Adsorption of Graft Copolymers onto Silica and Titania

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ABSTRACT: The adsorption of graft copolymers of poly(acrylamide) (PAAm, backbone) and poly(ethylene oxide) (PEO, side chains) from aqueous solution onto silica and titania was studied with reflectometry. Two high-molar-mass copolymers were used with different PEO graft densities (10 and 18% w/w PEO in copolymers G10 and G18, respectively). On titania only the PAAm backbone adsorbs and the PEO does not. This results in adsorbed amounts of 0.83 and 0.85 mg m^{-2}, respectively, which is about the same as that for a PAAm homopolymer. On silica the situation is reversed: now the PEO side chains adsorb and the PAAm backbone does not. The adsorption as a function of time shows a maximum, before the stable plateau is reached. The adsorbed amount on silica is much higher than that on titania: in the final plateau it is 1.35 and 1.2 mg m^{-2} for G18 and G10, respectively. On silica the polymers form longer loops and tails so that more molecules can be accommodated at the surface. The overshoot on silica depends on the polymer concentration, suggesting that it is not caused by a conformational change of the adsorbed layer but by exchange with polymer molecules from solution. Differences in graft distribution and graft density in the polymer sample are probably responsible for the displacement. The average number of grafts per polymer is rather low. On statistical grounds there should be an appreciable polydispersity in graft distribution and in graft density. Molecules in which the grafts are clustered in a few groups can displace molecules with more regularly separated grafts, and molecules with a high graft density can displace those with a lower number of side chains. The newly arriving molecules can then adsorb in a flatter conformation with a lower adsorbed amount as the extra loss in conformational entropy is compensated by the gain in adsorption energy.

Introduction

Polymers are extensively used for the stabilization of colloidal dispersions. By forming a protective layer around the particles, they can prevent these particles from aggregating by van der Waals forces.[1,2] Especially diblock copolymers can be very effective in forming a thick stabilizing layer. This feature arises from the fact that only a small part of the molecule, the anchor block, adsorbs to the surface. The other part, the buoy block, protrudes into the solution and forms a long dangling tail. For good steric stabilization it is necessary that the polymer tails protrude far into the solution, as these tails determine the thickness of the adsorbed layer.[2] From this point of view, it is interesting to consider another type of copolymer, a *graft copolymer*. Such copolymers, also called comb copolymers, have a main chain of one type of segment and side chains grafted to it consisting of another type of monomer units. Each graft copolymer then has many tails which makes them suitable as steric stabilizers of colloidal dispersions. So far, the adsorption and stabilization by graft copolymers has received relatively little attention in the literature.[3−6]

In a few theoretical papers the behavior of graft (co)-polymers was considered. Van der Linden et al.[6] found with a numerical self-consistent-field theory that graft *homopolymers* (with the same types of segments in backbone and side chains) adsorb preferentially with their backbone, with the side chains dangling in the solution. These authors suggested that the opposite result found by Balasz and Siemasko[3] may be due to insufficient equilibration in the Monte Carlo simulations. In both studies it was found that graft homopolymers form a thinner adsorbed layer than the equivalent linear polymer with the same total number of segments. Although the graft polymer has many more tails than the linear polymer, the extension of these tails into the solution is limited by the adsorption of the backbone. When the side chains are relatively long compared to the backbone spacing, a thick brush of nonadsorbing tails could be formed, comparable to that formed by diblock copolymers. Increasing the total length of the graft polymer eventually results in a thick layer because the backbone chain ends are no longer adsorbed and behave as tails (with attached side chains).[6] In the case of a graft *copolymer* with an adsorbing backbone and nonadsorbing grafts, the results are more or less similar to that obtained with the graft *homopolymer*. The picture, however, changes considerably for a graft copolymer with adsorbing grafts and a nonadsorbing backbone. In this case, the side chains adsorb to the surface and parts of the backbone dangle in the solution as loops and tails. The backbone prevents some of the side chains from adsorbing for entropical reasons. The loops and tails therefore contain both backbone and some grafts. The resulting layer is less dense close to the surface, and it extends further away in the solution than for a graft copolymer with nonadsorbing grafts. The adsorbed amount is mainly determined by the density in the first few layers and is therefore lower for a polymer with adsorbing side chains than for one with an adsorbing backbone.

In two experimental studies, adsorption of graft copolymers was investigated. Eremenko et al.[4] considered the adsorption of copolymers of poly(acrylamide) grafted to poly(vinyl alcohol) and its effect on the electrokinetic potential of silica and the hydrodynamic layer thickness. They found that the adsorbed amount of the polymer with more adsorbing side chains is considerably higher. However, the graft density of their polymers is very low (2−6 side chains per molecule).

