Adsorption of Nanocolloidal SiO_2 Particles on PEO Brushes

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Introduction. The interactions between polymers at interfaces and the environment is of the utmost importance for numerous processes in biomedical applications, but also in the food industry and in paint applications.[1,2] The past two decades polymers end-grafted to interfaces at high densities, so-called *polymer brushes*, have been recognized as interesting objects from an academic point of view.[2−6] Recently, numerous studies have examined brushes as promising candidates to modify the adsorption properties of surfaces in contact with heterogeneous solutions.[7−10] For instance, the adsorption of proteins and bacteria on surfaces, also known as *biofouling*, may be suppressed via grafting of hydrophilic polymers.[11]

However, advancement in the field of brushes in contact with heterogeneous media seems to be slow due to two reasons: (a) the difficulty of experimentally preparing well-characterized polymer brushes and (b) the current lack of model systems to study brush−particle interactions. In recent papers we reported a novel method of preparing polymer brushes on solid substrates, based on the Langmuir−Blodgett (LB) technique.[12−14] Also, in the past the interaction between silica surfaces and PEO-homopolymers has been examined in detail.[15] Using reflectometry to measure the adsorption of nanocolloidal SiO_2 particles onto brushes prepared via the LB-technique, we believe to have the first brush−particle system in which the polymer−polymer, polymer−particle, and particle−particle interactions can be varied independently via the pH, grafting density, and ionic strength, respectively. In this communication, we report the first results for this model system and compare the results with predictions of theoretical models.

Materials and Methods. Diblock copolymers consisting of PS(38)−PEO(700) were received from Dr. G. Riess, Mulhouse, France (the numbers denote the number of monomers in the blocks).[16] The PS−PEO was dissolved in chloroform (1 g L^{-1}) and deposited on the air/water interface of a Langmuir trough via a micropipet. The PS−PEO monolayer was compressed to the desired density, characterized by the surface pressure.[17,18] Silicon wafers were hydrophobised using styrene as described in refs 19 and 20. On top of the styrene monolayer a PS layer of thickness 60 to 70 nm was spin-coated at 3000 min^{-1} from a 14 g L^{-1} solution in toluene. Subsequently, the PS−PEO monolayer was transferred onto the coated wafer via the well-known LB-technique.[21] The interaction between the PS-groups on the block copolymer and the spin-coated PS layer is strong enough to provide stable PEO-brushes, irrespective of the solution conditions.[13] Via this method, wafers with irreversibly grafted layers of PEO chains at predetermined grafting densities were prepared. We refer the reader for further details of this process to refs 12−14.

A 156 g L^{-1} solution of SiO_2 particles of radius 8 nm, as determined via dynamic light scattering, was received from Akzo Nobel. This solution was diluted by a factor of 10 000, corresponding to a silica particle density 2.77 μm^{-3} and the pH was set at the desired value between 2.5 and 11 using NaOH and HCl. No salt was added; the overall ionic strength was therefore $I \sim 10^{-pH}$.

The adsorption of these silica particles on each of the PEO brushes was measured at various pH values via reflectometry. A detailed discussion of this optical technique may be found in ref 22. A silicon wafer modified with PS−PEO was preincubated at the desired pH in the reflectometer cuvette. When the intensities of the normal (I_s) and parallel (I_p) polarization components of the reflected laser beam were stable, a solution containing nanocolloidal silica at the same pH was injected and the adsorption on the modified wafer was followed in time. The overall adsorbed amount of silica was calculated from the change in I_p/I_s relative to the initial value. For calculation of the adsorbed amount, the Abeles matrix technique was used.[22]

Results. The adsorption of nanocolloidal SiO_2 particles on grafted PEO layers was observed to occur rapidly and varied strongly as a function of the pH. By way of illustration we plot the adsorption, as determined from the change in reflected intensities, as a function of time for various pH values and a grafting density of 7.4 nm^2 per PEO chain in Figure 1. As can be deduced, the overall adsorbed amount decreases strongly with increasing pH. Moreover, it is seen that the adsorbed amount does not increase indefinitely, but levels off at a plateau, the value of which depends on the pH value.

