

Communications to the Editor

Adsorption of Protonated Poly(vinylpyridine) on Silica. Correlation between Interfacial Conformation and Colloid Stability

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Introduction. It is known that polyelectrolyte adsorption on the oppositely charged solid substrate is followed by chain reconfiguration. At the first step of the diffusion-controlled fast adsorption, conformation of an adsorbed coil is the same as the conformation in solution. At the second step a slow reconfiguration is observed. The chain becomes progressively flatter until the process is terminated due to excluded surface effects resulting from the adsorbed molecules in the neighborhood (semidiluted surface concentration regime).¹ Recently it was shown theoretically and experimentally (by employing contact angle measurements) that the surface coverage has extrema (maximum/minimum) at the transition region from the diluted to semidiluted surface concentrations for adsorption of homopolymers² and a copolymer.³ It was assumed that this behavior reflects the evolution of the polymer conformation in the adsorbed layer with increasing surface coverage. Such a behavior originates from the competition between the intra- and intermolecular correlation, which may be attributed to the interfacial chain reconfiguration.²

The time required for the interfacial structures to attain equilibrium was found to be very long, as this involved a slow exchange between the adsorbed and unadsorbed chains.^{4,5} When the adsorbed chain needs some delay to change its conformation in order to become desorbable, kinetic parameters may determine the overshoot regime.⁶ Consequently, the existence of extreme conditions could result from the kinetic effects and/or from the chain interactions in the adsorption layer. A detailed experimental study of such phenomena requires investigations at very long time scales and extremely low concentrations.

Here we report the investigation of the above-mentioned phenomenon in the case of polyelectrolyte adsorption on silica from aqueous solutions of different concentrations. Adsorption of water soluble polymers may result from the establishment of electrostatic and hydrophobic interactions as well as hydrogen bonds.^{7,8} To understand the polyelectrolyte/adsorbent interaction

it was essential to choose an experimental system for which only electrostatic forces were responsible for the adsorption. This situation corresponds to a “true” polyelectrolyte, whose solution behavior is determined only by electrostatic interactions between charged chain elements and whose adsorption behavior at charged solid–liquid interfaces is caused by interactions between polyion and surface charge. Poly(4-vinylpyridine) (PVP) at pH = 3 was found to combine these solution and interfacial characteristics.⁸ We report the behavior of PVP adsorbed on silica observed at a wide concentration range—from the very diluted to the plateau adsorption value—(i) by measuring the contact angle on the dried PVP coated silicon wafers and (ii) by determining the extent of aggregation–fragmentation processes in the aqueous suspensions initially containing dispersed PVP coated colloidal silica particles.

Experimental Section. Materials. PVP characterized by a number average molecular weight of 3.6×10^5 was synthesized in ethylene glycol using azobisisobutyronitrile as an initiator.⁹ Fractionated silica powder (Merck) with a mean diameter of 1.2 μm and a specific surface area of 2.4 m^2/g was used as a substrate for the aggregation/fragmentation experiments. Fractionation was performed to eliminate particles of diameters less than 0.6 μm which cannot be counted in the dispersed form by the Coulter counter technique.¹⁰ Contact angle measurements were performed on Si wafers with a top silica layer carefully washed with double distilled water. The wafers were immersed in water for a week, rinsed again, and then dried with dust-free nitrogen.

Adsorption Procedure and Sample Preparation. PVP 0.1% solution in water was prepared at pH = 2. The series of PVP solutions of different concentrations were prepared by dilution of the 0.1% solution with water at pH = 3 to obtain a final pH of 3. The silica powder (1 g) was added to 15 mL of the solution, and the mixture was stirred for 48 h. Then the suspension was allowed to settle for 36 h. Si wafers were carefully immersed into the clear supernatant above the sediment and kept immersed for 72 h. This procedure was used to reproduce identical polymer interfaces on the wafers and silica particles. The polymer-coated wafers were taken out of the solutions and rapidly rinsed six times in water and then dried with nitrogen at room temperature.

