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Mixed Surface Micelles of Polystyrene-*b*-poly(2-vinylpyridine) and Polystyrene-*b*-poly(methyl methacrylate)

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ABSTRACT: We report on mixed surface micellization behavior of two diblock copolymers: PS-*b*-P2VP (M_w = 56 000, w_{PS} = 50%) and PS-*b*-PMMA (M_w = 50 000, w_{PS} = 50%). Both diblock copolymers were synthesized by sequential anionic polymerization and have narrow molecular weight distributions. PS-*b*-P2VP and PS-*b*-PMMA were spread at the air−water interface in dilute chloroform solution (0.5 mg/mL) by two different methods: (1) spreading of a premixed solution and (2) separate spreading of each block copolymer solutions sequentially. The $\pi-A$ isotherms were measured at different subphase pH, and the morphology of the surface micelles was investigated by atomic force microscopy after transferring to a Langmuir−Blodgett film onto a silicon wafer. The ionization of the P2VP block induced different morphology at low pH from which the aggregated structure of block copolymers in micelles could be delineated. When PS-*b*-P2VP and PS-*b*-PMMA are spread as a premixed solution, two block copolymers form surface micelles sharing a PS core and mixed corona of P2VP and PMMA chains while independent PS-*b*-P2VP micelles and PS-*b*-PMMA micelles coexist when the block copolymers were spread separately. These results indicate that the surface micellization takes place rapidly after spreading, and there is no observable exchange of the block copolymers between the micelles in a reasonable time span.

Introduction

Many amphiphilic block copolymers self-assemble at the air−water interface into a microphase-separated structure, which is called as surface micelle. The hydrophobic blocks aggregate to form isolated structures of different shapes depending on relative block lengths, and they are stabilized by surface-active hydrophilic blocks residing on the water surface.[1−15] The surface micelle is a two-dimensional analogue of block copolymer micelles in solution.

Recently, a variety of mixed block copolymer micelles have been realized by mixing two or more different diblock copolymers.[16−23] A typical approach to make mixed micelles is mixing two micelle-forming block copolymers of A−B and A−C type with a common insoluble A block, which may form a micelle with a core of aggregated A block and mixed coronas of B and C chains. In many cases, the B and C chains behave differently to environmental changes, and various potential applications could be anticipated with such mixed micelles. In addition, physical chemistry of chain mixing in such a confined geometry is also a subject of interest. However, the formation of mixed micelles is not a trivial process since the B and C chains are usually incompatible in the absence of favorable interactions.

There are several successful reports overcoming the huddle in the literature. For example, Zhang et al. reported on mixed micelle formation from premade polystyrene-*b*-poly(acrylic acid) and polystyrene-*b*-poly(aminopropylene glycol methacrylate) micelles in water.[23] They observed the exchange of block copolymers between the premade block copolymer micelles, which is rare unless there is a strong affinity between the corona chains. The driving force for chain mixing in this case was attributed to H-bond formation between the poly(acrylic acid) and poly(aminopropylene−glycol methacrylate) blocks in the coronas. Hui et al. prepared mixed block copolymer micelles of polystyrene-*b*-poly(2-vinylpyridine) (PS-*b*-P2VP) and poly(ethylene oxide)-*b*-P2VP (PEO-*b*-P2VP) with mixed corona chains of PS and PEO. The driving force for the formation of mixed micelle in this work was the cross-linking reaction of P2VP blocks by addition of 1,4-dibromobutane as the cross-linker in DMF. This mixed micelle is stable in water as well as in organic solvent such as 1,4-dioxane.[16] Hu and Liu reported on the preparation of mixed micelles of poly(*tert*-butyl acrylate)-

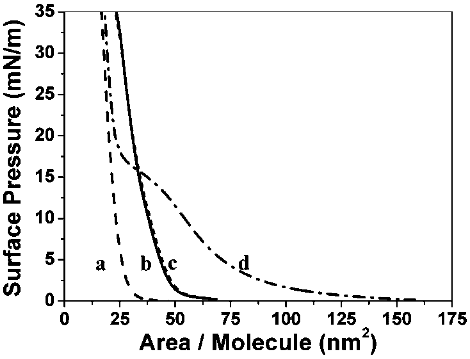

Figure 1. $\pi-A$ isotherms of PS-*b*-P2VP (a, d) and PS-*b*-PMMA (b, c) diblock copolymers at two different subphase pH (a and b: pH 1.8; c and d: pH 5.3).

