Macromolecules **1994,** *27,* 5271-5276

Rate of Adsorption of Diblock Copolymers from Micellar Solutions on Solid-Liquid Interfaces

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Received November 17, 1993; Revised Manuscript Received March 28, 1994®

ABSTRACT: We present results relative to the kinetics of adsorption of the diblock copolymer poly(vinylpyridine)-polystyrene on silica from toluene solution using a radiolabeled polymer. The investigations are carried out by controlling the rate of the polymer supply to the adsorbent to determine the kinetic coefficient $K(N_s)$ as a function of the number of adsorbed copolymers N_s. The bulk concentration N is monitored by controlling either the concentration of the polymer solution injected into the reactor or the rate of injection. The variation of $K(N_s)$ *vs* N_s is correlated to the decrease in the surface area available to the solute polymer. The first step in the adsorption is purely to fill the surface by depositing the polymer chains on free surface areas. Over a degree of coverage close to 35%, the adsorption is mainly controlled by limited surface accessibility and also retarded by the diffusional transfer through the dangling polystyrene chains. Experiments carried out with copolymers of different size asymmetry ratios show that the relative size of the polystyrene coil anchored at the surface controls this adsorption mechanism. As the solution is composed of unimers and micelles whose relative concentration is a function of the total copolymer concentration, this parameter is varied to investigate the characteristics of the adsorption of unimers and micelles. We determined that the two constituents adsorb on the surface in a zigzag conformation.

Introduction

Diblock copolymers are considered to be very efficient agents for colloid stabilization due to their ability to provide, in selective solvent, two macromolecular moieties with very different chain solubilities. Our investigation concerns the rate of adsorption of the block copolymer poly(2-vinylpyridine)/polystyrene (PV2P/PS) on silica/toluene interfaces in order to determine the mechanism of the adsorption and the structure of the copolymer layer. Previous work has shown that the PV2P block binds strongly to silica whereas the PS chain is stretched away from the surface.[1] This schema has been refined by experiments with surface force apparatus which has determined that the PV2P block binds strongly to mica in a flattened configuration and that the stretched PS chains exert long-ranged, mutually repulsive forces when two layers are brought to a separation causing overlap of the chains.[2] Further information was obtained by determining the surface density of the block copolymer as a function of the block size asymmetry ratio.[3] This study evidenced that for copolymer of moderate asymmetry the surface density is influenced by the molecular weight of the PVP block while for copolymers of large asymmetry the surface density is determined by the molecular weight of the larger PS block. These observations agreed with theoretical models.[4]

Investigations by surface plasmons on the kinetics of adsorption of block copolymers from solutions below and above the critical micelle concentration (cmc) revealed that unimers and micelles contribute to surface coverage.[5] The kinetic properties of the process were not modeled on the Langmuir kinetic model. These authors also note the higher rate of surface coverage above the cmc as proof of the direct adsorption of micelles and concluded that the first stages of the adsorption correspond to the adsorption of micelles whereas longer times involve adsorption of unimers. In previous work, we also investigated the kinetics of adsorption of unimers and we evidenced the existence of a fast and a slow rate of surface coverage.[6,7] We determined that the interfacial area of the adsorbed block might be schematized by a disk like structure, and we used this geometrical conformation to model the rate of adsorption using the random sequential adsorption algorithm.[8] This localized adsorption mechanism, which corresponds to the fast adsorption process, showed the important role of the excluded surface effect in the rate of surface coverage. It also indicated that the fast rate of adsorption only applied to a degree of coverage close to 0.35.

The adsorptivity of micelles has been theoretically analyzed for spherical micelles in a highly selective solvent, where the corona blocks surround the core and are radially stretched.[9] Taking into account thermodynamic considerations, the authors concluded that the core of the micelle should be protected from adsorption by the highly solvated corona. The rate-limiting process seemed to be the relaxation kinetics of the single chain expulsion accompanying the disappearance of the unimers due to adsorption. The mechanism of the expulsion was described and the scaling law of the process was obtained.[10]

In the present work, we have investigated the rate of adsorption from micellar solutions by continuously determining the concentration of the polymer in the liquid phase. From the balance between the injected and the nonadsorbed material, we were able to describe the rate of adsorption $\Delta N_s/\Delta t$ by introducing the kinetic coefficient K which is only correlated to the degree of surface coverage expressed by the number of adsorbed macromolecules N_s per square centimeter:

$$\Delta N_s/\Delta t = K(N_s)N \qquad (1)$$

where N is the instantaneous bulk concentration expressed in moles per square centimeter of the adsorbent area. We expect that the determination of the kinetics of the adsorption leads to information on the interfacial structure of the unimers and the micelles.

