

Pressure-Induced Order Transition in Nanodot-Forming Diblock Copolymers at the Air/Water Interface

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S Supporting Information

ABSTRACT: Understanding and controlling the processes in block copolymer (BC) monolayers at the air/water interface during surface area compression is a key issue for producing ultrathin films of predetermined morphology with well-defined order and known dimensions. Langmuir isotherms of nanodot-forming BC monolayers generally display a plateau indicative of a 2D phase transition, which has been the subject of various interpretations in the literature. Here, based on investigations of Langmuir–Blodgett and Langmuir–Schaefer nanodot films of PS-P4VP mixed with 3-*n*-pentadecylphenol (PDP), we show by atomic force microscopy (AFM) that it involves a change in nanodot packing order (from quasi-hexagonal to quasi-square), argued to be a general phenomenon for nanodot BC monolayers. It is accompanied by system-specific conformational changes (as discussed in previous literature), which, in the present case, implicate PDP alkyl chain ordering, as deduced previously from *in situ* infrared data and indirectly supported here by AFM imaging.

Block copolymers (BCs) are quintessential nanostructure-forming materials thanks to their self-organizing capabilities.¹ This provides for a large variety of potential technological applications that take advantage of the different ordered morphologies produced.² To exploit these morphologies, it is essential to know and understand the factors that control them and the transitions between them. In the bulk, it is well known that the BC composition (block ratio, molecular weight, block interaction parameters) and temperature are controlling factors.¹ In thin films, typically obtained by spin-casting or dip-coating procedures, the interfacial energies with, usually, air and a solid substrate as well as the film thickness relative to the bulk periodicity are additional controlling factors.³

Ultrathin BC films that are effectively monolayer films (and which might be viewed as the equivalent of the “wetting layer”, i.e., adsorbed layer, in solid substrate-supported thin films obtained by spin- or dip-coating) are typically obtained by a single transfer from a pressure-controlled air/water interface to a solid substrate using the Langmuir–Blodgett (LB) technique. Here, surface pressure is another potential controlling parameter. Composition control of LB monolayer BCs has been shown to give rise to at least three distinct morphologies: planar, strand (elongated, rod-like), and nanodot (spherical) surface micelles in order of increasing hydrophilic block content,⁴ along with variations

attributed to kinetic effects.^{5,6} To date, there is little documentation of pressure control of morphological transitions.^{6–8} However, BCs with nanodot morphologies (in contrast to planar and strand morphologies) generally give rise to Langmuir compression isotherms featuring a plateau, first reported for alkylated polystyrene-block-poly(4-vinylpyridine) (PS-P4VP), i.e., PS-P4VP⁺R_nX⁻, where R_n refers to a linear alkyl substituent of *n* carbons on the pyridine moiety and X⁻ refers to the counterion.⁹ Such a plateau, according to the surface phase rule, is indicative of a surface pressure-induced first-order phase transition, with two phases coexisting at the plateau pressure.⁴ It should be interjected here that it is generally agreed upon that the nanodot morphology is formed of isolated nodules (micelle centers) composed of a defined number of hydrophobic blocks (light-colored dots in the images shown here) dispersed (or dewetted) on a monolayer with a thickness on the order of 1 nm and composed of the hydrophilic blocks adsorbed to the water surface.^{4,10–12} It must be emphasized that there is a single layer of nanodots in these monolayers, distinguishing them from thin films obtained by spin- or dip-coating, where three-dimensional structure must always be considered.

The isotherm plateau in nanodot-forming BCs has been the subject of several interpretations. It was initially proposed to be a transition from surface-adsorbed to subphase-solubilized hydrophilic blocks, also called the “starfish → jellyfish” transition (particularly in connection with PS-P4VP⁺R_nX⁻)⁹ or the “pancake → brush” transition [particularly in connection with polystyrene-poly(ethylene oxide) (PS-PEO)].¹³ Later, this interpretation was ruled out for PS-P4VP⁺R_nX⁻ by *in situ* (i.e., air/water interface) synchrotron X-ray and neutron reflectivity, which indicated insufficient thickening of the P4VP⁺R_nX⁻ layer with pressure (and no discontinuity) to support subphase solubilization.¹² Instead, *in situ* FTIR showed greater alkyl trans character at higher surface pressure, indicating a disorder–order change of the alkyl side chains.^{12a} The plateau transition for PS-PEO was alternatively interpreted as involving a dehydration/conformational change of surface-adsorbed PEO,¹⁴ as for PEO homopolymer.¹⁵

