

Surface Micelle Formation of Polystyrene-*b*-Poly(2-vinyl pyridine) Diblock Copolymer at Air-Water Interface

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Abstract: We have studied the surface micelle formation of polystyrene-*b*-poly(2-vinyl pyridine) (PS-*b*-P2VP) at the air-water interface. A series of four PS-*b*-P2VPs were synthesized by anionic polymerization, keeping the PS block length constant (28 kg/mol) and varying the P2VP block length (1, 11, 28, or 59 kg/mol). The surface pressure-area (π -A) isotherms were measured and the surface morphology was studied by atomic force microscopy (AFM) after Langmuir-Blodgett film deposition onto silicon wafers. At low surface pressure, the hydrophobic PS blocks aggregate to form pancake-like micelle cores and the hydrophilic P2VP block chains spread on the water surface to form a corona-like monolayer. The surface area occupied by a block copolymer is proportional to the molecular weight of the P2VP block and identical to the surface area occupied by a homo-P2VP. It indicates that the entire surface is covered by the P2VP monolayer and the PS micelle cores lie on the P2VP monolayer. As the surface pressure is increased, the π -A isotherm shows a transition region where the surface pressure does not change much with the film compression. In this transition region, which displays high compressibility, the P2VP blocks restructure from the monolayer and spread at the air-water interface. After the transition, the Langmuir film becomes much less compressible. In this high-surface-pressure regime, the PS cores cover practically the entire surface area, as observed by AFM and the limiting area of the film. All the diblock copolymers formed circular micelles, except for the block copolymer having a very short P2VP block (1 kg/mol), which formed large, non-uniform PS aggregates. By mixing with the block copolymer having a longer P2VP block (11 kg/mol), we observed rod-shaped micelles, which indicates that the morphology of the surface micelles can be controlled by adjusting the average composition of block copolymers.

Keywords: surface micelle, polystyrene, poly(2-vinyl pyridine), block copolymer, Langmuir-Blodgett film.

Introduction

Many amphiphilic block copolymers are surface active to form Langmuir monolayers at the air-water interface, and the monolayer property and the morphology after the deposition of the Langmuir-Blodgett (LB) film have been studied extensively.¹⁻¹⁴ Amphiphilic block copolymers can self-assemble at the air-water interface into a micro-phase separated structure, which is called surface micelles. The hydrophobic blocks aggregate to form an isolated phase of various shapes and it is stabilized by the corona of hydrophilic blocks spread on the water surface. For example, Zhu *et al.* studied the surface micelle formation of polystyrene-*b*-poly(4-vinyl pyridine) quaternized with decyl iodide.¹ They observed circular, rod, and plane shaped phases of the PS domain

depending on the relative block lengths,² and calculated the aggregation number of circular micelles.³ The aggregation number decreased as the block length of P4VP/C₁₀I increased. As the Langmuir monolayer of the block copolymer was compressed by reducing the surface area, the hydrophilic block submerges into the subphase, which makes a transition region in the surface pressure-area (π -A) isotherm. They described the transition as a starfish to a jellyfish type transition,³ but recently reported that the dissolved chain remains adsorbed to the water surface.¹⁵ Also the research group has reported the similar surface micelle behavior for other block copolymers such as PS-*b*-poly(butyl methacrylate),¹⁶ PS-*b*-poly(ethylene oxide),¹³ and PS-*b*-poly(alkyl acrylate)s.¹²

Another surface active block copolymers, whose surface micelle behavior was extensively studied, are polystyrene-*b*-poly(ethylene oxide) (PS-*b*-PEO) and polystyrene-*b*-poly(methyl methacrylate) (PS-*b*-PMMA). Goncalves da Silva

