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Kinetics of Block Copolymer Adsorption

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ABSTRACT: The kinetics of adsorption of diblock copolymers of poly(2-vinylpyridine) and polystyrene from toluene solutions on silica was investigated by using radiolabeled polymers. To study the relaxation of the anchoring block, only copolymers with a large pyridine block were selected. Adsorption was performed from solutions at concentrations below the cmc. Fast adsorption was observed for initial adsorption on bare silica, which became fully covered by chain segments of pyridine blocks. A slow rearrangement of the interfacial layer then followed, the surface relaxation being faster for copolymers with larger pyridine blocks.

Introduction

The adsorption of diblock copolymers onto solid-liquid interfaces has recently gained renewed interest due to the ability of these polymers to perfectly stabilize colloidal suspensions. As for low molecular weight surfactants, one part of the copolymer is able to strongly interact with the solid phase and therefore provides an irreversible anchoring for the second block. Properties of this picture are generally referred to for interpretation of the features of the system. In the present work, we were interested in the mechanism and kinetics of interfacial layer formation in a system involving adsorption of a diblock copolymer of 2-vinylpyridine and styrene from toluene solutions onto silica. The process leading to layer formation in these case may be nontrivial in contrast to adsorption processes involving homopolymers. Elements of response have been obtained in adsorption studies by varying the type of adsorbent (hydrophobic and hydrophilic silica) and the nature of the polymer solvent (solvent and nonsolvent for the blocks).[1] As a general feature, in a polar solvent, the protonated vinylpyridine group is able to interact with the acidic group of silica, leading to formation of a strong and permanent link. In organic media, nonelectrostatic polar forces between sorbent and polymer may originate from Lewis acid-base interactions. Thus unmodified silica gave an adsorption of 1.75 mg/m^2, whereas silanized silica retained only 0.07 mg/m^2 from the same toluene solvent. This indicates that copolymer adsorption may be blocked if the active sites of the sorbent are unavailable. Toluene constitutes a good solvent for the styrene block and is a nonsolvent for the pyridine sequence. The copolymer solubilized below the critical micelle concentration (cmc) may have a segregated structure where, as usually assumed, the poly(2-vinylpyridine) block is protected from precipitation by the polystyrene chain. Considering the adsorption mechanism of these unimers, one may wonder how the internal moiety, segregated and protected from solvent, is able to interact with the solid surface. On the other hand, above the cmc, one may question the capacity for adsorption of the copolymer micelles, when one observes that full surface coverage has been obtained only for high concentrations of the supernatant solution.[1] This finding may lead to the conclusion that micelles themselves cannot adsorb, as postulated by Johner and Joanny.[2] However, the opposite was concluded by Tassin et al. from kinetic measurements of copolymer adsorption.[3] We believe that solid/polymer interactions are possible only when the distance of closest approach between the core block and the sorbent lies in the range of the polystyrene layer surrounding one unimer. The mechanism of copolymer adsorption in the presence of micelles appears to be open to continuous investigation.

The object of the present study was to determine the rate of establishment of the interfacial layer when polymer transfer starts from very dilute solutions, below the cmc. We believe that our model is valid for many other systems, such as mica and oxides, where strong interactions are expected to occur.[4-6] To show the importance of structural relaxation of the anchoring PVP block, experiments were carried out with copolymers having a relatively large PVP block.

The device and experimental procedure used to determine the correlation between adsorption rate and surface coverage have been described.[7] At each time, adsorption is calculated from the residual polymer concentration in the liquid phase. The kinetic coefficient of the adsorption process is discussed in terms of surface occupation.

Materials and Methods

Two-Block Copolymers. The copolymers PVP-PS were kindly provided by the Ecole d'Application des Hauts Polymères (EAHP, Strasbourg). They were prepared by classical anionic polymerization of styrene with functional end groups in tetrahydrofuran, followed by polymerization in situ of the 2-vinylpyridine component. Average molecular weights for PS and PVP sequences, respectively, were determined by light scattering in tetrahydrofuran solution. Precise determination of the polymer concentration in the liquid phase was obtained using radiolabeled samples. To label the copolymer, trace quaternization of the PVP sequence was carried out with $^{14}CH_3I$ in tetrahydrofuran, leading to 0.1-0.3% pyridinium iodide groups. The copolymer characteristics are given in Table I, including the polymer reference according to the now classical definition taking into account the degree of polymerization x of the two blocks PVP and PS. To prevent the polymer from adsorbing moisture, the samples were maintained over P_2O_5.

