Self-Assembly of Polystyrene-block-Poly(Ethylene Oxide) Copolymers at the Air–Water Interface: Is Dewetting the Genesis of Surface Aggregate Formation?

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Block copolymer self-assembly at the air–water interface is commonly regarded as a two-dimensional counterpart of equilibrium block copolymer self-assembly in solution and in the bulk; however, the present analysis of atomic force microscopy (AFM) and isotherm data at different spreading concentrations suggests a nonequilibrium mechanism for the formation of various polystyrene-b-poly(ethylene oxide) (PS-b-PEO) aggregates (spaghetti, dots, rings, and chainlike aggregates) at the air–water interface starting with an initial dewetting of the copolymer spreading solution from the water surface. We show that different spreading concentrations provide kinetic snapshots of various stages of self-assembly at the air–water interface as a result of different degrees of PS chain entanglements in the spreading solution. Two block copolymers are investigated: MW = 141k (11.4 wt % PEO) and MW = 185k (18.9 wt % PEO). Langmuir compression isotherms for the 185k sample deposited from a range of spreading concentrations (0.1–2.0 mg/mL) indicate less dense packing of copolymer chains within aggregate cores formed at lower spreading concentrations due to a competition between the interfacial adsorption of PEO blocks and the kinetic restrictions of PS chain entanglements. From AFM analysis of the transferred Langmuir–Blodgett films, it is clear that PS chain entanglements in the spreading solution also affect the morphological evolution of surface aggregates for both samples, with earlier structures being trapped at higher concentrations. At the highest spreading concentration for the 141k copolymer, the coexistence of long spaghetti aggregates with cellular arrays of holes, along with various transition structures, indicates that various surface aggregate evolutions occur from networks of rims formed as a result of dewetting of the evaporating spreading solution from the water surface.

Introduction

Nonlithographic techniques leading to controllable and potentially functional structures occupy a fundamental niche in modern materials science. For this reason, there has been considerable interest in systems that spontaneously organize into predictable surface patterns, including significant research focused on the self-assembly of amphiphilic diblock copolymers at the air–water interface. When deposited onto the surface of water, polymeric amphiphiles form nanoscale surface aggregates with a range of morphologies, including dots, long strands (spaghetti), planar structures (continents), ring and chainlike aggregates, and interconnected networks of spaghetti. The predominant surface features obtained depend on a number of controllable factors, including the nature and relative lengths of the two blocks, the surface pressure, and the concentration of the spreading solution. It is commonly suggested that these various two-dimensional (2D) aggregates are analogous to the diverse array of three-dimensional (3D) block copolymer structures that form under equilibrium conditions in selective solvents and in the solid state; however, recent research suggests that at least some of the observed morphological diversity at the air–water interface can be attributed to kinetic effects related to chain entanglements between hydrophobic blocks in the spreading solution. Despite the immense potential offered by block copolymer self-assembly at the air–water interface for patterning surfaces with polymeric and composite features, several key aspects of 2D aggregate formation continue to be poorly understood, especially compared to the vast theoretical and empirical literature on 3D block copolymer morphologies: What is the detailed microstructure of block copolymer aggregates at the air–water interface, including the relative positions and conformations of both blocks? Are these structures actually 2D analogues of the various 3D micelle morphologies that form under equilibrium conditions? What is the mechanism of formation of the various surface morphologies? Perhaps the most widely studied system of diblock copolymer self-assembly at the air–water interface is based on a hydrophobic

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molecular areas can be determined, describing the average surface properties of the two regions of increasing concentration of PS and PEO as the spreading solvent evaporates. Additional water surface and repulsive interactions between PS and water (the so-called “pancake” conformation)10,11. At low surface density, these aggregates consist of a raised core of clustered PS chains, in either a collapsed or fine structure from the isotherms.

This paper presents Langmuir isotherm and hysteresis data for various spreading concentrations of a high molecular weight and hydrophobic PS-b-PEO copolymer with a somewhat higher PEO content than that investigated in our previous study: MW \( = 185k, 18.9 \text{ wt } \% \text{ PEO (denoted 185k). For this copolymer, Langmuir compression isotherms show a clear pancake-to-brush phase transition, allowing the effect of spreading concentration on the limiting areas of the pancake and brush conformations (A}_p, and A}_b, respectively) to be assessed for the first time. This provides the basis for a model of the fine structure of surface aggregates under different conditions of chain entanglements during spreading. As well, we compare the spreading concentration dependence of the morphologies of transferred aggregates in LB films of the 141k and 185k copolymers. For both copolymers, morphology evolution at the air-water interface is kinetically impeded by chain entanglements in the spreading solution. As a result, higher spreading concentrations result in lower chain mobilities before the aggregates are ultimately trapped by vitrification, providing earlier “snapshots” in the process of block copolymer aggregate formation.

The kinetic trapping of PS-b-PEO surface aggregates via variations in the spreading concentration has led us to the first direct evidence for a mechanism of spontaneous copolymer self-assembly at the air-water interface. Insight into a mechanism of block copolymer self-assembly is offered by a relatively high spreading concentration for the 141k sample, which provides a very early snapshot of aggregation at the water surface. AFM images of the resulting LB films show a coexistence of long and interconnected spaghetti aggregates with cellular networks of holes in relatively low continent-like regions, with the holes surrounded by raised rims. These network structures are strongly reminiscent of patterns formed from the dewetting of ultrathin films of homopolymers from solid23–32 and liquid33,34 surfaces.