With the “starfish → jellyfish” transition ruled out for at least PS-P4VP⁺R_nX⁻, the process underlying the isotherm plateau appears to involve only some kind of molecular rearrangement, the type depending on the specific system. However, the lack of a unifying element in the process seems unsatisfactory, given the generality of the isotherm plateau for nanodot-forming BCs. The

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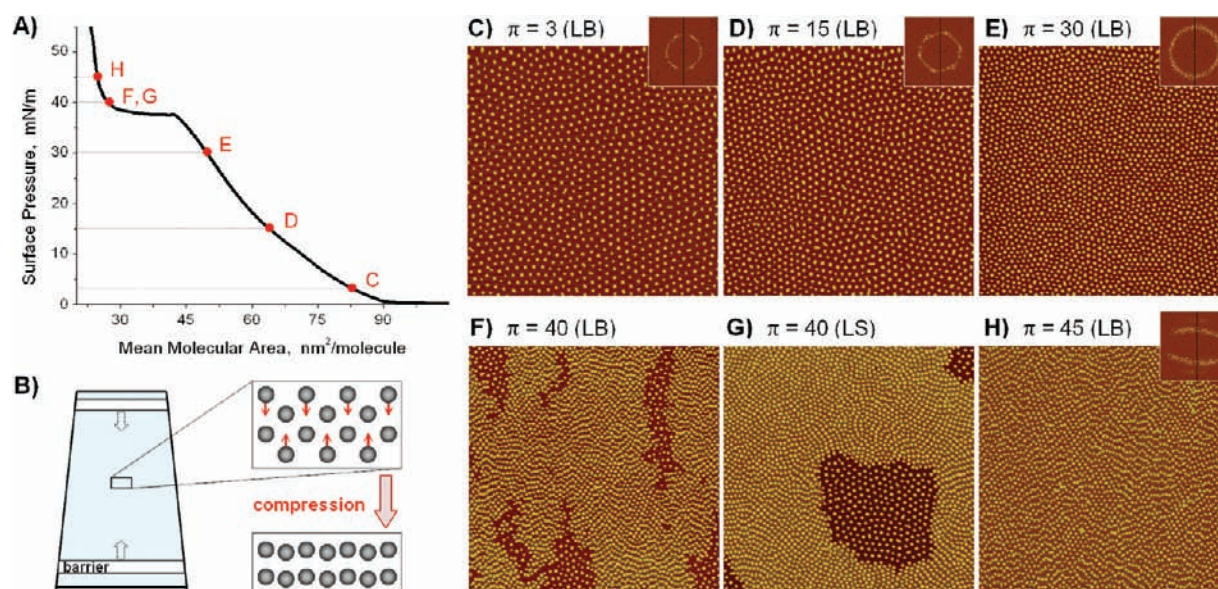


Figure 1. (A) Langmuir compression isotherm of PS-P4VP(29%)/PDP at the air/water interface. (B) Model of order–order transition as a result of barrier compression (see text for details). The image illustrates a Langmuir trough (arrows show direction of barrier compression) and the nanodot morphology below (top, with red arrows indicating dot movement upon compression) and above (bottom) the plateau pressure. (C–H) AFM height images ($5 \times 5 \mu\text{m}^2$) of Langmuir-Blodgett (LB, in C–H) and Langmuir-Schaefer (LS, in G) monolayer films transferred at the surface pressures (π) indicated. Corresponding 2D FFTs are given in the upper right corner for C–E and H. The direction of transfer (for C–F and H), coincident with the barrier compression direction (for C–H, including G), is along the Y-axis.

present Communication shows that there is, in fact, a morphological change in nanodot order (i.e., a phase change) that occurs at the plateau, and this is considered to be the general element underlying the transition. It is accompanied (necessarily) by system-specific molecular rearrangement, as discussed in previous literature.

