Aggregation Behaviors of a Polystyrene-*b*-poly(methyl methacrylate) Diblock Copolymer at the Air/Water Interface

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ABSTRACT: Aggregation behaviors, in particular, surface micelle formation, of a diblock copolymer A−B, where the A block is polystyrene (PS, surface inactive and water insoluble) and the B block is poly(methyl methacrylate) (PMMA, surface active, but water insoluble), at the air/water interface have been examined. The block length ratio of PS:PMMA was 140K:646K. With the aid of a Langmuir film balance and an atomic force microscope (AFM), surface pressure isotherms, as well as the hysteresis and temperature effects on the isotherms and aggregation numbers, were determined, and a self-consistent picture of the surface morphology and the aggregation phenomena was obtained. Analogous to the critical micelle concentration in a bulk solution of a surfactant, the surface aggregation of the block copolymer took place only at a certain surface mass density and resulted in small circular micelles with an aggregation number around 6−7, as determined by AFM. The small aggregation number is attributed to the longer block length of PMMA relative to that of PS.

Introduction

A considerable interest in polymer monolayers spread on air/water (A/W) interfaces has arisen because of both the molecular details accessible in monolayer experiments and the technological applications of ultrathin polymer layers.[1−10] Polymer monolayers spread on A/W interfaces have also played an important role in our understanding of the factors that control polymer−polymer and polymer−interface interactions.[11−20] Among polymer monolayers, block copolymers monolayers are particularly interesting because the blocks can be chosen to give the molecule a pronounced amphiphilic character.[21−30] In view of this, monolayers of diblock copolymers have received considerable attention in recent years.[31−40] Monolayers are quasi-two-dimensional by virtue of the adsorbed layer having a finite thickness; hence, their behaviors are expected to be different from those in three-dimensional space (in melts or solutions).[38,39] The values of the dimensional scaling parameters are different, but they have counterparts in different dimensional spaces. One is a phase separation and micelle formation.[2−9] A remarkable property of block copolymers is their ability to self-assemble in the melt into a variety of ordered structures with nanoscale periodicities.[35] These structures can be controlled by varying the composition of the block copolymers or the segregation between blocks. The properties of ordered structures in block copolymer melts were subjects of recent intensive experimental and theoretical studies.[36]

Micellization also occurs in dilute solutions of block copolymers in a selective solvent at a fixed temperature above a concentration called the critical micelle concentration.[41] At a high concentration above the critical gel concentration, the micelles can order into a lattice. Self-assembly of diblock copolymers into ordered structures was observed in two dimensions ("surface micelles") as well as in three dimensions.[2−14] Surface micelles have been observed for a number of ionic block copolymers by Eisenberg and co-workers.[2−9,33,34] Direct evidence was first obtained using a transmission electron microscope and an atomic force microscope (AFM) for polystyrene/poly(4-vinylpiridine) diblock ionomers, quaternized with decyl iodide (P(S-*b*-VP/C_{10}I)), spread as a monolayer on an A/W interface.[2] Depending on the relative chain length of each block, different morphologies were observed.[2−9] Phase transitions distinct from those in the bulk were observed with increasing asymmetry in a strongly segregated block copolymer. On the other hand, circular surface micelles were also observed for nonionic block copolymers.[9,33,34,37] The polymorphism (circular, rodlike, or large planar segregates) observed in the surface micelles of ionic block copolymers was determined by a balance between block sizes.[3] The polymorphism is evidently affected by the solubility of the hydrophilic part in block copolymers. Eisenberg et al.[5] describe spherical aggregates with a core−shell structure as "star" micelles if the corona block is much longer than the core and other aggregates whose soluble block is much shorter than the insoluble block as "crew cut" micelles.[21] As the soluble blocks are made progressively shorter, the morphology of the aggregate changes from spherical to rodlike, lamellar, or vesicular and finally to large compound vesicles and large compound micelles.[2,5,6] For some other diblock copolymers, it is reported that different interactions between the blocks induce surface aggregation under compression.[44−46]

All previous studies reported to date have been concerned with block polyelectrolytes or block copolymers in which one block is hydrophobic and the other is polar but nonionic. The relative contributions made by the hydrophobic "buoy" block and the water-soluble polyelectrolyte/polyhydrophilic block have been addressed.[11−17] When the surface monolayers are compressed, polymorphism appears and depends on the relative solubility or the affinity of one block with the

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subphase (water). If both blocks are hydrophobic, the block copolymer molecules remain on the water surface. The resulting morphology of the block copolymer monolayer is expected to depend on the interaction between the blocks, the chain length of each block, and the concentration.[34,37] This happens also to nonamphiphilic block copolymers. Rice and co-workers used static and dynamic evanescent wave light scattering to report that spread films of polystyrene-*b*-poly(methyl methacrylate) diblock copolymers (PS−PMMA) formed "thin disklike aggregates containing about 240 molecules".[37] No region of their surface pressure/area isotherm was found to correspond to isolated copolymer chains. However, this was for a PS−PMMA diblock copolymer having a PS block (M_w = 880 000) which was longer than the PMMA block (M_w = 290 000). They also remarked that, in monolayers of PS−PMMA having an M_w of 450 000 for both blocks, no aggregates of a disklike type were found. By noting that the attraction between collapsed PS blocks drives the copolymer aggregation, they concluded that if the PMMA blocks were large enough to keep the PS blocks from coming close together, no aggregates would be formed.

In this study, we investigated the monolayer behavior at an A/W interface of PS−PMMA diblock copolymers having a molecular weight different from that investigated by Rice et al.[37] Whether the block copolymers formed surface micelles, and if they did, what the shapes of the micelles would be were our main interests. These monolayers can stay on the water surface even at high concentration. We used a block copolymer having a molecular weight (M_n) of 140 000 for the PS block and 656 000 for the PMMA block. This diblock copolymer is different from that used by Rice et al.[37] in the sense that the PMMA block was much longer than the PS block. Hence, we expected different micelle morphology for this diblock copolymer at an A/W interface. As a part of continuing efforts to enhance our understanding of the micelle behavior of diblock copolymers, we report the details of the surface micellization of a PS−PMMA diblock copolymer at an A/W interface as measured by using a Langmuir film balance technique and an atomic force microscope.

