Self-assembly of an ultra-high-molecular-weight comb block copolymer at the air–water interface

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The self-assembly of a newly synthesized, amphiphilic comb block copolymer (CBCP) at the air–water interface was systematically explored using the Langmuir–Blodgett (LB) technique. The CBCP had an ultra-high molecular weight (\(M_n = 510 \times 10^3\) g mol\(^{-1}\)) with polystyrene arms grafted along one block of long hydrophilic backbone. At the air–water interface, the CBCP molecules spontaneously assembled into ribbon-like structures and cellular patterns at zero surface pressure when a volatile solvent (i.e., chloroform) and a less volatile solvent (i.e., toluene) were used, respectively. This spontaneous self-assembly behavior of the CBCP was induced by the dewetting process. The mechanism for the morphological change as a function of surface pressure was scrutinized and further confirmed by compression–expansion cycle and solvent vapor annealing studies. To the best of our knowledge, this is the first study of self-assembly of ultra-high-molecular-weight, amphiphilic CBCPs at the air–water interface. As such, it provides insight into the design of controllable pattern formation using amphiphilic copolymers.

Introduction

Because of their broad range of potential applications in microlithography,\(^1\) devices,\(^2\) and biomimetic thin films,\(^3\) controlled patterning of amphiphilic copolymers at the air–water interface is attracting considerable attention. Upon deposition of amphiphilic copolymers on the water surface, the unfavorable interfacial interaction between the hydrophobic block and the water leads to the aggregation of hydrophobic blocks, forming different morphologies to reduce the overall free energy of the system. On the other hand, the hydrophilic block tends to adsorb on the water surface, forming starfish-like structures for amphiphilic copolymers.\(^4,6\) To date, a variety of amphiphilic copolymers at the air–water interface, including linear block copolymers,\(^1,4,5,7,8\) star copolymers,\(^8–13\) and dendritic polymers,\(^1,4,7,14–16\) have been investigated, and a wide range of morphologies, for example dots,\(^6,13,15,17\) spaghetti,\(^6,16,18\) ribbons,\(^1,15,16,19\) islands,\(^13,15,16\) and continents,\(^1,18\) were observed. These surface features were heavily dependent upon a number of parameters, including the polymer structure, surface pressure, and temperature,\(^1,4,5,7,19\) and have been extensively studied. However, due to the limited size and amorphous nature of these copolymers, it is often challenging to determine the microstructure of aggregates and their initial self-assembly process at zero surface pressure, which is critical for designing or predicting controllable patterns of newly synthesized polymers. Unlike the familiar self-assembly process of block copolymers in three dimensions under equilibrium conditions, amphiphilic copolymers at the air–water interface are kinetically trapped in their ‘frozen state’ after solvent removal,\(^1,18\) dictated by the chain entanglement between hydrophobic blocks in the spreading solution.\(^1,18\)

Recently, an ultra-high-molecular-weight, amphiphilic comb block copolymer (CBCP) with a degree of polymerization along the backbone exceeding 1100 units was successfully synthesized [Fig. 1(a)].\(^20,21\) The block with polystyrene arms assumed a rigid rod shape due to steric crowding between the arms, resulting in elongation of the backbone polymer in that block [Fig. 1(b)].\(^21\) The large molecular size and well-defined molecular structure make this CBCP an excellent candidate to study the microstructure of aggregates and their formation mechanism. In this paper, the self-assembly process of this newly synthesized CBCP is presented. The morphological changes influenced by the surface pressure, the assembly time, and the spreading solvent were systematically explored. The mechanism for surface-pressure-induced morphological changes was explored and further confirmed by compression–expansion cycle and solvent annealing studies.

Experimental

Previously synthesized CBCP with an ultra-high molecular weight of 510 kg mol\(^{-1}\) was utilized in the present study.\(^20,21\) The

