes are found to be at  $Q_z > 0$  Å<sup>-1</sup> (Figure 2 and Table 1), indicating a rectangular lattice of alkyl chains tilted toward next-nearest neighbors (NNN).

The transition from the NN-tilted to the NNN-tilted phase gives rise to a sudden reorientation of molecules, resulting in local reflectivity changes that can be detected by BAM<sup>8,9</sup> (Figure 3). This allows a precise determination of the transition pressure. It is about 14.5 mN/m at 18 °C. The temperature dependence of this phase transition studied by BAM is displayed in Figure 4. The transition to the phase with upright oriented chains, which was found at 22 mN/m using GID (Figure 2), was determined precisely by the vanishing of the anisotropy contrast in the BAM images. Similar to the behavior of fatty acids,<sup>11</sup> this transition pressure was found to be almost independent of temperature and shifts only from about 20 mN/m at 18 °C to 19 mN/m at 28 °C. For fatty acids and other simple amphiphiles the idea of a generic phase diagram is discussed.<sup>11</sup> Following this idea, homologues with long alkyl chains behave at a higher temperature like homologues with a shorter alkyl chain. In the present study the high-temperature/short alkyl chain range of the phase diagram of alkyl acetates is studied. The cross-sectional area of the alkyl chains varies from 19.8 to



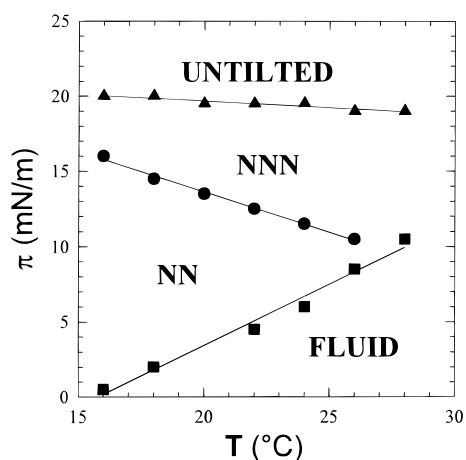
**Figure 3.** Reorientations induced by the transition from the NN-tilted to the NNN-tilted phase at 24 °C. The monolayer is shown before (a) and immediately after the transition (b). Within less than 1 s the pattern induced by the transition anneals to large patches of homogeneous orientation (c). The bar represents 100  $\mu\text{m}$ .

**TABLE 1: Reflex Positions (Bold) and fwhm (below the Reflex Positions) of a Palmityl Acetate Monolayer at 18 °C**

palmityl acetate, 18 °C [mN/m]	$Q_{xy}$ [ $\text{\AA}^{-1}$ ] $Q_z$ [ $\text{\AA}^{-1}$ ]		$Q_{xy}$ [ $\text{\AA}^{-1}$ ] $Q_z$ [ $\text{\AA}^{-1}$ ]	
	02		11, $1\bar{1}$	
4	<b>1.491</b>	<b>0</b>	<b>1.417</b>	<b>0.57</b>
	0.016		0.039	0.23
12	<b>1.501</b>	<b>0</b>	<b>1.466</b>	<b>0.41</b>
	0.017		0.030	0.25
17	<b>1.493</b>	<b>0.26</b>	<b>1.507</b>	<b>0.13</b>
	0.020	0.27	0.016	0.30
22	<b>1.517</b>	<b>0</b>		
	0.014			

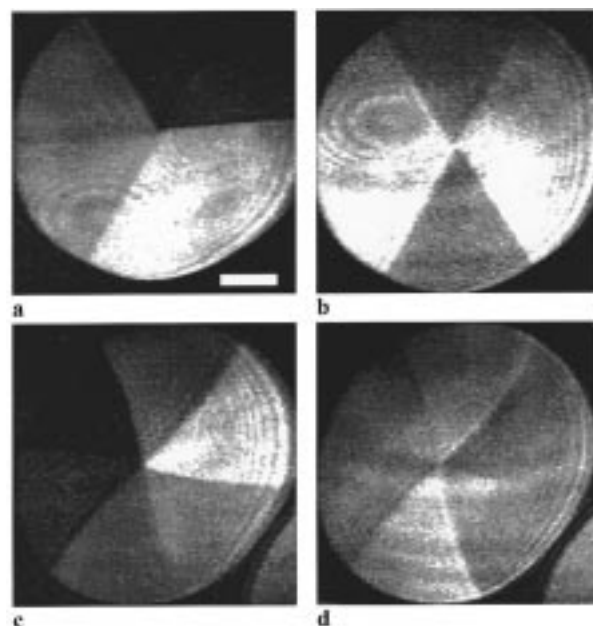
**TABLE 2: Lattice Parameters of a Palmityl Acetate Monolayer at 18 °C**

