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Surface Property of the Langmuir-Blodgett Films of Polymers Modified with Perfluoroalkyl Groups by Ether Bonds

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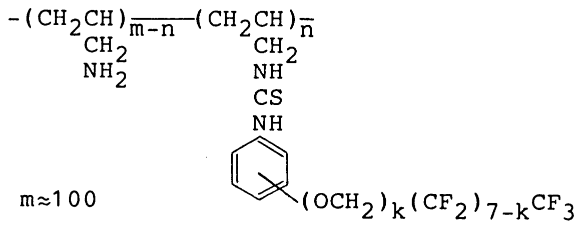
o- And p-1,1-dihydroperfluoroalkoxyphenyl groups were introduced to polyallylamine and Langmuir-Blodgett films of the polymers were successfully prepared. Characterization of the films indicated that the surface energy becomes lower by introduction of perfluoroalkyl chains by ether bonds instead of carbon-carbon bonds in the polymer, and very low γc value, less than 10 dyn cm^{-1}, was achieved.

Langmuir-Blodgett (LB) method$^{1)}$ is one of the most useful method for control of molecular ordering. If molecular ordering can be controlled as designed, it is expected that property of molecule itself clearly appear in the material and that the material with superior function can be obtained. Accordingly, LB method is suitable for arrangement of functional groups. On the other hand, long chain perfluoroalkyl (Rf) groups show excellent surface properties, for instance, low surface energy, low friction, high oxygen affinity, and so on, so that the thin film which possesses Rf groups as functional groups is expected to be useful as surface coating, film separation, and so on. And in the light of practical use, polymer film is suitable as these materials because it is thermally and mechanically stabler than monomer one. From these points of view, LB films of polymer containing Rf groups are expected as functional thin films, and concerning these LB films, photopolymerized LB films$^{2)}$ and polyion complex type LB films$^{3)}$ were reported. Recently we have succeeded in introducing Rf groups to hydrophilic polymers by covalent bonds and first achieved preparation of LB films of the polymers modified with Rf groups by covalent bonds.$^{4)}$ And we demonstrated that these LB films show excellent surface properties which are characteristic of Rf groups, and that chemical structure of the polymer has an influence on the molecular ordering and the surface properties of the films.$^{4-8)}$ Here we report the influence of flexibility of the ether bond on the property of LB films of polymers modified with Rf groups, which is first example that shows the relation between molecular structure and material's function concretely by the value of critical surface tension.

The polymers modified with benzene rings linked to Rf chains by ether bonds (o- and p-PAPEFs) were synthesized by the reaction between polyallylamine (Mw = 5200 — 6700) and o- and p-1,1-dihydroperfluorooctyloxyphenyl isothiocyanates,$^{9)}$

respectively. The various modified polymers, n/m = 0.05, 0.2, 0.4 (o- and p-PAPEF5 ,20, 40) were obtained by control of the added amount of 1,1-dihydroperfluorooctyloxyphenyl isothiocyanates. Figure 1 shows the surface pressure - surface area (F-A) isotherms for the monolayers of o- and p-PAPEFs at 290 K. The monolayers of PAPEFs were spread from the benzene / methanol or benzene / trifluoroethanol solution on the water surface. The deposition of monolayers of PAPEFs was attempted under surface pressure of 20 mN m^{-1} on slide glasses, and Y type multilayers were obtained. The monolayers' thicknesses of these films were measured by the X-ray diffraction.

The limiting areas (A_0) of perfluoroalkyl unit at zero pressure and the monolayers' thicknesses of PAPEFs are compared with those of PAPHFs[8] in Table 1 and Table 2, respectively. Both A_0 values and monolayers' thicknesses of PAPEFs shows similar tendency to those of PAPHFs. This