Experimental Section

A. Materials. A PS−PMMA diblock copolymer was purchased from Polymer Source Inc. (Canada). It has molecular weight (M_n) of 140 000 for the PS block and 656 000 for the PMMA block. Its polydispersity index was 1.32. Neat polystyrene (PS) and poly(methyl methacrylate) (PMMA) were purchased from Pressure Chemicals Co. The molecular weight (M_n) of the polystyrene was 200 000, and the polydispersity index was less than 1.05. The molecular weight (M_n) of the poly(methyl methacrylate) was 255 000, and the polydispersity index was less than 1.15. Spectrograde chloroform was used without further purification to make dilute solutions (0.1 mg/mL).

B. Surface Pressure Measurement. Polymer monolayers were formed at the A/W interface using 0.1 mg/mL stock solutions of polymers dissolved in chloroform. The aqueous subphase was purified and deionized using a Millipore Milli-Q system (18 MΩ) equipped with an organic removal cartridge. The surface pressure isotherms were measured using a Langmuir film balance (KSV5000, Helsinki, Finland). The temperature of the subphase was maintained using a Lauda circulating water bath. Care was taken to clean the film balance before the measurement. The surface of the water was swept several times until a satisfactory isotherm was obtained for a clean surface. A blank experiment was done by spreading pure solvent on the water surface. Precisely measured volumes of the solutions were spread on the water surface using a SGE gastight microliter syringe. After complete evaporation of the solvent (20 min), the layer floating on the subphase was symmetrically compressed by using two mobile barriers at a predetermined constant speed. Most surface pressure−area ($\pi-A$) isotherms were measured several times. The typical reproducibility at a given area was ±0.2 mN/m.

C. Atomic Force Microscope (AFM) Measurement. A monolayer on the water surface was deposited onto freshly cleaved mica by pulling it out of the water while compressing the film at a constant pressure (the vertical dipping method). The samples were observed in air by using a commercial AFM (AutoProbe LS, PSI-LS) equipped with microfabricated V-shaped silicon nitride cantilevers (force constant: 0.05 mN/m) on a 5 μm scanner using the contact mode. The transfer of a monolayer from the surface of the water to a solid substrate did not introduce any artifacts. This was checked by comparing the micrographs obtained at different pulling-out speeds. The mean height and root-mean-square roughness were obtained from the height histograms of the AFM images, which were attained from the cross-sectional profile of individual domains. After excluding 10% area each from both ends, the rest 80% area was scanned.

D. Aggregation Number of Surface Micelles. It is well-known that block copolymers or polyelectrolytes form aggregates or surface micelles on the subphase surface. As Eisenberg et al. noticed,[3] at low surface pressure, these micelles consist of aggregates of one block at the core (core block) with arms of the other block radiating outward from the core block on the surface of water. As in all aggregation phenomena, the degree of aggregation or the aggregation number is of particular importance. While there are several methods to calculate the aggregation number of the micelles,[3] we adopt a method applicable to AFM pictures. The method is based on the assumption that no deformation of the film occurs in the transfer process and that a 1:1 correspondence exists between the Langmuir film and the film adsorbed on the air/water interface. It is the total area method used by Eisenberg et al.[3] From a quantitative analysis of the atomic force micrographs, one can determine the total area of the micrograph and count the total number of micelles in that area. The area per micelle is obtained by dividing the area of the micrograph by the number of micelles in the micrograph. From the deposition conditions and $\pi-A$ measurements, one also knows the area per molecule at the pressure at which the film was transferred. The area per micelle divided by the area per molecule gives the number of molecules per micelle.

Results and Discussion

Surface Pressure Measurement. In this paper, we present detailed surface pressure measurements to elucidate the structural properties of PS−PMMA diblock copolymer molecules and to investigate the structural rearrangement of the interfacial self-assembly of this material. Isotherms obtained at 23 °C for homopolymers (PS and PMMA), a block copolymer, and a PS/PMMA binary mixture (20:80) on pure water are shown in Figure 1. The surface pressure of the block copolymer falls between those of the PMMA and the PS homopolymers. The isotherm of a binary mixture, which has the same weight ratio as the diblock copolymer, follows that of PMMA more closely at high surface pressure. This is because of a different phase behavior as explained below. In the compression stage, the isotherm of a binary mixture shows a monotonically increasing surface pressure with decreasing surface area whereas that of a block copolymer shows a plateau at the surface pressure between 15 and 20 mN/m, which appears to be diffuse first order in nature.[42] The plateau appears more vividly in the decompression stage (Figure 1b). This is reproducible under controlled experimental conditions. In the decompression process, a hysteresis

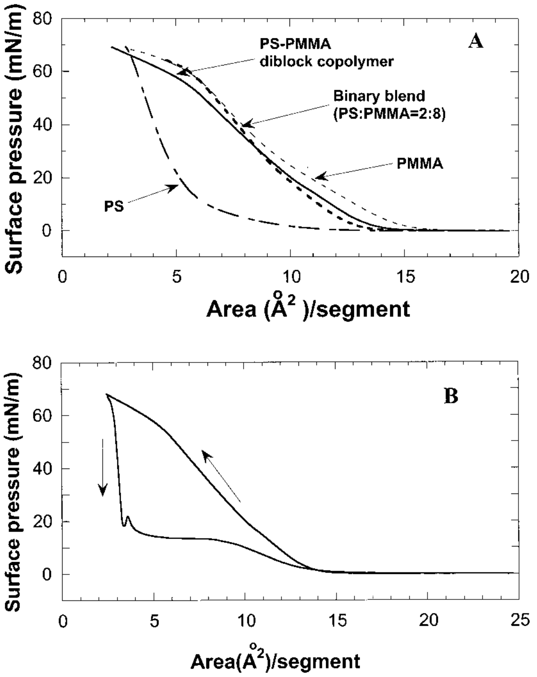


Figure 1. (a) $\pi-A$ isotherms (23 °C) obtained by compressing monolayers of PS homopolymer (— - —), PMMA homopolymer (- - -), PS−PMMA diblock copolymer (—), and 2:8 binary mixture of the PS and the PMMA homopolymers (- - -) at the air/water interface. b) $\pi-A$ isotherm of PS−PMMA diblock copolymer in a compression and expansion cycle.

