Spreading Behavior of Poly(*N*-dodecylacrylamide-*co*-styrene) Monolayers and Langmuir–Blodgett Multilayer Formation[1]

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ABSTRACT: The spreading behavior of poly(*N*-dodecylacrylamide-*co*-styrene)s (PDDASt) with various copolymer compositions on a water surface was investigated by measurements of the surface pressure (π)–area (A) isotherms. The stability of the copolymer monolayers depends strongly on the styrene (St) content in the copolymers; the monolayer becomes unstable, and the collapse pressure in the π–A isotherms decreases linearly as the styrene mole fraction increases. A closely packed condensed monolayer was formed for copolymers having a styrene content up to 0.6 mole fraction. This is due to the excellent monolayer formation property of the *N*-dodecylacrylamide (DDA) monomer unit. A linear relationship between the average limiting surface area per monomer unit and the styrene mole fraction is observed, indicating that additivity of the surface area of DDA and St holds; that is, DDA and St monomer units are mixed, with each having its own surface area, 0.28 and 0.16 nm^2, respectively, in the copolymer monolayers on water. This corresponds to an ideal mixing. The condensed polymer monolayers could be transferred successively onto solid supports such as a quartz slide by both downward and upward strokes with a transfer ratio of unity, giving Y-type uniform polymer LB films having an aromatic moiety applicable to various functionalities. An extension to a method for the introduction of various useful functional comonomers into the polymer LB films is also described.

Introduction

Langmuir–Blodgett (LB) films have received much attention from the viewpoint of functional utlrathin films.[2] The LB method is one of the best ways to prepare thin films with a controlled thickness at a molecular size and well-defined molecular orientation.[3] Many kinds of amphiphilic compounds such as long-chain fatty acids have been investigated and applications to many electronics devices is to be expected.[2–4] These LB films, however, have poor mechanical and thermal stabilities or poor resistance to dissolution by organic solvents. In order to overcome these weaknesses, many efforts to prepare polymeric LB films have been carried out.

Three methods (A–C in Scheme I) may be considered for preparation of polymer LB films. Method A: First the polymerizable amphiphilic monomer is spread onto a water surface and the condensed monomer monolayer is transferred onto a solid support (deposition), and then the polymer LB film is obtained through polymerization of the monomer LB film by some appropriate treatment such as UV irradiation, electron beam, or γ-ray irradiation. On this method, the polymerization of vinyl monomers, acrylate monomers, or diacetylene monomers with long alkyl chains has been attempted.[5–11] In general, however, these polymer LB films have cracks and defects caused by internal stress and reorganization brought about by polymerization under restricted mobility in the LB films. Method B: First amphiphilic monomers are polymerized separately by the usual polymerization method and the resulting amphiphilic polymers[12–14] or copolymers[15–19] are spread onto a water surface, forming condensed polymer monolayers, and then the deposition of the monolayer gives the desired polymer LB film. Method C: This is intermediate between methods A and B: that is, a monomer monolayer is formed in the same way as by the A method, and the polymerization of the condensed monolayer on the water surface yields a polymer monolayer; the deposition of the polymer monolayer in the same way as in B results in a polymer LB film. There are a few reports by this method.[20]

We have been interested in the preparation of polymer LB films and have succeeded in the preparation of fairly uniform films using the *N*-alkylacrylamide series by methods A and B. For method A, we have found that *N*-octadecylacrylamide (ODA) forms a stable condensed monolayer, which can be deposited onto solid supports with a transfer ratio of unity. The monomer LB multilayers are polymerized completely by UV irradiation,[21] and the possibility of application to a new type of high-resolution resist (a deep UV- and EB-sensitive negative resist) has also been indicated.[22] For method B, poly(*N*-dodecylacrylamide) forms a stable condensed monolayer, which can be deposited onto solid supports, giving a fairly uniform polymer LB film,[23] which has been used as a permselective membrane for oxygen.[24] As an extension of these studies, we have tried to introduce various functional groups into the polymer (PDDA) LB film and have proposed that various functional monomers, which have no ability to form monolayers, are introduced into the polymer LB film as a comonomer of *N*-dodecylacrylamide.[2] The resulting copolymers are expected to form a stable monolayer.

In this work, the introduction of styrene, which is the most popular monomer having the potential to introduce various functional groups as a substituent of the aromatic ring, is examined as a comonomer. Styrene is copolymerized with DDA in various mole fractions, and the spreading behavior of the copolymers (Chart I) on a water surface and the formation of the polymer LB films are investigated.