Adsorbent. The adsorbent was nonporous glass beads (Verre et Industrie). The particle diameter lay between 10 and 80 μm as determined by Coulter Counter, and the volume averaged mean harmonic diameter was 34 μm, which furnished a specific area of 7.8×10^{-2} m^2/g. The glass beads were treated with hot hydrochloric acid to generate a surface bearing only SiOH groups. They were then washed free of acid with distilled water, and excess water was evaporated under reduced pressure at 40 °C. This mild drying process maintained the silica surface in the silanol form, without physisorbed water. It also precluded formation of siloxane bridges on the surface, which would have occurred under drying at higher temperatures. The number of silanol groups accessible for alkaline neutralization was found to be 7.9/nm^2.[8] This value will be considered to be the density of anchoring sites for pyridine adsorption. It corresponds in fact to the sites located in the first and second arrays of the silica planes, but both types of site may be considered as displaying similar interactions forces toward adsorbing polymers.

Adsorption Procedures. The copolymer solutions were prepared by dissolving a given weight of polymer in a weighed

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Table I
Characteristics of Diblock Copolymers

PVP-PS	$M_{w,PVP}$, g/mol	$M_{w,PS}$, g/mol	radioactivity, cpm/μg
[771–314]	81 000	32 700	220
[412–179]	43 300	18 600	544
[863–177]	90 600	18 400	244
[1580–177]	166 000	18 400	610

mass of solvent. These preparations were left standing for at least 24 h at 25 °C.

(a) Determination of the Rate-Limiting Step. One gram of silica beads suspended in toluene was introduced into 70 g of copolymer solution at 5 μg/g, and a second solution was prepared similarly. We proceeded as follows. One milliliter of the supernatant solution was taken from solution I and analyzed for radioactivity every 6 min. For solution II, the liquid phase was entirely withdrawn from the bead sediment and brought into contact with 1 g of silica beads free of adsorbed polymer every 6 min. The polymer concentration was successively determined. This procedure was carried out near to zero concentration in solution II.

(b) Determination of Fast Adsorption Kinetics. We used the cell described in ref 7. We recall that the polymer solution of concentration C_0 is introduced at the rate J_V into the cell reactor of fixed volume V. The effluent leaves the cell through an aperture fitted with a filter that retains the beads in the cell. The sampling time Δt is 2 min, and determination of the radioactivity of the effluent permits adsorption to be calculated as a function of time. Completion of adsorption corresponds to achievement of an exponential variation of the polymer concentration with time. This procedure allows determination of surface-controlled adsorption rates because stirring of the suspension rules out diffusion-limited transfer from solution to sorbent.

(c) Determination of Slow Adsorption Kinetics. The bead suspension was left in contact with the solution for a prolonged period. Care was taken to prevent moisture penetrating the vessel, and the suspension was periodically mildly stirred to homogenize the liquid phase. As before, the progress of adsorption was recorded by determination of the polymer concentration in the supernatant solution. These experiments were carried out over about 2 months to obtain a nearly constant value of the polymer adsorption. We note that procedure c differs from b because in c adsorption onto the surface is limited by diffusive transfer from the solution to the sediment of thickness less than 1 mm. This retardation of the mass transfer from solution to surface may have an influence on the number of adsorbed molecules necessary to obtain full coverage of the bare surface in the case of structural relaxation of the PVP block.

Results and Discussion

Determination of the Rate-Limiting Process. The range of micellar concentrations of block copolymers PVP–PS has been determined by Tassin et al. using the light-scattering technique; for 05–60 and 60–60 samples, the cmc was 65 μg/mL.[3] To determine the rate-limiting process in the adsorption of unimers in the absence of micelles, procedure a was implemented. Figure 1 shows the temporal evolution of the amount of copolymer [771–314] being adsorbed in solutions I and II during successive periods of 6 min. One observes that in solution I adsorption is rapidly stopped, whereas in solution II, although the increment of adsorbing copolymers decreases with time because the supernatant becomes poorer in polymer, the copolymer concentration declines slowly to zero. We conclude that an excluded surface effect must exert a role of prime importance in the kinetics of the adsorption process when the procedure described in a is implemented. From the result that all copolymers initially present in the liquid phase are adsorbed when the surface/volume ratio is sufficiently large, and according to the value of the cmc determined by Tassin et al.,[3] we conclude that the solution contained unimers only at this low concentration of about 4–5 μg/mL. In the present work, the concentration range 4–40 μg/mL (below the cmc) constitutes the domain of investigation.

