Preparation and Characterization of Poly(*N*-1H,1H-pentadecafluorooctylmethacrylamide) Langmuir–Blodgett Film

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ABSTRACT: The monolayer behavior of poly(*N*-1H,1H-pentadecafluorooctylmethacrylamide) (pC7F15MAA) spread on the air–water interface was investigated by measurement of surface pressure–area isotherm at different sub-phase temperatures. The monolayer of pC7F15MAA was transferred onto solid substrates as Y-type Langmuir–Blodgett (LB) film and the monolayer thickness was calculated by X-Ray diffraction techniques and surface plasmon measurements. Wettability and the surface structure of the LB film were investigated by measuring the static contact angle ($\cos \theta$) of water on the surface. The wettability varied slightly with increasing temperature. The critical surface tension measurement suggests that the surface of pC7F15MAA LB film covered mainly with CF₃ groups.

KEY WORDS Langmuir–Blodgett Film / Fluorinated Polymer / Surface Plasmon Resonance / Wettability /

The Langmuir–Blodgett (LB) technique is an excellent method for preparation of ultrathin films with controlled thickness at a molecular size and well-defined molecular orientation.¹ Recently, polymeric LB films have received much attention due to their superior mechanical and thermal stability than those of low molecular weight LB films² and the applications especially in the fields of coatings, optics, and electronics have been discussed.^{3,4} The simplest method to fabricate the polymeric LB film is by deposition of preformed polymer monolayers.^{5–7} For the fabrication of polymeric LB films, comb-like polymers with well-defined hydrophilic groups and hydrophobic hydrocarbon side chains are mostly studied.^{8–14} Monolayer formation and LB film preparation in these polymers are determined by the balance of hydrophilic and hydrophobic interactions.

Langmuir–Blodgett films of comb-like polymers with fluorocarbon side chains are attracting much recent attention due to their characteristic properties such as low friction, excellent insulation, excellent durability, and so on.^{15,16} The fluorocarbon chains are also hydrophobic and have rigid character (stiffness of the C–F bond), which are suitable factors for stable monolayer formation. However, the deposition of the monolayer on solid substrates is difficult because of the weak interactions among the monolayer due to the low surface energy of fluorinated materials. Nonetheless, a few papers have been reported about monolayers and the fabrication of LB films from comb-like polymers with fluorocarbon side chains.^{17–21} In previous works, we have found that polyacrylamide struc-

Figure 1. Structural formula of poly(*N*-1H,1H-pentadecafluorooctylmethacrylamide) (pC7F15MAA).

ture is suitable for stable LB film formation due to the self-assembly property based on hydrogen bonding of amide group.^{14,22,23} Using this excellent property of the acrylamide backbone, we have demonstrated that poly(*N*-fluoroalkylacrylamide)s form stable monolayers at the air–water interface and fairly uniform polymer LB films can be easily prepared.²⁴ In this work, we investigated the spreading behavior of poly(*N*-1H,1H-pentadecafluorooctylmethacrylamide) (Figure 1) on the water surface to prepare stable polymer LB film and tried to determine its monolayer thickness by X-ray diffraction method and surface plasmon resonance measurements. The surface of the resulting polymer LB film was characterized by wettability measurements, and the surface structure was evaluated from the critical surface tension measurement.

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EXPERIMENTAL

Materials

AK-225 (a mixture of $\text{CF}_3\text{CF}_2\text{CHCl}_2$ and $\text{CClF}_2\text{CF}_2\text{CHClF}$) and 1,1,1,3,3,3-hexafluoro-2-propanol (HFIP) were purchased from Asahi Glass Company and Central Glass Co., Ltd., respectively and used as received. 1H,1H-Pentadecafluorooctyl amine was purchased from Daikin Co., Ltd. *N*-(1H,1H-Pentadecafluorooctylmethacrylamide) was synthesized from the reaction of methacryloyl chloride with the corresponding amine in the presence of triethylamine in chloroform at room temperature. The reaction mixture was washed sequentially with hydrochloric acid, sodium carbonate, and saturated sodium chloride aqueous solution and then dried with anhydrous sodium sulfate. The crude product was recrystallized from *n*-hexane and dried under vacuum at room temperature. The pC7F15MAA was prepared by free-radical polymerization in tetrahydrofuran at 60°C with α,α -azobis(isobutyronitrile) as an initiator. The polymer was purified by reprecipitation from HFIP into a large excess of acetonitrile in twice and dried under vacuum at room temperature.