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et al. investigated the Langmuir monolayer property of PS-*b*-PEO in detail and observed the transition behavior similar to the quaternized PS-*b*-P4VP.^{6,8} Baker *et al.* reported that the aggregation number of PS-*b*-PEO surface micelles decreases as the PEO portion increases and the aggregation number does not change with surface pressure.¹¹ Lin *et al.* used evanescent wave light scattering to investigate the surface monolayer of PS-*b*-PMMA.⁵ Seo *et al.* reported on the π -A behavior of PS-*b*-PMMA monolayers and the surface morphology of LB film transferred to silicon wafers.^{9,10} Kumaki *et al.* spread PS-*b*-PMMA at extremely low concentration to observe the AFM image of a single polymer chain from the LB film deposited at very low surface pressure.¹⁷

The overall monolayer behavior and surface morphology is similar for these amphiphilic block copolymers. The shape of surface micelles depends on the composition of block copolymers. Circular micelles are formed at high hydrophilic block composition and prevails to as low as 15-20% content. As the composition of the hydrophilic block is reduced further, rod-shaped micelles are preferentially formed. If the hydrophilic block content is reduced as low as 5%, the uniform structure of surface micelles is no longer observed. As the film is compressed, the area occupied by hydrophilic chains spread on the air-water interface is reduced and it reaches a point at which the hydrophilic chains form a dense monolayer. Then the film goes through a transition at which the π -A diagram shows a plateau. The high compressibility of the film in the transition region has been understood as the hydrophilic corona chains dissolve into the subphase or make conformation transition.¹⁸

Regarding the surface micelle formation mechanism, the surface micelles seem to form above the critical surface concentration as *three dimensional* micellization does.⁹ However, various conditions such as compression speed and concentration of spreading solution also affect the micellization behavior.¹⁹ Mobility of polymer chains forming surface micelle appears more restricted than three dimensional micelles. Cox *et al.* reported that block copolymers having a hydrophobic and a hydrophilic block forms micelles irreversibly soon after they were spread on the water surface.¹³ And aggregation number in a surface micelle does not seem to change much with compression. On the other hand, Baekmark *et al.* observed that poly(2-ethyl-2-oxazoline)-*b*-poly(2-nonyl-2-oxazoline) did not form surface micelles at low surface pressure, and surface micelles were formed as the surface pressure was increased.⁷

The *three dimensional* micellization of PS-*b*-PVP in selective solvents has been studied extensively for potential applications of the microphase-separated structures.²⁰⁻²³ The PVP block domain of the micelles is useful to capture various counter anions to generate nano-structures of various metals or compounds. However, there is no report on the surface micelle behavior of PS-*b*-PVP except for the extensive

works of Lennox and coworkers on the PS-*b*-P4VP with quaternized PVP block. We found that it is not necessary to quaternize PVP block with alkyl chains but PS-*b*-PVP block copolymer itself is surface active to form surface micelles. In this study, we investigate the surface micelle formation of polystyrene-*b*-poly(2-vinyl pyridine) (PS-*b*-P2VP) diblock copolymers at the air-water interface.

Experimental

Materials. PS-*b*-P2VP diblock copolymers were synthesized by sequential anionic polymerization keeping the PS block length constant at 28 kg/mol and varying the P2VP block length at -78 °C under Ar atmosphere using *sec*-BuLi and THF as an initiator and a solvent, respectively. Details of the apparatus and the polymerization procedure were reported previously.^{24,25} After the polymerization of styrene block was completed, 2-vinylpyridine (2VP) was added for the polymerization of the P2VP block. After the polymerization of PS block, an aliquot of the reaction mixture was taken for the characterization. Subsequently, a series of diblock copolymers with variable P2VP block length were obtained by withdrawing aliquots of the reaction mixture after each 2VP monomer addition. The block copolymers were precipitated in methanol. The degree of polymerization of the PS blocks and the polydispersities of the diblock copolymers were determined by size exclusion chromatography (SEC). The PS-*b*-P2VPs used in this study were summarized in Table I.

