Molecular Weight Effect on the Behaviors of Polystyrene-*block*-poly(methyl methacrylate) Diblock Copolymers at Air/Water Interface

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ABSTRACT: Diblock copolymer (A−B) behaviors in quasi-two-dimensional space have been examined where the A block is polystyrene (PS) and the B block is poly(methyl methacrylate) (PMMA). The length of the PMMA block was varied while that of the PS block was kept almost the same. The surface pressure isotherms were determined with the aid of a Langmuir film balance. The surface pressure isotherms exhibited two phase transitions attributed to surface micelle formation at low surface pressure and to further assembly of surface micelles at high surface pressure. Atomic force microscope images are correlated with the aggregates of the chains forming the quasi-two-dimensional surface micelles at low surface pressure. Chains having shorter PMMA block than PS block form the micelles with many block copolymer molecules (ca. 430 molecules) whereas chains having 4 times longer PMMA block than PS block form the micelles with several molecules. High compression led the micelles to have a more compact structure. The new structure of crowds of micelles by further compression was observed by a Brewster angle microscope. This does not correspond to big aggregates formation since its structure appearance was reversible whereas the surface micelle formation was irreversible. All the block copolymers used in this study exhibited a hysteresis. In the slow expansion process, the surface pressure of the long chain showed a minimum. Because of the micelle formation in the first cycle of compression and expansion, the hyteresis was remarkably reduced in the consecutive cycles.

Introduction

The presence of block copolymers at surfaces and interfaces plays a crucial role in many industrial applications ranging from adhesion, lubrication, stabilization of colloidal dispersions, and surfactancy to lower interfacial tensions of polymer blends.[1−3] Besides these specific technical applications, clear scientific interest exists in the study of block copolymers at interfaces because of general polymer conformation and dynamics in confined geometries. In view of this, the properties of the interfacial layers formed by block copolymers have received considerable attention. [4−8] Theories to predict the volume fraction profile of a polymer at an interface, as well as the excess free energy (surface pressure), have been proposed by de Gennes,[4] Alexander[5] (scaling theory), Milner et al.,[6] Zulina et al.,[7] and Shull[8] (self-consistent mean-field theory). The adsorption of a block copolymer at the interface is very interesting because the structural evolution of the adsorbed layer depends on the molecular characteristics of the separate blocks.[9] Several experimental studies have been carried out to verify the theoretical predictions, most of which focused on solid−liquid interfaces.[10−16] Unfortunately, the interfacial chain density, an important parameter, cannot be controlled very well for these systems. A better approach would be to use air−liquid interfaces.[9] For such interfaces, the chain density can be continuously varied by compression or expansion of the interface; thus, the amount of polymer spread on the interface can be precisely controlled if a polymer forms insoluble monolayers. A vast amount of literature exists that deals with the equilibrium behaviors of polymer monolayers at air/liquid and liquid/liquid interfaces.[9−23]

Depending on the chain densities and the extent of intermolecular interactions, block copolymers are postulated to assume different geometries, resulting in varying manifestations of surface viscoelasticity.[9] For instance, we can focus on a diblock copolymer A−B that spread on the air/liquid (A/L) interface, which consists of a surface active soluble block A connected to a surface inactive and insoluble block B. Such a block copolymer as a monolayer at an A/L interface will give rise to different conformations for block A relative to the surface mass density. For instance, it can be a flat, pancake-like conformation in the low-density limit but a brush or mushroom-like conformation in the high-density limit.[14] If the insoluble block B is longer than the soluble block A, surface micelles will form.[24−30] Some recent examples are diblock copolymers of polystyrene (PS) and poly(ethylene oxide) (PEO) [14−16] for an A(inactive, insoluble)−B(active, soluble) type, PS and poly(dimethylsiloxane) (PDMS)[17−19] for an A(inactive, insoluble)−B(active, insoluble) type though this system was investigated at air/organic liquid interface rather than air/water interface, and PEO and poly(methyl methacrylate) (PMMA)[20] for an A(active, soluble)−B(active, insoluble) type. PEO and PDMS are very surface active polymers while PS is not,[11,14] and the surface properties can vary depending on the relative chain lengths of the surface-active A and the surface-inactive B blocks.

Block copolymers have been extensively studied in regards to their phase separation and self-assembly

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Table 1. Molecular Weight Data for PS−PMMA Diblock Copolymers

sample[a]	product name	M_n of PS	M_n of PMMA	PDI[b]	tacticity in PMMA block		
					syndio	iso	atactic
P70	P722	146 700	70 700	1.11	0.79	0.002	0.208
P155	P224	143 800	154 800	1.12	0.813	0.004	0.183
P392	P309	154 800	392 300	1.08	0.818	0.003	0.179
P656	P419	140 000	656 000	1.32	0.450	0.000	0.550

[a] The numbers after P means the molecular weights of PMMA segment in kilo units. [b] Polydispersity index = M_w/M_n.

propensity.[24] Block copolymer molecules adsorbed at an A/L interface were found to self-assemble into aggregates composed of many diblock molecules.[25−30] Depending on the relative chain length of each block, polymorphism of the aggregates was observed.[24−30] Most previous studies were concerned with diblock copolymers in which one block was hydrophobic while the other was hydrophilic (or water-soluble). The surface behavior of the PS−PMMA diblock copolymer is quite interesting because the PS block does not have an affinity for water, and the PMMA block is also hydrophobic though less so than PS.[14,17−22] Though the behavior of PS−PMMA diblock copolymers at the PS/PMMA homopolymer blend interface has been studied very intensively due to the wide variation of its properties with the molecular weight and the block length ratio,[31−34] the monolayer behavior has not received much attention.[23] PS−PMMA diblock copolymers are expected to stay on the water surface.[36] However, PMMA behaves as a condensed-type monolayer whereas the previously studied block copolymers (PS−PEO[14−16] and PS−PDMS[17−19]) had PEO and PDMS blocks which exhibited an expanded-type monolayer. In view of this, PS−PMMA is particularly suited for studying the behavior of a diblock copolymer in the quasi-two-dimensional (2D) domain. It is important to point out that the terms “2D” and “quasi-2D” refer to the molecular dimensionality and not strictly to the spatial dimensionality of these aggregates.[27] For example, while the PS of the surface micelles are 2−3 nm high for our samples, they are in fact less than the thickness of one collapsed PS random coil of the same molecular weight.[35] As Eisenberg et al. asserted, the surface micelles are therefore conveniently referred to as being 2D because the PS−PMMA diblock copolymers occupy only a surface adsorbed state, and the PS core is an aggregate of surface-adsorbed PS blocks.[27]