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Scheme I

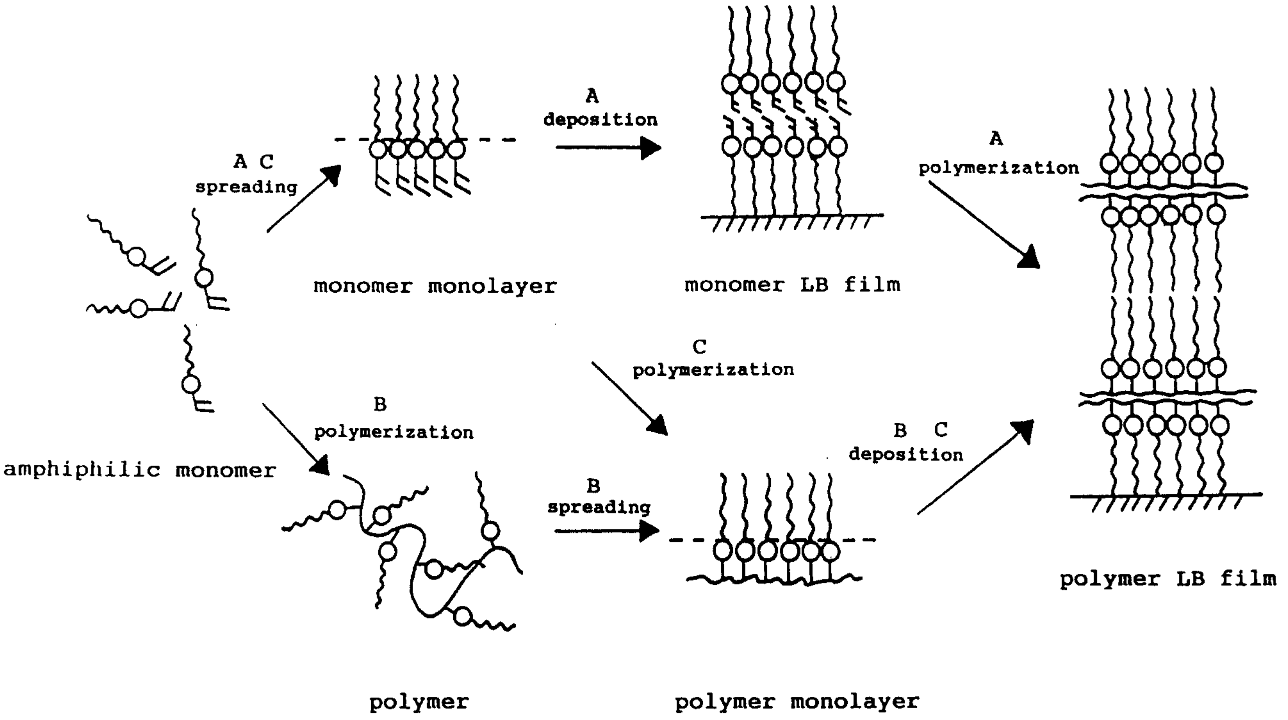


Chart I

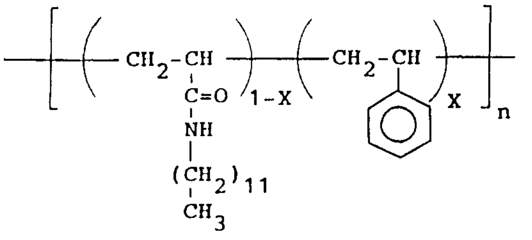


Table I
Copolymer Composition, Number-Average Molecular Weight, and Polydispersity of Various Poly(*N*-dodecylacrylamide-*co*-styrene)s

styrene content in PDDASt (X)	M_n	M_w/M_n
0	3 700	1.24
0.18	12 000	1.98
0.24	30 000	1.76
0.33	20 000	1.40
0.58	17 000	1.41
0.75	30 000	1.44
0.80	30 000	1.42
0.38	7 400	1.26
0.38	27 000	1.37
0.38	55 000	1.29

Experimental Section

N-Dodecylacrylamide monomer was synthesized by the reaction of acryloyl chloride and dodecylamine in the presence of triethylamine in 1,2-dichloroethane. The product was purified by column chromatography and by recrystallization from *n*-hexane. Poly(*N*-dodecylacrylamide-*co*-styrene)s (PDDASt; Chart I) were prepared by free-radical polymerization of styrene with *N*-dodecylacrylamide in benzene at 60 °C with 2,2′-azobis(isobutyronitrile) as a thermal initiator. The copolymers were purified by reprecipitation from a filtered chloroform solution into a large excess of methanol and dried under vacuum at room temperature. Molecular weights were determined by a Toyo Soda gel permeation chromatograph (GPC) using a polystyrene standard. The styrene mole fraction was determined by ^{1}H NMR and UV spectroscopy (Table I).

