# Long-Range Tilt Orientational Order in Phospholipid Monolayers: A Comparative Study

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ABSTRACT  Monolayers of dipalmitoyl-phosphatidyl-$N$-monomethylethanolamine (DPP(Me)E) and dipalmitoyl-phosphatidyl-$N,N$-dimethylethanolamine (DPP(Me$_2$)E) are studied and compared with dipalmitoyl-phosphatidylethanolamine (DPPE), dimyristoyl-phosphatidylethanolamine (DMPE), and dipalmitoyl-phosphatidylcholine (DPPC) to characterize the influence of the headgroup size. The properties of the condensed phases of DPP(Me$_2$)E and DPP(Me)E are between those of DPPC and DMPE or DPPE. DPPC domains are elongated and the orientation changes continuously, whereas DMPE domains are compact and the orientation jumps at curved lines. The domains of DPP(Me$_2$)E and DPP(Me)E are compact, and not elongated. The orientation changes continuously by 360° around a point in the centered domains, and jumps of the orientation occur only in the case of twinning. Furthermore, the size of the headgroup influences the erection of the aliphatic chains. For DPPC and (DPP(Me$_2$)E), no complete erection of chains occurs, whereas for DPP(Me)E the surface pressure required for the complete erection of chains is much higher than for DPPE. The same tendency is found for the collapse. DPPC monolayers do not collapse. DPP(Me$_2$)E monolayers collapse at a much higher surface pressure than those of DPP(Me)E and DPPE.

## INTRODUCTION

Long-range orientational order in condensed phases of Langmuir monolayers was first observed for dipalmitoyl-phosphatidylcholine (DPPC) by fluorescence microscopy, using head-labeled dyes and illuminating the probe from the side with polarized laser light (Moy et al., 1986, 1988). For many years, however, no further studies in this field appeared in the literature. The recently developed Brewster angle microscope (BAM) (Hönig and Möbius, 1991; Henon and Meunier, 1991) now allows direct characterization of the long-range orientational order, owing to the optical anisotropy induced by the tilted aliphatic chains (Hönig et al., 1992). A study of dimyristoyl-phosphatidylethanolamine (DMPE) monolayers (Weidemann and Vollhardt, 1995a) revealed a structure deviating from that in DPPC monolayers, which encouraged a detailed comparison of the order for the two lipids (Weidemann and Vollhardt, 1995b).

Shape and texture of the domains are very different for phosphatidylethanolamines and phosphatidylcholines. The molecular structures of the two lipids are different with respect to headgroup size. A phosphatidylcholine deviates from a phosphatidylethanolamine by having the three methyl groups at the nitrogen atom instead of the hydrogen (Fig. 1). Two phospholipids with one and two methyl groups at the nitrogen are available, dipalmitoyl-phosphatidyl-$N$-monomethylethanolamine (DPP(Me)E) and dipalmitoyl-phosphatidyl-$N,N$-dimethylethanolamine (DPP(Me$_2$)E). The properties of the con-

densed phases of these lipids are expected to be shifted from those of DMPE or dipalmitoyl-phosphatidylethanolamine (DPPE) toward those of DPPC.

The orientational order in monolayers of these substances has been studied by electron microscopy of transferred layers and fluorescence microscopy (Hui and Yu, 1993). However, these techniques are not very suitable for such a study, because the orientation can be determined for only a few points in the domain. Thus, it was not possible to distinguish between continuous change of orientation, as in DPPC domains, and jumps, as in DMPE domains. In this study, furthermore, the domains were very irregularly shaped, indicating a state far from equilibrium. Therefore, one cannot discount the possibility that these domains were deformed during the transfer process.

## EXPERIMENTAL

The monolayers were visualized with a Brewster angle microscope (BAM1) from NFT (Göttingen, Germany) mounted on a Langmuir film balance from Lauda (Lauda-Königshofen, Germany) (FW2). The images obtained with the BAM1 are mirror images of the water surface due to a mirror in the reflected beam path. The observation at the Brewster angle results in a distortion of the BAM images. To correct for this, the video images of the charge-coupled device camera were digitized and treated with an image-processing software. The low anisotropy contrast of the phospholipid monolayers has been increased with the software. The lateral resolution of the Brewster angle microscope is about 4 $\mu$m. Only a small part of the image is sufficiently sharp and well illuminated. Thus a section of 500 $\mu$m × 500 $\mu$m is used in the present work.