Fig. 1 (a) Chemical structure, and (b) schematic representation of the newly synthesized CBCP, which can be viewed as a triblock polymer. Each block is labeled as A (within a thick dotted circle), B (within a thin dotted circle), or C, respectively.
dimensions of the CBCP were estimated from molecular models
by performing energy minimization using Material Studio 4.1.
Chloroform (99.9%), toluene (99.8%), and carbon disulfide
(99.8%) were purchased from Fisher Chemicals and used without
further purification. CBCP solutions in chloroform and toluene
at a concentration $c = 6.29 \mu M$ were prepared. Surface
pressure–area ($\pi$–$A$) isotherms and polymer monolayers were
obtained with a R&K Langmuir–Blodgett (LB) system (Riegler
& Kirsten, GmbH, 160 cm$^2$ Teflon trough). The trough was
carefully cleaned with $1 : 1$ H$_2$O$_2$:NH$_3$OH solution overnight and
subsequently rinsed with DI water (NanoPure, > 18 M$\Omega$ cm) 5
times. A 5 $\mu$L aliquot of the CBCP in chloroform or in toluene
was gently placed on the water surface to ensure initial gas
state.\textsuperscript{11} After allowing the solvent to evaporate for 30 min, the
monolayer film was compressed at a rate of 150 $\mu$m s$^{-1}$.

The Si substrates used for depositing LB films were cleaned
with a mixture of sulfuric acid and Nonchromix, followed by
rinsing with DI water and blown dry with N$_2$. For LB deposi-
tions, the Si substrate was withdrawn at a rate of 35 $\mu$m s$^{-1}$
while keeping the pressure constant. Solvent vapor annealing
was performed by placing the deposited film onto an elevated plat-
form in a sealed container with approximately 10 mL of solvent
in the reservoir.

The morphologies of the LB films were examined by atomic
force microscopy (AFM; Dimension 3000) in tapping mode. The
scanning rate was 2 Hz. Each sample was imaged at more than 5
locations to ensure the reproducibility of features observed. The
average height and surface coverage of the LB films were
obtained by performing the bearing analysis.

**Results and discussion**

The chemical structure of the CBCP is depicted in Fig. 1(a). It
can be regarded as a triblock copolymer with one hydrophobic
PS block as the arm (i.e., C block) and two hydrophilic blocks in
the backbone (i.e., short A block and long B block with very
short alkyl side-chains).

**Effect of surface pressure**

A Langmuir isotherm, i.e., surface pressure vs. area ($\pi$–$A$) plot,
of the CBCP is shown in Fig. 2. The continuous pressure rise was
indicative of the formation of a LB monolayer. The entire
isotherm can be divided into four regions; the (i) gas state at
$\pi = 0$, (ii) extended liquid state, (iii) plateau region at $\pi = 22$ mN
m$^{-1}$, and (iv) condensed-state region. Similar isotherms were
observed for both the chloroform solution and the toluene
solution, suggesting that the solvent had no effect on the
monolayer formation (Fig. 2). Representative AFM height
images of LB monolayers obtained from the four regions are
shown in Fig. 3. Table 1 summarizes the height of self-assembled
structures and the resulting surface coverage.

**Region (i) gas state ($\pi = 0$).** Ribbon-like structures with
a broad size distribution were observed at the surface pressure
$\pi = 0$ [Fig. 3(a)]. The height of the ribbons was about 4.36 nm.
These ribbons represented aggregates of the raised PS chains
[i.e., C block in Fig. 1(a)] due to the hydrophobic characteristics
of PS.\textsuperscript{17,18} Since pressure has not yet been applied to the CBCP,
the aggregation of PS blocks was a direct consequence of the
spontaneous self-assembly of PS chains. The driving force for the self-
assembly was an interplay of the attractive interaction
between hydrophilic chains (i.e., B blocks) and the water phase,
and the repulsive interactions between PS chains and water as
well as between PS chains and hydrophilic chains as the chlo-
roform evaporated.\textsuperscript{6,22} With no surface pressure applied, the self-
assembled ribbons were highly dispersed as shown in Fig. 3(a).

![Pressure–area isotherms of the LB monolayer of the CBCP obtained from the chloroform solution (solid line) and the toluene solution (dash line), respectively. The four regions are labeled as (i) gas state, (ii) extended liquid state, (iii) plateau region, and (iv) condensed-state region. $A_b$ and $A_p$ are the area of brush-like structures and the area of pancake-like structures, respectively.](Image)

