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Langmuir-Blodgett Films of Polyvinylamine Modified by Perfluoroacylation. Preparation of Super Thin Films

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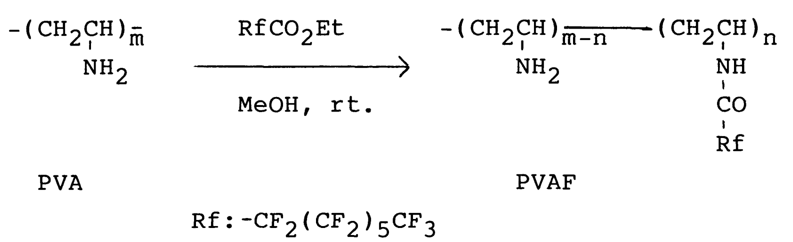
Long chain perfluoroalkyl groups were introduced to polyvinylamine by perfluoroacylation. Langmuir-Blodgett films of the fluorinated polymer were successfully prepared. The thickness of monolayer of the films were super thin and it was about 8 Å. Characterization of the films were attempted.

The films which are modified by long chain perfluoroalkyl group are useful materials for oil repellent coating, insusceptible coating to dust deposition, membrane separation, insulator, and so on. To use these films for surface coating as higher performance materials, thin films are necessary. For instance, insulating film for metal-insulator-semiconductor type device1) and surface coating of floppy disk. In the previous communication2) we have reported Langmuir-Blodgett (LB) films of fluorinated polyallylamine. The characterization of these films indicated the extremely good surface properties because they have a highly oriented molecular ordering, and also thermal stability3) of the polymer LB films compared with monomeric ones. We wish to report another example of polymer LB film of polyvinylamine which was modified by the perfluoroacylation and that the thickness of monolayer was super thin.

Low molecular weight polyvinylamine hydrochloride4) was prepared5) from polyacrylamide (Mw≈7100: viscometric average molecular weight) which was prepared6) from acrylamide. Polyvinylamine modified by perfluoroacylation (PVAF) was synthesized under similar reaction condition as previously reported.2) The reaction scheme and synthesized polymer are shown as follows:



$$-(CH_2\underset{NH_2}{CH})_m \xrightarrow[\text{MeOH, rt.}]{RfCO_2Et} -(CH_2\underset{NH_2}{CH})_{m-n}-(CH_2\underset{\substack{NH\\CO\\Rf}}{CH})_n$$

PVA PVAF

Rf: $-CF_2(CF_2)_5CF_3$

n/m	PVAF
0.09	PVAF9
0.18	PVAF18
0.37	PVAF37
0.56	PVAF56
0.65	PVAF65

The structure of this polymer (PVAF) is determined by the infrared spectrum (amide absorption2) at 1700 cm^{-1}) and the elemental analysis. The ratio of perfluoroalkyl groups to amino groups in PVA can be controlled by the added amount of ethyl perfluorooctanoate. PVAF9 - 56 are soluble in solvent and use for preparation of LB films.

Figure 1 shows the surface pressure-area (F-A) isotherms for the monolayers of the PVAF9 - 56 at 290 K. The monolayers of PVAF were spread from the benzene / methanol (2 : 1; PVAF9 - 37, 1 : 1; PVAF56) solution ($3.5X10^{-3}$ mol dm^{-3}) on the water surface. The monolayers were stable up to 55 mN m^{-1} and the limiting areas (A_0) of perfluoroalkyl unit at zero pressure for PVAF9, 18, 37, 56 were 78, 64, 49, 35 $Å^2$, respectively. These A_0 values were larger than section area of CF_2[2)] (28 $Å^2$).

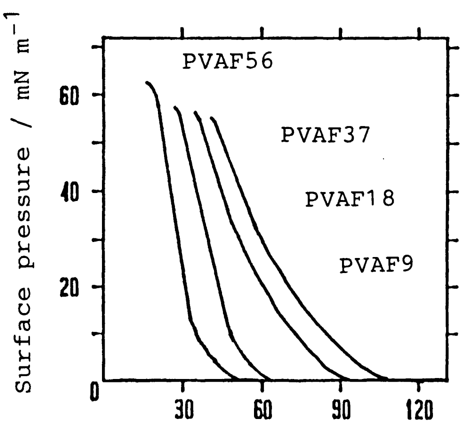


Fig. 1. F-A isotherms of PVAF.

The deposition of monolayers of PVAF was attempted at 20 mN m^{-1} on slide glasses and the LB films characterized as a Z type (transfer ratio, 1 ± 0.1) were obtained. X-Ray analysis of the LB films (10 layers) was carried out and the X-ray diffraction patterns were observed. The monolayer's thickness was calculated by Bragg's expression and it was super thin (6.4, 8.4, 8.0, 8.0 ± 0.5 Å for PVAF9, 18, 37, 56, respectively), compared with previously reported[2)] film of modified polyallylamine (≈ 30 Å). The monolayer's thickness was also calculated by Talystep[2)] and it was around 6 - 7 Å.

The γc value of Zisman plot was measured with n-alkanes on the LB film surface in usual manner.[2)] γc values of PVAF9, 18, 37, 56 were 16.9, 16.9, 16.4, 13.9 for monolayers and 14.9, 14.9, 14.8, 13.1 dyn/cm for 3 layers, respectively. These values, which are lower than those at surface of polytetrafluoroethylene (18.5 dyn/cm), indicate that some CF_3 groups existed on the surface of LB film. γc values of monolayers were larger than 3 layers values, indicating that LB films were super thin and slide glass surface had an effect on the γc values.

It is considered that the polymer LB films were stabilized by the formation of 6 membered ring by hydrogen bond of NH group in PVA polymer chain.

References

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