While AFM yields important information on the lateral morphology of the surface aggregates, Langmuir compression isotherms of PS-b-PEO monolayers at the air-water interface can offer additional insight into the aggregate fine structure, including the interfacial conformation of PS and PEO blocks.10,13,17,18 At low surface density, these aggregates consist of a raised core of clustered PS chains, in either a collapsed or somewhat brushlike state,13,17 with some of the PEO chains radiating from the periphery of the aggregate in a 2D corona at the water surface (the so-called “pancake” conformation).10,11 Cox et al. pointed out that PEO should also reside underneath the PS core, and proposed a model describing a coherent film of PEO buffering unfavorable interactions between PS and water.11 When aggregates on the water surface are laterally compressed, the surface density (\( \Gamma \)) increases until PEO chains in neighboring corona eventually overlap, resulting in an increase in the surface pressure (\( \pi \)), which is the difference between the surface tension of pure water and the surface containing the film (\( \pi = \gamma_0 - \gamma \)). As the surface area (A) continues to decrease, overlapping PEO chains submerge into the subphase at constant \( \pi \sim 10 \text{ mN/m} \) to form a PEO brush, as evidenced by a break (pseudoplateau) in the \( \pi - A \) isotherm, a conformational change commonly described as the “pancake-to-brush” phase transition. Further compression results in the overlap of the relatively incompressible cores and a sharp increase in \( \pi \). From the two regions of increasing \( \pi \), two distinct limiting mean molecular areas can be determined, describing the average surface area of chains in the pancake and brush conformations of the aggregates (\( A_0p \) and \( A_0b \), respectively).6 The extent of the pseudoplateau has been found to be dependent on the PEO content: for copolymers with less than \( \sim 15 \text{ wt } \% \text{ PEO, the PEO pancake-to-brush transition is impeded by the large surface area of the PS cores, such that no break is observed in the isotherm.}^13

For identical amounts of the 141k PS-b-PEO copolymer deposited at the water surface, we previously reported that the spreading concentration significantly affected the Langmuir compression isotherms, indicating differences in chain conformations within various trapped aggregates.17 It was found that the limiting mean molecular area (\( A_0 \)) increased sharply below a critical spreading concentration (\( c \leq 0.25 \text{ mg/mL} \)), corresponding to the appearance of chainlike and ring morphologies in the LB films. This increase in \( A_0 \) was tentatively ascribed to an increase in the interfacial adsorption of PEO blocks within the aggregates due to a decrease in entanglement of PS blocks during spreading. However, because of the relatively low PEO content of the copolymer in that study (11.4 wt %), no pseudoplateau was observed under any of the experimental conditions investigated, limiting the elucidation of aggregate fine structure from the isotherms.
In addition, various intermediate structures point to the formation of spaghetti aggregates via the disconnection of junctions within networks of rims. On the basis of this evidence, we outline a new nonequilibrium mechanism for the formation and evolution of block copolymer surface aggregates, beginning with an initial dewetting of copolymer solutions from the air—water interface. We believe that this mechanism may be generally applicable to the formation of various 2D copolymer morphologies at the air—water interface, and has been elucidated in the present system due to slow polymer dynamics relative to the time scales of spreading and solvent evaporation. This is attributed to relatively long PS blocks leading to strong chain entanglements and low PEO contents leading to slow copolymer spreading.

Experimental Section

Materials. The two PS-b-PEO copolymers used in this study were obtained from Polymer Source Ltd. and were characterized by the manufacturer (Table 1), where \( M_n \) is the number-average molecular weight, \( M_w/M_n \) is the polydispersity index, and \( x_n \) indicates the degree of polymerization of each block.

Stock solutions of each copolymer (\(~5 \text{ mg/mL}\)) were prepared by weighing an appropriate amount of the polymer (dried overnight in a dark desiccator at room temperature) into new glassware that had been cleaned three times with acetone and three times with spectroscopic-grade chloroform (Aldrich, 99.9\%); a specific amount had been cleaned three times with acetone and three times with spectroscopic-grade chloroform (Sigma-Aldrich, 99.9\%); then added gravimetrically. Spreading solutions of various concentrations were prepared by diluting appropriately weighed quantities of this stock solution; all solutions were prepared 24 h prior to use to allow for equilibration and used within 2 days for isotherm trials and within 7 days for dipping studies. Prepared solutions were sealed with Teflon and refrigerated in the dark. Solid copolymer samples were stored in a sealed vial covered in aluminum foil at \(-20 ^\circ \text{C}\). These precautions were necessary to minimize the degradation of the PEO block via oxidation.\(^{35}\)

Table 1. Characteristics of the Copolymers Used in This Study

<table>
<thead>
<tr>
<th>PS-b-PEO</th>
<th>(M_n) (g/mol)</th>
<th>PEO wt %</th>
<th>(M_w/M_n)</th>
<th>(M_n,\text{PEO}) (g/mol)</th>
<th>(M_n,\text{PS}) (g/mol)</th>
<th>(x_n,\text{PEO})</th>
<th>(x_n,\text{PS})</th>
</tr>
</thead>
<tbody>
<tr>
<td>141k</td>
<td>141 100</td>
<td>11.4</td>
<td>1.04</td>
<td>16 100</td>
<td>125 000</td>
<td>370</td>
<td>1200</td>
</tr>
<tr>
<td>185k</td>
<td>185 000</td>
<td>18.9</td>
<td>1.09</td>
<td>35 000</td>
<td>150 000</td>
<td>800</td>
<td>1440</td>
</tr>
</tbody>
</table>

