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Effects of Ionic Strength and Counterion Valency on Adsorption of Hydrophobically Modified Polyelectrolytes

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I. Introduction. Polymer adsorption is a versatile process in the control of surface properties. It has been used in a wide range of technologies, including adhesion, lubrication, biocompatibilization, stabilization, and controlled flocculation of colloidal dispersions.[1−4] Polyelectrolytes are linear macromolecule chains bearing a large number of charged or chargeable groups when dissolved in a suitable polar solvent, generally water,[5] and are used for the control of surface properties in these media. The steric effects of large size and electrostatic interactions, together with water solubility, make polyelectrolytes attractive candidates for constructing drug delivery vehicles, biomembranes, enzyme carriers, and other biomaterial surfaces and interfaces.[6−9]

Diblock copolymers, with one anchoring block which adsorbs onto surfaces and a functional block which delivers desired properties to the surface, form a particularly rich and promising class of surface modifiers.[10] Diblock copolymers consisting of a hydrophobic block and an electrically charged block form a special group of polyelectrolytes, which we term here, hydrophobically modified polyelectrolytes. The adsorption of poly(*tert*-butylstyrene)-*block*-sodium poly(styrenesulfonate) (PtBS−NaPSS) onto silica surfaces in aqueous solutions has been studied using ellipsometry and atomic-force microscopy (AFM).[11] Compared to a NaPSS homopolymer of comparable molecular size, much higher adsorbed amounts were measured, demonstrating the importance of the hydrophobic block in anchoring the diblock to the silica surface. No adsorption (≤0.1 mg/m^2) was observed in pure water without any added salt. When the NaCl concentration was increased to 1 M, adsorption could be readily observed, in a two stage process, starting with a diffusion-limited phase, followed by a stage limited in rate by the physical barrier of the accumulating layer. In this paper, we will continue to explore the role played by salt concentration in adsorption. We demonstrate that added salt can be a virtual on−off switch for adsorption.

II. Experimental Section. Materials. PtBS−NaPSS synthesized by anionic polymerization with molecular weight 160 000 and polydispersity 1.04 is used in this study. This molecule was referred to as "MT3" in a previous paper.[11] The PSS block was sulfonated to the 87% level after the preparation of the tBS−styrene block copolymers.

This polymer is highly asymmetric with 27 hydrophobic tBS units and 727 hydrophilic styrene units to ensure the water solubility of the copolymer. In aqueous solution, we expect that the hydrophobic block forms a compact globule, while the hydrophilic block dissolves with a characteristic coil dimension that depends *inter alia* on the size of the block and salt concentration in solution.[12] Above a certain concentration (CMC), the polymer chains begin to self-assemble into micellar structures.[13] Solution preparation and silica surface treatment are described in an earlier paper.[11]

Table 1. Effect of NaCl Concentration

[NaCl] (M)	1/κ (Å)	A (mg/m^2)	R (Å)	R_h (Å)	σ/σ^*
2	2.2	1.4	77.0	97.2	1.59
1	3.0	1.12	81.6	100.9	1.52
0.8	3.4	1.05	85.4	102.2	1.43
0.25	6.1	0.74	106.5	108.9	1.04
0.15	7.9	0.73	107.5	112.0	1.02
0.12	8.8	≤0.1			
0		≤0.1			

[a] ≤0.1 means this adsorbed amount is not detectable by the ellipsometry method. [b] R_h is calculated using a linear function of log(R_h) with log [NaCl] based on the data in ref 12. [c] σ/σ^* is calculated as $(R_h/R)^2$.