We reported in a separate study[36] the surface aggregation behavior of a diblock copolymer (PS-*b*-PMMA: M_n = 140 000:656 000 g/mol). Using an atomic force microscope, we could describe a self-consistent picture of the surface micelle morphology and aggregation phenomena. In this work, we investigated the nature of different PS−PMMA diblock copolymers at the air−water interface as well as their micelle formation and relaxation phenomena. The length of the PMMA segment was varied while that of the PS segment was kept almost the same. By doing this, we tried to figure out a structural evolution scheme for the PS−PMMA diblock copolymers and more experimental evidence for our previous claims.[36]

Experimental Section

Materials. The PS−PMMA diblock copolymers were purchased from Polymer-Source Inc. (Canada). Table 1 lists some characteristics of these block copolymers. As can be seen from columns 3 and 4 of Table 1, they have similar PS block lengths (ca. 147000 ± 7000) but mainly differ in the molecular weights of the PMMA blocks and in their tacticity. P70 has shorter PMMA block (M_n = 70 000) than the PS block. P155 has almost the same block length (M_n = 155 000) as the PS block whereas P392 and P656 have longer PMMA blocks (M_n = 392 000 and 656 000, respectively) than PS blocks. The numbers after P means the molecular weights of PMMA segment in kilo units.

Measurements. As the spreading solvent, spectrograde chloroform (Aldrich) was used without further purification. Distilled water was deionized by using a Millipore Q2 system and was used for the subphase. A Teflon trough with internal dimensions of 110 mm × 285 mm × 12.5 mm was filled to its brim with the subphase. The dynamic surface pressure measurement was done using a computer-controlled film balance equipped with an electrobalance (Cahn, model 2000). After the surface was cleaned by several passages of the Teflon float, a sandblasted platinum plate (11 mm × 26 mm × 0.1 mm), previously soaked in a HNO_3/H_2SO_4 mixture and washed thoroughly with pure water, was carefully hung on the suspending wire of an electrobalance (Cahn, model 2000). The voltage output of the electrobalance control unit was read directly by using a digital voltmeter. The final precision of the surface-pressure measurements was estimated to be ±0.02 dyn/cm. No significant surface pressure was detected before spreading the polymer solution upon compressing the area to 3% of its initial value. A stepping motor was used to move the Teflon float forward and backward. The speed was preset at a predetermined value (15 mm/min). When the surface pressure reached a predetermined value, the motion of the float was reversed, and it returned to its starting position; after a preset interval, the process was repeated.

The polymer monolayer was spread on the subphase surface by applying a suitable volume of polymer solution with a Hamilton microsyringe. To obtain a stable monolayer on the subphase, we allowed at least 20 min for the solvent to evaporate after each spreading. The temperature of the subphase was controlled by circulating thermostated water through a glass coil placed in the bottom of the trough. The temperature of the circulating water was maintained at 23.0 ± 0.1 °C by using a Lauda bath (Lauda RM6).

The monolayer morphology was observed using a commercial atomic force microscope (AutoProbe CP, Park Scientific Instruments Co.) with the contact mode in air and at 23 °C. The microscope was equipped with microfabricated V-shaped silicon cantilever (force constant: 0.03 mN/m) on a 5 μm scanner. The monolayer was deposited on a cleaned silicon wafer. Cleaning was done by putting it in the 1/3 solution of 30% H_2O_2/concentrated H_2SO_4 at room temperature for 15 min and rinsing with Millipore deionized water. The monolayer was transferred on the wafer at the constant surface pressure under a constant vertical lifting speed of 1 mm/min. It is known that no apparent structural defects in the transferred monolayers arise if the lifting rate is kept below 5 mm/min.[24]

The morphology of the floating monolayer at high surface pressure was observed using a Brewster angle microscope (BAM) because of its ability to examine the in-situ organizations of the amphiphilic molecules forming the monolayers at the A/L interface.[21,22] The instrument was a commercial miniunit (Nanofilm technologie Gmbh, Göttingen, Germany) equipped with a 688 nm diode laser (30 mW) for p-polarized light and had a field of view of 4.8 × 6.4 mm^2. Surface images were captured by using a CCD camera. The lateral resolution of the optical system in the plane of the water surface was limited to about 20 μm.

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,[24−30] 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,[25]

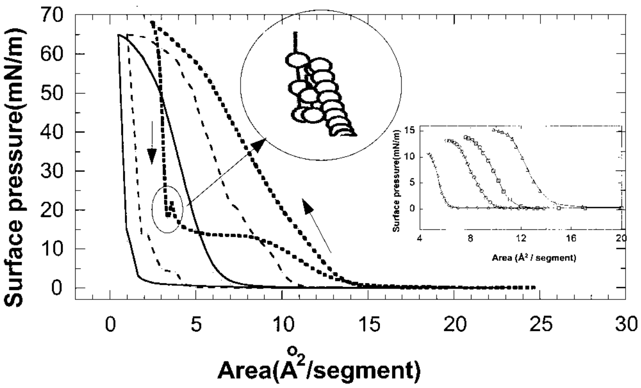

Figure 1. Surface pressure−area ($\pi-A$) isotherms for PS−PMMA diblock copolymers monolayers at 23 °C: (−) P70, (− −) P155, and (- - -) P656. The surface pressure was measured compressing and expanding the monolayer. The inset is the ($\pi-A$) isotherms for PS−PMMA diblock copolymer monolayers at 23 °C obtained using the continuous addition method:[12,19] (◇) P70, (○) P155, (□) P392, (△) P656. Dynamic surface pressure measurement represents the block copolymers reaction to external constraints rather than showing their true equilibrium properties. Lines are guides for the eyes. For long diblock copolymers (P656 and P392), the surface pressures increase less rapidly.