Measurements

Surface pressure (π)-area (A) isotherm measurements and the deposition of pC7F15MAA monolayer were carried out with a computer-controlled Langmuir trough (FSD-110 and 111, USI). Distilled and deionized water ($>17.5\text{ M}\Omega\text{cm}$, CPW-101, Advantec) was used as the subphase. The polymer for π -A isotherm measurement was dissolved in AK-225 containing 5% HFIP at a concentration of about 1 mM (monomer unit). Appropriate amount of the solution (200 μL) was spread on the water surface and the monolayer was then compressed at a speed of $14.0\text{ cm}^2\text{ min}^{-1}$. The deposition of monolayer was carried out at a surface pressure of 30 mN m^{-1} at 25°C. Glass slides were cleaned ultrasonically with chloroform, acetone, and finally UV-O₃ cleaner (NL-UV253, Nippon Laser Electronics) and made hydrophobic with octadecyltrichlorosilane (ShinEtsu Chemical Co., Ltd.). Cast film of pC7F15MAA was prepared by pipetting a AK-225 solution of pC7F15MAA onto a glass slide and allowing to evaporate the solvent at room temperature. For the surface plasmon measurement, a silver layer (*ca.* 50 nm) was thermally evaporated onto glass substrates in a vacuum chamber (V-KS200, Osaka Vacuum Ltd.) below $2.0 \times 10^{-4}\text{ Pa}$; then monolayer was transferred on the silver layer by vertical dipping method at dipping

speed 10 mm min^{-1} . The substrate was coupled with a prism (BK-7, $n_{632.8} = 1.515$) through an index match fluid ($n_D^{20} = 1.516$, Kargille Inc.) in Kretschmen configuration.²⁵ A linearly polarized He-Ne laser beam (*p*-light, $\lambda = 632.8\text{ nm}$) impinged upon the LB film and the incident angle was changed by a stage controller (TDR-120, Sigma Koki). The intensity of the reflected light was measured by a photodiode detector (S3590-01, Hamamatsu) as a function of incident angle; data were recorded on personal computer. X-Ray diffraction (XRD) was carried out using MAC Science M18XF²²-SRA instrument with Cu-K α (0.154 nm) as a target. FT-IR transmission and reflection absorption (RAS) spectra were measured with JASCO FT/IR-230 operated at a resolution of 4 cm^{-1} . CaF_2 and Au-evaporated glass substrates were used for transmission and RAS measurement, respectively.

Contact angle on the surface of LB film was measured at 30 s after dropping distilled water by the sessile drop method with a CA-X contact angle meter (Kyowa Interface Science Co., Ltd.) at 20°C and ambient humidity. The contact angles were the average of five measurements at different positions for one sample. To monitor effect of temperature on the wettability of pC7F15MAA LB film (10 layers employed as sample) and cast film were heated to a range from 20 to 300°C in air inside a temperature controlled oven system. After heating 10 min, each sample was subjected to analysis by static contact angle measurements. The resulting data were averaged over five random measurements on a given surface. The contact angles for droplets of various *n*-alkanes such as hexane, octane, decane, dodecane, and tetradecane on the LB film and cast film were measured to obtain the critical surface tension (γ_c). The value of γ_c was determined by extrapolating a linear regression analysis of the data to $\cos \theta = 1$ (Zisman plot).²⁶

RESULTS AND DISCUSSION

Monolayer Behavior of pC7F15MAA at the Air–Water Interface

The pC7F15MAA is white amorphous solid and insoluble in most common organic solvents. It is soluble in fluorinated solvents like AK-225, Freon113, trifluoroacetic acid (TFA), and 1,1,1,3,3,3-hexafluoro-2-propanol (HFIP) but only swelled in tetrahydrofuran. The polymer, pC7F15MAA dissolved in AK-225 was spread on the water surface for the π -A isotherm measurements at different subphase temperatures. Figure 2 shows the π -A isotherms of pC7F15MAA monolayers at different subphase temperatures. All the π -

Figure 2. π -A isotherms of pC7F15MAA at different subphase temperatures.