The Results and Discussion section of this paper is divided into the following parts: In the first part, we describe the effect of spreading concentration on the compression isotherms of the 185k copolymer; these results, together with previous isotherm data from the 141k copolymer,\(^{17}\) are used to develop a model describing the packing and conformation of hydrophobic and hydrophilic blocks within PS-b-PEO surface aggregates for different spreading concentrations. The second part describes the spreading concentration dependence of isotherm hysteresis. This is followed by a description of the spreading concentration dependence of aggregate morphologies in LB films, including a comparison of morphology evolution in the 141k and 185k copolymers. We finally present AFM data of surface aggregates for the 141k polymer obtained at a high spreading concentration (\(c = 2.0 \text{ mg/mL}\)) showing evidence that various surface morphologies of PS-b-PEO evolve from patterns formed by

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dewetting of the evaporating solution from the water subphase.

On the basis of this evidence, we propose a nonequilibrium mechanism for PS-\textit{b}-PEO self-assembly at the air–water interface, involving an initial dewetting step, following by subsequent morphology evolution driven by interfacial PEO adsorption.

Compression Isotherms. Compression isotherms obtained for the more hydrophilic 185k copolymer all showed a pseudo-plateau at $\pi \sim 10$ mN/m, consistent with a pancake-to-brush transition for overlapping PEO chains during compression. Representative isotherms of Langmuir films cast from $c = 0.10-1.0$ mg/mL spreading solutions of the 185k copolymer are shown in Figure 1a, highlighting a marked spreading concentration dependence of the isothermal film behavior. For each spreading concentration, the limiting mean molecular areas of the pancake and brush conformations ($A_{0,p}$ and $A_{0,b}$ respectively) were determined by extrapolating tangents to the inflection points in the two regions of increasing $\pi$ to $\pi = 0$, as shown in Figure 1b. For the range of spreading concentrations, the isotherms in Figure 1a show a constant initial onset in the surface pressure increase and a constant pancake limiting area $A_{0,p}$; the latter value is plotted versus the spreading concentration in Figure 2a, with errors determined from repeat runs carried out on separately prepared Langmuir films. When we normalize the determined $A_{0,p}$ values with respect to the number of EO repeat units in the copolymer, we obtain an average value of $\sim 31$ Å$^2$ per EO monomer over the range of spreading concentrations. This value is consistent with the pancake limiting areas reported for PS-\textit{b}-PEO copolymers of various compositions\textsuperscript{6,7,12,13} and is significantly lower than the limiting areas reported for PEO homopolymer at the air–water interface (40–48 Å$^2$ per EO).\textsuperscript{36}

In contrast to the constant limiting area of the pancake conformation, the isotherms in Figure 1a clearly show a progressive increase in the brush limiting area $A_{0,b}$ with decreasing spreading concentration. The earlier onset of the brush region with constant onset of the pancake region results in a clear decrease in the extent of the pseudo-plateau as the spreading concentration decreases, which appears as only a slight break in the isotherm for $c = 0.10$ mg/mL. The dependence of the spreading concentration on the brush limiting area (Figure 2b) shows that $A_{0,b}$ is relatively constant for higher spreading concentrations ($c \geq 1.0$ mg/mL), although it starts to increase considerably for $c \leq 0.5$ mg/mL. Interestingly, this trend in $A_{0,b}$ with respect to spreading solution concentration is similar to that observed previously for $A_0$ values determined from compression isotherms of the 141k copolymer, which were constant for a range of spreading concentrations but sharply increased for $c \leq 0.25$ mg/mL.\textsuperscript{17}

The observed spreading concentration dependence of compression isotherms points to significant differences in chain conformations and packing within surface aggregates of the 185k copolymer following solvent evaporation. Figure 3 shows a qualitative model, based on the observed trends in the isotherm data, describing the effect of spreading concentration on the conformations of PS and PEO blocks within surface aggregates.

after solvent removal, before and after compression past the
pancake-to-brush transition. This picture assumes that the PS
cores are vitrified after solvent evaporation, so that, upon
compression, peripheral PEO chains extending from the cores
can undergo a pancake-to-brush transition, but no fundamental
rearrangement of chains within the cores can occur. Consistent
with the model of PS-b-PEO surface aggregates described
previously by Cox et al., 11 Figure 3 shows PEO blocks (dark
blue) located both in a corona at the periphery of the PS core
(red) and also in a sublayer underneath the core. The key feature
of the present model is the difference in copolymer packing
densities within the aggregates under different spreading condi-
tions and the consequential differences in the PEO chain
conformation within the sublayer. For concentrated spreading
(Figure 3a), the packing of copolymers within the core is relatively
dense, resulting in a high local density of PS blocks inside the
cores. The surface concentration of PS blocks directly affects the
nature of the interaction between EO monomers and the interface,9
such that strong repulsive interactions are expected underneath
the densely packed cores, forcing PEO chains in the sublayer to
submerge into the water, even before the aggregates are
compressed. Upon compression, the peripheral PEO chains
overlap as aggregates are brought into contact, and will eventually
undergo a pancake-to-brush transition until the neighboring cores
start to overlap. In contrast, for dilute spreading (Figure 3b), the
packing density of copolymers within the cores is significantly
lower, with weaker repulsion between the EO monomers and the
interface underneath the aggregates reflected in the partial
interfacial adsorption of PEO chains in the sublayer. When these
aggregates are compressed, peripheral PEO begins to overlap at an
areal density similar to that in the concentrated spreading
case; however, the less dense cores occupy a larger area per
molecule, and will begin to overlap at an earlier stage of
compression (Figure 3b) compared to the cores from concentrated
spreading (Figure 3a). The earlier overlap of aggregate cores
will impede compression-induced desorption of PEO chains in the
corona, explaining the decrease in the extent of the pseudoplateau
as the spreading concentration decreases (Figure 1a). Although this model is based on trends in  \( \Delta A_{0p} \) and \( \Delta A_{0b} \)
measured from compression isotherms for the 185k copolymer,
the previously reported concentration dependence of the limiting
area of the 141k copolymer17 suggests that a similar picture of
copolymer packing from different spreading conditions is
generally applicable to copolymers in which chain entanglements
influence surface self-assembly on the time scale of solvent
evaporation, as discussed below.

