Formation of Polymerizable Monomer Langmuir−Blodgett Films with Polyfluorocarbon Chains for Use in High-Resolution Negative Resists

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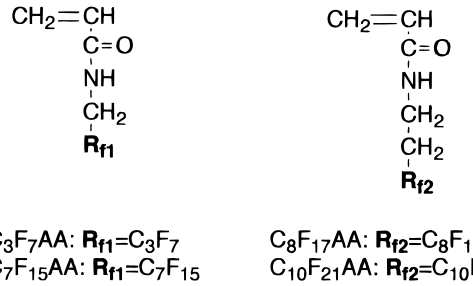
Recently, polymerization of monomer Langmuir−Blodgett (LB) films has received much attention due to its promise in high-resolution lithography and spatially addressable immobilization of various functional groups.[1,2] Since LB films have attractive features, such as a molecularly ordered structure and controllability of film thickness on the order of molecular sizes, they are expected to provide a high resolution and sensitivity in lithography. A large difference in solubility against organic solvents between monomer and polymerized LB films is required to achieve fine-pattern lithography. In general, a high degree of polymerization in the solid phase as seen in LB films is problematic because of the defects and the grain boundary of the films. There are several reports on fine-pattern drawing using polymerizable monomer LB films such as *N*-octadecylacrylamide,[3−5] ω-tricosenoic acid,[6] α-octadecylacrylic acid,[7] and octadecyl acrylate. All of these amphiphiles require long hydrocarbon chains for the formation of stable LB films. These long alkyl chains are inferior as resist materials because of low stability against solvents, plasma etching, heating, etc. Since fluorocarbon chains have a strong hydrophobic character, they can be used instead of hydrocarbon chains in LB films. Fluorocarbon materials are of great interest because of their low friction coefficient, excellent insulation characteristics, excellent durability, and so on.[8−11] So far, only a few investigations on polymerization of LB films with fluorocarbon chains have been reported.[12] There is no study on lithography involving monomer LB films consisting of fluoro compounds. In a previous study,[3] it was found that *N*-alkylacrylamide monomers form stable monolayers on the surface of water and that the resulting monomer LB films can be used as high-resolution negative resists due to their high degree of polymerization. In the present work, we employed poly[*N*-(fluoroalkyl)acrylamide]s as fluorinated monomer amphiphiles and investigated the properties of poly[*N*-(fluoroalkyl)acrylamide] monolayers with different fluorocarbon chain lengths, in order to identify fluorinated monomer LB films appropriate for high-resolution lithography. It has been found that *N*-2-(perfluorodecyl)-ethylacrylamide forms a stable condensed monolayer on the surface of water. Moreover, LB films built-up from the monolayer showed high reactivity of the polymerization to UV light irradiation.

Poly[*N*-(fluoroalkyl)acrylamide] monomers with different fluorocarbon chain lengths, *N*-1*H*,1*H*-heptafluorobutylacrylamide (C_3F_7AA), *N*-1*H*,1*H*-pentafluorooctylacrylamide ($C_7F_{15}AA$), *N*-2-(perfluorooctyl)ethylacrylamide ($C_8F_{17}AA$), and *N*-2-(perfluorodecyl)ethylacrylamide ($C_{10}F_{21}AA$) were synthesized as follows: Polyfluoroalkyl iodide was reacted with sodium azide in *N*,*N*-dimethylformamide.[13] The resulting azide compound was reduced by suspending lithium aluminum hydride in dry ether to obtain the corresponding amine. Then the resulting amine was reacted with acryloyl chloride in the presence of triethylamine in dichloromethane at room temperature. The crude products were recrystallized from hexane and dried under vacuum at room temperature.



C_3F_7AA: $R_{f1}=C_3F_7$ $C_8F_{17}AA$: $R_{f2}=C_8F_{17}$
$C_7F_{15}AA$: $R_{f1}=C_7F_{15}$ $C_{10}F_{21}AA$: $R_{f2}=C_{10}F_{21}$

Figure 1. Structural formulas of poly[*N*-(fluoroalkyl)acrylamide] monomers with different fluorocarbon chain lengths.

