CHEMISTRY LETTERS, pp. 1027-1030, 1990.

Langmuir-Blodgett Films of Polymers Modified with Perfluoroalkyl Groups by Covalent and Ionic Bonds

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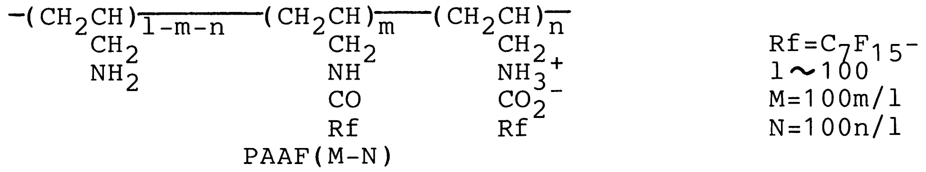
Long chain perfluoroalkyl groups were introduced to polyallylamine by both amide and ionic bonds, and Langmuir-Blodgett films of these polymers were successfully prepared even if the modification ratio of perfluoroalkyl groups was much higher than polymer LB films modified with perfluoroalkyl groups by covalent bonds. Characterization of the LB films indicated that these LB films showed better water-repellency than ion complex type LB films.

The polymer thin films containing long chain perfluoroalkyl (Rf) groups are expected as useful materials for oil and water repellent coating, film separation, and so on because of excellent surface properties of Rf group. Concerning polymer Langmuir-Blodgett (LB) films containing Rf groups, polyion complex type LB films have been reported.[1] In the previous papers,[2-7] we have reported that new type LB films of polymers modified with Rf groups by covalent bonds are successfully prepared, and the molecular ordering and surface energy of the LB film can be controlled by slight change of chemical structure of the polymer. When modification ratio of Rf groups to the polymer increase, however, solubility of the polymer in organic solvents decrease because of water- and oil-repellency of Rf groups. And in some cases the polymer does not have enough solubility to prepare the polymer solution, so that the LB films of the polymer can not be prepared by spreading the polymer solution on the water surface. For example, PAAF[2,3] is soluble in methanol when 20% of amino groups of polyallylamine are modified by perfluoroacylation, while, the polymer become insoluble when 30% of amino groups are modified.

In this paper we wish to report that LB films of the polymer modified with Rf groups by both covalent and ionic bonds were successfully prepared. And these LB films could possess higher content of Rf groups than the LB



Scheme 1. Structural formula for PAAF(M-N).

films of PAAF, which were modified by only covalent bonds. We also describe that polymer chain extend with increasing the content of the Rf groups introduced by ionic bonds, and that the LB films show higher water-repellency than polyion complex type LB films.

As preliminary study, the polymers modified with Rf groups by ionic bonds (PAAF0-N, N = 5, 20, 40, shown in Scheme 1.) were prepared by the reaction between polyallylamine (Mw = 5200 — 6700) and perfluorooctanoic acid. The benzene / methanol (1 : 1) solution of PAAF0-N were spread on the water surface at 290 K, and the surface pressure - surface area (F-A) isotherms were measured. The F-A isotherms are shown in Fig. 1. The limiting areas of perfluoroalkyl unit at zero pressure (A_0(Rf)) for PAAF0-5, 0-20, and 0-40 were 54, 46, and 38 $Å^2$, respectively. The deposition of surface monolayers on slide glasses was attempted under surface pressure of 20 mN m^{-1}, and Z type multilayers were obtained. The γc values of Zisman plot were measured with n-alkanes on the surface of the LB films (1 layer) in usual manner,[2] and the γc values of PAAF0-5, 0-20, and 0-40 were 17.1, 16.9, and 16.2 dyn cm^{-1}, respectively. Contact angles of water on the surface of the LB films (1 layer) were also measured, and those for PAAF0-5, 0-20, and 0-40 were 77, 83, and 84 deg., respectively.

Next, the polymer modified with Rf groups by both amide and ionic bonds (PAAF10-N, N = 0 — 50) were prepared by the reaction between PAAF10-0, which was synthesized by perfluoroacylation of polyallylamine,[2] and perfluorooctanoic acid. All these polymers were soluble in methanol and the benzene / methanol (1 : 1) solution of the polymers were spread on the water surface at 290 K. The F-A isotherms for PAAF10-0, 10-5, 10-15, 10-40, and 10-50 are shown in Fig. 2 and A_0(Rf) values were 75, 67, 52, 35, 26 $Å^2$, respectively. The A_0(Rf) value decreased to the section area of Rf group (28 $Å^2$)[2] with an increase in N

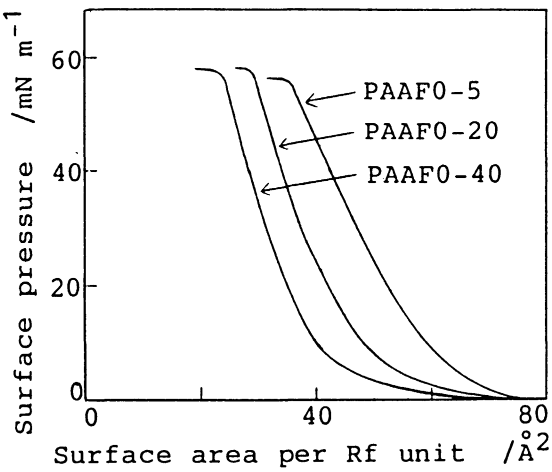


Fig. 1. F-A isotherms for PAAF0-N.

