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Spreading and transfer behavior of poly(2-acrylamidohexadecylsulfonic acid-co-styrene) monolayers

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Abstract

The spreading behavior of poly(2-acrylamidohexadecylsulfonic acid-co-styrene) ($PAMC_{16}SSt$) random copolymers with various compositions was investigated by measurements of the surface pressure–area (π–A) isotherms. The random copolymers formed stable condensed monolayers with a high collapse pressure (about 40 mN m^{-1}) over a wide range of styrene contents. The collapse pressure increased somewhat with increase in the styrene content. These facts indicate that more hydrophobic units can be incorporated into a stable copolymer monolayer if 2-acrylamidohexadecylsulfonic acid is used as an amphiphilic comonomer instead of *N*-dodecylacrylamide. A linear relationship between the average limiting surface area per monomer unit and the styrene mole fraction was observed up to about 0.6 styrene mole fraction. The addition of $CdCl_2$ into the water subphase had little effect on the spreading behavior of $PAMC_{16}SSt$ monolayers. The transfer of $PAMC_{16}SSt$ was affected by the subphase and the copolymer composition. In the case of $CdCl_2$ aqueous solution (1 mmol L^{-1}), all the monolayers could be transferred onto a hydrophilic glass substrate by an upward stroke with a transfer ratio of unity. However, the transferred monolayers were lost in the downward stroke.

1. Introduction

Copolymerization of an amphiphilic monomer with a functional monomer or monomers is opening up many avenues towards the synthesis of polymeric LB materials with specially designed functionalities [1–3]. Miyashita and co-workers [1, 2] found that a carbazole or styrene (St) chromophore up to 0.33–0.58 mole fraction could be introduced into copolymer Langmuir–Blodgett (LB) films by using amphiphilic *N*-dodecylacrylamide (DDA) as the comonomer, and that the copolymer monolayer became unstable as the St content in the random copolymer increased. We have synthesized and characterized a new amphiphilic monomer, 2-acrylamidohexadecylsulfonic acid ($AMC_{16}S$) and its homopolymer poly(2-acrylamidohexadecyl sulfonic acid) ($PAMC_{16}S$) [4, 5]. It was expected that more chromophoric monomer could be incorporated into stable copolymer monolayers if $AMC_{16}S$ is used as a comonomer instead of DDA, since $AMC_{16}S$ is more hydrophilic [6]. In this work, St was copolymerized with $AMC_{16}S$ in various mole fractions, and the spreading and transfer behaviors of the copolymers were investigated.

2. Experimental details

$AMC_{16}S$ was synthesized by the reaction of 1-hexadecylene, acrylonitrile and oleum as described previously [4]. $AMC_{16}S$ was further purified by recrystallization in acetone–water (acetone:water = 20:1 v/v) mixed solvent. St was washed with 10% NaOH aqueous solution and water and then dried over silica gel, followed by vacuum distillation. Poly(2-acrylamidohexadecylsulfonic acid-co-styrene) ($PAMC_{16}SSt$) copolymers were prepared by free radical polymerization of $AMC_{16}S$ with St in tetrahydrofuran (THF) at 70 °C with 2,2′-azobis(isobutyronitrile) (AIBN) as the initiator. THF was dried over CaH_2 and distilled under N_2, and AIBN was recrystallized from methanol. The resulting copolymers were isolated by precipitation in petroleum ether and washed with petroleum ether and HCl aqueous solution (2 mol L^{-1}) successively.

The copolymers were further purified by reprecipitation from a filtered THF solution into a large excess of petroleum ether and dried under vacuum at about 50 °C. The intrinsic viscosities were measured in THF at 30 ± 0.05 °C, using a Ubbelohde viscometer. The composition of the copolymers was determined by ^1H

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TABLE 1. Characteristics of $PAMC_{16}SSt$ copolymers with the following copolymerization conditions: 0.08 g AIBN; 50 ml THF; reaction temperature, 70 °C

Sample	Monomer			Reaction time (h)	Copolymer		
	$AMC_{16}S$ (g)	St (g)	St mole fraction		Yield (g)	$[\eta]$ (ml g^{-1})	St mole fraction
a	1.0	4.0	0.935	8	0.8	12.2	0.796
b	1.7	3.3	0.875	5	1.7	12.1	0.694
c	2.5	2.5	0.783	3	2.5	12.1	0.445
d	3.3	1.7	0.650	2	3.2	12.5	0.409
e	4.0	1.0	0.474	2	4.2	11.5	0.205
f	4.5	0.5	0.286	2	4.7	11.5	0.111

nuclear magnetic resonance (JEOL FX-100 NMR spectrometer; $CDCl_3$ as solvent). The copolymerization conditions and copolymer characteristics are listed in Table 1. For comparison, a sample of $AMC_{16}S$ homopolymer NP-2 ($[\eta] = 17.7$ mL g^{-1}; THF; 30 °C) [5] was used.

