Construction of Two-dimensional Single Crystal of Fatty Acid by Two-step Cooling Crystallization Method

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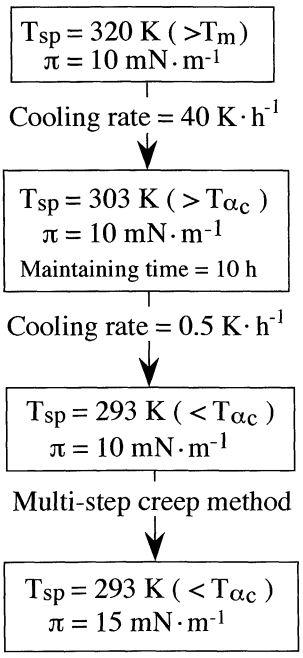
(Received January 16, 1997; CL-970031)

A two-step cooling crystallization method for constructing two-dimensional single crystal of stearic acid was proposed on the basis of thermal characteristics of the monolayer on the water surface. The amorphous monolayer was cooled down to a higher crystallization temperature to form a small number of crystalline nuclei at the first step, and then, the monolayer was further cooled down to a lower crystallization temperature to form large crystallites at the second step. The crystallite size and the crystallographical regularity of the monolayer were remarkably progressed by the two-step cooling crystallization method.

For the applications of Langmuir-Blodgett films as molecular assembly devices, it is necessary to construct the defect-free monolayer of organic molecules.[1] However, the structural defects such as crystallographical distortion, crystallographical incontinuity, crystal dislocation and voids at interfacial regions among crystalline domains are easily formed in the fatty acid monolayer which is prepared by the conventional method.[2-4] One of structural regularization methods based on thermal molecular motion is a cooling crystallization method, which is effective for the construction of the defect-diminished monolayer.[5] In this paper, a novel cooling crystallization method was proposed on the basis of transmission electron microscopic observations.

A benzene solution of stearic acid with a concentration of 3×10^{-3} mol l^{-1} was spread on the water surface. A crystallized monolayer was prepared by two-step cooling crystallization on the basis of the crystal growing method of a small number of seed crystallite. Scheme 1 shows the preparation process for the stearic acid monolayer by two-step cooling crystallization method. The amorphous monolayer was prepared on the water surface at a subphase temperature, T_{sp} of 320 K above the melting temperature, T_m of the stearic acid monolayer,[5] 317 K. Then, the amorphous monolayer was compressed to a surface pressure of 10 mN m^{-1}. After that, T_{sp} was reduced to a temperature of 303 K above the crystalline relaxation temperature, $T\alpha_c$,[6] 298 K at 10 mN m^{-1} at a speed of 40 K h^{-1}. After maintaining at 303 K about 10 h, the monolayer was cooled down to 293 K ($<T\alpha_c$) at a speed of 0.5 K h^{-1} and then, was compressed to 15 mN m^{-1} by the multi-step creep method.[7] The morphological crystallite size and the crystallogaraphical continuity of the crystallized monolayer prepared by the two-step cooling crystallization method were compared with those for the crystalline monolayer prepared by the conventional method, that is, the continuous compression method at T_{sp} of 293 K and 15 mN m^{-1}. These two kinds of monolayer were transferred onto hydrophilic SiO substrate by the horizontal drawing-up method.[8] Electron diffraction, ED pattern was taken with a Hitachi H-7000 transmission electron microscope which was operated at an acceleration voltage of 75 kV and a beam



Scheme 1. Preparation process for crystallized monolayer of stearic acid by the two-step cooling crystallization method.

