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Studies on the Molecular Overturn during Compulsory Z-Type Deposition of LB Films Using Double Gates

Teiji KATO
Department of Applied Chemistry, Faculty of Engineering,
Utsunomiya University, 2753, Ishii-machi, Utsunomiya 321

Overturn of molecules during the compulsory Z-type deposition using double gates was investigated by in-situ photopolymerization of a film material and by contact angle measurements of resultant LB films with water. The experimental results made inferable that molecules should overturn three times in total for every two cycles of the compulsory Z-type deposition.

Some amphiphilic materials did X- or Z-type deposition by the conventional vertical dipping method, but many of the resultant LB films exhibited the Y-type structure. This means that film molecules should overturn during or after these types of deposition. Some investigators considered this problem and suggested some molecular overturn mechanisms,[1-4] but they were not confirmed by the experiments.

We have developed a microcomputer-controlled instrument for making complex LB films fully automatically using a double gates system.[5] The gate consisted of a pair of double loops of PTFE thin sheet and their PTFE made holders which were set in head-on arrangements at the water surface in a Langmuir trough. Two pairs of gates permit the passage of a solid substrate of LB films, but supress insoluble monolayers to leak through. By using these double gates, one can perform compulsorily a Z-type deposition of LB films of desired film materials as follows.[5] A solid substrate goes down vertically through a clean water surface. Then, it moves horizontally passing through the gates from a clean water surface area to a monolayer-covered water area, and goes up through the monolayer maintained at constant surface pressure. Here, it takes one layer of the film molecules by a Z-type deposition. Finally, it comes back to a starting position by moving horizontally in air, and one compulsory Z-type deposition cycle is completed. Repeating this cycle, one can deposit a desired number of layers of LB films by the complete Z-type deposition compulsorily. An insoluble monolayer of arachidic acid on the water containing cadmium ions was deposited onto a hydrophobic glass substrate very regularly by this method. X-Ray diffraction from the resultant LB film was not so strong, but it revealed that the structure of the film was that of Y-type. This means that film molecules must overturn once at least for every twice compulsory Z-type depositions.

This paper will reveal when molecules do overturn during the Z-type deposition by fixation of film molecules through in-situ photopolymerization of a film material at every elementary deposition process, and by contact angle measurements with water of the separately prepared, fixed structure LB samples to determine the direction of molecules in the outermost layers of the LB films.

The film material used in this study was 10,12-pentacosadiynoic acid(abbreviated hereafter as PA) which was purchased from Wako Chemicals(mp, 63.0-64.0 °C). No impurity was detected by the high pressure liquid chromatography(column; Inert sil, solvent; methanol, eluent; acetonitrile) and the material was used without further purification. Benzene of an absorption-grade(Dojin Chemicals) was used as a spreading solvent. Reagent-grade cadmium acetate(Wako Chemicals) was used to prepare the subphase water containing 10^{-3} M of cadmium ions. X-Ray patterns of LB films were measured with a conventional Rigaku Denki horizontal powder diffractometer(Geigerflex model 3300), employing Cu K_α radiation. PA can be photopolymerized by UV irradiation when molecules are arranged in the regular manner such that in crystals, monolayers or in LB films. A 150 W Xe-lamp(Ushio Denki Co.Ltd.) was used as a UV light source for photopolymerization of the LB films and a fused-quartz lens system focused the light on them.