appears which strongly depends on the surface pressure at which the film expansion is initiated. If expansion begins prior to the plateau pressure being achieved, then virtually no hysteresis occurs. If compression goes beyond the plateau surface pressure, hysteresis is evident. In a separate study, we attributed this to the rearrangement of PMMA segment.[43] Since no quantitative differences were observed in the isotherms for different delay times (waiting time after spreading) longer than 20 min, this is not a solvent-induced effect. We checked the effect of the compression rate, and it was found not to be very remarkable.[43] The films showed more expanded monolayer behavior when compressed slowly but had similar plateau surface pressures (π_t) in the experimental range. The effect of the compression rate diminished at high surface pressures above π_t. Also, a minimum appeared during the expansion process. It is manifest that the compressed film expanded at a slower rate than the rate of area increase. A similar observation was made for the isotherms of the polyelectrolyte polystyrene-*b*-poly(decylated vinylpyridinum iodide) (P(S-*b*-VP/C_{10}I)).[2−6] Eisenberg et al. also pointed out that a film of (P(S-*b*-VP/C_{10}I)) taken through a compression/expansion cycle could, if compressed immediately after decompression and compressed below the transition range, exhibit a compression isotherm superimposed on the returning portion of the prior expansion curve.[2,3] This is not applicable when the compression is above the transition value. Unless the macromolecule's primitive structure is fully recovered, superimposition of a compression isotherm on the returning portion of the prior expansion curve never happens, which is the case for a PS−PMMA copolymer monolayer as well as for (P(S-*b*-VP/C_{10}I)) (see Figure 5 in ref 6).

Figure 2 is a schematic representation of the possible mechanism for the conformation change in a diblock copolymer. (A) When the solution was spread on the water surface, few aggregates were formed because of the long PMMA block. This is obvious in the AFM photos (see Figure 6). (B) As soon as the compression started, a self-assembly of diblock copolymers on a two-dimensional surface occurred to form "surface micelles". The PMMA segments were radially extended. (C) In the compression process, a detectable rise in the pressure above the baseline occurred when the branches from different surface aggregates began to interact with each other. The free space between aggregates (called "macro void"[43]) was compressed to form a more compact and uniform film. This shows up as the plateau in slow compression. (D) Further compression forces the PMMA segment into a more compact conformation. This structural change was verified by using an AFM.

The isotherm is fully reversible up to the transition process. This indicates that the two-dimensional chain alignment between the coronae segments (PMMA segments) in an aggregate would be a low-energy process and should have rapid kinetics associated with them.[32] However, further compression after the rearrangement is a kinetically slow process, as evidenced by almost no decrease in the surface area per segment. Highly compressed aggregates (Figure 2D) require some time to return to their more relaxed states in expanded areas.[6,43] Hence, the surface pressure reaches a minimum as soon as the expansion starts and then recovers some surface pressure due to the molecule's structural change (Figure 1b).

A comparison of isotherms acquired at different temperatures provides an insight into the nature of the monolayer phase transition. Figure 3 shows the effect of temperature on the dynamic behavior of the PS−PMMA monolayer in the experimentally accessible temperature range (7−40 °C). This is qualitatively similar to that for (P(S-*b*-VP/C_{10}I)) reported by Eisenberg et al.[7] However, there is a subtle difference from the (P(S-*b*-VP/C_{10}I)) results. The isotherm for (P(S-*b*-VP/C_{10}I)) exhibits a clear plateau pressure at each temperature while the PS−PMMA film manifests a plateau for temperatures higher than 30 °C. This is attributed to the difference in the structural change between the PMMA segment and the P(S-*b*-VP/C_{10}I) segment. The broad plateau in the P(S-*b*-VP/C_{10}I) isotherm is due to molecular reorganization occurring in the monolayer, which was termed a "starfish" to "jellyfish" transition by Eisenberg and co-workers.[2,3,6] At the starting point of the plateau, the monolayer is made up of PS cores and PVP/C_{10}I chains adsorbed to the surface. Beyond that point, further compression forces the decylated PVP$^+$ moieties into the aqueous subphase, and at the final point of the plateau, the ionic chains are for the most part dissolved into the subphase.[6,7] In contrast, PMMA chains are not soluble in water; thus, they stay on the water surface. The micelles can be made to touch each other by removing the empty space between the micelles (Figure 2). When the temperature is low, at the plateau area, the monolayer becomes more homogeneous. Beyond this point, further compression causes the PMMA block rearrangement to be in a more compact conformation. As the temperature goes up, the micelles move more freely and easily make the rearrangement after removing the free space; thus, the plateau appears more apparently. The plateau