In Figure 2, the calculated adsorbed amount is plotted in time under varying solvency conditions and a higher grafting density of 4.9 nm^2 per chain. Initially, the solution in the cuvette consisted of pure water at pH 3.8. After introduction of a solution at the same pH containing silica particles, the adsorbed amount increased rapidly to a high value (regime i). After 843 s the solution in the cuvette was changed to a silica containing solution at pH 12 (regime ii). The adsorbed amount can be seen to drop quickly to the baseline, i.e., zero adsorbed amount. After changing back to a silica containing solution at pH 3.8 the same plateau of the adsorbed amount was regained (regime iii). Again, changing back to a silica containing solution at pH 12 resulted in zero adsorption (regime iv). When a solution without SiO_2 particles at pH 3.8 was inserted, a small resultant adsorption was observed (regime v). This is believed to stem from SiO_2 particles that remain in the cuvette of the reflectometer. Again, switching to pH 12 (regime vi), back to 3.8 (regime vii), and finally to 12 (regime viii) showed a remnant adsorption.

In Figure 3, we show the overall plateau value of adsorbed amount of SiO_2 particles as a function of the PEO grafting density at pH 2, 8, 9, 10, and 11. The curves drawn through the points are a guide to the eye. It is observed that all curves exhibit a maximum in the adsorbed amount as a function of the grafting density. The overall adsorbed amount increases continuously

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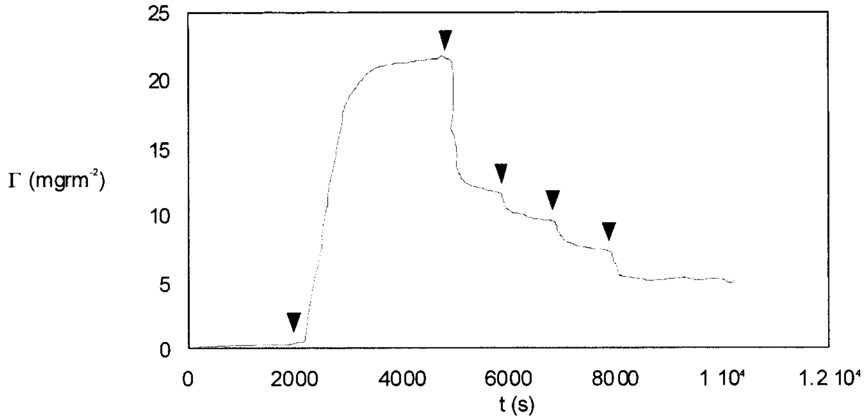

Figure 1. Adsorbed mass of SiO_2 in time at various pH valuesof the silica solution. At the arrows, silica solutions of differing pH values were injected in the cell. These values were 2.5, 8, 9, 10, and 11, respectively. The grafting density of the PEO brush was 7.4 nm^2 per chain.

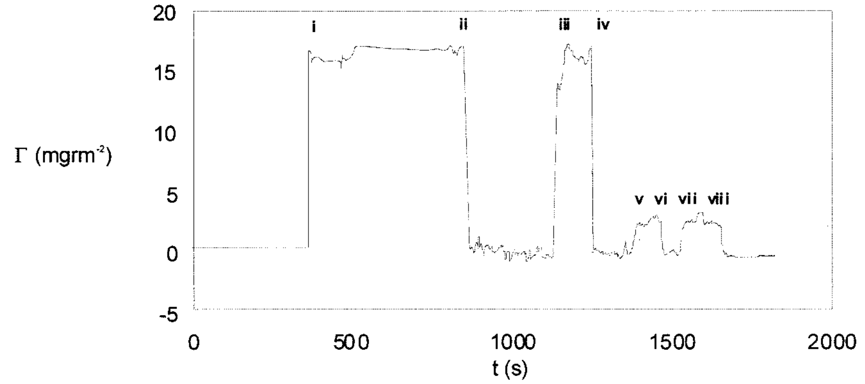

Figure 2. Adsorbed mass of SiO_2 in time upon switching the pH between 3.8 and 12, as explained in the text. The grafting density of the PEO brush was 4.9 nm^2 per chain.

