# Hydrodynamic Thickness of Interfacial Layers Obtained by Adsorption of a Charged Diblock Copolymer on a Selective Surface from Aqueous Solutions

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ABSTRACT: The solution properties of the asymmetric diblock copolymer poly(styrenesulfonate)−poly(vinylpyridine) were investigated using light scattering, viscometry, and fluorescence probing. Adsorption on neutral and electrically charged (selective sorbent) materials was determined using radiolabeled polymer, and the hydrodynamic thickness of adsorbed layers was measured by quasi-elastic light scattering measurements. In water, the copolymer displayed dual hydrophobic properties. Its strongest hydrophobic character, responsible for adsorption on the neutral material poly(tetrafluoroethylene) (Teflon), was abolished by addition of very small amounts of electrolyte, while the volume of the less hydrophobic moieties was pH dependent. The solubility domain of the copolymer was limited to the pH range between 2.5 and 3.8 and an ionic strength of less than 0.01. Micelles formed in water or 0.001 M NaCl solution showed a maximum value of the radius of gyration close to 220 nm. Partially reversible adsorption on positively charged polystyrene latex particles bearing amidine surface groups could involve both hydrophobic and ionic interactions, while the hydrodynamic thickness of the residual interfacial layer after rinsing with solvent was dependent on the initial copolymer concentration in the supernatant phase and on the pH and electrolyte concentration of the final suspending phase. The adsorbed copolymer layer appeared to be well suited to the stabilization of colloids in electrolyte media due to its electrosteric protective effect, which increased with electrolyte concentration.

## Introduction

Diblock copolymers in selective solvents constitute complex systems where solubility and structure depend on critical polymer and solvent parameters.[1,2] Since a selective solvent is a nonsolvent for one polymer block and a good solvent for the second block, this situation leads to well-organized systems in which unimers and micelles coexist when the polymer concentration is greater than the critical micelle concentration. At relatively low concentrations, micelles take the form of a sphere where the core consists of a compact assembly of the nonsoluble blocks and the outer shell of a corona of the soluble blocks.[3] Generally, these soluble micelles are relatively monodisperse in size and mass.[4]

Diblock copolymers of styrenesulfonate and vinylpyridine constitute a class of polymers of well-defined properties. When the blocks are of equal length and relatively short (less than 200 monomers), the copolymer is water soluble between pH 1 and 7 and presents typical solution characteristics ranging from a monomolecular to a micelle conformation with decreasing pH.[5,6] If the length of the soluble stabilizing vinylpyridine block is greater than that of the anchoring styrenesulfonate block as in the present system, the situation is more complex. The first part of the present paper is thus devoted to a presentation of the solution characteristics of this diblock copolymer. Since the aim of the study was to determine the conditions leading to colloid stabilization,[7] the interfacial characteristics of colloid−polymer complexes were determined, and these are presented in the second part of the paper. As a model colloid, we chose a polystyrene latex bearing positively charged amidine groups whose surface density, as calculated from the electrophoretic mobility of the latex particles, was found to be constant in the pH range of interest.

The initial problem was to determine the solution characteristics of the water-soluble asymmetric copolymer. According to the usual schematic representation of a micelle, we conjectured that optimal protection of the core against polymer aggregation would be provided by a large shell offering the greatest electrosteric protection and that this situation should be attained for a vinylpyridine block long and highly protonated as can be the case in strongly acidic medium. In fact, under such conditions we found the copolymers to be nonsoluble in water even after heating the mixture for long periods. When the degree of protonation was relatively low, the copolymer was soluble in water and aggregated in the presence of electrolyte. However, at very low degrees of protonation the micelles once again become nonsoluble. Solubility was also found to depend on the length of the vinylpyridine block, sequences shorter than that of the molecule employed in the present study being insufficient to solubilize the copolymer. This could arise from the relative hydrophobicity of the polymeric material in aqueous media, as such problems do not occur in organic media.

On the other hand, the present system displays similarities to complex polyelectrolytes, where strong electrostatic interactions induce great modifications in the solubility of the individual constituents.[8] Certain similarities to polyampholytes are also apparent. These latter polyelectrolytes, which present neutral, negative, and positive groups coexisting along the polymer backbone, have been shown to require strong electrical charge screening for solubility and may therefore be considered to display an antipolyelectrolyte character.[9] Our diblock copolymer constitutes a particular type of polyampholyte where one short block contains only negatively charged styrenesulfonate groups while a second long block contains neutral pyridine and positively charged pyridinium groups in a statistical distribution. The ionic strength of an aqueous solvent would be expected to play an important role in the solubility

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and interfacial conformation of such a copolymer, and this point is discussed in the third part of our paper.