The spreading and transfer behaviors of $PAMC_{16}SSt$ together with the homopolymer NP-2 were studied on a KSV-5000 twin-compartment trough at room temperature (about 18 °C). The polymers were spread from chloroform solution (1 mg mL^{-1}). The subphase was deionized water or $CdCl_2$ aqueous solution (1 mmol L^{-1}). The average limiting surface area per monomer unit was obtained from the isotherms by extrapolating the steeply rising part of the surface pressure to zero surface pressure. Glass slides were cleaned in a $K_2Cr_2O_7$ (about 5 wt.%) solution in concentrated H_2SO_4 and treated in Soxhlet's extractor with isopropanol. The transfer speed was kept at 5 mm min^{-1}.

3. Results and discussion

The spreading behavior of $PAMC_{16}SSt$ random copolymers on a water surface or a $CdCl_2$ solution (1 mmol L^{-1}) was investigated by measuring the surface pressure–area (π–A) isotherms.

Figure 1 shows the π–A isotherms of the random $PAMC_{16}SSt$ copolymers on a pure water subphase. Generally, monolayers with a collapse pressures of approximately 20 mN m^{-1} or higher are sufficiently stable to permit assembly into multilayer films [7, 8]. As shown in Fig. 1, the $PAMC_{16}SSt$ copolymers formed condensed monolayers and had collapse pressures of about 40 mN m^{-1}, indicating that they have the prerequisite for construction of LB films.

It is most important to note, however, that the collapse pressure of $PAMC_{16}SSt$ copolymers increases somewhat with increase in the St mole fraction in the copolymers over a wide range of St contents (up to about 0.8 St mole fraction), as depicted in Fig. 2. This behavior is very different from that observed by Mizuta

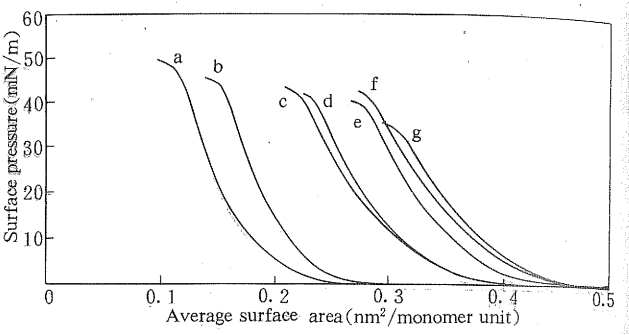


Fig. 1. π–A isotherms of $PAMC_{16}SSt$ copolymers (curves a–f) and $AMC_{16}S$ homopolymer NP-2 (curve g) on pure water for various St mole fractions: curve a, 0.796; curve b, 0.694; curve c, 0.445; curve d, 0.409, curve e, 0.205; curve f, 0.111; curve g, 0.

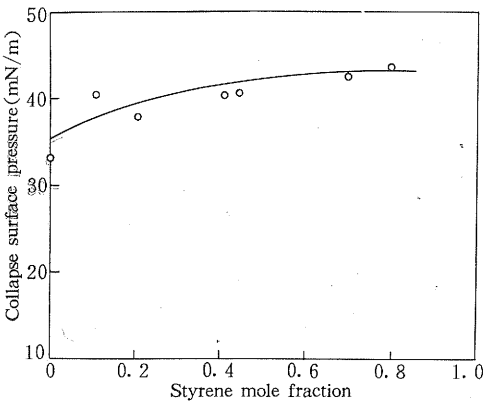
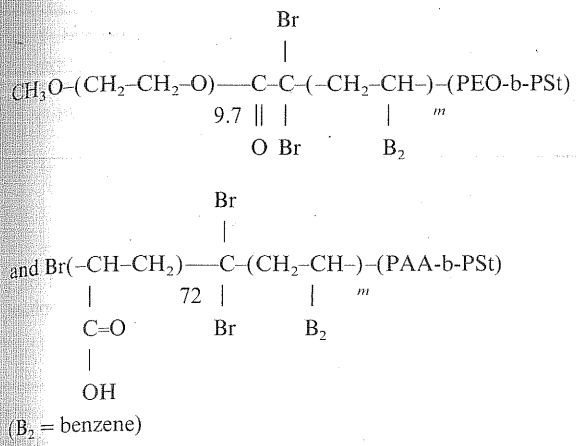


Fig. 2. Collapse surface pressure as a function of polymer composition (on pure water).

et al. [2], where the monolayer spreading behavior of poly(*N*-dodecylacrylamide-co-styrene)s (PDDASt) depended strongly on the St content in the polymers, where the collapse pressure in the π–A isotherms decreased linearly as the St mole fraction increased and where the collapse pressure for the copolymer with about 0.6 St mole fraction was less than 20 mN m^{-1}.