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.[25] From a quantitative analysis of the atomic force photomicrographs, 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

It is well-known that vinyl polymers with sufficiently hydrophilic pendant groups, such as poly(vinyl acetate), form ideal monolayers on A/W interface with every repeating unit being tightly adsorbed.[12] In contrast, vinyl polymers without hydrophilic groups, such as polystyrene, do not spread to form a monolayer on A/W interface.[38] The surface pressure−area curves ($\pi-A$ curves) of the latter polymers show extraordinarily small limiting areas compared with their molecular structures, indicating that the polymers exist on the water surface as flakes or multilayers.[39−41] PMMA has the propensity in between these two types. It forms a condensed-type monolayer.[12]

Figure 1 shows that two transitions appear in the isotherms of P155 and P656, both in the compression and in the expansion processes, though the molecular weights of the PMMA segments were different and those of the PS blocks were almost the same. The PS block is not significantly deformed even after the collapse.[36,38,41] The transitions in the compression process are attributed to a reorganization of the block copolymer molecules, i.e., to surface micelle formation and to reorganization of the micelles into a more compact form. The structural reorganization is discussed again later in relation to the morphology. Figure 1 also shows that there is a hysteresis in the isotherm. The expansion curve does not follow the compression curve: the pressure drops sharply at the beginning of the expansion process and approaches the compression pressure−area isotherm only at large area (almost 0 mN/m). This hysteresis reveals some facts about the response of the chain molecules to a dynamic external constraint. In the expansion process, highly compressed micelles do not disperse fast enough to cover the expanded area; hence, the pressure drops rapidly. This is ascribed to the large viscosity of the monolayer[37] and to the slow dispersion of compressed micelles on the surface. Later this will be discussed again. Though the compression−expansion cycle is a dynamic process, only small effects due to speed variation were observed. Only the transition in the expansion process for long polymers (P656) subsided slightly with the expansion speed of 10 times faster.

It is worthy of note that the isotherm of P656 (the highest molecular weight chain) exhibited an unusual minimum when the expansion was done very slowly. The appearance of the minimum in the slow expansion process evidently indicates that the highly compressed monolayer and the local structure obtained in the high compression are not disturbed during the expansion run. It is a dynamic phenomenon. This is supported by the BAM images shown later. A minimum was also observed in the expansion isotherm for the PS−PEO monolayer[14] at the air/water interface, but the trend was different. According to the explanation of Gonçalves et al., the PS−PEO polymer chains, although highly hydrated, retain part of their helical structure.[14,44] This organization is favored by the shorter PEO block because water is not such a good solvent for PEO chains at higher polymer concentrations. The minimum disappears with increasing PEO chain length. For PS−PMMA block copolymers, however, the minimum was observed for chains having longer PMMA blocks (P656). This can be explained by some structural rearrangement at the minimum, possibly a rearrangement of the micelle structure (from the locally crowded structure), and/or by a return from the looping structure in air. Recent neutron scattering experiments[45,46] report that all of the syndiotactic PMMA rests on the water surface while some of the isotactic molecules are immersed in the subphase (water) as loops and tails because of different solvent condition. On the basis of the neutron reflectometry data, Henderson et al.[45] concluded that the isotactic polymer is in good solvent conditions whereas the atactic and syndiotactic isomers are in thermodynamic environments that are worse than “Θ” conditions. Thus, the ester groups in isotactic PMMA tend to point downward toward the water phase while those in syndiotactic PMMA tend to point sideways. This was also revealed in the surface pressure measurement of the PMMA monolayer at the air−water interface.[13] On the basis of neutron reflectometry results, Henderson et al.[45] argued that more compression of syndiotactic PMMA chains in the compact state causes them to loop in air. Taking into consideration the tacticites of these block copolymers (Table 1), we can plausibly suppose that PMMA segments in long chains may loop in air at a high compression state after the second transition rather than dip into the water. This looping is rapidly relieved in the expansion process. Thus, the minimum indicates relaxation of long-chain conformation. In Figure 1, it is worthwhile noticing that, depending on the chain length, different transition behaviors appear during the expansion process. For

