

Monolayer Behavior of Poly(*N*-decylacrylamide-*co*-*N*-1*H*, 1*H*-pentadecafluorooctylacrylamide) on Water and Surface Characterization of Their Langmuir–Blodgett Films

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ABSTRACT: The spreading behaviors of poly(*N*-decylacrylamide-*co*-*N*-1*H*, 1*H*-pentadecafluorooctylacrylamide) (DAPF) copolymers with various copolymer compositions at the air–water interface were investigated by measurement of surface pressure–surface area isotherms to prepare a high quality fluorinated polymer Langmuir–Blodgett (LB) film for developing a new type of solid lubricant. The monolayer property depended strongly on the copolymer composition. The copolymer monolayers can be transferred onto solid substrates giving uniform polymer LB films. The surface wettability and the critical surface tensions of the LB films were investigated by measuring the contact angle (θ) of a water droplet on the surface. The friction coefficients of the LB films were measured as a function of the copolymer composition. The friction coefficient for the DAPF copolymer LB films decreases with the content of *N*-decylacrylamide (DA). The frictional properties in the copolymer LB films are discussed from various factors, such as packing density and chemical composition.

KEY WORDS Polymer Langmuir–Blodgett (LB) Film / Acrylamide / Friction / Surface Tension / Fluorocarbon /

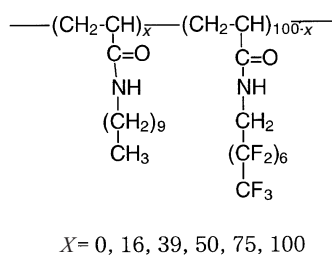
Recently, in order to reduce friction and wear which are one of the most important requirements for improving the performance of moving components in many technological devices, various kinds of lubricants have been developed. Many experimental and theoretical studies have been carried out on the rheology and tribology of ultrathin lubricant films composed of organic molecules.^{1–5} Since the Langmuir–Blodgett (LB) technique is known to provide organic ultrathin films with controlled thickness of molecular scale and with well-defined molecular orientation,⁶ the surface improvement of solid substrate with LB films is receiving much attention in surface nanotechnology. Molecularly smooth surface of LB films is especially expected for application to no-wear and low frictional lubricant in high-density magnetic recording systems, where it is essential that the spacing between the magnetic layer and the recording head is desired to be very thin, typically no more than 10 nm. There are many studies describing the use of LB films for lubricants.^{7–9} Moreover, in the experiments using LB films, it has been achieved to measure friction on an atomic resolution by atomic force microscopy (AFM). Overney and co-workers reported that the frictional force on fluorocarbon areas is about three or four times as large as on hydrocarbon areas in the friction measurement of the phase-separated mixed LB films with C₉F₁₉–C₂H₄–O–C₂H₄COOH and C₁₉H₃₉COOH on Si surface.^{10–13}

Briscoe and Evans¹⁴ also found that the frictional force divided by the real area of contact shear on partially fluorinated carboxylic acids is about five times as large as that of hydrocarboxylic acids. It is concluded that the frictional force of perfluorocarbon and semifluorocarbon compounds are larger than those of hydrocarbons although perfluorinated polymers are widely used as low frictional lubricants.^{15–17} This is also supported by the studies of theoretical calculations.^{18, 19}

Polymer LB films have higher thermal and mechanical stability and high resistance to dissolution by organic solvents compared with low molecular weight LB film.²⁰ In previous works, we have found that polyacrylamide structure is suitable for stable LB film formation due to the self assemble property based on hydrogen bonding.^{21–23} We have succeeded in the preparation of a series of poly(*N*-perfluoroalkylacrylamide) LB films in order to utilize them for an ultrathin lubrication film of hard-disk with higher storage density.^{24, 25} In the fluorinated acrylamide polymer LB films, very low critical surface energy characteristic of highly orientation of the perfluoroalkyl chains and of the surface covered by CF₃ were observed.²⁴ The friction coefficient of the fluorinated polymer LB films decrease with the perfluorocarbon chain length.²⁴

In the present work, the monolayer properties of the copolymers of *N*-decylacrylamide (DA) and *N*-1*H*, 1*H*-pentadecafluorooctylacrylamide (PF) with various copolymer compositions (Figure 1) were investigated

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$$X = 0, 16, 39, 50, 75, 100$$

Figure 1. Chemical structure of poly(*N*-decylacrylamide-*co*-*N*-1*H*,1*H*-pentadecafluorooctylacrylamide) copolymers.

by surface pressure–area isotherms. The surface properties, such as critical surface tension and frictional force response, of the LB films are discussed as a function of the copolymer composition aiming at finding a new solid lubricant film.