It is easily understandable that the hydrophile–lipophile balance (HLB) is a very important factor

influencing the monolayer formation of amphiphilic polymers as well as low molecular amphiphiles. Niwa *et al.* [9] prepared a well-defined block-type amphiphilic copolymer of



with systematically different chain lengths of polystyrene segment and found that the $\pi-A$ isotherms of these copolymers strongly depended on the hydrophobic chain length m. In the case of PAA-b-PSt, the collapse pressure increased with increase in hydrophobic chain length m from 14.0 to 112.7. In the case of PEO-b-PSt, the collapse pressure was kept at almost the same in the m range 6.7–109.7. Miyashita and co-workers [10, 11] studied the effect of alkyl length on the spreading behavior of *N*-alkylacrylamide monomers and their comb-type amphiphilic polymers, and found that *N*-octadecylacrylamide formed a stable condensed monolayer in the monomer series [10] and poly(*N*-dodecylacrylamide) (PDDA) formed the most stable condensed monolayer in the series of comb-type amphiphilic polymers [11]. Poly(3-alkylthiophene)s cannot form stable and uniform monolayers, just because the thiophene ring is not sufficiently hydrophilic to promote true monolayer formation, and well-defined LB films were fabricated from these materials by mixing them with a proportion of an amphiphile, say stearic or arachidic acid [12, 13]. We have found that $PAMC_{16}S$ could form a condensed monolayer on a pure water surface, whereas its monomer $AMC_{16}S$ could not, owing to the good water solubility of $AMC_{16}S$ [6, 14].

Therefore it can be concluded that an HLB region exists, beyond which the collapse pressure would decrease markedly and a stable monolayer cannot be obtained. We can imagine that $PAMC_{16}S$ and PDDA may serve as two opposite critical examples in comb-type amphiphilic polymers, and that the monolayer-forming ability of those polymers, which are more hydrophilic than $PAMC_{16}S$ or more hydrophobic than PDDA, would become worse. As a result, introducing hydrophobic units into a DDA homopolymer chain or extending its substituted alkyl to a longer chain would destroy the proper HLB of PDDA and decrease the ability to form a monolayer. Also, more hydrophobic chromophoric monomers can be incorporated into a stable copolymer monolayer when $AMC_{16}S$ is used as an amphiphilic comonomer instead of DDA, just as expected previously [6].

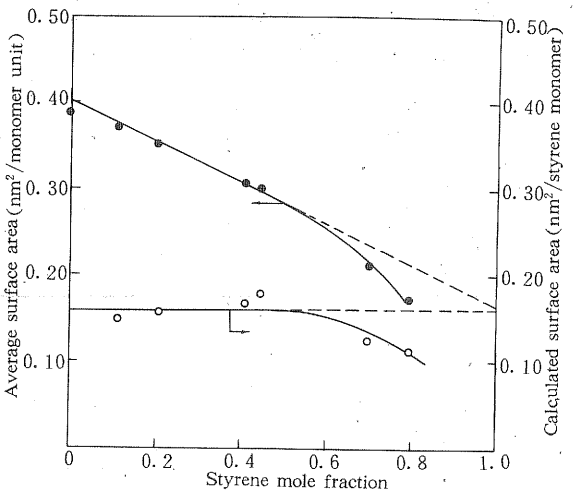


Fig. 3. Average limiting surface area per monomer unit and calculated area per St monomer unit as a function of St mole fraction (subphase, pure water).

Figure 3 shows the variation in the average limiting surface area per monomer unit with St mole fraction. Similar to PDDASt copolymers [2], a straight line is obtained up to about 0.6 St mole fraction. This means that the copolymer chains have no coiled form on the water surface up to 0.6 St mole fraction and the St unit in the copolymer monolayer occupies a constant surface area. As shown in Fig. 3, the calculated surface area of the St unit in the $PAMC_{16}SSt$ copolymers up to about 0.6 St mole fraction is 0.16 nm^2, which is consistent with the value estimated from the CPK model where the copolymer main chain is laid horizontally on the water surface and the benzene rings are oriented perpendicular to the surface [2]. In general, a linear relationship between the average limiting surface area and the mole composition for mixed monolayers is observed in a situation where either ideal mixing or phase separation occurs [15]. In the mixed monolayers of long-chain fatty acids with a chromophore compound, the chromophore forms aggregates even at a concentration of a few per cent [16]. Now, in the case of random copolymers, each monomer unit is linked to the polymer chain randomly and the aggregation of the St monomer units is suppressed, resulting in the uniform distribution of St units in the monolayer.

