CHEMISTRY LETTERS, pp. 1277-1280, 1988.

Langmuir-Blodgett Films of Polyallylamine Modified with Long Perfluoroalkyl Chains by Urea Bonds.

Novel LB Films of Highly Fluorinated Polymer

Masanori TAMURA, Hiroyasu ISHIDA, and Akira SEKIYA*
National Chemical Laboratory for Industry,
Higashi, Tsukuba, Ibaraki 305

Long perfluoroalkyl chains were introduced to polyallylamine by urea bonds. Langmuir-Blodgett films of the polymers were successfully prepared even in the case of highly fluorinated polymer. Characterization of the films indicated that highly fluorinated polymer shows the unusually small limiting area and thick monolayer.

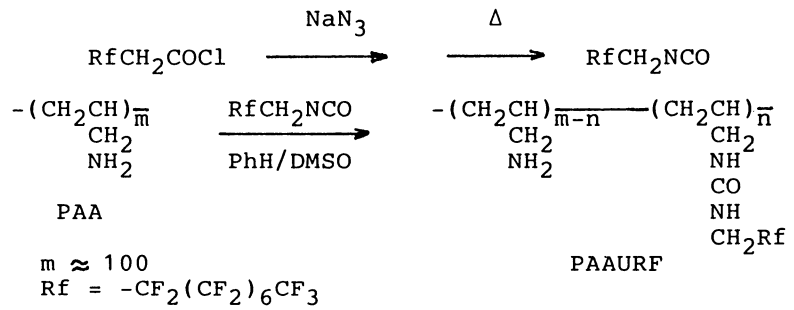
Polymer Langmuir-Blodgett (LB) films are expected as very useful material for functional membranes because they are uniform ultra-thin films which have higher thermal and mechanical stability compared with monomeric ones and highly oriented molecular ordering. Especially LB films of polymer containing long perfluoroalkyl chains have excellent properties, such as water- and oil-repellency, low friction, insulation, and so on, which are characteristic of long perfluoroalkyl chains.1)

Recently some investigations were made concerning the LB films of polymer containing long perfluoroalkyl chains. Ringsdorf et al. reported photopolymerization of monomeric LB films.2) Kunitake et al. showed LB films of ion complex which consist of anionic polymer and cationic monomers containing perfluoroalkyl chains,3) and on the other hand, Fujihira et al. reported different ion complex type LB films of cationic polymer and anionic monomers containing perfluoroalkyl chains.4) But further investigations are desired in order to obtain more stable films which have novel molecular ordering.

In our research the LB films of polyallylamine (PAA) modified with perfluoroalkyl chains by amide bonds (PAAF) were reported.[5,6] These films 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. However it was found that PAAF could not be preserved in the solution because the amide bonds of PAAF were gradually hydrolyzed.

In this paper we wish to report that LB films of new polymers modified with perfluoroalkyl chains by urea bonds were successfully prepared and that in the case of highly modified polymers the LB films had the unusually small limiting areas and thick monolayers.

1,1-Dihydroperfluorononyl isocyanate was prepared from corresponding acid chloride by Curtius reaction. The new polymers modified with perfluoroalkyl chains by urea bonds (PAAURF) were synthesized by the reaction between PAA (Mw = 5200 — 6700)[7] and 1,1-dihydroperfluorononyl isocyanate in the mixed solvent of benzene and dimethylsulfoxide(3 : 5). The reaction route is summarized in Scheme 1. The structure of these polymers were determined by the infrared spectrum (urea absorptions at 1660, 1585 cm^{-1}) and the elemental analysis. The modification ratio to amino groups in PAA could be controlled by the added amount of 1,1-dihydroperfluorononyl isocyanate, and the various modified polymers, n/m = 0.12, 0.16, 0.24, 0.38, 0.58 (PAAURF12, 16, 24, 38, 58) were synthesized. These polymers were insoluble in usual organic solvents, but soluble in trifluoroethanol even though the modification ratio was high,[8] and the solution could be preserved.



$RfCH_2COCl \xrightarrow{NaN_3} \xrightarrow{\Delta} RfCH_2NCO$

$-(CH_2CH(CH_2NH_2))_m- \xrightarrow[PhH/DMSO]{RfCH_2NCO} -(CH_2CH(CH_2NH_2))_{m-n}-(CH_2CH(CH_2NHCONHCH_2Rf))_n-$

n/m	PAAURF
0.12	PAAURF12
0.16	PAAURF16
0.24	PAAURF24
0.38	PAAURF38
0.58	PAAURF58

Scheme 1. Synthesis of PAAURF.

Figure 1 shows the surface pressure-area (F-A) isotherms for the monolayers of PAAURF12, 16, 24, 38, and 58 at 290 K. The monolayers of PAAURF's were spread from the benzene / trifluoroethanol (3 : 2 — 2 : 1) solution (2.4 — 8.6

x 10^{-4} mol dm^{-3}) on the water surface. The monolayers were stable up to more than 55 mN m^{-1} and the limiting area (A_0) of perfluoroalkyl unit at zero pressure for PAAURF12, 16, 24, 38, and 58 were 40, 28, 14, 13, and 12 Å^2, respectively. The A_0 value of PAAURF16 equals to the section area of CF_2 (28 Å^2).[5] This indicated that perfluoroalkyl chains stand side by side vertically. The larger A_0 value of PAAURF12 indicated that perfluoroalkyl chains lean somewhat. On the other hand, the A_0 value of highly modified PAAURF24, 38, 58 were lower than the section area of CF_2, which shows that perfluoroalkyl chains are put one upon another.

