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Langmuir-Blodgett Films of Polyallylamine Modified with (Perfluoroalkyl)phenyl Groups

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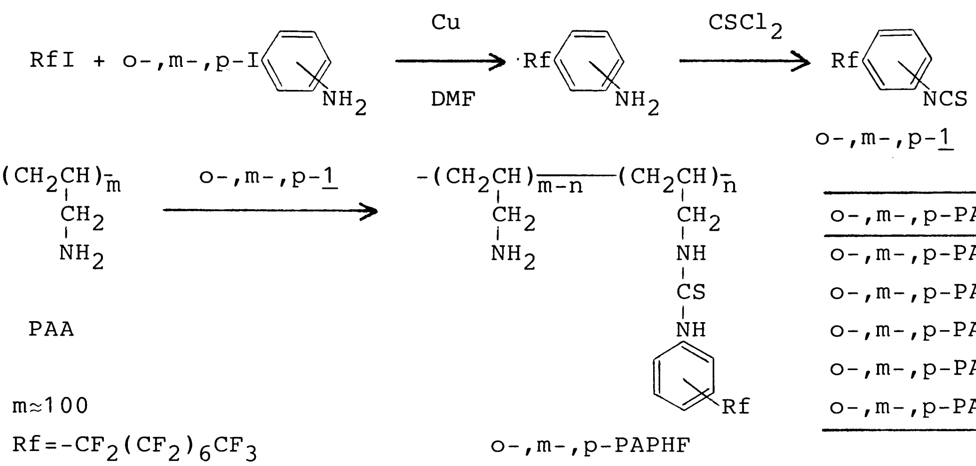
(Perfluoroalkyl)phenyl groups were introduced to polyallylamine by thiourea bonds. Langmuir-Blodgett (LB) films of the polymers were successfully prepared. Characterization of the films indicated that structural isomerism of substituted benzene has an effect upon the molecular ordering in the LB film and that the limiting area and critical surface tension of the LB films become smaller in the order, ortho, meta, and para isomers.

If fluorine atoms are introduced to the surface of the film, it shows excellent surface properties, such as water- and oil-repellency, low friction, insulation, and so on, because the fluorine atom has characteristic properties, the highest electronegativity of all atoms, very low polarizability, and so on. Accordingly if the surface of the film can be covered with functional groups containing fluorine atoms and if density or ordering of the functional groups can be controlled freely, it is possible to make the film which has new controlled surface properties coming from fluorine atoms. The Langmuir-Blodgett (LB) film has highly oriented molecular ordering and it is suitable for arrangement of functional groups. Therefore, the LB films of polymer containing perfluoroalkyl groups are expected as higher performance materials for surface coating, film separation, and so on, and some investigations were made.1,2) In the previous papers we have reported new type LB films of polymers to which long perfluoroalkyl chains were introduced by covalent bonds. The LB films of polyallylamine (PAA) modified by perfluoroacylation (PAAF) showed excellent low surface energy, and the ratio of perfluoroalkyl chain to the polymer had an effect on molecular ordering and the surface control was realized.3) Moreover, cross linked LB films were successfully prepared.4) When polyvinylamine (PVA) was used instead of PAA, the LB films of PVA modified by perfluoroacylation (PVAF) had quite different molecular ordering and the thickness of monolayer of the LB film was super thin.5) On the other hand, the LB films of PAA modified with perfluoroalkyl chains by urea bonds (PAAURF) have unusually thick monolayer.6) These results suggest that a slight structural difference of the polymer has a great influence upon the molecular ordering in the LB film.

In this paper we wish to report that LB films of new polymers modified with (perfluoroalkyl)phenyl groups by thiourea bonds were successfully prepared and that the molecular ordering of the LB film is influenced by structural isomerism of substituted benzene.