The observed differences in chain conformations within
aggregates formed from different spreading concentrations can be
explained by increased entanglements between PS blocks in
more concentrated spreading solutions. On the basis of the model
in Figure 3, the interfacial adsorption of EO monomers should
provide a driving force for the system to decrease the density
of packing within the aggregates, although this tendency can be
kinetically impeded by the overlap of PS blocks in the spreading
solvent if chain entanglement effects are significant: when the
spreading concentration is relatively high, the polymer chain
dynamics will be slower, such that denser, less energetically
favorable aggregate conformations are ultimately trapped by
solvent removal and vitrification. We note that the structures in
Figure 3 describe only differences in the average density of
copolymer cores within aggregates from various spreading solutions,
as inferred from isotherm data, and do not address the spreading
concentration dependence of the lateral morphologies of the
aggregates. The latter related issue will be discussed in connection
with the AFM data of transferred LB films of self-assembled
PS-b-PEO.

Hysteresis. Hysteresis effects have proved to be very
informative in elucidating the dynamic behavior of amphiphilic
systems under variable stress at air—liquid6—8,37—43 and liquid—
liquid interfaces.44 It has been observed that PS-b-PEO copoly-
mers at the air—water interface have compression isotherms that
can be significantly different from the subsequent expansion
isotherms.6—8 Goncalves da Silva et al.6 studied hysteresis in
PS-b-PEO monolayers at both high and low surface pressures
(brush and pancake regimes, respectively) through a series of
compression/expansion isotherms on PS-b-PEO copolymers of
variable PEO block length. However, the effect of spreading
concentration on the hysteresis of PS-b-PEO monolayers has not
been previously investigated.

Hysteresis of the 185k copolymer in the pancake regime
(compression to \( \pi = 10 \) mN/m, just above the plateau region,
followed by expansion) was found to show a clear spreading
concentration dependence, as shown by representative compression/expansion cycles for spreading concentrations of 0.25 and
0.50 mg/mL (Figure 4a). This hysteresis was quantified by

\[ \Delta A_{0p} = \text{mean molecular area} (\text{Å}^2) \]

\[ \text{Spreading concentration (mg·mL}^{-1}) \]

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\[ \begin{align*}
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0.50 \, \text{mg/mL} & , 0.50 \, \text{mg/mL} \\
\end{align*} \]

\[ \begin{align*}
0 & , 0.25 \, \text{mg/mL} \\
0.50 \, \text{mg/mL} & , 0.50 \, \text{mg/mL} \\
\end{align*} \]
calculating the difference $\Delta A_{0,p} = A_{0,p} - A'_{0,p}$, where $A'_{0,p}$ is the pancake limiting area determined from the expansion isotherm. Figure 4b shows $\Delta A_{0,p}$ to be constant in the range of high spreading concentrations, but decrease sharply for monolayers cast from spreading solutions below $0.50 \text{ mg/mL}$ (Figure 4b), corresponding to the increase in $A_{0,b}$ in Figure 2b. Hysteresis in the pancake regime can be explained by PEO entanglement during the pancake-to-brush transition.6 We note that the extent of PEO entanglements during compression will depend on the amount of PEO that undergoes the pancake-to-brush transition. On the basis of the model in Figure 3, less extensive PEO entanglements should therefore form upon compression for lower spreading concentrations, since earlier overlap of less densely packed cores will impede the conformational transition of peripheral PEO chains. The observed trend in $\Delta A_{0,p}$ therefore supports the proposed differences in chain packing and conformation within aggregates under different spreading conditions. Another possible cause of hysteresis at low pressures is the irreversible desorption of PEO homopolymer impurity from the interface.6,37 We carried out multiple compression–expansion cycles in the pancake regime of the isotherm (Supporting Information) and found that $\Delta A_{0,p}$ decreases steadily with each cycle for all spreading concentrations, although significant hysteresis persists after the first cycle. This indicates that PEO homopolymer may contribute to $\Delta A_{0,p}$, although it is not the main cause of hysteresis in this system.