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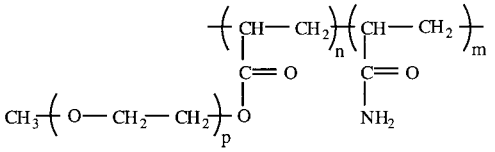

Figure 1. Structural formula of the PAAm−PEO graft copolymers. The PEO side chains are more or less randomly distributed along the main chain. For both polymers G10 and G18, the number of EO units per side chain (p) is 144. The number of side chains n is roughly 15 for G10 and 30 for G18, and the total molar mass is on the order of 1000 kg mol^{-1}.

Liang et al.[5] studied the adsorption of graft copolymers with a poly(methyl methacrylate-*co*-methacrylic acid) backbone and poly(ethylene oxide) side chains onto latex particles. The adsorbed amount and layer thickness increased with increasing graft density. This result is unexpected because the graft density mainly determines the density of the adsorbed layer, i.e., the adsorbed amount, but hardly affects the layer thickness. For a better interpretation of the data, more information about molar mass and graft density is essential.

In this study we compare the adsorption of graft copolymers with an adsorbing backbone and nonadsorbing side chains to the reverse situation of adsorbing side chains and a nonadsorbing backbone. To make a meaningful comparison, we used a single type of graft copolymer on two different surfaces, with different affinities for the backbone and graft segments. The effect of graft density could be investigated by using two graft copolymers with about the same molar mass but different numbers of side chains. The graft copolymers had a poly(acrylamide) backbone and poly(ethylene oxide) side chains. The graft density was low, with a weight percentage of the side chains of 10 and 18% for the two polymers used. The adsorption of these polymers was studied with reflectometry. The adsorbent surfaces were silica, on which only the side chains adsorb, and titania, for which only the backbone has affinity.

Experimental Section

Polymers. The polymers used in this study were graft copolymers of poly(acrylamide) (PAAm) and poly(ethylene oxide) (PEO), which where synthesized and kindly made available by Prof. M. Möller (Twente University, Enschede, The Netherlands, presently at Ulm University, Ulm, Germany). The polymers were synthesized by radical copolymerization of acrylamide with a small amount of a PEO macromonomer which had been end-functionalized with an acrylate moiety.[7] The PEO side chains had a molar mass of 6.34 kg mol^{-1} and a polydispersity index $M_w/M_n = 1.11$. Two polymer samples were used, differing in graft density. The PAAm−PEO graft copolymer with the highest PEO graft density (18% in weight) is denoted as G18. The other graft copolymer, G10, has a weight percentage PEO of 10%. Considering the molar mass of the PEO side chains, this means that a backbone part between two side chains has, on average, rather high molar masses of 59 and 30 kg mol^{-1} for G10 and G18, respectively. The total molar mass of the copolymers is on the order of 1000 kg mol^{-1}. The molar mass of G18 is expected to be higher than that of G10 because of the presence of more side chains, despite the fact that the total length of the main chain is probably slightly smaller. The ratio m/n (number m of backbone units divided by the number n of grafts) is 832 for G10 and 416 for G18. The average number of grafts is therefore roughly 15/molecule for G10 and about 30/molecule for G18. However, on statistical grounds there should be an appreciable dispersity in graft density. The structural formula of the graft copolymers is given in Figure 1, and a schematic impression of a chain of G10 and G18 is sketched in Figure 2.

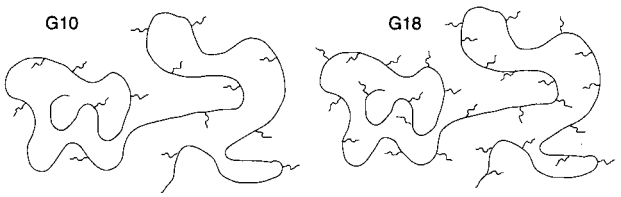

Figure 2. Schematic representation of copolymers G10 and G18. The side-chain density is rather low, but the molar mass per side chain is relatively high (6.34 kg mol^{-1}).

For both polymers G10 and G18 the number of EO units per side chain (p) is 144. The number of side chains n is roughly 15 for G10 and 30 for G18, and the total molar mass is on the order of 1000 kg mol^{-1}.

The polymers are soluble in water, although cross-linking reactions may render the polymer insoluble.[8] It is possible that the main chain PAAm is, to a very small extent, hydrolyzed so that the polymer contains a few acrylic acid groups. The ester link between the main chain and the PEO side chains can easily be hydrolyzed with acid or base, resulting in a solution with a mixture of two soluble homopolymers: PAAm with a very high molar mass and PEO with a molar mass of 6.34 kg mol^{-1}. This polymer mixture is used to study the adsorption behavior of the individual building blocks of the graft copolymers.