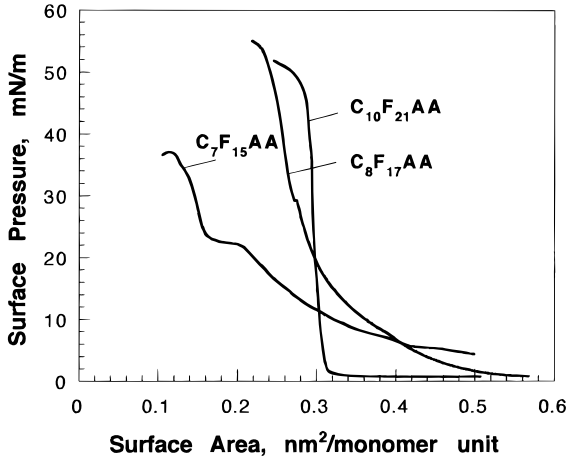


Figure 2. Surface pressure−area isotherms of poly[*N*-(fluoroalkyl)acrylamide] monomers with different fluorocarbon chain lengths at 20 °C.

Measurement of the surface pressure−surface area ($\pi-A$) isotherms was carried out using a computer-controlled Langmuir trough (FSD-110, USI). Pure distilled water with a resistivity higher than 17 MΩ cm^{-1}, purified by a Milli-QII system, was used as the subphase. The poly[*N*-(fluoroalkyl)acrylamide] monomers for $\pi-A$ isotherm measurement were dissolved in trichlorotrifluoroethane (Freon 113). Appropriate amounts (200 μL) of the solutions were spread on the water surface, and then the monolayers on the water surface were compressed at a speed of 14.0 cm^2/min. The $\pi-A$ curves were measured using different compression speeds and different spreading volumes in order to ensure the reproducibility of the isotherms.

Figure 2 shows $\pi-A$ isotherms for the monolayers of poly[*N*-(fluoroalkyl)acrylamide] monomers with different fluorocarbon chain lengths at 20 °C. It is clear that the isotherms vary according to the fluorocarbon chain length. The C_3F_7AA monomer monolayer shows no surface pressure at any molecular area due to dissolution into the water subphase. The $C_7F_{15}AA$ monolayer isotherm shows an expanded monolayer at low surface pressure. A transition from an expanded to a condensed phase is observed at 22 mN/m. However, the condensed monolayer is unstable and collapses under constant surface pressure. The $C_8F_{17}AA$ monolayer isotherm shows a relatively steep rise in surface pressure with a transition from an expanded monolayer to a condensed

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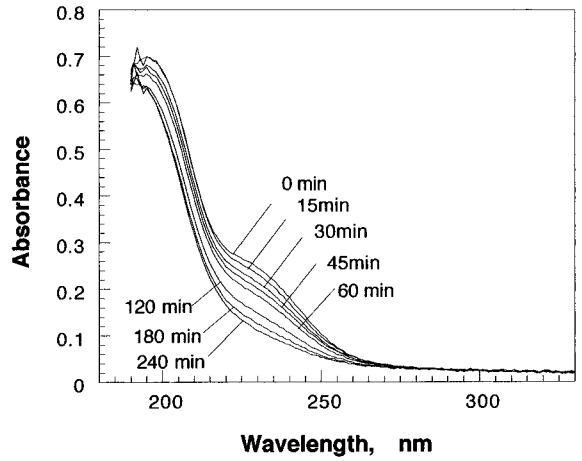

Figure 3. UV absorption spectra of a $C_{10}F_{21}AA$ monomer LB film with 40 layers on a quartz slide with various irradiation times under a xenon light.