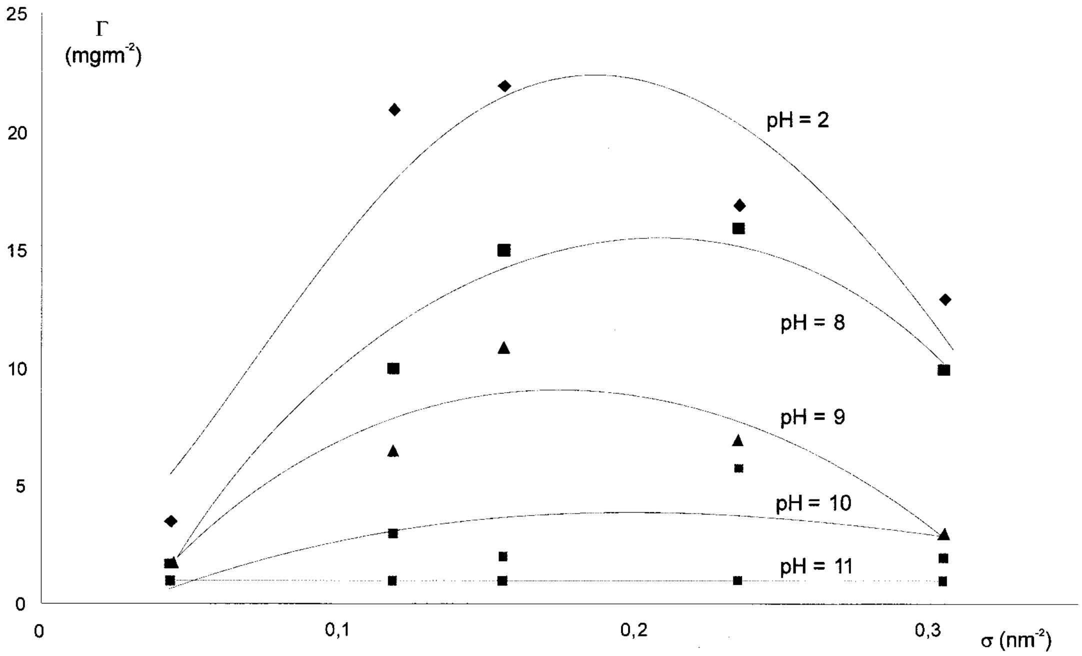

Figure 3. Overall adsorbed mass of SiO_2 as a function of the grafting density for 5 pH values.

with decreasing pH. Note that the maximum adsorbed amount, 22 mg m^{-2}, corresponds to 3.9×10^{-3} particles per nm^2; i.e., adsorbed on the order of 40 grafted PEO chains are available per SiO_2 particle.

Discussion. From Figures 1 and 2, it may be concluded that the PEO brush – nanocolloidal SiO_2 system allows us to reversibly vary the adsorption of nanoparticles on a brush of a given grafting density via the pH. The attractive interactions that result in SiO_2 adsorption on PEO are evidently the same as those believed to result in the adsorption of PEO homopolymer on silica surfaces, namely hydrogen bonds.[15] According to van der Beek et al., at low pH the protonized silica may form hydrogen bonds with the oxygen in the PEO. With increasing pH, the density of hydrogen groups on the silica decreases, resulting in less strong SiO_2–PEO