Table 1. Characterization Results of PS-*b*-P2VP and PS-*b*-PMMA Diblock Copolymers

polymer	M_w[a]	composition[b] (PS), %	M_w/M_n[a]
PS-*b*-P2VP	56 000	50	1.10
PS-*b*-PMMA	50 000	50	1.08

[a] Measured by SEC/MALLS. [b] Determined by ^{1}H NMR.

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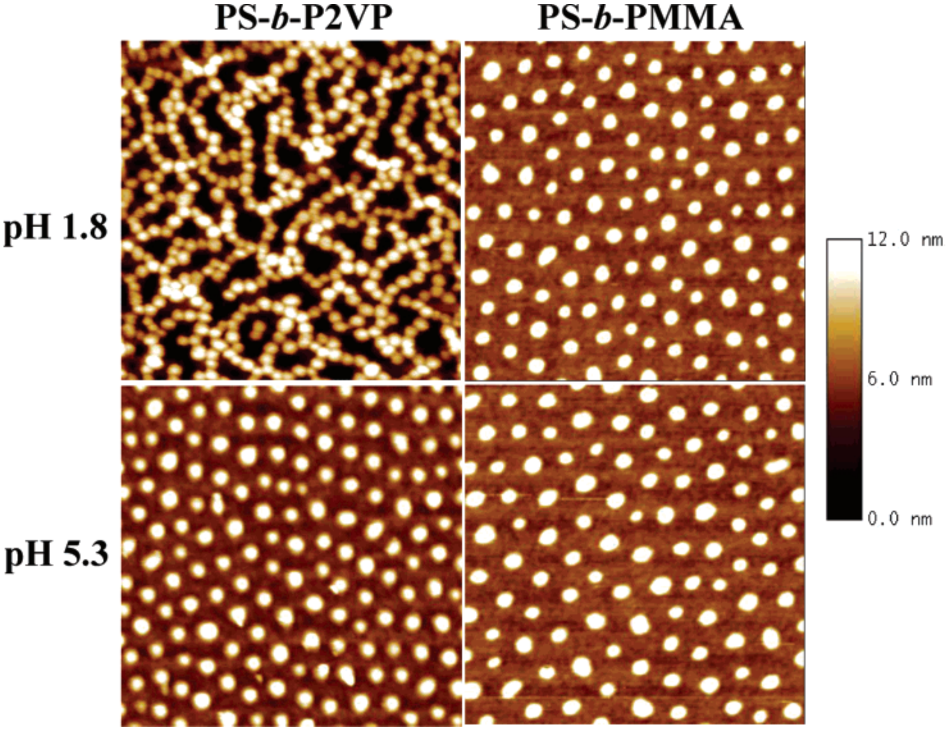

Figure 2. AFM images (1 × 1 μm) of the surface micelle morphology of PS-*b*-P2VP and PS-*b*-PMMA at different subphase pH. The LB films were deposited at π = 2 mN/m.

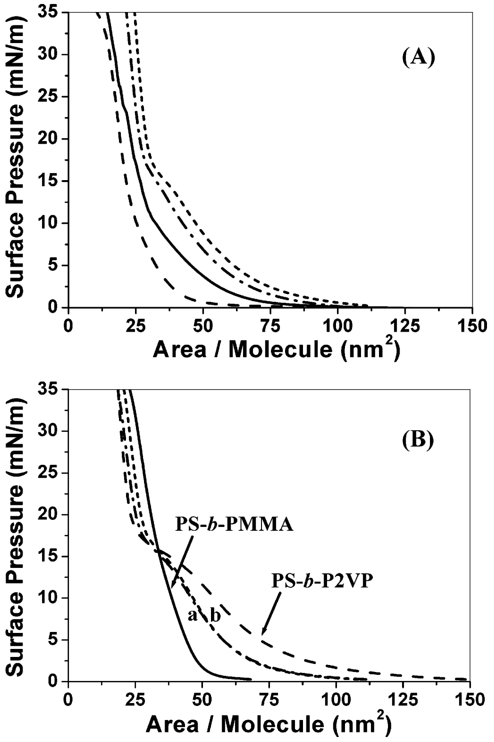

Figure 3. π−*A* isotherms of PS-*b*-P2VP and PS-*b*-PMMA mixture spread separately. (A) Dashed line: pH 1.8 (PS-*b*-P2VP:PS-*b*-PMMA = 2:1, w/w); solid line: pH 1.8 (1:1); dash-dotted line: pH 5.3 (1:1); dotted line: pH 5.3 (2:1). (B) π−*A* isotherms of surface micelles of individual PS-*b*-P2VP (dashed line), PS-*b*-PMMA (solid line), 1:1 mixture of two diblock copolymers at pH 5.3 (a: dash-dotted line), and the average area calculated from the π−*A* isotherms of PS-*b*-P2VP and PS-*b*-PMMA (b: dotted line).