## Materials and Methods

**Copolymers.** The polystyrene–polyvinylpyridine copolymer was synthesized by anionic polymerization of styrene with functional end groups in tetrahydrofuran, followed by polymerization in situ of the 2-vinylpyridine component. Average indexes of polymerization of respectively 177 and 1581 for the polystyrene and poly(vinylpyridine) blocks were calculated from light scattering measurements performed in tetrahydrofuran, first on the living block polystyrene and after on the diblock, the variation of the refractive index with the concentration being quite similar for each block. The polystyrene block was sulfonated using the technique of Turback with a triethyl phosphate–sulfur trioxide complex, which enabled the reduction to a minimum of parasite reactions and polymer degradation and gave a sulfonation yield close to completion. Details of this procedure have been given elsewhere.[5,10] Radiolabeling of the polymer was performed in aqueous solution by quaternization with $I^{14}CH_3$ of two pyridine groups in every thousand, after which the solution was heated to 80 °C for 24 h and then centrifuged for 4 h at 20 000 rpm to eliminate aggregates and/or insoluble polymer. The loss in specific radioactivity was of the order of 5–10% in dilute solution. Quasi-elastic light scattering measurements showed the presence of two molecular populations of distinctly different mobility, while classical light scattering revealed two species of different radii of gyration appearing as determined in the domains of large and small scattering angles. The larger species seemed to be relatively monodisperse in size and was assumed to represent micelles.

**Colloid.** Latexes of two different sizes were used. A spherical polystyrene latex bearing amidine groups $C(=N^+H_2)(NH_2)$ (ADC, Portland, OR), of particle diameter 225 nm and surface charge density 4.28 $\mu C/cm^2$, was selected as a positively charged colloid suitable for a precise determination of the hydrodynamic thickness of adsorbed copolymer layers. Adsorption experiments were carried out using polystyrene latex bearing amidine groups of diameter 1150 nm bearing a surface charge density 14.2 $\mu C/cm^2$. These larger particles were more suitable for determination of the amount of adsorbed polymer than the small particles since centrifugation of large particle suspensions yielded a clear supernatant, essential for the determination of polymer adsorption by the depletion method. As the copolymer could be expected to adsorb on a wide variety of materials, its adsorption characteristics were studied in containers composed of the hydrophobic neutral sorbent Teflon.

**Hydrophobic Domains.** The presence and relative extent of hydrophobic domains are usually evaluated by fluorescence probing.[11–13] Fluorescence emission spectra of pyrene solubilized in copolymer solutions were recorded using a Hitachi F-4010 spectrofluorimeter in the range 350–500 nm at an excitation wavelength of 335 nm and pyrene concentrations sufficiently low to ensure the absence of excimers. The existence of hydrophobic microdomains was monitored from the ratio $I_1/I_3$ of the intensities of the first and third vibronic peaks, which decreases when the average microenvironment of pyrene molecules becomes less polar. Reference values of $I_1/I_3$ were obtained in water and cyclohexane.[14]

**Relative Viscosity.** The relative viscosity of copolymer solutions was determined by linear extrapolation to zero shear of the shear rate dependent viscosity measured in a Low Shear 30 rheometer (Contraves).

**Titration.** In the case of poly(acrylic acid) and poly(methacrylic acid),[15] the presence of hydrophobic microdomains has been shown to modify the shape of the usual Henderson–Hasselbach plot of the titration curves. While this may be valid for the titration of ionized and protonated blocks of the present copolymer, it is impossible to attribute departure from the usual curves to the dissociation of a given ionic group due to the strong interaction always existing between two oppositely charged moieties. Nevertheless, the copolymer solution in water (solution I) and the copolymer solution in electrolyte solution (solution II) were concomitantly titrated over a predefined pH range by adding constant aliquots of hydrochloric acid to solutions I and II. Solutions I and II were connected by a 0.001 M KCl bridge, this low salt concentration being chosen to reduce the pollution of the copolymer solutions in water by KCl being at the saturation point in the filling liquid of the usual standard electrodes. Differences in electrical potential were recorded between two identical glass electrodes plunged in solutions I and II.[16]

**Hydrodynamic Thickness.** The hydrodynamic thickness HT of adsorbed polymer layers was calculated from the decrease in Brownian mobility resulting from the presence of the polymer on the surface of initially bare colloid particles. The Brownian motion causes the intensity of light scattered from the particles to vary with time. The polymer-coated particles move more slowly than the bare particles so that the rate of fluctuation of the light scattered from them is also slower. Mobilities were determined using a Malvern Zeta Sizer III apparatus and an automatic method. Analysis of the autocorrelation function over a period of time enables the translational diffusion coefficient of particles undergoing Brownian motion to be calculated. From the diffusion coefficient, together with the temperature and viscosity of the suspending liquid, the particle size can be measured. The hydrodynamic thickness of the adsorbed polymer corresponds to the difference between the radius of the bare colloid and the radius of the hard sphere with hydrodynamic characteristics equivalent to those of the polymer-coated particle.