monolayer at 29 mN/m. The limiting area of the condensed monolayer is 0.31 nm^2, which is almost the same as the area calculated (0.28 nm^2) from the CPK model for a polyfluorocarbon side chain. However, the $C_8F_{17}AA$ monolayer cannot be transferred onto solid supports. The $C_{10}F_{21}AA$ monolayer also shows a very steep rise in surface pressure with a high collapse pressure of 50 mN/m. The limiting area per molecule estimated by extrapolation of the linear part is 0.30 nm^2/molecule. In conclusion, only the condensed $C_{10}F_{21}AA$ monolayer can be transferred onto solid supports from the water surface. The successive deposition can be carried out at 35 mN/m in up/down strokes with a transfer ratio of unity, suggesting the formation of a typical Y-type LB film. The results suggest that a polyfluorocarbon chain length greater than eight is necessary to form a stable LB film in the present acrylamide monomers. Similar results are reported in the literature for perfluorinated alkanoic acids and for 2-(perfluoroalkylethyl)-2-oxazolines.[15]

The UV−vis absorption spectrum of a 40 layer $C_{10}F_{21}$-AA monomer LB film deposited on a quartz glass shows a typical absorption band around 230 nm, due to the $\pi-\pi^*$ transition of the vinyl group.[3a] Under light irradiation with a xenon lamp, the absorption band of the LB film, 230 nm, decreases, indicating polymerization of the LB films (Figure 3). FT-IR spectra of a 160 layer $C_{10}F_{21}AA$ monomer LB film deposited on a CaF_2 substrate also exhibit polymerization of the LB films with the exposing light as shown in Figure 4. The vinyl stretching absorption band at 1626 cm^{-1} decreases with the time of light irradiation. The absorption bands of the carbonyl stretching at 1657 cm^{-1} and of the NH bending at 1552 cm^{-1} also become broad with the time of light irradiation. On the other hand, the absorption bands of the CF_2 symmetric stretching at 1150 cm^{-1} and the asymmetric stretching at 1204 cm^{-1} do not vary after the light irradiation. The results indicate that the structure of the amide group in the LB film is varied whereas the structure of the fluoroalkyl chain is maintained by polymerization of the acrylamide group. The dissolution of the polymerized LB film was examined by observing the change of the absorption spectrum after dipping in various solvents. As can be seen from Table 1, the polymerized $C_{10}F_{21}AA$ LB film has a high resistance against solvents, and there is a large difference in solubility between the unpolymerized (monomer) and the polymerized $C_{10}F_{21}AA$ LB film.

