CHEMISTRY LETTERS, pp. 399-402, 1991.

Langmuir-Blodgett Films of Polyacrylic Acid Modified with Perfluoroalkyl Groups

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Long chain perfluoroalkyl groups were introduced to polyacrylic acid, and Langmuir-Blodgett films of the polymers were successfully prepared. The preparation of the polymer LB films containing metal ions was achieved by spreading the polymer solution on the aqueous solution of metal salt. Characterization of the films was attempted.

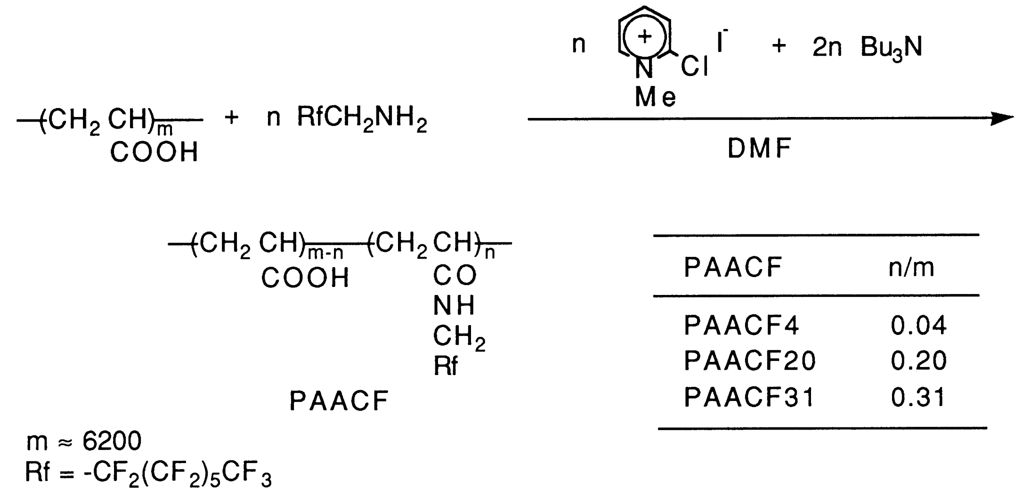
Long chain perfluoroalkyl (Rf) groups show excellent properties which are quite different from corresponding alkyl groups, such as excellent low surface energy, oxygen affinity, etc. Therefore, Rf groups are expected to be very useful for the functional thin films like surface coating films, separation films and so on. From this viewpoint, we have demonstrated the new type Langmuir-Blodgett (LB) films of polymers modified with Rf groups by covalent bonds, and that the molecular ordering and surface energy can be controlled by slight change of chemical structure of the polymer.[1-6)]

On the other hand, it is well known that LB film of fatty acid salt is obtained by spreading the fatty acid solution on the aqueous solution containing metal ion such as calcium ion, and many investigations had been made concerning the LB films of fatty acid salt. Blodgett made the first report of the LB film of fatty acid salt and described that it became possible to deposit more than 200 layers on a glass plate by metal ion in the subphase.[7)] Concerning the LB film of perfluoroalkanoic acid, it was reported that the monolayer of perfluoroalkanoic acid salt can be deposited onto a substrate by using the subphase containing aluminum ion although perfluoroalkanoic acid itself is difficult to be deposited.[8)] These facts suggest that, if the solution of polymer which has carboxyl groups as hydrophilic groups is spread on the subphase containing metal ion, the LB film of polymer containing metal ion as metal salt should be formed and show different properties from the LB film of the polymer itself. But the study of the effect of metal ions in the subphase on the polymer LB films has not been made. Especially in the case of the polymer LB films containing Rf groups, even the polymer which possesses carboxyl groups has not been synthesized yet. Only polymerization of carboxylic acid containing double bond in the monolayer was reported as the polymer LB film containing both Rf groups and carboxyl groups, however, the effect of metal ions in the subphase was not investigated.[9)]

In this paper, we wish to report that the LB films of the polymers containing Rf groups which have carboxyl groups were successfully prepared and that the LB films of metal salts of the polymers were obtained by using aqueous solution containing metal ion as the subphase. We also describe that metal ion in the subphase influenced the molecular ordering and the properties of the LB films.