palmityl acetate, 18 °C [mN/m]	$a$ [ $\text{\AA}$ ]	$b$ [ $\text{\AA}$ ]	$A_{xy}$ [ $\text{\AA}^2$ ]	$t$ [deg]	TA	$A_0$ [ $\text{\AA}^2$ ]
4	5.214	8.428	22.0	25	NN	19.8
12	4.986	8.366	20.9	18	NN	19.8
17	4.825	8.417	20.3	10	NNN	20.0
22	4.782	8.284	19.8	0		19.8

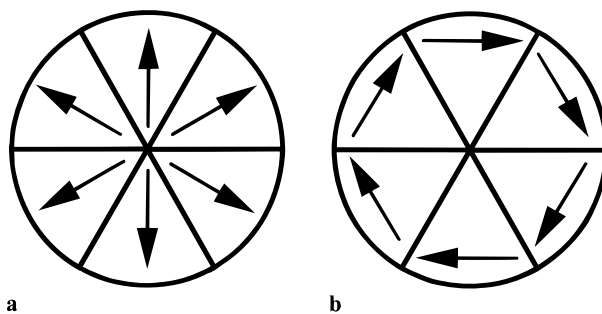


**Figure 4.** Phase diagram of palmityl acetate in the temperature region studied.

20.0  $\text{\AA}^2$  in the condensed phases of palmityl acetate monolayers, which is typical for the free-rotator phase of *n*-alkanes.<sup>11</sup> The positional correlation length calculated from the reflex at low  $Q_z$  varies from 140 to 120  $\text{\AA}$ , corresponding to that found for palmitic acid and their methyl and ethyl esters.<sup>12</sup> Only a minor deviation from the phase diagram of fatty acids is observed. At high temperatures a condensed phase with NNN-tilted alkyl chains is formed directly from the fluid phase. However, palmityl acetate monolayers behave quite similarly to those of palmitic acid with respect to the cross-sectional area of alkyl chains, the positional correlation length, the extent of the tilt of the alkyl chains, and its variation with surface pressure.<sup>12</sup>

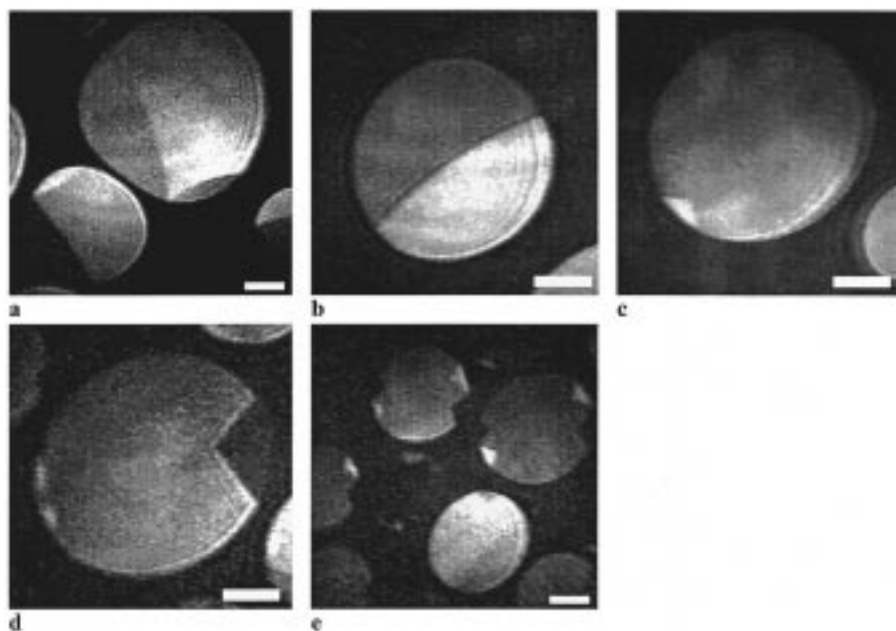


**Figure 5.** Six-fold-subdivided condensed-phase domains at 22 °C (a, b) and 24 °C (c, d). The left images (a, c) are taken at an analyzer angle of about 55°. The right images (b, d) show the same domains at parallel polarizers. The bar represents 100  $\mu\text{m}$ .