b-poly((2-cinnamoyloxyethyl methacrylate)-*ran*-(2-(1′-thyminylacetoxyethyl methacrylate))) and PS-*b*-poly((2-cinnamoyloxyethyl methacrylate)-*ran*-(2-(1′-adeninylacetoxyethyl methacrylate))). Their strategy was overcoming the repulsion between the PS and PtBA blocks by increasing the affinity between the core forming PCEMA blocks by tagging the poly(2-cinnamoyloxyethyl methacrylate) blocks of two diblock copolymers with a H-bonding pair of adenine and thymine.[18]

While the mixed block copolymer micelles in solution have attracted wide attention recently, few studies have been made on the mixed surface micelles at the air−water interface. This paper reports on the mixed surface micelle formation of A−B and A−C type block copolymers at the air−water interface. The core forming A block is hydrophobic polystyrene while B and C blocks are surface-active P2VP and poly(methyl methacrylate) (PMMA), respectively.

Experimental Section

Materials. PS-*b*-P2VP was synthesized by sequential anionic polymerization in THF at −78 °C under Ar atmosphere using *sec*-BuLi (Aldrich) and THF (Mallinckrodt) as an initiator and a solvent, respectively. Details of the apparatus and the polymerization procedure were reported previously.[24,25] PS-*b*-PMMA was also synthesized by sequential anionic polymerization of styrene and methyl methacrylate in THF at −78 °C under Ar atmosphere. The initiator was *sec*-BuLi, and 10 equiv of LiCl was added to suppress the side reaction in the polymerization of PMMA block.[26] The two diblock copolymers were characterized by ^{1}H NMR spectroscopy (Bruker, DPX-300) for the composition and by size exclusion chromatography (SEC) for the molecular weight. For the SEC analysis, two PS gel columns (Polymer Lab., PL-mixed C) were used, and the mobile phase was THF at a flow rate of 0.8 mL/min. For the analysis of PS-*b*-P2VP, 2 vol % trimethylethylenediamine (Aldrich) was added to the mobile phase to prevent the adsorption of P2VP to the stationary phase. SEC chromatograms were recorded by a refractive index detector (Wyatt, Opti-Lab) and a multiangle laser light scattering detector (Wyatt, mini-Dawn). The molecular characteristics of the synthesized diblock copolymers are summarized in Table 1.

***π*−*A* isotherms and Langmuir−Blodgett (LB) Films.** Surface micelles of PS-*b*-P2VP and PS-*b*-PMMA were formed at the air−water interface on a LB film apparatus (KSV 5000) by spreading dilute polymer solutions in chloroform (0.5 mg/mL). The aqueous