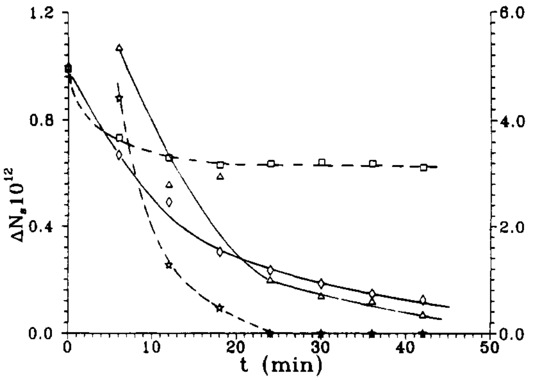

Figure 1. Determination of excluded surface effects for copolymer [771–314]: (– – –) adsorption onto the same adsorbent (case of solution I); (—) adsorption onto renewed adsorbent (case of solution II). Left ordinate: number of copolymer adsorbed during each period of 6 min: (☆) solution I; (△) solution II. Right ordinate: copolymer concentration in the supernatant as a function of contact time t: (□) solution I; (◇) solution II.

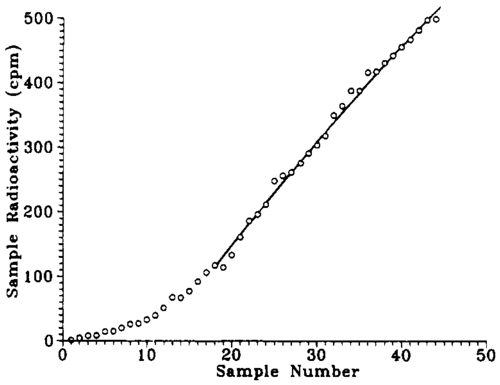

Figure 2. Representation of the radioactivity of the effluent (0.6 mL) as a function of the sample number. Copolymer [771–314], J_V = 0.3 mL/min, C_0 = 8.5 μg/mL. The full line describes the exponential regime corresponding to dilution of the injected copolymer solution.

Characteristics of the Fast Adsorption Regime. (1) Number of Adsorbed Copolymers. Procedure b was used to determine the fast adsorption kinetics. Figure 2 displays the characteristic variation of the effluent radioactivity (cpm) as a function of the number of the collected sample, for a typical experiment of adsorption of copolymer [771–314]: V = 48 mL, C_0 = 8.5 μg/mL, Δt = 2 min, and J_V = 0.3 mL/min. One observes that the adsorption stops after sample 20. According to the injection rate, the adsorption time is 40 min; no adsorption was observed during the following hour even in the presence of supernatants of increasing concentration. This corresponds to the amount of polymer adsorbed at the end of fast adsorption, and we postulate that this indicates full surface coverage.

Similar experiments were performed using different concentrations C_0 of the injected copolymer [771–314] solution at a constant rate J_V of 0.3 mL/min. As shown in Table II, the number of adsorbed molecules at the end of the fast adsorption regime does not depend on the solution concentration in the range 5–40 μg/mL. This implies that the rate of polymer supply does not influence the structure of the adsorbed layer at the end of adsorption. Schematically, the solute unimer is composed of a central PVP core surrounded by the solubilized PS sequence. In

Table II
Copolymer [771–314] Adsorbed under Different Rates of Polymer Supply (J_V = 0.3 mL/min)

C_0, μg/mL	$10^{11}N_0$, mol/mL	$10^{12}N_s$, mol/cm^2
8.49	7.46	1.14
14.64	12.87	1.06
15.45	13.59	1.15
38.19	33.58	1.02
39.35	34.61	1.08