k=0 : o-, p-PAPHF(M) ; M = 100n/m

k=1 : o-, p-PAPEF(M) ; M = 100n/m

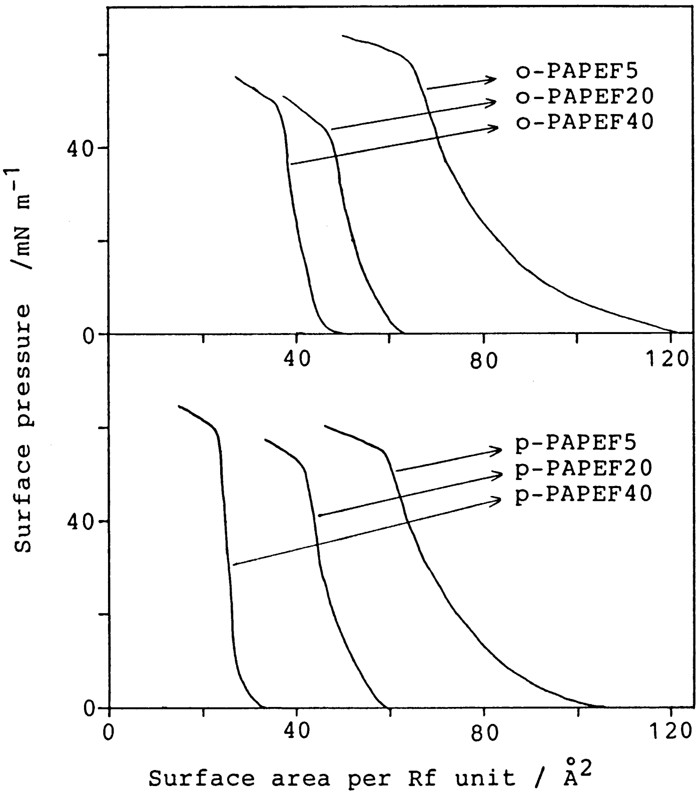


Fig. 1. F-A isotherms of o-,p-PAPEF.

Table 1. The limiting area of Rf unit A_0 /Å^2

PAPEF	o-	p-	PAPHF	o-	p-
PAPEF5	87	79	PAPHF5	87	71
PAPEF20	56	46	PAPHF20	63	32
PAPEF40	43	27	PAPHF40	45	11

Table 2. The monolayer's thickness /Å

PAPEF	o-	p-	PAPHF	o-	p-
PAPEF5	37	18	PAPHF5	27	20
PAPEF20	19	34	PAPHF20	18	22
PAPEF40	18	37	PAPHF40	17	57

indicate that the ordering of benzene ring of PAPEF is similar to that of PAPHFs, that is, the benzene ring is in lying position in o- isomer and standing up as the modification ratio becomes higher in p- isomer.$^{8)}$ And in the case of p-PAPEF40 Rf groups stand side by side, since A_0 value consists with the section area of Rf group (28Å^2).$^{4)}$ While, in the case of p-PAPHF40 A_0 value is smaller than the section area of Rf group, indicating that Rf groups are put one upon another.$^{8)}$

The γc values of Zisman plot were measured with n-alkanes on the LB films (1 layer) surface in usual manner.$^{4)}$ The γc values of o-PAPEF5, 20, 40 were 19.5, 17.7, 15.8 and those of p-PAPEF5, 20, 40 were 17.8, 14.8, 9.8 dyn cm^{-1}, respectively.

A plot of A_0 value versus γc value for p-PAPEFs and p-PAPHFs is shown in Figure 2, where, p-PAPHF40 is excepted since its film has different structure from others. p-PAPEFs indicate smaller γc values compared with p-PAPHFs at the same A_0 value, and the difference of γc values between both polymers becomes greater as the A_0 value becomes smaller. The γc value should be influenced by the molecular ordering in the film and also by the density of Rf groups. However, the LB films of p-PAPEFs have similar molecular ordering to that of p-PAPHFs as mentioned above, and the density of Rf groups on the LB films of both polymers is considered to be the same when both A_0 values are the same. Accordingly the difference in γc values is

