Letters

Surface Behavior of Amphiphilic Heteroarm Star-Block Copolymers with Asymmetric Architecture

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We study the surface behavior of the asymmetric amphiphilic heteroarm poly(ethylene oxide) (PEO)/ polystyrene (PS) star polymer on solid substrate. These star polymers differ in both architecture (four- and three-arm molecules, PEO-*b*-PS₃ and PEO-*b*-PS₂) and in the length of PS chains (molecular weight from about 10 000 up to 24 000). We observed that, for a given chemical composition with a predominant content of hydrophobic blocks, the compression behavior of the PS domain structure controls the surface behavior and the final morphology of the monolayers. New features of the surface behavior of star-block copolymers are high stretching of the PS arms from the interface and enhanced stability of the circular PS domain structure, even at high compression. We suggest that for asymmetric star-block copolymers both architecture and chemical composition heavily favor the formation of highly curved interfaces and, thus, more stable circular domain structure with stretched PS arms.

Introduction

Functionalized amphiphilic block copolymers are widely explored for their ability to form organized micellar aggregates with different morphologies in polymer solutions, in the bulk state, and in thin polymer layers at surfaces and interfaces, which are critical for many modern applications.[1–5] One of the most-exploited types of amphiphilic block copolymers is composed of poly(ethylene oxide) (PEO) and polystyrene (PS) blocks. The properties of these PEO–PS block copolymers, with variable mo-

lecular weight and chemical composition, are widely studied in the terms of their micellar structures in water[6] and organic solvents of different qualities[7–9] The interfacial behavior and the microstructure of PEO–PS block copolymers at both air–water and air–solid interfaces have been widely studied during the past few years.[10–19]

The surface behavior of these block copolymers is mainly controlled by the volume ratio of hydrophilic and hydro-

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phobic blocks, as was discussed in numerous publications.[12,20-22] Discussion of possible scenarios involved in the restructuring of the monolayers included initial spontaneous aggregation and changing conformation of the PEO chains and their regimes of submerging in the water subphase. Although some important details of structural reorganization are still under discussion, a general understanding of the surface behavior of these linear block copolymers includes long PEO chains adsorbed at the air–water interface as the main reason for the formation of the characteristic plateau region on the surface-pressure isotherm. In contrast, the long PS block (longer than the PEO block) should dominate the surface behavior, demonstrating conventional "gas–liquid" behavior during compression with transition from scarce, isolated, circular domains to dense, packed domains, which transform to cylindrical shapes at elevated pressures.[12] In the past years, a number of novel types of amphilihic block copolymer were synthesized and investigated: branched PEO–PS block and graft copolymers,[23] heteroarm (miktoarmed) copolymers,[24] multi-armed symmetrical copolymers,[22,25,26] Gemini,[27] and Janus-type[28] copolymers. However, to date, very limited data are available on how the confined architecture of these novel heteroarm star-block copolymers could affect their interfacial behavior and if the general trends known for linear block copolymers are held for analogous star-block copolymers.

In this work, we report on the interfacial behavior of four different amphiphilic heteroarm star-block copolymers, PEO-b-PS$_3$ and PEO-b-PS$_2$ (Figure 1). These star-block copolymers represent a case when the dimensions of the PEO chains, as is shown by computational models of star polymers in Figure 1, remain virtually unchanged for all star-block copolymers, with PS blocks dominating the overall shape for higher-molecular-weight molecules.

The overall length of PS arms is either comparable below or much higher than that for PEO arm (Table 1). The role of the star architecture and of the crowding of the multiple PS chains in the vicinity of a junction point at these two different regimes is the main focus of this work, with a detailed description of observed surface morphologies to be published elsewhere.[29]