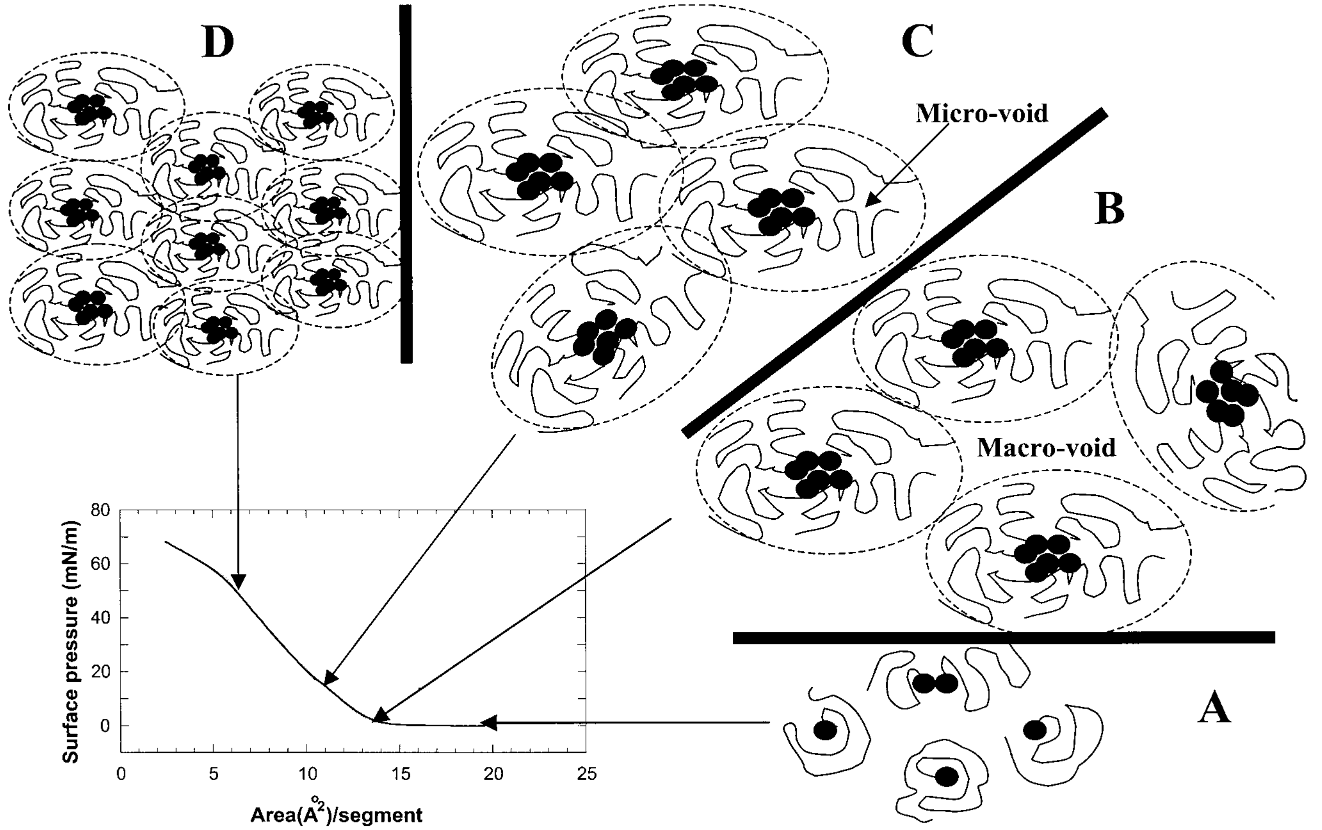


Figure 2. A schematic representation of the PS−PMMA diblock copolymer micelles at different surface pressures. (A) When the solution is spread on the water surface, few aggregates are formed because of long PMMA block. (B) As soon as the compression starts, self-assembly of diblock copolymers in two dimension occurs to form "surface micelles". PMMA segments are radially extended to accept the space restriction. We termed the free space between micelles as "macro void". (C) In the compression process, a detectable rise in pressure above the baseline occurs when the branches from different aggregates begin to sterically interact with each other. The free space between aggregates is compressed to remove the "macro voids" and, hence, to form a more compact and uniform film (transition). (D) Further compression above the transition surface pressure forces the PMMA segment in a more compact conformation by removing the micro voids in the PMMA corona.

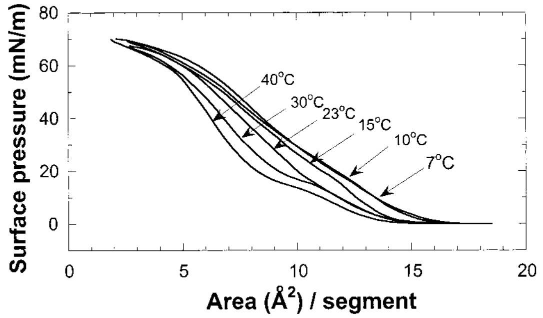
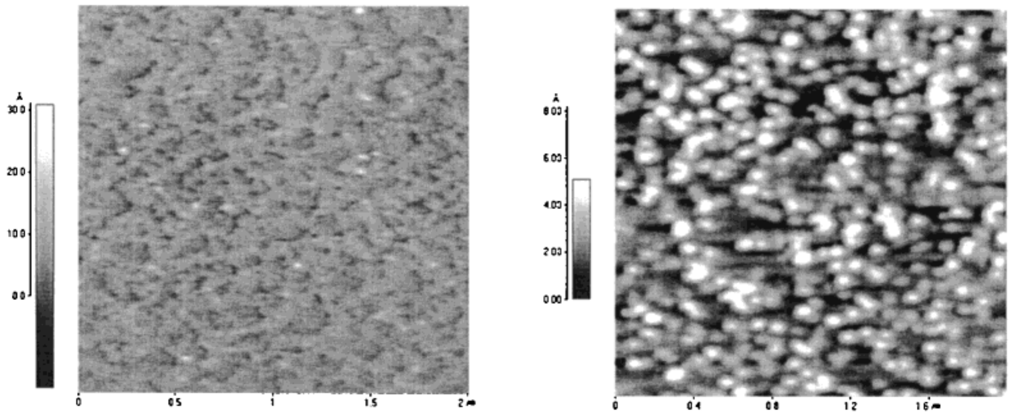


Figure 3. $\pi-A$ isotherms at different subphase temperatures obtained by compressing the PS−PMMA monolayer at the air/water interface.

surface pressure between structural rearrangement, therefore, decreases with increasing temperature. This is confirmed below by the surface micelle morphology.

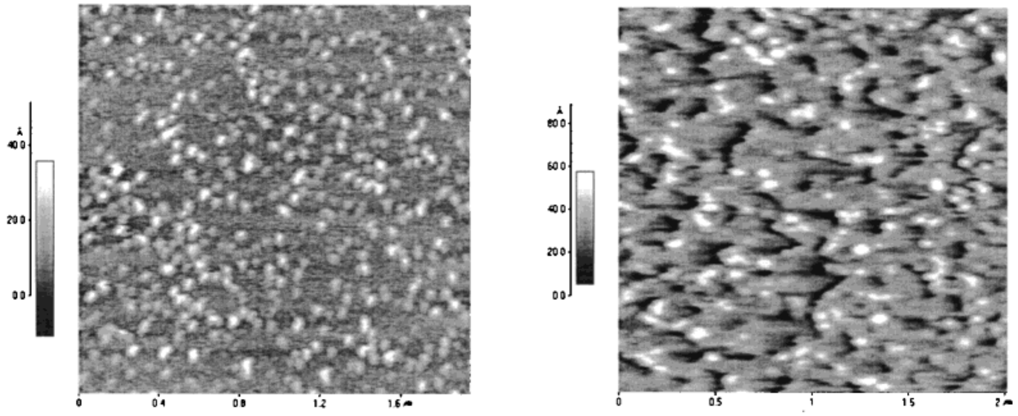
Morphology of Langmuir Films. The atomic force microscope visualizes the polymer morphology in the compression/expansion process. Eisenberg and co-workers have extensively studied block polyelectrolytes (P(S-*b*-VP/C_{10}I)) in regard to their spontaneous self-assembly to form aggregates (surface micelles) at an A/W interface.[2−11] Different morphologies were observed depending on the block composition of the polyelectrolyte. They were related to the solubility of the P(VP/C_{10}I) segment. Our film is different from this polyelectrolyte in that both the PS and the PMMA segments are hydrophobic and the PMMA segment (corona block) is much longer than the PS segment (core block). In addition, the molecular weights of both blocks are much higher than those of the P(S-*b*-(VP/C_{10}I)) used by Eisenberg et al. Hence, we do not expect structures like the jellyfish-type surface micelles of P(S-*b*-(VP/C_{10}I)) because of the insolubility of the PMMA block, nor do we expect large disklike aggregates. (Rice et al.[37] insisted that they observed some disklike aggregates as big as 20 μm.) Other morphologies are not expected due to the much longer corona block. If PS−PMMA diblock copolymers form micelles, we can easily anticipate only spherical or oval surface micelles because PS−PMMA diblock copolymer molecules mostly stay on the water surface.