**Copolymer Adsorption.** Adsorption experiments with radiolabeled copolymer were performed using suspensions of a fixed latex concentration in order to allow measurement of the hydrodynamic thickness of the polymeric interface with nonlabeled polymer under identical conditions of volume to surface area ratio. Amounts of copolymer adsorbed on the Teflon container and on the combined latex and Teflon surfaces were calculated by the depletion method. In the latter case, the copolymer solution was poured into the container and left at rest for 3 days to ensure the establishment of an initial adsorption equilibrium on the Teflon surface, after which the latex suspension was added to allow adsorption on the latex particles. Adsorption equilibrium was assumed to be established on the two sorbents when the Teflon and amidine latex were at equilibrium with the same final concentration of copolymer. In some instances, the quantity of polymer adsorbed could be obtained only with relatively poor accuracy due to the limited areas available for adsorption: 15 $cm^2$ for the container and 120–300 $cm^2$ for the latex. Nevertheless, despite the low area of the Teflon container, an absence of adsorption could be verified by comparison of the specific radioactivities of the liquid phase before and after transfer into the container, the limit of radiodetection by liquid-scintillation spectroscopy (Tricarb, Packard) permitting the distinction between zero and 5 $\mu g/m^2$ adsorption.

## Results and Discussion

**Solution Characteristics. Existence of Hydrophobic Domains.** The pyridine groups of the homopolymer poly(vinylpyridine) are protonated below pH 4.0. When these pyridine groups belong to a block connected to a poly(styrenesulfonate) block, under conditions allowing the association of an average of one pyridine group with one sulfonate group, the protonation domain is shifted toward higher pH values (Figure 1).[5] This leads to a situation where below pH 4.0 all pyridine groups are protonated while above pH 4.0 the degree of protonation decreases with pH. As a result, a fall in pH induces a strong decrease in copolymer size and an increase in the degree of micellization, as determined by viscometry and neutron scattering.[6] In light of these observations, we conclude that in the present situation, where the polymerization index of the pyridine block is close to 10 times that of the styrenesulfonate block, the sulfonate groups should be fully neutralized and the presence of sulfonate/pyridinium ion

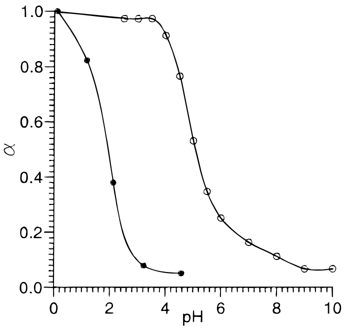

**Figure 1.** Representation as a function of pH of the degree of protonation of the vinylpyridine groups belonging to a homopolymer of poly(vinylpyridine) (●) and to a symmetric poly(styrenesulfonate)-poly(vinylpyridine) copolymer (○).

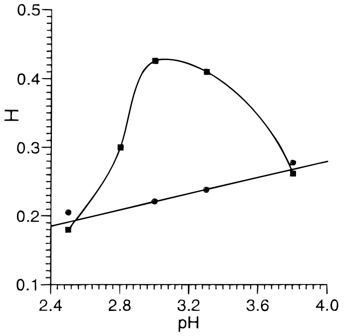

**Figure 2.** Representation of the degree of hydrophobicity $H$ (eq 1) of the copolymer as a function of pH in water (■) and in $10^{-3}$ M NaCl solution (●). $H = 0$ and $H = 1$ correspond to the response of the pyrene probe in water and in cyclohexane, respectively.

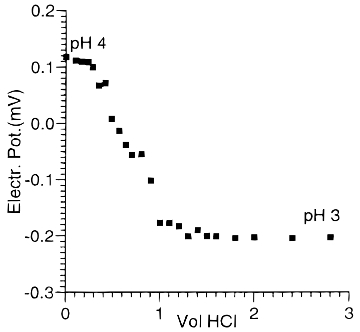

**Figure 3.** Representation of the electrode potential of the system [glass electrode−copolymer in water||KCl, 0.001 M||copolymer in 0.001 M NaCl−glass electrode] as a function of the volume of HCl concomitantly added to the two solutions over the pH range 3−4.

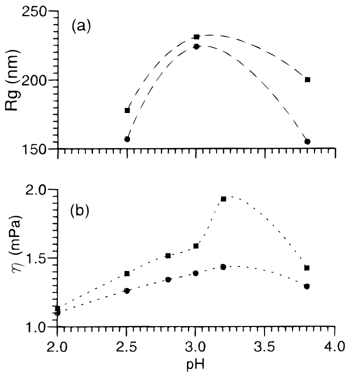

**Figure 4.** Representation of the radius of gyration of the copolymer micelles (a) and the viscosity of the solution (b) as a function of pH in water (■) and in $10^{-3}$ M NaCl solution (●).