Hysteresis was also observed in the high surface pressure region of the 185k copolymer isotherm (brush regime) by compression to $\pi = 40 \text{ mN/m}$ followed by expansion. For both spreading concentrations shown in Figure 5a (0.10 and 0.50 mg/mL), a sharp drop in the surface pressure is observed upon expansion, followed by a shallow minimum (inset). A similar minimum was previously observed in expansion isotherms obtained by Goncalves da Silva et al. for PS-\textit{b}-PEO monolayers expanded from 35 mN/m, and was attributed to the local ordering and cohesion of helical PEO chains in the brush conformation.6 To compare hysteresis for different spreading concentrations, we calculated $\Delta A_{0,b} = A_{0,b} - A'_{0,b}$, analogous to the determination of $\Delta A_{0,p}$. As shown in Figure 5b, the observed trend in $\Delta A_{0,b}$ with decreasing spreading concentration is the opposite of that found for $\Delta A_{0,p}$, increasing for spreading concentrations below $0.50 \text{ mg/mL}$. An increase in hysteresis in the brush regime for lower spreading concentrations can also be explained in terms of the conformational differences described in Figure 3. In the dilute spreading case, the increased compressibility of less densely packed cores should lead to improved organization and cohesion of submerged PEO chains upon compression to high surface pressures, explaining the observed increase in hysteresis compared to aggregates from more concentrated spreading.

**Aggregate Morphologies in Langmuir–Blodgett Films.** Figure 6 summarizes the spreading concentration dependence of LB film topologies for both 141k and 185k copolymers, showing AFM images of aggregates obtained from spreading concentrations of 1.0 mg/mL (a,b), 0.50 mg/mL (c,d), 0.25 mg/mL (e,f). Transfer pressures, $\pi = 2.0 \text{ mN/m}$ (a,c,e) and $\pi = 5.0 \text{ mN/m}$ (b,d,f). Images are $10 \times 10 \mu\text{m}$. **Figure 5.** (a) Representative compression–expansion cycles of the 185k copolymer in the brush regime (compression to $\pi = 40 \text{ mN/m}$) following spreading from 0.10 mg/mL (solid line) and 0.50 mg/mL (dashed line) copolymer solutions in chloroform. The inset details the pressure minimum during expansion for the 0.50 mg/mL case. (b) Hysteresis in the brush regime $\Delta A_{0,b}$ versus spreading concentration.

**Figure 6.** AFM images of LB films of 141k (a,c,e) and 185k (b,d,f) copolymers deposited at the air–water interface from various spreading concentrations: 1.0 mg/mL (a,b), 0.50 mg/mL (c,d), 0.25 mg/mL (e,f). Transfer pressures, $\pi = 2.0 \text{ mN/m}$ (a,c,e) and $\pi = 5.0 \text{ mN/m}$ (b,d,f). Images are $10 \times 10 \mu\text{m}$.
morphology of aggregates as they existed at the air—water interface. Evidence for the kinetic stability of aggregates at the air—water interface, attributed to the glassy nature of high-$T_g$ PS chains following solvent evaporation, was provided by AFM film morphologies obtained under identical spreading conditions but for different surface pressures during transfer ($\tau = 2.0-20.0$ nN/m). Compression to higher surface pressures before transfer resulted in a significant decrease in the distance between features, although the observed aggregate morphologies were found to be identical (Supporting Information).

For both the 141k and 185k copolymer samples, clear morphology changes are observed as a function of the spreading concentration. Both samples show a mixture of dots and spaghetti from 1.0 mg/mL spreading (Figure 6a,b), with longer spaghetti and fewer dots observed for the 141k sample than for the 185k sample. The mean widths of dots and spaghetti for the two copolymers are the same within error (Table 2), although the 185k sample forms dots and spaghetti that are somewhat taller (20 and 15 nm, respectively) than those formed from the 141k sample (16 and 12 nm, respectively), consistent with a somewhat taller brush from the longer PS blocks in the 185k copolymer. For both the 141k and 185k copolymer samples, clear morphology changes are observed as a function of the spreading concentration. Both samples show a mixture of dots and spaghetti from 1.0 mg/mL spreading (Figure 6a,b), with longer spaghetti and fewer dots observed for the 141k sample than for the 185k sample. The mean widths of dots and spaghetti for the two copolymers are the same within error (Table 2), although the 185k sample forms dots and spaghetti that are somewhat taller (20 and 15 nm, respectively) than those formed from the 141k sample (16 and 12 nm, respectively), consistent with a somewhat taller brush from the longer PS blocks in the 185k copolymer.

Table 2. Mean Dimensions of PS-b-PEO Surface Aggregates Observed by AFM

<table>
<thead>
<tr>
<th>141k</th>
<th>185k</th>
</tr>
</thead>
<tbody>
<tr>
<td>dots</td>
<td>16 ± 2</td>
</tr>
<tr>
<td>spaghetti</td>
<td>12 ± 2</td>
</tr>
<tr>
<td>rings/chains (walls)</td>
<td>10 ± 2</td>
</tr>
<tr>
<td>dots</td>
<td>170 ± 30</td>
</tr>
<tr>
<td>spaghetti</td>
<td>160 ± 20</td>
</tr>
<tr>
<td>irreg. aggs.</td>
<td>10 ± 3</td>
</tr>
</tbody>
</table>

Errors represent the standard deviation of at least 75 measured surface features.