Materials

Diblock Copolymers. The copolymers PV2P/PS of different size asymmetry ratios were identical to those previously used in ref 6. The methods of the synthesis and the radiolabeling of the

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® Abstract published in *Advance ACS Abstracts,* August 1, 1994.

Table 1. Molecular Characteristics

code	M_w[a]	$M_{w,Ps}$[a]	$M_{w,PV2P}$[a]	n_{PS}[b]	N_{PV2P}[b]	β_m[c]	β_s[d]
552	113700	32700	81000	314	771	3.4	1.1
555	61900	18600	43300	179	412	3.0	1.1
569	184400	18400	166000	177	1581	1.9	0.5
568	109000	18400	90600	177	863	2.3	0.5

[a] g/mol. [b] Polymerization index of the corresponding block. [c] Bulk size asymmetry ratio: $\beta_m = (n_{PS})^{0.6}/(n_{PV2P})^{0.33}$. [d] Surface size asymmetry ratio: $\beta_s = (n_{PS})^{0.6}/(n_{PV2P})^{0.5}$.

polymer have been described elsewhere. Their code and characteristics are given in Table 1.

Preparation of the Solutions. The copolymer solutions were prepared by dissolving a given weight of polymer in a weighed mass of solvent. These preparations were left standing for at least 24 h at 25 °C for solutions below the cmc and for at least 1 week for solutions above the cmc. This ageing of the solutions led to reproducible determination of light scattering intensity. On the other hand, no differences were found between the polymer concentrations determined by radioactivity counting before and after high-speed centrifugation of the solutions.

Adsorbents. The adsorbent was nonporous glass beads. The acidic and thermal treatment prior to adsorption is described in ref 6 and was carefully conducted to obtain adsorbents of constant surface characteristics. The number of silanol surface groups accessible for alkaline neutralization was found to be 7.9 per nm^2. These acidic silanol groups are the anchoring sites for pyridine group adsorption. In actual fact, the copolymer was found to strongly adsorb on this hydrated silica (1.75 mg/m^2) whereas silanized silica retained only 0.07 mg/m^2.[1]

Methods

I. Experimental Determination of the Adsorption Rate. The sorbent and the solvent were introduced into a cell reactor of volume V close to 50 mL. Homogenization of the suspension was achieved by stirring with a magnetic bar. At time zero, the radiolabeled polymer solution at concentration C_0 (cpm/mL) was injected at constant rate J_v (mL/min) into the reactor (containing the sorbent of area S) using a regularly driven calibrated glass syringe. Simultaneously, the liquid phase flowed through the reactor outlet after filtration through a filter fitted to retain the sorbent inside the cell reactor. This effluent was collected for a time Δt (min), and successive samples n were analyzed for radioactivity. In the case of the very slow injection rate, pure solvent was injected in the pipe at a constant rate at the outlet of the reactor to obtain sizeable volumes of the radioactive effluent. On the other hand, for experiments carried out below the cmc and with very dilute solutions, the polymer concentration C_0 was corrected by the amount adsorbed on the wall of the vessel.

The increase in adsorption ΔA_s for a time increment Δt is obtained from the relationship

$$[\Delta A_s]_{n+1} = J_v C_0 \Delta t - A_{n+1} - \frac{V}{2J_v\Delta t}(A_{n+2} - A_n) \qquad (2)$$

where A_n represents the radioactivity of the nth sample. At time $t = 0$, $n = 0$. It is important to note first that insofar as the polymer concentration in the liquid phase suspending the glass beads progressively changes during adsorption, there is no simple relationship between the variation of the adsorbed amount as a function of time when the rate of the polymer injection is changed. The rate of the adsorption increase is more clearly expressed by (1). Second, in (2), it is implicitly assumed that the injected polymer is instantaneously distributed throughout the volume V of the liquid phase contained in the reactor. The volume V could be separated into two volumes $(V - \delta S)$ and δS, where δS represents the unstirred interfacial liquid layer of thickness δ surrounding the adsorbent of area S.[11] We took into account the influence of the retardation effect of the unstirred layer by assuming a concentration gradient in the stagnant layer around each bead by combining (1) with Fick's laws of diffusion. We obtained that the calculated diffusion-layer thickness is close to 4 molecular diameters, so that the kinetic coefficient values do not depart significantly from those determined by assuming negligible diffusion effects. This theoretical result can be confronted to the following experimental results. In the presence of nonadsorbing glass beads, the variation of the radioactivity of the effluent as a function of time is strictly equal to that calculated by assuming that the polymer is instantaneously diluted in the volume V.[11] In the presence of an adsorption involving strong interactions, all of the injected polymer is instantaneously adsorbed, the limit of detection in the liquid phase being of the order of 10 ng.[8] The experimental procedure thus eliminates all retardation effects resulting from the diffusional polymer transfer from the bulk phase to the adsorbent surface.