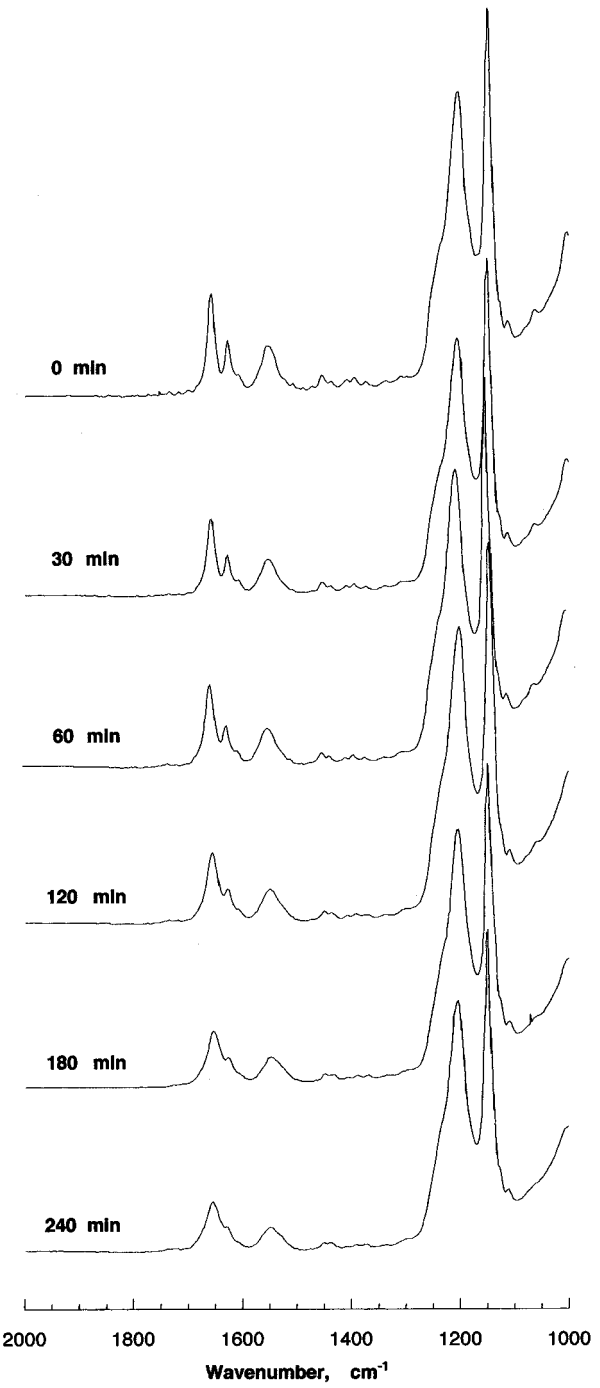

Figure 4. FT-IR absorption spectra of a $C_{10}F_{21}AA$ monomer LB film with 160 layers on a CaF_2 substrate with various irradiation times under a xenon light.

Table 1. Comparison of Stability against Various Solvents between Monomer and Polymerized $C_{10}F_{21}AA$ LB Films

	chloroform	Freon 113[a]	THF	HFIP[b]
polymerized LB film	−[c]	−	−	s[c]
monomer LB film	−	s	s	s

[a] Trichlorotrifluoroethane. [b] Hexafluoro-2-propanol. [c] s, soluble; −, insoluble.

This large difference in solubility suggests the possibility of application of the LB film in a negative-type photolithography. UV light was irradiated onto an 80 layer $C_{10}F_{21}AA$ monomer LB film through a photomask on which various test patterns were drawn. After irradiation, the LB film was rinsed with Freon 113 solvent to expose patterns in the polymerized LB film.

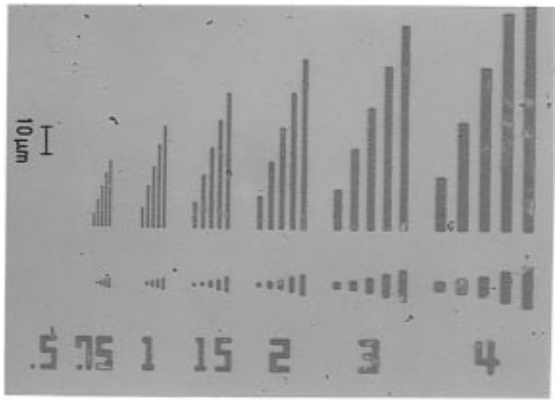

Figure 5. Optical micrograph of a fine negative pattern of a $C_{10}F_{21}AA$ monomer LB film with 80 layers on a silicon wafer.

Fine negative patterns appeared clearly, due to polymerization of the $C_{10}F_{21}AA$ monomer, as shown in Figure 5. Lines 0.75 μm in width, which is the limit of resolution of the photomask, were visible. The microscopic photograph shows that the surface of the photopolymerized LB film is uniform. This means that no contraction of the LB film occurs as a result of UV irradiation. It is evident that the $C_{10}F_{21}AA$ LB film could be used as a new material for high-resolution lithography.

In summary, the $C_{10}F_{21}AA$ monomer forms a stable monolayer on the surface of water and can be transferred onto a solid support with a transfer ratio of unity, yielding a Y-type LB film. This $C_{10}F_{21}AA$ monomer LB film can be polymerized by UV irradiation, rendering it insoluble in typical organic solvents. The polymerized LB film retains fine patterns when developed by a solvent which dissolves the monomer LB film. Further investigation regarding the mechanism of photopolymerization of the fluorinated monomer LB film and the stability of the fluorinated LB film against oxygen plasma is currently under way.

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