

## Fully Extended Polyelectrolyte–Amphiphile Complexes Adsorbed on Graphite

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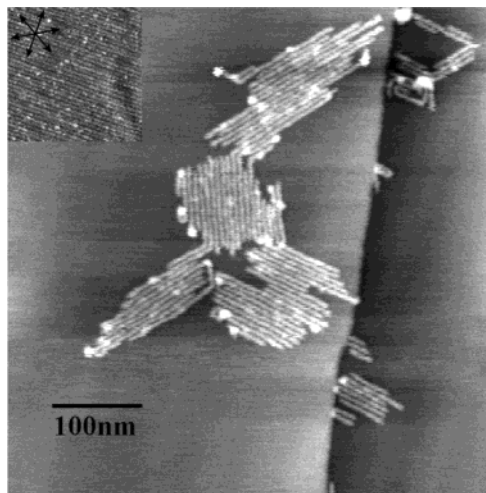
Polyelectrolyte–amphiphile complexes (PACs) have attracted considerable attention due to their interesting properties and potential applications in pharmaceuticals and environmental science.<sup>1,2</sup> Since most biopolymers are polyelectrolytes and as lipids are of amphiphilic nature, PACs are also of fundamental interest for biology. The formation of PACs is driven by electrostatic interactions of the charged polyelectrolyte backbone and the oppositely charged headgroups of the amphiphiles. The resulting PACs have completely different properties than the native polyelectrolytes, e.g. with respect to solubility and phase behavior.<sup>3–5</sup>

The interaction of PACs with interfaces<sup>6</sup> is of fundamental interest in wetting and adhesion.<sup>7</sup> The adsorption of a macromolecule at an interface generally affects the conformation of the polymer, which may give rise to a variety of artifacts such as shrinkage of the polymer.<sup>8,9</sup> In addition, the length distribution of polymers in solutions and adsorbed on surfaces can be different.<sup>10,11</sup> Due to the great size, macromolecules often get kinetically trapped at the interface, which effectively prohibits reversible self-assembly processes and (long-range) ordering of macromolecules.<sup>12</sup> Even shape persistent macromolecules, such as DNA or proteins, exhibit generally only short-range ordering in surface-confined architectures.<sup>13</sup>

On the other hand, numerous molecules can self-assemble on suitable interfaces, such as long-chain alkanes on graphite, giving rise to highly ordered structures.<sup>14</sup> We therefore asked if it is possible to utilize molecular self-assembly to organize macromolecules at interfaces in predictable ways. The strategy pursued here utilizes a PAC with a molecular component, which can self-assemble on the underlying substrate. We present results of two PACs with distinct length distributions adsorbed on graphite. Scanning force microscopy (SFM) provides information on the structure of single PAC as well as assemblies of PACs on the surfaces. In addition, we use SFM to determine the length distribution of the adsorbed PACs and to compare it to that of the native polyelectrolyte.

Atactic poly(sodium 4-styrenesulfonate) (PSS) was chosen as parental polyelectrolyte. Using size exclusion chromatography (SEC) with light scattering and refractive index detection the length distribution profiles of two samples was determined (Sample A (Aldrich):  $M_n = 72.820$ ,  $M_w = 98.870$ ,  $D = 1.36$  and Sample B (Scientific Polymer Products):  $M_n = 107.500$ ,  $M_w = 109.800$ ,  $D = 1.02$ ). PACs were prepared from PSS and trimethylhexadecylammonium bromide (THA Br) as described before,<sup>15</sup> except that water was used for washing the PACs. PAC was spin coated from chloroform solution on a freshly cleaved graphite surface followed by annealing for 15 min at 35 °C. SFM was performed in tapping mode.<sup>16</sup>

SFM images show a graphite surface covered with 2D raft-like structures consisting of straight, tightly packed rods (Figure 1). The



**Figure 1.** Representative SFM image of PAC on graphite (sample A). Single straight PAC rods pack in “raft”-like structures. (Inset) Representative SFM image of THABr on graphite. Arrows denote orientation of graphite lattice.

spacing between the rods is  $6 \pm 0.2$  nm. The rods are predominantly oriented along three directions enclosing angles of  $120^\circ$ , which reflects the symmetry of the underlying graphite substrate. The height of the structures is approximately 0.8 nm. Notably, no crossing molecules are observed.<sup>17</sup>

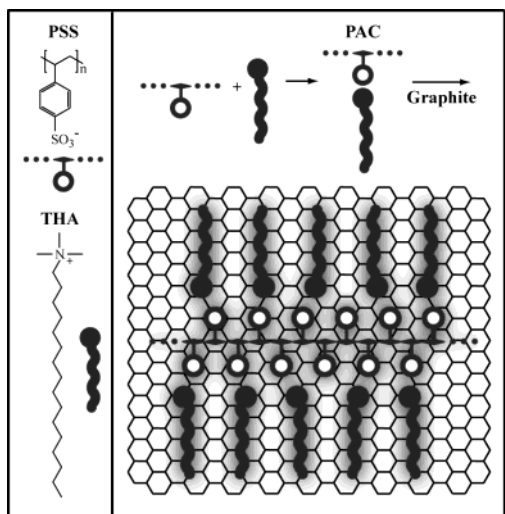
Neat monolayers of THABr on graphite show lamellae with a spacing of  $4.8 \pm 0.1$  nanometers (Figure 1, inset). A fully extended THA molecule has a length of approximately 2.3 nm, indicating that a lamella consists of THABr dimers, as is often the case for amphiphilic molecules.<sup>18</sup> The absence of such lamellae in PAC images indicates that there is no significant excess THABr present in PAC samples.