**Figure 6.** Sketch of the tilt orientation in the two types of 6-fold-subdivided domains: (a) low-temperature type; (b) high-temperature type.

Focusing attention on the domain textures, one finds that some of the domains formed in the phase coexistence region are subdivided into six segments of different reflectivity (Figure 5). Depending on the temperature two different types of domains are observed. The texture in parts a and b of Figure 5 occurs at  $T \leq 22$  °C, whereas the texture in parts c and d of Figure 5 forms at  $T \geq 24$  °C. Studying the low-temperature texture with parallel polarizers, one finds the lowest reflectivity in the segments at the top and at the bottom. In these segments the chains are tilted perpendicular to the plane of incidence



**Figure 7.** Characteristic domains that show no subdivision into six parts at 22 °C (a), 24 °C (b, c), 26 °C (d), and 28 °C (e). The bars represent 100  $\mu\text{m}$ .

(which is horizontal in the images). Thus, the chains are tilted along the bisector of the segments (Figure 6a). In the high-temperature texture these segments are the brightest for parallel polarizers. Consequently, the chains are tilted perpendicular to the bisector of the segments (Figure 6b). The latter is also confirmed by the observation of left- and right-handed domains by BAM as discussed in a recent paper.<sup>6</sup>

From the phase diagram (Figure 4) it becomes evident that the transition from one texture to another between 22 and 24 °C is not related to the phase transition from the NN-tilted to the NNN-tilted phase. The condensed phase formed from the fluid phase is NN-tilted over this temperature range. At 24 °C the high-temperature texture already appears. However, upon further compression the sudden reorientation (Figure 3) corresponding to the phase transition is still observed. The domains are formed at a surface pressure between 6 and 8 mN/m, whereas the NN–NNN phase transition occurs at about 11.5 mN/m.

The reason for the transition from one texture to the other can be deduced from the temperature-dependent behavior of the domains, which are not subdivided into six segments (Figure 7). These domains undergo a continuous transition from one texture to the other. The domains are separated into three parts of different orientation at 22 °C. Besides the defect lines at which the orientation jumps, slight continuous changes of orientation are also observed. The tilt azimuth is preferentially oriented perpendicular to the boundary as in the 6-fold-subdivided domains. At 24 °C some domains are separated into two parts of different orientation; other domains show some inclusions of different orientation. At 26 °C all domains show such inclusions. At 28 °C almost all domains show a regular arrangement of inclusions at two opposite sides of the domain. Such a texture was found first in ethylpalmitate monolayers.<sup>6</sup> It indicates a preferred orientation of the molecules parallel to the domain boundary. The latter is in agreement with the molecular orientation of the high-temperature texture of the 6-fold-subdivided domains.

A preferred orientation of the molecules with respect to the domain boundary can be described by an anisotropic line tension (i.e., the energy of the domain boundary per boundary length). The anisotropic line tension  $\Lambda$  is a periodic function and can

be expanded into a Fourier series:

$$\Lambda = a_0 + \sum a_k \cos(k\varphi) + \sum b_k \sin(k\varphi)$$

where  $\varphi$  is the angle included by the tilt azimuth and the normal to the domain boundary. A rectangular lattice requires a mirror symmetry in two dimensions. Since only the cosine function has this symmetry and not the sine function, all  $b_k$  are zero. At low temperatures one minimum of the line tension at  $\varphi = 0^\circ$  is observed according to  $\Lambda = a_0 + a_1 \cos(\varphi)$  with a negative  $a_1$ . A similar behavior was found for fatty acids, fatty acid methyl esters, and 1-monoglycerides. At high temperatures two minima at  $\varphi = 90^\circ$  and  $\varphi = 270^\circ$  and two maxima at  $\varphi = 0^\circ$  and  $\varphi = 180^\circ$  appear according to  $\Lambda = a_0 + a_2 \cos(2\varphi)$  with a positive  $a_2$  (for a detailed discussion see ref 6). The evolution of the domains that are not separated into six parts suggests a continuous change of the coefficients of the Fourier series with increasing surface pressure or with decreasing polar tilt angle. The continuous change of the Fourier coefficients gives rise to a crossover in the preferred molecular orientation with respect to the domain boundary and causes an abrupt transition from one 6-fold texture to the other. Such behavior indicates two opposing contributions to the anisotropy of line tension, both being influenced by the magnitude of the polar tilt angle. Such contributions could arise for instance from interactions of molecular dipoles whose alignment depends on the polar tilt angle or from an anisotropic roughness of the boundary, which is affected by the tilt of the molecules.