Experimental Section

The amphiphilic heteroarm PEO-b-PS$_3$ and PEO-b-PS$_2$ star-block copolymers were synthesized by the "core first" approach.[30] The anionic polymerization of ethylene oxide was followed by the atom transfer radical polymerization (ATRP) of styrene, as has been reported in detail elsewhere (Table 1).[31] These star-block copolymers have relatively low polydispersity indexes (1.16–1.3), as was confirmed by gel-permeation chromatography (GPC) (Table 1). The solid substrates were freshly cleaned, atomically smooth, [100] silicon wafers of a high quality.[32] Wafer preparation was conducted in a class 100 Cleanroom to avoid air contaminations. Langmuir isotherms were collected and Langmuir–Blodgett (LB) monolayer deposition was conducted using an LB trough (R&K 1). The effective thickness of the deposited monolayers was measured with a COMPEL Automatic Ellipsometer (InOmTech, Inc.). The LB monolayers were studied with atomic force microscopy (AFM) by using Dimension-3000 and Multimode microscopes (Digital Instruments, Inc.) in the light tapping mode in accordance with the usual procedure adapted in our lab.[33,34] Molecular models were built using Materials Studio 3.0 and Cerius² 3.8 on an SGI workstation. For a more detailed description, see Supporting Information.

Results and Discussion

The surface pressure–area isotherms obtained for different amphiphilic heteroarm star polymers are shown in Figure 2. All isotherms showed a steadily increasing surface pressure upon compression that is indicative of the formation of stable Langmuir monolayers.[35] We did not observe any hysteresis of monolayers of the PEO-b-PS$_3$-1 and PEO-b-PS$_2$-1 up to 5 mN/m, although hysteresis was observed for PEO-b-PS$_3$-2 and PEO-b-PS$_2$-2 star polymers, even at low surface pressure, which can be explained by PS chain interactions, especially when the monolayer is compressed to its collapsed state.

The shape of these isotherms is slightly different from the surface-pressure isotherms obtained for linear diblock PEO–PS copolymers with a relatively low content of hydrophilic block.[10,14] The isotherms for PEO-b-PS$_3$-1 and PEO-b-PS$_2$-1 showed some evidence of the phase transition of PEO at low (<10 mN/m) surface pressure (pseudoplateau). In contrast, for PEO-b-PS$_3$-2 and PEO-b-PS$_2$-2 star polymers, we did not observe any pseudoplateau on the isotherms due to a low PEO content and a relatively short PEO block, unlike the traditional block copolymers with higher PEO content described in the literature.[10,14,16] It has been shown in numerous publications that the plateau characterized phase transition of the PEO chain from pancake to brush structure upon compression.[8-16] Detectable increase of the surface pressure was observed for surface area per molecule below 40–60 nm², with a

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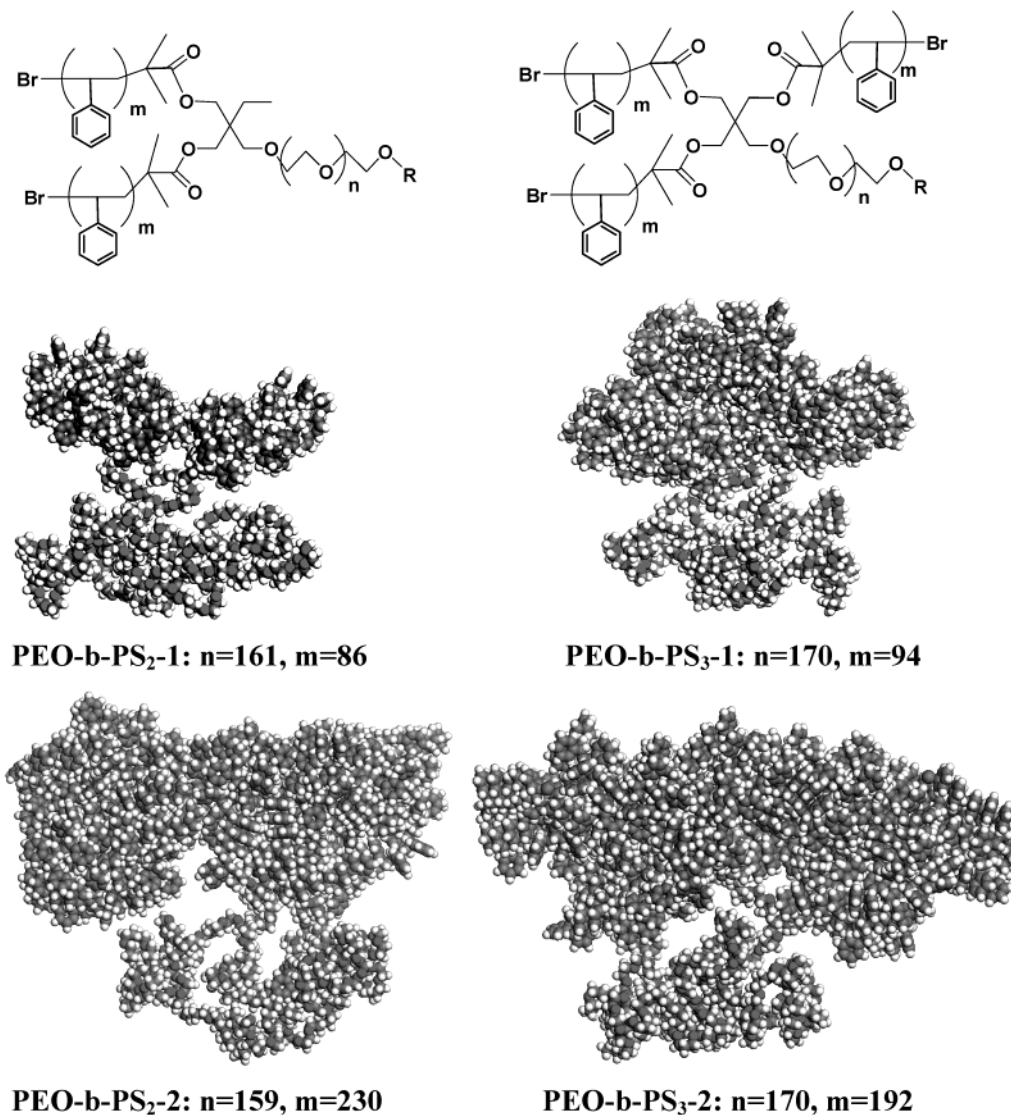
PEO-b-PS$_2$-1: n=161, m=86