EXPERIMENTAL

Materials

The preparation of *N*-1*H*,1*H*-pentadecafluorooctylacrylamide and *N*-decylacrylamide monomers are described in detail in previous papers.^{21,24} All of the homopolymers and copolymers were prepared by free radical polymerization in tetrahydrofuran at 60°C with α,α -azobis(isobutyronitrile) as an initiator. The polymers were purified by reprecipitation from a tetrahydrofuran or freon solution into a large excess of methanol and dried under vacuum at room temperature. Molecular weights were determined by a Toyo Soda gel permeation chromatography (GPC) using a polystyrene standard. The mole fractions of DA in the copolymers were determined by element analysis.

Monolayer and LB Films Formation

Measurement of surface pressure (π)–area (A) isotherms and the deposition of monolayer were carried out with a computer-controlled Langmuir trough (FSD-110, USI). Distilled water with a resistivity of higher than 17 M Ω cm purified by a Milli-QII system was used. The polymers for π -A isotherm measurement were dissolved into freon. Appropriate amounts of the solution (0.2 mL) were spread on a water surface at 20°C, and then the monolayers formed were compressed at a speed of 14.0 cm² min⁻¹. The condensed monolayer on the water surface were transferred onto a hydrophobic slide glass at a surface pressure of 30 mN m⁻¹. Glass slides, on which LB multilayers are deposited, were cleaned in a boiling HNO₃ and made hydrophobic with trichloromethylsilane.

Measurements

Contact angle measurements were carried out at 30 s after dropping distilled water onto the surfaces of LB

Table I. Copolymers of DA and PF with various copolymer compositions

Polymer	DA content		
	(mol%)	$M_n (\times 10^4)$	M_w/M_n
PolyPF	0	–	–
DAPF-16	16	–	–
DAPF-39	39	2.87	2.9
DAPF-50	50	1.93	3.3
DAPF-75	75	1.08	2.2
PDA	100	1.23	2.3

films with 6 layers at 20°C in ambient humidity with a CA-X contact angle meter (Kyowa Kaimen Kagaku). The contact angles were the average of three measurements at different positions for one sample. The advancing angles were determined immediately by injecting a 5 μ L liquid drop, and the static contact angles were read from a drop of 5 μ L solvent in the surface. The contact angles for droplets of various alkanes such as hexane, octane, decane, dodecane, and tetradecane on the LB films were measured to obtain critical surface tension (γ_c). The value of γ_c was determined by extrapolating a linear regression analysis of the data to $\cos \theta = 1.00$ (Zisman plot).²⁶

The frictional force of the polymer LB films were measured with a back-to-forth sliding friction meter (HEIDON14D, Shintoukagaku) using a sapphire tip at a sliding speed of 1.0 mm s⁻¹ under a loading weight of 10 g in eleven transits. The LB film with 2 layers onto a hydrophobic slide glass were used as a sample. The kinetic friction coefficients (μ) of the polymer LB films were calculated by dividing the average frictional force (F) in the tenth transit by the loading weight (W), *i.e.*, $\mu = F/W$.

RESULTS AND DISCUSSION

Monolayers of poly(*N*-Decylacrylamide-*N*-1*H*,1*H*-pentadecafluorooctylacrylamide) Copolymers at the Air-Water Interface and LB Film Formation

Poly(*N*-decylacrylamide-*co*-*N*-1*H*,1*H*-pentadecafluorooctylacrylamide) with various copolymer compositions were prepared by radical copolymerization (Table I). The copolymers with the DA content less than 16% were insoluble in usual organic solvents such as tetrahydrofuran. The copolymers dissolved in a fluorinated solvents (freon) were spread on the water surface at 20°C for π -A isotherm measurement. The π -A isotherms show that the monolayer properties vary with the copolymer compositions (Figure 2). It is clear that the isotherm curves are shifted toward smaller surface area with increasing DA mol%, accompanied by a decrease in collapse pressure. No hysteresis behavior was observed in the isotherms. The limiting surface