Figure 4 shows AFM images of a PS−PMMA monolayer and a binary mixture of PS and PMMA. As already mentioned, there is a subtle difference between the two morphologies. For the binary mixture film, particles exist on the subphase surface even when the surface pressure is zero. Since the binary mixture film has a separate phase in itself, polystyrene aggregates in its own domain. Using a transmission electron microscope, Kumaki observed that the PS monomolecular particles formed on the water surface even when the surface pressure was zero.[27−31] On the other hand, the PS−PMMA diblock copolymer film exhibits very few aggregates when the surface pressure is zero. However, as soon as the surface pressure increases (0.3 mN/m), more aggregates are observed. When the surface pres-



PS-PMMA 0 mN/m

PS-PMMA 0.3 mN/m



PS-PMMA 7 mN/m

Binary mixture of PS and PMMA. 0 mN/m

Figure 4. AFM images of the PS−PMMA diblock copolymer film (23 °C) at different surface pressures. AFM image of the binary mixture (PS:PMMA = 2:8) at 0 mN/m is also shown for comparison. The binary mixture film shows separate domains of the PS at 0 mN/m while very few aggregate domains are observed in the image of diblock copolymer film at 0 mN/m.

sure goes over 7 mN/m, no new aggregates seem to be formed.

For the block copolymer aggregates, different mechanisms for the formation of surface micelles have been proposed such as a transfer of micelles in the spreading solution to the surface,[34] a compression-induced surface aggregation which is formed when a critical micelle concentration driven by compression is reached,[44] and a spontaneous surface aggregation process which is neither compression nor spreading-solvent dependent (see Figure 3 of ref 33). All these mechanisms are possible, depending on the molecular weight of each block and the solution concentration. Since dynamic light scattering shows no large aggregates at the present solution concentration, the first mechanism seems inappropriate. The second mechanism is more plausible for this system than the last one (spontaneous surface aggregation) because very few aggregates were observed when the solution was spread on the water surface. Most surface micelles were formed after the compression started (Figure 4). For further evidence, AFM images were taken at the subphase temperature of 10 °C to reduce the mobility of the macromolecules. Figure 5 shows that no aggregates were formed when the surface pressure was zero. There were some holes in the film, which were reminiscent of the macro voids between micelles.[43] A more homogeneous film was obtained by removing these holes by compression. At 10 °C, a homogeneous flat film still existed even when the surface pressure was 0.2 mN/m, and no aggregates were observed. Aggregates appeared when the surface pressure reached 0.3 mN/m. It is evident that the polymer chains rearranged themselves during the compression at low temperature to form the aggregates. At high temperatures, some molecules, when they came into contact with the water surface, rearranged themselves to form a few aggregates from the solution configuration because of increased activity. The driving force for the surface micelle is the balance of the interactions between the air, the water, and the two polymer blocks, analogous to the surface-induced phase separation in thin films of diblock copolymers.[12−14,33] According to a recent theoretical investigation, the conformation of PMMA blocks in surface aggregates is nearly Gaussian,[1] which implies that PS chains in micelles remain practically unperturbed. This is essentially different from what is found for the usual case of three-dimensional micelles in block copolymer melts.[2,36] The repulsion of