The measurement of surface pressure–area isotherms and the deposition of the monolayers were carried out with an automatic Langmuir trough (Kyowa Kaimen Kagaku HBM-AP using a Wilhelmy type film balance). Distilled, deionized water was used for the subphase. The chloroform used for spreading the monolayer on the water surface was of spectroscopic grade. Glass slides, on which LB multilayer was deposited, were cleaned in a boiling H_2SO_4–HNO_3 (2:1) solution and made hydrophobic with dichlorodimethylsilane.

Results and Discussion

Surface Pressure–Area Isotherms. Copolymers with various copolymer compositions were prepared (Table I). The Q and e values for DDA monomer were measured as 0.51 and 0.73, respectively.[25] From these values, the reactivity ratios for the styrene copolymer were calculated to be r_1(styrene) = 0.57, r_2(DDA) = 0.17, and r_1r_2 = 0.097. The mean styrene sequence length, for example, for the 1:1 copolymer was found to be 1.46. These values indicate that the styrene copolymers have a tendency toward alternation. The surface pressure–area isotherms for the copolymers that were spread on a water surface from a chloroform solution are shown in Figure 1. Apparently, the isotherms change with styrene mole fraction: the slope for the rise in surface pressure becomes smaller, and the collapse pressure also decreases with the mole fraction of styrene (Figure 2). This indicates that the copolymer monolayers become unstable as the styrene content in the copolymers increases. This is attributed to the hydrophobic nature of the styrene monomer. Introduction of the styrene unit into PDDA decreases the ability of the monolayer formation of PDDA. It is, however, of interest that even the copolymers with ca. 0.6 styrene mole fraction show a rise in surface pressure, indicating the formation of a fairly stable monolayer. The average limiting surface area per monomer unit was defined as the water surface area occupied by a monomer unit of the monolayer. It was estimated from the isotherms by extrapolating the steep rising part of the surface pressure curves to zero surface pressure. The surface area obtained was plotted against the styrene mole fraction, giving a straight line up to 0.6 styrene mole fraction (Figure 3). From the linear relationship, the surface area per styrene monomer unit can be calculated at various copolymer compositions by

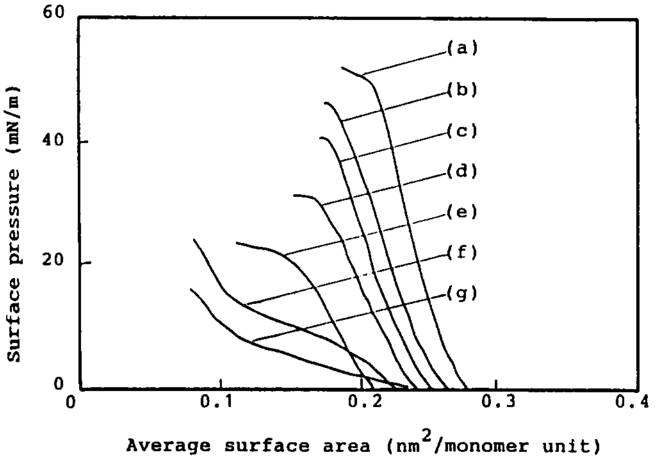


Figure 1. Surface pressure–area isotherms of PDDA homopolymer (a) and PDDASt copolymers (b–g); (b) St mole fraction: 0.18, (c) 0.24, (d) 0.33, (e) 0.58, (f) 0.75, (g) 0.80.