Table III
Influence of the Molecular Weight on the Copolymer Adsorption

sample [x_{PVP}–x_{PS}]	$10^{12}N_s$, mol/cm^2	$10^{10}x_{PVP}N_s$, monomol/cm^2	$10^{13}\bar{n}_s$, mol/h
[771–314]	1.10	8.5	1.8
[412–179]	2.30	9.5	
[863–177]	1.62	14.0	2.0
[1580–177]	2.07	32.7	3.2

the adsorbed state, the PVP chain has many segments in direct contact with the sorbent, whereas the PS chain protrudes in the solvent phase.[3,9] This structural change should be a fast process here. In fact, when the structural relaxation is slow compared to rate of surface coverage, the amount of adsorbed copolymers may depend on the rate of polymer supply to the solid surface. The adsorbed polymers have different areas depending on the adsorption time; as a result, the mean area depends on the rate of surface covering. Our experimental device allows us to artificially retard the surface covering and thus leads to determination of the temporal variation of the interfacial area of the adsorbed polymer.[10–12] In the present case, as for the system polystyrene/silica/carbon tetrachloride,[13] the structural change during adsorption should be fast, and we infer that during this fast adsorption regime, the copolymer [771–314] immediately adopts a metastable conformation.

These fast adsorption experiments were repeated with the different copolymer samples listed in Table I. Table III presents the values of N_s, the number of adsorbed macromolecules (mol/cm^2), in the second column and the values of $x_{PVP}\,N_s$, the number of adsorbed segments of the PVP block in the third column. We first consider the adsorption of copolymers [771–314] and [412–179], which are characterized by the same asymmetry ratio of about 2.40. For the smaller copolymer, the number of adsorbed moles is twice as large. We calculate that the number of adsorbed segments $x_{PVP}\,N_s$ is about 9 × 10^{-10} mol/cm^2 for both copolymers. This value is to be correlated with the number of hydroxyl groups located on the silica surface, 7.9 × 10^{14}/cm^2, to which we suppose an identical number of PVP chain segments to be opposed. In fact, 5.4 × 10^{14} segments are adsorbed, corresponding to a coverage of 68%. This value is not far from the random packing limit (78%), when disks are randomly deposited onto a plane surface and compacted.[14] The last process requires the adsorbed block to be able to move freely on the surface and from previous considerations, we postulate that chains of the PVP block are adsorbed in a flat conformation, each pyridine site facing one silanol group by Lewis acid–base interaction.

A second observation is relative to the adsorption of three copolymers with increasing length of the PVP block [412], [863], and [1580] and constant PS sequence length [177]. A clear effect on the number of adsorbed copolymers is not obtained, but one observes that the number of segments adsorbed increases strongly. Clearly, the thickness of the adsorbed "pancake" increases with the length of the PVP block. For the copolymer [1580–177], a 4-fold increase in layer thickness was calculated as compared to the [412–179] sample. This result demonstrates that, in spite of the strong interaction existing between the pyridine group and the surface silanol responsible for the formation of flat pancakes in the case of copolymers of low molecular weight, chain–chain interactions of PVP blocks in nonsolvent media preclude total flattening of the large molecule, at the present injection rate. We believe that the transition between the two structures depends only on characteristics of the PVP block.

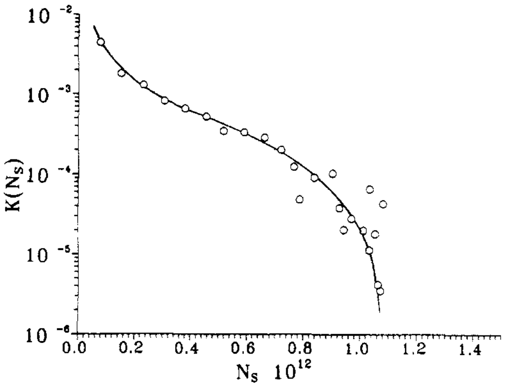

Figure 3. Representation of the kinetic coefficient $K(N_s)$ (cm·s^{-1}, relation 2) as a function of the surface coverage N_s (mol/cm^2) for adsorption of copolymer [771–317] (fast adsorption regime).