Surface Pressure Measurement and LB Films. As a spreading solvent, HPLC grade chloroform (Mallinckrodt) was used without further purification. PS-*b*-P2VP monolayer was spread at the air-water interface by dropping 100 μ L of 0.5 mg/mL chloroform solution on deionized water and the surface pressure-area (π -A) isotherms were measured after complete evaporation of the solvent (~15 min) using an LB film apparatus (KSV 5000) at the compression rate of 5 mm/min. The temperature of the subphase was maintained at 25 \pm 0.2 °C using a circulating water bath (Neslab, RTE-110).

Atomic Force Microscope Measurement. LB film of the polymer monolayer was transferred onto RCA-treated Si wafer by pulling it out of the subphase with a constant speed

Table I. Molecular Characteristics of PS-*b*-P2VP^a

PS- <i>b</i> -P2VP	M_n (PS, kg/mol)	M_n (P2VP, kg/mol)	M_w/M_n
28k-1k	28	1	1.10
28k-11k	28	11	1.08
28k-28k	28	28	1.05
28k-59k	28	59	1.05

^aDetermined by SEC with light scattering detection.

of 5 mm/min while maintaining a constant surface pressure. The surface morphology of the LB films were examined by a tapping mode AFM (Digital Instruments, Nanoscope III). Each sample was imaged at a number of locations on the wafer to examine the reproducibility of the features observed in the images. A 10 μm scanner and silicon tips (125 μm tip length) were used. Images shown were plane-fitted, flattened in a few cases, to maximize image presentability. Measurements of height, width, and spacing were taken from sectional analyses of the images. All images are 1 μm on a side, with heights and gray scale chosen to optimize presentability.

Aggregation Number of Surface Micelles. The area per micelle is obtained from the number of micelles in the AFM images. The area per block copolymer molecule is determined from the π -A isotherm by dividing the surface area by the number of spread polymer molecules at the surface pressure where the film was transferred. Then the area per micelle divided by the area per molecule yields the number of the block copolymer molecules per micelle.

Results and Discussion

π -A Isotherm. Figure 1 shows the π -A isotherm of PS-*b*-P2VPs of four different P2VP block lengths. For the block copolymers with short P2VP block lengths (28k-1k and 28k-11k), the π -A isotherm does not show any special feature but rises steeply at small molecular area. It is a typical behavior of polymers without sufficient length of hydrophilic blocks. For PS-*b*-P2VPs with a longer P2VP block length, typical π -A characteristics of amphiphilic block copolymers are observed. At low surface pressure, a typical expanded Langmuir film behavior is observed for PS-*b*-P2VP (region 1). In this region surface pressure increases gradually as the film is compressed. The film is more expanded for longer P2VP blocks, which indicates that the hydrophilic P2VP chains spread on the water surface.

As the film is compressed further, transition region appears where the film compressibility becomes very high (region 2). The longer the P2VP block is, the wider the transition zone is. It is because the hydrophilic blocks occupying a larger surface area reorganize their structure. For the case of water insoluble hydrophilic blocks such as PMMA, it is not expected that PMMA blocks dissolve into the subphase and does not show a transition region. On the other hand, the water-soluble hydrophilic chains in PS-*b*-PEO or quarterized PS-*b*-PVP would dissolve into the subphase at the transition region. The jelly fish (or brush) type chain conformation was proposed earlier, but recently it was reported that the dissolved hydrophilic chains remains adsorbed to the water surface.¹⁵ After the transition zone, the surface pressure increases very steeply indicating that most of the surface area is occupied by hard PS domain (region 3).

In Figure 2, the π -A isotherms of the block copolymers

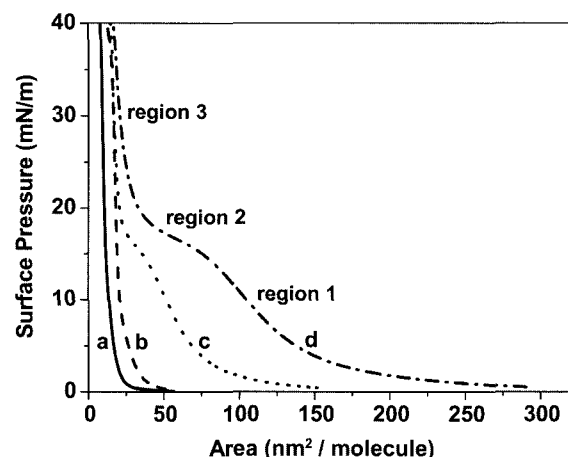


Figure 1. π -A isotherms of four different PS-*b*-P2VP samples. a: 28k-1k, b: 28k-11k, c: 28k-28k, d: 28k-59k.