The question arises of whether the texture transition is a unique feature of palmityl acetate monolayers or a common feature in monolayers of simple amphiphiles. In ethyl palmitate monolayers no such texture transition is observed.<sup>6</sup> This is, however, not unexpected, since the polar tilt angle is always below  $16^\circ$  in ethyl palmitate monolayers and the texture transition in palmityl acetate monolayers occurs at a tilt angle of about  $23^\circ$ . Consequently, only the domain type occurring in palmityl acetate monolayers at low polar tilt angles (Figure 6b) is present in ethyl palmitate monolayers. In methyl palmitate monolayers a transition from one texture to the other is observed;<sup>7</sup> however, its origin is not yet clear, since existing

domains were studied while the temperature was varied. Domains formed at different temperatures as in the present work are expected to have the equilibrium shape, but existing domains do not necessarily transform immediately into their equilibrium shape. Thus, the conclusion may be right that in this case the texture transition in methyl palmitate monolayers is accompanied by a phase transition.<sup>7</sup> Recently, also in fatty acid monolayers a transition in the preferred molecular orientation was reported.<sup>13</sup> Until now in fatty acid monolayers the molecules were known to be tilted preferentially perpendicular to the domain boundary.<sup>3</sup> However, the domain type in Figure 6b was observed in myristic acid monolayers at temperatures exceeding 23 °C and in palmitic acid monolayers at temperatures exceeding 43 °C.<sup>13</sup> Unfortunately, there is no sharp transition between the two textures in Figure 6, since the domain type in Figure 6a does not occur at lower temperatures.<sup>3</sup> For 1-monopalmitin monolayers it is again not surprising that no texture transition was detected.<sup>4</sup> In these monolayers the polar tilt angle does not fall below 26° at  $\pi < 30$  mN/m. On the whole, the texture transition does not seem to be a unique feature of palmityl acetate monolayers. The molecules are preferentially tilted perpendicular to the domain boundary for high polar tilt angles and parallel for low polar tilt angles.

## Conclusions

In palmityl acetate monolayers, domains subdivided into six equal segments are formed. With an increase of temperature (corresponding to an increase of surface pressure) a transition from a texture with chains tilted along the bisector of the segments to another texture with chains tilted perpendicular to the bisector of the segments occurs. A transition between phases with tilted alkyl chains can be ruled out as the reason for the texture transition. A continuous change of the anisotropy of the line tension with surface pressure, as concluded from the continuous change of the textures in domains without the 6-fold subdivision, can explain this texture transition. The results on monolayers of other simple amphiphiles suggest that the anisotropy of the line tension is determined by the polar tilt angle. A preferred molecular tilt perpendicular to the boundary is observed in monolayers of substances with high polar tilt angle, and for substances with weakly tilted alkyl chains the molecules are preferentially tilted parallel to the boundary.

Although this texture transition is not correlated to the phase transition, sudden reorientations and the vanishing of the anisotropy contrast allow the detection of phase transitions by BAM. A phase diagram was drawn for palmityl acetate combining BAM with GID measurements that provides information on the nature of the phases. At low surface pressures a phase with NN-tilted chains is observed. Over the temperature

range studied a phase with NNN-tilted chains is present at higher pressures. At high temperatures this phase is formed directly from the fluid phase. With respect to this detail, the behavior of palmityl acetate clearly differs from that of fatty acids.<sup>2</sup> However, palmityl acetate monolayers are quite similar to those of palmitic acid with respect to the extent of the tilt of the alkyl chains and its variation with surface pressure.<sup>12</sup> At about 20 mN/m the alkyl chains become upright in palmityl acetate layers.

Altogether we have shown that texture changes may not only occur as a consequence of a structure change but also as an accidental degeneracy of line-tension anisotropy.

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