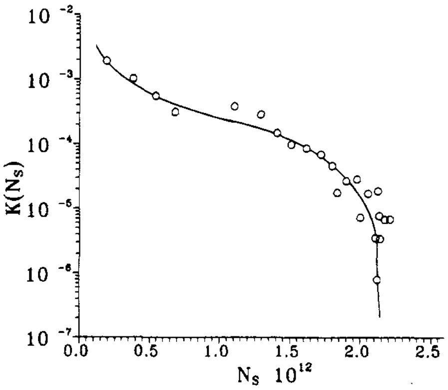

Figure 4. Representation of the kinetic coefficient $K(N_s)$ (cm·s^{-1}, relation 2) as a function of the surface coverage N_s (mol/cm^2) for adsorption of copolymer [1580–177] (fast adsorption regime).

(2) Kinetics of Adsorption. Assuming that the adsorption process corresponds to first-order kinetics

$$N(\text{solution}) \rightarrow N_s(\text{interface}) \qquad (1)$$

the elementary description of the kinetics is the following:

$$\mathrm{d}N_s/\mathrm{d}t = N(t)\,K(N_s) \qquad (2)$$

where $N(t)$ represents the instantaneous concentration of the copolymer in the liquid phase and $K(N_s)$ is the kinetic coefficient related to the coverage N_s at time t according to the rate-limiting effect of the available surface. Results are presented on the basis of eq 2, and the shape of the variation of log $K(N_s)$ versus N_s is reported in Figures 3 and 4 for adsorption of copolymers [771–314] and [1580–177], respectively. For copolymer [771–314], the variation of $K(N_s)$ with N_s does not depend on the concentration C_0 of the injected solution. This implies the validity of eq 2 and completes the result of Tassin et al., who fail to describe the kinetic behavior of the diblock copolymer. Departure from the first order in copolymer concentration (relation 2) reported in ref 3 seems to be correlated to structural changes during adsorption, as reported below.

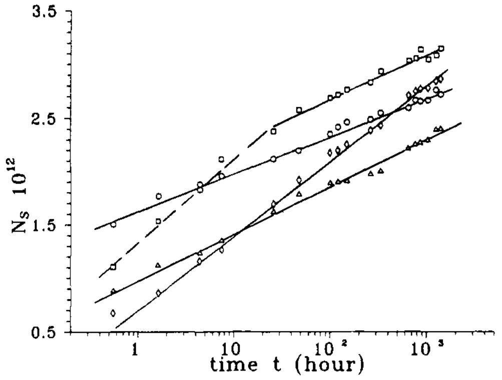

Figure 5. Representation of the number of copolymer adsorbed N_s (mol/cm^2) as a function of log t for different copolymers; (○) [771–314]; (□) [412–179]; (△) [863–177]; (◇) [1580–177] (slow adsorption regime).

The shape of the variation of $K(N_s)$ with N_s is comparable to that obtained for adsorption of polystyrene onto silica beads under poor solvent conditions, in carbon tetrachloride at 4 °C.[13] We conclude that in spite of the two different interfacial structures that result at the end of fast adsorption, the adsorption mechanism brings into play a unique process: the segregated PVP block apparently adsorbs onto the surface like a disk of variable thickness. No slow structural relaxation could be demonstrated by varying the injection rate for the smallest copolymer which always occupied the maximum number of available surface sites. This does not seem to be true for copolymers of higher molecular weight, as determined by using procedure c.

Characteristics of the Slow Adsorption Regime. We observed that the end of the fast adsorption regime does not constitute a state of thermodynamic equilibrium. This surface area saturation may be compared to the S-shaped kinetics evidenced in ref 3, where adsorption goes through a plateau for intermediate times. To define the slow adsorption process, we used procedure c. Figure 5 shows the number of adsorbed copolymers as a function of log t, where t represents the solid/liquid contact time. The proportionality between N_s and log t implies that the adsorption rate may be expressed by the relation of Arrhenius, where the adsorption energy depends only on the thermodynamic characteristics of the layer and may be described in terms of surface coverages at time t and in the equilibrium state. The adsorption rate is given by relation 3, where $\bar{n}_s$ is the mean number of moles adsorbed

$$dN_s/dt = \bar{n}_s/t \quad (3)$$

per hour and t the adsorption time. The values of $\bar{n}_s$ are reported in Table III.