(the modification ratio of Rf groups by ionic bonds, see Scheme 1.), indicating that arrangement of Rf groups gradually changed from lying position to standing position with increasing the modification ratio of Rf groups by ionic bonds. The A_0(Rf) value was smaller than the section area of Rf group in the case of PAAF10-50, which indicates that Rf groups put one on another when the modification ratio of Rf groups become too high.[5] The limiting areas of monomer unit in polyallylamine at zero pressure (A_0(PAA)) were calculated and relation between A_0(PAA) and N is shown in Fig. 3. With an increase in N, the A_0(PAA) value increased at first, reached maximum, and then decreased. This indicates that the polymer chain extended with increasing the modification ratio of Rf groups introduced by electrostatic force. But when the modification ratio of Rf groups exceeded a certain value, the polymer chain extended to the limit and the molecular arrangement change as that Rf groups overlapped one another, resulting that the A_0(PAA) value decreased.

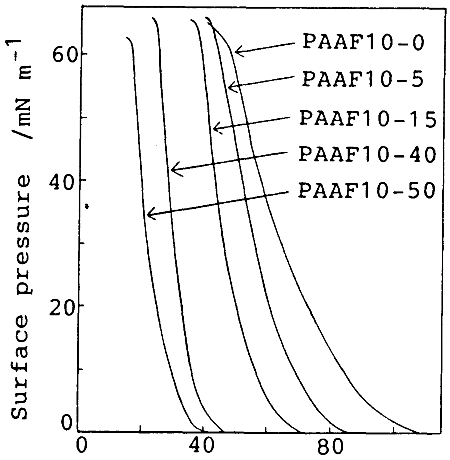


Fig. 2. F-A isotherms for PAAF10-N.

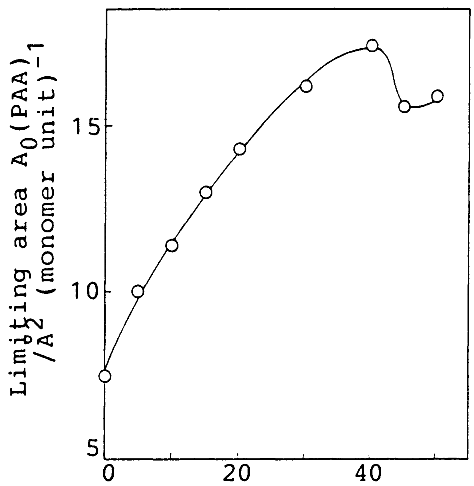


Fig. 3. Relation between A_0(PAA) and N for PAAF10-N.

The deposition of the surface monolayers on slide glasses was attempted under surface pressure of 20 mN m^{-1}. Y type multilayers were obtained in the case of PAAF10-0 and 10-5. The type of the deposition changed from Y type to Z type with an increase in N. In the case of PAAF10-15, midway type multilayer was obtained, namely, transfer ratio of downward deposition was less than that of upward deposition, and multilayers of PAAF10-40 and 10-50 were Z type. The result agrees with the fact that the LB films of PAAF(M-0), which is modified by amide bonds, were Y type[2] and the LB films of PAAF0-N, which modified by ionic bonds, were Z type as mentioned above.

The γ_c values and contact angles of water for the LB films (1 layer) of PAAF10-N were measured, and the results are shown in Table 1. The γ_c

values are smaller than that of polytetrafluoroethylene (18.5 dyn cm^{-1}), indicating that Rf groups are arranged and that CF_3 groups exist on the surface of the LB film.[2)] The γc value decreased with an increase in N. This suggests that Rf groups gradually take more standing position with an increase in N, which agrees with the result that A_0(Rf) value decreased with an increase in N.

Table 1. The γc values and contact angles of water for the LB films

PAAF(M-N)	γc /dyn cm^{-1}	Contact angle of water /deg.
PAAF0-20	16.9	83
PAAF0-40	16.2	84
PAAF10-0	17.3	102
PAAF10-5	16.6	105
PAAF10-15	15.6	108
PAAF10-40	14.3	104
PAAF10-50	14.2	99

Concerning water-repellency, the above-mentioned polyion complex type LB films of PAAF0-N showed smaller contact angles of water than PAAF10-0, which is modified with Rf groups by amide bonds, as shown in Table 1. Compared with these polyion complex type LB films, the LB films of PAAF10-N showed higher water-repellency, for example, contact angle of water for the LB film of PAAF10-5 was higher than that of PAAF0-20 by more than 20 deg. though the ratio of Rf groups for PAAF10-5 is somewhat less than PAAF0-20. It is assumed that hydrophilicity of ionic bonds makes water-repellency of polyion complex type LB films lower, however, water-repellency of PAAF10-N was maintained because Rf groups introduced not only by ionic bonds but also by covalent bonds. The contact angle of water increased at first, reached maximum, and then came to decrease with an increase in N. Increase of Rf groups make water-repellency higher, however, increase of ionic bonds make water-repellency lower. The result would be explained by these two opposite effect.

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(Received March 22, 1990)