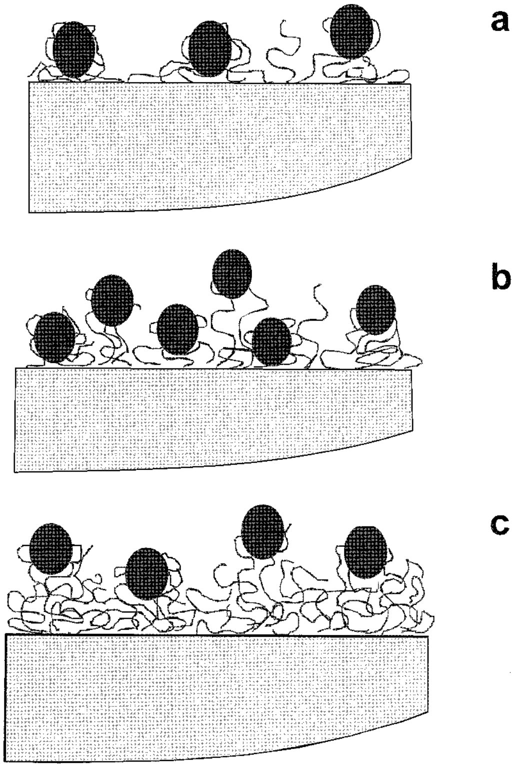

Figure 4. Schematic illustration of the adsorption of SiO_2 nanocolloidal particles on a PEO brush at (a) low grafting density, (b) intermediate grafting density, and (c) high grafting density.

attraction. The effective decrease in adsorption strength was observed to occur in the pH regime 8−11. Their results correlate nicely with the observed decreasing SiO_2 adsorption on PEO brushes with increasing pH in Figure 3.

The generic maximum in the adsorbed amount is the most interesting result found in our study. Clearly, the increasing adsorbed amount at low grafting densities is due to the increasing density of grafted PEO chains, i.e., the increasing number of adsorption sites for the SiO_2 particles. At high grafting densities the steric interactions between the densely grafted PEO chains result in a high osmotic pressure within the brush. In this regime, the attractive PEO−SiO_2 interactions may not compensate the increased steric interactions upon insertion of a SiO_2 particle in the brush. The result is that the SiO_2 particles are excluded from the proximal (inner) part of the brush and reside in the distal (outer) and less dense part of the brush. The balance of increasing number of adsorption sites and increasing steric interactions results in a maximum in the adsorbed amount as a function of the grafting density, as illustrated schematically in Figure 4.

Recently, we proposed an analytical model to mimic the adsorption of nanocolloidal particles on polymer chains in a brush conformation, so-called brushes with excluded volume interactions.[23,24] In this model a single chain is assumed to be able to reversibly complex with a large number of particles, i.e., form a necklace. Examples of such necklaces in solution are polymer−micelle and polymer−protein complexes.[25,26] In the case of strong repulsive steric interactions between adsorbed particles, a maximum in the adsorbed amount in the brush was predicted as a function of the grafting density. Clearly, the assumption of polymeric necklaces is not valid for the PEO−SiO_2 system investigated here, as at the maximum in the adsorbed amount the number of chains per particle is on the order of 40, whereas in our model each chain is assumed to complex with a large number of particles. Nevertheless, the interactions responsible for the maximum in the model (attractive polymer−particle interactions vs repulsive particle−particle and polymer−polymer steric interactions) are believed to be responsible for the observed maxima in the PEO−SiO_2 system as well.

We conclude that the combination of PEO brushes and SiO_2 particles forms an interesting model system to study brush−particle interactions, due to the control of the PEO−SiO_2 attraction via the pH. In future work we intend to focus on the influence of other parameters, for instance the ionic strength. It should be interesting to examine the influence of the ionic strength on the electrostatic interactions between the SiO_2 particles and the subsequent influence on the adsorption. Other parameters that may be varied are the chain length (is there a critical chain length for adsorption) and the polydispersity (i.e., bimodal brushes).