When the St content in the $PAMC_{16}SSt$ copolymer increases further to 0.7–0.8 St mole fraction, deviation in the surface area of the St unit from the constant value is observed (Fig. 3), indicating that the

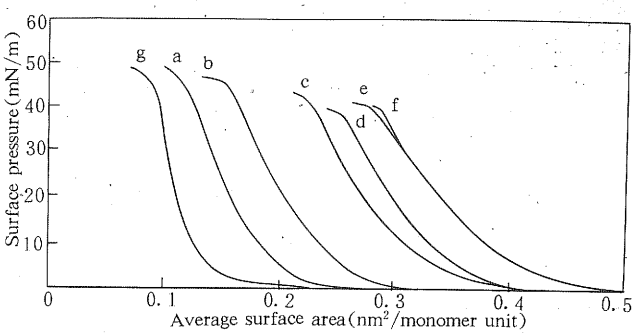


Fig. 4. $\pi-A$ isotherms of $PAMC_{16}SSt$ copolymers (curves a–f) and $AMC_{16}S$ homopolymer NP-2 (curve g) on a $CdCl_2$ aqueous solution (1 mmol L^{-1}).

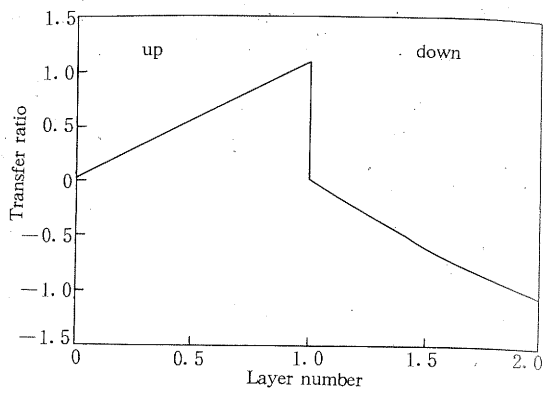


Fig. 5. Transfer curve of $PAMC_{16}SSt$ monolayer (sample e) on a hydrophilic glass slide by upward and downward strokes (subphase, $CdCl_2$ solution (1 mmol L^{-1})).

polystyrene segments begin to take a folded or coiled form on the water surface.

Figure 4 shows the $\pi-A$ isotherms of $PAMC_{16}SSt$ copolymers as well as the $AMC_{16}S$ homopolymer NP-2, spread on a $CdCl_2$ aqueous solution (1 mmol L^{-1}). It can be seen that the subphase has a strong effect on the spreading behavior of the $AMC_{16}S$ homopolymer NP-2, and the limiting area per monomer unit decreases markedly when the subphase contains $CdCl_2$. This phenomenon is in agreement with the results obtained previously [6, 14]. It means that $PAMC_{16}S$ can form more closely packed monolayers when the subphase contains multivalent cations. Interestingly, the addition of $CdCl_2$ to the water subphase has little effect on the spreading behavior of $PAMC_{16}SSt$ copolymers, even for the copolymer with a St mole fraction as low as about 0.1. This result suggests that no phase separation of $PAMC_{16}S$ segments occurs in the $PAMC_{16}SSt$ monolayers.

There is a lack of rules governing the transfer of polymeric monolayers. As new random-copolymer-type amphiphilic polymers with a broad composition range, $PAMC_{16}SSt$ copolymers are of special interest. It was found that the molecular areas of the spread monolayers of both $PAMC_{16}S$ and $PAMC_{16}SSt$ changed little when the surface pressure was kept constant (30 mN m^{-1}), indicating that the monolayers were sufficiently stable for transfer. However, in the case of the pure water subphase, the apparent transfer ratio of the $AMC_{16}S$ homopolymer and $AMC_{16}S$-rich copolymers (samples e and f) by the upward stroke was much larger than 1; this is probably due to the strong hydrophilicity of $AMC_{16}S$ units. As the St content increased, the copolymer monolayers could be transferred with a transfer ratio of about 1. In the case of a $CdCl_2$ aqueous solution (1 mmol L^{-1}), the monolayer transfer of all the copolymers was achieved by the upward stroke with transfer ratio of about 1. However, all the transferred monolayers were lost in the downward stroke, as depicted in Fig. 5. Neither Y-type nor Z-type LB films were transferred on the hydrophilic glass substrate.

It was reported that the self-assembled monolayers of $PAMC_{16}S$ homopolymer on gold surfaces (both clean and anodized gold) exhibited great adsorption stability, even during faradaic reactions [14]. However, the similarly self-assembled monolayer on glass or quartz was found to be lost easily when the monolayer-coated plate was rinsed with water. This is due to the pronounced hydrophilic nature of $PAMC_{16}S$ and the weak interaction of its monolayer with the surface of glass or quartz; these factors are also responsible for the difficulty of LB film construction of $PAMC_{16}SSt$ on a glass substrate.

Acknowledgments

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