Measurements. The adsorption of the graft copolymers was measured with a reflectometer equipped with a stagnation point flow cell, a technique that has been described extensively elsewhere.[9,10] Macroscopically flat silicon wafers from Aurel GmbH (Germany) were used. By thermal oxidation, we obtained an SiO_2 layer with a thickness of about 110 nm. A TiO_2 layer with a thickness of about 25 nm was deposited on a silicon wafer by reactive sputtering of Ti in an oxygen atmosphere. This was carried out at Philips Laboratories in Eindhoven, The Netherlands. Strips cut from these wafers were cleaned by oxidation with UV ozone and could be cleaned and reused many times. Fresh solutions of the copolymers were stored in the refrigerator and used within 1 week. The adsorption measurements were performed with polymer concentrations varying from 5 to 100 mg L^{-1} in demineralized water. To screen the effect of any charged groups present, we added KNO_3 up to a total concentration of 10 mM, except for one series of measurements where we studied the effect of different concentrations of salt. All measurements were performed at room temperature ($T = 294 \pm 1$ K).

Results and Discussion

Reflectometry is a suitable tool to study the kinetics of polymer adsorption at time scales varying from a few seconds up to several hours. This technique measures the adsorbed amount of polymer at the surface, but any conformational changes at constant adsorbed amount are not detected.

The homopolymers PEO and PAAm have different affinities for silica and titania surfaces. From earlier studies it is known that PEO has a high adsorption affinity for silica,[9−11] but we found no affinity at all for titania (results not shown). For the acrylamide homopolymer, the adsorption behavior is the opposite: it has almost no affinity for silica, the adsorbed amount is very low, and on titania we found an adsorbed amount between 0.5 and 1 mg m^{-2} (results not shown). For the graft copolymers of PAAm−PEO, we measured the adsorbed amount on both silica and titania as a function of time. In Figure 3 we show an example of kinetic adsorption curves of the copolymer with the higher graft density, G18, on both surfaces. Figure 4 gives similar data for the copolymer with the lower graft density, G10.

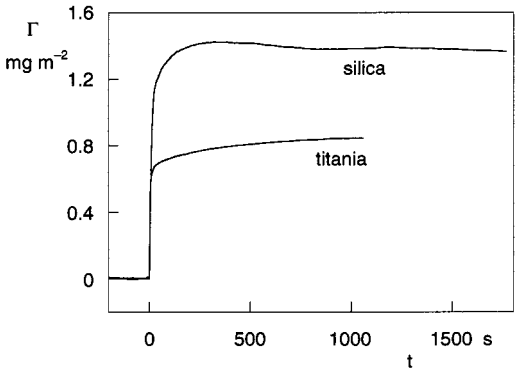

Figure 3. Kinetic adsorption curves of G18 on silica and titania. The polymer concentration is 50 mg L^{-1} in a 10 mM KNO_3 solution at pH 6.

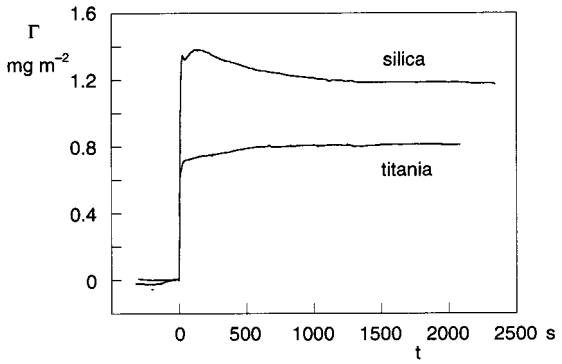

Figure 4. Kinetic adsorption curves of G10 on silica and titania. The polymer concentration is 50 mg L^{-1} in a 10 mM KNO_3 solution at pH 6.

The adsorption curves of G18 and G10 on titania are very similar. In the initial stages of the adsorption, the adsorbed amount increases linearly with time, as expected for diffusion-limited adsorption in a stagnation point flow. Toward saturation of the surface, the adsorption rate decreases abruptly, and eventually the adsorbed amount does not change any longer: a plateau is reached. The plateau adsorbed amount for titania is almost equal for both copolymers: 0.84 and 0.81 mg m^{-2} for G18 and G10, respectively. This adsorption behavior resembles that of a linear PAAm homopolymer with a molar mass of 500 kg mol^{-1}: the plateau adsorbed amount for this sample was 0.7 mg m^{-2} at the same salt concentration and pH. Apparently, the presence of the PEO side chains, which have no affinity for the titania surface, hardly affects the adsorption behavior of the copolymers. The copolymers adsorb with the PAAm backbone to the surface and, as the graft density is low, the adsorption is similar to that of a linear PAAm homopolymer. This is in agreement with theoretical predictions by Van der Linden et al.,[6] who found that, upon increasing the backbone spacing between the grafts, the polymer behaves more and more as a linear homopolymer.