Contact Angle Measurements. The static contact angles Θ of water (double distilled) or diiodomethane (DIM) from Merck were determined by the sessile drop method using Krüss G40 equipment. The drop was rested on the substrate for 1 min before measurements. For each sample three successive measurements were made on two wafers. In most cases the root-mean-square deviation did not exceed 2°.

Aggregation/Fragmentation Rate Measurements. The technique and methodology employed for the de-

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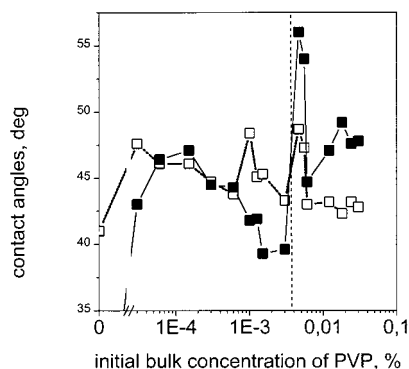


Figure 1. Contact angle dependence vs initial bulk concentration (c_0) of PVP obtained with the two wetting liquids: water (■) and DIM (□).

termination of the aggregate mass frequency have been described elsewhere.¹¹ We note that the number average mass is derived from the histogram given by this technique. The suspension containing silica powder and polymer was homogenized by stirring and two aliquots taken from the suspensions after 24 and 168 h were analyzed by the particle counting technique (Coulter counter) to determine the average mass of the aggregates (the average number of particles per aggregate). After 168 h, aliquots of the different silicon/polymer suspensions were diluted 10 times and a gentle rotation was sustained for 192 h. Periodically, the diluted suspensions were analyzed to determine the variation in the colloidal stability resulting from the modification of the surface characteristics induced by the 10-fold dilution.

All experiments were performed at 25 °C.

Results and Discussion. The plot of the contact angle for wetting of the PVP covering, obtained from the adsorption experiment on Si wafers, against the initial (before adsorption) concentration c_0 of PVP in aqueous solution at pH = 3 is shown in Figure 1. The contact angles of water and DIM on bare Si wafer amount to $20 \pm 2^\circ$ and $41 \pm 1^\circ$ respectively, while on the surface of the PVP thick and dried films (with thickness of about 200 nm, prepared by spin-coating technique) the contact angles are $59 \pm 2^\circ$ and $46 \pm 2^\circ$ respectively. Consequently, the change of contact angle within these limits shows the variation of the adsorbed chain conformation when the wetting liquid can contact with both the uncovered substrate and polymer chains.¹² The fraction of the substrate surface, covered by polymer, should be proportional to $1 - \cos \Theta$. In some cases the contact angle for adsorbed layers is higher than that a PVP film. This can be explained by a specific chain conformation, when the polar groups are preferentially oriented to the substrate. The plateau adsorption value for PVP at 25 °C and pH = 3 was found to be 0.3 mg/m² at the surface saturation after 24 h. The polymer has an exceptionally strong affinity to the substrate.¹³ Thus, for the chosen solution-to-adsorbent ratio of 15:1 we assume the total amount of PVP to be adsorbed on the substrate is up to $c_0 = 5 \times 10^{-3}\%$ so that in this concentration range c_0 can be taken to be the same as the adsorbed polymer amount. The latter can be seen from the following estimations. The amount of PVP in solution at $c_0 = 5 \times 10^{-3}\%$ is equal to $15 \times 5 \times 10^{-3}/(100 \times 1000) = 0.75$ mg per 1 g of the silica powder or 0.31 mg/m². Consequently, at a very high affinity, almost all PVP was adsorbed as has been obtained elsewhere.¹³

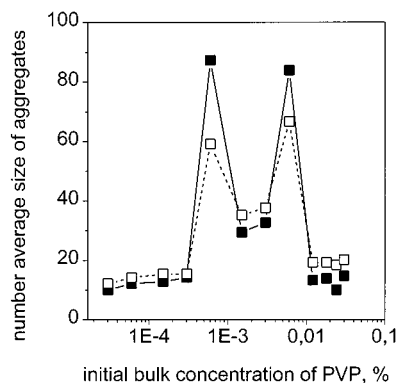


Figure 2. Number average mass of (silica + polymer) aggregates as function of the initial bulk concentration c_0 determined after 24 h (□) and 168 h (■).