Considering shape and lateral and vertical dimensions, we attribute the rods to individual PACs. On the basis of these findings we propose that PACs self-assemble on the basal plane of graphite. Most likely, the alkyl chains of THA assemble along the lattice axis of graphite. The incorporation of PSS into the lamellae results in a widening of the spacing compared to monolayers of neat THABr (Scheme 1). We therefore conclude that the underlying graphite surface acts as a template for PAC. This self-assembly process results in an almost complete straightening of the PSS main chain as we will see below.

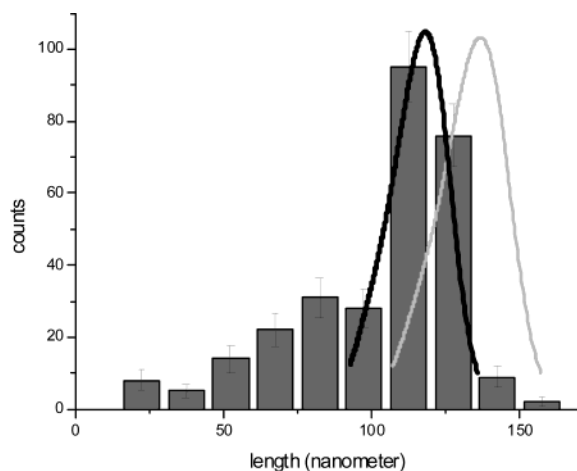
For the length distribution analysis we will focus on sample B because it is made from a PSS standard with a narrow and mono modal mass distribution. The length distribution profile of PAC is estimated from the contour length of all rods that can be clearly traced from beginning to end. The lengths of the PAC rods are directly determined from SFM images with standard image analysis software (Figure 2). To compare the molecular length distribution obtained by SFM with the molar masses distribution from SEC,

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**Scheme 1.** Formation of PAC and Its Self-Assembly on Graphite<sup>a</sup>

<sup>a</sup> THA molecules bind electrostatically with their positively charged head group to the negatively charged PSS backbone (left). On graphite, the alkyl chains of THA most likely assemble along the lattice axis of the underlying graphite surface. The self-assembly process completely unfolds and straightens the polymeric backbone of PAC at the interface. In addition, PAC rods can at least initially diffuse on the surface to form well-ordered, oriented aggregates. On the basis of our previous investigations on metallo-supramolecular PACs,<sup>6</sup> it becomes clear that this approach is of general utility to control the adsorption of macromolecular assemblies on a surface in a predictable way, which represents significant advance toward the design and construction of nanotechnological systems through molecular self-organization. Further experimental and theoretical studies shall elucidate this.



**Figure 2.** Length distribution profiles for PAC (sample B) for 295 rods. The histogram represents the SFM data, and the solid lines are the SEC data; gray line: assuming PSS repeat unit length 0.25 nm, black line: assuming a PSS repeat unit length of 0.216 nm. The weight fraction provided by SEC is recalculated to number fraction to compare with SMF molecular counts.

the molar masses are divided by the weight of the PSS repeat unit and multiplied by its length. The repeat unit ( $C_8H_7SO_3Na$ ) has a molar mass of 206 g/mol and in the case of an all-trans conformation the length amounts to 0.25 nm. The gray line in Figure 2 shows the resulting molecular length distribution. We see that the experimentally determined length distribution is shorter, which we attribute to the steric repulsion of adjacent phenyl groups preventing an all-trans conformation. As a result, the actual contour length is shorter. For example, in crystalline isotactic polystyrene the backbone adopts a helical conformation with three units per turn ( $3_1$  helix), yielding a projected contour length of  $6.5/3 = 0.216$  nm.<sup>19</sup> The formation of a secondary structure, therefore, causes a length reduction of 0.86. The solid line in Figure 2 shows the length

distribution profile based on the assumption of a helical secondary structure of the PSS backbone. While the atactic PSS used here cannot adopt an all-helical structure, it can be viewed as a polymer consisting of short helical segments. Therefore, the actual contour length of PAC will also be reduced with respect to a theoretical all-trans conformation.

Within the experimental error the data strongly suggest that the molar mass distributions of parent PSS and adsorbed PAC agree with each other. This means that the PSS backbone in PAC rods on graphite is fully extended. Such a structure is an intriguing and surprising result because there is no reason to assume that PAC in solution is completely straight.<sup>20</sup> The adsorption process involves a molecular ordering mechanism, which completely unfolds and straightens the polymeric backbone of PAC at the interface. In addition, PAC rods can at least initially diffuse on the surface to form well-ordered, oriented aggregates. On the basis of our previous investigations on metallo-supramolecular PACs,<sup>6</sup> it becomes clear that this approach is of general utility to control the adsorption of macromolecular assemblies on a surface in a predictable way, which represents significant advance toward the design and construction of nanotechnological systems through molecular self-organization. Further experimental and theoretical studies shall elucidate this.

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**Supporting Information Available:** Preparation of PACs and SEC characterization. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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