The adsorption onto silica can, in contrast to that on titania, only occur through the presence of the PEO side chains. The initial parts of the adsorption curves of G18 and G10 increase again linearly with time, and the adsorption rate is the same as that found on titania. This is the expected behavior since the limiting step in this stage of the adsorption is the mass transport toward the surface. The low graft density does not reduce the initial attachment rate of the copolymer. The presence

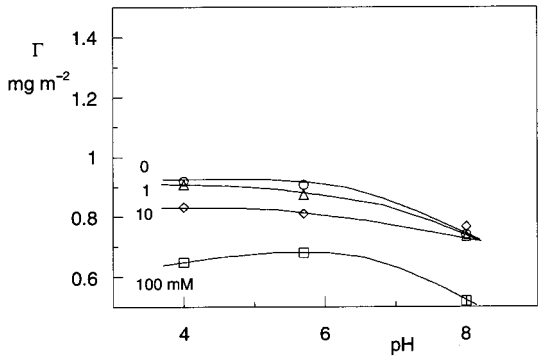

Figure 5. Adsorbed amount in the plateau of the adsorption curve of G10 on titania as a function of pH at different concentrations of KNO_3: 0 (circles), 1 (triangles), 10 (diamonds), and 100 mM (squares). The polymer concentration is 50 mg L^{-1}.

of a few long PEO side chains is already sufficient to "trap" the polymer when it arrives at the surface. After the initial stage of the adsorption, a maximum in the adsorbed amount is reached. After that, the adsorbed amount decreases to the final plateau level, where the adsorbed amount remains constant in time. The "overshoot" around the maximum is far more pronounced for G10 than for G18: the difference in the adsorbed amount between the maximum and the plateau is 0.2 and 0.05 mg m^{-2}, respectively. This overshoot is a very interesting phenomenon, which has only been reported occasionally before. A few cases have been observed for compact proteins.[12−14] For these proteins, the overshoot was interpreted as a slow change of conformation of adsorbed molecules which spread on the surface and slowly displace later-arriving weakly adsorbed protein molecules. Johnson et al.[15] found an overshoot for the adsorption of poly(dimethylsiloxane) and *cis*-poly(isoprene) onto germanium oxide and silica and interpreted it as a surface-induced crystallization of the adsorbed homopolymers. We will return to the overshoot further on. The adsorbed amount on silica found for G10 in the maximum is slightly higher than that found for G18, but at the plateau the adsorbed amount of G18 is higher. Both polymers have a considerably higher adsorbed amount on silica than on titania.

Ionic Strength and pH. Before discussing the above results in more detail, we first consider the effect of the salt concentration and pH. For G10 we studied the adsorption from a 50 mg L^{-1} solution onto silica and titania as a function of pH at different concentrations of KNO_3. In Figure 5 we give the adsorbed amount in the final plateau of the adsorption curves on titania, and in Figure 6 we plot the adsorbed amount in the maximum of the adsorption curves on silica.

Even though the polymers carry almost no charge, the salt concentration and pH can have an effect on the adsorption behavior of the graft copolymers as the amide group has a delocated electron pair which makes the oxygen slightly negatively charged and the amine positive. In addition, some of the amides may be hydrolyzed and converted into acidic carboxyls.

As can be seen from Figure 5 the pH has an effect on the adsorbed amount in the plateau of the adsorption curve. The highest adsorption is found at a low pH (with the exception of the highest salt concentration), which coincides with the iso-electric point of titania which is at pH 4.[16] The surface is then only weakly charged, and the polymer carboxyl groups, if present, are dissociated

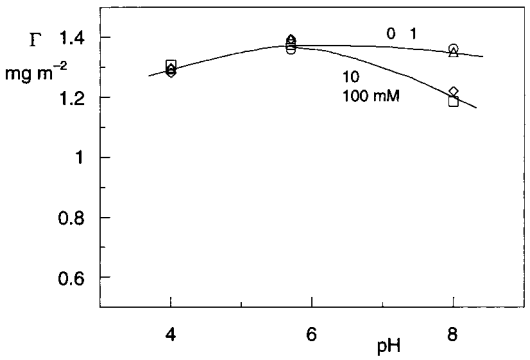

Figure 6. Adsorbed amount in the maximum of the adsorption curve of G10 on silica as a function of the pH at different concentrations of KNO_3: 0 (circles), 1 (triangles), 10 (diamonds), and 100 mM (squares). The polymer concentration is 50 mg L^{-1}.