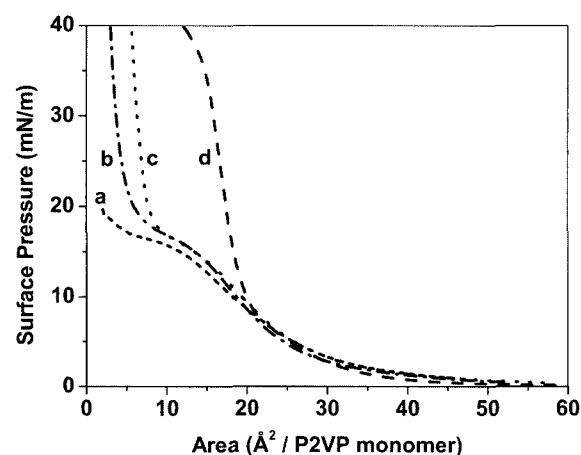


Figure 2. π -A isotherms of P2VP homopolymer (a) and PS-*b*-P2VP diblock copolymers (b-d). a: 35.9 kg/mol, b: 28k-59k, c: 28k-28k, d: 28k-11k.

are re-plotted against the surface area per P2VP monomer unit. Also plotted is a π -A isotherm of a P2VP homopolymer (a, $M_w = 35.9$ kg/mol). They show very similar π -A behaviors at the low pressure regime (region 1). The identical surface area occupied by the P2VP segments for homo-P2VP and PS-*b*-P2VP indicates that the entire surface area is covered by P2VP block for PS-*b*-P2VP. It is more clearly illustrated in Figure 3(A) displaying the limiting surface area occupied by a PS-*b*-P2VP molecule as a function of the molecular weight of P2VP block. The limiting area was determined at two regions of the π -A isotherm (region 1 and region 3) by extrapolating the π -A isotherm to the zero surface pressure and Figure 3(B) shows an example how the limiting areas were obtained for the 28k-28k sample. As shown in Figure 3(A), a very good linear relationship is found in region 1 between the limiting surface area per block copolymer

molecule and the P2VP block molecular weight (squares). Two homo-P2VP (9.1 and 35.9 kg/mol) data points (triangles) are included to confirm the observation made in Figure 2. Also the extrapolation of the line to the zero molecular weight approaches the zero surface area. This indicates that P2VP blocks occupy practically the entire surface area of the Langmuir film and the PS blocks contribution to the surface area is negligible in region 1. Therefore the micelle cores of PS aggregates (AFM images will be shown later) have to lie on the P2VP monolayer and do not contribute to the surface area in region 1. The general observation is similar to PS-*b*-PEO reported by Goncalves da Silva *et al.*, but the limiting area of PS-*b*-PEO (0.27 nm²) was significantly different from that of homo-PEO (0.40-0.48 nm²).⁶ Therefore, there must exist a clear difference in the structure of the hydrophilic chains between PS-*b*-P2VP and PS-*b*-PEO.