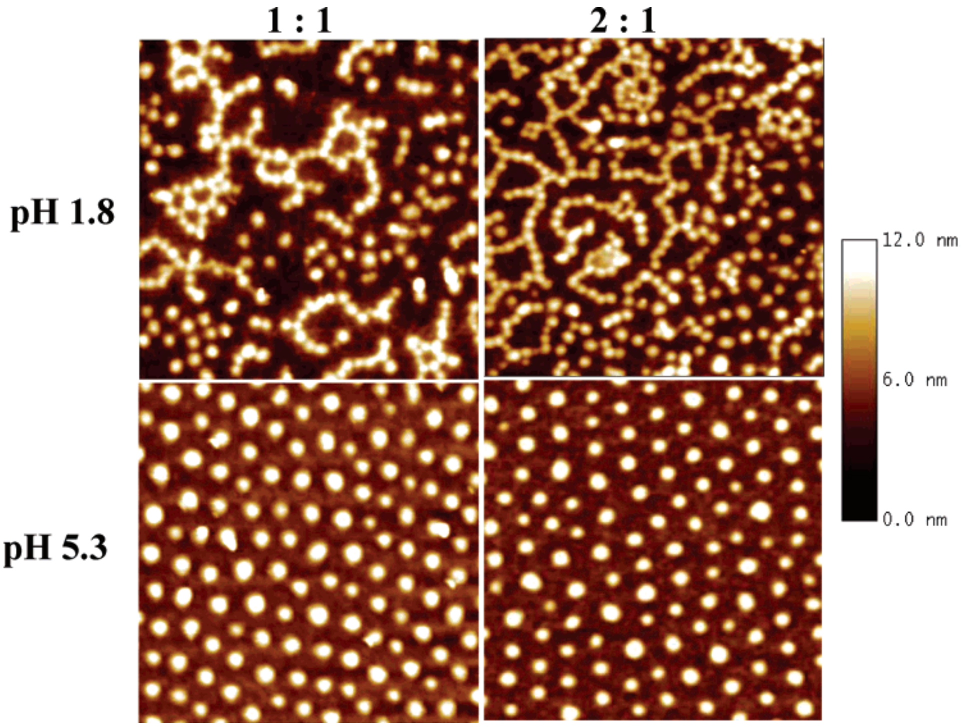

Figure 4. AFM images (1 × 1 μm) of the LB films of block copolymer mixture of different composition (PS-*b*-P2VP:PS-*b*-PMMA = 1:1 and 2:1, w/w) prepared by the separate spreading method at different subphase pH. The LB films were deposited at $\pi = 2$ mN/m.

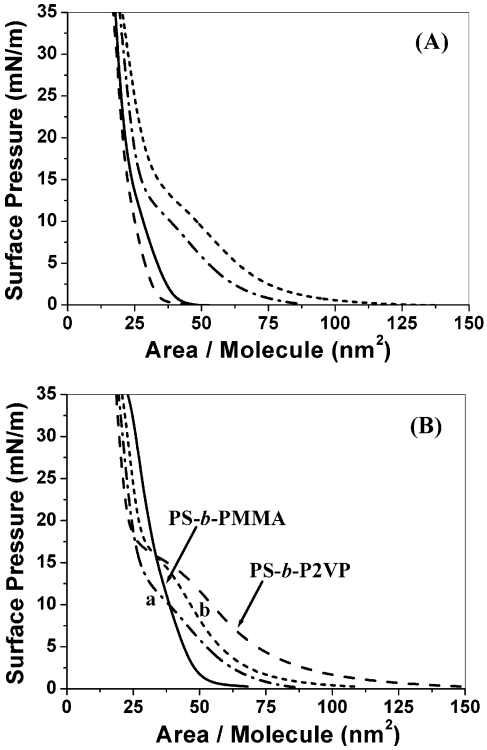

Figure 5. $\pi-A$ isotherms of PS-*b*-P2VP and PS-*b*-PMMA mixture prepared by the premixed spreading method. (A) Dashed line: pH 1.8 (PS-*b*-P2VP:PS-*b*-PMMA = 2:1, w/w); solid line: pH 1.8 (1:1); dash-dotted line: pH 5.3 (1:1); dotted line: pH 5.3 (2:1). (B) $\pi-A$ isotherms of surface micelles of individual PS-*b*-P2VP (dashed line), PS-*b*-PMMA (solid line), 1:1 mixture of two diblock copolymers at pH 5.3 (a: dash-dotted line), and the average area calculated from the $\pi-A$ isotherms of PS-*b*-P2VP and PS-*b*-PMMA (b: dotted line).

subphase was either deionized water or sodium phosphate buffer solution (0.2 M). The $\pi-A$ isotherms were obtained at a compression rate of 5 mm/min. The temperature of the subphase was maintained at 25 °C using a circulating water bath.

LB films were transferred onto RCA-treated Si wafers at a constant vertical lift speed of 5 mm/min while keeping the surface pressure constant at 2 mN/m by feed back controlled compression. The transfer ratio was close to unity. The equilibration time at the target pressure before the LB film transfer is 20 min.

Sample Spreading Methods. Two different sample spreading methods were used: premixed and separate spreading. In the premixed spreading method, PS-*b*-P2VP and PS-*b*-PMMA are dissolved in chloroform at a mass ratio of 1:1 or 2:1. The 0.5 mg/mL (total concentration) chloroform solution was spread at the air–water interface. In the separate spreading method, the spreading solutions of PS-*b*-P2VP or PS-*b*-PMMA in chloroform prepared separately at a concentration of 0.5 mg/mL each. The PS-*b*-P2VP and PS-*b*-PMMA solutions were spread sequentially. About 15 min was allowed between each spreading for complete evaporation of chloroform and the formation of surface micelles.