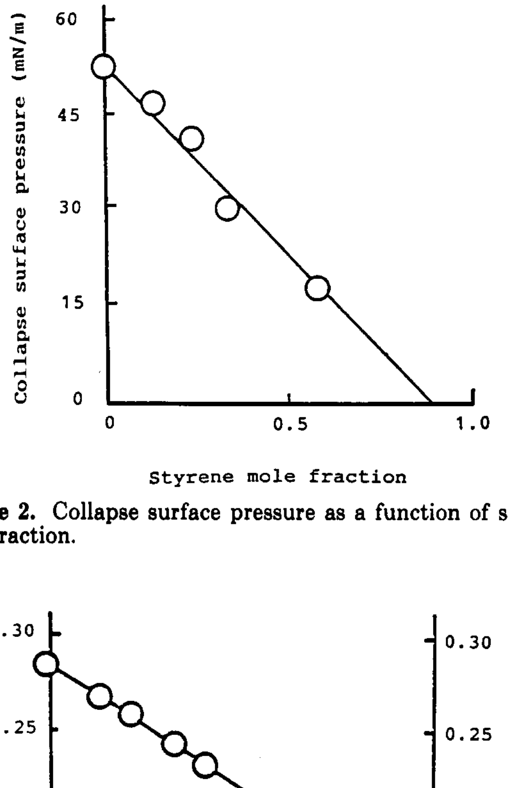


Figure 2. Collapse surface pressure as a function of styrene mole fraction.

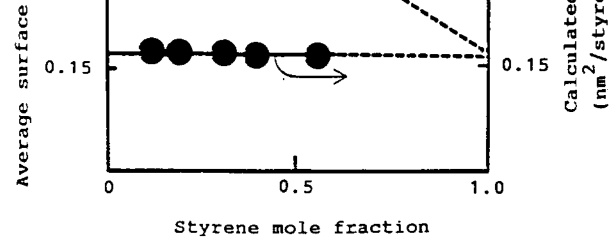
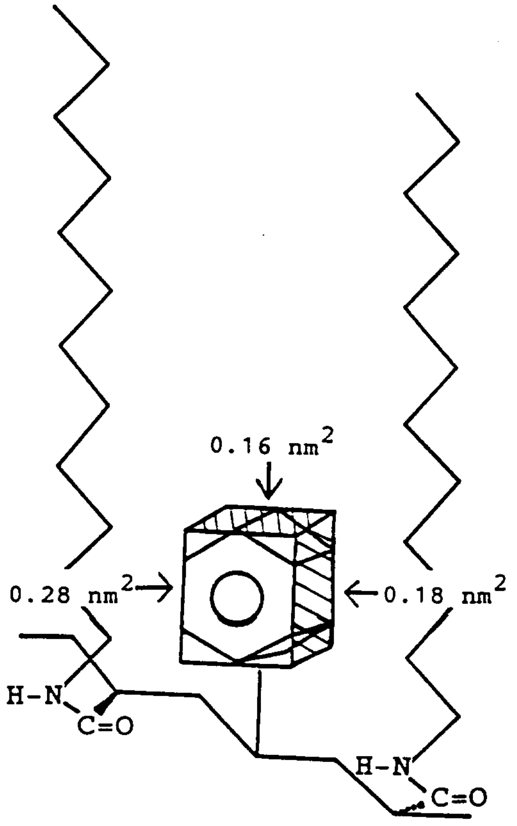


Figure 3. Average limiting surface area per monomer unit (○) and calculated surface area per styrene monomer unit (●) as a function of styrene mole fraction.

Chart II



assuming the area of a DDA monomer unit to be 0.28 nm^2/monomer, which has been determined from the isotherm of the DDA homopolymer.[19] A constant value of 0.16 nm^2/St monomer unit was obtained over a wide range to 0.6 styrene mole fraction (Figure 3). This means that the styrene monomer unit in the copolymer monolayer occupies a constant surface area on the water surface, irrespective of the copolymer composition (up to 0.6 St content) and also shows that the copolymer chains have no coiled form on the water surface. If the copolymer chain has a folded or coiled form on the water surface, the area allotted to the styrene monomer unit would become smaller and change with copolymer composition. The surface area (0.16 nm^2) is consistent with the value estimated from the CPK model where the polymer main chain is laid horizontally on the water surface and the benzene rings are oriented perpendicular to the chain (Chart II). As styrene is hydrophobic, the benzene ring tends to orient far from a water surface. The orientation of the copolymers shown in Chart II is supported also from analogy with the PDDA homopolymer and the carbazole copolymer.[23,26] The surface area allotted to a repeating monomer unit in polymer monolayers has varied with the size of the pendant chromophore and the conformation of polymer chains.[18,26,27] In the study of carbazole–DDA copolymer monolayers, the surface area for the carbazole chromophore has been obtained to be 0.34 nm^2, as expected from CPK models based on a similar conformation shown in Chart II.[26]