pair complexes could lead to the formation of hydrophobic microdomains. The existence of such microdomains may be deduced from the value of the ratio $I_1/I_3$, which is equal to 1.88 in water and to 0.66 in the apolar medium cyclohexane. Using the following definition of the degree of hydrophobicity $H$:

$$H = \frac{1.88 - I_1/I_3}{1.88 - 0.66} \tag{1}$$

this parameter is shown in Figure 2 as a function of pH for the copolymer solutions containing NaCl concentrations of 0 and $10^{-3}$ M. In the presence of $10^{-3}$ M NaCl, $H$ increases progressively with pH. On the contrary, a strong transitory rise in the extent of hydrophobic microdomain formation is observed at approximately pH 3.1 in the absence of NaCl. Two points are worthy of note: (i) this phenomenon only occurs in the absence of salt insofar as an increase in ionic strength of up to 0.05 did not induce any modification of the curve recorded at $10^{-3}$ and (ii) the phenomenon responsible for the increase in hydrophobicity between pH 3.8 and 3.1 is inhibited below pH 3 by the rising concentrations of hydrogen and chloride ions. Titration of the copolymer with HCl in water and in $10^{-3}$ M NaCl solution reveals a small difference in the energy of pyridine group protonation in the pH range 3.8−3.1, whereas initial and final plateau values indicate protonation of the pyridine groups in water or electrolyte solution to require equal energies outside this pH range, charge shielding by $10^{-3}$ M NaCl appearing to be without effect (Figure 3). According to the sign of the potential drop, protonation of the pyridine groups requires more strongly acidic conditions in water than in the presence of $10^{-3}$ M NaCl. Clearly, the presence of hydrophobic microdomains in the absence of electrolyte may account for this effect. On the other hand, the degree of hydrophobicity in $10^{-3}$ M NaCl solution and its linear increase with pH cannot be correlated with a modification of the interaction of pyrene molecules with the polymer skeleton resulting from progressive replacement along the polymer chain of “hydrophilic” pyridinium groups by “hydrophobic” pyridine groups. Indeed, in electrolyte solutions of poly(vinylpyridine) or a mixture of poly(styrenesulfonate) and poly(vinylpyridine) of composition close to that of the copolymer, the probe response is similar to its response in water over the same pH range. Thus the pyrene probe does not reveal the existence of hydrophobic microdomains in such systems. The different levels of hydrophobicity of copolymeric systems therefore most likely result from the presence of organized structures of well-differentiated nature, which are not present in polyelectrolyte complexes.

**Sizes of Micelles and Their Solution Characteristics.** Variations in the extent of the hydrophobic microdomains with electrolyte and hydrogen ion concentrations do not appear to be simply correlated to the size and total volume of the micelles present in the liquid phase (Figure 4). The radius of gyration of the micelles is plotted in Figure 4a as a function of pH in water and in $10^{-3}$ M NaCl solution. A large difference in size is observed only at pH 3.8, where there is no great difference in hydrophobicity, while maximum values of 220 and 230 nm are observed respectively in the presence and absence of electrolyte at pH 3.0, where the difference in hydrophobicity is most important. Figure 4b shows the viscosity at zero shear of copolymer solutions in pure water and in 0.001 M NaCl solution

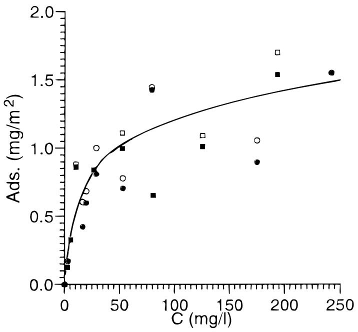

**Figure 5.** Adsorption of the copolymer (mg/m$^2$) on Teflon (exposed area 15 cm$^2$) as a function of the polymer concentration in the liquid phase at adsorption equilibrium at pH 2.5 (■) and 3.0 (●) and after equilibration with solvent at pH 2.5 (□) and 3.0 (○).

as a function of pH. Application of Einstein's law for the viscosity of suspensions of spheres indicates that the volume fraction increases almost linearly with pH below pH 3 and that a lower ionic strength leads to a greater increase in volume fraction. The viscosity in water strongly increases above pH 3 and lower values of the volume fraction are obtained at pH 3.8 in both situations.

We note that the copolymer solubility around pH 3 results from the formation of organized micelles whose size is very pH dependent. As the pH decreases, the micelle size strongly decreases and we assume that (i) as long as the polymer remains soluble, the degree of micellization progressively decreases and (ii) when the polymer becomes nonsoluble, the formation of micelles is inhibited. Slow precipitation from the liquid phase occurs below pH 2 (degree of protonation close to 0.9), with progressive formation of a cloudy suspension from which polymer can be recovered only by centrifugation. Insofar as the homopolymer poly(vinylpyridine) is soluble in this pH range, the nonsolubility of the copolymer should be attributed to the presence of hydrophobic domains which attract each other and slowly form aggregates of small size. Above pH 4 (degree of protonation close to 0.1), the copolymer becomes nonsoluble, precipitates rapidly, and sediments easily. This observation demonstrates that the presence of the poorly soluble outer shell induces strong attractive forces which becomes efficient at each encounter initially between the macromolecules and after between the aggregates. Therefore, the presence of hydrophobic microdomains and the degree of protonation of the free pyridine chain play an essential role in the structure of the solution (micelles or aggregates) and its stability.