![AFM height images of the CBCP LB monolayers obtained from the four chloroform at various transfer pressures: (a) $\pi = 0$, (b) $\pi = 10$ mN m$^{-1}$, (c) $\pi = 22$ mN m$^{-1}$, and (d) $\pi = 45$ mN m$^{-1}$. Chloroform was allowed to evaporate for 30 min before the LB deposition. Scan size $= 10 \times 10$ $\mu$m and z-scale $= 30$ nm for all images. Scan size $= 3 \times 3$ $\mu$m for the inset in (c).](Image)
Region (ii) extended liquid state region (\( \pi = 0 \sim 22 \text{ mN m}^{-1} \)). A typical AFM height image of a LB film deposited at surface pressure \( \pi = 10 \text{ mN m}^{-1} \) is shown in Fig. 3(b). Compared with the sample obtained at \( \pi = 0 \), the ribbon length dramatically increased. However, the average width and height of the ribbons did not change within the error limit (Table 1; i.e., \( h = 4.47 \text{ nm} \) at \( \pi = 10 \text{ mN m}^{-1} \) vs. \( h = 4.36 \text{ nm} \) at \( \pi = 0 \)). At \( \pi = 10 \text{ mN m}^{-1} \), the ribbons were still separated from each other, indicating that the hydrophilic chains (i.e. B blocks) formed a corona around the ribbons (i.e., aggregates of PS blocks) as schematically illustrated in Fig. 4(a),7 and the elastic repulsive force between the hydrophilic corona distanced PS ribbons.10 The scratch tests showed no height difference between the inter-ribbon area, occupied by the hydrophilic corona and the Si substrate. Similar to other typical amphiphilic block copolymers,5,6 the CBCP exhibited a so-called pancake-like structure with hydrophilic B blocks adsorbed on the water surface [Fig. 4(a)]. The pancake surface area \( A_p \) was 795 nm\(^2\), determined by extrapolating the initial pressure rise from 0 to 22 mN m\(^{-1}\) (Fig. 2); the large \( A_p \) was consistent with the ultra-high-molecular-weight nature of the CBCP.

Region (iii) plateau region (\( \pi = 22 \text{ mN m}^{-1} \)). The plateau at surface pressure \( \pi = 22 \text{ mN m}^{-1} \) can be attributed to a ‘pancake-to-brush’ transition (i.e., a first-order phase transition)7 as the hydrophilic B chains desorbed from the water surface and submerged into the water subphase upon further compression, forming a brush-like structure [Fig. 4(b)].10 While the shape of PS ribbons was retained, the ribbons coalesced side-by-side, as shown in the inset of Fig. 3(c). This led to an increase in the height of the ribbons, yielding \( h = 5.57 \text{ nm} \) (Table 1).

Region (iv) condensed-state region (\( \pi > 22 \text{ mN m}^{-1} \)). Continued compression of the CBCP led it to the condensed state. The hydrophilic B blocks completely submerged into the water subphase and the hydrophobic PS chains remained on the water surface. The incompressible PS chains further overlapped and the surface pressure increased dramatically as a result of compression. A representative AFM height image obtained at \( \pi = 45 \text{ mN m}^{-1} \) is shown in Fig. 3(d). The ribbon-like structures disappeared; surface morphology was dominated by island-like domains. The average domain height markedly increased, yielding \( h = 10.45 \text{ nm} \) (Table 1).

Effects of assembly time and solvent at zero surface pressure

The spontaneous self-assembly of the CBCP at \( \pi = 0 \) for longer times was investigated. After being placed on the water surface, the CBCP solution was allowed to evaporate for 2 h, rather than 30 min as described above (Fig. 3). Fig. 5(a) shows a typical AFM height image of the resulting LB film after the evaporation of chloroform for 2 h. In comparison with the surface morphology assembled after 30 min [Fig. 3(a)], the longer assembly time led to a substantial elongation of the ribbons [Fig. 5(a)]; the surface coverage of ribbons increased from 24% to 30% (Table 1). The ribbon width, however, remained constant within the error limit, suggesting that more CBCP molecules diffused to the tip of the ribbons to enable growth into longer ribbons. The diffusion of free CBCP molecules was enabled by the trapped solvent around the ribbons. The sample after an even longer evaporation time (i.e., 3 h) was also measured; notably, no further increase in the ribbon length was observed. The growth of ribbons was locked after complete solvent evaporation (i.e., 2 h). The morphological change [comparing Fig. 3(a) with Fig. 5(a)] signified that the aggregation (i.e., self-assembly) of polymers at the air–water interface for a short period of time was not in its equilibrium state but rather represented a kinetically trapped situation.17

The solvent was found to exert a profound influence on the self-assembly of the CBCP at \( \pi = 0 \). Chloroform is a highly volatile solvent with the boiling point, bpt = 61.2 °C, thus the CBCP had a much shorter time to self-assemble before being

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**Table 1** Height and surface coverage of the CBCP ribbons obtained from AFM images