In region 3, a quite different behavior from region 1 is

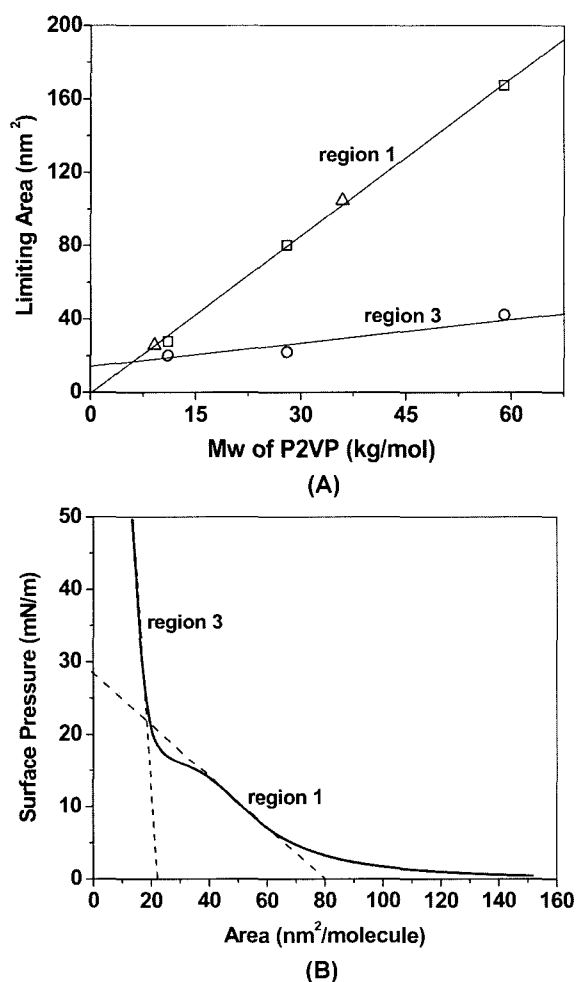


Figure 3. (A) Plot of limiting surface area vs. molecular weight of P2VP chain (PS-*b*-P2VP: □, homo-P2VP: △) in region 1, and in region 3 (PS-*b*-P2VP: ○) after the transition. (B) Diagram showing how the limiting surface area was determined for the 28k-28k sample as an example.

observed. The limiting surface area is about 20 nm², and the dependence on the molecular weight of P2VP block is much weaker than that in region 1. This indicates that in region 3 the P2VP chains contribute little to the limiting area. Kumaki measured the surface area of homo-PS film spread on water surface as 0.04 x M (molecular weight, in g/mol) in Å² for a wide molecular weight range from 4,000 to 2.06 × 10⁷.²⁶ The extrapolation of the line to the zero P2VP block molecular weight approaches ~14 nm², which is similar to the homo-PS value (11 nm² for 28 kg/mol PS). The small difference is seemingly due to the residual effect of the P2VP block.

Morphology of Langmuir-Blodgett Monolayer Films. Figure 4 displays the AFM images of the monolayer LB films of the PS-*b*-P2VPs transferred at a surface pressure of