**Interfacial Characteristics. Interactions with Teflon.** The most striking result of this study concerns the interactions of the copolymer with Teflon. Whereas strong and irreversible adsorption of about 1.5 mg/m$^2$ of copolymer was observed in water at pH 2.5 and 3.0, no adsorption could be detected in $10^{-3}$ M NaCl solutions under the same pH conditions. In Figure 5, the adsorption at equilibrium from water is represented by filled symbols and the adsorption after rinsing with solvent by open symbols. The absence of desorption when the supernatant solution was replaced by solvent indicates that hydrophobic interactions are responsible for the adsorption of the copolymer on Teflon in water, since electrostatic interactions led to reversible adsorption in the case of poly(vinylpyridine) in contact with poly(styrenecarboxylate) latex at pH 3.[17] A very low concentration of electrolyte is sufficient to modify the solution conformation and stability of the copolymer micelles to the point where no interaction with Teflon is possible. These experiments demonstrate the energy difference between the adsorbed and nonadsorbed states to be small at the molecular level, as confirmed by the data of Figure 3, where modification of the degree of hydrophobicity can be seen to require only a very low electrostatic potential energy and should involve only a few pyridine groups. This suggests that addition of a small amount of electrolyte leads to the disappearance of the hydrophobic domains responsible for irreversible adsorption of the copolymer on neutral materials. The remaining hydrophobic microdomains, which exist in water at pH 2.5 and 3.8 and in $10^{-3}$ M NaCl solutions at all pH values and slightly increase in density with pH, do not appear to contribute significantly to the hydrophobic adsorption process.

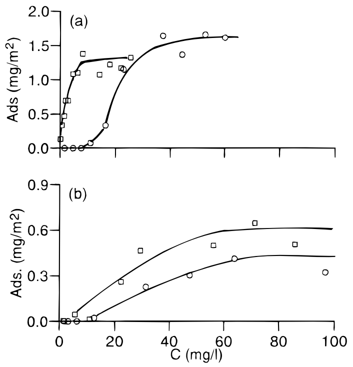

**Figure 6.** Adsorption of the copolymer (mg/m$^2$) on a polystyrene latex bearing positively charged amidine surface groups as a function of the polymer concentration at adsorption equilibrium in water (a) (exposed area 120 cm$^2$) and in $10^{-3}$ M NaCl solution (b) (exposed area 300 cm$^2$) at pH 2.5 (□) and 3.0 (○).

**Interactions with Polystyrene Latex Bearing Amidine Surface Groups.** Figure 6a shows isotherms for adsorption of the copolymer on the model polystyrene latex in water at pH 2.5 and 3.0. Although plateau levels are close to 1.5 mg/m$^2$, adsorption at pH 3 only begins at a concentration threshold of 10 mg/L. Similar thresholds are observed for adsorption from $10^{-3}$ M NaCl solutions under the same pH conditions, leading in this case to a lower surface concentration of 0.4 mg/m$^2$ in the plateau region (Figure 6b). The adsorption is not completely irreversible insofar as some desorption was detected at both pH values when the supernatant solution was replaced with solvent. Partial reversibility is characteristic of adsorption involving ion exchange processes, where the small anions of the solution which are present at constant concentration irrespective of the polymer concentration compete for adsorption with the poly(styrenesulfonate) block of the copolymer at finite and at infinite polymer dilutions. Desorption is limited in water to about one-quarter of the adsorbed macromolecules, possibly due to the presence of the hydrophobic microdomains. Indeed, there is a greater extent of desorption in $10^{-3}$ M NaCl solutions, where only one-third of the initially adsorbed macromolecules remain irreversibly adsorbed at the interface. The existence of a threshold concentration in the adsorption isotherms could result from the stability of the organized micellar structure, which would tend to oppose adsorption on a surface bearing electrical charges of the same sign. In this sense, adsorption on a selective surface of asymmetric diblock copolymers may require prior relaxation of micelles to release free unimers,[18,19] as proposed by

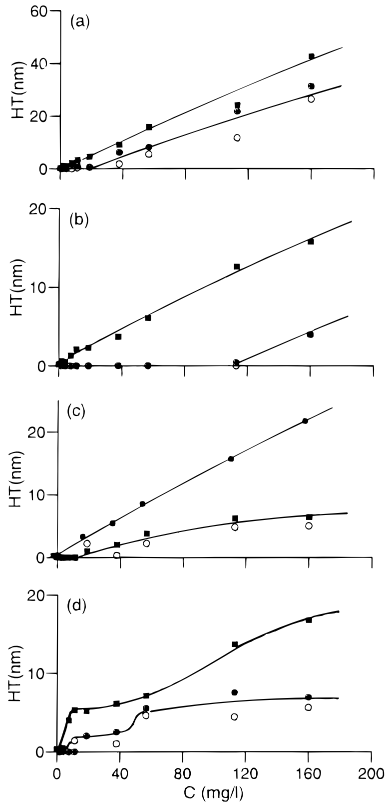

**Figure 7.** Representation of the hydrodynamic thickness HT (nm) of the adsorbed copolymer layer as a function of the polymer concentration in the liquid phase at pH 2.5 (a), 2.8 (b), 3.0 (c), and 3.6 (d). The upper curves (■) correspond to the situation where the layer was in equilibrium with the copolymer solution at concentration *C* (mg/L), while the lower curves correspond to the situation where the copolymer solution was replaced by solvent and the layer thickness determined after 15 min (●) and 4 days (○).