Figure 1 shows records of the compulsory Z-type deposition of a PA monolayer on the subphase containing 10^{-3} M cadmium acetate using double gates. The solid substrate(50x20x1 mm microscopic glass slide) was hydrophobitized as follows. A clean glass slide deposited one layer of PA compulsorily by the Z-type deposition, and then deposited two layers of Y-type of PA by the conventional vertical dipping. If the substrate was hydrophobitized with ferric stearate by rubbing, no deposition of PA occured by the compulsory Z-type deposition. Other experimental conditions are written in the figure captions. The curves (a) and (b) show an area reduction of the monolayer with time and a pressure fluctuation during deposition,respectively. As seen from the figure, the area reduction by deposition was very regular and one layer of PA molecules was always deposited at every upward process with transfer ratio of almost unity. X-Ray diffraction data from the LB film(20 layers) made under the conditions in Fig. 1 were as follows(angles and intensities at diffraction peaks); 1st(1.63°, 3400 cps), 2nd(3.14°, 1950 cps), 3rd(4.72°, 3500 cps), 4th(6.30°, 1140 cps), 5th(7.88°, 1220 cps), 6th(9.49°, 270 cps), 7th(11.07°, 400 cps), 8th(12.68°, 100 cps), 9th(14.28°, 200 cps), 10th(15.90°, 50 cps), 11th(17.48°, 50 cps).

The peaks were observed up to 14th and the LB film had very high molecular regularity. The long spacing of the LB film calculated from the above data(averaged from 2nd to 9th peak) was 5.60 nm which corresponded well to that of a Y-type structure; the value obtained from the LB film of PA made by the conventional vertical dipping method was

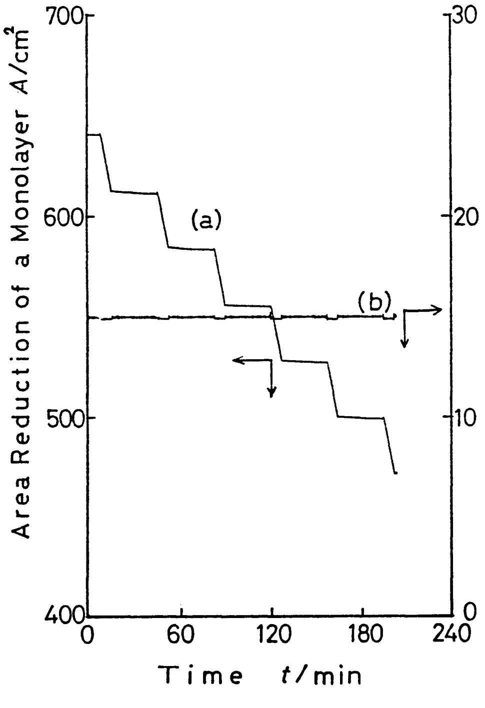

Fig.1. Records of the compulsory Z-deposition of a PA monolayer on the water containing cadmium ions(15 °C, pH 6.1, 15 mN/m, 10 mm/min).
(a), (b) See Text.

5.61 nm, being an averaged value calculated from 2nd to 7th X-ray diffraction peaks. The film molecules must also do overturn during the compulsory Z-type deposition of PA as arachidic acid molecules should do.

Molecules in the LB films were photopolymerized in-situ during deposition by UV light irradiation for 30 min in air and for 60 min in water. The LB films became blue at first and then red by polymerization. The long spacing of the LB film made by the compulsory Z-type deposition changed a little by photopolymerization from 5.60 nm to 5.64 nm, because of the topochemical character of polymerization of PA in LB films.

Contact angles of the in-situ photopolymerized LB films with water were measured by the method of adhering bubble in water. A bubble adhered to the LB film was enlarged by a magnification of 30 with a projection system. Accuracy of the reading was ±1°. When measurements were done in pure water, contact angles changed very rapidly with time, and the LB films were destroyed in a short time from a three-phase line of water, air(a bubble) and the LB film. Therefore, measurements were done with water containing cadmium acetate of the same concentration to the sub-phase water for deposition. Contact angles changed gradually with time after a sample was immersed into water and a bubble was set, probably due to the adsorption of acetic acid molecules or ions onto the LB films in water. So, the extrapolated values to zero time were taken as the contact angles of polymerized LB films.