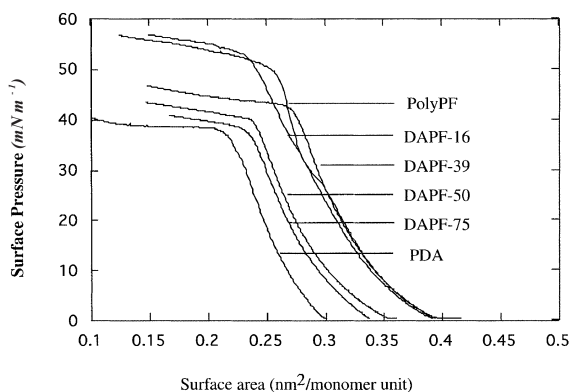


Figure 2. Surface pressure–area isotherms of (a) PolyPF, (b) DAPF-16, (c) DAPF-39, (d) DAPF-50, (e) DAPF-75, and (f) PDA at 20°C.

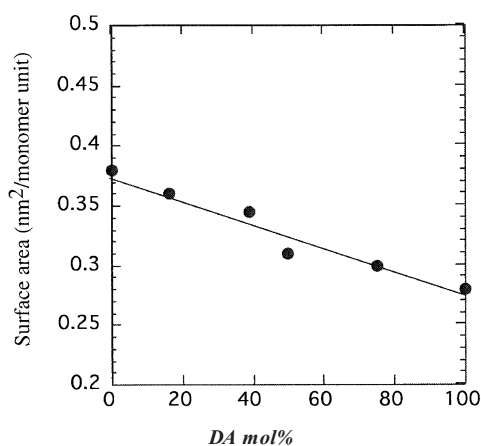


Figure 3. Change of surface area for DAPF copolymers as a function of the DA composition.

area per repeating unit can be obtained by extrapolation of a linear part of the isotherm to zero pressure. It is of interest that a linear relationship between the surface area and DA mol% was obtained (Figure 3), that is, an ideal mixing of DA and PF monomers in the monolayer occurs. This indicates that both monomer unit have their respective molecular occupied surface areas in the monolayers and the copolymer chains do not form an entangled or coiled form on the water surface. The copolymer monolayers were transferred onto a solid support, giving the polymer LB films. The copolymers except of DAPF-50 were transferred onto a solid support with both down and up strokes with a transfer ratio of nearly unity giving a Y-type LB films. The DAPF-50 monolayer was transferred only with down stroke with a transfer ratio of unity giving a X-type LB film.

Wettability of Copolymer LB Films

The wettability of surface of the copolymer LB films on a glass slide was investigated by measurement of advancing and static contact angles of a water droplet on the LB films. The LB films with six layers were

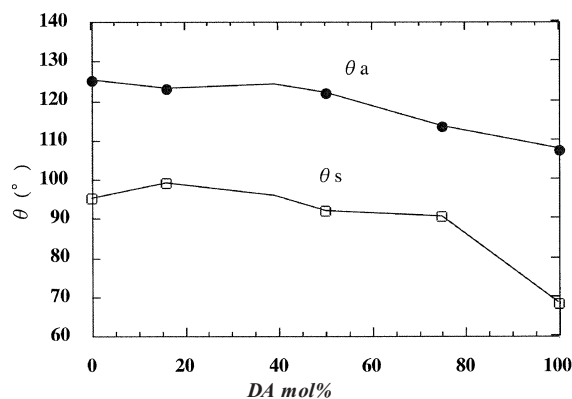


Figure 4. Contact angles of DAPF LB films as a function of the DA composition (θ_a and θ_s are the advancing and static contact angles, respectively).

employed as samples. Figure 4 shows the contact angles of the copolymer LB films as a function of DA content. The contact angle increases by introduction of PF monomer, meaning that the surface becomes more hydrophobic. The contact angle, however, becomes nearly constant for the copolymers with more than 40 mol% PF. The surface of the copolymer LB films shows higher contact angle (122°) and more hydrophobic than the surface of polytetrafluoroethylene (115°), of which surface is known to be covered with $-\text{CF}_2$ group. The higher water contact angles for the surface of the copolymer LB films with more than 40% PF are predominantly contributed from $-\text{CF}_3$ group.