We define the number N of nonadsorbed polymers per square centimeter of the adsorbent area averaged over the period Δt and the number ΔN (mol/cm^2) of macromolecules which are supplied to 1 cm^2 of adsorbent during the period Δt of injection.

$$\Delta N = J_v N_0 \Delta t/S \qquad (3)$$

with

$$N_0 = C_0/R_s M_w \qquad (4)$$

The corresponding increase in adsorption ΔN_s (mol/cm^2) is related to ΔA_s through

$$\Delta N_s = \Delta A_s/(S R_s M_w) \qquad (5)$$

where S, R_s, and M_w are respectively the area of the adsorbent, the specific radioactivity (cpm/g), and the mean molecular weight of the polymer. The mean adsorption rate $\Delta N_s/\Delta t$ (min^{-1}) is related to the kinetic coefficient $K(N_s)$ as indicated in (1).

II. Random Sequential Adsorption (RSA) as a Model of Localized Adsorption. RSA was first used to calculate the maximal coverage when disks are randomly deposited onto a plane. More recently, it has been used to determine the corresponding rate of surface coverage.[12,13] The model assumes that a disk is deposited onto a plane when the corresponding area is free of adsorbed disks. When the selected position is already occupied, adsorption does not occur and, as in our experimental procedure, the disk is counted among those remaining in the "liquid phase". Clearly, in simulation, it is needless to take a sample from the "liquid phase" to determine the disk concentration. We used a model which allows about 1230 disks of radius r to be deposited onto a rectangular plane surface of dimension $60r \times 120r$.

To correlate computer simulation and experiments, the relative importance of the rate of polymer transfer from the solution toward the sorbent surface and the rate of the polymer supply to the liquid phase contained in the reactor should be estimated. The computer time and calculation of the adsorption rate in simulation were determined as follows:

At time $t = 0$, ΔN_c disks are placed in the vicinity of the plane. Each disk is assumed to carry out only one attempt to adsorb before the time is incremented by Δt_c. The simulation indicates that after one period Δt_c, ΔN_{cs} disks succeed in adsorbing while N_c disks fail. During a second period Δt_c, the constant number of attempts ΔN_c is increased by the number N_c which failed in the first period. As in the experiments, the nonadsorbed disks remain in the system and again attempt to adsorb during each period Δt_c. Our simulation still indicates the new values ΔN_{cs} and N_c after $(\Delta N_c + N_c)$ attempts. This procedure is continued until the full surface of the plane is fully covered with disks. The time increment Δt_c was chosen equal to 1.

The correlation between computer "time" and physical time is easily established because the mass transfer rate is limited by controlling the rate of polymer supply: one time unit may be measured by the number of macromolecules being injected into the reactor per unit area of adsorbent or by the number of successive attempts to deposit the disks on the plane area. To determine quantitatively the influence of ΔN_c on the variation of the kinetic coefficient $K(N_{cs})$, a wide range of supply rates was investigated. As one might expect, different values of ΔN_c lead to different patterns when the surface coverage is represented as a function of time. We are only interested in determining the kinetic coefficient as a function of the surface coverage, and we define a mean kinetic coefficient which, as in the experimental procedure, determines the probability of adsorption onto the plane area if N_{cs} are previously adsorbed at random:

$$K(N_{cs}) = (\Delta N_{cs}/N_c) \qquad (6)$$

In the following section, the results and discussion mainly concern the similarity existing between the different patterns of the kinetic coefficient $K(N_s)$.

Results and Discussion

The selectivity of toluene toward the PV2P–PS copolymer has been evidenced by analysis of the relative composition of the two phases coexisting at equilibrium for a concentrated mixture of the two homopolymers PS (15 g) and PV2P (15 g), both of a molecular weight close to 20 000 in 70 g of toluene. The dense gel phase containing the PV2P (15 g) retained only 5 g of toluene while the liquid phase containing the PS (15 g) retained 65 g of the solvent.[14] On the other hand, the compatibility of the homopolymer PV2P and toluene has been found to depend on the molecular weight. Homopolymers of a molecular weight under 7000 are readily soluble while those of a molecular weight over 60 000 appear to be nonsoluble.[3] Therefore, toluene should be a selective solvent for our copolymers. The formation of associated molecules is a property of dilute solutions of block copolymers in selective solvent. Micellization of block copolymers leads to a closed association where the micelles are characterized by a narrow distribution of micellar size and mass. The coexistence of the molecularly dispersed and associated components supports the concept of the critical micelle concentration (cmc).[15] This concentration can be obtained with different techniques, and a large disparity in the mass of the micelles has been determined, probably due to the different degrees of dryness of the solvent.[16] For our system, we could estimate the degree of micellization to be between 10 and 20 from light scattering measurements, but we were unable to determine the cmc. From surface exclusion chromatography, we estimated the cmc to be close to 10^{-10} mol/mL. This value should be compared to the value of 5×10^{-10} mol/mL determined by Tassin *et al.* for the same system but of relatively larger PS moiety.[5]

