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# Reconformation and Metallization of Unimolecular Micelles in Controlled Environment

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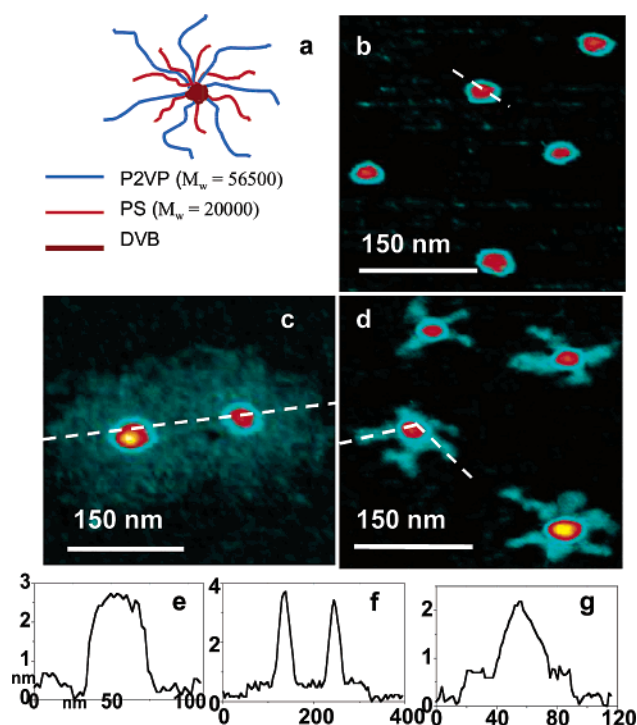
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## ABSTRACT

Unimolecular micelles constituted from the star-shaped PS<sub>7</sub>–P2VP<sub>7</sub> polystyrene/poly(2-vinylpyridine) block copolymer single molecules were studied with molecular resolution using AFM. In selective solvent the unimers show core–shell structures with very pronounced segregation into the collapsed core and the extended shell formed by stretched polymer arms of P2VP and PS in water and toluene, respectively. Metallization of P2VP arms of the copolymer leads to the organic–inorganic nanocomposite with 1–3 nm in diameter palladium clusters localized in the outer shell of unimers, forming starlike structures with metallized arms and improving the contrast to resolve the fine molecular morphology.

**Introduction.** Block copolymers composed of hydrophilic and hydrophobic segments form in aqueous media a micellar structure with a hydrophobic inner core and a hydrophilic outer shell.<sup>1</sup> The micelles are widely used for stabilization of colloidal dispersions and in drug delivery systems when the lipophilic core is used as a “microcontainer” for hydrophobic drugs.<sup>2</sup> However, the micelles are unstable below a critical concentration that limits their possible applications. Star-shaped block copolymers in which hydrophobic and hydrophilic arms are connected together demonstrate behavior of unimolecular micelles stable in aqueous solution in a wide range of concentrations.<sup>3</sup> This unique behavior of the unimers is very promising for the development of drug delivery systems, catalytic systems, electron and energy transfer units, and nanoelectronic devices.<sup>4</sup>

It was shown that polystyrene/poly(2-vinylpyridine) heteroarm star copolymers (PS<sub>7</sub>–P2VP<sub>7</sub>, where 7 is number of arms; Figure 1a) undergo micellization in acidic solutions. The association number is much smaller as compared to corresponding linear diblock copolymers,<sup>5</sup> giving evidence that in dilute solution the molecules predominately form unimolecular micelles. Although conformations and properties of PS<sub>7</sub>–P2VP<sub>7</sub> and other star copolymers were theoretically predicted<sup>6</sup> and widely studied using light scattering (LS), NMR, and other methods,<sup>3,4</sup> there are still no direct experimental data about the morphology of the micelles



**Figure 1.** Schematic representation (a) and representative AFM images and cross-sections of unimers adsorbed on mica: from THF (b, e); from THF-acidic aqueous solution (1:10) after 120 min stirring (c, f); from THF-toluene solution (1:10) after 30 min stirring (d, g).

formed in different environmental conditions. The mixed starlike block copolymers may be considered as a mixed

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brush of a spherical geometry. It was recently shown that the morphology of mixed brushes on a flat substrate is effected by a subtle interplay between lateral and perpendicular phase segregation. The structure of the mixed brush is strongly influenced by selectivity of solvents.<sup>7</sup> The mechanism of microphase segregation in mixed spherical brushes is still not fully understood.<sup>8</sup>