We conclude that the average limiting surface area (A_{av}) of the copolymer monolayers can be expressed by

$$A_{av} = A_{DDA}(1 - X) + A_{St}X \qquad (1)$$

where A_{DDA} and A_{St} are the surface areas of DDA (0.28 nm^2) and St (0.16 nm^2), and X is the mole fraction of St. This equation means that the additivity of the surface area of DDA and that of St in the copolymer monolayers holds. A linear relationship for mixed monolayers like the above equation is observed in a situation where ideal mixing or phase separation occurs.[18] In general, the average surface area for mixed monolayers deviates upward or downward from a straight line, depending on inter-

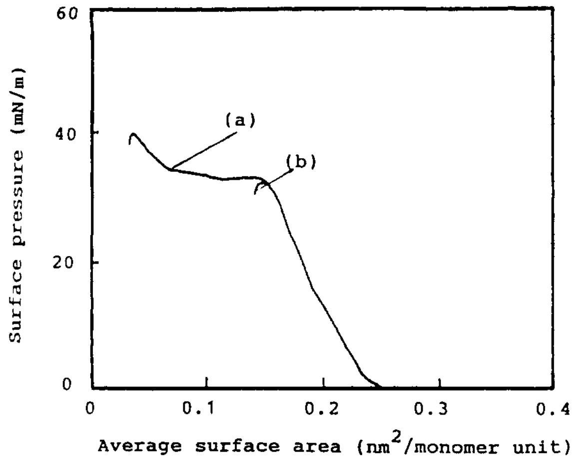


Figure 4. Surface pressure–area isotherms of PDDASt with various molecular weights, M_n: (a) 55 000 and 27 000, (b) 7400.

Table II
LB Film Formation from PDDASt Monolayers

styrene content in PDDASt (X)	surface pressure, mN/m	transfer ratio up	transfer ratio down
0	40	1.0	1.0
0.18	30	1.0	1.0
0.24	30	1.0	1.0
0.33	30	1.0	1.0
0.58	15	0.9	0.9
0.75		0	0
0.80		0	0

molecular interaction.[4,27] Aggregate formation is characteristic of mixed monolayers consisting of low molecular weight compounds.[19,28] In the mixed monolayer of long-chain fatty acids with a chromophore compound, the chromophore forms aggregates even at a few percentage concentration.[28] In the present case, however, each molecule is linked to the polymer chain randomly and the aggregation of the styrene monomer unit is suppressed. Moreover, the DDA monomer unit interacts strongly with the water and tends to spread on the water surface. The copolymer chains are closely packed, taking the orientation shown in Chart II on the water surface. As a result, a uniform distribution of styrene is found. In contrast, the average limiting surface area of the copolymers with mole fractions of more than 0.6 deviates from this relationship and gives a smaller surface area, indicating that the copolymer takes a coiled form partially and/or the polymer chains overlap with each other. Because the aggregation force (cohesive force) due to hydrophobicity of styrene sequences overcomes the spreading force of DDA monomer sequences at this copolymer composition, the copolymers hardly spread uniformly on the water.

Figure 4 shows the surface pressure isotherms of various molecular weight copolymers. The isotherm in the condensed state is not influenced by molecular weight. This result also suggests that the polymer chain does not form an aggregation or a coiled form.

LB Multilayer Formation. The condensed monolayer of the copolymers could be transferred onto a solid support, giving the polymer LB films. Table II shows a transfer ratio of the copolymer monolayers with various styrene mole fractions. The condensed monolayers of the copolymers up to 0.33 mole fraction could be transferred onto a solid support with both down and up strokes with a transfer ratio of unity. Even the copolymer with a 0.58 mole fraction could be transferred onto a solid support with both down and up strokes with a transfer ratio of 0.9. It is noteworthy that the polymer LB films with styrene contents over 50% could be obtained. This is apparently due to a superior ability of the DDA molecule in monolayer and LB multilayer formation. It is expected that styrenes having various substituents on the aromatic ring can be introduced by the same way, and the polymer LB films with various functionalities formed. An extension to other aromatic monomers is currently under way.

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Registry No. PDDASt, 134971-22-5; $H_2C{=}CHC(O)Cl$, 814-68-6; $Me(CH_2)_{11}NH_2$, 124-22-1; $H_2C{=}CHC(O)NH(CH_2)_{11}Me$, 1506-53-2; $(H_2C{=}CHC(O)NH(CH_2)_{11}Me)_x$, 33827-81-5.