The perfluoroalkyl chain was introduced to benzene ring by Ullmann reaction and o-, m-, and p-(perfluorooctyl)anilines were synthesized. o-, m-, and p-(Perfluorooctyl)phenyl isothiocyanates were prepared from the corresponding (perfluorooctyl)anilines by the use of thiophosgene. Three types of the new polymers modified with each isomer of (perfluoroalkyl)phenyl group by thiourea bonds (o-, m-, and p-PAPHF) were synthesized by the reaction between PAA (Mw = 5200 — 6700)[7] and o-, m-, and p-(perfluorooctyl)phenyl isothiocyanates respectively. The reaction route is summarized in Scheme 1.



o-,m-,p-PAPHF	n/m
o-,m-,p-PAPHF5	0.05
o-,m-,p-PAPHF10	0.1
o-,m-,p-PAPHF20	0.2
o-,m-,p-PAPHF30	0.3
o-,m-,p-PAPHF40	0.4

Scheme 1. Synthesis of o-,m-,p-PAPHF.

The infrared spectra of these polymers were measured and ν_{C-F} absorption (1300 — 1100 cm^{-1}), ν_{C-H} (aromatic) absorption (3060 cm^{-1}), and ν_{N-H} absorption (3300 cm^{-1}) were observed. The modification ratio to amino groups in PAA could be controlled by the added amount of (perfluorooctyl)phenyl isothiocyanate, and the various modified polymers, n/m = 0.05 — 0.4 (o-, m-, and p-PAPHF5 — 40) were synthesized.

Figure 1 shows the surface pressure-area (F-A) isotherms for the monolayers of o-, m-, and p-PAPHF at 290 K. The monolayers of PAPHF were spread from the benzene / methanol (1 : 1) or benzene / trifluoroethanol (3 : 2 — 6 : 5) solution on the water surface. The stable monolayers were formed and the limiting areas (A_0) of perfluoroalkyl unit at zero pressure are shown in Table 1. The benzene ring is considered as a disk which have ca. 44 $Å^2$ area[8] and 3.4 Å thickness. The A_0 values of o-PAPHF are larger than the benzene ring's area, and it is assumed that the benzene ring is in lying position. On the other hand, in the cases of m- and p-PAPHF the A_0 values of higher modified polymers become smaller than the benzene ring's area, which suggests that the benzene ring is standing up as the modification ratio becomes higher. However the A_0 values are larger than the section area from the side direction of a benzene ring (ca. 25 Å^2)[8] except for p-PAPHF40, which indicates that the benzene ring does not stand quite vertically. Concerning the ordering of perfluoroalkyl chain, larger A_0 values than the section area of CF_2 chain (28 Å^2)[3] shows that perfluoroalkyl chain also does not stand quite vertically, except for p-PAPHF40. The A_0 value of p-PAPHF40 is smaller than both the section area from the side direction of a benzene ring and that of CF_2 chain, which shows that perfluoroalkyl chains are put one upon another.[6]

The deposition of monolayers of PAPHF was attempted under surface pressure of 20 mN m^{-1} on slide glasses, and Y type multilayers were obtained. The γc values of Zisman plot were measured with n-alkanes on the LB films (1 and 5 layers) surface in usual manner.[3] The results are summarized in Table 2. The γc values of 1 layer films are almost equal to those of 5 layer films, and the γc values decrease as the modification ratio of the polymers becomes higher. The γc values of m-PAPHF5 and p-PAPHF5 are close to that of polytetrafluoroethylene, 18.5 dyn cm^{-1}, which indicated that perfluoroalkyl chains almost lie on the surface. On the other hand, the γc values of o-PAPHF5 and o-PAPHF10 are higher than 18.5 dyn cm^{-1}. In these cases it is considered that the benzene ring or PAA has an effect on the surface of the films. When the polymers with the same modification ratio are compared, the γc value decreases in the order, ortho, meta, and para isomer. This suggests that perfluoroalkyl chains are arranged more vertically in this order.