Protocol for Adsorption. Freshly cleaned wafers were placed in a trapezoidal quartz cell. Then the cell was filled with solution and monitored ellipsometrically. All measurements were done at a wavelength of 5893 Å and $T = 232$ °C. FORTRAN software was used to extract the adsorbed amount numerically. Since the change in ellipsometric angles due to adsorption is small [$O(1°)$], and taking into account the uncertainty in the ellipsometric angles [$O(0.1°)$], unique values for refractive index (n) and thickness (d) of the adsorbed layer could not be found. Instead, a reasonable value for refractive index was guessed, and the computed corresponding ellipsometry readings were compared to the experimental data. Among the two ellipsometric angles, ψ and δ, we found by systematic examination of our data that δ is more sensitive to this polymer adsorption. Thus, when there is no perfect match, we choose the best fit for the δ value. The adsorbed amount A was calculated by

$$A = \frac{d_1(n_1 - n_0)}{\left(\frac{\mathrm{d}n}{\mathrm{d}c}\right)_\mathrm{p}} \tag{1}$$

where d_1 is the thickness of the polymer layer, n_1 is the refractive index of the layer, n_0 is the refractive index of the solvent, and dn/dc is the refractive index increment of the medium due to the addition of polymer. For this polymer, dn/dc is 0.168 mL/g.[14] The adsorption of 1 M NaCl is also examined using this method. During the 30 h test period, there is no detectable adsorption of salt on the surface.

III. Results and Discussion. (1) NaCl as the Added Salt. The concentration of NaCl, which determines the ionic strength of the solution and thus the electrostatic screening effect, was varied between 0 and 2 M. The corresponding adsorbed amounts are listed in Table 1 and shown in Figure 1. In Table 1, the Debye screening length, κ^{-1}, measures the electrostatic screening effect of the ionic strength in solution:

$$\kappa^{-1} = \left(\frac{\epsilon_\mathrm{r}\epsilon_0 kT}{\sum (Z_i e)^2 C^*_{i0}}\right)^{1/2} \tag{2}$$

where ϵ_r is the dielectric constant of the solvent, ϵ_0 is that of vacuum, Z_i is the valence of ion i, and C^*_{i0} is the bulk molecular electrolyte concentration.

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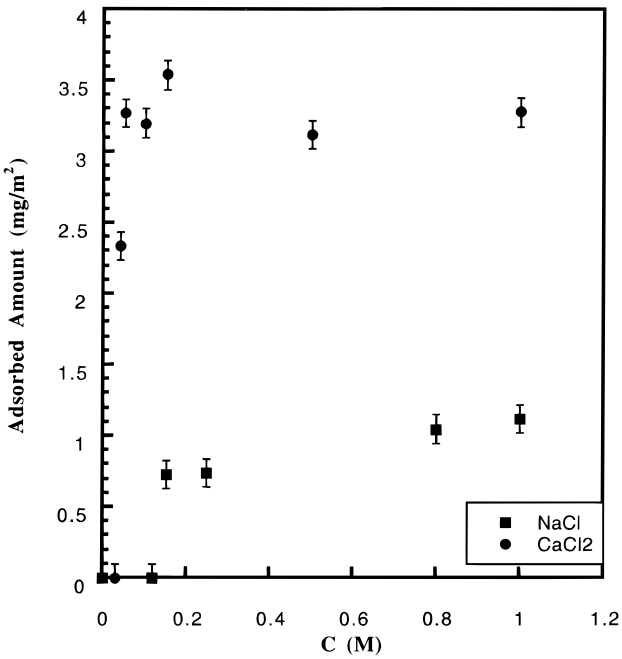

Figure 1. Effect of NaCl and $CaCl_2$ concentration on polyelectrolyte adsorption. Polymer concentration is 3.9×10^{-7} M for both salts.

R in Table 1 represents half of the distance between points of attachment of the tethered polyelectrolyte chains, estimated using the equation

$$R = \sqrt{\frac{M}{AN_{av}\pi}} \quad (3)$$

where M stands for the molecular weight, A stands for the adsorbed amount, and N_{av} is Avogadro's number. σ/σ^* is the tethering density (σ) over the overlap density (σ^*), a measure of the degree of crowding in the polyelectrolyte brush based on the NaPSS homopolymer hydrodynamic radius R_h[12] in the corresponding salt concentration.

