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Langmuir-Blodgett Films of Polyallylamine Modified by Fluorocarbon

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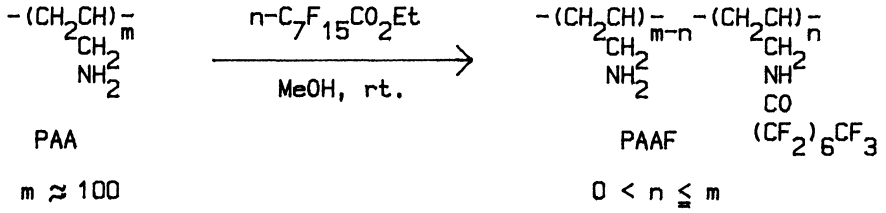
Fluoroalkyl groups were introduced to polyallylamine by the treatment with ethyl perfluorooctanoate. Langmuir-Blodgett films of the fluorinated polymer were successfully prepared. Characterizations of the films were attempted.

A strong attention has been focussed on the functionalized Langmuir-Blodgett (LB) films which show excellent properties because they have a highly oriented molecular ordering. Polymer LB films which possess higher thermal and mechanical stability compared with monomeric ones are useful materials for surface coating. On the other hand, a long chain perfluoroalkyl group on the surface shows extremely good properties as oil resistance, low friction and so on. At this point, LB films of polymer containing fluorocarbon chains should have excellent surface properties. The polymerization by UV irradiation for monomeric LB films containing carbon-carbon double bond and fluorocarbon chains was recently reported.[1,2] We wish to report the first example of polymer LB films prepared from polymer which was modified with the perfluoroalkyl group, and that the surface control is achieved by changing the content of fluorocarbon chain in these films.

Polyallylamine hydrochloride (Mw = 8500 - 11000) was treated with sodium methoxide in the methanol solution and precipitates of sodium chloride were separated. To this solution ethyl perfluorooctanoate was added[3] and fluorinated polymer was formed as follows:



PAA PAAF

$m \approx 100$ $0 < n \leq m$

The structure of this polymer (PAAF) is determined by the infrared spectrum (amide absorptions[4] at 1712 and 1550 cm^{-1}) and the elemental analysis. The ratio of perfluoroalkyl groups to amino groups in PAA can be controlled by the added amount of ethyl perfluorooctanoate. The polymer which was modified by a high content of fluorocarbon was not soluble in methanol. The soluble polymers less fluorinated, n/m = 0.2 (PAAF20) and 0.05 (PAAF5), were synthesized in order to prepare LB films.

Figure 1 shows the surface pressure-area (F-A) isotherms for the monolayers of the PAAF20 and PAAF5 at 290 K. The monolayers of PAAF were spread from the benzene / methanol (1 : 1) solution ($5.5X10^{-3}$ mol dm^{-3}) on the water surface. The monolayers were stable up to 60 mN m^{-1} and the limiting areas (A_0) of perfluoroalkyl unit at zero pressure for PAAF20 and 5 were 28 and 69 $Å^2$, respectively. The section area of CF_2[2] is 28 $Å^2$. The A_0 value of PAAF20 indicates that fluoroalkyl chains stand side by side. The large A_0 value of PAAF5 shows fluoroalkyl chains somewhat laid on the surface.

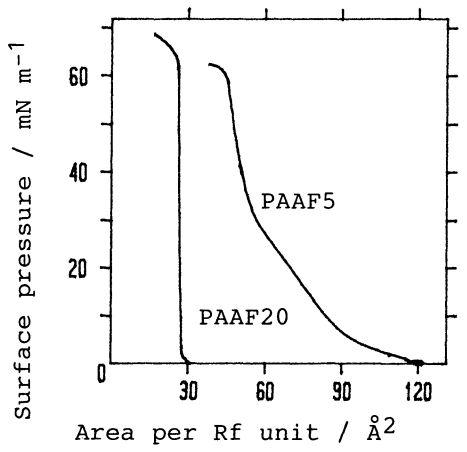


Fig. 1. F-A isotherms of PAAF.

The deposition of monolayers of PAAF20 and PAAF5 was attempted at 20 mN m^{-1} on slide glasses and the LB films characterized as a Y type (transfer ratio, 1 ± 0.1) were obtained. The thickness of the film was measured by Talystep (Rank Taylor Hobson Co., Ltd.) with a needle of point size 125 Å. The thicknesses of PAAF20 and PAAF5 were 27.1 and 21.5 Å, respectively. This result suggests that a thicker film was obtained in the case of fluoroalkyl chains stood side by side on the surface.

The γc value of Zisman plot was measured with n-alkanes on the LB film surface in usual manner.[5] γc value of PAAF20 (1, 3, 5, 7 layers) and PAAF5 (1, 7 layers) were 16.4, 16.5, 16.6, 16.2 and 18.5, 18.6 dyn/cm, respectively. Compared with γc value of polytetrafluoroethylene, 18.5 dyn/cm,[5] the surface of PAAF5 LB film is considered to be covered with CF_2 (the middle of fluorocarbon chain), and the low γc value of PAAF20 LB films indicats that the surface was covered with CF_3 (the end of fluorocarbon chain). The higher γc value of PAAF20 LB films, compared with the films which is covered with CF_3 (γc = 13.0 dyn/cm[6]), suggests that the unreacted amino groups under the fluorocarbon are effected to the surface.

Attempts to use as surface controlled films for membrane separation are in progress.

References

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