Atomic force microscopy (AFM) was successfully used to resolve the fine structure of single polymer molecules. First successful results were obtained for polymer chains with bulky side groups and for molecular brushes.<sup>9</sup> Recently, we reported the visualization of flexible polyelectrolyte (PE) single molecules using AFM.<sup>10</sup> Rapid evaporation of solvent in the moment of the PE molecule deposition on solid substrate allows to freeze the solution conformation in 2D projection. We also have described conditions to metallize PE molecules in different conformations.<sup>11</sup> Here we present the AFM study of star-shaped PS<sub>7</sub>–P2VP<sub>7</sub> as single-molecule entities, its reformation on a response to controlled environment, and show the direct evidence of the intramolecular phase segregation. Mineralization of unimers<sup>12</sup> adsorbed onto Si wafer leads to star-shaped nanocomposites in which palladium clusters of several nanometers are localized on P2VP arms, improving contrast for AFM investigations of unimers.

**Experimental Section. Preparation of Samples on Mica.** Solution of PS<sub>7</sub>–P2VP<sub>7</sub> in tetrahydrofuran (THF) (0.01 g/L) was diluted by slow addition of the 10-fold excess of acidic water (pH 2, HCl) or toluene. After stirring during 3, 15, or 120 min, we set a drop of the solution onto the surface of freshly cleaved mica for 1 min and afterward removed the rest of the drop with centrifugal force and investigated the dry sample with AFM.

**Metallization on Si Wafers.** Highly polished Si wafers (obtained from Wacker-Chemitronics) were first cleaned in an ultrasonic bath three times for 5 min with dichloromethane (DCM), placed in the cleaning solution prepared from NH<sub>4</sub>OH and H<sub>2</sub>O<sub>2</sub> at 60 °C for 1 h. (Note: the NH<sub>4</sub>OH/H<sub>2</sub>O<sub>2</sub> solution reacts violently with organic compounds. Caution should be used when handling this solution.) Samples were finally exposed to 50% sulfuric acid for 15 min and then rinsed several times with Millipore water (18 MQxcm). Pd(OAc)<sub>2</sub> (PA), DMB, and DCM were used as received from Aldrich.

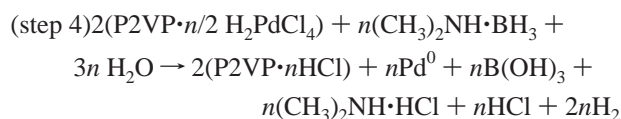
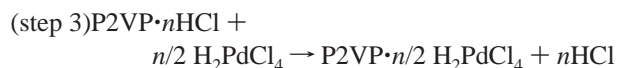
To obtain a saturated PA aqueous solution, 5 mg of PA in 30 mL of water was placed in an ultrasonic bath for 30 min and then the unsolved PA was precipitated by centrifugation for 5 min at 2000 g. A solution of PS<sub>7</sub>–P2VP<sub>7</sub> in THF (0.01 g/L) was diluted by a slow addition of the 10-fold excess of acidic water (pH 2, HCl). After stirring during 120 min, we set a drop of the solution on the surface of the cleaned Si wafer for 1 min and afterward removed the rest of the drop with centrifugal force. Then, in the second step, the Si wafer was rinsed several times with water and placed into the PA solution (pH 2) for 1 min for the formation of the P2VPH<sup>+</sup>⋯(PdCl<sub>4</sub>)<sup>2-</sup> composite. In the third step, the Si wafer was thoroughly rinsed with water and placed for 15 s into the reduction solution, which contained 1.0 mg/mL of

**Table 1.** Characteristics of the PS<sub>7</sub>–P2VP<sub>7</sub> Sample

$M_w(\text{PS}_{\text{arm}})$	by SEC	20000
$M_w(\text{P2VP}_{\text{arm}})/\text{number of arms}$	by LS/ calculated	56500/6.9
$W_{\text{P2VP}}$ , fraction of P2VP	by NMR	66%
$M_w(\text{PS}_7\text{--P2VP}_7)$ , g/mol	by LS	544000

DMB. Finally, the Si wafer was cleaned with water and dried with an argon flux.