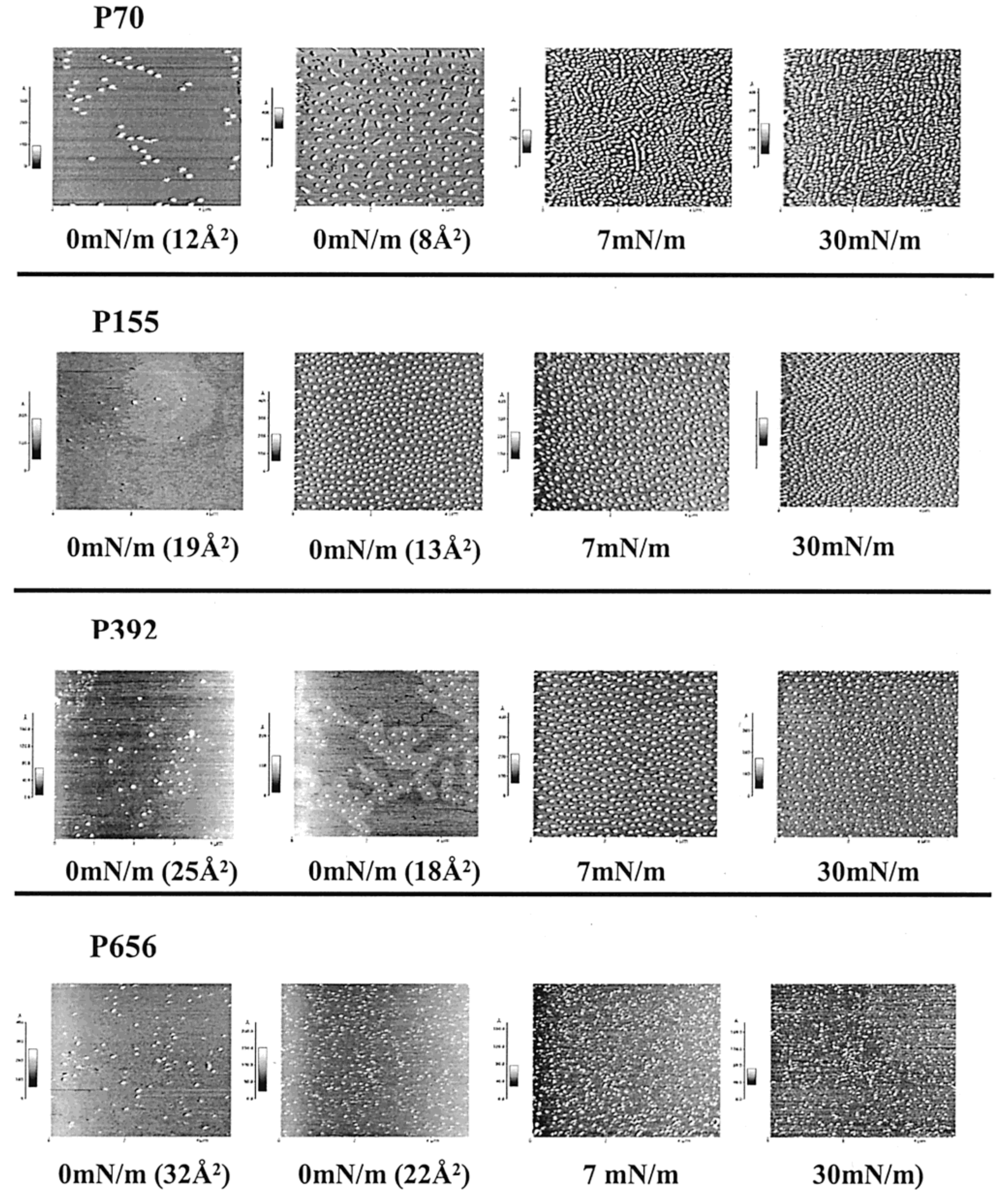

Figure 2. AFM images of PS−PMMA diblock copolymer monolayers. The white domains correspond to micelle cores (aggregated PS blocks). For short polymer chains (P70), the morphology appears very irregular in the sense that some of the PS domains are small while some others are relatively big. Domain size and shape become more uniform for long chains.

short PMMA chains (P70), the isotherm looks to pass through the transition almost continuously whereas for long PMMA chains (P656), it has a plateau of the transition between micelle expanded state and micelle condensed state. This is ascribed to less voids exist between the micelles for short chains because of small corona.[36] Thus, no stable intermediate state was observed.

Figure 2 shows AFM images of PS−PMMA monolayers. All films exhibit very few aggregates when spread on the water surface. As the surface area decreases (hence, the surface pressure increases), vividly appear more domains. The white domains correspond to aggregated PS blocks. PS−PMMA block copolymer molecules spread on the water surface have separate PS and PMMA domains which overlap very little.[38,41]

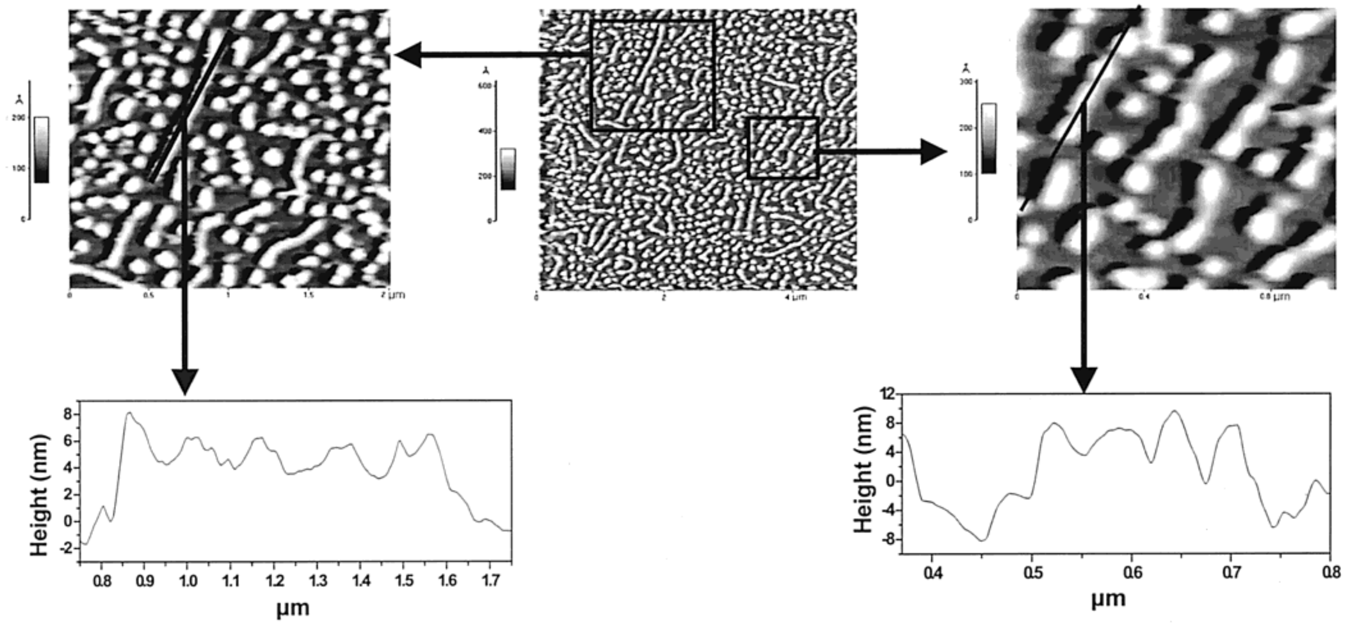

Figure 3. Enlarged AFM image of PS−PMMA diblock copolymer (P70) monolayer at 7 mN/m.

As the surface pressure increases, the number of aggregates rapidly increases until the surface pressure reaches about 7 mN/m. Afterward , fewer micelles seem to be formed. This confirms Eisenberg et al.'s assertion that the surface micellization is a very general one in that it occurs for the nonionic block copolymers as long as the block copolymer molecules are surface-adsorbed.[25,28] The attraction between the PS blocks and the repulsion of the PS block against both water and the PMMA block drives the PS block to aggregate. Evidently the 2-D assembly of the hydrophobic PS blocks provides enough enthalpy to overcome the substantial entropy losses attendant with the orientation of PMMA blocks into highly defined, close-packed geometry.[28]