<table>
<thead>
<tr>
<th>Pressure/mN m(^{-1})</th>
<th>Time/h</th>
<th>Height, h/(\text{nm})</th>
<th>Surface Coverage (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chloroform solution</td>
<td>(\pi = 0)</td>
<td>4.36</td>
<td>24</td>
</tr>
<tr>
<td></td>
<td>(\pi = 10)</td>
<td>4.47</td>
<td>30.7</td>
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<tr>
<td></td>
<td>(\pi = 20)</td>
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<td>31.5</td>
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<td></td>
<td>(\pi = 22)</td>
<td>5.57</td>
<td>55.1</td>
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<td></td>
<td>(\pi = 45)</td>
<td>10.45</td>
<td>43.3</td>
</tr>
<tr>
<td>Toluene solution</td>
<td>(\pi = 0)</td>
<td>5.54</td>
<td>30</td>
</tr>
<tr>
<td></td>
<td>(\pi = 20)</td>
<td>4.44</td>
<td>21.4</td>
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<tr>
<td></td>
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<td>40.5</td>
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<tr>
<td></td>
<td>(\pi = 20)</td>
<td>13.57</td>
<td>54</td>
</tr>
<tr>
<td>CS(_2) annealing</td>
<td>(\pi = 0)</td>
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<td>93.1</td>
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<td>Methanol annealing</td>
<td>(\pi = 0)</td>
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<td></td>
<td>(\pi = 20)</td>
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<td>(\pi = 20)</td>
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**Fig. 4** Schematic illustration of the packing of microstructures at different surface pressures. (a) in the low-pressure region (i.e., between region (i) and region (ii); Fig. 2), where two ribbons were yielded; (b) in the plateau region (i.e., region (iii); Fig. 2); and (c) in the condensed-state region (i.e., region (iv); Fig. 2). B block (see Fig. 1) = hydrophilic block, and C block (see Fig. 1) = PS block (i.e., arms).

**Fig. 5** AFM height images of the CBCP LB monolayers obtained after solvent evaporation for 2 h. (a) from chloroform solution, and (b) from toluene solution. The deposition pressure, \(\pi = 0\). Scan size = 10 × 10 \(\mu\text{m}\) and z-scale = 30 \text{ nm} for both images.
kinetically trapped in its ‘frozen state’ upon complete solvent evaporation. In contrast, toluene is a less volatile solvent with bpt = 110.6 °C. Therefore, compared to the CBCP chloroform solution, when toluene was used as the spreading solvent, it was possible to achieve a state that was relatively close to the final equilibrium state by providing the CBCP molecules with a longer time to self-assemble, yielding a cellular pattern [i.e., interconnected network structures; Fig. 5(b)] composed of ribbons of the same width and height as those shown in Fig. 5(a).

We now turn our attention to further illustrating the mechanism for the formation of dispersed ribbons at zero applied surface pressure and the mechanism for morphological change as a function of surface pressure as follows.

**Mechanism for self-assembly at \( \pi = 0 \)**

Ribbon-like structures have been observed in LB depositions of amphiphilic copolymers, for example, in the arborescent graft copolymer polystyrene-g-poly(ethylene oxide) (PS-g-PEO in which PS and PEO were the core and the shell, respectively). They were formed by the pressure-induced association of these dendritic molecules. The formation of ribbons was reversible; upon the release of pressure, the ribbons dissociated into dendritic graft copolymers. In stark contrast, the ribbons produced from the CBCP were inherently stable structures: they yielded at \( \pi = 0 \) and can grow with time at that pressure [Fig. 5(a)] or at higher pressure [Fig. 3(a)–(c)]. Steric crowding between the hydrophobic PS blocks caused the hydrophilic A block to stretch [Fig. 1(b) and Fig. 4(a)]. As a result, the A chain appeared as a rigid rod. The length of the rigid A block was about 53.6 nm, estimated using Material Studio.

As depicted in Fig. 4(a), two of the CBCP molecules aggregated head-to-head to yield a pair (i.e., B blocks on the top and the bottom with C blocks in the middle). Then this polymeric pair assembled side-by-side with adjacent pairs to form a long ribbon [for example, ribbon 1 in Fig. 4(a)]. The long hydrophilic B chains were adsorbed on the water surface because when the film was transferred onto the Si substrate, the ribbon height from roughly 4.5 nm to 5.57 nm. This is because when the film was transferred onto the Si substrate, the hydrophilic chains in the water subphase were trapped between the PS chains and the Si substrate. As a result, the PS ribbons were situated on a layer of hydrophilic B blocks, giving rise to a larger height.