Marques *et al.*, who considered micelles to be no more than reservoirs of unimers,[20] and as taken into account by Johner and Joanny in their study of the adsorption kinetics.[21]

**Hydrodynamic Thickness of the Copolymer Layer Adsorbed on Polystyrene Latex Bearing Amidine Surface Groups as a Function of the Polymer Concentration.** Parts a–d of Figure 7 present the hydrodynamic thickness of the adsorbed layer as a function of the polymer concentration at adsorption equilibrium in water at pH 2.5, 2.8, 3.0, and 3.6. At each pH value, the upper curve corresponds to the situation where the supernatant is at the adsorption equilibrium concentration, while the lower curve corresponds to the situation where the supernatant has been replaced by solvent and the hydrodynamic thickness determined after intervals of 15 min and 4 days. There is a decrease in layer thickness due to partial desorption following replacement of the supernatant by solvent but the contact time seems to play a minor role. The interfacial stability is found to depend on the equilibrium concentration, and the most relevant case corresponds to the situation at pH 2.8, where the threshold concentration giving rise to electrosteric protection of the latex is close to 0.1 g/L after rinsing of the latex–copolymer complex. Plateau values of hydrodynamic thickness approaching 5 nm are obtained above pH 3.

The hydrodynamic thickness of the adsorbed copolymer layer is presented in Figure 8 as a function of the polymer concentration at adsorption equilibrium in $10^{-3}$ M NaCl solution at pH 2.5 (a), 2.8 (b), and 3.0 (c). A common curve is obtained when the supernatant is replaced with solvent and the hydrodynamic thickness determined after 15 min and 4 days. Whereas an extremely thick layer 50 nm deep is observed at pH 2.5, values of about 7 and 4 nm are obtained at pH 2.8 and 3.0, respectively. Since these hydrodynamic thicknesses are smaller than the half radius of gyration of micelles in solution (Figure 4a), this result would indicate the interfacial density of the adsorbed copolymer to be lower than the chain density inside the micelle corona and constitutes evidence in support of the proposed relaxation of micelles prior to adsorption.

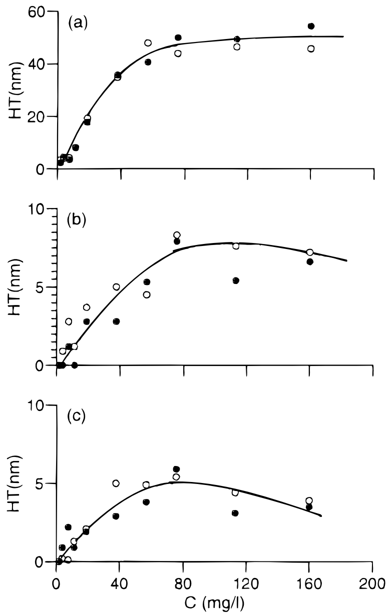

**Figure 8.** Representation of the hydrodynamic thickness HT (nm) of the adsorbed copolymer layer as a function of the polymer concentration in the liquid phase at pH 2.5 (a), 2.8 (b), and 3.0 (c). The common curves correspond to the layer thickness when the equilibrium copolymer solution at concentration *C* (mg/L) was replaced by solvent and the layer thickness determined after 15 min (●) and 4 days (○).

Strong electrostatic repulsion between highly protonated pyridinium groups belonging to projecting blocks could account for the relatively large values of hydrodynamic thickness observed at pH 2.5 in water and in $10^{-3}$ M NaCl solutions, a decrease in protonation with rising pH inducing a strong decrease in layer thickness. Dissociation of sulfonate/vinylpyridinium ion pairs in a solution of ionic strength greater than $10^{-3}$ could also contribute to compression of the adsorbed layer.