A isotherms showed a steep rise in surface pressure with high collapse pressure, increasing slightly with increasing subphase temperatures. The limiting surface area per monomer unit of the monolayer is 0.32 nm^2 at 20°C ; determined by extrapolating the linear portion of the steep rise in the π -A curve to zero surface pressure. This value appears to be larger than the estimated value for molecular cross-sectional area (0.28 nm^2) of the fluorocarbon chain.^{27,28} A possible explanation for the larger area can be suggested:

(i) Fluorocarbon chains, such as $-(\text{CF}_2)_6\text{CF}_3$ can adopt a helical structure²⁹ and then a slight increasing of the molecular cross-sectional area can be expected.
 (ii) Another interpretation is that pC7F15MAA side chains are in tilted arrangement. The limiting surface area of pC7F15MAA (monomer unit) is slightly larger than that of poly(*N*-fluorooctylacrylamide) LB film (0.30 nm^2).²⁴ This indicates that the α -methyl group at the polymer backbone exerts steric hindrance, thus disturbing the packing of the fluorocarbon chain. The monolayer of pC7F15MAA on the water surface can be transferred onto solid supports under a surface pressure 30 mN m^{-1} as Y-type LB film with a transfer ratio of almost unity at both downward and upward strokes.

Characterization of Layer Structure in pC7F15MAA LB Film

The layer structure and thickness of pC7F15MAA LB film were investigated by X-ray diffraction measurement (XRD). The XRD pattern of the pC7F15MAA LB film with 46 layers has Bragg peaks as shown in Figure 3. The pC7F15MAA LB film consists of bilayer periodical architecture and monolayer thickness (d) is estimated to be 1.31 nm from the Bragg peaks. This value is smaller than the theoretical molecular length (l), estimated to be 1.5 nm from the Corey–Pauling–Koltun (CPK) model,³⁰ where fluoroalkyl chain takes all-*trans* structure and is oriented perpendicular to the plane of the substrate. The

Figure 3. X-Ray diffraction pattern of pC7F15MAA with 46 layers.

Figure 4. Probable orientation of pC7F15MAA monolayer on water surface.

FT-IR measurement (transmission, and reflection absorption) of pC7F15MAA LB multilayer (60 layers) showed that the ratio of absorption intensities of $\nu_{\text{as}} \text{CF}_2$ (1246 cm^{-1}) and $\nu_{\text{s}} \text{CF}_2$ (1149 cm^{-1}) in transmission mode and reflection absorption mode are 3.20 and 7.0 respectively indicating all-*trans* structure in fluoroalkyl chain. One possible explanation may be suggested for this deviation that fluorocarbon chain is in tilted orientation on the surface.³¹ Using the formula $l \cos \theta = d$, where d is the monolayer thickness and l is the theoretical molecular length, the tilt angle of fluorocarbon chain in pC7F15MAA LB film can be calculated to be 29° (Figure 4).

To determine the thickness of pC7F15MAA LB film surface plasmon resonance (SPR) measurements were also carried out. SPR reflectivity measurements are surface-sensitive, spectroscopic methods that can be used to characterize the thickness and refractive index of ultrathin organic and biopolymer films at noble metal (Au, Ag, Cu) surfaces.³² The angle dependent reflect-

Table I. Dielectric constant and pC7F15MAA LB film thickness determined from Fresnel fits

Layer	ϵ'	ϵ''	Thickness (nm)
Prism	2.296	0	—
Ag	-17.050	0.55	50.1
pC7F15MAA (2 layers)	2.10	0	3.2
pC7F15MAA (4 layers)	2.10	0	5.4
pC7F15MAA (6 layers)	2.10	0	7.8
pC7F15MAA (8 layers)	2.10	0	10.6
pC7F15MAA (10 layers)	2.10	0	12.5
Air	1.0	0	—

Figure 5. Angle-dependent SPR reflectivity curves of pC7F15MAA as a function of number of deposited layers symbols are experimental points ; solid lines are theoretical curves.

tivities of pC7F15MAA LB films were measured as a function of the number of deposited layers (Figure 5). The minimum of the reflectivity curve shifts from an incident angle 42° to higher angles after deposition of LB films. The dielectric constant (ϵ) and LB film thickness were determined by fitting the theoretical calculation based on Fresnel's equation³³ to the experimental data (Table I). We assumed that the dielectric constant of pC7F15MAA LB film was constant. The thicknesses of the pC7F15MAA LB film obtained in this way are shown in Figure 6 as a function of the number of layers and exhibit a linear relationship, indicating successive regular deposition of the monolayer. The average monolayer thickness is estimated to be 1.30 nm which is in good agreement with the value obtained from XRD measurement. Using the relation $n = \sqrt{\epsilon}$ the refractive index (n) of pC7F15MAA LB film has been found to be 1.449.