We see that structural relaxation starts from the monolayer situation for the copolymer [771–314]. For the sample [412–179], which possesses a short PVP sequence, we fail to explain the observed increase in adsorption. For copolymers characterized by larger PVP blocks, relatively longer periods (10–50 times) are necessary to obtain the coverages that correspond to the end of fast adsorption in procedure b. In procedure c, we recall that polymer transfer from solution to adsorbent is hindered in comparison with the convective transfer in procedure b. As observed for strongly interacting systems, we postulate that the adsorbing unimer undergoes extreme flattening, since the adsorption rate is limited by diffusive transfer. One expects the number of copolymers necessary to fully cover the initially bare surface to become smaller under diffusive transport conditions[10,11] and the effect to be amplified with increasing length of the PVP block. This assumption is in agreement with the experimental results, where with increasing length of the PVP sequence, [863–177] and [1580–117], the number of adsorbed copolymers at the beginning of the slow relaxation process decreases. In fact, the corresponding number of adsorbed chain segments is about 5 × 10^{14}, equal to the value calculated for the surface density of one monolayer. We conclude that diffusion strongly influences the layer conformation in this metastable equilibrium.

Table IV
Layer Characteristics at the End of the Slow Adsorption Regime

sample [x_{PVP}–x_{PS}]	$10^{12}N_{s,max}$, mol/cm^2	$10^{10}x_{PVP}N_{s,max}$, monomol/cm^2	N_H
[771–314]	2.72	20.9	2.3
[412–179]	3.15	13.0	1.5
[863–177]	2.40	20.7	2.3
[1580–177]	2.86	45.2	5.0

However, diffusive transfer should not influence the kinetics of the process when interfacial relaxation becomes rate limiting. The log normal representation was selected because it furnished a linear variation of the adsorption with time, and it is evident that establishment of the thermodynamic equilibrium requires a very long time. The amount of copolymer adsorbed N_s after 2 months is indicated in Table IV for the different copolymers.

Since the surface occupation does not correspond to maximum coverage, we discuss only the different variations of N_s with log t. The slow increase in adsorption, which represents thickening of the anchoring block, seems to be faster when the anchoring sequence is large, as shown in Figure 5. This consideration enables us to decide the rate-limiting factor in this adsorption regime. However, this observation does not support the classical view where formation of the dense brush consecutively induces slower adsorption rates.[2,15] Fast adsorption would be expected to occur for small unimers when the macromolecules have to reptate through the anchored PS chains. Tassin et al. have reported the slow increase of the copolymer adsorption for solution below the cmc, during the long-time kinetics.[3] From observations over 10–12 h, the increase was found to be faster for 60/60 than for 60/180 copolymers. This result shows an important retardation effect resulting from the existence of the brush for this class of PS-PVP copolymers. In our case, the thickening of PVP chains in the slow regime, corresponding to the formation of an interfacial melt, permits (i) a decrease in the number of chain segments of the anchored block in contact with the solvent and (ii) a more efficient protective action of the solubilized PS chain. According to this scheme, we note that after an incubation period of 2 months, the radius of the adsorbed pancake is comparable to the calculated value of the radius of gyration (4 nm) of polystyrene having a polymerization index of 177. The last column of Table IV furnishes the number of multilayers in the melt.[16] It is thus possible that the two sequences determine, by combined action, the kinetic and thermodynamic characteristics of the adsorption process.

Conclusions

The use of radiolabeled polymers in these adsorption studies allowed precise determination of the amount of polymer adsorbed and the adsorption dynamics when the interfacial layer was formed by copolymers derived from solutions of concentration below the cmc. Fast and slow kinetics were observed.

In the fast regime, the density of adsorbed chain segments was used to characterize the adsorbed layer. Under controlled conditions of solution-to-surface transfer of copolymer, the thickness of the adsorbed (collapsed) PVP chain increased with the polymerization index of the PVP block. This constituted a first indication of the structural relaxation affecting the copolymer conformation. A second indication was obtained from measurements carried out under diffusive transfer conditions. We observed that structural relaxation always started from a monolayer conformation, and limited coverages under fast adsorption resulted only from excluded surface effects.

Adsorption measurements run for up to 2 months displayed unusually slow interfacial relaxation and a significant increase in copolymer adsorption. In fact, copolymer interfaces obtained by adsorption from solutions below the cmc need an indefinitely long time to reach surface completion. The adsorbed anchor thickens up to the thickest layer that (i) is permitted by surface and internal cohesive forces of the PVP sequence and (ii) is compatible with the dimension of the solubilized PS block.

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