Table 1 summarizes the contact angle data. A contact angle of polyethylene is included as a representative value of a hydrophobic surface. Values for the LB films of PA made by the conventional vertical dipping deposition and polymerized in air or polymerized in water and taken out through a clean water surface using gates are also included in the table. The LB sample number 4 was made by the vertical dipping deposition and was photopolymerized in-situ in water after it was immersed through a clean water surface. By comparing the contact angles of samples number 2,3, and 4, it is natural to consider that PA molecules in the outermost layer should overturn when it passes across the clean water surface. As seen from the table, the surfaces of the in-situ photopolymerized,separately prepared LB films during the compulsory Z-type deposition are hydrophilic(No.5), hydrophobic(6), hydrophilic(7) and hydrophobic(8) in regular order of the deposition process, respectively.

Table 1. Contact angles of in-situ photopolymerized LB films of PA with water

Sample conditions			Contact angle[a)]	Surface
No.		polymerized[b)]		
1	polyethylene		86-89°	hydrophobic
2	vertical dipping	in water	53-55°	hydrophilic
3		in air	87-89°	hydrophobic
4		in water[c)]	52-54°	hydrophilic
5	compulsory Z	in water	53°	hydrophilic
6	(odd cycle)	in air	75-77°	hydrophobic
7	compulsory Z	in water	45-47°	hydrophilic
8	(even cycle)	in air	76-78°	hydrophobic

a) With water containing 10^{-3}M of cadmium acetate.
b) 30 min in air and 60 min in water. c) See text.

Figure 2 shows schematically the most plausible overturn mechanism that is compatible with all of our experimental results; one layer of PA molecules always deposited at every upward process; an X-ray diffraction profile exhibits a higher molecular order of Y-type structure; the surface of the LB film changed according the order of hydrophilic, hydrophobic, hydrophilic and hydrophobic during completion of one Y-type layer by Z-type deposition using double gates.

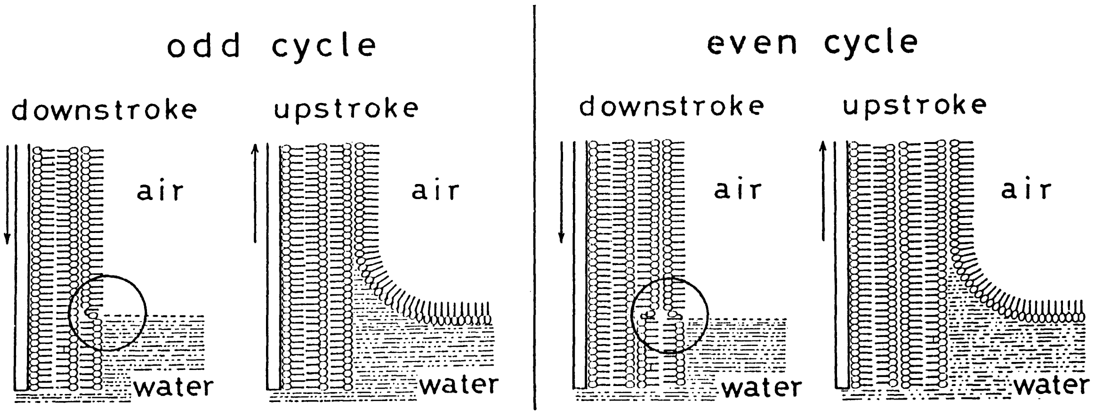

Fig.2. The most plausible molecular overturn mechanism during a complete Z-type deposition that is compatible with all of our experimental results.

At the downward process in an odd cycle, molecules in the outermost layer attached at the preceding upward process overturn once when they pass across the water surface and the surface of the LB film becomes hydrophilic. This is the reason why PA molecules could not be deposited by compulsory Z-type deposition onto a glass slide hydrophobitized with ferric stearate. At the upward process in the same cycle, one layer of molecules attaches onto the substrate by the Z-type deoposition.
At downward process in the next even cycle, molecules in the outermost two layers overturn together at the same time to form Y-type structure. At the upward process in the same cycle, one layer of PA molecules is taken up and surface becomes hydrophilic. The experimental results thus make inferable that film molecules should overturn three times in total for every two cycles of compulsory Z-type deposition, and this overturn mechanism can be applicable in general to Z-type deposition that affords Y-type structure.

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