CHEMISTRY LETTERS, pp. 1515-1516, 1989.

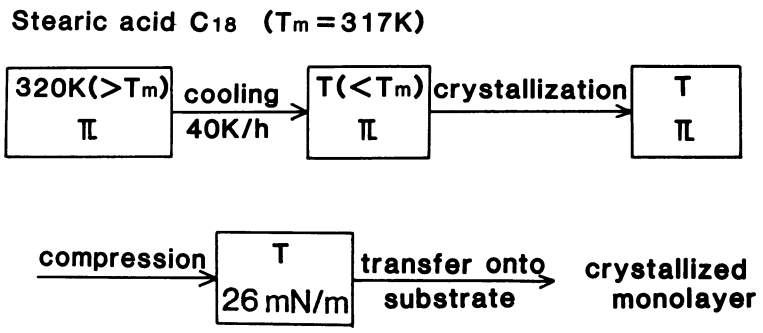
Construction of High-Quality Monolayer by Crystallization on the Water Surface

Tisato KAJIYAMA,* Kazuo UMEMURA, Motoko UCHIDA, Yushi OISHI, and Ryutaro TAKEI†
Department of Applied Chemistry, Faculty of Engineering, Kyushu University,
6-10-1 Hakozaki, Higashi-ku, Fukuoka 812

Defect-diminished fatty acid monolayer was constructed by cooling the amorphous monolayer on the water surface down to a temperature region below the melting temperature of the monolayer.

Fatty acid monolayers on the water surface have been classified into a crystalline monolayer and an amorphous one, depending on the subphase temperature, T_{sp} below and above the melting temperature, T_m of the monolayer, respectively.[1] Formation of the crystalline and amorphous monolayers is irrespective of the magnitude of surface pressure. Furthermore, the crystalline monolayer is composed of small crystallites with large fraction of crystalline defect due to incomplete crystallographic sintering at their boundary surfaces among the crystallites during compression.[2] It is indispensable to construct the defect-free monolayer for applications of LB films as functional ultra-thin films. In this study, defect-diminished fatty acid monolayer was constructed by cooling the amorphous monolayer down to a temperature region below T_m. The crystalline size and crystalline distortion (corresponding to the fraction of crystalline defect) in a direction along the monolayer surface were quantitatively evaluated by a single line method[3,4] based on the Fourier analysis of electron diffraction profiles.

A benzene solution of stearic acid of 3.5×10^{-3} mol·l^{-1} was prepared as a spreading solution. Scheme 1 shows the preparation process for crystallized monolayer of stearic acid. The amorphous monolayer was prepared on the pure water surface at T_{sp} of 320 K above T_m of 317 K[5] and then, was compressed to the surface pressure of 15 mN·m^{-1}. With maintaining the surface pressure at 15 mN·m^{-1}, T_{sp} was reduced to the temperature of 303 K below



Scheme 1. Flow sheet describing the construction for crystallized monolayer.

†On leave from Asahi Glass Electronic Products R&D Center Co.Ltd., Yokohama 221

T_m at the speed of 40 $K \cdot h^{-1}$ and then, the monolayer was further crystallized for 3 h on the water surface. This monolayer was again compressed to the surface pressure of 26 $mN \cdot m^{-1}$, at which the stearic acid monolayer was confirmed to be morphologically homogeneous.[1] The monolayer constructed by this method was designated the crystallized monolayer. In order to compare the crystalline distortion and crystalline size of the crystallized monolayer with those of the crystalline monolayer, the crystalline monolayer was prepared at T_{sp} of 293 K below T_m and 26 $mN \cdot m^{-1}$. These two kinds of monolayer were transferred onto collodion-covered electron microscope grids by a vertical dipping method. The transfer ratio was one. Electron diffraction, ED patterns were taken with a Hitachi H-500 transmission electron microscope. Crystalline size, L_{lat} and crystalline distortion in a direction along the monolayer surface, D_{lat} were evaluated by a modified single line method[3,4] based on the Fourier analysis of ED profiles.

Table 1 shows the values of D_{lat} and L_{lat} for the crystalline and crystallized monolayers of stearic acid. The magnitude of D_{lat} and L_{lat} for the crystallized monolayer was much smaller and larger than those for the crystalline monolayer, respectively. Though the magnitude of D_{lat} for the crystallized monolayer is comparable with that of high density polyethylene single crystal or spherulite, L_{lat} of the crystallized monolayer is 5-8 times as large as that of high density polyehylene.[6] Therefore, it is clear that the monolayer with crystallographically superior quality can be constructed by crystallizing the amorphous monolayer on the water surface. On the other hand, in the case of the crystalline monolayer, crystallographical sintering (fusion) at the boundary surfaces among crystallites did not occur by the compression, which suppressed the formation of the structural defect-diminished monolayer.

Table 1. Crystalline distortion and crystalline size for crystalline and crystallized monolayer

	Crystalline distortion D_{lat} / %	Crystalline size L_{lat} / nm
Crystalline monolayer	4.9	6.4
Crystallized monolayer	1.5	120

In conclusion, crystallization of the amorphous monolayer on the water surface is remarkably effective to construct a two-dimensional crystallized monolayer with large crystalline size and small fraction of crystalline defects.

References

1)T.Kajiyama, Y.Tanimoto, M.Uchida, Y.Oishi, and R.Takei, Chem.Lett., 1989, 189.
2)Y.Oishi, K.Umemura, M.Uchida, T.Kajiyama, and R.Takei, submitted to J.Phys.Chem.
3)D.Hofmann and E.Walenta, Polymer, 28, 1298(1987).
4)T.Kajiyama, I.Hanada, K.Shuto and Y.Oishi, Chem.Lett., 1989, 193.
5)T.Kajiyama, N.Morotomi, M.Uchida, and Y.Oishi, Chem.Lett., 1989, 1047.
6)T.Kajiyama, T.Okada, and M.Takayanagi, J.Macromol.Sci.-Phys., B9, 35(1974).

(Received June 10, 1989)