AFM Measurement. The surface morphology of the LB films was observed by a tapping mode AFM (Digital Instruments, Nanoscope III) housed in a vibration-resistant case. Each sample was imaged at a number of different locations on the wafer to examine the reproducibility of the surface morphology. A 100 μm scanner and silicon tips (125 μm tip length) were used.

Results and Discussion

Individual Block Copolymers. Figure 1 shows the $\pi-A$ isotherms of individual PS-*b*-P2VP and PS-*b*-PMMA at two different subphase pH. The pH 5.3 corresponds to deionized water in contact with air, and the subphase of pH 1.8 was a 0.2 M sodium phosphate buffer. The PS-*b*-PMMA monolayer film (b and c) did not show a noticeable difference at two different pH as expected for a nonionizable polymer. The $\pi-A$ isotherms of PS-*b*-PMMA show a characteristic of the condensed film showing a steep increase of surface pressure upon compression.

On the other hand, the isotherms of PS-*b*-P2VP show a quite different behavior at two different subphase pH due to the

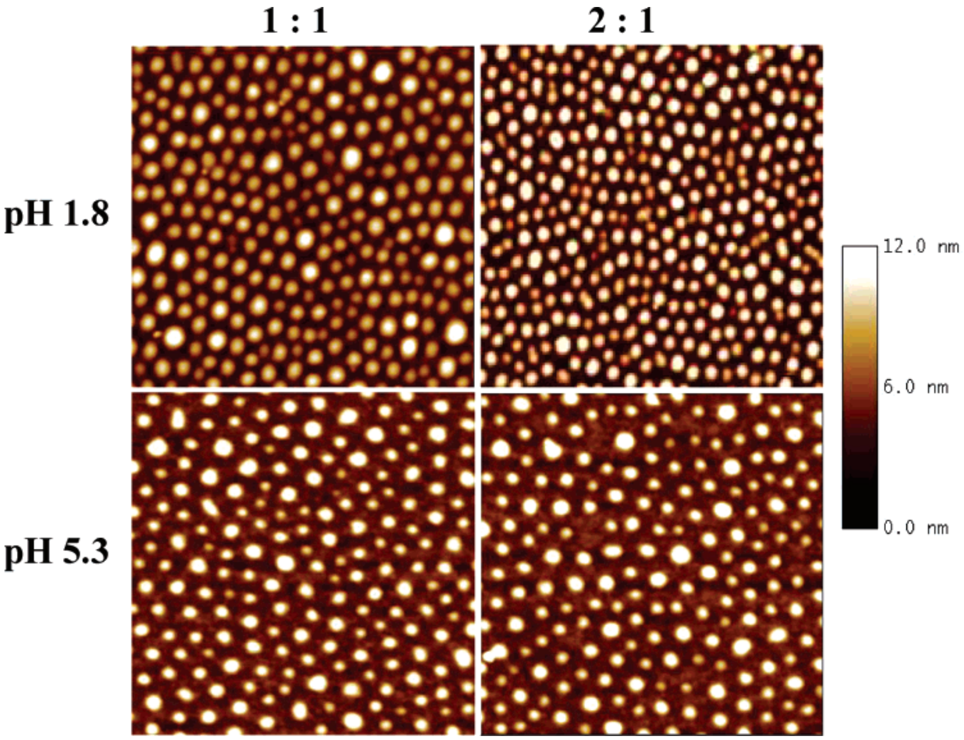

Figure 6. AFM images (1 × 1 μm) of the LB films of block copolymer mixture of different composition (PS-*b*-P2VP:PS-*b*-PMMA = 1:1 and 2:1, w/w) prepared by the premixed spreading method at different subphase pH. The LB films were deposited at $\pi = 2$ mN/m.

ionization of the P2VP block.[10,12] At pH 5.3 (d), P2VP corona chains are partially ionized and the surface micelles exhibit an expanded film behavior showing a slow rise of the surface pressure upon compressing the film. A transition region shows up at $\pi \approx 15$ mN/m due to the submerge of the partially ionized P2VP block upon compression of the Langmuir film.[10] At pH = 1.8 (a), the $\pi-A$ isotherm is much different from the one observed at pH 5.3. The fully ionized P2VP blocks submerge into the subphase, and the surface micelles exhibits a condensed film behavior. At low surface pressure, the surface area at pH 1.8 is far smaller than pH 5.3 due to the fact that the molecular area pervaded by the P2VP corona at the air−water interface decreases with increasing solubility of P2VP at low pH.[27] At high surface pressure, the molecular area becomes similar at two different pH, reflecting the submergence of the PVP chains at the highly compressed state.