Figure 2 reveals that different shapes come out depending on the chain length and, hence, the molecular weight. P656, the longest diblock copolymer, forms the surface micelles of small cores. PS core size is not uniform for this block copolymer, which is ascribable to its wider polydispersity than others (Table 1). P155 and P392 produce surface micelles of relatively uniform size and shape while P70 having a shorter PMMA block than PS block shows different geometry at high surface pressure. Some of them have the rod shape. In the Langmuir−Blodgett film investigation of surface micelles formed from a series of block polyelectrolytes based on polystyrene and decylated poly(vinylpyridine), Eisenberg and co-workers have discovered three morphologies of starfish, rod, and planar structures, which are corresponding to spherical, cylindrical, and lamellar morphologies of block copolymers in three-dimensional solid state.[24−27] It seems that the rod shape of P70 at high surface pressure is different from the rod shape that Eisenberg and co-workers observed. The rod structure of P70 seems to be formed by further aggregation of the surface micelles (Figure 3) whereas the rod shape observed by Eisenberg and co-workers[29] was formed in the micelle formation process. The rod shape in this study looks like a string of micelles. This rod shape was not observed for P155, which has almost equal molecular weights for PS and PMMA blocks. This indicates that further aggregation between the PS block cores is possible when the PMMA block length is shorter than PS block length; hence, the assembly of the hydrophobic PS cores provides enough enthalpy to overcome the substantial entropy loss attendant with the orientation of PMMA corona into highly close-packed geometry. In contrast, when the PMMA block length is longer than PS block, entropic losses are too big to be overcome by the enthalpy gain. Therefore, the rod shape micelles were not formed. This can be further corroborated by the observation of the surface micelles formed from the blend solution of P70 and P392 (50:50 ratio). Figure 4 shows the mixture surface morphology with the surface pressure. When the surface pressure is low, P70 and P392 form their own micelles. Different micelles are evidently existent. After further compression, the mixture monolayer shows more or less similar shape micelles. The rod shape observed in P70 monolayer was not observable. We infer that the enthalpic energy gains by PS blocks in different block copolymers were not enough to overcome the entropic losses attendant with the orientation of different length PMMA blocks. Once formed, surface micelles were not disassembled into block copolymer molecules even when the surface area was fully expanded (the surface pressure returned to zero), and then a long time (72 h) has elapsed. This supports Eisenberg et al.'s assertion that, once formed, the surface aggregates are kinetically stable, and therefore unimer−micelle exchange, if any, is very slow.[24]

For a PS−PMMA diblock copolymer having different molecular weight (M_w of PS block = 880 000 and PMMA block = 290 000) from our samples, Rice et al. reported that no region of the surface pressure−area isotherm corresponded to isolated molecules.[23] Since the PMMA block was much shorter than the PS block, their polymer molecules formed self-aggregates as soon as spread on the water surface, and the polymers self-assembled into aggregates containing about 240 molecules. 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 molecules, and the boundary was determined by the PMMA portion. According to their results, the dense core of the PS portions oriented themselves so that the collapsed PS blocks were

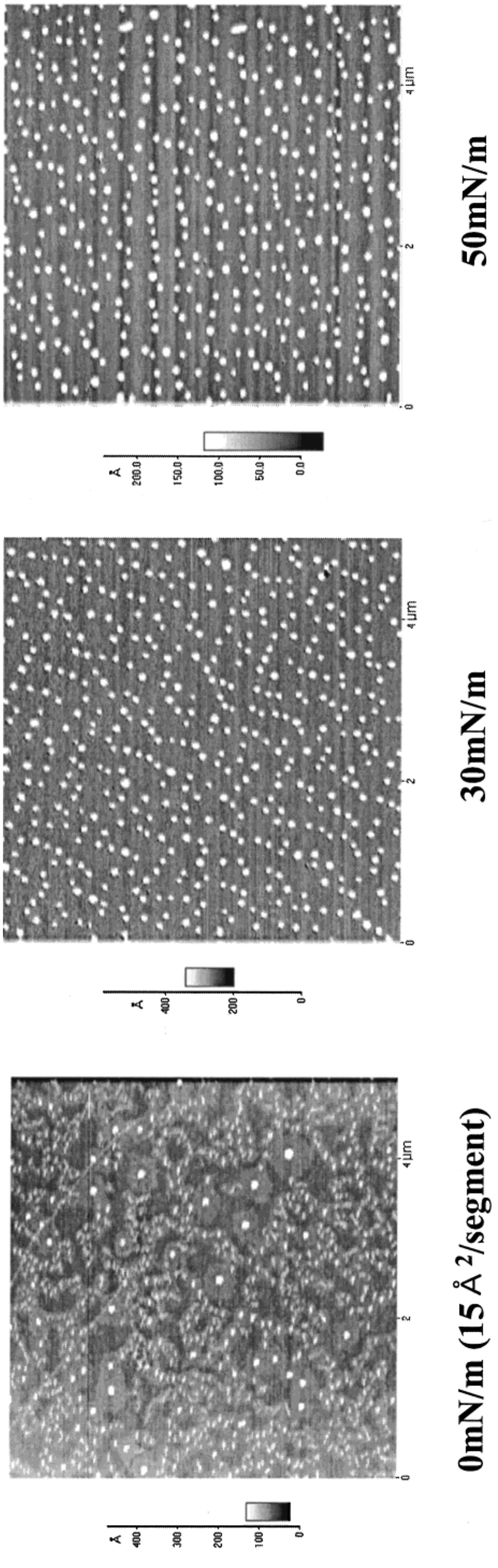

Figure 4. AFM images of P70/P392 mixture (50:50 ratio) monolayers.

in the air, while the PMMA blocks were at the air/water interface. 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.[23] Our results are somewhat different. When the molecules were spread on the water surface, few aggregates were formed (or aggregates were too small to be detected by AFM) for other polymers except P70. Even P70 did not show many aggregates (Figure 2). Most surface micellization proceeded with the surface compression. This implies that self-attraction of PS blocks is not so strong to lead to micelle formation. However, slight compression is enough to induce the aggregation of block copolymer molecules.