From Figure 1, we see that not only at zero-added-salt but also below a certain finite salt concentration (<0.15 M), there is no adsorption observed. Above this salt concentration, the adsorbed amount jumps to a substantial and readily detectable value. Adding salt to the system will promote adsorption in two ways: (1) The salting-out effect, which worsens the solvent quality for both blocks, increases the adsorbed amount. It was estimated that above about 0.1 M, salting-out effects can become important.[15] (2) A diminishment of long-range electrostatic interactions reduces the penalty for close approach of chains. Considering these facts, we interpret the results in the following way. At low salt concentrations, the driving force for adsorption is weaker than the electrostatic factors that oppose it. With increasing salt concentration, the adsorption driving forces are enhanced and the electrostatics are diminished. Around 0.15 M, there is a turning point where the driving forces are larger than the opposing forces. Evidently, this point displays some character as a switch for the control of the diblock adsorption.

A concentration of 0.15 M NaCl for PSS solution has been found to be significant in other work. It has been reported[12] that 0.15 M NaCl water solution behaves as a Θ solvent for NaPSS homopolymer, which can be interpreted as the point where the pure quality of the solvent is just compensated for by the polymer intrachain repulsion. At 1 M, the screening length (3 Å) is comparable to the charge−charge distance and neutral block copolymer behavior is expected. The average half-distance between surface-attached chains in 1 M salt is smaller than the approximate 100 Å radius of the PSS block.[12] This means that the polymers have some degree of overlapping. σ/σ^* is about 1.5 in 1 M NaCl, so that these layers are weakly crowded brushes in high salt concentrations.

Table 2. Effect of $CaCl_2$ Concentration

$[CaCl_2]$ (M)	$1/\kappa$ (Å)	A (mg/m²)	R (Å)	R_h (Å)	σ/σ^*
1	1.8	3.28	50.8	95	3.50
0.5	2.5	3.12	52.1	99	3.61
0.15	4.5	3.54	48.9	105.5	4.65
0.1	5.6	3.2	51.4	107.8	4.40
0.05	7.9	3.27	50.9	112.0	4.84
0.04	8.8	2.34	60.14	113.4	3.56
0.03	10.1	≤0.1			

[a] R_h for NaPSS in $CaCl_2$ is calculated with the assumption that the same ionic strength gives the same R_h as NaCl.

(2) $CaCl_2$ as the Added Salt. Counterion valency has been found to be very important for polyelectrolyte behavior.[16−18] We studied the effect of a divalent salt: calcium chloride. The $CaCl_2$ concentration was varied from 0 to 1 M. Adsorbed amounts as well as the corresponding Debye length are listed in Table 2 and also plotted in Figure 1. As with NaCl, when the $CaCl_2$ concentration is lower than a certain value (<0.04 M), there is no adsorption detected. Above this concentration, adsorption is readily observed. Again, $CaCl_2$ contributes to the free energy change by modifying the solvent−diblock interactions and the electrostatic interactions. Around 0.04 M, the decreasing solubility and screened electrostatic repulsion compensate for the loss of entropy, to produce substantial adsorption.

Compared to NaCl, however, the corresponding plateau-adsorbed amount reached at high salt concentrations is higher for $CaCl_2$. This might be caused by the ability of the divalent calcium ions to produce association between polymer chains, reducing repulsions in a way which monovalent sodium ions cannot do. A fraction of the calcium ions are in close proximity to segments on the polymer chain, conferring to this region a net positive charge. This will induce a short range attraction between such monomers and those that retain bare negative charge.[16]

The much lower threshold salt concentration for adsorption is also caused by the valency difference. From eq 2, we know that at the same concentration, the denominator for $CaCl_2$ is 3 times that of NaCl. That means, for the same electrostatic screening effect, only one-third the molar concentration is needed when using $CaCl_2$ relative to NaCl. If we take 0.15 M for NaCl, then the concentration for $CaCl_2$ is $0.15/3 = 0.05$ M, quite close to the value of 0.04 M in our results.