All phospholipids were obtained from Sigma (approximately 99%; Deisenhofen, Germany) and spread from a chloroform solution, or from a chloroform/methanol 3:1 solution in the case of DMPE and DPPE. The chloroform was received from J. T. Baker (p.a. grade; Deventer, Holland), and the methanol was from Merck (p.a. grade; Darmstadt, Germany). The subphase water was purified by reverse osmosis, using a MilliQ unit (pH = 5.5).
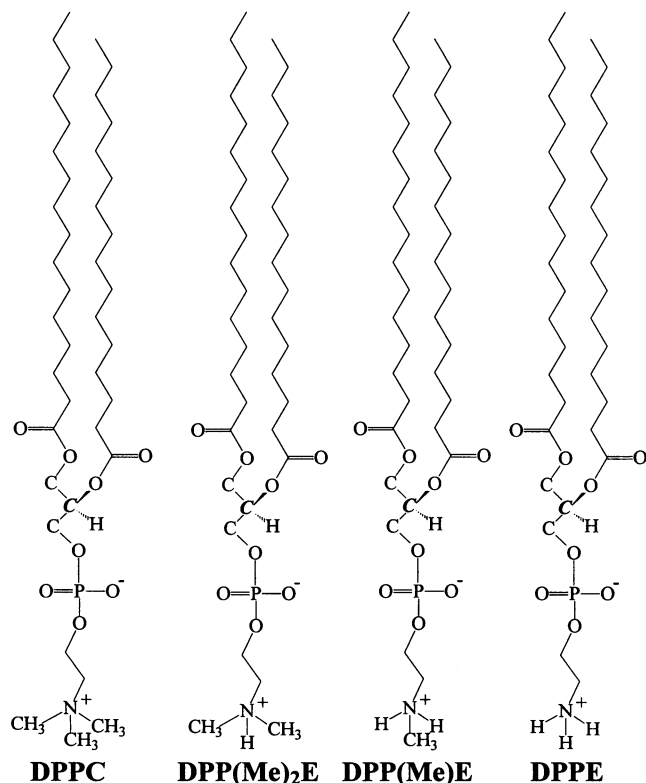
FIGURE 1   The molecules studied are different with respect to the numbers of methyl groups at the nitrogen. DPPC has three methyl groups, DPP(Me₂)E two, DPP(Me)E one, and DPPE (as well as DMPE) has no methyl group.
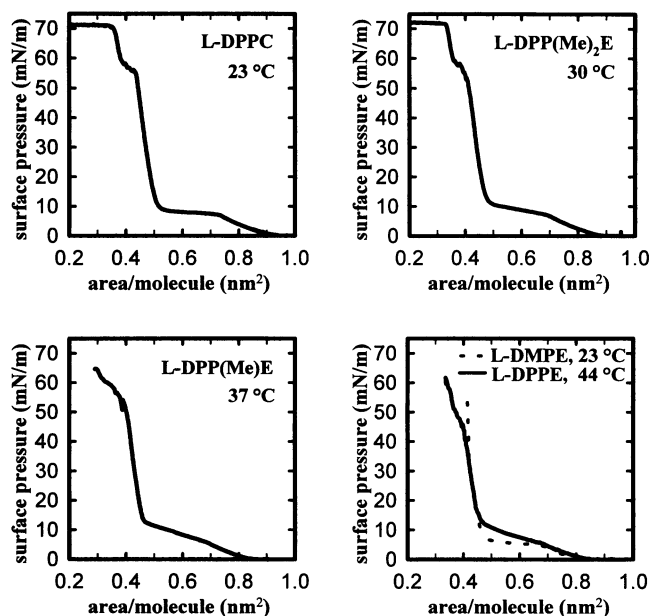


FIGURE 2   The isotherms of the substances investigated show a comparable plateau at different temperatures. For DMPE and DPPC the monolayers were studied at 23°C, DPP(Me₂)E was studied at 30°C, DPP(Me)E at 37°C, and DPPE at 44°C. The decrease of area below 0.4 nm² molecule$^{-1}$ at high pressures corresponds to a leakage. This part of the isotherm is only intended to illustrate that it is possible to achieve sufficiently high pressures for the BAM to be used to investigate whether the monolayer collapses or the anisotropy contrast vanishes.

## RESULTS AND DISCUSSION

A characterization of the orientational order in a condensed phase of a Langmuir monolayer requires that the observed textures occur under well-defined conditions. Domains formed during a first-order phase transition from a fluid phase to a condensed phase are most suitable. Domains appearing during such a phase transition exhibit characteristic textures. A first-order phase transition is characterized by a coexistence region, resulting in a plateau in the π-A isotherm. Such a plateau is not present in the π-A isotherm of DPP(Me₂)E at room temperature. The isotherm does, however, show a pronounced plateau at 30°C (Fig. 2 *b*). For DPP(Me)E and DPPE, a plateau becomes apparent at higher temperatures (Fig. 2, *c* and *d*). In the case of DPP(Me)E the studies were carried out at 37°C and the DPPE monolayers were studied at 44°C.

As observed previously for DMPE and DPPC (Weidemann and Vollhardt, 1995a,b) the domains of all observed phospholipids grow with an unstable domain wall, not only at high compression rates, but also at intermediate compression rates of less than $1 \times 10^{-2}$ nm² molecule$^{-1}$ min$^{-1}$. However, the shapes of these branched domains can be quite different (Fig. 3). The shape is fractal-like for DPPC, DPP(Me₂)E, and DMPE. In this growth regime the growing tips are not correlated to crystallographic directions of the

two-dimensional lattice. Thus, the domain shape does not reflect the chirality. Domains of DPP(Me)E and DPPE grow dendritically. For these the growth directions follow dense rows of the two-dimensional crystal lattice. The dendrites of these substances are curved for the pure enantiomers. A large number of domains have been observed, all with the same sense of curvature. However, in DL-DPPE monolayers straight dendrite arms are observed. The absence of a curvature in the dendrite arms of racemate suggests that the curvature is an effect of the chirality and not a characteristic of the observed texture. The curved dendrite arms correspond to the curvature of the defect lines in the L-DMPE domains (Fig. 4) (Weidemann and Vollhardt, 1995a,b). Both dendrite arms and defect lines run along lattice directions, and thus their curvature reflects that of the crystal lattice. Consequently, the curvature of the dendrite arms of L-DPPE has the same sense as the curvature of the segment boundaries in L-DMPE. The dendrites of L-DPP(Me)E and L-DPPE are curved in the same sense, indicating a similar influence of the chirality on the crystal structure for the nonmethylated and methylated ethanolamines.