In order to obtain the critical surface tension (γ_c) of the copolymer LB films, the contact angles for droplets of various alkanes such as hexane, octane, decane, dodecane, and tetradecane on the LB films were measured. A good linear relationship between the contact angle and the surface tension of the alkane molecule employed was observed for all the copolymer LB films (Figure 5). By extrapolation of the line to $\cos \theta = 1.0$, the critical surface tensions (γ_c) can be estimated to be 11, 12, 14, and 16 mN m^{-1} for the DAPF-16, DAPF-39, DAPF-50, and DAPF-75 LB films, respectively. These values are lower than that of polytetrafluoroethylene (18 mN m^{-1}).²⁶ The low critical surface tensions support that the polyfluoroalkyl chains are closely packed in the copolymer LB films.

Frictional Property of Copolymer LB Films

The frictional force response of the copolymer LB films were measured with a back-to-forth sliding friction meter using a sapphire tip at a sliding speed of 1.0 mm s^{-1} under a loading weight of 10 as shown in Figure 6. Figure 7 shows the frictional force response for the DAPF-50 LB film with 2 layers deposited on a glass substrate as a typical example when a sapphire tip under a loading weight of 10 as shown in Figure 6 slides

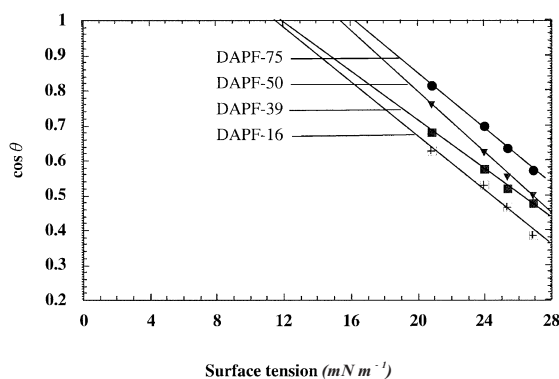


Figure 5. A linear relationship between the contact angles of copolymer LB films and the surface tension of *n*-alkane molecules.

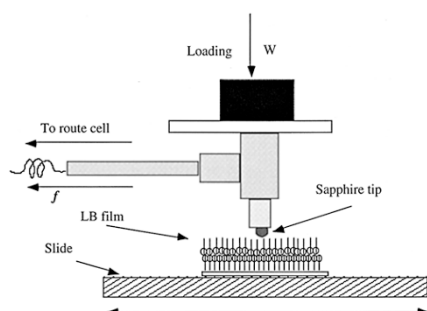


Figure 6. A schematic illustration for friction force measurement.

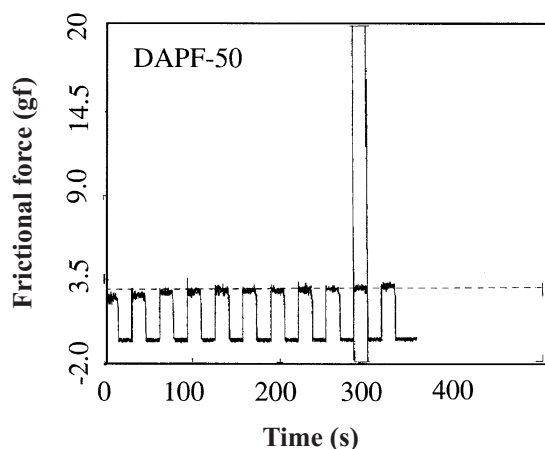


Figure 7. A typical frictional force response of DAPF-50 LB films.

back-to-forth in eleven times of transits. It is clear that the frictional forces are stable during sliding and independent of the number of transits, keeping a constant force. A surface with fair smoothness and toughness is formed in the copolymer LB films. In order to investigate the lubricating durability in detail, we examined the influence of repeating cycle of sliding on the friction coefficients of polyPF, DAPF-16, and DAPF-36 LB films (Figure 8). The friction coefficient of polyPF LB film gradually increases after about 200-time transits, indicating that the surface becomes rough. This is attributed to removal of LB films from the substrates