Figure 2 displays the AFM images of the LB films of individual PS-*b*-P2VP and PS-*b*-PMMA deposited at $\pi = 2$ mN/m at two different subphase pH (1.8 and 5.3). For the PS-*b*-PMMA, there is hardly any morphological difference at the two different pH. Isolated circular micelles with a quasi-hexagonally packed structure were observed, which is the commonly observed circular surface micelle morphology for amphiphilic block copolymers with a large enough hydrophilic block. In contrast, a big morphological difference shows up for PS-*b*-P2VP LB films at two different pH. At pH 5.3, the surface micelle morphology is similar to that of PS-*b*-PMMA because the solubility of P2VP chains is low at this pH. At pH 1.8, the morphology is distinctively different in which circular micelles form a laced network structure. This is due to the submerge of the fully ionized P2VP corona leaving PS cores unscreened from the hydrophobic interaction, which induces an interesting association of the surface micelles.[12] This characteristic morphology of PS-*b*-P2VP surface micelle at low pH helps delineate the aggregated structure of mixed micelles as described later.

Separate Spreading. Figure 3A displays the $\pi-A$ isotherms of PS-*b*-P2VP and PS-*b*-PMMA spread separately. Four $\pi-A$ isotherms were obtained for two different diblock copolymer composition (PS-*b*-P2VP:PS-*b*-PMMA = 2:1 and 1:1, w/w) at two different subphase pH. The average area per molecule increases in the sequence of (2:1, pH 1.8), (1:1, pH 1.8), (1:1, pH 5.3), and (2:1, pH 5.3). The film of the 2:1 mixture (PS-*b*-P2VP:PS-*b*-PMMA) is more condensed than the 1:1 mixture at pH 1.8 while more expanded at pH 5.3. It can be understood from the fact that a partially ionized P2VP corona chains at pH 5.3 pervades a larger area than the PMMA chain while a fully ionized P2VP corona chain at pH 1.8 occupies a smaller area than the PMMA chain at the air−water surface, as seen in Figure 1.

The two isotherms obtained at pH 5.3 show a transition behavior at the surface pressure of $\pi \sim 15$ mN/m, which is the same as of the neat PS-*b*-P2VP although it is not as conspicuous as the case of neat PS-*b*-P2VP. The transition region becomes more distinct as the PS-*b*-P2VP content increases. It appears that the $\pi-A$ isotherms of mixed micelles show an intermediate property of individual micelles. In order to find whether the $\pi-A$ isotherms represent the average surface area of the individual surface micelles, the $\pi-A$ isotherm of 1:1 mixed surface micelle is compared with the average $\pi-A$ isotherm of individual block copolymers in Figure 3B. The average molecular area at a given surface pressure is calculated by the following formula

$$\text{average area} = n_{\text{PS}-b-\text{P2VP}}(\text{area/PS-}b\text{-P2VP}) + n_{\text{PS}-b-\text{PMMA}}(\text{area/PS-}b\text{-PMMA}) \quad (1)$$

where $n_{\text{block copolymer}}$ is the number fraction of each block copolymers. Indeed, the number-average $\pi-A$ isotherm of the two individual block copolymers matches near perfectly at low surface pressure with that of the 1:1 mixture spread separately. At high surface pressure above the transition surface pressure of PS-*b*-P2VP (~15 mN/m), the agreement is not as good. Although not shown, a similar behavior is observed for the 2:1 mixture at pH 5.3. On the other hand, we could not find such