For both copolymers, clear morphology changes are observed as a function of the spreading concentration. Both samples show a mixture of dots and spaghetti from 1.0 mg/mL spreading (Figure 6a,b), with longer spaghetti and fewer dots observed for the 141k sample than for the 185k sample. The mean widths of dots and spaghetti for the two copolymers are the same within error (Table 2), although the 185k sample forms dots and spaghetti that are somewhat taller (20 and 15 nm, respectively) than those formed from the 141k sample (16 and 12 nm, respectively), consistent with a somewhat taller brush from the longer PS blocks in the 185k copolymer. As described in our earlier paper, a decrease in the spreading concentration of the 141k sample results in a progress from spaghetti (Figure 6a), to “budding spaghetti” (Figure 6b) with dimples at the ends and depressions along the length of the aggregates, to a predominance of interesting rings and chainlike aggregates (Figure 6c). In contrast, for the 185k sample, decreasing the spreading concentration results in an increase in the number of dots relative to spaghetti, with transition structures (Figure 6f, inset) indicating that dots are formed by pinching from spaghetti aggregates. In addition, as the spreading concentration decreases, the 185k sample shows a dramatic increase in the number of structures classified as small irregular aggregates (Figure 6d,f), with lateral dimensions significantly smaller than dots (<125 nm) and irregular, noncircular topologies. Unlike the 141k sample, no rings or chainlike aggregates were observed from the 185k copolymer for any of the spreading concentrations studied.

These AFM data from different spreading concentrations indicate that varying degrees of PS chain entanglement, resulting in different copolymer mobilities in the spreading solvent, can significantly influence the aggregate morphologies. The dependence of chain entanglements on the observed surface aggregates strongly suggests that they are nonequilibrium structures, kinetically trapped at different stages of morphology evolution upon solvent removal; this sharply contrasts the situation of block copolymer micelles in solution where a thermodynamic balance of interfacial energy and chain stretching determines the aggregate size and morphology.53–49 AFM images obtained for higher spreading concentrations, where chain mobilities are more restricted before freezing, can therefore be regarded as earlier snapshots in the evolution of aggregate morphology. From the predominance of spaghetti aggregates at higher concentrations for both the 141k and 185k copolymers, along with the observed transition morphologies at lower concentrations, it can be concluded that spaghetti forms at a relatively early stage of self-assembly for both copolymers, and then evolves by different pathways in a manner that depends on the composition. Since isotherm data and the resulting chain-packing model (Figure 3) suggest that changes in copolymer packing are driven by an increase in interfacial PEO adsorption underneath the aggregates, this same driving force should play an important role in directing the evolution of spaghetti aggregates into the various observed morphologies. In the 141k system, the development of dimples (budding spaghetti, Figure 6c) and then holes along the length of spaghetti (chainlike aggregates, Figure 6e) should allow PEO blocks trapped underneath the aggregates to become adsorbed. In the 185k system, the pinching of dots from spaghetti will increase the contact line of the aggregates at the air—water interface, also allowing submerged PEO to become adsorbed. Another driving force for the pinching of dots from spaghetti will be provided by a more favorable PS surface-to-volume ratio, similar to the development of a Rayleigh instability in a liquid ribbon.31 The different pathways for the two copolymers may be explained by the more hydrophobic character of the 141k sample, which results in slower chain dynamics upon spreading compared to the more hydrophilic 185k copolymer; on the basis of this argument, it is possible that the formation of budding spaghetti and then chainlike aggregates (141k copolymer) requires less lateral movement of chains than the pinching of dots from spaghetti (185k copolymer).

An important feature of the copolymer packing model in Figure 3 that cannot be confirmed by isotherm measurements is the relative heights of the aggregates from high and low spreading concentrations. For concentrated spreading, where the average packing of copolymers in the cores is found to be relatively dense, the aggregates should be, on average, higher than when the spreading concentration is more dilute, where the average packing of copolymers in the cores is found to be relatively sparse. The relative occurrence and heights (Table 2) of the features observed by AFM from high and low spreading concentrations of both copolymers appear to support this conclusion. For the 141k copolymer, the rings and chainlike features formed at low spreading concentrations are significantly lower (10 nm) than the dots and spaghetti formed at higher spreading concentrations (16 and 12 nm) and are closer to the expected height of an individual collapsed PS coil from the Kumaki area (8 nm).50 For the 185k copolymer, dots, spaghetti, and small irregular aggregates are observed at all spreading concentrations, although the occurrence of small irregular aggregates increases significantly as the spreading concentration decreases (Figure 6d,f); these irregular aggregates are much lower (10 nm) than the corresponding dots and spaghetti (20 and 15 nm), further

supporting the conclusion from isotherm data that the average density of chain packing decreases with the spreading concentration.

Mechanism of the Formation of PS-b-PEO Surface Aggregates: Dewetting-Induced Self-Assembly at the Air–Water Interface. The results discussed in previous sections demonstrate that, for both 141k and 185k block copolymers, spaghetti aggregates appear to be a common starting point from which a number of other surface aggregates evolve (dots, chainlike aggregates, rings, and small irregular aggregates). However, this conclusion gives rise to the question, How do spaghetti aggregates initially form? Long surface aggregates with high aspect ratios (termed spaghetti, rods, worms, or strands in various references) are often regarded as 2D counterparts to 3D rodlike block copolymer micelles, which form under conditions of a dynamic equilibrium between single chains and a thermodynamically optimum morphology. However, the observed spreading concentration dependence of surface behavior and aggregate morphology reported here makes a strong case that spaghetti aggregates, unlike 3D block copolymer cylindrical micelles, are frozen rather than equilibrium structures. In this section, we consider compelling evidence that dewetting of evaporating copolymer solutions from the air–water interface initiates self-assembly and the formation of the various aggregate morphologies.