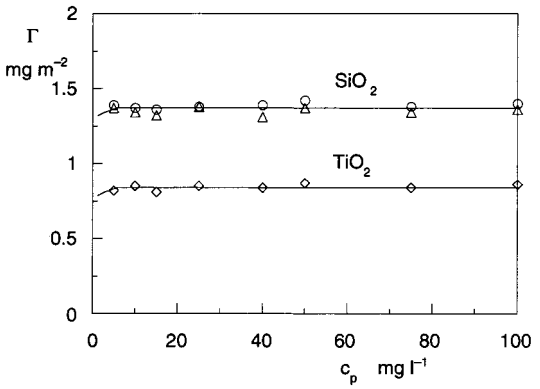

Figure 7. Adsorption isotherms of G18 on titania (diamonds) and on silica (triangles). For silica we give also the adsorbed amount in the maximum of the adsorption curve (circles), which in this case is not much higher than the plateau value. The solutions contain 10 mM KNO_3, and the pH is around 6.

for a small part, rendering the polymer main chain slightly negatively charged. The adsorption at this pH is mainly determined by the nonelectrostatic interaction between the polymer and the surface. When the pH is increased to 5.7, the surface and the polymer are both negatively charged, which reduces the adsorbed amount (except for 100 mM, where the screening of electrostatic interactions is strongest). A further decrease of the adsorbed amount found at pH 8 can also be explained by the increase of charge on both adsorbent and adsorbate. However, these effects are small, from which we conclude that there are only a few acidic groups present in the polymer. This is confirmed by the adsorption rates at different pH's, which are, within experimental error, not affected by the pH of the solution. Increasing the ionic strength decreases the importance of electrostatic interactions between the polymer and the surface. If this screening is the only effect, it would show up in the results as an increase of the adsorbed amount at a pH above 4, and no effect would be expected around pH 4. However, this does not hold for the results shown in Figure 5. Clearly the role of salt is more complicated. For example, the ions can interfere with the polar amide groups of the main chain. Such an interference will affect the adsorption because it is this group which is probably responsible for the adsorption onto titania.

The adsorption curves of G10 onto silica at different pH's and salt concentrations were all similar to the one plotted in Figure 4; the only difference is the adsorbed amount. The shape of the curves is the same, as is the relative difference between the adsorbed amounts in the maximum and at the plateau of the curve. In Figure 6 we see again an effect of varying pH and ionic strength of the solution. However, the effects are smaller than those for the adsorption on titania. The ionic strength and the pH can have a direct effect on the acrylamide groups responsible for the adsorption on titania. For PEO, which is the adsorbing group on silica, we hardly expect any effect of salt and pH on the adsorption in the range in which we varied these parameters. Indeed, the pH has only a small effect on the adsorbed amount, and the ionic strength does not affect the adsorbed amount at pH 4 or 6. At pH 8, however, we find a small decrease in the adsorbed amount at the two higher ionic strengths. The small differences in the adsorbed amounts found on silica are probably caused by a change in solution properties of the PAAm main chain. The results of varying pH and ionic strength for G18, with a higher graft density, are very similar to those obtained with G10; we do not show these results. For the remainder of the experiments we used polymer solutions with an ionic strength of 10 mM KNO_3 and a pH of 6.

Adsorption Isotherms. The adsorption isotherm of a polymer is usually of the high-affinity type, because of the many segments that can contribute to the adsorption.[2] In Figure 7 we plot the adsorption isotherms of G18 on silica and on titania. The isotherm on titania shows that there is hardly any dependence on the polymer concentration used. The adsorbed amount in the plateau of the isotherm is around 0.85 mg m^{-2}, similar to what we found for the adsorption of a PAAm homopolymer.

For silica we give also the adsorbed amount in the maximum of the adsorption curve (circles), which in this case is not much higher than the plateau value. The solutions contain 10 mM KNO_3, and the pH is around 6.

For the adsorption of G18 on silica, also a high-affinity isotherm is found. The difference between the adsorbed amounts in the maximum and in the plateau of the adsorption curves is small for this polymer, and it hardly depends on the polymer concentration. The adsorbed amount in the plateau of the isotherm is 1.35 mg m^{-2}, which is considerably higher than that on titania. Apparently, the polymer conformations at the two types of surfaces are different.

The analogous results for G10 are given in Figure 8. For this polymer the overshoot on silica is much larger than that for G18, and the drop in Γ following the overshoot is around 0.2 mg m^{-2} over the entire concentration range.