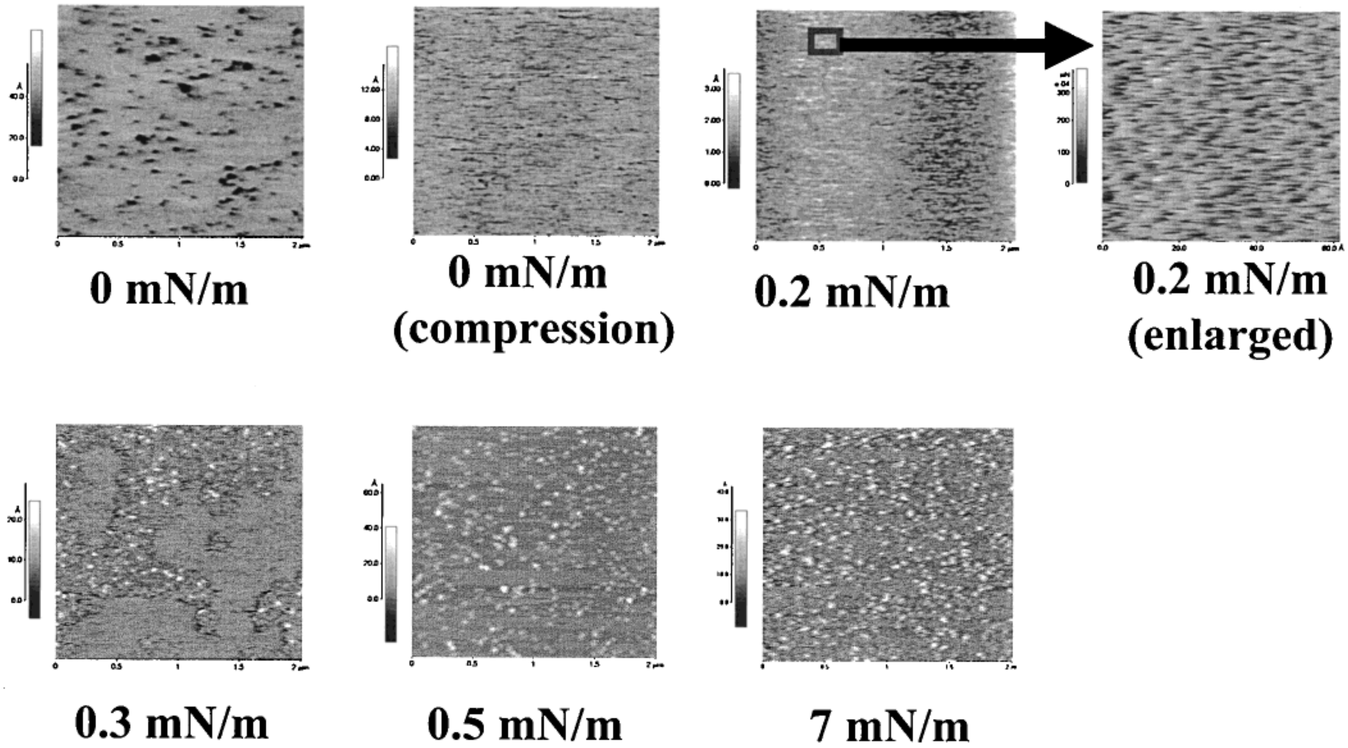


Figure 5. AFM images of the PS−PMMA monolayers at different surface pressures. The subphase temperature was 10 °C. No aggregate is seen at the surface pressure of 0.2 mN/m.

the PS block against both the water and the PMMA block drives the PS block to aggregate. After the aggregate formation, further compression forces the PMMA segment to go underneath the PS core. Thus, the PS core was lifted further to reduce its contact with the water. This is evident in the core height change. The domain height was 15 Å at 0.3 mN/m, 20 Å at 0.5 mN/m, and 16 Å at 7 mN/m. Evidently, this shows that there was not much of the PMMA segment under the PS core when the micelles formed. After the PS aggregates formed, further compression forced the PMMA segment to move under the PS core; hence, the PS domain to be lifted (or extended) into the air. Thereafter, the PMMA segments were compressed further to form a thicker layer; hence, the domain height decreased. There was a relatively large compression in the PMMA segments until the transition region, after which less compression occurred. This is consistent with our separate report.[43]

As already mentioned, since the diblock copolymer in this study has a longer PMMA segment (corona) than the PS segment (core), only small spherical aggregates appear. After 7 mN/m, no apparent variation in the number of domains was noticed (Figure 6). The root-mean-square roughness of the film was 1.7 Å when spread. A slight compression (0.2 mN/m) reduced the roughness to 0.4 Å, which means the formation of a flatter and more uniform film. However, the root-mean-square roughness increased to 0.7, 5.5, and 7.1 Å for surface pressures of 0.3, 7, and 50 mN/m, respectively. The average domain diameter changed slightly with compression, but it was almost constant (700 Å) after 7 mN/m. This means further merging between different micelle cores did not occur and indicates that the PS block aggregates could not overcome the entropic energy loss for PMMA coronae.

Aggregation Number of Surface Micelles. For a diblock copolymer (PS−PMMA) having different molecular weights (M_w of PS block = 880 000 and M_w of PMMA block = 290 000) from ours, Rice et al. [37] reported that no region of the surface pressure−area isotherm corresponded to isolated molecules. Since the PMMA block was much shorter than the PS block, their polymer molecules formed self-aggregates as soon as they were spread on the water surface, and the polymers self-assembled into aggregates containing about 240 molecules.[37] Rice et al. described these aggregates as “furry disks” with dense cores and brushlike boundaries. The core was determined by the PS portion of the molecule and the boundary by the PMMA portion. According to their results, the dense cores of the PS portions oriented themselves so that the collapsed PS blocks were in the air, while the PMMA blocks were at the air/water interface. In the work of Rice et al., because of the relatively short PMMA segment, the PMMA blocks attached to molecules in the center of disk lay almost entirely beneath the dense core. The PMMA blocks attached to molecules on the perimeter of the disk were considerably extended at the air/water interface, as in a “starfish” molecule. Our results are totally different. When the molecules were spread on the water surface, few aggregates (or aggregates too small to be detected by AFM) were formed because the PMMA segment was longer than the PS block (Figures 2 and 4). Surface micellization proceeded with the surface compression. The form of surface aggregation depended on the relative lengths of the two blocks in a fashion similar to that observed for block copolymers in solvents and in bulk.[35,36,40,41] The rodlike or large lamellar aggregates observed in the surface micelles of P(S-*b*-VP/C_{10}I)[3−10] or the large furry disk shape observed by Rice et al.[37] in the surface micelles of PS−PMMA were not observed in this study. In those other studies, the 2-D self-assembly of the hydrophobic PS blocks provided enough enthalpy to overcome the substantial entropy losses attendant with the orientation of a number of non-PS blocks into a highly defined, closely packed