**Hydrodynamic Thickness of the Copolymer Layer Adsorbed on Polystyrene Latex Bearing Amidine Surface Groups as a Function of pH.** The hydrodynamic thickness of the interfacial copolymer layer was determined after the latex–polymer complex formed in $10^{-3}$ M NaCl solution at pH 2.5, 2.8, or 3.0 had been rinsed with solvent and equilibrated at varying pH. A first measurement was performed after 15 min (Figure 9a) and a second after 4 days (Figure 9b). Figure 9a shows that adsorption at pH 2.8 yields the lowest hydrodynamic thicknesses and adsorption at pH 3.0 the highest hydrodynamic thicknesses at pH values greater than 3.0, while adsorption at pH 2.5 leads to a strong decrease in layer thickness with pH. The system remains stable after adsorption at pH 3.0. However, as reported in Figure 9b, following adsorption at pH 2.5, the initially stable copolymer layer decreases from 15

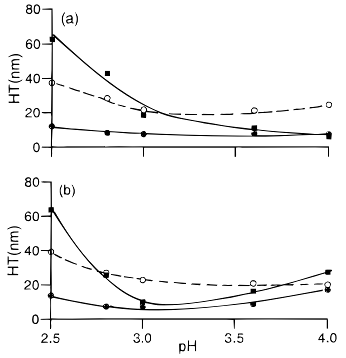

**Figure 9.** Representation of the hydrodynamic thickness HT (nm) of the adsorbed copolymer layer when the layer initially formed in $10^{-3}$ M NaCl solution at pH 2.5 (■), 2.8 (●), or 3.0 (○) was rinsed and equilibrated for 15 min (a) or 4 days (b) with $10^{-3}$ M NaCl solution of the pH indicated on the abscissa.

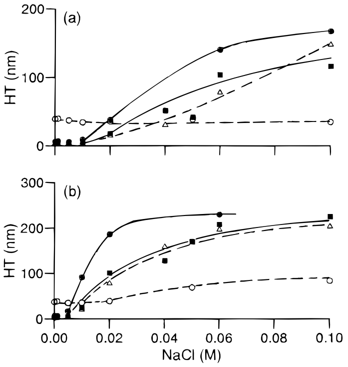

**Figure 10.** Representation of the hydrodynamic thickness HT (nm) of the adsorbed copolymer layer when the layer initially formed in $10^{-3}$ M NaCl solution at pH 2.5 (○), 3.0 (△), 3.2 (■), or 3.6 (●) was rinsed and equilibrated at identical pH for 15 min (a) or 4 days (b) with a NaCl solution of the molarity indicated on the abscissa.

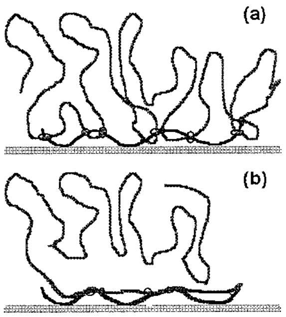

**Figure 11.** Representation of the conformation of the copolymer chain in the adsorbed state, with ion pair links (circles) distributed statistically (a) or in sequence (b) along the vinylpyridinium block.

min to 4 days when the pH falls below 3.5 and increases with time when the pH rises above 3.5. The temporal evolution is small for adsorption at pH 2.8, and only the hydrodynamic thickness measured at pH 4.0 increases with time from 7 to 17 nm. These slow expansions and contractions of the interfacial layer can only result from structural modifications within the layer, as the amount of polymer adsorbed remains constant or can only decrease with changes in the characteristics of the liquid phase. Finally, such pH-induced reorganization of the adsorbed layer constitutes a very slow process.

**Hydrodynamic Thickness of the Copolymer Layer Adsorbed on Polystyrene Latex Bearing Amidine Surface Groups as a Function of the Electrolyte Concentration.** Insofar as an adsorbed polymer layer is thought to provide extremely efficient electrostatic stabilization of colloids suspended in media of high ionic strength, we determined the hydrodynamic thickness of the adsorbed copolymer layer when a latex–polymer complex formed under given reaction conditions was washed with solvent and suspended in aqueous solutions of high electrolyte concentration. Parts a and b of Figure 10 show the hydrodynamic thickness measured after 15 min and 4 days of contact respectively for latex–polymer complexes formed in water at pH 2.5, 3.0, 3.2, and 3.6. The most striking result is that the interfacial copolymer layer greatly expands with electrolyte concentration, in contrast to the usual contraction of adsorbed polyelectrolyte layers in the presence of solutions of increasing electrolyte concentration.[22] Hence such copolymers should be well suited to the electrosteric stabilization of colloidal systems even in concentrated electrolyte solutions. The phenomenon responsible for chain expansion could be the electrolyte-induced dissociation of the pyridinium/styrenesulfonate ion pairs, chlorine ions interacting with the pyridinium groups of one block and sodium ions with the sulfonate groups of the second block. A similar mechanism has been found to be responsible for the solubilization of polyampholytes in concentrated electrolyte solutions.[9] This large chain expansion will only be possible if the pyridinium groups involved in ion pairing are statistically distributed along the vinylpyridine block in the manner indicated in Figure 11a. Electrolyte-induced breakage of pyridinium sulfonate ion pairs then leads to a large increase in chain volume whereas the alternative conformation represented in Figure 11b would attain maximal chain expansion in water as in the case of a polyelectrolyte grafted at one end of the macromolecule.