I. Influence of the Rate of the Copolymer Supply J_vN_0/S to the Adsorbent on the Coefficient of the Adsorption Rate $K(N_s)$. 1. The Concentration C_0 Is Equal to 10^{-10} mol/mL and Corresponds to the cmc. Copolymer 552 [171–314] was chosen for this study because, first, in solution it is characterized by a size asymmetry ratio equal to 3.4 and, in the adsorbed state, it is characterized by a size asymmetry ratio close to 1. This means that the retardation of the adsorption kinetics due to excluded surface area effects cannot be differently controlled by the adsorbed block PV2P and the soluble PS chain, if the interfacial reconformation rate is fast. With this assumption, the adsorbed diblock looks like a cylinder protruding from the surface, with a radius close to the radius of gyration of the PS block. In the soluble state, the PV2P block is in the collapsed state, and one may conclude that the copolymer adsorbs by interfacial deposition, only if the available free area is close to the cross-sectional area of the PS coil in the solution.

Figure 1 shows the kinetic coefficient $K(N_s)$ as a function of the amount of macromolecules already adsorbed N_s. The concentration of the polymer solution was equal to 0.9×10^{-10} mol/mL and the injection rate 6×10^{-12} mL/min. The curve of Figure 1 may be superimposed onto that of Figure 3 of ref 6, and the amount N_s of the polymer adsorbed at the end of the fast adsorption tends to 1.1×10^{-12} mol/cm^2. We assume that the solution is free of micelles at 0.9×10^{-10} mol/ml. Figure 2 represents one possible schematic representation of the polymer layer at the end of this adsorption process, which leads us to consider that the adsorption kinetics may be determined from the rate of the random sequential adsorption of disks on a plane surface. This information is also is given in Figure 1, and we note that the experimental rate of surface coverage and that determined by simulation may be strictly superimposed. The ratio of the area effectively covered by the adsorbed disks to the total available surface area is close to 0.35. This value is equal to the degree of coverage experimentally determined when the density of adsorption at the end of the fast adsorption regime, 1.1×10^{-12} mol/cm^2, is compared to that at full surface coverage, 2.75×10^{-12} mol/cm^2.[7]

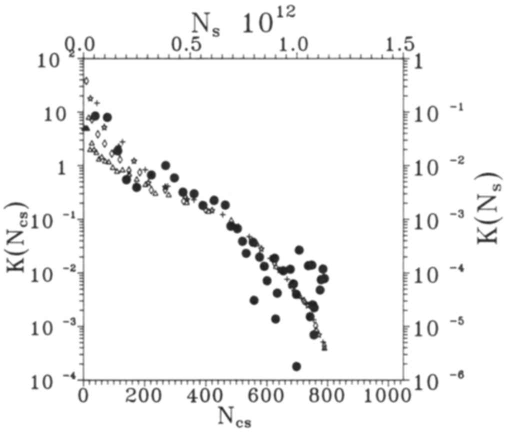

Figure 1. Representation of the kinetic coefficient $K(N_{cs})$ as a function of the number N_{cs} of adsorbed disks in an adsorption process developing with features of the random sequential adsorption model for different rates of disk supply ΔN_c: (△) 5; (◇) 20; (★) 50; (+) 100 (left ordinate). Adsorption of copolymer 552: representation of the kinetic coefficient $K(N_s)$ (s^{-1}) from a solution of 0.9×10^{-10} mol/mL as a function of the number N_s of moles already adsorbed (•) (right ordinate).

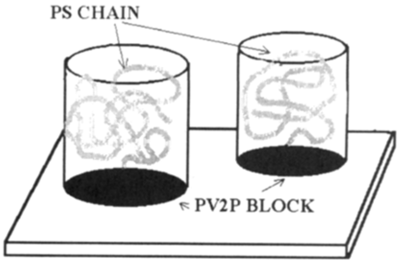

Figure 2. Representation of the copolymer layer at a small degree of surface coverage showing the limitation inherent in the model of the random deposition of disks.