AFM micrographs provide more information by access to the aggregation number of surface micelles. We applied the total area method to calculate the aggregation number at the constant surface pressure of 7 mN/m. The calculated aggregation number was 430 ± 20, 115 ± 10, 60 ± 8, and 7 ± 2 for P70, P155, P392, and P656 samples, respectively. A relatively large error in P656 is inferred due to their polydispersity. Since the core size of P70 is not uniform, P70 also introduces some large errors in the counting of surface micelles. Despite their uncertainty, it is unquestionable that more molecules aggregate for shorter PMMA segment molecules. This is consistent with expectations based on the limitations of PMMA block conformation. Because it has to take the 2D “ random coil” conformation on the water surface, the longer chains have to adopt a much wider footprint; hence, fewer molecules aggregate for long chains.[23,27,28] Also, as we mentioned above, the interaction between PS blocks and repulsion between PS and PMMA blocks should participate in the determination of the aggregation numbers. The large aggregation number of P70 is speculated to reflect further aggregation between micelles. Rice et al. reported that thin disklike aggregates contains about 240 molecules of aforementioned PS−PMMA diblock copolymer.[23] They suggested that the furry disks could aggregate to form even “larger” islands of disks. Dynamic light scattering results showed that there were two different contributions to the intensity fluctuations, which is consistent with the idea that some of the micelles on the surface formed much larger networks of islands.[23] When the PMMA segment is longer than PS segment, such a large aggregation was not formed. This is also in agreement with Rice et al.’s observation. Even at the very high surface pressure, the surface micelles did not show any formation of large aggregates even though it showed a crowd of micelles.

To look into more details of the hysteresis, we repeatedly measured the dynamic surface pressure. Figure 5 shows the $\pi-A$ curves of the longest diblock copolymer (P656). They were obtained as follows: The monolayer was compressed to a surface pressure of 18 mN/m, expanded to a surface pressure of 0 mN/m (an area of 40 Å^2/repeating unit), and then compressed and expanded again (Figure 5a). In the second experiment, the monolayer was compressed to a surface pressure of 33 mN/m, where the surface pressure was over the transition region, then expanded to a surface pressure of 0 mN/m (an area of 40 Å^2/repeating unit), and then compressed and expanded again (Figure 5b). In the

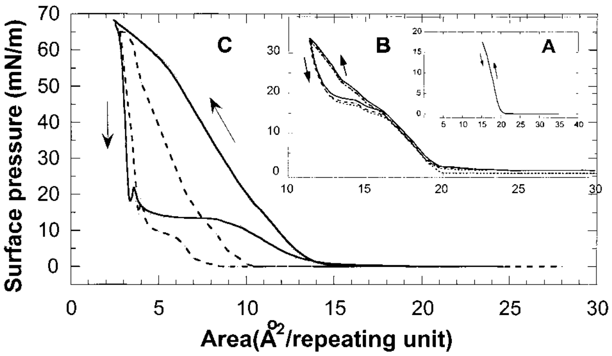

Figure 5. π−A curves of the longest diblock copolymer (P656) monolayers: (A) The isotherm was obtained after compressing the monolayer to a surface pressure of 18 mN/m, expanded to a surface pressure of 0 mN/m (an area of 40 Å^2/repeating unit), and then compressed and expanded again. (B) The monolayer was compressed to a surface-pressure of 33 mN/m, where the surface pressure was over the transition region, then expanded to a surface pressure of 0 mN/m (an area of 40 Å^2/repeating unit), and then compressed and expanded again. (C) The monolayer was compressed all the way to 65 mN/m and then relaxed to 0 mN/m. After waiting for 24 h, it was compressed and expanded again. Solid lines (—) represent the first runs, and dashed lines (- - -) represent the second runs.

third experiment, the monolayer was compressed all the way to 65 mN/m and then relaxed to 0 mN/m (an area of 40 Å^2/repeating unit). From Figure 5a,b, we can see that there is no hysteresis at all when the PMMA segments in the micelles are not compressed further than 18 mN/m. However, a hysteresis occurs when the micelles are in a highly compressed state. (The surface pressure is above the second transition for further aggregation of micelles which appears as the plateau in the expansion process.) Once the surface pressure is low (below the second transition pressure), the micelles just touch on the brim. When the external pressure is relieved, the repulsion between different PMMA coronae enacts them to push each other, thus dispersing the micelles rapidly. On the other hand, when the PMMA coronae are compressed above the transition surface pressure (Figure 5b), the micelles do not follow the same isotherm. This is in agreement with the explanation by others.[14,25] High compression puts the PMMA coronae into a dense conformation, forming a large thin film on the water surface; hence, the micelles do not disperse rapidly when the external pressure is removed. This is further confirmed by looking into the behavior of the shortest block copolymer. The monolayer of P70 shows a hysteresis when it is compressed to 7 mN/m and then expanded, which is more similar to the behavior of the PS chain.[38] This is a sign of less void between the short chain micelles due to the short PMMA segment length. This large assembly of micelles is kinetically unstable; thus, once the pressure is relieved they are disassembled into the micelles. In contrast, as we mentioned above, once formed micelles do not disassemble into block copolymer molecules after returning to zero surface pressure even after quite a long time.[13] This is corroborated by the fact that when the same monolayer was recompressed after waiting for 24 h (Figure 5c), the isotherm did not follow the first run. This means that the original chain conformation in the quasi-2D surface could not be recovered after the molecules had experienced the micelle formation. The transition also appears less vividly in the second compression isotherm, which looks like that of a condensed film. Figure 6 shows repeated cycles for P70 diblock copolymer monolayer. Though less obvious than P656 case, it shows similar behavior. The hysteresis diminishes with further cycle, indicating that the monolayer becomes more homogeneous.

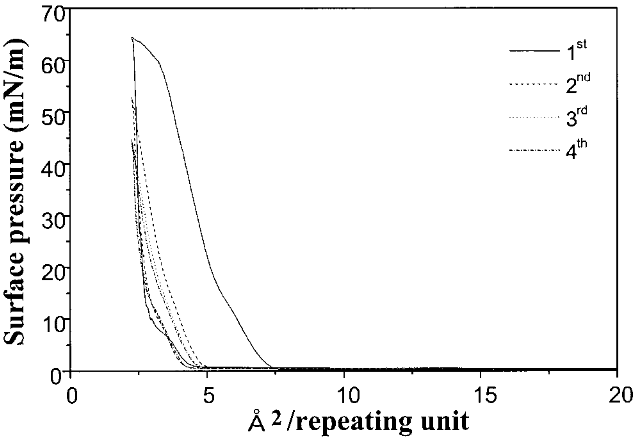

Figure 6. Repeated π−A curves of the P70 monolayer: (—) first cycle, (- - -) second cycle, (· · ·) third cycle, (— · —) fourth cycle.