PEO-b-PS$_3$-1: n=170, m=94

PEO-b-PS$_2$-2: n=159, m=230

PEO-b-PS$_3$-2: n=170, m=192

Figure 1. Chemical formulas of the heteroarm star polymers (top) studied in this work with corresponding molecular models and corresponding abbreviations (bottom). R is *tert*-butyldiphenylsilyl (*t*-Bu(Ph)$_2$Si-) protecting group.

Table 1. Properties of Heteroarm Star Polymers

	total		PEO arm				PS arm			experiment		
	M_n 10^3	PDI[a]	M_n 10^3	N[b]	L_{arm} nm	φ	M_n 10^3	N	L_{arm} nm	A_o nm^2	A_o/PEO unit nm^2	A_o/PS unit nm^2
PEO-*b*-PS$_3$−1	37.0	1.16	7.5	170	65	0.18	9.8	94	24	21	0.33	0.074
PEO-*b*-PS$_3$−2	67.0	1.19	7.5	170	65	0.10	20.0	192	48	31	0.28	0.054
PEO-*b*-PS$_2$−1	25.0	1.29	7.1	161	61	0.26	8.9	86	22	11	0.23	0.064
PEO-*b*-PS$_2$−2	54.8	1.18	7.1	159	61	0.11	23.9	230	58	24	0.30	0.052

[a] Polydispercity index is determined from GPC data. [b] N is the number of monomeric units, φ is a volume fraction of PEO block, and L is the length of the corresponding arm.

sharp rise above 10 mN/m, indicating the formation of the condensed monolayer state observed for surface areas below 10−30 nm^2. Surface pressure increase is caused by interaction of hydrophobic PS blocks, even for comparable dimensions of PS and PEO chains. In fact, all pressure−area isotherms for star-block copolymers are consistently shifted to higher surface areas with increasing molecular weight of the PS arms (Figure 2). The surface area per molecule, A_0, calculated for all monolayers by the extrapolation of the steep rise in the surface pressure to a zero level, was in the range of 11−24 nm^2, with increasing values observed for the copolymers with a higher molecular weight of PS arms (Table 1).[36]

To gain additional insight into the surface behavior of the monolayers, we analyzed the surface morphology of the LB monolayers transferred at the solid substrate at different surface pressure (Figure 2). For all monolayers studied here, we evaluated the overall effective thickness of the monolayers from ellipsometry and the PS domain heights and their surface coverage from AFM images (Figure 3). The initial monolayer spreading results in the instant formation of the well-developed domain morphology with circular domains (see representative images of PEO-*b*-PS$_3$-1 star polymer at different surface pressures