The adsorption isotherm of G10 on titania is almost the same as that for G18, with an adsorbed amount in the plateau of the isotherm around 0.83 mg m^{-2}, slightly lower than that found for G18. This would agree well with the fact that the molar mass of G18 is somewhat higher than that of G10. However, the small difference is perhaps not significant, as it is within the experimental error of the technique used.

For silica we give also the adsorbed amount in the maximum of the adsorption curve (circles). The solutions contain 10 mM KNO_3, and the pH is around 6.

Also for sample G10 the adsorption on titania is thus similar to that of a PAAm homopolymer. The difference in graft density hardly affects the adsorbed amount, as in both cases the number of side chains is low. The

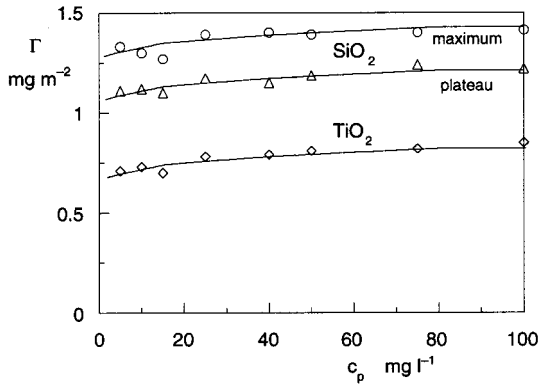

Figure 8. Adsorption isotherms of G10 on titania (diamonds) and on silica (triangles). For silica we give also the adsorbed amount in the maximum of the adsorption curve (circles). The solutions contain 10 mM KNO_3, and the pH is around 6.

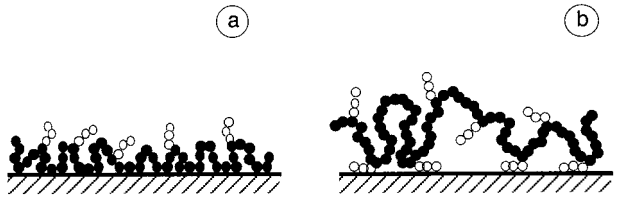

Figure 9. Schematic presentation of the adsorbed layer of PAAm−PEO graft copolymers on titania (a) and on silica (b). The PAAm main chain is represented by filled circles and the PEO grafts by open circles.

result of Liang et al.,[5] in which the adsorbed amount (and layer thickness) increases with the density of nonadsorbing grafts, suggests that the graft density in their system is much higher. The similar behavior of our copolymers and a PAAm homopolymer on titania suggests that the copolymers have a conformation which is not much different from that of an adsorbed homopolymer. Only a few PEO side chains protrude into the solution, but their contribution to the adsorbed amount is small. A pictorial representation of the structure of the adsorbed polymer layer on titania is given in Figure 9a.

The adsorbed amount in the maximum of G10 on silica is about the same as that of G18. The decrease of the adsorbed amount following the overshoot is larger than that for G18, which corresponds to a lower plateau value for G10. On silica the graft copolymers probably have a configuration in which only part of the side chains are adsorbed at the surface. The polymer would lose a considerable amount of configurational entropy if all grafts would have to be in contact with the surface. The surface is therefore only partly covered with PEO chains. The reason for the higher adsorbed amount on silica is that the graft copolymer forms longer loops and tails. Only a fraction of the PEO chains is in contact with the surface, yet these adsorbed grafts attach the whole chain firmly to the surface because of the relatively high adsorption energy of the (long) PEO chains. The PEO chains used in this study do indeed adsorb strongly on silica,[11] and they are probably long enough to secure attachment of the whole molecule. The resulting polymer layer could then be similar to that of a brush formed by the adsorption of diblock copolymers, where only one block attaches to the surface and the other protrudes into the solution.[17,18] The difference is that the graft copolymer used has a very high molar mass and that the brush contains many loops and not just tails. Consequently, the brush density is not very high. The configurations of the two polymers used in these experiments are probably similar as the adsorbed amounts do not differ much. As the graft density of G10 is lower than that of G18, fewer side chains per polymer are adsorbed to the surface. A sketch of the possible structure of the adsorbed layer on silica is given in Figure 9b.

The PAAm main chain is represented by filled circles and the PEO grafts by open circles.