Dendritic growth indicates an anisotropic line tension. An anisotropic line tension is characteristic for the crystalline state, whereas absence of an anisotropic line tension is typical for disordered systems. Dendritic growth is observed for DPPE and DPP(Me)E, but does not occur in DPP(Me₂)E and DPPC monolayers. As a result, it can be concluded that the crystallinity of the condensed phase decreases from
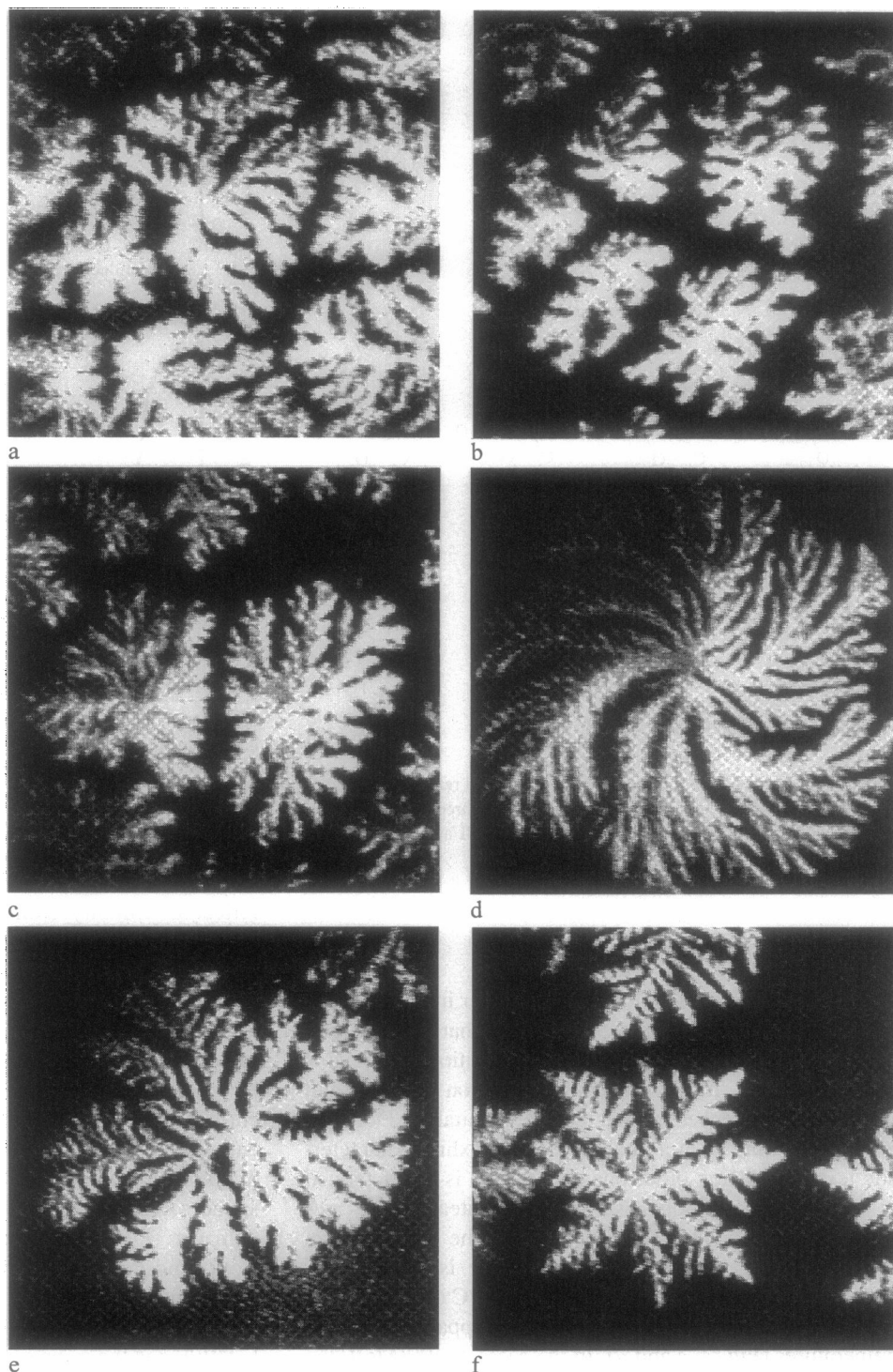
FIGURE 3 The branched domains of the phospholipids studied have different morphologies. For DMPE (a), DPPC (b), and DPP(Me$_2$)E (c), the domains are fractal-like. Domains of DPP(Me)E (d) and DPPE (e and f) are more dendritic and reflect the chirality of the molecules in the case of L-DPP(Me)E (d) and L-DPPE (e). For DL-DPPE (f) the arms of the dendrites are straight. The compression rate was about $1 \times 10^{-1}$ nm$^2$ molecule$^{-1}$ min$^{-1}$.

DPPE to DPPC. Because dendritic growth is also not observed in DMPE monolayers, the crystallinity of a monolayer is also affected by the chain length. The condensed phase is less crystalline for shorter chains, even at the lower temperature of an equivalent plateau pressure.