Wettability of pC7F15MAA LB Film Surface

The wettability of the pC7F15MAA LB film surface was investigated by contact angle measurement of a water droplet. Figure 7 shows contact angles of the pC7F15MAA LB film as a function of number of layers and it is clear that the contact angle is higher in the LB films with the even number of layers than with the odd number of layers. This indicates that hydrophobic and hydrophilic surfaces are produced alternately by

Figure 6. A linear relationship between the thicknesses of pC7F15MAA LB film and the number of layers. **Figure 7.** Contact angles of pC7F15MAA LB film as a function of the number of layers.

the deposition of the monolayer. This "odd-even" effect in the wettability of the built-up LB film supports Y-type structure. The hydrophobic and hydrophilic properties could be attributed to the fluorocarbon chain and amide group respectively. This phenomenon is similar to the contact angle measurement for the poly(*N*-dodecylacrylamide) LB film.²¹ However, in the case of the fluorinated alkyl acrylamide polymer LB film showed no alternation in contact angles²⁴ which is possibly attributed to the inversion (overturn) phenomena as reported in the LB films of low molecular weight fatty acids such as stearic acid.³⁴ Pronounced alternation in contact angles of pC7F15MAA LB film shown in Figure 7 implies that the inversion did not occur. Figure 8 shows the effect of temperature on wettability

Figure 8. Plot of static contact angle of pC7F15MAA (LB film and cast film) vs. incubation temperature.

of pC7F15MAA LB film and cast film indicating that wettability of pC7F15MAA LB film changed slightly with increasing temperature. This might be attributed to the stable surface formation resulted from enhanced intermolecular van der Waals interactions between the chains in the LB film upon heating. However, in the case of cast film the change of contact angle with increasing temperature is larger than the LB film mainly due to the disordering of the fluorocarbon chain upon heating leading to expose of groups other than CF_3 , e.g., CF_2 on the surface.

In order to derive the critical surface tension (γ_c) of pC7F15MAA LB film and cast film, the contact angles for droplets of various *n*-alkanes such as hexane, octane, decane, dodecane, and tetradecane on the LB film and cast film were measured. The LB films with 10 layers were employed as samples. A good linear relationship between the contact angle ($\cos \theta$) and the surface tension of the *n*-alkane molecules employed was observed for both pC7F15MAA LB film and cast film (Figure 9). By extrapolation of the linear plot to $\cos \theta = 1.0$, the critical surface tension (γ_c) can be estimated to be 12.5 mN m^{-1} for pC7F15MAA LB film. This value is lower than that of the polytetrafluoroethylene (PTFE, 18 mN m^{-1}).³⁵ This reveals that the surface of pC7F15MAA LB is composed of mainly CF_3 groups. The cast film showed a critical surface tension 17 mN m^{-1} , which is larger than the LB film. This indicates that the surface of pC7F15MAA cast film composed of CF_3 and CF_2 groups resulted from the random orientation of fluorocarbon chain in the cast film. However, the critical surface tension of pC7F15MAA LB film is slightly larger than that poly(*N*-fluorooctylacrylamide) LB film (11.0 mN m^{-1}).²⁴ This difference in the γ_c values might be attributed to the packing of the fluorocarbon side chain resulted from the steric hindrance of α -methyl group in pC7F15MAA LB film.

Figure 9. A linear relationship between the contact angles of pC7F15MAA (LB film and cast film) and the surface tension of *n*-alkane molecules.

CONCLUSION

The poly(*N*-1H,1H-pentadecafluorooctylmethacrylamide) (pC7F15MAA) forms stable monolayer on the water surface in which the methacrylamide backbone is at the water surface and the fluorocarbon chain is tilted toward the air. Uniform LB film as Y-type with thickness 1.31 nm could be obtained by deposition of the monolayer onto solid substrates. The pC7F15MAA LB film showed “odd-even” effect in contact angle and changed alternately between 114° (even) and 111° (odd). The fluoroalkyl chain is densely packed at the surface of the pC7F15MAA LB film and takes highly oriented structure in which CF_3 groups exposed to surface, leading to low critical surface tension compared with PTFE.

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