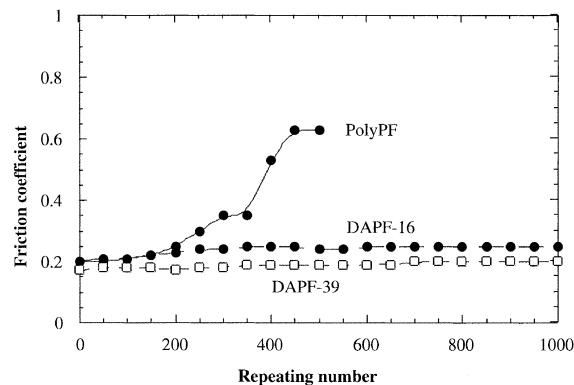


Figure 8. Kinetic friction coefficients of polyPF, DAPF-16, and DAPF-39 LB films as a function of the number of repeating transits. Loading weight: 10 g.

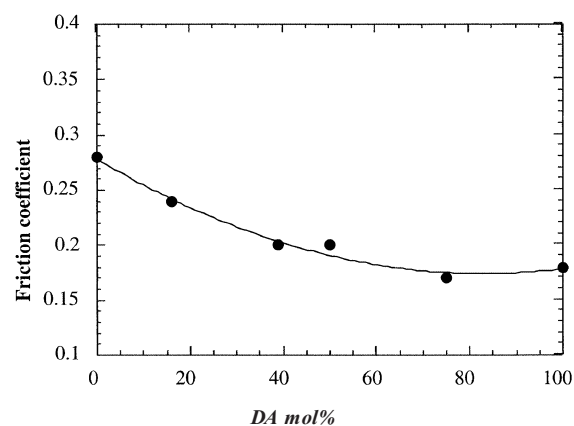


Figure 9. Kinetic friction coefficients of DAPF copolymer LB films as a function of the DA composition.

during the transits. On the other hand, the friction coefficients of the DAPF-16, and DAPF-36 LB films remain almost constant, indicating higher durability of the copolymer LB films, compared with the fluorinated homopolymer. The lower durability of the PolyPF LB film is attributed to peeling off from the substrate because of the weak interaction of fluorinated polymer with glass slide. The improvement of durability by the copolymer is explained by increase in the interaction between the copolymer and the glass by adhesive force that is derived from the hydrocarbon chains.

Figure 9 shows the kinetic friction coefficient of the copolymer LB films as a function of DA mol%. Apparently, the friction coefficient decreases with increasing DA mol%. It is of interest that the coefficient is reduced from 0.28 of polyPF to 0.24 in the presence of only 16% DA monomer. The decrease in the friction coefficient by the introduction of hydrocarbon into fluorinated compound is consistent with the theoretical calculation^{18,19} and experimental results^{10–13} obtained by AFM method: the frictional forces of perfluorocarbon and semifluorocarbon chain surface are larger than those of hydrocarbons. Despite the fact that

fluorocarbon-based materials exhibit higher frictional coefficients than analogous hydrocarbon-based materials, fluorocarbons are used as lubricants because of their high chemical, thermal, and mechanical stability.

A number of molecular-level phenomena such as packing density,^{4,5} local disorder,²⁷ and chemical structure¹⁷ have been proposed to account for higher frictional properties in fluorinated films. As shown in Figure 3, the surface area per repeating unit decreases linearly with DA mol%. The additional rule of the respective monomer area is kept. This indicates that the molecular packing density is almost the same with all the copolymer monolayers, irrespective of the copolymer compositions. All the copolymer monolayers are keeping a condensed state. From the fact, the decrease in the friction coefficient with DA content is not explained in terms of the molecular packing. In the present study, the friction coefficient apparently decreases with increasing DA mole fraction. It is explained by the fact that the hydrocarbon is more flexible and the deformation energy is lower than the corresponding fluorocarbon in the case where the friction force is determined by the deformation of molecule in the surface.