References and Notes

(1) Fleer, G. J.; Cohen Stuart, M. A.; Scheutjens, J. M. H. M.; Cosgrove, T.; Vincent, B. *Polymers at Interfaces*; Chapman & Hall: London, 1993.
(2) Alexander, S. *J. Phys. Fr.* **1977**, *38*, 983.
(3) de Gennes, P−G. *Macromolecules* **1980**, *13*, 1069.
(4) Milner, S. T.; Witten, T. A.; Cates, M. E. *Macromolecules* **1988**, *21*, 2610.
(5) Zhulina, E. B.; Borisov, O. V.; Priamitsyn, V. A.; Birshtein, T. M. *Macromolecules* **1991**, *24*, 140.
(6) Carignano, M. A.; Szleifler, I. *Macromolecules* **1995**, *28*, 3197.
(7) Halperin, A. *Langmuir* **1999**, *15*, 2525.
(8) Jeon, S. I.; Lee, J. H.; Andrade, J. D.; de Gennes, P−G *J. Colloid Interface Sci.* **1991**, *142*, 149. Jeon, S. I.; Andrade, J. D. *J. Colloid Interface Sci.* **1991**, *142*, 159.
(9) McPherson, T.; Kidane, A.; Szleifer, I.; Park, K. *Langmuir* **1998**, *14*, 176.
(10) Sofia, S. J.; Premnath, V.; Merrill, E. W. *Macromolecules* **1998**, *31*, 5059.
(11) See, for instance: Courtney, J. M.; Lambda, N. M. K.; Sundaram, S.; Forbes, C. D. *Biomaterials* **1994**, *15*, 737 and references therein.
(12) Currie, E. P. K.; Sieval, A. B.; Avena, M; Zuilhof, H.; Sudhölter, E. J. R.; Cohen Stuart, M. A. *Langmuir* **1999**, *15*, 7116.
(13) Currie, E. P. K.; Van der Gucht, J.; Borisov, O. V.; Cohen Stuart, M. A. *Pure Appl.Chem.* **1999**, *71*, 1227.
(14) Currie, E. P. K.; Sieval, A. B.; Fleer, G. J.; Cohen Stuart, M. A. *Langmuir* **2000**, *16*, 8324.
(15) van der Beek, G. P.; Cohen Stuart, M. A.; Cosgrove, T. *Langmuir* **1991**, *7*, 327.
(16) Haruska, Z.; Hurtrez, G.; Walter, S.; Riess, G. *Polymer* **1992**, *33*, 2447.
(17) Bijsterbosch, H. D.; de Haan, V. O.; de Graaf, A. W.; Mellema, M.; Leermakers, F. A. M.; Cohen Stuart, M. A.; van Well, A. A. *Langmuir* **1995**, *11*, 4467.
(18) Currie, E. P. K.; Leermakers, F. A. M.; Cohen Stuart, M. A.; Fleer, G. J. *Macromolecules* **1999**, *32*, 487.
(19) Sieval, A. B.; Demirel, A. L.; Nissink, J. W. M.; Linford, M. R.; van der Maas, J. H.; de Jeu, J. H.; Zuilhof, H.; Sudhölter, E. J. R. *Langmuir* **1998**, *14*, 1759.
(20) Sieval, A. B.; Vleeming, V.; Zuilhof, H.; Sudhölter, E. J. R. *Langmuir* **1999**, *15*, 8292.
(21) Roberts, G., Ed. *Langmuir−Blodgett Films*; Plenum Press: New York, 1990.
(22) Dijt, J. C.; Cohen Stuart, M. A.; Hofman, J. E.; Fleer, G. J. *Adv. Colloid Interface Sci.* **1994,** *50*, 79.
(23) Currie, E. P. K.; Van der Gucht, J.; Borisov, O. V.; Cohen Stuart, M. A. *Langmuir* **1998**, *14*, 5740.
(24) Currie, E. P. K.; Cohen Stuart, M. A.; Fleer, G. J.; Borisov, O. V. *Europ. Phys. J. E* **2000**, *1*, 27.
(25) Cabane, B. *J. Phys. Chem.* **1977**, *81*, 1639.
(26) Linse, P.; Piculell, L.; Hansson, P. In *Polymer-Surfactant Systems*; Kwak, J. C. T., Ed.; Surfactant Science Series 77; Marcel Dekker: New York, 1998.

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