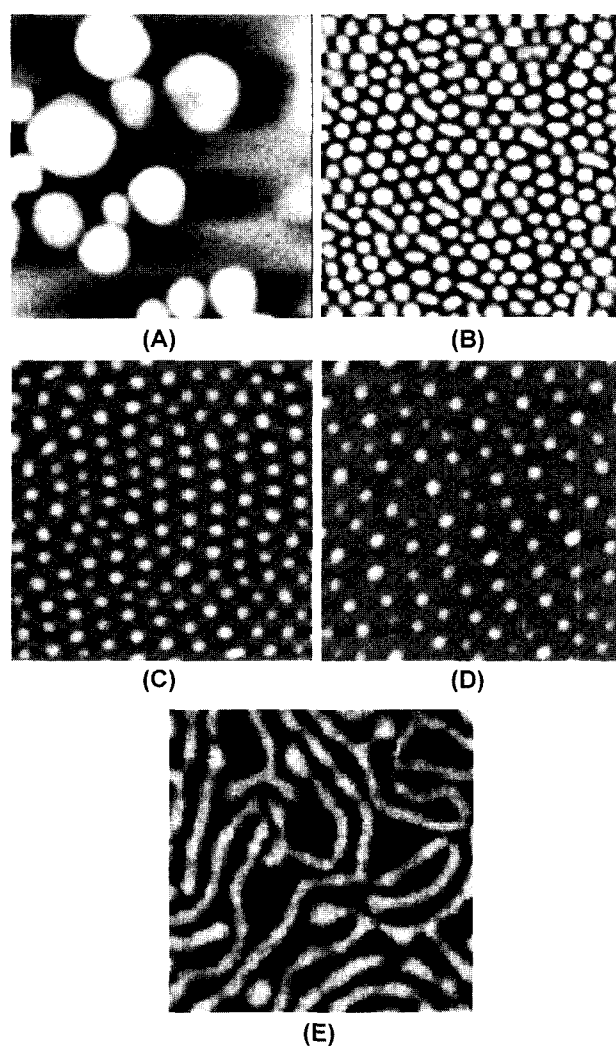


Figure 4. AFM images (1 × 1 μm) of the LB monolayer films of different molecular weight PS-*b*-P2VP (A~D) and a block copolymer mixture (E). (A) 28k-1k, (B) 28k-11k, (C) 28k-28k, (D) 28k-59k, (E) 28k-1k/28k-11k (5/5, w/w). Deposition surface pressure was 2 mN/m.

2 mN/m. The irregular circular aggregates were observed for 28k-1k sample (A), which indicates that the molecular weight of P2VP block is too low to make well-defined surface micelles. As the P2VP block length increases, more homogeneous circular micelles are formed. For 28k-11k sample (B), circular micelles and elongated micelles coexist and the distance between the micelles is not large. For 28k-28k (C) and 28k-59k (D) samples, well-developed circular micelles are observed, of which the radius is 25~40 nm and the height is 3~4 nm. The distance between the surface micelles increases with the P2VP block length.

Zhu *et al.* reported that the transition region in the π -A diagram was observed for the block copolymers which form circular micelles, which is consistent with this work.² They also found rod shaped micelles for PS-*b*-P4VP/C₁₀I with P4VP content of 6-14 mol% or less and plane morphology at P4VP content below 6%. Since it is expected that rod shaped micelles would appear for PS-*b*-P2VP with a P2VP block length between 1 and 11 kg/mol, we mix the equal weights of the 28k-1k and 28k-11k samples to make a sample

of 17.6 wt% P2VP content and observe the morphology of the surface micelles. As displayed in Figure 4(E) the mixture made rod-shaped micelles. The bulk morphology of block copolymer mixtures does not always follow the average composition and a more systematic study is needed to fully understand how the morphology of surface micelles varies in such mixture systems. In any event, we report that a different morphology of surface micelles can be developed by adjusting the average composition by mixing two block copolymers.

Next, the effect of surface pressure on the micelle morphology was investigated. Figure 5 displays the AFM images of the LB films of 28k-59k and 28k-28k samples deposited at two different surface pressures of 2 and 10 mN/m, respectively. The surface pressure of 10 mN/m is still much below the transition pressure (~15 mN/m) as can be seen in Figure 1. As the polymer film is compressed, the distance between the micelle cores (area per micelle) decreases. The height of the PS micelle cores remains at ~3-4 nm, almost independent of molecular weight or surface pressure. To compare the