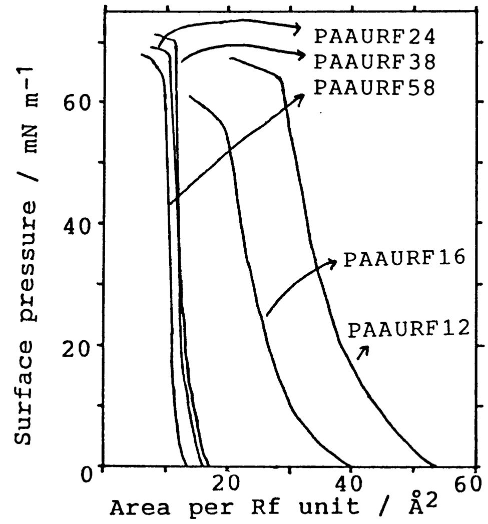


Fig. 1. F-A isotherms of PAAURF.

The deposition of these surface monolayers of PAAURF's was attempted at 20 mN m^{-1} on slide glasses, and Z type multilayers were obtained in almost all cases.[9] The γc values of Zisman plot were measured with n-alkanes on the LB films (1 and 3 layers) surface in usual manner.[5,10] The results are summarized in Table 1. The γc values of 1 layer films of PAAURF's are about 16 dyn cm^{-1}, and that of 3 layers are about 15 dyn cm^{-1}. These γc values are lower than that of polytetrafluoroethylene, 18.5 dyn cm^{-1},[10] which indicates that CF_3 groups (the end of perfluoroalkyl chain) exist on the surface of the films.

The monolayer's thickness of these films was measured by the X-ray diffraction[11] and Talystep (Rank Taylor Hobson Co., Ltd.) with a needle of point size 125 Å. The results are summarized in Table 2. The monolayer's thickness of polymers less modified with perfluoroalkyl chains, PAAURF12 and 16, are about 30

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

PAAURF	1 Lay	3 Lay
PAAURF12	16.6	15.5
PAAURF16	16.3	15.1$^{a)}$
PAAURF24	16.1	15.3
PAAURF38	15.9	14.8
PAAURF58	15.5	14.5

a) 5 Lay.

Table 2. Monolayer's thickness of the PAAURF LB films / Å

PAAURF	X-Ray	Talystep
PAAURF12	30	20~30
PAAURF16	35	20~35
PAAURF24	70	30~50
PAAURF38	80	70~120
PAAURF58	80	80~110

Å. Compared with these values, the monolayer's thickness of higher modified polymers, PAAURF24, 38, and 58, are thicker, more than 70 Å.

These results suggest the following conclusion. In the LB films of the less modified polymers (PAAURF12 and 16) perfluoroalkyl chains stand side by side on the hydrophilic PAA chain expanding on the surface, vertically in PAAURF16, and lean somewhat in PAAURF12. On the other hand, in the case of higher modified polymers (PAAURF24, 38, and 58) many perfluoroalkyl branches sterically made the change of PAA chain's conformation difficult and the interaction between PAA chain and the water surface was weakened because the branches covered PAA chain. Accordingly PAA chain could not expand on the surface and was bent at some points and folded as a whole. This reflects the low A_0 values and the thick monolayers.

References

1) W. A. Zisman, Adv. Chem. Series, 43, 1 (1976).
2) R. Elbert, T. Folda, and H. Ringsdorf, J. Am. Chem. Soc., 106, 7687 (1984).
3) N. Higashi, T.Kunitake, and T. Kajiyama, Polym. J., 19, 289 (1987).
4) H. Yamada, Y.Goto, and M. Fujihira, 54th National Meeting of the Chemical Society of Japan, Tokyo, April 1987, Abstr., No. 3VII42.
5) A. Sekiya, H. Ishida, M. Tamura, and M. Watanabe, Chem. Lett., 1987, 1593.
6) A. Sekiya, M. Tamura, M. Watanabe, and H. Ishida, Chem. Lett., 1988, 527.
7) PAA is obtained by neutralization of polyallylamine hydrochloride; see Ref. 5.
8) Highly fluorinated polymer is difficult to dissolve in solvents. For example, see Ref. 5.
9) In the case of PAAURF16 Y type multilayer was obtained. References 5 and 6 indicated that both Y and Z type LB films had been obtained under slightly different conditions of the deposition of surface monolayers in the case of PAAF. Similarly in this case it is suspected that Z type LB film can be obtained by subtle change of the conditions.
10) Y. Kitazaki, Hyoumen, 14, 116 (1979).
11) The weak and broad diffraction peaks were observed in the X-ray diffraction. The values in Table 2 are approximate estimates from the broad peaks.

(Received April 21, 1988)