Compact phospholipid domains can be obtained at very low compression rates or as a result of a shape relaxation (about 2 h after the compression stopped for DMPE or DPP(Me$_2$)E, and more than 5 h for DPP(Me)E) of a branched domain grown at intermediate rates of compression (approximately $2 \times 10^{-2}$ nm$^2$ molecule$^{-1}$ min$^{-1}$). Influence of the compression rate on the structure was found only for DPPC (Weidemann and Vollhardt, 1995b). Because the effect of temperature fluctuations can exceed the effect of a very slow compression at the high temperatures used for the studies of DPP(Me$_2$)E, DPP(Me)E, and DPPE,

FIGURE 4 Under conditions close to equilibrium DMPE domains are compact (*a*). The domains are subdivided into segments by curved lines at which the orientation jumps. Furthermore, a continuous change of orientation between these lines can be observed. DPPC domains are elongated at very low compression rates ($2 \times 10^{-3}$ nm$^2$ molecule$^{-1}$ min$^{-1}$) (*b*). The orientation changes continuously within the domain arms. The lines running through the arms mark no jump of orientation, as they are shifted if the analyzer is rotated.
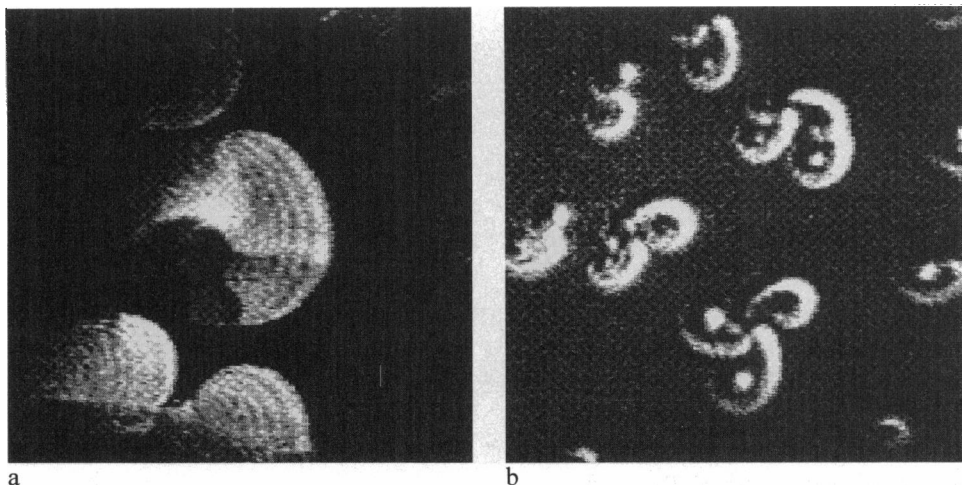
the condensed phase domains presented here were generated by a shape relaxation.

A comparison of L-DMPE and L-DPPC monolayers reveals very different domain textures. L-DMPE domains are characterized by sharp lines at which the orientation jumps (Fig. 4 *a*). These lines are joined together at a point inside the domain or at the edge of the domain. In the former case the domains are circular and bean-shaped for the latter case (Weidemann and Vollhardt, 1995a). All lines at which the orientation jumps are curved. Furthermore, the orientation changes continuously in the regions between the lines. L-DPPC domains consist of elongated arms (Moy et al., 1986, 1988; Weidemann and Vollhardt, 1995b). The lines running through the arms mark a strong continuous change of orientation (Fig. 4 *b*). In DPPC domains jumps of orientation occur only at the twin boundaries between the arms of the domain (Weidemann and Vollhardt, 1995b). Therefore the question arises whether jumps of the orientation occur in domains of DPP(Me$_2$)E and DPP(Me)E. To be able to distinguish between jumps of orientation and a continuous change of orientation, careful observation must be made whether the lines that separate dark and bright areas remain at a fixed position or are shifted, respectively, when the analyzer is rotated. Although this is not easy to visualize in single images, it is easy to observe from a video sequence.

In DPP(Me$_2$)E monolayers centered domains (Fig. 5 *a*) and noncentered domains (Fig. 5 *c*) occur, as in the DMPE monolayers. In the centered domains the orientation changes continuously by 360° around a point inside the domain (Fig. 5 *a*) and by less than 360° around a point at the edge of the domain in the noncentered domains (Fig. 5 *c*). From this point lines of equal brightness run radially to the domain boundary. However, lines that separate dark and bright areas are not sharp but diffuse. By a rotation of the analyzer the lines are continuously shifted (Fig. 5, *a* and *b*). Thus, no defect lines are present at which the orientation jumps. The domains reveal a certain similarity to the shell defect observed in liquid crystal films (Langer and Sethna, 1986) and in monolayers of pentadecanoic acid at the air-

water interface (Hönig et al., 1992). Under equilibrium conditions, the centered DPP(Me$_2$)E domains have a circular shape and the noncentered domains are bean shaped, like DMPE domains (Weidemann and Vollhardt, 1995a). In contrast to DMPE, the centered domains do not occur frequently.

The absence of the jumps of orientation impedes an evaluation of the effect of the chirality on the lattice at the air-water interface. Nevertheless, the course of the lines of equal brightness reflects changes in the orientation. The same sense of curvature of these lines in all centered domains of the pure L-enantiomer clearly reflects the chirality. The same curvature is found in the noncentered domains apart from the distortions at the edges of the domains. The curvature of the lines of equal brightness is affected by the course of the domain wall at the edges of the noncentered domains. The absence of the curvature of the lines in the domains of the racemate (Fig. 5 *d*) confirms that the curvature results from chirality. All lines separating dark and bright areas are straight. Unfortunately, the domains of the racemate are always much smaller than that of the pure enantiomer, thus complicating a more detailed study of the reflectivity in the domains.

In DPP(Me$_2$)E monolayers, the orientation jumps in a way similar to that of DPPC at the boundaries between the individuals of twinned domains (Fig. 6). The contact lines of the twinned individuals are straight and remain at a fixed position if the analyzer is rotated. In addition to the curvature of the lines of equal brightness, the outer shape of the twinned domains is affected by the chirality for the pure L-enantiomer. Twins consisting of two individuals are always S-shaped, threefold domains show a slight similarity to the DPPC-triskelions, and the curvature of the domain parts has the same sense as for DPPC.