We said that further core aggregation between micelles was not observed even at the high surface pressure. This is experimentally confirmed by BAM. Figure 7 gives the BAM images of P656 at different pressures. The BAM images at low surface pressures are almost the same as those obtained for the bare subphase (water) because the block copolymer has a homogeneous phase and a low reflectivity. When the surface pressure goes above the second transition surface pressure for micelles aggregation, some bright domains are observed, which means a different structure has evolved.[47] The radius of the ‘big island” in Rice et al.’s work was roughly 20 μm.[23] This was estimated using the evanescent wave light scattering technique. It was consistent with the static light scattering measurements. Since the lateral resolution of the BAM images in this study was limited to 20 μm, the white domain size is much bigger than the micelle size. The density of bright domains increases with the surface pressure. These bright domains substantiate the rearrangement of micelles into a more tightly packed state (possibly a hexagonal structure[25]). This was reproducible. Repeated experiments showed the reversible appearance of these domains. They are neither experimental artifacts nor impurities. However, this is not a further core aggregation of micelles but a lump of crowded micelles. This can be confirmed by the fact that the bright domains diminished with decreasing surface pressure. Also, it was observed that the density of the bright image at 18 mN/m during the expansion isotherm was higher than that during the compression at the same surface pressure, which means a hysteresis. In two-dimensional space, since chain entanglement is not expected,[42,47−49] the large white image disappears when the pressure is removed. The appearance of bright domains by the crowded micelles was also observed for short chains (P70 and P155), and they also disappeared after expansion.

The appearance of a different structure, not any further micelles aggregation, on the water surface can be ascribed to a poor solvent condition. This is in contrast to the interfacial behavior of PS−PEO diblock copolymer monolayers at an air−water interface.[14,49] PEO forms an expanded-type monolayer on a water surface. PEO is soluble in water, and much softer than

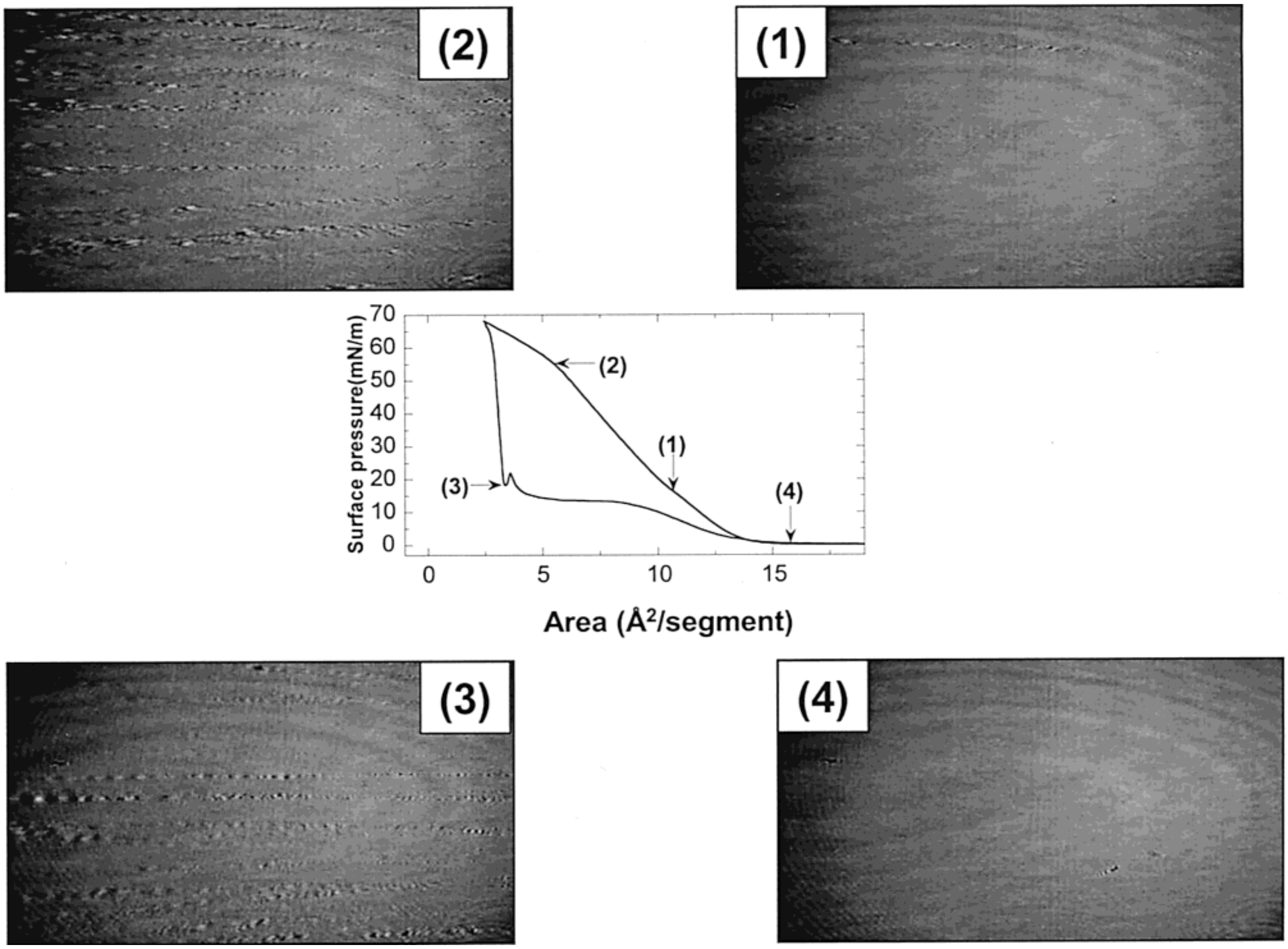

Figure 7. BAM (Brewster angle microscope) images of the longest block copolymer (P656) monolayer at different surface pressures. The bright domains substantiate the rearrangement of micelles into a more tightly packed state. Since the lateral resolution of the BAM images is limited to 20 μm, the white domain size is much bigger than the micelle size. This was reproducible. Separate experiments showed the reversible appearance of these domains. They are neither experimental artifacts nor impurities.