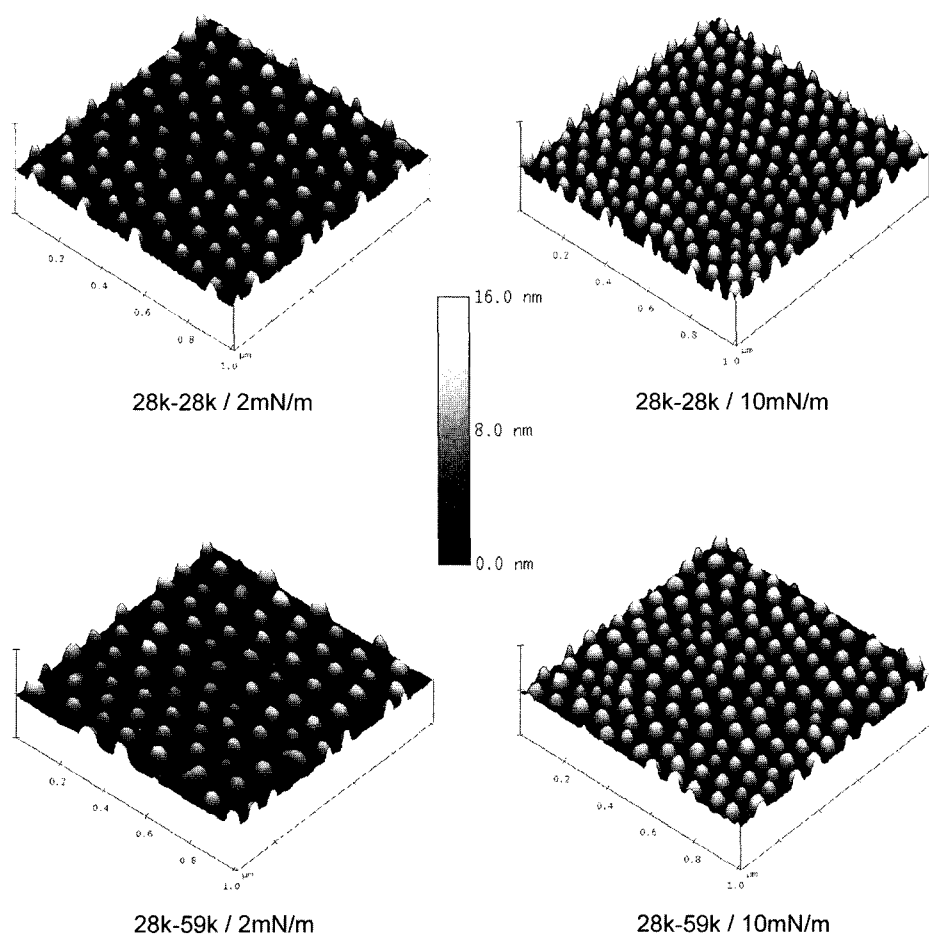


Figure 5. AFM images ($1 \times 1 \mu\text{m}$) of the LB monolayer films of 28k-28k and 28k-59k samples deposited at two different surface pressures.

Table II. Aggregation Number in a Surface Micelle^a

PS- <i>b</i> -P2VP/ Deposition Pressure	Number of Micelles/ μm^2	Area Per Micelle (10^3 nm^2)	Area Per Molecule (nm^2) ^b	Aggregation Number
28k-28k/2 mN/m	143 ± 2	6.99 ± 0.1	94.4	74 ± 1
28k-28k/10 mN/m	320 ± 16	3.13 ± 0.2	51.4	61 ± 3
28k-59k/2 mN/m	103 ± 2	9.71 ± 0.2	191	51 ± 1
28k-59k/10 mN/m	202 ± 8	4.95 ± 0.2	104	48 ± 2

^a Standard deviation obtained from the analysis of four separate AFM images.

^b Measured from π -A isotherm.

micelle size quantitatively, the aggregation number per micelle was determined by the method described in the experimental section and listed in Table II. The aggregation number decreases as the molecular weight of P2VP block increases. This is a general trend observed for surface micelles as well as for *three dimensional* micelles. Among the available data on the aggregation numbers of different block copolymers with comparable block lengths, we could find 190 for PS-*b*-PnBMA (27.1k-29.0k) and 125 for PS-*b*-P4VP/C₁₀I (27.1k-25.2k)¹⁶ to compare with 74 for PS-*b*-P2VP (28k-28k). It remains to be answered why the aggregation number for PS-*b*-P2VP is significantly less than the other polymers. It appears that there is no simple way to predict the aggregation number of surface micelles yet. Zhu *et al.* also reported that the aggregation number of PS-*b*-P4VP/alkyl iodide showed no simple trend with the alkyl chain length.⁴

While the aggregation number of the 28k-59k sample is almost independent of surface pressure, but the 28k-28k sample shows a noticeable decrease in the aggregation number at high surface pressure. It is due to the appearance of small sized micelles at 10 mN/m for 28k-28k sample as observed in Figure 5. Baker *et al.* reported a similar observation on the surface micelle behavior of PS-*b*-PEO that the size of surface micelles decreases with surface pressure increase for PS-*b*-PEO with low PEO content (15.5%) while it becomes independent of molecular weight at high PEO content.¹¹ However, it is generally accepted for block copolymers forming glassy surface micelle cores of surface micelles to form micelles irreversibly soon after they were spread on the water surface.¹³ Therefore, the surface pressure dependence of the aggregation number remains to be investigated further to understand the origin of this behavior.