The surface pressure-induced nanodot order transition, which is the primary point of this Communication, was discovered by atomic force microscopy (AFM) investigations of LB monolayer films of a PS-P4VP diblock copolymer [$M_n(\text{PS}) = 41\,500$, $M_n(\text{P4VP}) = 17\,500$, 29.4 mol % VP] mixed with 3-*n*-pentadecylphenol (PDP; 1:1 VP:PDP molar ratio), where PDP hydrogen-bonds to the VP moieties to form effective side chains in the P4VP block.^{6,16} This system is architecturally similar to PS-P4VP⁺R_nX⁻, but without the ionic groups and with noncovalent instead of covalent links between the alkyl side chains and P4VP main chain. Since it is known that these LB monolayers are formed from a single layer of nanodots, whether below or above the plateau (until collapse),¹² AFM is an appropriate technique to investigate their 2D order, having the necessary nanoscopic lateral resolution to access directly (with no model dependence) the positional and orientational arrangement of the nanodots and their dimensional parameters as a function of surface pressure. The long alkyl chains of PDP allowed for a secondary observation by AFM that suggests alkyl chain reorientation from prone to vertical, thus supporting the alkyl chain disorder–order change previously inferred from the above-mentioned *in situ* FTIR analysis of PS-P4VP⁺R_nX⁻.^{12a}

The compression isotherm for PS-P4VP/PDP at 21 °C is given in Figure 1A. It shows an obvious plateau at a surface pressure of $38 \text{ mN} \cdot \text{m}^{-1}$, comparable to the plateau pressures observed in nanodot-forming PS-P4VP⁺R₁₀I⁻ diblock copolymer isotherms.⁴ LB monolayers were transferred to mica at five

Table 1. Average Dimensions of the Nanodots in the PS-P4VP/PDP LB Films Transferred at Various Surface Pressures (π)

π ($\text{mN} \cdot \text{m}^{-1}$)	height (nm ± 0.5)	width (nm)	spacing (nm)
3	7.5	65 ± 5	150 ± 10^b
15	7.5	65 ± 5	130 ± 10^b
30	7.5	65 ± 10	105 ± 5^b
40	8.0, 5.0 ^a	65 ± 10	$80\text{--}120^c$
45	5.5	60 ± 5	$80\text{--}110^c$

^a Values relative to the lower and higher backgrounds, respectively.

^b Obtained from the FFTs. ^c Variable; see text for details.

different surface pressures, three below and two above the isotherm plateau (specified by red dots in Figure 1A). Characteristic topography images of the films, one for each surface pressure, are shown in Figure 1C–F,H. Films transferred below the plateau pressure have quasi-hexagonal nanodot order, as typically observed for nanodot-forming BCs,^{4,10,17} indicated also by the fast Fourier transforms (FFT) of the images of the films transferred at 3 and 15 $\text{mN} \cdot \text{m}^{-1}$. Table 1 shows that the nanodot heights and widths are little influenced by pressure; only their average spacing decreases with increasing pressure due to being pushed closer together by barrier compression, in accordance with previous work on LB nanodot films of BCs.^{4,9,12} There appears to be somewhat more disorder in the film transferred at 30 $\text{mN} \cdot \text{m}^{-1}$, as suggested by its FFT and as might be expected preceding a transition in nanodot order at a critical lateral pressure.

The images of the LB films transferred at 40 and 45 $\text{mN} \cdot \text{m}^{-1}$ (Figure 1F,H) indicate that the nanodot morphology itself is conserved; however, clearly, it no longer shows hexagonal order. The type of high-pressure order is less evident, given the

insufficient long-range positional order. On one hand, the short range of the order can be interpreted as indicative of disorder, thus implying an order–disorder transition. On the other hand, it is striking that in many places the nanodots tend to a local square lattice arrangement with dimensions of about $100(\pm 10)$ nm. In others, the local order appears more rectangular-like, describable also as well-separated rows of closely spaced nanodots (particularly in Figure 1H), where the dimensions are 70–80 nm and 110–120 nm for the short and long rectangular sides (or within and between the closely spaced rows), respectively. In these cases, the transition is one of order–order (the presence of some areas of darker-colored backgrounds in Figure 1F,G will be addressed below).