PMMA, considering their surface elasticity values.[9,12] Because of this difference, the hysteresis behaviors in the compression−expansion cycle are totally different. For PS−PEO block copolymers, the π−A isotherm shows several regions which can be ascribed to different conformations of the polymer chains:[14,44] a pancake structure at low surface pressures, an intermediate mushroom structure when the PEO segments are solubilized in the subphase, and a brush structure for low surface areas where the PEO chains stretch away from the interface to avoid overlapping.[14] For PS−PEO, inclusion of water in the chain prevents the chain from returning to its original position and conformation. Hence, hysteresis appears. As already mentioned, syndiotactic and attactic PMMA are not immersed in the water at high compression.[45,46] Due to the topological constraints, they stay in two-dimensional space where crossovers and entanglements of the individual polymer coils will not occur.[48−50] In contrast to the three-dimensional analogues of the PS−PEO block copolymers, the PS−PMMA micelles do not readily intertwine with each other; the only way to do so would be through a partial alignment of the corona chains, which would cost a substantial amount of conformational entropy.[42,49] Instead, they form a lump of compressed micelles only when it is highly compressed. Once the pressure is relieved in the expansion, the repulsion between PMMA coronae to recover their conformations disperses the aggregated micelles.

Summary

With the aid of a Langmuir film balance, an atomic force microscope and a Brewster angle microscope, the monolayer behaviors of a series of a diblock copolymer (A−B), where the A block is polystyrene (PS, surface interactive and water insoluble) and the B block is poly(methyl methacrylate) (PMMA, surface active but water insoluble), have been examined on the air/water interface. The PMMA block length was varied while the PS block length was kept almost the same. We investigated the peculiar features of the PS−PMMA monolayers from a quasi-two-dimensional point of view.

Dynamic surface pressure measurements show the response of a quasi-two-dimensional monolayer to an external force as well as micelle formation and aggregation. The surface pressure measurements show that short PMMA segment chains (P70) more closely follow the behavior of a pure PMMA monolayer, but long PMMA segment chains (P656) show a less-condensed behavior. Since PS and PMMA are immiscible, this is a natural consequence. Because of the structural change, the dynamic isotherms showed a hysteresis. The hysteresis was observed when the surface pressure went over the second transition. Once the micelles were pushed together, they did not disperse rapidly; thus, a hysteresis appeared. In a slow expansion process, the surface pressure of a long chain (P656) showed a minimum, which is a dynamic effect. After the first compression−expansion cycle, the original conformation of the PMMA segments in the two-dimensional surface could not fully recover their original conformation, even after a very long time had elapsed following the return to zero surface pressure. As a consequence, the second compression isotherm did not follow the first one. A transition for the micelles condensation was more clearly observable for the long diblock copolymers (P155 and P656). The transition is ascribed to the removal of large voids between the micelles.[36] Above the plateau surface pressure, a more uniform monolayer is formed due to removal of the large voids and further compression forces the PMMA coronae into a more condensed state. This structural evolution is consistent with experimental results obtained by using the surface laser light scattering method.[37] On the other hand, the short PMMA chain's (P70) isotherm did not distinctly show the plateau; no stable intermediate state was observable. It also showed a hysteresis when the compressing surface pressure reached much lower values compared to the long chains. This indicates that less void exists between the micelles of the short chains because of the small coronae.

AFM images evidently show that the PS segments of block copolymer chains aggregate to form surface micelles. The PS blocks form the core while the PMMA blocks form the corona. Once formed, the surface micelles did not disperse as separate chains, even after the surface pressure returned to zero, and remained there for a long time. Depending on the molecular weight, different images were observed. Domain size and shape were a little bit irregular for the longest chain (P656), probably due to its wide polydispersity. The calculated aggregation number was decreased with the chain length. P70, which has a shorter PMMA segment than PS segment, has a large aggregation number of ca. 430. P70 also showed some rod-shaped aggregates at high surface pressure, which was not observed in others morphology. More uniform size and shape appeared in other polymers (P155 and P392).

From the dynamic experimental results, we conclude that even at a high surface concentration, PS−PMMA block copolymers do not form complicated entanglements on water surface. Instead, they form irreversible two-dimensional surface micelles. This micelle formation was an irreversible process in the sense that each molecules conformation was not recovered after the surface pressure had returned to zero. BAM images showed that a further coalition between micelles did not occur. It showed some new structures at high surface pressure, but this structure is a lump of crowded micelles. It is a dynamic effect due to further compaction of PMMA coronae surrounding the micelle cores.

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(43) With the assumption that the PS particles on the water surface form a continuous film with bulk density of 1 g/cm^3, the apparent thickness of the film, d_{app}, was calculated as 2.6 nm, which is quite close to the value of 2.5 nm measured by Kumaki et al.[32] (A single-chain conformation of a polystyrene-*b*-poly(methyl methacrylate) copolymer, the same one

as P392, was observed with an atomic force microscope (AFM).[32] The limiting area A_0 of P392 measured in this study was 11.5 Å^2/segment and was in good agreement with the data of Kumaki et al.[32]) From the measured A_0 of P392, the limiting area/molecule was calculated as 6.96×10^2 nm^2/molecule, which is also in good agreement with the AFM measurement by Kumaki et al. If we assume a uniform thickness, the PMMA segment in a free block copolymer chain occupies an area of 20.5 times the limiting area of a homo-PMMA monolayer of the same molecular weight at the air/water interface,[12] which means the PMMA segment in the block copolymer is very expanded. When we plotted the limiting area of the block copolymer molecules versus the PMMA portion, the limiting area fell on a linear interpolation between the limiting areas of PMMA (15.8 Å^2/repeating unit)[12] and PS (4 Å^2/repeating unit).[38] This implies that the PS block is on the water surface with very few contacts with the PMMA block. The limiting areas of block copolymer was determined by extrapolating the linear portion of the $\pi - A$ isotherms to $\pi = 0$. When the limiting areas of the PMMA segments were plotted as a function of the composition of the block copolymer, they were almost constant, close to the value of PMMA homopolymer. This means that, in all cases, the numbers of PS and PMMA segmental contacts are low in these block copolymers.[27] The limiting area of polystyrene was obtained from the empirical equation of Kumaki.[38] For a wide molecular weight range from 4000 to 2.06×10^7 g/mol, he observed that the limiting areas of PS were linearly proportional to the molecular weights ($A_0 = 0.04M$ Å^2/molecule). This indicates that the limiting area per repeating unit is constant, 4 Å^2/repeating unit, and is much smaller than the area of the molecular structure of polystyrene. Kumaki ascribed this to the multilayered structure of the polystyrene chains in the particles on the water surface.[38]

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