The adsorbed amounts on silica are higher than these on titania, which could lead to the conclusion that the adsorption of side chains is more favorable than that of the backbone. This seems to be in contradiction with the numerical self-consistent-field results presented by Van der Linden et al.[6] These authors concluded that the adsorbed amount is higher for an adsorbing backbone, although the layer thickness is less. However, their results were obtained with graft copolymers that did not differ in the relative amount of adsorbing segments, whereas in our system the ratios of the mass of potentially adsorbing segments to the total molar mass are 0.10 and 0.18 for silica and 0.90 and 0.82 for titania, respectively. If we would have decreased the relative number of adsorbing segments on titania, i.e., increased the graft density, this most likely would have given rise to an increase in the adsorbed amount, which eventually would have been higher than that for silica in these experiments. We could not check these conjectures because graft copolymers with a higher graft density were not available.

Hydrolysis. The copolymers can easily be hydrolyzed at the ester connection between the PAAm main chain and the PEO side chains by acid or base. We hydrolyzed the grafts by adding NaOH to the stock solution of both G10 and G18 until a pH of 11 was reached. The solution was kept at this pH for 1 h after which it was diluted to the desired concentration, and the pH and the ionic strength were again adjusted to 6 and 10 mM, respectively. From these solutions, which contain a mixture of short PEO homopolymers and long linear PAAm homopolymers, we measured the adsorption to both silica and titania. For both G10 and G18 we found on silica an adsorbed amount of 0.4 mg m^{-2}, which agrees well with earlier results obtained with PEO homopolymers with a similar molar mass.[9,19] On titania the adsorbed amount was, within experimental error, the same as that found for the graft copolymers. These results clearly demonstrate that the adsorbance of the graft copolymer is a result of combining the two different segment types into one single molecule.

Overshoot. In almost all cases, the adsorption of a polymer is accompanied by a partial flattening or spreading of the molecule. For flexible polymers, this is usually a very fast process, much faster than the rate of supply from solution. Therefore, highly coiled transient states with big loops are usually not observed on the experimental time scale. However, some spreading processes are relatively slow, such that they become comparable in rate to the polymer supply. Under such conditions overshoots may appear; some examples are found with compact molecules such as proteins[12−14] and with surface-induced crystallization of polymers.[15] It is characteristic for these kinds of overshoots that they only appear for sufficiently high polymer supply rate. If the polymer supply is slow, the polymer can assume its most favorable conformation before all surface sites

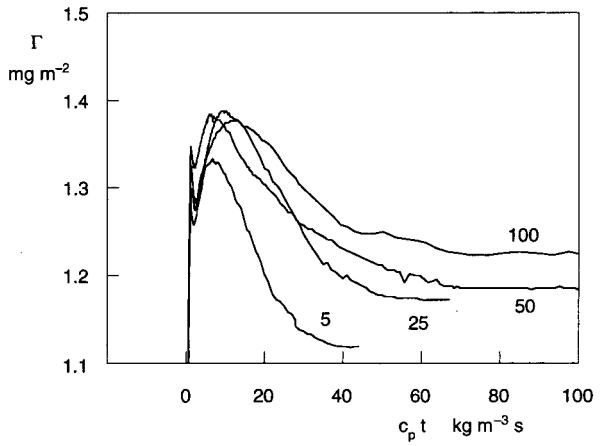

Figure 10. Part of the adsorption curves of G10 on silica as a function of the polymer flux for different polymer concentrations, which are indicated in the figure and are expressed in mg L^{-1}. The measurements were performed at an ionic strength of 10 mM and pH 6.

are occupied, and there is no need to displace some of the already adsorbed polymers to obtain that conformation. The adsorption curves of PAAm−PEO graft copolymers show a measurable overshoot, which is most pronounced for the polymer with the lower side-chain density.

To get a better insight into the overshoot phenomenon, we take a closer look at the adsorption kinetics of the graft copolymers on silica. We plot a part of the adsorption curve of G10, the polymer with the lower graft density and a large overshoot, for different polymer concentrations in Figure 10. In this case we normalize the variable time by multiplying it with the polymer concentration; the abscissa then represents the integrated polymer flux, i.e., the total mass of polymer supplied.

The maxima in the adsorption curves of Figure 10 are all, by approximation, located at a constant $c_p t$, which means that the moment when the maximum is reached is mainly controlled by the integrated polymer flux. We also observe that the decay rate of the adsorbed amount after the maximum depends on the polymer concentration. This implies that it is the transport rate which controls the decay rate of Γ rather than a process occurring at the surface. Another very important result seen in Figure 10 is that the overshoot does not disappear when the polymer is added very slowly, i.e., for low polymer concentrations.