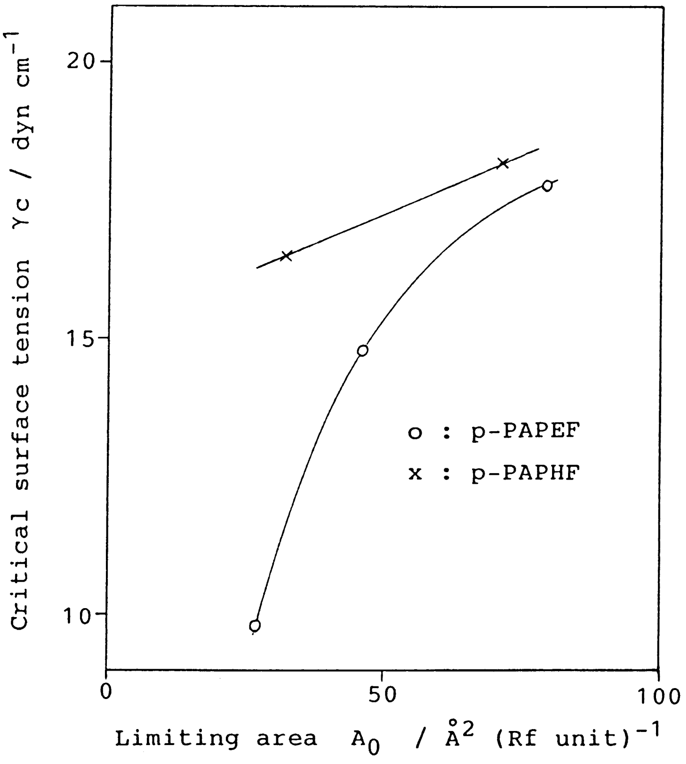


Fig. 2. A_0 - γc plot for p-PAPEFs and p-PAPHFs.

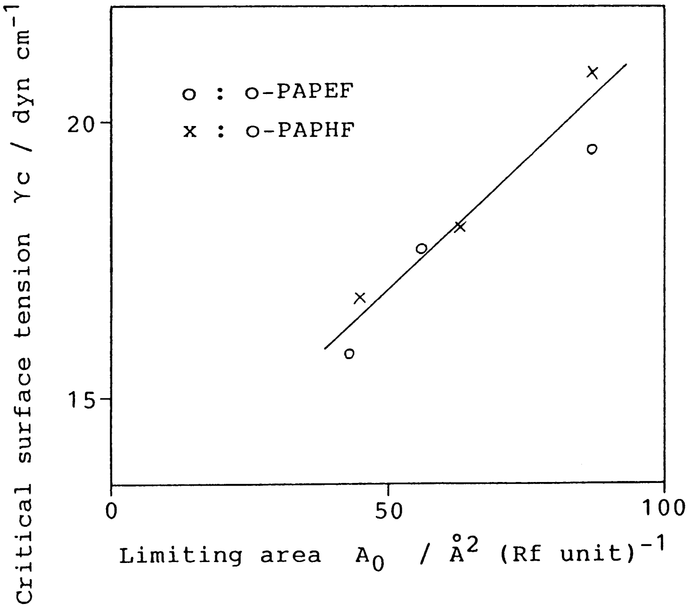


Fig. 3. A_0 - γc plot for o-PAPEFs and o-PAPHFs.

ascribed to the difference in molecular structure between p-PAPEFs and p-PAPHFs, that is, whether Rf groups are modified by ether bonds or not. In the case of p-PAPEFs, Rf groups and benzene rings are arranged in standing position and Rf groups are linked to benzene ring by flexible ether bonds, so that these Rf groups are assumed to have freedom of rotation at ether bonds enough to sweep wide area of the surface. Therefore, the properties of Rf groups should be reflected on the surface more effectively by flexibility of ether bonds to decrease the surface energy. When A_0 value is large, that is, when the density of Rf groups is low, Rf groups can not cover the surface sufficiently even if Rf groups rotate at ether bonds so that the decrease of the surface energy should be small. However, as A_0 value becomes smaller, more effectively Rf groups can cover the surface to afford very low γc value, less than 10 dyn cm^{-1}.

Figure 3 shows a plot of A_0 value versus γc value for o-PAPEFs and o-PAPHFs. The A_0 - γc plot for both polymers is almost on a straight line. This indicates that flexible ether bonds have no effect on the surface energy. In the case of o-PAPEFs, the benzene rings are assumed to be arranged in lying position. Consequently it is suspected that Rf groups can not sweep the surface so that the effect of ether bond disappear.

As mentioned above, we can clearly demonstrate the effect of ether bond in the polymer on the property of the LB film. Namely, flexibility of ether bond makes Rf group rotate freely to decrease the surface energy, and if flexibility of ether bond is restricted, this effect disappears. This effect should be brought about even if Rf groups are not contained, and be able to applied widely in preparing the materials which possess superior functions.

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