Domains with a more compact shape do not occur in DPP(Me)E monolayers in less than 2 h, and even after 5 h the domains have an uneven boundary and are not circular. The domains are, however, compact enough to allow the inner structure to be studied. The orientation again changes

FIGURE 5   In compact L-DPP(Me₂)E domains, the orientation changes by 360° around a point inside the domain (*a* and *b*) or at the edge of the domain (*c*). The orientation changes continuously and no jumps of orientation are observed. The lines of equal brightness are shifted from *a* to *b*, which are taken at different positions of the analyzer. These lines are curved for the pure enantiomer. For DL-DPP(Me₂)E no curvature of these lines is observed (*d*).
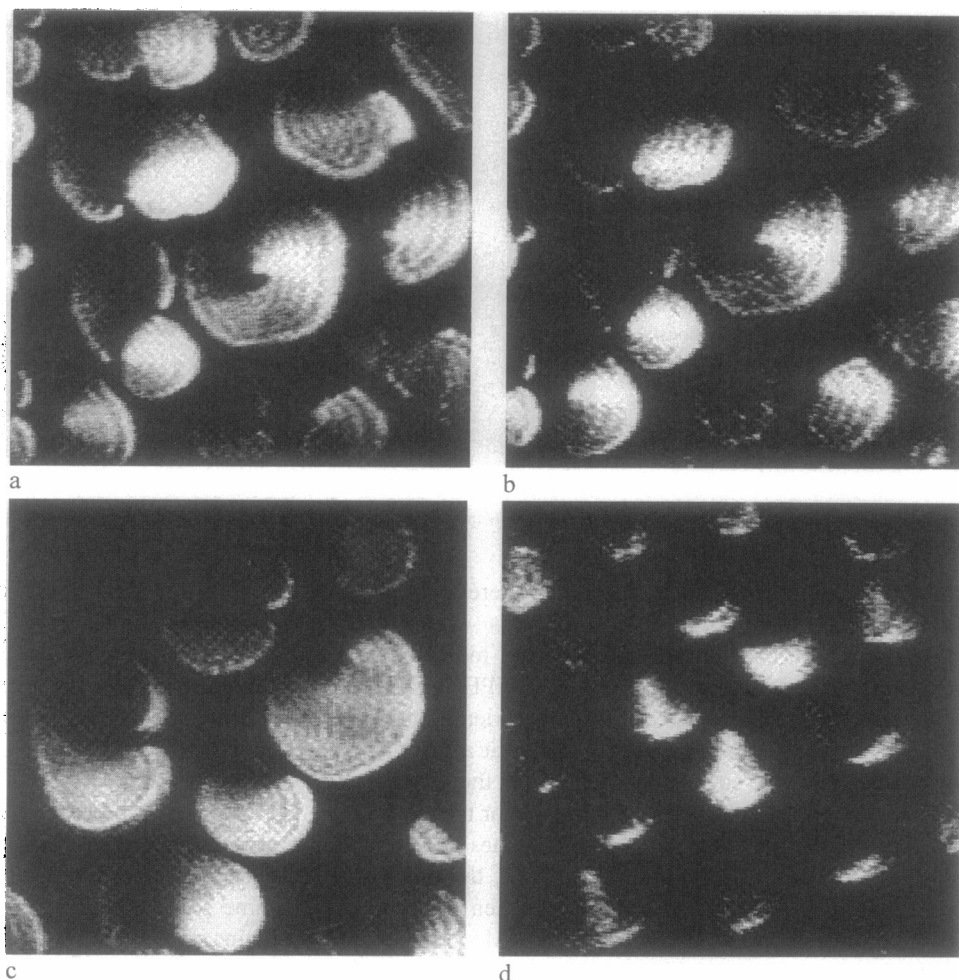
continuously by 360° around a point inside the centered domains (Fig. 7 *a*) and by less than 360° around a point at the edge of the noncentered domains (Fig. 7 *b*). Again the lines separating dark and bright areas are continuously shifted by rotating the analyzer, although this shift is not so clear because of the branching of the domains. Lines remaining at a fixed position typical for jumps of the orientation are not observed. The textures of DPP(Me)E domains are, therefore, quite similar to that of DPP(Me₂)E.

An alternative way to evaluate the textures of the condensed phase is a very rapid compression ($2.5 \times 10^{-1}$ nm² molecule$^{-1}$ min$^{-1}$) of the monolayer to a pressure at which the whole monolayer is in the condensed state (about 15 mN/m). The domains then become highly branched. The branches of the domain are thinner than 5 $\mu$m. When the domains come into contact at the end of the plateau, the branches can easily be deformed, leading to a condensation of the material between the arms. A condensed monolayer with many points at which the orientation changes by 360° results from the compression of the highly branched domains (Fig. 8, *a* and *b*). These changes of orientation are irregular but can anneal to a more ordered state. For DPP-(Me)E, the result is a mainly continuous change of orientation. Apart from the lines that separate the former branched

domains, only some irregular discontinuity lines remain (Fig. 8 *c*). The latter are already present immediately after the compression stop (Fig. 8 *a*) and result from the deformation of the branched domains. The monolayer was observed for more than 1 h, and no significant changes of the texture occurred.