If indeed an order–order transition, the absence of long-range positional order can be rationalized as follows. (a) First, the hexagonal order at lower pressures is similarly not long-range (i.e., there are many grains and defects, with imperfections introduced also by polydispersity in nanodot size and shape, attributable to kinetic and statistical effects¹⁸), making it inevitable that imperfect long-range order is carried through to the high-pressure morphology. Two other possible causes (points b and c below) can be related to the observation that the rows of closely spaced nanodots (on the quasi-rectangular lattice) tend to be roughly perpendicular to the (coincidental) compression and transfer directions. (b) The process from quasi-hexagonal to quasi-rectangular/square order can be viewed as resulting from the nanodots in a given row of the hexagonal lattice being pushed between the nanodots in a neighboring row by barrier compression (illustrated schematically in Figure 1B), in which case much of the P4VP/PDP monolayer may be forced into the space separating the rows of closely spaced nanodots, preventing further mutual approach of the rows, thereby producing a rectangular-type lattice. This asymmetric arrangement of P4VP/PDP around the nanodots is unlikely to be an equilibrium arrangement and thus could experience a tendency to re-equilibrate toward a more symmetric square lattice, which however may be slow due to the polymeric character of the monolayer. In addition, further disorder may be introduced by the forced merging of rows of nanodots when this occurs at an angle to the rows. (c) The act of transfer from the water surface, where the monolayer is under conditions of high lateral pressure, to the rising substrate, where the lateral pressure is released, may disturb the order. On one hand, the release of pressure may allow some local relaxation to occur in the fraction of time between lift-off from the water surface and strong adsorption to the solid substrate. On the other hand, in the event that a square lattice is much more prevalent on the water surface than on the substrate, the opposing effects of gravity and surface adsorption, or shear forces, during the transfer may stretch the film somewhat. This can result in the lattice being pulled apart slightly in the transfer direction and simultaneously contracted in the orthogonal direction, leading to a more rectangular-like lattice. This effect may explain the greater component of more rectangular character (or lines of closely spaced nanodots) in the image in Figure 1H for the film transferred well above the plateau pressure.

It must be emphasized here that it is generally assumed that the transfer process does not affect the overall morphology of LB films (supported by *in situ* X-ray and neutron reflectivity data¹²), although it may cause local perturbation of the types indicated in the previous paragraph. Possible distortion by shear forces during transfer can be avoided by using the Langmuir–Schaefer (LS) technique, where the film is transferred in a horizontal manner.

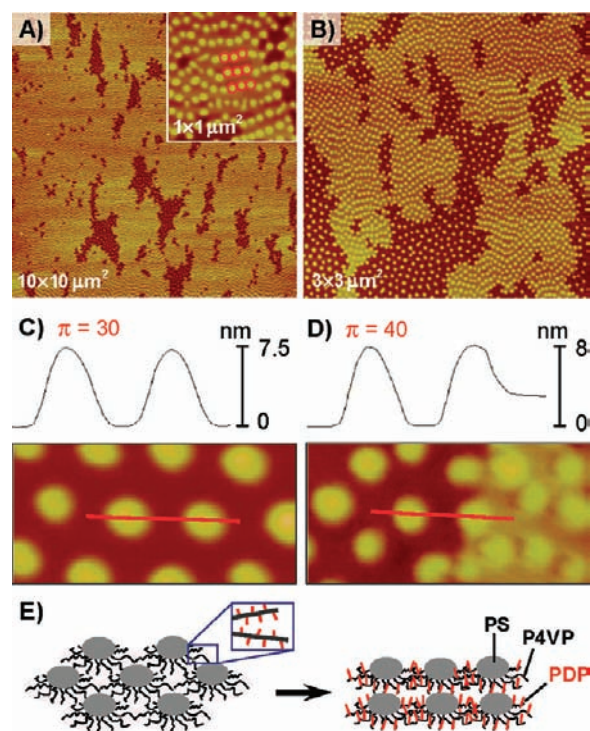


Figure 2. (A,B) AFM height images of a PS-P4VP/PDP LB monolayer film transferred at $40 \text{ mN}\cdot\text{m}^{-1}$, illustrating the presence of a minority lower background and majority higher background; the inset in A shows the short-range nanodot order in the higher background (highlighted by red circles). (See also Figure SI-1.) (C,D) Height profiles accompanying close-up AFM images ($500 \times 250 \text{ nm}^2$), for comparison of LB films transferred at 30 and $40 \text{ mN}\cdot\text{m}^{-1}$, respectively. (E) Model illustrating the changes that occur at the plateau transition: nanodot reorganization accompanied by alkyl chain (red lines) reorientation from prone to vertical.

The AFM image of an LS film of PS-P4VP/PDP transferred at $40 \text{ mN}\cdot\text{m}^{-1}$ is shown in Figure 1G. It is clearly similar to the image in Figure 1F, thus confirming the observations in LB films. It appears to have more square-like order (about $90 \times 90 \text{ nm}^2$), in contrast to more rectangular-like order for the LB film, which may be rationalized by point b above (the longer exposure time to the transfer pressure in the LS technique may allow sufficient time for re-equilibration) or point c above (slight film distortion during LB transfer is avoided); both of these possibilities support quasi-square nanodot order as the equilibrium order above the plateau.¹⁹ Below the plateau pressure, the LS films, like the LB films, have quasi-hexagonal order.