The monolayer's thickness of these films was measured by the X-ray diffraction. The results are summarized in Table 3. The monolayer's thickness of

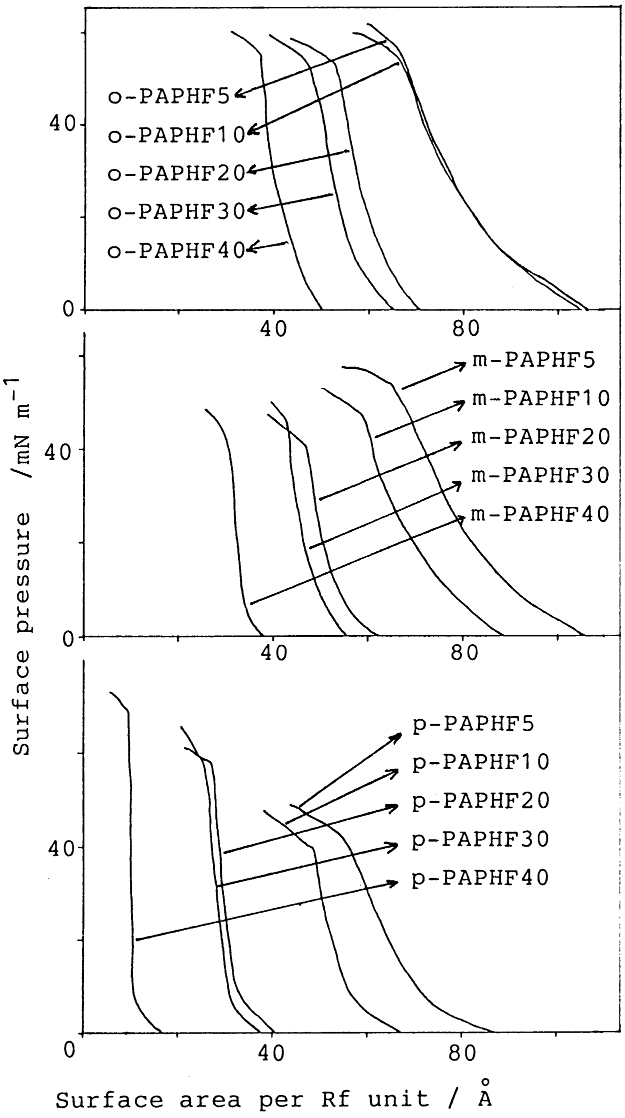


Fig. 1. F-A isotherms of o-,m-,p-PAPHF.

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

PAPHF	o-	m-	p-
PAPHF5	87	88	71
PAPHF10	87	74	57
PAPHF20	63	54	32
PAPHF30	57	48	31
PAPHF40	45	33	11

Table 2. The γc values of the PAPHF LB films /dyn cm^{-1}

	o-		m-		p-	
PAPHF	1Lay	5Lay	1Lay	5Lay	1Lay	5Lay
PAPHF5	20.9	20.8	18.7	18.7	18.2	18.2
PAPHF10	19.9	19.4	17.8	17.8	17.6	16.9
PAPHF20	18.1	18.0	17.4	16.9	16.5	16.1
PAPHF30	17.4	17.1	16.2	16.1	15.2	15.1
PAPHF40	16.8	16.8	15.7	15.4	16.3	16.1

Table 3. Monolayer's thickness of the PAPHF LB films /Å

PAPHF	o-	m-	p-
PAPHF5	27	21	20
PAPHF10	19	24	35
PAPHF20	18	22	22
PAPHF30	17	21	22
PAPHF40	17	16	57

o-PAPHF are almost smaller than 20 Å, while those of m-PAPHF and p-PAPHF are thicker than o-PAPHF. Thinner monolayer of o-PAPHF indicated that (perfluoroalkyl)phenyl groups are arranged in a leaning position compared with m-PAPHF and p-PAPHF.

It is assumed that small angle between the perfluoroalkyl chain and thiourea group of o-PAPHF makes the perfluoroalkyl chain difficult to stand vertically, and that the perfluoroalkyl chain is more easy to stand vertically as this angle becomes larger.

References

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7) PAA is obtained by neutralization of polyallylamine hydrochloride ; see Ref. 3.
8) The area and the section area from the side direction of benzene ring are calculated from its molecular model.

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