For L-DPPE such a continuous change of orientation breaks down to lines at which the orientation jumps (Fig. 8 *d*), similar to the curved defect lines in the compact L-DMPE domains (Weidemann and Vollhardt, 1995a). The curvature of the lines is now much higher, resulting in spiral-shaped textures (Fig. 8 *d*). There are several kinks in the spiral arms. The origin of these kinks is not quite clear, but might result from defects. A spiral arm could be free to move, but a defect could stop the propagation of a spiral arm, resulting in a kink at the defect at which the spiral arm is fixed. Lines at which the orientation jumps appear after approximately 5 min. They are, however, very irregular and need about 30 min to form the regular spirals in Fig. 8 *d*. The structures observed after 30 min are stable and show no further tendency to change with time.

Similar spiral structures are observed in monolayers of pentadecanoic acid (Qiu et al., 1992b) and myristic acid (Ruiz-Garcia et al., 1993), and have been correlated to a
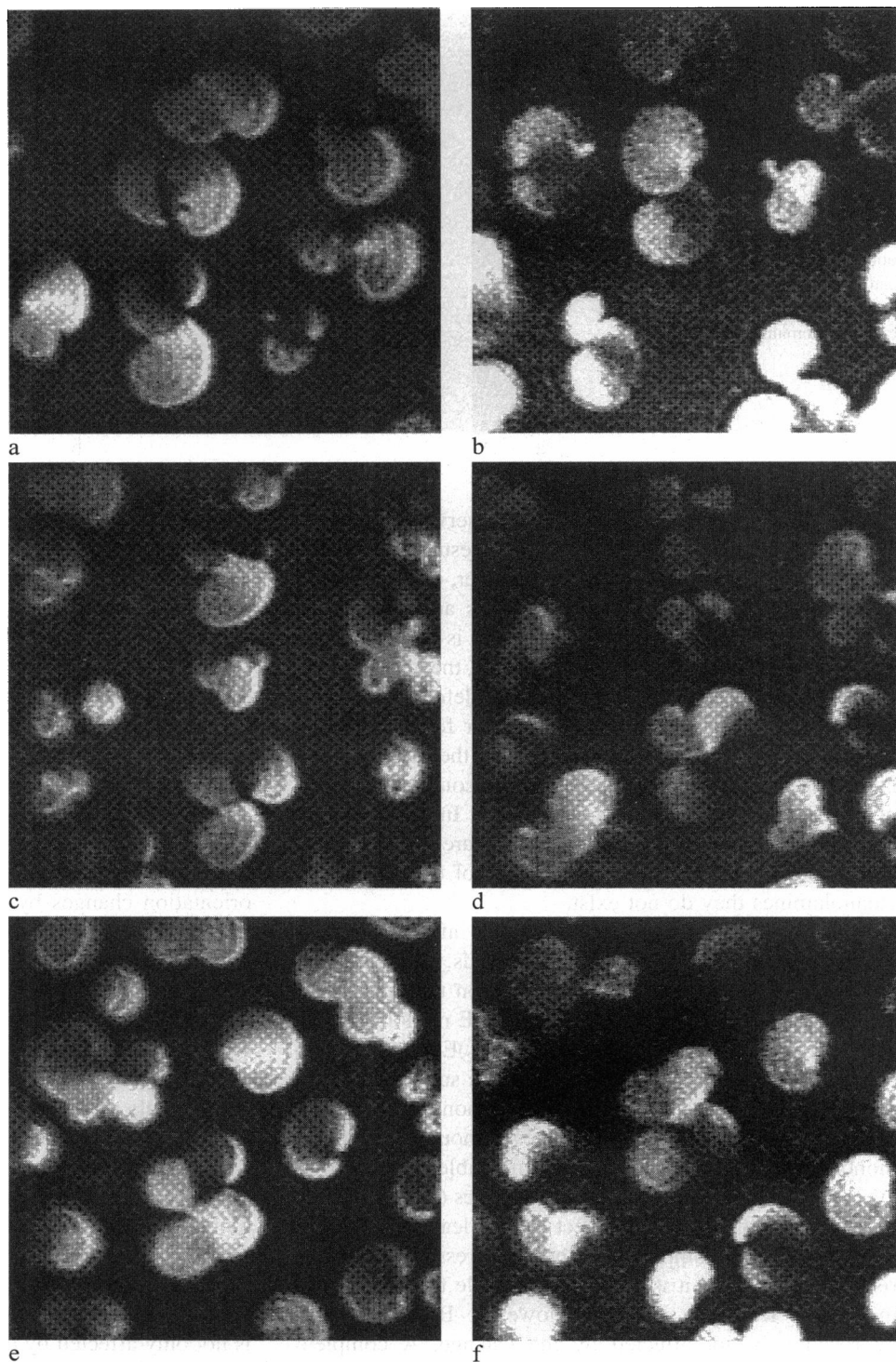
FIGURE 6 Some domains in DPP(Me$_2$)E monolayers can be regarded as twins. Domains consisting of two individuals are always S-shaped (a and b). Twins consisting of three parts are similar to the initial state of the triskelions in DPPC monolayers (c and d). Some twins consist of four parts (e and f). Each domain is shown for two opposite positions of the analyzer. The orientation jumps at the twin boundaries. This becomes evident from the fixed position of these lines at different positions of the analyzer.