CONCLUDING REMARKS

We synthesized a series of poly(*N*-decylacrylamide-*co-N*-1*H*,1*H*-pentadecafluorooctylacrylamide) copolymers that exhibit a good resistance to dissolution by organic solvents while DA content in copolymers is low. The copolymers with a wide range of composition form a stable monolayers on the water surface and the monolayers can be easily deposited onto solid substrates yielding the polymer LB films. The surface properties such as wettability and friction force varied with the copolymer composition. The surface of the copolymer LB films becomes more hydrophobic and lower critical surface energy by the introduction of PF monomer. On the other hand, the friction coefficient decreases with DA content and also the durability in the friction measurement is improved by the introduction of DA monomer. A new type of solid lubricant thin film that has not only a low friction but also low-energy, rupture resistance and high resistance to organic solvents can be expected to the copolymer LB films with

the copolymer composition precisely controlled.

REFERENCES

1. Z. Suzuki, Y. Saotome, and M. Yanagisawa, *Thin Solid Films*, **160**, 453 (1988).
2. T. Miyamoto, R. Kaneko, and T. Andoh, *ASMEJ Tribology*, **112**, 567 (1990).
3. S. Miyaki and R. Kaneko, *Thin Solid Films*, **212**, 256 (1992).
4. V. DePalma and N. Tillman, *Langmuir*, **5**, 868 (1989).
5. M. K. Chaudhury and M. J. Owen, *Langmuir*, **9**, 29 (1993).
6. G. Roberts, "Langmuir–Blodgett Films", Plenum Press, New York, N.Y., 1990.
7. A. I. Bailey and J. S. Courtney-Pratt, *Proc. R. Soc. London, Ser. A*, **227**, 500 (1955).
8. V. Novotny and J. D. Swalen, *Langmuir*, **5**, 485 (1989).
9. J. N. Israelachvili and D. Tabor, *Wear*, **24**, 386 (1973).
10. R. M. Overney, E. Meyer, J. Frommer, H. J. Guntherodt, G. Decher, J. Reibel, and U. Sohling, *Langmuir*, **9**, 341 (1993).
11. R. M. Overney, E. Meyer, J. Frommer, D. Brodbeck, R. Luthi, L. Howald, H. J. Guntherodt, M. Fujihira, H. Takano, and Y. Goton, *Nature*, **359**, 133 (1992).
12. R. M. Overney, E. Meyer, J. Frommer, H. J. Guntherodt, M. Fujihira, H. Takano, and Y. Goton, *Langmuir*, **10**, 1281 (1994).
13. R. M. Overney, H. Takano, M. Fujihira, E. Meyer, and H. J. Guntherodt, *Thin Solid Films*, **240**, 105 (1994).
14. B. J. Briscoe and D. C. Evans, *Proc. R. Soc. London, Ser. A*, **380**, 389 (1982).
15. O. Levine and W. A. Zisman, *J. Phys. Chem.*, **61**, 1188 (1957).
16. S. Yamada and J. Israelachvili, *J. Phys. Chem. B*, **102**, 234 (1998).
17. H. I. Kim, T. Koini, T. R. Lee, and S. S. Perry, *Langmuir*, **13**, 7192 (1997).
18. A. Koike and M. Yoneya, *J. Chem. Phys.*, **105**, 6060 (1996).
19. A. Koike and M. Yoneya, *Langmuir*, **13**, 1718 (1997).
20. T. Miyashita, *Prog. Polym. Sci.*, **18**, 263 (1993).
21. T. Miyashita, Y. Mizuta, and M. Matsuda, *Br. Polym. J.*, **22**, 329 (1990).
22. Y. Mizuta, M. Matsuda, and T. Miyashita, *Langmuir*, **9**, 1158 (1993).
23. T. Miyashita, X. D. Li, and A. Aoki, *Polym. J.*, **27**, 1154 (1995).
24. X. D. Li, A. Aoki, and T. Miyashita, *Langmuir*, **12**, 5444 (1996).
25. F. Fan, X. D. Li, and T. Miyashita, *Thin Solid Films*, **348**, 238 (1999).
26. W. A. Zisman, *Adv. Chem. Ser.*, **43**, 1 (1964).
27. X. Xiao, J. Hu, D. H. Charych, and M. Salmeron, *Langmuir*, **12**, 237 (1996).