The adsorption kinetics below the cmc has been considered by Ligoure and Leibler, and the authors focus attention on the penetration of chains through the brush protecting the wall.[17] The theory addresses copolymers characterized by a large size asymmetry ratio, so that the anchoring chain is very short. Before brush overlapping (the range covered by our study), there is essentially no activation barrier and the adsorption is controlled by chain diffusion in the solution. Above the overlap concentration, further adsorption requires some stretching and this phenomenon constitutes a potential barrier opposing the penetration of the chains.

We conclude that the rate of the polymer adsorption as a function of the number of adsorbed macromolecules may thus be estimated from simulation using the algorithm of the random sequential adsorption model. Insofar as the model requires that the adsorbed molecule remains fixed

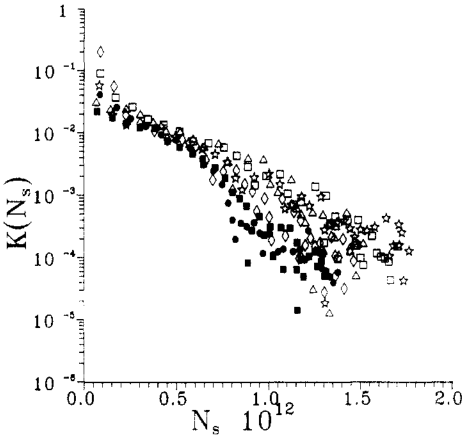

Figure 3. Representation of the kinetic coefficient $K(N_s)$ (s^{-1}) *vs* the surface occupation N_s expressed in mol/cm^2 for experiments carried out with the copolymer 552 at the cmc (10^{-10} mol/mL) at two rates of copolymer supply: (solid symbols, two experiments) 1.6×10^{-11} mol/min; (open symbols, four experiments) 3.6×10^{-11} mol/min.

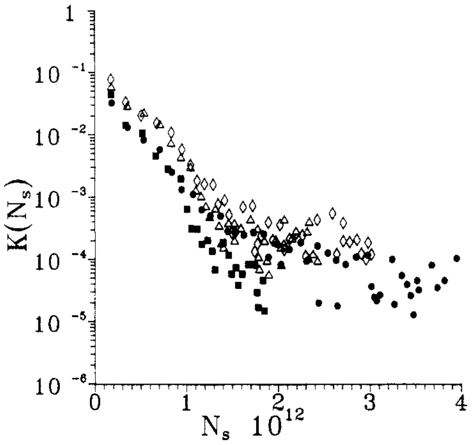

Figure 4. Representation of the kinetic coefficient $K(N_s)$ (s^{-1}) *vs* the surface occupation N_s expressed in mol/cm^2 for experiments carried out with the copolymer 552 at the concentration of 3.5 × cmc (3.5×10^{-10} mol/mL) at two rates of copolymer supply: (solid symbols, two experiments) 2.0×10^{-11} mol/min; (open symbols, two experiments) 10^{-10} mol/min.

at the impact point, without the possibility of moving in the adsorption plane, this result is in agreement with the observation that the adsorbed molecules do not exchange with those in solution, as indicated by Parsonage *et al.*[3] The mechanism of the copolymer adsorption (localized adsorption) obviously presents some similarity with that of the adsorption of polystyrene onto glass beads but is really different from that of the adsorption of a polyelectrolyte onto a charged adsorbent in aqueous medium (mobile adsorption).[8] Insofar as the representation of the increase of the amount of polymer adsorbed as a function of time cannot be clearly discussed when the polymer concentration is continuously changed, we chose to express the result of the adsorption kinetics by the representation of the kinetic coefficient $K(N_s)$ as a function of the amount of macromolecules already adsorbed N_s. This representation enabled the adsorption mechanism to be clearly determined.

Figure 3 shows $K(N_s)$ *vs* N_s for a set of experiments carried out by injecting polymer solutions at identical concentrations but at two different rates of injection equal to 1.6×10^{-11} (two experiments) and 3.8×10^{-11} mol/min (four experiments), respectively. The shape of the curves is similar to that of Figure 1. However, at a given degree of surface coverage, an increase in the injection rate leads to a higher adsorption rate.

2. The Concentration N_0 Is Larger Than the cmc. Figure 4 shows the variation of $K(N_s)$ *vs* N_s for experiments carried out using N_0 equal to 3.6 × (cmc) at the two rates of polymer injection equal to 2×10^{-11} (two experiments) and 10^{-10} mol/min (two experiments), respectively. One clearly observes that a fast rate of injection leads to fast total adsorption.