spontaneous chiral symmetry breaking. The lattice of the L-DPPE monolayer is chiral, owing to the chirality of the molecules. The chirality of the lattice has been assumed to give rise to a faster annealing of defects (Bibo and Peterson, 1992). This can explain the observations for DL-DPPE monolayers, in which the defects anneal very slowly and the textures formed are very irregular. However, at slightly lower compression rates (5.0 × 10$^{-1}$ nm$^2$ molecule$^{-1}$

min$^{-1}$), a texture similar to the segment structures in monolayers of fatty acids (Henon and Meunier, 1993), fatty acid ethyl and methyl esters (Qiu et al., 1991, 1992a,b; Overbeck et al., 1994), and 1-monoglycerides (Vollhardt et al., 1993; Weidemann et al., 1995; Gehlert et al., 1995; Brezesinski et al., 1995) occurs (Fig. 8 e). The change of orientation breaks down into straight lines at which the orientation jumps, but many inclusions of deviating orientation remain. The an-

FIGURE 7 In DPP(Me)E monolayers, the domains become compact very slowly. Even after 2 h the domains are quite branched. However, in the center of the domain a continuous change of orientation by 360° can be observed and no jumps of orientation occur. Centered (a) and noncentered domains occur (b).

a

b
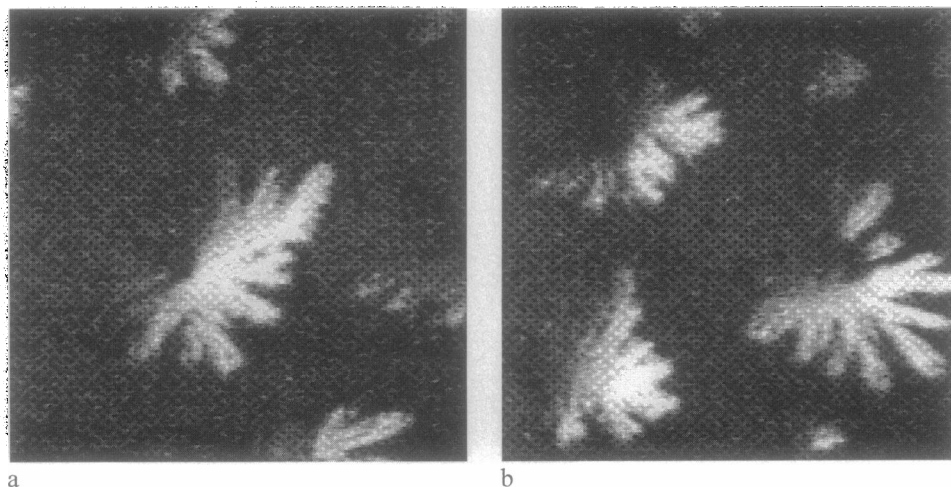
nealing of these defects is too slow to observe. Finally, for L-DMPE the same spirals as for L-DPPE result, as expected (Fig. 8 f). The anisotropy contrast, however, decreases with decreasing chain length. Thus the spirals are much more difficult to visualize. A slight difference is the decreased width of the arms for DMPE. Furthermore, the arms are less kinked, indicating a higher mobility of defects in DMPE monolayers. One finds the same behavior for the textures that result from the rapid compression of the monolayer to higher pressures and the textures in the compact domains observed in the phase coexistence region. In ethanolamine monolayers regular arrangements of lines are formed where the orientation jumps, but in monolayers of the methylated ethanolamines they do not exist.

Morphology is not the only property affected by the different headgroups of the phospholipids. The different headgroup sizes have a direct influence on the erection of chains. The behaviors of DPPC and DMPE monolayers are quite different. For DPPC and DPP(Me$_2$)E, no complete erection of chains can be observed until a surface pressure of $\pi = 71$ mN/m has been reached. The monolayers cannot be compressed to these high pressures without leakage. The monolayer starts to float around the movable barrier; however, even at intermediate compression rates ($5 \times 10^{-2}$ nm$^2$ molecule$^{-1}$ minute$^{-1}$) the effect of the leakage is lower than that of the compression and the pressure continues rising. In this state, it is no longer possible to evaluate the monolayer from the isotherm; however, Brewster angle microscopy is not affected by the leakage. A complete erection of the chains is indicated by the disappearance of the anisotropy contrast. In DPP(Me)E monolayers, the transition to a state with vertical chains occurs at 55 mN/m and for DPPE at 39 mN/m. The complete erection of chains at a slightly lower surface pressure of 32 mN/m for DMPE shows that not only the headgroup affects the transition to vertical chains. Nevertheless, the influence of the headgroup is dominant; a larger headgroup hinders the erection of chains.

A similar relation occurs for the collapse of the monolayers. DPPC monolayers have never been observed to collapse, even at a surface pressure of 71 mN/m. DPP(Me$_2$)E monolayers collapse at 71 mN/m, DPP(Me)E monolayers at 61 mN/m, and DPPE monolayers at 58 mN/m. The collapse of the monolayer is clearly indicated in the microscope images by the appearance of collapse lines (Weidemann and Vollhardt, 1995a). Again the influence of the chain length is not so strong. Collapse of DMPE monolayers has been observed at about 60 mN/m.

## CONCLUSIONS

For both DPP(Me$_2$)E and DPP(Me)E quite similar textures have been found under conditions close to equilibrium. The orientation changes by 360° in the centered domains. No jumps of orientation occur, apart from twinning as in DPPC. However, the shape of the domains is compact, as in DMPE, and is no longer elongated. The influence of the chirality on the domain structure is not as pronounced as in DPPC or DMPE domains, but it is present nevertheless. The lines of equal brightness in the domains are curved, and in DPP(Me$_2$)E monolayers the twins consisting of two individuals are always S-shaped.

The branched domains at high and intermediate rates of compression are fractal-like for DPPC and DPP(Me$_2$)E and more dendritic for DPP(Me)E and DPPE, suggesting an increase of the crystallinity from DPPC to DPPE. The absence of dendritic growth for DMPE shows that the crystallinity of monolayers at comparable plateau pressures is not only affected by the headgroup, but also by the chain length.