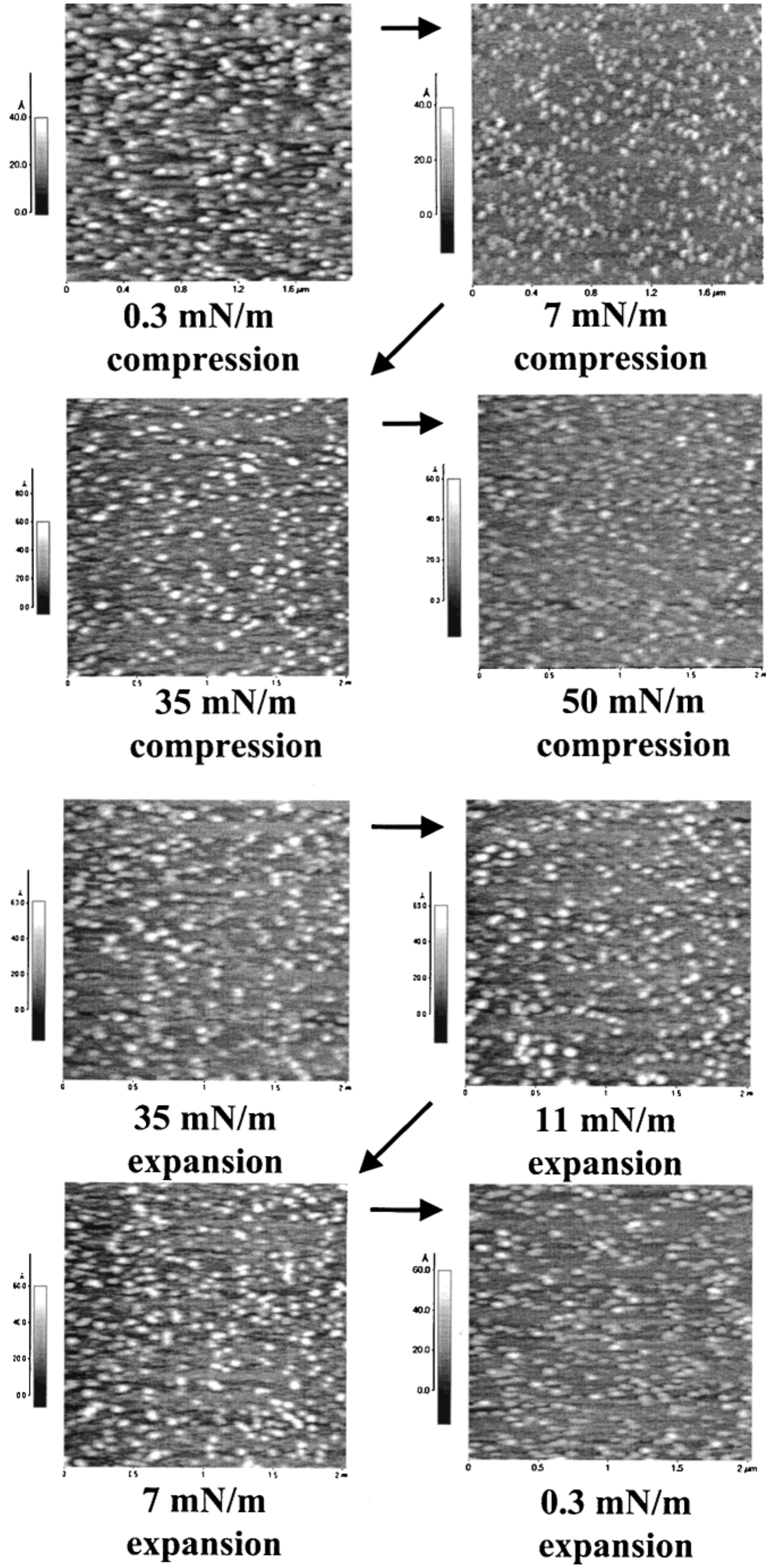


Figure 6. Morphology of the films at different surface pressures. The number of PS domains does not noticeably change with further compression above 7 mN/m. Also, no remarkable change in the number of micelles was observed during the expansion process.

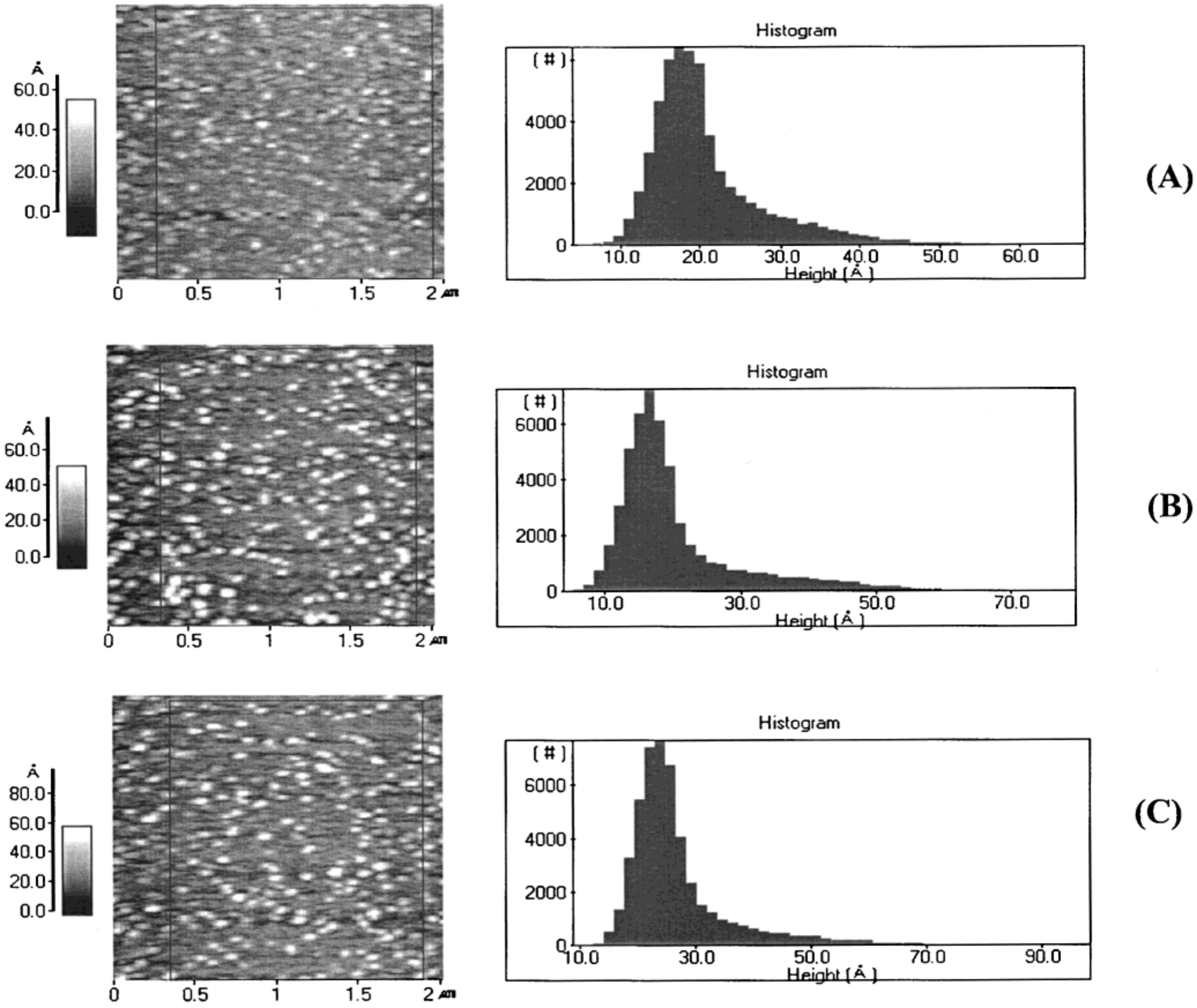


Figure 7. AFM images and the height histograms of PS−PMMA monolayers at different surface pressures in the expansion process: (a) 50, (b) 11, and (c) 3 mN/m.