Introduction of Rf groups to polyacrylic acid was carried out by the reaction between polyacrylic acid

(Mw ≈ 450,000) and 1, 1-dihydroperfluorooctylamine using 1-methyl-2-chloropyridinium iodide and tributylamine.[10)] The reaction route is shown in Scheme 1.



PAACF	n/m
PAACF4	0.04
PAACF20	0.20
PAACF31	0.31

Scheme 1. Synthesis of PAACF.

The structure of the polymer is determined by infrared spectrum (amide absorption : 1685, 1550 cm^{-1}, C-F absorption : 1300-1100 cm^{-1}) and elemental analysis of fluorine. The modification ratio of Rf groups to carboxyl groups could be controlled by added amount of 1, 1-dihydroperfluorooctylamine, and the various modified polymers, n/m = 0.04, 0.20, 0.31 (PAACF4, 20, 31) were synthesized.

The benzene / ethanol (1 : 1) solution (the concentration of Rf group : $0.2\text{-}1.1 \times 10^{-3}$ mol dm^{-3}) of PAACF was spread on the water surface at 290 K, and the surface pressure - surface area (F-A) isotherms were measured. The F-A isotherms on pure water surface are shown in Fig. 1 and the limiting areas of perfluoroalkyl unit at zero pressure (A_0) for PAACF4, 20, and 31 were 66, 39, and 5 Å^2, respectively. The A_0 values of PAACF4 and 20, which are larger than the section area of Rf group (28 Å^2),[1)] show that Rf groups are in somewhat lying position, and the larger A_0 value of PAACF4 than PAACF20 shows that Rf groups of PAACF4 are leaning more than PAACF20. The A_0 value of PAACF31, which is smaller than the section area of Rf group, indicates that Rf groups are overlapped one another.[4)] Next, the PAACF solutions were spread on the aqueous solution containing calcium chloride (4.0×10^{-4} mol dm^{-3}) and potassium hydrogencarbonate (4.0×10^{-4} mol dm^{-3}), and the F-A isotherms were measured. The F-A isotherms on the aqueous $CaCl_2$ are shown in Fig. 2 and the A_0 values for PAACF4, 20, and 31 were 96, 39, and 5 Å^2, respectively. The shape of the F-A isotherms changed by the presence of calcium ion in the subphase, especially in the case of PAACF4, the A_0 value also changed. The results suggest that calcium salts of the polymer were formed by calcium ion in the subphase. If calcium salt is formed, cross linking of polymer chain would occur because divalent calcium ion links two carboxyl groups. The cross linking would reduce the flexibility of polymer chain, accordingly, the cross-linked polymer film would be more rigid than the polymer film which is not cross-linked. Therefore, the surface area of cross-linked polymer film would be difficult to decrease when surface pressure increases. It is supposed that for this reason the slope of F-A isotherm on aqueous $CaCl_2$ is steeper than the corresponding F-A isotherm on pure water. Compared with PAACF20, PAACF4 showed greater difference between the F-A isotherm on pure water and that on aqueous $CaCl_2$. The results would be explained by that the cross linking by calcium ion had a greater influence on the F-A isotherm of PAACF4 than PAACF20 because the ratio of unmodified carboxyl group, which can cause cross linking, in PAACF4 polymer is higher than PAACF20. In the case of PAACF31, the difference between the F-A isotherm on pure water and that on aqueous $CaCl_2$ is very small, however, this would be due to the structure that Rf groups are overlapped.

The deposition of the surface films on slide glasses was attempted under surface pressure of 20 mN m^{-1}. In the case of the film on pure water, Y type multilayers were obtained. In contrast, the films of PAACF4 and 20 on the aqueous $CaCl_2$ afforded Z type multilayers. The film of PAACF31 on aqueous $CaCl_2$ afforded Y type multilayers, however, it is assumed that the different deposition type of PAACF31 is ascribed to the structure that Rf groups are overlapped one another.