Even though adding more salt to the system better screens the electrostatic repulsion, when the adsorbed amount is high, and chains are crowded (3.5 times the overlapping density in 0.04 M $CaCl_2$), the steric barrier to further adsorption becomes important. This may explain why further increasing the salt concentration beyond the threshold for adsorption is not able to cause a further increase in the adsorbed amount for $CaCl_2$.

(3) Check for Desorption under Zero-Added-Salt Conditions. Since the adsorption requires a threshold salt value, we studied the desorption of previous adsorbed layers exposed to zero-added-salt. After adsorption at high salt concentrations, we switched the solution into pure water for more than 24 h. No detectable desorption was seen in any case.

IV. Conclusions. We have found that the adsorption of hydrophobically modified polyelectrolytes requires a well-defined threshold ionic strength. The threshold appears so well-defined, and the difference of adsorbed amount above and below the threshold so great, that salt concentration acts as a virtual switch for adsorption. The threshold concentration for divalent salt is lower than for monovalent salt, consistent with ionic strength being the control parameter. Divalent salt produces much higher adsorbed amounts. These observations provide insight into the physics of assembly and interactions in polyelectrolyte brushes.

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References and Notes

(1) Napper, D. *Polymeric Stabilisation of Colloidal Dispersions*; Academic Press: London, 1983.
(2) Witten, T. A.; Pincus, P. A. *Macromolecules* **1986**, *19*, 2509.
(3) Scheutjens, J.; Fleer, G. J. *Macromolecules* **1985**, *18*, 1882.
(4) Lee, L. H., Ed. *Adhesion Science and Technology*; Plenum Press: New York, 1975.
(5) Hara, M. *Polyelectrolytes, Science and Technology*; Marcel Dekker, Inc.: New York, 1993.
(6) Kawashima, Y.; Handa, T.; Kasai, A.; Takenaka, H.; Lin, S. Y.; Ando, Y. *J. Pharm. Sci.* **1985**, *74*, 264.
(7) Davison, C. J.; Smith, K. E. *J. Bioact. Compat. Polym.* **1990**, *5*, 267.
(8) Dellacherie, E. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1991**, *32*, 602.
(9) Hair, M., Ed. *The Chemistry of Biosurfaces*; Marcel Dekker, Inc.: New York, 1971; Vols. 1, 2.
(10) Parsonage, E. E.; Tirrell, M.; Watanabe, H.; Nuzzo, R. G. *Macromolecules* **1991**, *24*, 1987. Watanabe, H.; Tirrell, M. *Macromolecules* **1993**, *26*, 6455.
(11) Amiel, C.; Sikka, M.; Schneider, J. W.; Tsao, Y.; Tirrell, M.; Mays, J. W. *Macromolecules* **1995**, *28*, 3125.
(12) Wang, L.; Yu, H. *Macromolecules* **1988**, *21*, 3498.
(13) Guenoun, P.; Davis, H. T.; Tirrell, M.; Mays, J. W.*Macromolecules* **1996**, *29*, 3965.
(14) Azzam, R. M. A.; Bashara, N. M. *Ellipsometry and Polarized Light*; NorthHolland, New York, 1977.
(15) Hesselink, F. T. *J. Colloid Interface Sci.* **1976**, *60*, 448.
(16) Olvera de la Cruz, M.; Belloni, L.; Delsanti, M.; Dalbiez, J. P.; Spalla, O.; Drifford, M. *J. Chem. Phys.* **1995**, *103*, 5781.
(17) Delsanti, M.; Dalbiez, J. P.; Spalla, O.; Belloni, L.; Drifford, M. *ACS Symp. Ser.* **1994**, *548*, 381.
(18) Nordmeier, E.; Dauwe, W. *Polym. J.* **1991**, *23*, 1297.

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