geometry. This was possible due to the relatively short non-PS block.[2,3,37] In contrast, the PS−PMMA molecules in our study do not have enough enthalpy to overcome the large entropy loss of PMMA blocks. As already mentioned, uniform aggregate size implies that there is a sharp transition between the free and the aggregated states. This indicates that a minimum number of pairs must associate before any aggregate is stabilized, thus resolving the competition between the entropy loss and the enthalpy change.[37,43] For monolayers from very diluted solutions, Kumaki and Hashimoto observed that the molecules of a PS−PMMA diblock copolymer whose M_w's were 155 000 and 390 000 for the PS and the PMMA blocks, respectively, existed as isolated molecules.[29] In our study, the PS blocks of different molecules aggregated with the compression, and the PMMA blocks were radially extended to accommodate the space restriction (Figure 2). Since the PS segments are strongly incompatible with air, monomeric units of PS blocks can be safely assumed to be densely packed in micelles so that their volume fraction in the aggregate is equal to unity.[3,6,28] PMMA blocks in different molecules do not penetrate each other.[38] A recent theoretical investigation reports that the aggregation process for surface molecules is favored by a gain in the surface free energy but is opposed by stretching of the corona blocks on the surface.[1] It is the interplay of these two factors that defines the state of the micelle. After micelle formation, further aggregation between different micelles is prevented by the PMMA block coronae. Even at high compression, the PMMA blocks in different micelles do not overlap much. Also, the PMMA chains of neighboring micelles do not penetrate each other.[38−40] This is supported by the fact that the number of PS domains (cores) does not change with further compression after 7 mN/m (Figure 6). Touching between solid cores seems to be almost impossible. If the non-PS block is ionic (as in P(S-*b*-VP/C_{10}I) molecules)[6,7] or soluble in water,[15−20] it tends to be highly extended in the water; hence, aggregation between different micelles is possible. Nonionic PMMA blocks should be reorganized on the water surface from 2D "random coils" to more extended narrow ones in order to accept further coalition between micelles.[15] The number of molecules per micelle is, therefore, expected to be very few. We also expect the lengths of the attached PMMA blocks in the micelles to be longer than the PMMA segment of an isolated molecule. An enlarged micrograph shows that the core of the micelle (PS domain) is oval-shaped rather than circular, which means the micelle is formed of several heads.[43]

AFM micrographs provide access to the aggregation number of surface micelles. Since the core sizes of the micelles are almost the same, we can safely assume that each micelle holds about the same surface area and apply the total area method to calculate the aggregation number.[3] The area per micelle varied with the surface pressure and was 2.6×10^4, 9.09×10^3, and 7.4×10^3 nm^2 for pressures of 0.3, 0.5, and 7 mN/m, respectively. The aggregation number after the plateau transition surface pressure was 6.4 molecules/micelle. At a surface pressure of 18 mN/m, the value of the area per PMMA segment, after subtracting the PS area, was about 850 nm^2, which is smaller than the area of a PMMA monomolecule of the same molecular weight (1026 nm^2).[1,29] This is a convincing evidence that the PMMA segments are in a more compact state than the free molecules at high surface pressures. The water surface is thus covered by aggregated PS−PMMA chains at the transition surface pressure. After the available free space between the micelles is removed, further compression puts the PMMA segments of different molecules in a micelle into a very compact form. In a very compressed state at a pressure above the transition surface pressure, some PMMA segments may have loops in the air rather than being immersed in the water.[47] The increase in the root-mean-square roughness with pressure supports this structure.

Once formed, the surface aggregates are kinetically very stable; therefore, unimer−micelle exchange, if it happenes, is very slow. No remarkable change in the morphology of the film (hence, the number of micelles) was observed at different surface pressures during the expansion process (Figure 6). Though the core domain size did not change noticeably, the mean height of the core domains shown in Figure 7 increased with expansion (21, 23, and 27.7 Å at 50, 11, and 3 mN/m, respectively) because of PMMA segment relaxation and micelle dispersion.

Conclusions

A comprehensive Langmuir film balance/atomic force microscope study of the surface aggregation behavior of a diblock copolymer (PS−PMMA: $M_n = 160\,000$:$646\,000$) has been carried out. The surface pressure isotherms, the hysteresis, temperature effects on the isotherms, and the aggregation numbers were determined, leading to a self-consistent picture of the surface morphology and aggregation phenomena.

The isotherm of the block copolymer falls between those of the PMMA and the PS homopolymers while that of the binary mixture follows the PMMA isotherm at high surface pressure because of micelle formation of the block copolymer in the compression process. A plateau clearly appears in the isotherm curve when the subphase temperature is high. As the temperature goes up, PMMA segments move more freely and easily make the rearrangement of removing the free space; thus, the plateau appearance becomes more obvious. At the plateau surface pressure, PMMA segments form a uniform monolayer.

AFM images reveal that the aggregates are mostly formed during compression, which is attributed to the long PMMA segment and is consistent with the result of a recent theoretical study: when the adsorbed blocks (PMMA) are much larger than the nonadsorbed blocks (PS), at some small value of the ratio of the degree of polymerization (N_{PS}/N_{PMMA}), and the concentration of the blocks on the surface is very small, it may become more favorable for the PS chains to form single globules rather than to aggregate into micelles.[1,29] The size of the core was almost uniform, which implies that there was a sharp transition between the free and the aggregated states. Analogous to the critical micelle concentration in a bulk solution of a surfactant, the surface aggregation of the block copolymer takes place only at a certain surface mass density, resulting in small circular micelles. Before any aggregate can become stabilized, a minimum number of molecule pairs must associate in such a way that the association energy overcomes the large entropy change. Because of the long PMMA segment, the difference between the energy change due to PS segment aggregation and the entropy loss due to PMMA segment extension and reorientation is so large that some extra energy, such as compression, is required to form aggregates.

AFM images show that 6−7 block copolymer molecules aggregate to form micelles. Energy restrictions prevent the large molecules from being in a “furry disk” or from having a rodlike or lamellar morphology. The absolute and the relative lengths of each block in a diblock copolymer significantly affect the aggregate morphology on the water surface. A large PMMA chain coronae surrounding the PS cores also do not allow the dense cores to touch one another. Hence, they maintain mostly in a small spherical morphology. When the surface micelles are formed, relatively few segments of the PMMA block are under the PS core because of the immiscibility between PS and PMMA. After aggregation, further compression pushes the PMMA segments beneath the PS core to lift it, which reduces undesirable contacts with the water surface. Once formed, the surface aggregates are kinetically very stable; therefore, unimer−micelle exchange does not occur, or if it does, it is very slow.

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