Our interpretation of the relative increase in the total adsorption rate with the increase of the polymer injection rate is based on the assumption of the existence of two adsorption mechanisms which may be more or less concomitant. The first one can be schematically represented by the random sequential adsorption model which allows the macromolecules to be freely deposited and adsorbed on the still free surface portions. The rate of the second mechanism has been described by Joanny and Johner, who assumed the diffusion mechanism through the already formed layer to be rate controlling.[9] The adsorption probability during this slow adsorption regime, when the copolymer diffuses through the dangling PS chain, is, however, limited by the interfacial area of each small free portion remaining between the already adsorbed PV2P blocks. At a given N_s coverage, the total interfacial area of these free portions may depend on the rate of the structural reconformation of the adsorbed polymer if one assumes that, once the polymer is adsorbed, the radius of the cross-sectional area of the anchoring PV2P block slowly increases from its value in solution $R_{\mathrm{PV2P}} \approx (M_{\mathrm{PV2P}})^{1/3}$ to its interfacial equilibrium value $R_{\mathrm{s,PV2P}} \approx (M_{\mathrm{PV2P}})^{1/2}$, while the limitation arising from the presence of one PS block is not modified and proportional to $R_{\mathrm{s,PS}} \approx (M_{\mathrm{PS}})^{2/3}$. If the relaxation time of the reconformation is of the order of the period of the polymer injection, it may result that, at a given coverage N_s, the free area available by diffusion through the polymer layer, is larger for the higher rate of polymer injection than for the very slow one. Actually, reconformation is able to control the amount of polymer adsorbed.[18-20] This mechanism of structural reconformation may induce a faster interfacial diffusion-limited coverage at the higher rate of injection than at the slower one.

II. Influence of the Diblock Copolymer Asymmetry Ratio on the Pattern of the Variation of the Kinetic Coefficient $K(N_s)$ *vs* $N_s n_{\mathrm{PV2P}}$. To obtain information on the interfacial structure of the adsorbed layer, the kinetic coefficient was analyzed as a function of $N_s n_{\mathrm{PV2P}}$, n_{PV2P} being the polymerization index of the PV2P block.

One set of experiments was carried out to determine the retardation effect resulting from the copolymer diffusion through the interfacial PS layer. Figure 5 shows the variation of $K(N_s)$ *vs* $N_s n_{\mathrm{PV2P}}$ for the adsorption of copolymers 569 [1581–177] and 552 [771–314] at a rate of injection close to 5×10^{-11} mol/min. Copolymer 569 is characterized by a size asymmetry ratio in the adsorbed state equal to 0.5 whereas that of copolymer 552 is equal to 1.13. A quite similar result is obtained for copolymers 555, 568, and 569, characterized by an identical molecular weight of the PS block and a different polymerization index of the PVP2 block, 412, 863, and 1581, respectively. The variation of $K(N_s)$ *vs* $N_s n_{\mathrm{PV2P}}$ is reported in Figure 6 for experiments carried out at a constant rate of polymer injection equal to 7×10^{-11} mol/min. All of the curves are superimposed in a large domain of $N_s n_{\mathrm{PV2P}}$. At a given value close to 10^{-9}, deviation occurs, indicating that the less dense PS layer of copolymer 569 weakly opposes the diffusional transfer whereas the more dense layer of

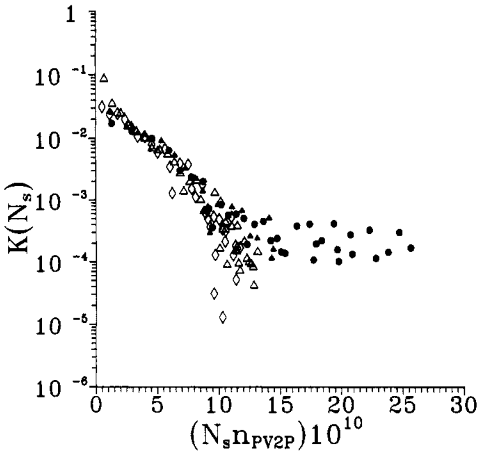

Figure 5. Representation of the kinetic coefficient $K(N_s)$ (s^{-1}) *vs* the surface occupation $N_s n_{PV2P}$ expressed in mol of PV2P chain segments/cm^2 for experiments carried out at the concentration of 1.2×10^{-10} mol/mL and at a rate of polymer supply of 3.8×10^{-11} mol/min for the copolymer 552 (open symbols, two experiments) and at the concentration of 2×10^{-10} mol/mL and at a rate of polymer supply of 6.0×10^{-11} mol/min for the copolymer 569 (solid symbols, two experiments).