The conditions and mechanism for the dewetting of liquid polymer films from surfaces have been widely studied in recent years. The stability of a thin (∼1 μm) liquid film on a surface is governed by a combination of long-range and short-range intermolecular forces. Under conditions where long-range van der Waals interactions predominate, the tendency of a thin film to undergo dewetting is determined by the sign of the effective Hamaker constant, $A = A_{\text{LL}} - A_{\text{SL}}$, where $A_{\text{LL}}$ is the Hamaker constant for liquid–liquid interactions within the film and $A_{\text{SL}}$ is the Hamaker constant for substrate–liquid interactions. If $A$ is positive, then cohesive interactions within the film are stronger than interactions between the film and the substrate, and the film will dewet below a critical thickness to minimize contact with the substrate. Film rupture results in the formation of holes throughout the unstable or metastable film, via either spinodal decomposition or nucleation by local defects or impurities; the holes then expand as material flows from wet regions into raised rims surrounding the growing holes. Advancing rims eventually come into contact, forming a polygon pattern of interconnected liquid ribbons that finally breaks down into droplets via a Rayleigh instability.

Figure 7 shows AFM images of LB films of the 141k copolymer obtained from a spreading concentration of 2.0 mg/mL, which is twice as concentrated as the spreading solution from which the spaghetti aggregates in Figure 6a were prepared. The large number of chain entanglements present in this solution gives rise to an even earlier snapshot of the self-assembly process, which shows a large number of long and interconnected spaghetti aggregates, in addition to cellular networks of holes in relatively low continent-like regions. These networks of polygonal holes are strongly reminiscent of patterns formed in the intermediate stages of dewetting of thin polystyrene films from solid surfaces, and provide evidence that the evaporating film of copolymer solution underwent dewetting from the air–water interface before vitrification. Moreover, the coexistence of spaghetti aggregates with the apparent dewetting patterns, along with various intermediate structures, suggests that spaghetti evolves from the networks of merging rims formed by hole formation and growth.

Figure 8 shows close-up images of transition structures in different regions of the 141k LB film from a 2.0 mg/mL spreading concentration, representing various stages of the formation of spaghetti aggregates. Investigation of the various structures within this film suggest a series of kinetic snapshots in which the earliest structures are networks of holes in a continuous film (Figure 8a, i) with holes surrounded by raised rims (Figure 8a, ii). The pattern in Figure 8a is very consistent with the intermediate stages of liquid film dewetting described by Reiter, showing regions where advancing rims are about to come into contact (Figure 8a, ii), along with strands formed by the merging of two rims (Figure 8a, iii). As described for other dewetting films, the developing network consists of polygonal holes with vertexes connecting three edges. Another transition structure (Figure 8b) shows a region where a portion of the resulting network of rims has broken into large chains (on a larger length scale than the chains observed for the same sample at low spreading concentrations), with buds of accumulated material on the chains arising from the breaks in connectivity (Figure 8b, iv). Other regions indicate that the large chains then break at junction points to form spaghetti, with sharp bends in the spaghetti (Figure 8c, v), suggesting their former connectivity within the large chains. This evolution of spaghetti aggregates from a network of rims arising from a dewetting process is supported by a topographic line profile revealing that the heights (∼12 nm) and widths (∼150 nm) of the walls of a “broken” network and the neighboring spaghetti are nearly identical. As well, the height and width of spaghetti aggregates from this higher spreading concentration (2.0 mg/mL) of the 141k copolymer are completely consistent.
with spaghetti aggregates observed for the same copolymer under more dilute spreading (e.g., Figure 6a). Contrasting the 141k copolymer, the 185k copolymer did not reveal dewetting patterns even at the highest investigated spreading concentration of 2.0 mg/mL, which resulted in a mixture of mainly spaghetti with some dots (not shown). This is explained by faster chain dynamics during spreading of the more hydrophilic polymer, with a larger PEO content resulting in a stronger driving force for aggregate evolution against the restrictions of PS entanglements. However, considering the similarities of spaghetti aggregates observed for the two copolymers, it is reasonable to conclude that spaghetti within the 185k films also formed via a dewetting process, although the early dewetting patterns could not be trapped on the time scale of solvent evaporation under the spreading conditions investigated.

The various kinetic snapshots provided by AFM and isotherm data at different spreading concentrations therefore suggest a mechanism for interfacial PS-b-PEO self-assembly (Figure 9). Immediately following deposition of the spreading solution on water, a continuous film of the copolymer solution forms at the air-water interface, stabilized by the positive spreading coefficient of chloroform on water. Within the film, PEO blocks (dark blue) will orient toward the water surface as chloroform evaporation occurs, resulting in the formation of a continuous monolayer of diblock copolymer, with the PS blocks (red) highly swollen with chloroform (Figure 9a). With further evaporation of chloroform, increasing contributions from unfavorable PS-water interactions eventually result in film dewetting and hole formation in various regions of the film (Figure 9b,c). As the holes expand, the monolayer material is pushed from the continuous wet regions into rims surrounding the holes, where the copolymer chains become more densely packed and brushlike as a result of the local lateral flow fields (Figure 9b). PEObeneath the rims is forced into the subphase by the local dense packing of PS blocks arising from the dewetting flow. The growth of holes will continue until the advancing rims merge to form a 2D network of merged rims (Figure 9d), with an internal structure best described by a densely packed brush of copolymer chains, once most of the chloroform has evaporated (Figure 9e). In most examples of dewetting of liquid films from solid substrates, the liquid ribbons that form from contact between advancing rims undergo immediate breakup into droplets via a Rayleigh instability, in a process driven by the surface tension of the liquid.23,24,31 In contrast, the evolution of the 2D network formed by dewetting of copolymer solutions from the water surface appears to follow a different path, with the network breaking at various junctions to form long spaghetti aggregates (Figure 9f), which then further evolve into chainlike aggregates (141k copolymer) or dots (185k copolymer) (Figure 9g). We point out that, although PS surface tension will be an important factor in the evolution of aggregates following the dewetting stage, our isotherm results suggest that increased adsorption of PEO chains trapped underneath the aggregates provides an additional driving force for aggregate evolution. Material flow toward the rims during dewetting can explain the initial dense packing of copolymer chains within the spaghetti aggregates and the resulting desorption of PEO chains under the aggregate cores. Thus, subsequent PEO adsorption, along with kinetic restrictions of PS entanglements, may account for the unique
structures formed via PS-\(b\)-PEO self-assembly at the air—water interface compared to the patterns of droplets formed in more conventional dewetting processes of single-component liquids.\(^{23,24,31}\)