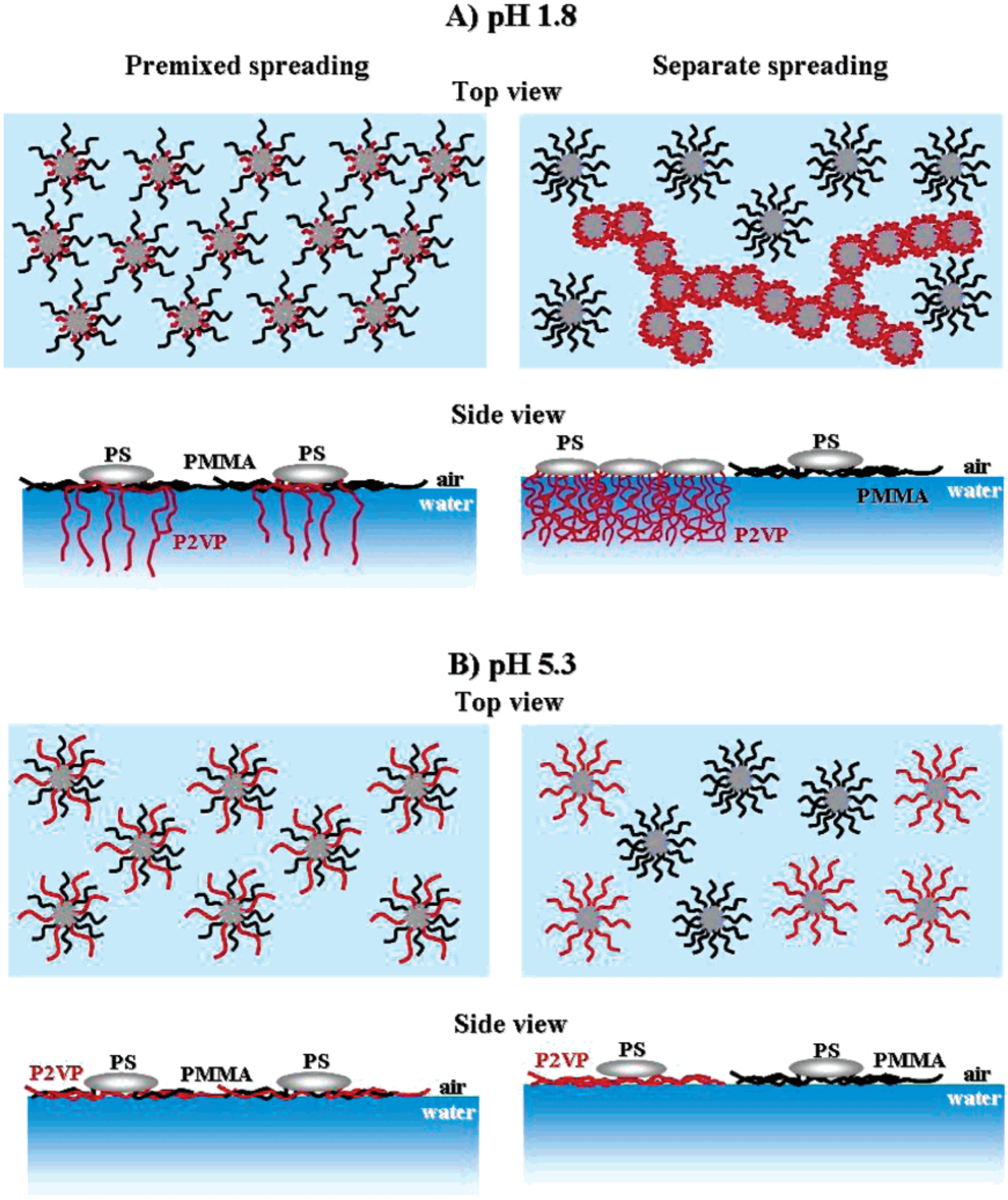

Figure 7. Schematic illustrations of the surface micelles prepared by spreading of premixed solution and separate spreading of PS-*b*-P2VP and PS-*b*-PMMA at pH 1.8 (A) and pH 5.3 (B).

a good additive behavior of the $\pi-A$ isotherm at pH 1.8.