Figure 6 shows the AFM images of the 28k-28k LB film near the transition region. At the surface pressure of 13 mN/m, the individual circular micelles exist intact as shown in Figure 6(A). As the film was compressed further to approach the transition region (16 mN/m), micelle cores get close and start to make contact one another. In the transition region, the large portion of P2VP blocks hides beneath the PS cores and the boundary of the cores becomes obscure as shown in Figure 6(B). The change shows up more clearly in

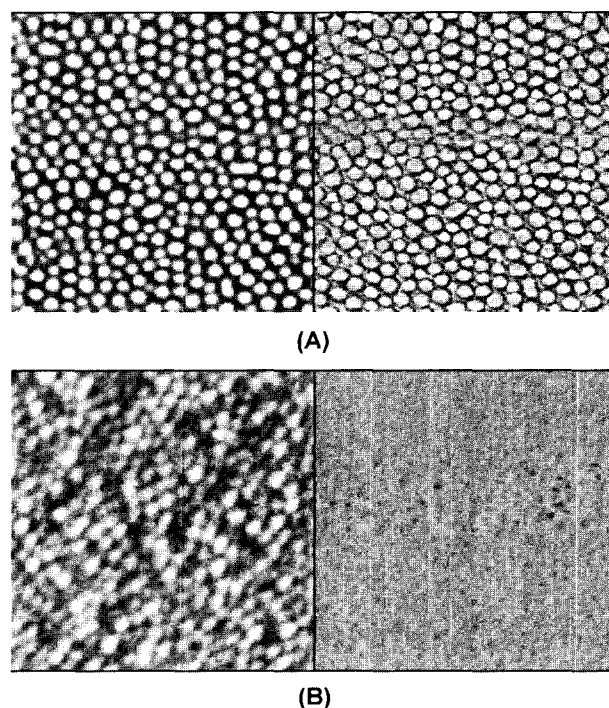


Figure 6. Height (left) and phase (right) mode AFM images ($1 \times 1 \mu\text{m}$) of 28k-28k LB films transferred at high surface pressures near the transition region. (A) 13 mN/m, (B) 16 mN/m.

the phase image, in which phase boundary between the PS cores is hardly observable. It indicates that practically the entire surface is covered with PS although the boundary of the micelle cores is still observable in the topographic image. This observation is consistent with the conclusion obtained from the limiting surface area that the surface area in region 3 is almost independent of P2VP block length (Figure 3 (B)). When the film is compressed further, the surface pressure increases very steeply due to the repulsion between hard PS cores.

In summary, we investigated the surface micelle behavior of a set of four PS-*b*-P2VPs with a constant PS block length at 28 kg/mol and varying P2VP block length of 1-59 kg/mol. PS-*b*-P2VP forms surface micelles well without quaternization of the pyridine groups. The general association behavior

of PS-*b*-P2VP at the air-water interface is not much different from the other amphiphilic block copolymers. We found that the limiting surface area at the surface pressure below the transition region is proportional to the P2VP chain length and identical to the homo-P2VP. It indicates that P2VP blocks form a dense monolayer on water surface and PS cores lie on the P2VP monolayer. At the surface pressure above the transition region the limiting area does not change much with the molecular weight of PS-*b*-P2VP. It indicates that the entire surface is covered by PS cores as confirmed by AFM. In addition, we found that a different surface micelle morphology can be formed by mixing block copolymers of different composition.

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