Comparison of the hydrodynamic thicknesses in parts a and b of Figure 10 indicates that electrolyte-induced reconformation of the interfacial layer is a very slow process. The threshold sodium chloride concentration inducing large chain expansion is close to 0.01 M and this expansion appears to stabilize near 0.05 M, while high initial protonation of the pyridine groups seems to limit the interfacial chain extension. Furthermore, stabilization by pyridinium groups is limited to the narrow pH domain between 2.5 and 3.6, where the copolymer is water soluble. Adsorption from more highly concentrated electrolyte solutions containing polymeric aggregates of large size was found to lead to interfacial deposition of aggregates at levels incompatible with the usual characteristics of adsorbed polymer layers.

## Conclusion

Stabilization of colloid particles in aqueous suspensions can be achieved as theoretically predicted by adsorption of diblock copolymers on selective surfaces. In the present case, the colloid surface bearing amidine groups of charge opposite those of the anchoring styrenesulfonate block should leave the stabilizing poly(vinylpyridine) block as a corona of diffuse chains projecting into the liquid phase. This model of the interface was however not fully attained in situations where adsorption of the copolymer required prior relaxation of micelles. Irreversible adsorption on noncharged materials such as Teflon resulted from the presence of hydrophobic microdomains. Adsorption on charged materials presenting a selective surface was found to be partially reversible, although the small amount of copolymer remaining irreversibly adsorbed on the surface after rinsing with solvent was nevertheless able to develop large hydrodynamic thicknesses sensitive to pH and ionic strength. The most striking result was that the thickness of the adsorbed layer increased with the electrolyte concentration of the suspending phase, contrary to the usual behavior of adsorbed polyelectrolyte layers. Interfacial reorganization was relatively slow in comparison to the kinetics previously observed for polyelectrolytes adsorbed on porous media.

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## References and Notes

(1) Halperin, A. *Macromolecules* **1987**, *20*, 2943.
(2) Halperin, A.; Tirrell, M.; Lodge, T. P. *Adv. Polym. Sci.* **1991**, *100*, 31.
(3) Birshtein, T. M.; Zhulina, E. B. *Polymer* **1989**, *30*, 170.
(4) Johner, A.; Joanny, J. F. *Macromolecules* **1990**, *23*, 5299.
(5) Varoqui, R.; Tran, Q.; Pefferkorn, E. *Macromolecules* **1979**, *12*, 831.
(6) Pefferkorn, E.; Varoqui, R.; Mathis, A.; Picot, C.; Schmitt, A. To be published.
(7) Rodrigues, K.; Mattice, W. L. *Polym. Prepr.* (*Am. Chem. Soc., Div. Polym. Chem.*) **1991**, *32*, 269.
(8) Zezin, A. B.; Lutzenko, V. V.; Rogacheva, V. B.; Aleksina, O. A.; Kalyuzhanaya, R. I.; Kabanov, V. A.; Kargin, V. A. *Polym. Sci. U.S.S.R.* (*Engl. Transl.*) **1974**, *14*, 857.
(9) Skouri, M.; Munch, J. P.; Candau, S. J.; Neyret, S.; Candau, F. *Macromolecules* **1994**, *27*, 69.
(10) Turbak, A. F. *Ind. Eng. Chem., Prod. Res. Dev.* **1962**, *1*, 275.
(11) Binana-Limbelé, W.; Zana, R. *Macromolecules* **1987**, *20*, 1331.
(12) Binana-Limbelé, W.; Zana, R. *Macromolecules* **1990**, *23*, 2731.
(13) Kiefer, J. J.; Somasundaran, P.; Ananthapadmanabhan, P. In *Polymer Solutions, Blends, and Interfaces*; Noda, I., Rubingh, D. N., Eds.; Elsevier Science Publishers B. V.: Amsterdam, 1992.
(14) Kalyanasundaram, K.; Thomas, J. K. *J. Am. Chem. Soc.* **1977**, *99*, 2039.
(15) Mandel, M.; Leyte, J. C. *J. Polym. Sci.* **1962**, *56*, S23.
(16) Ringenbach, E.; Chauveteau, G.; Pefferkorn, E. *J. Colloid Interface Sci.* **1993**, *161*, 223.
(17) Elaissari, A.; Haouam, A.; Huguenard, C.; Pefferkorn, E. *J. Colloid Interface Sci.* **1992**, *149*, 68.
(18) Halperin, A. *Europhys. Lett.* **1989**, *8*, 351.
(19) Halperin, A.; Alexander, S. *Macromolecules* **1989**, *22*, 2400.
(20) Marques, C.; Joanny, J. F.; Leibler, L. *Macromolecules* **1988**, *21*, 1051.
(21) Johner, A.; Joanny, J. F. *Macromolecules* **1990**, *23*, 5299.
(22) Pefferkorn, E.; Dejardin, P.; Varoqui, R. *J. Colloid Interface Sci.* **1978**, *63*, 353.

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