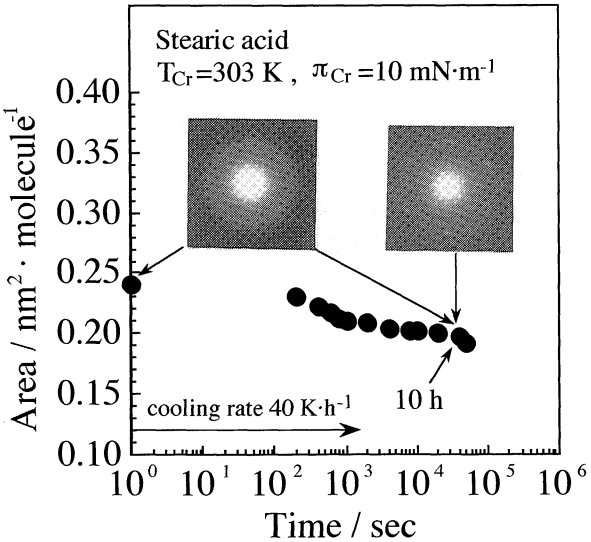


Figure 1. Molecular occupied area with time during crystallization at 303 K and 10 mN m^{-1}.

Table 1. Values of L_{lat} and morphological crystallite size for stearic acid monolayers in a crystalline state prepared by the two-step cooling crystallization method and the continuous compression method

	Crystallographical continuity, L_{lat}/nm	Morphological crystallite size/μm
Two-step cooling crystallized monolayer	30.2	500
Crystalline monolayer	6.2	10

current of 0.5 μA. The spot size of electron beam was 10 μm in diameter. The morphological crystallite size (corresponding to single crystal size) in a monolayer was estimated by the electron beam scanning over monolayer sample on grid.[9] The crystallographical continuity, L_{lat} in the monolayer was evaluated by the single line method based on the Fourier analysis of ED profiles.[3]

Figure 1 shows the crystallization time dependence at 303 K of the molecular occupied area corresponding to A of the π-A isotherm at the constant surface pressure of 10 mN m^{-1}. The molecular occupied area at 10 mN m^{-1} was gradually decreased with the crystallization time for the fast cooling from 320 K to 303 K (about 20 min) and then, was almost remained constant for 10 h where the monolayer morphology was still homogeneous on a TEM observation level. The ED pattern of the monolayer after 10 h showed an amorphous halo at a major portion of scan area in the monolayer, while a crystalline spot was slightly observed at a very small portion of scan area even though at 303 K. This indicates that the monolayer being cooled down to 303 K ($<T_m$) for the first step of crystallization is composed of a small number of crystallite and a large fraction of amorphous monolayer, even in a super-cooled state. Then, when the monolayer was further slowly cooled down to 293 K and compressed to 15 mN m^{-1} by the multi-step creep method, the ED pattern at every scan area of the monolayer revealed a crystalline state of the monolayer. The magnitude of morphological crystallite size of the monolayer was much larger than the electron beam radius as shown in Table 1. These indicate the crystal growth of small crystallites formed at the first step in the cooling crystallization process.

Table 1 shows the values of L_{lat} and the morphological crystallite size for stearic acid monolayers in a crystalline state prepared by the two-step cooling crystallization method and the continuous compression method. The magnitudes of L_{lat} and the morphological crystallite size for the crystallized monolayer prepared by the two-step cooling crystallization method were much larger than that for the crystalline monolayer prepared by the continuous compression method. The magnitude of L_{lat} for the crystallized monolayer is comparable to that of well-organized high density polyethylene single crystal or spherulite. The magnitude of crystallite size of the crystallized monolayer was about 500 μm. Therefore, the monolayer with crystallographically superior regularity can be successfully constructed by the two-step cooling crystallization of the amorphous monolayer on the water surface. On the other hand, in the case of the crystalline monolayer prepared by compression at a constant speed, crystallographical sintering at the boundary surfaces among crystallites imperfectly occurred by the simple compression, which suppressed the formation of the structural defect-diminished monolayer.

In conclusion, the two-step cooling crystallization method based on thermodynamic characteristics, crystallization process and mechanical characteristic of monolayer is remarkably effective to construct a two-dimensional crystallized monolayer with large crystallite size and small fraction of crystalline defects.

References and Notes

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9 After taking an ED pattern at a certain region, we took ED patterns at the other regions by successive scanning an electron beam. The morphological crystalline size was designated as the scanning area which diffraction spots on the ED pattern did not moved along azimuthal direction during the above process.