The different headgroup size has an influence not only on the domain shape but also on the phase behavior. A larger headgroup hinders the erection of chains. In DPPC and DPP(Me$_2$)E monolayers, the chains cannot be completely erected, and for DPP(Me)E, the transition to a state with vertical chains occurs at a higher pressure than for DPPE. The same tendency is observed for the collapse. DPPC monolayers have not been observed to collapse, and DPP(Me$_2$)E monolayers collapse at a much higher surface pressure than DPP(Me)E and DPPE. The effect of the chain
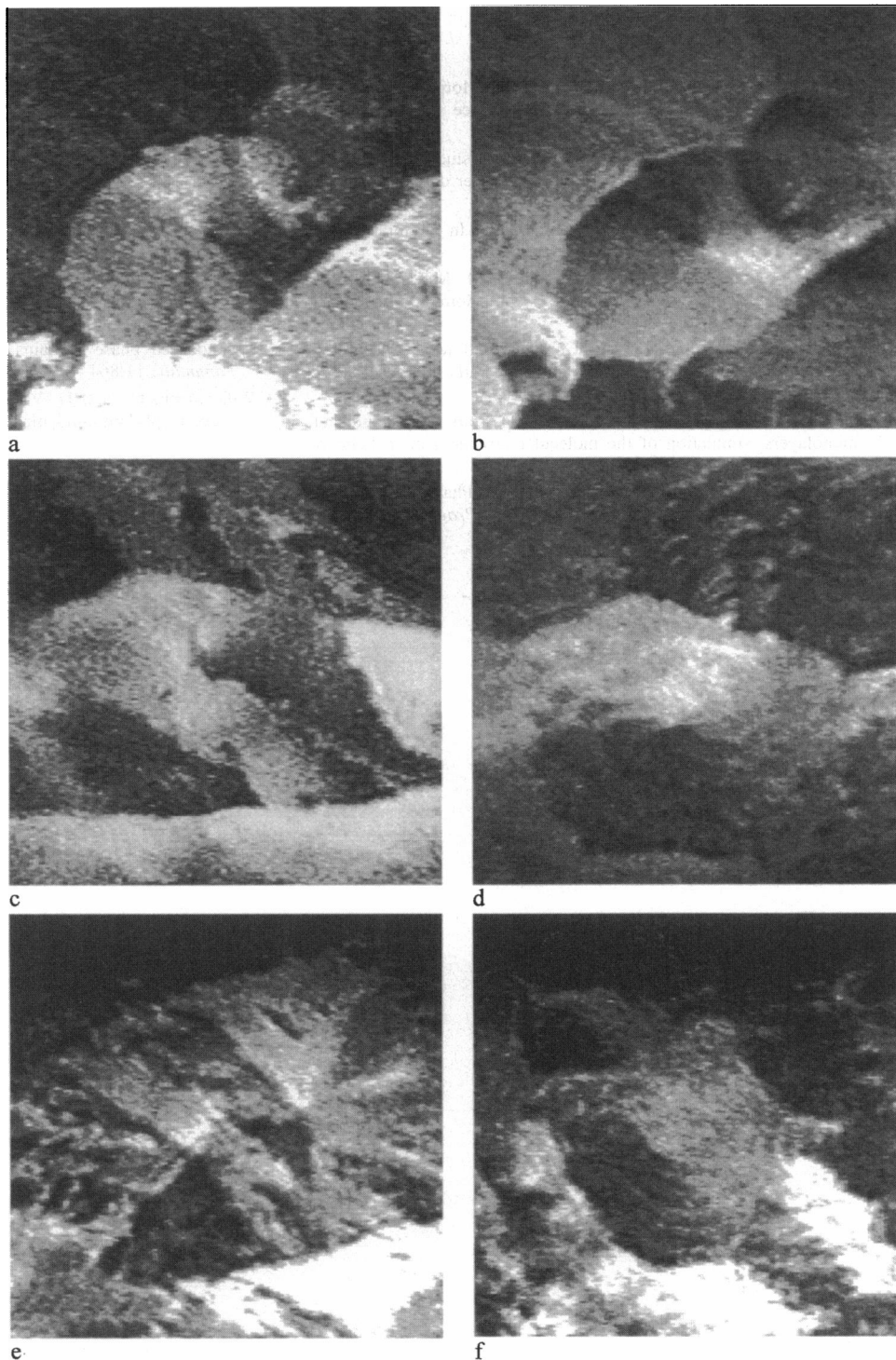
FIGURE 8 L-DPP(Me)E mono-
layer compressed to about 15 mN/m
with $2.5 \times 10^{-1}$ nm$^2$ molecule$^{-1}$
min$^{-1}$ at two opposite positions of
the analyzer (a and b). The orienta-
tion changes by 360° around the point
in the middle of the image. For the
other lipids a similar texture results
from such a rapid compression. In
DPP(Me)E monolayers a continuous
change of orientation results from a
relaxation, and no additional discon-
tinuity lines are created (c). For L-
DPPE the monolayer relaxes into
kinked spirals (d). For DL-DPPE the
annealing of defects is much slower.
At a slightly lower compression rate
$(5 \times 10^{-1}$ nm$^2$ molecule$^{-1}$ min$^{-1}$),
the change of orientation breaks
down along straight lines (e), but
many inclusions of different orienta-
tion remain. For L-DMPE again, spi-
rals are observed (f).



length on the erection of chains as well as on the collapse is
much smaller than that of the headgroup size.

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