The reason for the additive $\pi-A$ isotherm behavior can be found from the AFM images of the LB films shown in Figure 4. The topographic images obtained at pH 1.8 show combined AFM images of two individual diblock copolymers obtained at pH 1.8 in Figure 2, which unambiguously indicates the coexistence of the individual micelles of PS-*b*-P2VP and PS-*b*-PMMA. As the composition of PS-*b*-P2VP is increased, more laced structures are observed. Although it is not possible to find a similar clue from the surface micelle morphology at pH 5.3, in which only isolated circular micelles are observed, it would be safe to conclude that they also consist of individual micelles of PS-*b*-P2VP and PS-*b*-PMMA. At low surface pressure (at low micelle concentration), the interaction among the two different micelles is not strong, and such additivity of the surface area seems to be observed. At high surface pressure, however, the two different corona chains are forced to be in contact with one another, and the $\pi-A$ isotherm deviates from the "ideal" mixing behavior of two different surface micelles. The departure from the simple additive $\pi-A$ isotherm behavior at pH 1.8 can be understood in a similar manner since the PS-*b*-P2VP micelles with highly charged and submerged P2VP corona chains are highly incompatible with the PMMA corona chains in PS-*b*-PMMA micelles. The AFM images for the surface micelles at pH 1.8 in Figure 4 show irregular empty spaces, indicating that the two kinds of micelles do not fill the surface area homogeneously.

Premixed Spreading. When a premixed solution was spread at the air−water interface, as shown in Figure 5A, the general trend of the $\pi-A$ isotherms according to the subphase pH and the composition is similar to the case of separate spreading; the average area per molecule increases in the sequence of (PS-

b-P2VP:PS-*b*-PMMA = 2:1, pH 1.8), (1:1, pH 1.8), (1:1, pH 5.3), and (2:1, pH 5.3). However, the details of the $\pi-A$ isotherms are quite different, as displayed in Figure 3B for the 1:1 mixture at pH 5.3. The isotherm of 1:1 mixture (a) deviates significantly from the isotherm of average molecular area calculated from the isotherms of neat diblock copolymers (b). It indicates that the surface micelles of the block copolymer mixture have a structure different from the case of separate spreading. In addition, the transition surface pressure is lower than the case of separate spreading of neat PS-*b*-P2VP. Since the transition behavior is due to the submergence of partially ionized P2VP corona upon compression, the low transition pressure indicates that the number of P2VP corona chains per micelle would have changed.

In Figure 6 are displayed the surface morphology of the LB films prepared by the premixed spreading method at different subphase pH (1.8 and 5.3) and two different compositions of the block copolymer mixture (PS-*b*-P2VP:PS-*b*-PMMA = 2:1 and 1:1, w/w). All four AFM images show isolated circular surface micelles. The morphology at pH 5.3 is not much different from the separate spreading case (Figure 4), but the morphology at pH 1.8 is entirely different. The laced micelle structure of PS-*b*-P2VP observed in separate spreading at low pH disappeared, which indicates the absence of neat PS-*b*-P2VP micelles. The separate circular micelle structure at both low and high pH suggests the formation of mixed micelle of two bock copolymers sharing a common PS core.

Figure 7 schematically illustrates the structure of surface micelles prepared by two different spreading methods at pH 1.8. In a surface micelle formed by spreading of premixed solution, PS-*b*-P2VP and PS-*b*-PMMA aggregates sharing a PS core and mixed corona chains of P2VP and PMMA stabilize the surface micelle structure. Even at low pH, due to the pH-insensitive PMMA blocks spreading at the air−water interface, they can exist as isolated circular micelles despite the submergence of ionized P2VP chains. In contrast, the surface micelles formed from the separate spreading show the characteristics of the coexisting individual PS-*b*-P2VP and PS-*b*-PMMA micelles. At low pH, isolated circular surface micelles of PS-*b*-PMMA coexist with circular micelles of PS-*b*-P2VP which are associated into a laced structure due to the hydrophobic interaction of PS cores. At high pH, they also exhibit the characteristics of individual block copolymer micelles showing the average $\pi-A$ isotherm behavior of two neat block copolymers.

In summary, PS-*b*-P2VP and PS-*b*-PMMA form mixed micelles sharing a PS core when a premixed solution is spread on the air−water interface. The evidence of mixed micelle formation was confirmed by $\pi-A$ isotherm measurements and the surface micelle morphology after transferring to LB films. The mixed surface micelles with both P2VP and PMMA corona chains form isolated nanoscale dot patterns over wide pH range, which may find some useful applications with ionized P2VP chains. Such a structure is not realized with neat PS-*b*-P2VP at low pH. When the two block copolymers were spread separately, two kinds of micelles consisting of each block copolymers were formed. These results indicate that the surface micelle formation is a rapid process, and exchange of the block copolymers among the surface micelles is slow once the surface micelles are formed.

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