The images in Figure 1F,G show obvious regions of darker-colored background. These regions were also observed in LB films transferred at $40 \text{ mN}\cdot\text{m}^{-1}$, as illustrated in Figure 2A,B, though always to a much lesser extent than the lighter-colored background (see also Figure SI-1 in Supporting Information). They were not observed in the film transferred at $45 \text{ mN}\cdot\text{m}^{-1}$, suggesting that the plateau transition is not quite complete at $40 \text{ mN}\cdot\text{m}^{-1}$, thus leaving traces of the low-pressure phase morphology. The close-up height image in Figure 2D and the accompanying profile across two nanodots spanning the low and high backgrounds illustrate the topographical differences between the two regions. First, the average nanodot height in the

lower background is similar to that observed in Figure 2C for the film transferred below the plateau pressure. Second, the nanodot height in the higher background is unchanged relative to the lower background, whereas the background height itself increases by about 3 nm. In comparison, the elongated length of the PDP molecule is 2.6 nm. In light of the infrared data indicating alkyl chain ordering at the isotherm plateau for the architecturally similar PS-P4VP⁺R_nX⁻ ($n = 10, 18$),^{12a} the increase in background height can be interpreted as resulting from a reorientation of the PDP molecules from a disordered prone to an extended vertical conformation relative to the surface, as illustrated in Figures 2E and SI-2.²⁰ Reorientation of the P4VP chains (such as the VP rings reorienting from a flat to an edge-on conformation relative to the water surface⁹) might also occur and contribute a little to the increase in background height. It is noteworthy that the monolayer transferred at 45 mN·m⁻¹ (Figure 1H; see also Figure SI-3) shows only one type of background. The nanodot heights (Table 1) indicate that this is the high background, consistent with vertical alkyl chain orientation all over, as would be expected after completion of the transition.

In conclusion, the AFM images show clearly that there is a transition in nanodot order in the region of the high-pressure isotherm plateau, from quasi-hexagonal at lower pressures to, most likely we believe, quasi-square at high pressure. This change in order in the region of an isotherm plateau was observed also for a PS-P4VP BC of higher VP content, both with and without PDP present (Figures SI-3 and SI-4). A similar change in order was actually reported for a nanodot-forming PS-PEO BC some time ago,¹⁴ but no identification of the higher pressure order was made, nor was it associated with an isotherm plateau, probably due to none being clearly evident in the available isotherm. However, isotherms for other nanodot-forming PS-PEO BCs of similar composition do show a clear plateau (at a surface pressure of 7–10 mN·m⁻¹).^{13a,21} Even the initial report on LB films of PS-P4VP⁺R₁₀X⁻ indicated a different order above the plateau pressure (image similar to Figure 1H), but its significance appears to have been pre-empted by the then accepted “starfish → jellyfish” interpretation.⁹ Given this evidence for the same phenomenon in several different systems, it can be concluded that the pressure-induced order transition is a general phenomenon in nanodot-forming monolayers of diblock copolymers at the air/water interface. To accommodate the change in order, there are conformational or other molecular changes that are specific to each system, as mentioned above. In the present system (PS-P4VP/PDP) and also in PS-P4VP⁺R_nX⁻, it appears to involve alkyl chain ordering and reorientation, as concluded in ref 12a, and deduced indirectly here by AFM imaging. In systems without alkyl chains, such as PS-PEO and PS-P4VP, conformational changes involving the hydrophilic backbone probably occur (without ruling out the possibility of surface solubilization of PEO), as evoked above.

The discovery of the pressure-induced order transition is of fundamental importance for the understanding of LB films of BCs, and crucial for the intelligent manipulation of these films for applications. This transition can be compared with a similar order transition (hexagonal to disorder or square-like) in very thin solution-cast BC films induced by melt shearing²² and in confined BC films by strain effects,¹⁸ which also involve lateral forces. Moreover, an analogy can be made with 3D order–order transitions in sphere-forming BCs in the bulk.²³

■ ASSOCIATED CONTENT

S Supporting Information. Experimental details, additional AFM images, and a geometric model of P4VP/PDP segments on water. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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