The γ_c values of Zisman plot were measured with n-alkanes on the LB films (1 and 5 layer for Y type films, 1 and 3 layer for Z type films) in usual manner.$^{1)}$ The results are summarized in Table 1. The γ_c values of 1 layer films are almost equal to those of 5 layer films. In the case of LB film made by using pure water as the subphase, the γ_c values are lower than that of polytetrafluoroethylene (18.5 dyn cm^{-1}), indicating that CF_3 groups exist on the surface of LB films.$^{1)}$ The lower γ_c values of PAACF20 than PAACF4 indicate that the Rf groups of

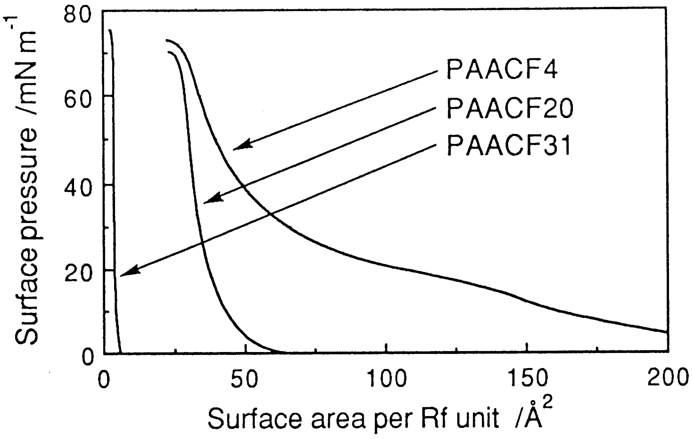


Fig. 1. F-A isotherms on H_2O.

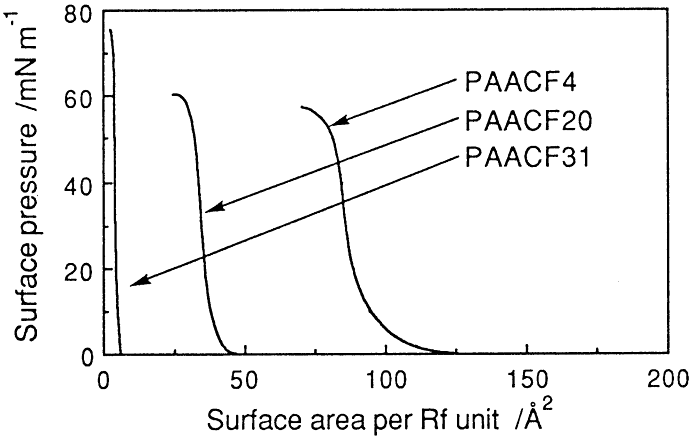


Fig. 2. F-A isotherms on $CaCl_2$ aq.

Table 1. The γ_c values of PAACF LB films /dyn cm^{-1}

	on H_2O		on $CaCl_2$ aq.	
PAACF	1 Lay	5 Lay	1 Lay	5 Lay
PAACF4	16.1	15.9	19.4	18.8$^{a)}$
PAACF20	15.0	15.0	17.1	16.8$^{a)}$
PAACF31	17.3	17.1	16.8	17.3

a) 3 Layer.

PAACF20 are leaning less than PAACF4. The γc values of PAACF31 are larger than the other PAACFs, however, this would be ascribed to that Rf groups are overlapped one another. The presence of calcium ion in the subphase increased the γc values of PAACF4 and 20. The results indicate that formation of calcium salt influenced the molecular ordering and the surface energy of the film. It is assumed that cross linking by calcium ion disordered the molecular ordering of Rf groups in the film, resulting that the increase of γc values. In the case of PAACF31, however, the γc values did not change by the presence of calcium ion. This is supposed to be ascribed to that the influence of formation of calcium salts upon the molecular ordering is small because the LB film of PAACF31 has the structure that Rf groups put one on another.

Table 2. Monolayer's thicknesses of PAACF LB films /Å^2

PAACF	on H_2O	on $CaCl_2$ aq.
PAACF4	32	35
PAACF20	16	18
PAACF31	220	290

The monolayer's thicknesses of these films were measured by X-ray diffraction. The results are summarized in Table 2. The LB films of PAACF31 were much thicker than those of PAACF4 and 20, because the LB films of PAACF31 have the structure that Rf groups are overlapped one another. And the results indicated that monolayer's thicknesses increase by formation of calcium salt.

In conclusion, we have demonstrated the LB films of polymers containing Rf groups as hydrophilic groups, and formation of polymer LB film containing metal ion by spreading the polymer solution on the subphase containing metal ion. Characterization of the LB film showed that the presence of metal ion in the subphase influenced the properties of the LB film.

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(Received November 28, 1990)