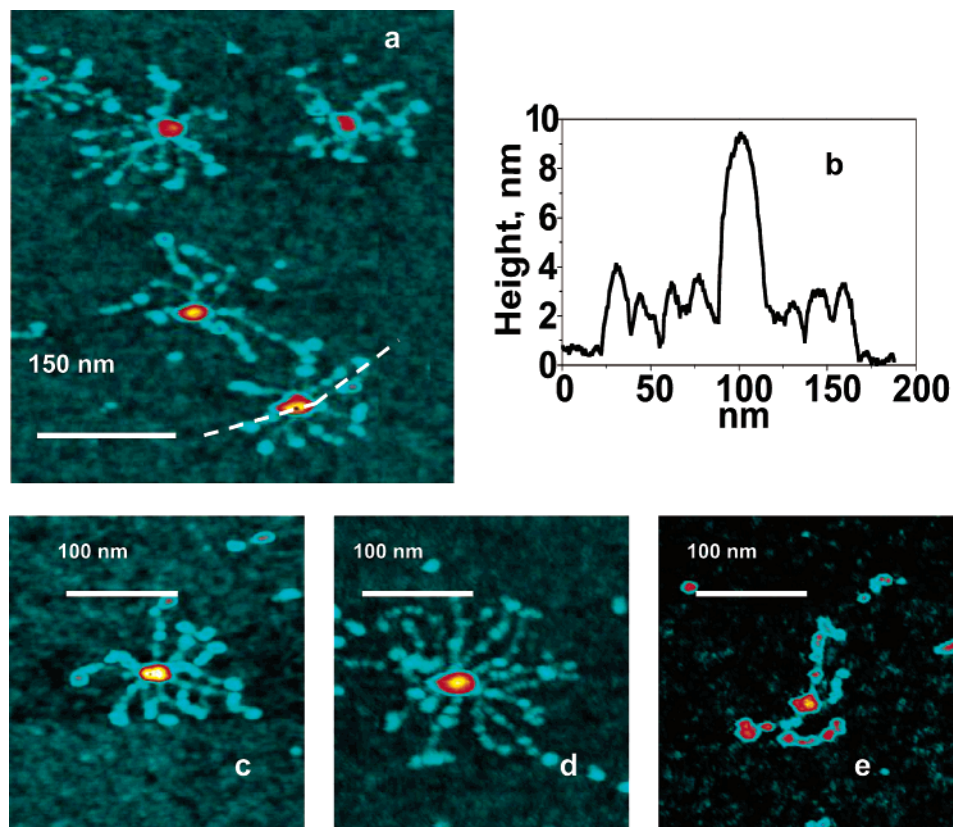
At pH 2 the surface of the Si wafer is positively charged (the measured isoelectric point was found at pH 3). Therefore, the starlike copolymer is attached to the solid substrate due to nonelectrostatic interactions. In these conditions we did not find Pd on the surface of the Si wafers after reduction. Pd clusters were formed only on the deposited molecules of PS<sub>7</sub>–P2VP<sub>7</sub>. A scheme of the reactions involved into the metallization process is presented below.



**AFM Experiments.** A Multimode AFM instrument (Digital Instruments, Santa Barbara) was operating in the tapping mode. Silicon tips with radius of 10–20 nm, spring constant of 30 N/m, and resonance frequency of 250–300 kHz were used after calibration with gold nanoparticles (diameter 5 nm) to evaluate the tip radius. The dimensions of structures obtained from AFM images were corrected (decreased) by the tip radius.<sup>13</sup>

**Results.** PS<sub>7</sub>–P2VP<sub>7</sub> (Table 1, Figure 1a) was prepared via three-step sequential “living” anionic polymerization using divinylbenzene linkage (DVB).<sup>14</sup> The block copolymer was initially solved in nonselective solvent (THF), and then the sample was diluted by a large excess of selective solvent (toluene or acidic water). Single molecules were deposited on mica or Si wafer as described in the Experimental Section.

In THF (good solvent for both P2VP and PS), PS<sub>7</sub>–P2VP<sub>7</sub> is molecularly dissolved and exists in near spherical conformation (Figure 1b, e). Averaged volume of PS<sub>7</sub>–P2VP<sub>7</sub> molecules adsorbed from THF roughly estimated on the base of AFM data equals to 884 nm<sup>3</sup> (the bulk volume calculated from molecular mass of PS<sub>7</sub>–P2VP<sub>7</sub> is 950 nm<sup>3</sup>). Addition of acidic water induces the intrasegregation when arms of protonated P2VP extend in outer direction due to the Coulombic repulsion,<sup>15</sup> while PS arms move inside the structure. We monitored the extension of P2VP arms in time: PS<sub>7</sub>–P2VP<sub>7</sub> unimolecular micelles underwent reformation during a stirring in the acidic aqueous solution (Table 2). At the final micelle-like state in 2 h, the arms of PS form a collapsed core which is stabilized by the protonated P2VP arms (Figure 1c, f). During segregation



**Figure 2.** AFM topographic images of Pd•••PS<sub>7</sub>–P2VP<sub>7</sub> nanocomposites on Si wafer: representative picture (a); cross-section taken along two arms of the star (b); molecules with different number of metallized P2VP arms: 7 (c); more than 10 (d); 4 (e).