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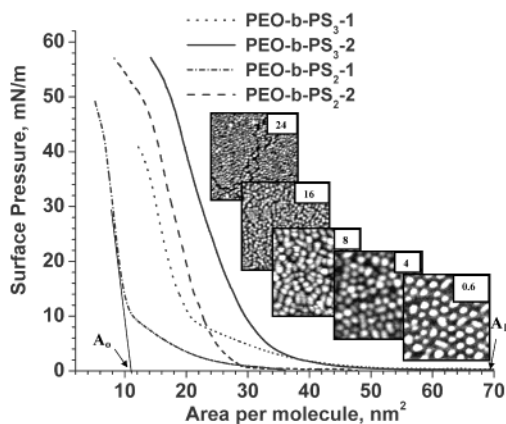
Figure 2. Pressure–area isotherms for Langmuir monolayers of amphiphilic heteroarm star-block copolymers and corresponding representative AFM images of surface morphologies of PEO-b-PS$_3$-1 star polymer at different surface pressures (the top right corner of the image shows the surface pressure, the first three AFM images are 500×500 nm^2 and the last two are 1×1 μm^2, the height scale is 10 nm).

in Figure 2). The predominant structural element at all surface pressures were round, relatively uniform circular micelles with the diameter ranging from 40 to 200 nm and the thickness of 0.5–6 nm for different block copolymers with overall thickness being higher for molecules with a higher molecular weight of PS chains and increasing number of PS arms (Figure 3). The modest compression of the monolayers results in increasing their effective thickness and the packing density of circular domains to 60–70% without significant changes in their shape and lateral dimensions (Figure 3). The effective monolayer thickness reached 2.5–5 nm for the different star-block copolymer at the highest pressure in the vicinity of the collapse where initial cracking was observed as a first sign of the monolayer pre-collapsed state (Figures 2 and 3). Despite significant scattering of the data, the increase of the monolayer thickness was consistent for all star-block copolymers with a systematic shift to higher values for molecules with a higher molecular weight of PS arms. In addition, an overall volume per molecule estimated from geometrical dimensions remains fairly unchanged, which implies no dramatic transformations of the micellar structure. Here, we should underline that the height of the PS domains did not change much upon compression, but the effective thickness of the LB monolayer increased significantly due to increasing mainly the concentration of the PS domains. An apparent discrepancy between AFM and ellipsometry data is related to different origins of the measured parameters. Indeed, the domain heights were obtained by cross-sectional analysis from AFM images under the assumption that domains were composed predominantly of PS phase surrounded by PEO phase.[37] The domain height was obtained as a difference between the surface and the surrounding of the domain, and the presence of other domains or their overall concentration do not affect this parameters. In contrast, ellipsometry measures the *effective thickness* of the whole surface layer. For modeling ellipsometry results, the combination of two materials must be considered to make up an "effective layer" with some intermediate index of refraction, which resulted in some average constant thickness for polymer layer, as described in detail in the
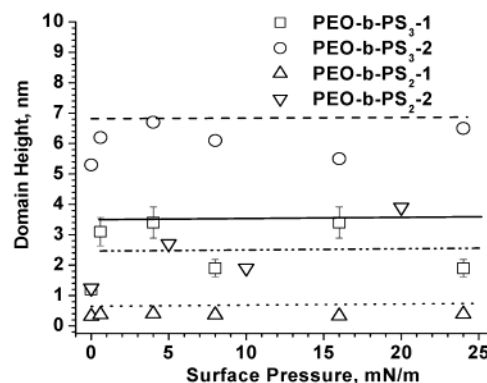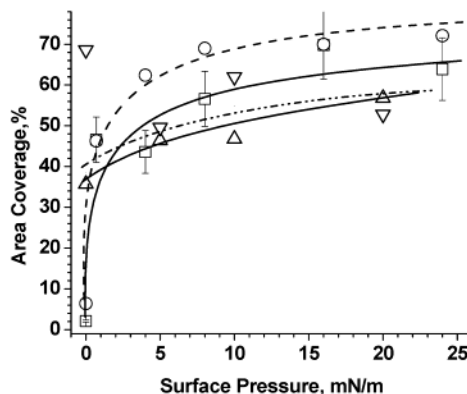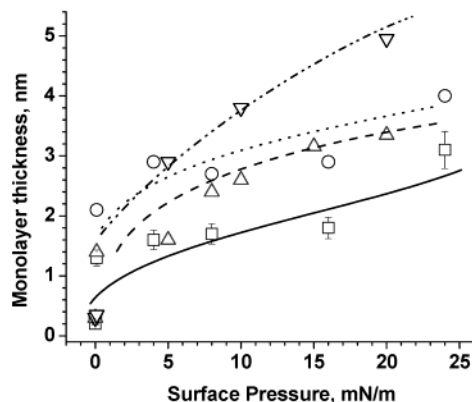