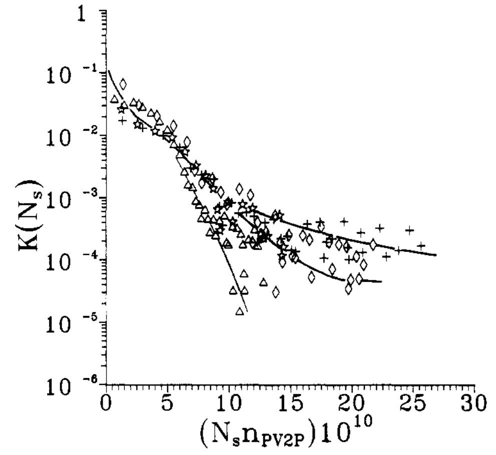

Figure 6. Representation of the kinetic coefficient $K(N_s)$ (s^{-1}) *vs* the surface occupation $N_s n_{PV2P}$ expressed in mol of PV2P chain segments/cm^2 for experiments carried out at the concentration of 2.0×10^{-10} mol/mL and at a constant rate of polymer supply of 7.0×10^{-11} mol/min for the copolymers 555 (△), 568 (◇), and 569 (★,+) (two experiments).

copolymer 552 strongly delays the beginning of this process. Obviously, above a critical coverage $N_s n_{PV2P}$ close to 10^{-9} mol/cm^2, the progress of the adsorption may result from the penetration of the unimers by a reptation-type diffusion as taken into account by Ligoure and Leibler.[17] Our result indicates that the kinetic coefficient of the process is of the order of 5×10^{-4} s^{-1} when the interfacial obstruction due to the dangling PS chains is relatively low. Otherwise, the rate leading to adsorption completion is very small[6] and cannot be determined by the present experimental procedure.

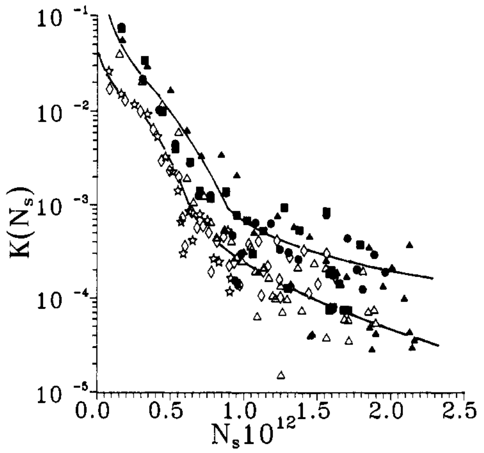

Figure 7. Representation of the kinetic coefficient $K(N_s)$ (s^{-1}) *vs* the surface occupation N_s expressed in mol/cm^2 for experiments carried out with the copolymer 569 at the concentrations of 2.2×10^{-10} mol/mL (open symbols, three experiments) and 9.5×10^{-10} mol/mL (solid symbols, three experiments) but with an equal rate of polymer of 1.6×10^{-11} mol/min.

The main result is that during the adsorption period controlled by the deposition of the macromolecules and the adsorption of the PV2P block, where the kinetics is controlled by the random sequential adsorption, the density of adsorbed PV2P chain segments is close to 10^{-9} and does not depend on the chain characteristics. This coverage is equivalent to 6×10^{14} pyridine groups opposing the 2.8×10^{14} silanol surface groups of the silica area already occupied at the end of the fast adsorption. A schematic view of the interfacial PV2P block should be the zigzag conformation (every second segment being adsorbed) of the flat adsorbed polymer chain determined by Killmann *et al.* for homopolymer and copolymer adsorption on silica surfaces and where hydrogen-bridged SiOH groups are responsible for the adsorption.[21] In the present situation, acid–base interactions are assumed to occur between the silanol and the pyridine groups.

III. Influence of the Micelle Concentration on the Kinetic Coefficient $K(N_s)$.

This set of experiments was carried out by injecting the solution of copolymer 569 [1581-177] at the two different concentrations of 2.2×10^{-10} and 9.5×10^{-10} mol/mL. Results of $K(N_s)$ *vs* N_s are represented in Figure 7, which shows that when the copolymer solution is enriched with micelles but injected at such a rate that the rate of polymer supply is constant (6×10^{-11} mol/min), the adsorption kinetics is faster. The following conclusion can be drawn.

If the micelles were able to relax quite instantaneously after being injected initially into the pure solvent and thereafter into an infinitely dilute solution, in order to give rise to unimers by the fission mechanism described by Halperin and Alexander,[10] the variation of $K(N_s)$ as a function of N_s should correspond to a unique curve.