**Table 2.** Average Dimensions of Unimers (averaged for 50 structures in 5 AFM images)

time (min) (after addition of acidic water)	diameter ( <i>D</i> ) and height ( <i>H</i> ) of shell		diameter ( <i>D</i> ), height ( <i>H</i> ), and volume ( <i>V</i> ) <sup>a</sup> of core		
	<i>D</i> , nm	<i>H</i> , nm	<i>D</i> , nm	<i>H</i> , nm	<i>V</i> , nm <sup>3</sup>
0	36 ± 10	2.4 ± 0.5	36 ± 10	2.4 ± 0.5	884
3	44 ± 15	1.1 ± 0.2	29 ± 10	3.4 ± 0.5	750
15	79 ± 25	0.8 ± 0.2	25 ± 10	3.1 ± 0.4	507
120	126 ± 35	0.3 ± 0.1	16 ± 7	2.9 ± 0.3	194

<sup>a</sup>  $V = 1/3H \times \pi(D/2)^2$ , for simplicity we used the geometry of a cone.

we observed the decrease of volume of the core from 884 nm<sup>3</sup> to 194 nm<sup>3</sup> (the bulk volume of the PS core calculated from molecular mass of PS equals to 250 nm<sup>3</sup>). We later confirmed the single-molecule origin of the observed structures. In toluene we obtained the inverse picture: the arms of P2VP formed a collapsed core ( $D = 36$  nm,  $H = 2.4$  nm; volume calculated from AFM data  $V_{\text{AFM}} = 813$  nm<sup>3</sup>; calculated from molecular weight  $V_{\text{calc}} = 670$  nm<sup>3</sup>), while the PS arms are stretched forming the shell ( $D = 80$  nm, Figure 1d, g).

To metallize PS<sub>7</sub>–P2VP<sub>7</sub> on the Si wafer surface, we employed a recently developed approach that is based on the ion exchange reaction between protonated (P2VPH<sup>+</sup>)Cl<sup>–</sup> and (2H<sup>+</sup>)PdCl<sub>4</sub><sup>2–</sup> (formed from PA and HCl) followed by reduction with dimethylamine borane.<sup>11</sup> Due to the reduction of Pd, atoms localized along the polymer chain build clusters. After metallization of PS<sub>7</sub>–P2VP<sub>7</sub> deposited from acidic

**Table 3.** Dimensions Pd•••PS<sub>7</sub>–P2VP<sub>7</sub> Nanocomposites (averaged from 52 structures in 6AFM images)

length ( <i>L</i> ), height ( <i>H</i> ), and number ( <i>N</i> ) of P2VP arms			diamter ( <i>D</i> ) and height ( <i>H</i> ) of PS core		diameter ( <i>D</i> ), height ( <i>H</i> ), and number ( <i>N</i> ) of Pd clusters per arm		
<i>L</i> , nm	<i>H</i> , nm	<i>N</i>	<i>D</i> , nm	<i>H</i> , nm	<i>D</i> , nm	<i>H</i> , nm	<i>N</i>
61 ± 15	1 ± 0.2	7 ± 1	9 ± 3	7.2 ± 2	3 ± 1	2.2 ± 1	3 ± 1

aqueous solution with fully extended P2VP arms, the Pd•••PS<sub>7</sub>–P2VP<sub>7</sub> nanocomposite appears in the good resolved star-shaped conformation (Figure 2). P2VP arms as well as Pd clusters are clearly observed in the AFM images and can be counted (Table 3).<sup>16</sup>

Consequently, the visualization and selective contrasting of the unimers with metal clusters allows to make the following conclusions. In selective solvent the unimers show the core–shell structures with very pronounced segregation into the collapsed core and the extended shell formed by stretched polymer arms of P2VP and PS in water and toluene, respectively. In nonselective solvent, microphase segregation results in more compact unimicelles. Details of the fine molecular morphology in nonselective solvent are still not resolved.

The data demonstrate that polymer molecules of a complicated architecture can be used as templates for metallization. This approach is promising for the fabrication of single molecule electronic devices.

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