As shown in Figure 1, the contact angle initially increases as c_0 increases. For the concentration equivalent to the surface coverage of 0.015 mg/m² ($c_0 = 10^{-4}\%$) which is 5% of the plateau adsorption value, the contact angle decreases with increase of c_0 and a minimum is observed. The lower point of the minimum corresponds to the adsorption value which is about 25% of the plateau adsorption value. The succeeding peak of the contact angle occurs at c_0 equal to $4 \times 10^{-3}\%$ and then the contact angle decreases and tends to a constant value at $c_0 = 5 \times 10^{-3}\%$. The difference between water and DIM above $3 \times 10^{-3}\%$ (extra peak in the case of DIM) could result from the difference in interaction of PVP with water and DIM. In contrast to DIM, water at pH = 6 does not dissolve PVP but can slightly swell the dried collapsed PVP layer.

In our opinion, the right part of the plot starting from $c_0 = 4 \times 10^{-3}\%$ (shown with the vertical dashed line) reflects the well-known behavior of the adsorbed polymer. When the adsorption value increases, the fraction of the attached segments decreases and the wetting liquid is able to penetrate through the layer and come into contact with the substrate.¹²

A subject of interest in this report is the left part of the plot (Figure 1) in the concentration range from $c_0 = 10^{-4}\%$ to $c_0 = 10^{-3}\%$. The observed minimum is assumed to reflect the reconfiguration of the adsorbed chains resulting from transition from the diluted to semidiluted surface concentration regime.² At this concentration the interaction between the chains and the substrates induces the change from a flat conformation to the conformation with a high fraction of loops and tails. This transition is followed by partial desorption of segments and, perhaps, even chains. As was mentioned earlier, similar phenomena were observed for the homopolymer and copolymer adsorption from organic medium.^{2,3} In this study the same effect is observed upon polyelectrolyte adsorption.

Polyelectrolyte adsorption induces the aggregation-fragmentation behavior of colloidal particles in water medium, which is usually characterized by a unique optimum flocculation dosage. The experiments carried out in the range of extremely low and medium surface coverage confirm these results (Figures 2 and 3). The data of Figure 2 show the average aggregate size in 24 and 168 h of aggregation of the suspension of the silica particles. The data of investigations of the fragmentation process are depicted in Figure 3. Two instability peaks in both figures correlate with the wetting data and obviously determine the correlation between poly-

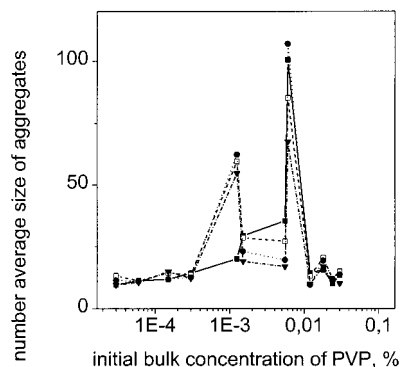


Figure 3. Number average mass of (silica + polymer) aggregates as function of the initial bulk concentration c_0 determined after 10-fold dilution of the suspension in 10 min (■), 48 h (□), 120 h (●), 192 h (▲).

mer reconfiguration effects and particles stability. We propose that (i) the first instability domain results from the neutralization of the silicon surface charge by the PVP adsorbed in a flat conformation and (ii) the second instability domain results from the usual bridging mechanism, when tails and bare sites on the surface are formed at higher surface coverages.^{1,14}

As shown in Figure 3, at the given polymer dosage the time dependence of the number average mass shows a nonmonotone behavior (oscillation). This oscillation is different for the two peaks. The same temporal behavior was found for the contact angle values.¹⁵ We may presume that the rate of the adsorption–desorption processes differs for different PVP concentrations, which could be an explanation for the obtained experimental data.

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