When the surface pressure was larger than 22 mN m\(^{-1}\), the hydrophilic chains were completely submerged in the water, leading to a dramatic increase in height from 5.57 nm to 10.45 nm (Table 1). Because no repulsive forces caused by hydrophilic chains were present, the PS chains could aggregate in any direction. Thus, an island-like morphology formed [Fig. 5(d)].

In order to verify the above proposed model for the surface-pressure-induced morphological evolution, compression–expansion cycle and solvent annealing studies were performed. Hysteresis effects have been proven to be very informative in
elucidating the dynamic behavior of amphiphilic polymers under different surface pressures. Before the plateau region (curve a in Fig. 6), a small hysteresis was observed, which may be caused by the rearrangement or overlap of hydrophilic chains on the water surface. The hysteresis in the plateau region was due to the desorption of hydrophilic chains from the water surface (i.e., partial submergence into the water subphase), and upon the release of surface pressure, these chains must overcome the energy barrier to become adsorbed again on the water surface (curve b in Fig. 6). After the release of surface pressure at \( \pi = 24 \text{ mN m}^{-1} \) in the condensed-state region, the pressure dramatically decreased to a minimum of 18 mN m\(^{-1}\) at the surface area of 240 nm\(^2\)/molecule and then increased again to form the hysteresis (curve c in Fig. 6). This may be due to the entanglement of hydrophilic B blocks in the brush-like structure [Fig. 4(c)]. Similar phenomena have been observed for a PS-\(b\)-PEO diblock copolymer.

**Effect of solvent vapor annealing on the morphology of the CBCP**

Selected solvents were used in the solvent vapor annealing of the deposited CBCP films. Specially, carbon disulfide (CS\(_2\)) and methanol were utilized to selectively swell the hydrophobic PS block and the hydrophilic blocks in the CBCP, respectively. Four LB films obtained at \( \pi = 20 \text{ mN m}^{-1} \) were annealed in CS\(_2\) and methanol vapors for 2 h and 7 h, respectively. The typical morphologies after annealing are shown in Fig. 7. Comparing the sample before annealing with one annealed in CS\(_2\) vapor, the height of ribbons remained unchanged (Table 1) and the morphology did not change perceivably. However, the surface coverage of ribbons increased to 40.5% (Table 1), resulting from the swelling of PS blocks laterally by CS\(_2\). For the annealing by methanol vapor, however, the morphology profoundly changed. The height of the ribbons increased dramatically from roughly 4.5 nm to 13.57 nm after annealing for 2 h. It further increased to 17.54 nm after annealed for 7 h. The methanol vapor annealing greatly enhanced the mobility of ribbons on the Si substrate by promoting the mobility of the hydrophilic A and C blocks which were anchored to the Si substrate for the LB film deposited at \( \pi = 20 \text{ mN m}^{-1} \). Additionally, upon methanol vapor annealing, the unfavorable interfacial interaction between the hydrophobic PS blocks and the hydrophilic Si substrate may drive the hydrophilic chains under the PS ribbons. This would form a continuous layer of hydrophilic chains between the PS blocks and the Si substrate and explain the large increase in the ribbon height. Taken together, the ribbons were dragged closer to one another, yielding a densely packed morphology. As a consequence, the surface coverage of ribbons markedly increased from 31.5% to 54% after 2 h and to 93.1% after 7 h methanol vapor annealing. Since methanol is non-solvent for PS, the shape of PS was not changed.

**Conclusions**

In summary, we have systematically explored the self-assembly of a newly synthesized amphiphilic CBCP at the air–water interface. The CBCP spontaneously assembled into ribbon-like structures on the water surface at zero surface pressure. Combining the Materials Studio modeling with the assembly time effect study, a possible model was proposed to illustrate the formation of ribbons. The dewetting process was found to play a key role in initiating the self-assembly process and leading to the formation of the dispersed ribbons. The morphological change of the LB films induced by the surface pressure was also scrutinized and was caused by the desorption of hydrophilic blocks on the water surface. This mechanism was supported by the compression–expansion cycle and the solvent vapor annealing experiments. The present study provides insight into the design of controllable pattern formation using amphiphilic copolymers.
Acknowledgements
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