Figure 3. Variation of the monolayer effective thickness (top), the surface coverage with PS domains (middle), and PS domain heights (bottom) with the surface pressure for four star-block copolymers. Lines are guides for an eye.

literature.[38,39] It means that the effective thickness of the polymer monolayer, as measured by ellipsometry, depends not only on the height of the domains but also upon their surface concentration. Therefore, the surface reconstruction resulting in changing domain concentration can (and it does in our case) show a constant domain height as measured by AFM and increasing effective monolayer thickness as measured by ellipsometry.

Although it is clear that the general trend in the formation of the interfacial morphology for star-block copolymers studied here is similar to that reported before for conventional linear block copolymers, we observe several distinguished features which we believe could be attributed to the peculiar architecture of these star-shaped molecules. For both star-block copolymers with a very

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low content of PEO block, a gradual increase in the surface pressure indicates the continuous formation of surface micelles (domains) with a limited number of molecules within an isolated domain.[40a] On the other hand, the isotherm shape with plateau, which is a signature of similar linear PEO−PS block copolymers, was observed only for the star-block copolymers with a modest content of PEO block (Figure 2). These two polymers exhibit an array of highly uniform, circular aggregates within LB monolayers, which confirmed the correlation between isotherms and AFM images describing the surface behavior of PVP−PS diblock copolymers.[40b,c] For the star polymers with lower PEO contents (about 10%, Table 1) where no plateau was observed in the isotherm, the LB monolayer was primarily composed of a polydisperse, very large, planar, circular structures with some rodlike micelles (See Supporting Information).

The onset of the initial stages of the formation of the monolayer is consistent with that expected for the linear block copolymers with hydrophilic block adsorbed at the air−water interface and is not affected by the presence of the multiple PS chains. In fact, the surface area per PEO unit for star-block copolymers (A_1 value, Figure 2, Table 1) is similar to the surface area estimated for the PEO monomeric units at the water surface hydrogen-bonded with 1−3 molecules of water (0.28 nm^2 for the PEO monomeric unit with two water molecules).[12,13,41] However, in the condensed monolayer state, the surface area per PS monomeric unit is within 0.05−0.07 nm^2/unit for star-block copolymers (Table 1). This value is well below the usual value of about 0.08−0.1 nm^2/unit observed for linear diblock copolymers. This behavior indicates that multiple PS chains connected to a single joint are more stretched because of the crowding of PS arms near the star junction point, as predicted for bulk structures.[27,42,43] This crowding also prevents the formation of cylindrical surface mor-phologies in LB monolayers compressed to high pressures and significant stretching of PEO chains usually observed for linear hydrophobic−hydrophilic molecules.[10,13−15]

Therefore, for the chemical composition studied here with a predominant content of hydrophobic blocks, we can conclude that the compression behavior of PS domains controls the surface behavior and the final morphology of the condensed monolayer with the hydrophilic block spread thinly between PS domains and the silicon surface. Star-block copolymers, especially ones with a high molecular weight of PS arms, show significant stability for a circular domain structure over a wide range of pressures and surface areas without forming the cylindrical domains under high compression, which occurs for linear block copolymers. This trend can be associated with the crowding state of the multiple PS chains tethered to a single joint point, resulting in a more stable state of the curved shape of the interface (hence, circular micellar structures) in asymmetrical star-block copolymers.[44] For asymmetric star-block copolymers, both architecture and chemical composition heavily favor the formation of highly curved interfaces and, thus, a more-stable circular domain structure of the monolayer, which sustains high compression of the monolayers. The trend toward higher stability of the curved interfaces associated with spherical domains is generally observed for solid state of star-block copolymers and is supported by theoretical considerations.[45,46]

Supporting Information Available: Experimental details, AFM images of LB monolayers, and topography images of LB monolayers. This material is available free of charge via the Internet at http://pubs.acs.org.

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