This dewetting mechanism for surface aggregate formation within PS-\(b\)-PEO monolayers also explains the observation of large continent structures previously observed in PS-\(b\)-PEO monolayers.\(^{10,13,19}\) From the discussion above, we propose that continents are simply extended regions of the original continuous film, which become frozen by solvent evaporation before undergoing dewetting or before being subsumed by an advancing rim. In fact, although we did not observe large continents from either of our samples at any of the studied spreading concentrations, the flat regions between rims in Figure 8a suggest smaller versions of the continents shown by Devereaux et al.,\(^{13}\) consisting of relatively low, flat aggregates surrounded by raised rims.

To our knowledge, only one previous paper has suggested dewetting as a mechanism for block copolymer aggregate formation at the air—water interface to explain the formation of 2D nanofoams from polystyrene-\(b\)-poly(sodium acrylate) block copolymers.\(^{5}\) Here we have shown evidence that dewetting appears to be the critical first step in the formation of a wide range of more common surface aggregates from self-assembly PS-\(b\)-PEO copolymers, including continents, spaghetti, and dots. Of course, dewetting as a mechanism for aggregate formation can only explain structures that form during solution spreading/evaporation, and cannot therefore account for features which have been recently observed to form at elevated surface pressures upon compression of PS-\(b\)-PEO starlike copolymers, that is, “micelle chaining”.\(^{21}\)

A key question arising from this investigation is, How general is the proposed dewetting mechanism for block copolymer self-assembly at the air—water interface? The main hurdle to answering this question by the current methodology is that, to trap the initial dewetting step by solvent evaporation, extremely slow chain dynamics are required. For the two copolymers investigated, both possess long PS blocks and therefore significant chain entanglements, and yet only the 141k copolymer showed trapped dewetting patterns and transitional structures at high concentrations, presumably due to its lower PEO content and slower spreading dynamics compared to the 185k copolymer. However, the similarity of spaghetti aggregates formed from both copolymers suggests a similar mechanism of formation. These two copolymers therefore highlight the possibility that the mechanism may be quite general, although its initial stages can only be observed ex situ via kinetic trapping, which, for normal rates of chloroform evaporation, requires a combination of long PS blocks and sufficiently low PEO content. Increasing the rate of solvent evaporation (e.g., by elevating the subphase temperature) may provide one avenue by which dewetting structures could be trapped for a wider range of copolymers, thus providing some insight into the generality of the mechanism.

**Concluding Remarks**

The apparent role of dewetting in the formation of PS-\(b\)-PEO surface aggregates emphasizes fundamental differences between diblock copolymer self-assembly in aqueous solutions (3D) and at the air—water interface (2D). While 3D block copolymer micelle morphologies represent, for the most part, equilibrium structures with minimum free energy, the 2D features described here and elsewhere appear to be frozen at various stages of a nonequilibrium process starting with a dewetting stage which seeks to minimize contact between an evaporating copolymer solution and the water surface. In fact, it appears that, for block copolymers exhibiting a variety of aggregate morphologies at the air—water interface, the resemblance with 3D structures formed from self-assembly in solution or in the bulk may be coincidental and not reflective of analogous formation mechanisms operating in two and three dimensions. It appears to be problematic, for example, to meaningfully compare the 2D spaghetti aggregates observed here with 3D cylindrical micelles formed from PS-\(b\)-PEO block copolymers in aqueous media—the former structures arising from the nonequilibrium convergence of rims in a dewetting film, and the latter structures representing an optimization of curvature and interfacial tension under equilibrium conditions. This insight into the role of dewetting in block copolymer self-assembly at the air—water interface should provide new understanding of surface aggregate formation in various systems, along with potentially new strategies of controlled patterning for specific applications.

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**Supporting Information Available:** Plots of hysteresis in the brush (\(\Delta k_{0,b}\)) and pancake (\(\Delta k_{0,p}\)) regimes for multiple compression/expansion cycles of the 185k copolymer at different spreading concentrations. AFM images of the 185k copolymer at constant spreading concentration (\(c = 0.50 \text{ mg/mL}\)) and various transfer pressures (\(\pi = 5.0, 10.0, \text{ and } 20.0 \text{ mN/m}\)). This material is available free of charge via the Internet at http://pubs.acs.org.

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