Direct X-Ray Study of the Molecular Tilt in Dipalmitoyl Lecithin Bilayers *

M. Hentschel ** ***, R. Hosemann **, and W. Helfrich ***

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Dedicated to Prof. Dr. W. Menke on the occasion of his 70th birthday

Direction and angle of molecular tilt in an ordered multilayer system of dipalmitoyl lecithin and water were directly determined by X-ray diffraction as a function of temperature in the gel phase with ca. 20 wt. % of water.

Early X-ray studies by Levine [1] and Tardien et al. [2] indicated that the hydrocarbon chains are tilted with respect to the layer normal in the gel phase of lecithin-water multilayer systems. Janiak et al. [3] obtained a temperature dependence of the tilt angle. Except the work of Levine, all these experiments were done with dispersions ("powders") and the tilt angle was deduced from the stacking period and the concentration of water. The latter was usually large enough ($\gtrsim 20\%$ by weight) to keep the pretransition and the main transition at the temperatures characteristic of the single bilayer, i. e. at 34 °C and 43 °C [4].

Stamatoff et al. [5] determined the tilt angle directly, using free-standing monodomain samples. However, the maximum concentration of water was only 10 wt.% and the data were analyzed on the assumption that all tilt directions were equally probable.

The following investigations were carried out with a "multisandwich" sample consisting of 100 mylar films alternating with multilayer systems of dipalmitoyl lecithin (DPL), both 5 µm thick. The multisandwich was prepared at 60 °C by compressing a mixture of DPL and 20 wt.% of water. At room temperature the 1 mm high sample was cut into a 1×10 mm strip. Polarizing microscopy showed the bilayers to be well-aligned parallel to the mylar films [6]. The sample was then allowed to stand for 50 h in water-saturated air at 4 °C, sealed in a thin quartz capillary, and finally mounted on the sample holder of an X-ray pinhole camera. When the temperature was changed, measurements were resumed only after at least one day.

The diffraction patterns confirmed the good alignment. With horizontal layers there were several orders of small-angle reflections indicating the stacking period along the vertical and wide-angle reflections from the hydrocarbon chain lattice near the equator. A density map of wide angle reflections is given in Figure 1. It suggests that the chains are tilted along one of the basic vectors of a hexagonal lattice (Case I) rather than along one of the bisectors (Case II). The two cases which are the most likely are sketched in Figure 2. The angle θ made by the reflected beam with the equator is related to the tilt angle φ by

$$\sin\theta = \begin{matrix} \pm\cos 30^\circ \sin\varphi \\ \pm 0 \end{matrix} \quad \text{in Case I}$$

and

$$\sin\theta = \begin{matrix} \pm\sin\varphi \\ \pm\cos 60^\circ \sin\varphi \end{matrix} \quad \text{in Case II}.$$

The tilt angle derived for Case I, the stacking period, and the spacing of the hydrocarbon chain lattice are

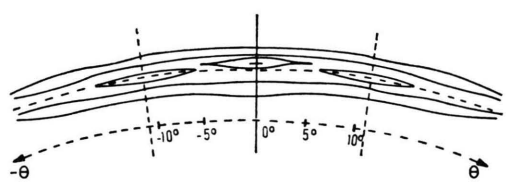

Fig. 1. Density map of hydrocarbon chain lattice reflections at 33.6 °C. 0° coincides with the equator of the diffraction pattern.

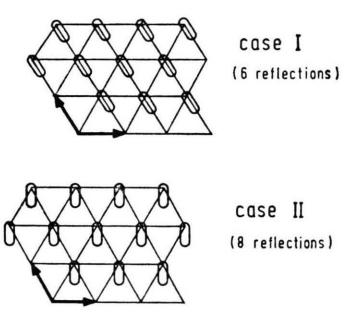

Fig. 2. Examples of the two most likely tilt directions (There are six of each).

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** Fritz-Haber Institut der MPG, Teilinstitut für Strukturforschung, Faradayweg 4–6, D-1000 Berlin 33.

*** WE 1B, FB Physik, Freie Universität Berlin, Königin-Luise-Str. 28/30, D-1000 Berlin 33.

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all plotted in Fig. 3 as functions of temperature. Figure 1 also indicates, that the tilt slightly distorts the hexagonal lattice, making it orthorhombic. The shape of the three reflections suggests that there is little or no correlation between neighbouring bilayers.

The temperature regions of Fig. 3 denote the known ranges [4] of the gel phase (I and II), the intermediate phase (III), and the fluid phase (IV and V). Signals of the gel or intermediate phase (dotted lines) persist through IV, indicating a phase separation. This seems to have been due to pronounced water absorption by the mylar film at elevated temperatures. The water content of the sample could not be measured directly, but was calculated from the stacking period and the tilt angle to be roughly 23 wt.% throughout the gel phase.

To obtain the tilt angle as accurately as possible we decomposed the pattern of Fig. 1 into three separate signals. This was done for all temperatures, although there was no central maximum in the density map near room temperature. Apparently the tilt direction was poorly defined in that region. Using there the analysis of Stamatoff et al. [5], we derived the same tilt angle as with our method.

Our measurements give the tilt direction and the tilt angle in the gel phase of DPL. There is saturation with water at least at 4 °C. In any detailed interpretation of the data one has to bear in mind the possible presence of defects such as the well-known spiraling steps [7]. These remnants of the ripple structure of the intermediate phase may heal

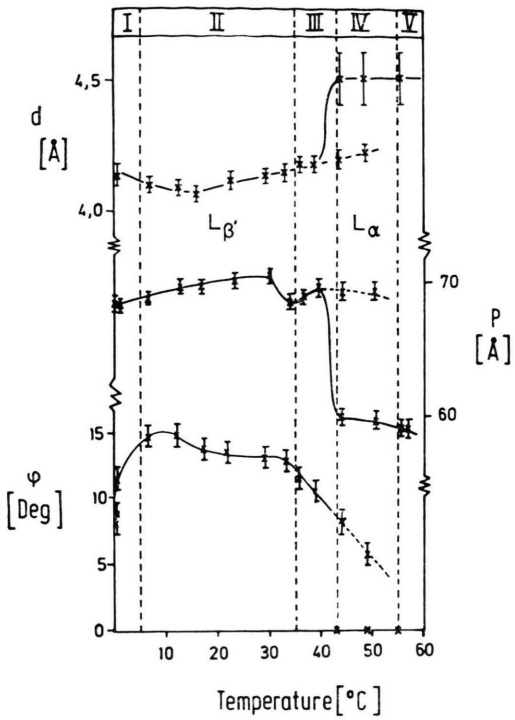

Fig. 3. Spacing d of Bragg planes of hydrocarbon chain lattice, stacking period P, and tilt angle φ as functions of temperatures.

very slowly. Independently of our work Levelut et al. [8] studied the X-ray diffraction of a multilayer system obtained by swelling a DPL single crystal in a wet atmosphere. Working only at room temperature, they found the same tilt direction, but a tilt angle of about 20°.

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