If, as assumed by Johner and Joanny,[9] the micelles are able to relax slowly with time to restore the equilibrium, the limiting step is the expulsion of chains by the micelles insofar as we demonstrated that the diffusional transfer is negligible in our experimental procedure. The kinetic coefficient $K(N_s)$ of the adsorption process obviously must be smaller when the concentration is large, as being limited by the micelle relaxation. The experimental result contradicts this assumption of the theory of Joanny and Johner, which most certainly addresses copolymers of higher asymmetry ratios. In favor of the adsorption of micelles is the result obtained from light scattering measurements. Though the corona of the micelle is in good solvent, the micelles behave as if they are in poor solvent: the second virial coefficient A_2 is of the order of (-1 to -4) $\times 10^{-4}$ g/mL. This negative value is not clearly understood insofar as A_2 is representative of the interactions between the micelles themselves as well as between the micelles and the unimers.[22] The resultant attractive interaction may explain why the behavior of the micelles toward the adsorbing surface is similar to that of the unimers.

Therefore we conclude that micelles are not submitted to relaxation prior to being adsorbed, so that even if the rate of polymer supply is equal in the two sets of experiments, the composition of the solution in unimers and micelles is different. The reason for the faster adsorption lies in the fact that, at a given degree of coverage N_s, the composition of the adsorbed copolymer layer in unimers and micelles also depends on the composition of the solution being injected. This may be simply explained by consideration of the random sequential adsorption process. The unimers are present at a relatively larger concentration in the dilute micellar solution. After adsorption, they may prevent a certain number of micelles from further deposition and adsorption by excluding a surface area much larger than the area effectively covered. On the other hand, for the micellar solution, a larger number of micelles may be adsorbed while allowing the unimers to progressively adsorb onto the areas from which the micelles are excluded due to their larger size. The aspect as well as the shape and relative size of the two components of the copolymer solution will be discussed in the companion paper.[23]

From the variation of the kinetic coefficient as a function of the number of adsorbed copolymers for experiments carried out below and above the cmc, we can conclude that the adsorption of both the micelles and the unimers proceeds by a localized adsorption mechanism, the adsorbed species strongly adhering to the adsorbent. We note that this mechanism implies that the adsorbed species cannot move in the interface as has been assumed to occur in the mobile adsorption processes.[8] This result is essential in the analysis of the results presented in ref 23.

Summary

Our investigations on the kinetics and mechanism of diblock copolymer adsorption on solid/liquid interfaces are only presented in terms of the variation of the kinetic coefficient $K(N_s)$ *vs* N_s. Actually, the degree of surface coverage was found to be the sole parameter managing the adsorption kinetics in the early state of the establishment of the polymer layer.[8] The bulk concentration of the polymer solution contributed only according to the mass action law. For the copolymer solution composed of unimers and associated species, the situation appeared to be more complicated. The demonstration that the kinetics of micelle and unimer adsorption can be apprehended by only using the total number of adsorbed copolymers N_s is essential to the understanding of the establishment of these interfaces.

We have demonstrated the benefit of controlling the rate of polymer supply to the adsorbent in the study of the mechanism and kinetics of diblock copolymer adsorption. The variation of the kinetic coefficient as a function of the degree of surface coverage determined from experiments carried out with very dilute solution (below the cmc) could be fitted with the result obtained by the random sequential adsorption model (localized adsorption). This mechanism was also found to describe the adsorption of micellar solutions. Data obtained from experiments carried out by varying the rate of polymer supply by only changing the rate of the liquid injection showed that the kinetic coefficient increased with this parameter, both at and above the cmc. This may be an outward sign of the existence of the reconformation of the adsorbed unimers and micelles.

By changing the asymmetry ratio of the copolymer, we could evidence the retardation effect on the slow adsorption process resulting from the presence of the PS coil. Actually, the progress of the adsorption was limited by the existence of this layer of variable chain segment density.

Data obtained from experiments carried out at constant rate of polymer supply with solutions of different concentrations led us to conclude that micelles, like unimers, adsorbed on the silica surface. A similar conclusion was drawn by Gast and co-workers for the system poly(ethylene oxide)/polystyrene adsorbing in cyclohexane onto sapphire.[24] Due to the existence of a slow adsorption regime limited mainly by the surface accessibility and occasionally by the diffusion through the dangling layer, in addition to that resulting from deposition and adsorption, which is highly irreversible, it appeared that it should be very difficult to obtain a true thermodynamic equilibrium situation for this class of adsorbed copolymers.

Acknowledgment. This work has been supported by the CNRS under project 936 GDR "Mesure des forces de surfaces". We thank Prof. J. F. Joanny, Dr. C. Marquez, and Dr. A. Johner for helpful discussions. Dr. J. M. Widmaier is acknowledged for kindly providing the copolymer samples and J. Widmaier for experimental assistance in radiolabeling the copolymer samples. We also gratefully acknowledge G. Maennel for devising the experimental equipment.

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