From Figure 9b we know that probably only part of the PEO side chains is adsorbed on the silica surface and that the surface is only partly covered with adsorbed chains. The polymer layer could therefore gain some adsorption energy if it could bring more of the grafts in contact with the surface. This could be achieved by a reconformation of the adsorbed polymers such that more of the grafts are adsorbed to the surface. The polymers would then have to flatten their structure, thereby releasing some of the already adsorbed polymers. This would then lead to a decrease of the adsorbed amount. However, the results shown in Figure 10 do not support that the overshoot is caused by a conformational change of the adsorbed polymers. The polymer supply and the time given to obtain this supply determine the decay rate of the adsorbed amount. This suggests that the decrease of the adsorbed amount is more likely to be caused by displacement of initially adsorbed polymer chains by newly arriving molecules from solution. Such a process must, of course, be driven by a decrease of the systems' Gibbs energy.

Differences in graft distribution and graft density in the polymer sample could be a reason for displacement by polymer molecules from solution. The average number of grafts per polymer is rather low, roughly 15 for G10 and 30 for G18. On statistical grounds there should be an appreciable polydispersity in graft distribution and in graft density. Thus, the distribution of side chains along the PAAm chain is probably irregular, and also the number of grafts is not the same in the various molecules. Molecules in which the grafts are clustered in a few groups can displace molecules with more regularly separated grafts, and molecules with a high graft density can displace those with a lower number of side chains. The newly arriving molecules can then adsorb in a flatter conformation as the extra loss in conformational entropy is compensated by the gain in adsorption energy. Accordingly, the adsorbed amount decreases as the total number of adsorbed molecules decreases.

The overshoot is most pronounced for the polymer with the lower graft density. This is to be expected as this polymer has probably a larger polydispersity in graft density and graft distribution. The adsorbed amount in the plateau of the adsorption curve of G18 is slightly higher than that of G10. This seems to be in contradiction with the fact that the higher chain density gives a higher adsorption energy and probably a more flattened conformation of the resultant polymer layer. However, the difference in plateau adsorbed amounts is only small and could possibly be explained by the difference in molar mass.

Conclusions

The adsorption of graft copolymers of PAAm and PEO from an aqueous solution onto silica and titania was studied with reflectometry. Two high-molar-mass polymers (M_w of around 1 million g mol^{-1}) were used with different PEO side-chain densities: G10 with a weight percentage of 10% PEO side chains and G18 with 18% (w/w) PEO grafts. On titania, only the PAAm backbone adsorbs and the PEO chains do not. This results in an adsorbed amount of 0.85 and 0.83 mg m^{-2} for G18 and G10, respectively, which is about the same as that found for a PAAm homopolymer. This outcome is in agreement with self-consistent-field calculations reported by Van der Linden et al.[6] for a graft polymer with a low graft density and an adsorbing backbone.

On silica, the PEO side chains adsorb and the PAAm backbone has no affinity for the surface. In the initial part of the adsorption curves, the adsorption rate is the same as that on titania. For both polymers we observed a maximum in the adsorption as a function of time, after which the adsorbed amount decreases and a plateau is reached. The overshoot is small for G18 (0.05 mg m^{-2}) and more pronounced for G10 (0.2 mg m^{-2}). Such an overshoot phenomenon has only incidentally been reported before.[12−15]

The adsorbed amount on silica is much higher than that found on titania: in the plateau the adsorbances are 1.35 and 1.2 mg m^{-2} for G18 and G10, respectively. Upon adsorption the graft copolymers adapt a conformation in which only part of the side chains are adsorbed. Following the overshoot, both graft copolymers show a decrease in the total adsorbed amount. The

overshoot depends on the polymer concentration, which suggests that it is not caused by a conformational change of the adsorbed layer but by exchange with polymer molecules from solution.

Differences in graft distribution and graft density in the polymer sample could be a reason for displacement by polymer molecules from solution. The average number of grafts per polymer is rather low, roughly 15 for G10 and 30 for G18. On statistical grounds there should be an appreciable polydispersity in graft distribution and in graft density. Molecules in which the grafts are clustered in a few groups can displace molecules with more regularly separated grafts, and molecules with a high graft density can displace those with a lower number of side chains. The newly arriving molecules can then adsorb in a flatter conformation with a lower adsorbed amount as the extra loss in conformational entropy is compensated by the gain in adsorption energy. The overshoot is most pronounced for the polymer with the lower graft density. This is to be expected as this polymer has probably a larger polydispersity in graft density and graft distribution.

The high adsorbed amount of the graft copolymers on silica makes it very probable that they can effectively be used as steric stabilizers of aqueous silica dispersions.[20] An advantage of these polymers above diblock copolymers is that the latter usually form micelles in solution. The occurrence of micelles can form a kinetic barrier which slows down the adsorption process,[21] which is, for many applications, a major disadvantage. The adsorption of graft copolymers onto silica is a transport-limited process so that a stabilizing steric layer may be obtained much faster than with block copolymers.

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