Sequential Adsorption of Polymers. Displacement or Trapping?

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Received May 30, 1997; Revised Manuscript Received November 12, 1997

ABSTRACT: Sequential adsorption of carboxylated pullulan and pullulan on polystyrene-coated wafers was studied by reflectometry. The incoming pullulan partially displaced the preadsorbed carboxylated pullulan from the surface. Mixed adsorption layers were formed. By increasing the pH of the solution the carboxylated pullulan dissociated and desorbed, whereas the neutral pullulan was not influenced and remained adsorbed. A positively charged polyelectrolyte (quaternized poly(vinylpyridine)) was used as a probe for detecting the amount of trapped, negatively charged carboxylated pullulan remaining on the surface after the desorption step. This trapped carboxylated pullulan is retained by *pure* entanglement effects. By a mass balance calculation, the fractions of displaced, desorbed, and trapped carboxylated pullulan could be found for pullulans with different molecular weights. The shorter pullulans did not displace any carboxylated pullulan but trapped about half of the layer; the other half could desorb rapidly upon pH increase. Longer pullulan molecules could displace up to 70% of the carboxylated pullulan layer, so that smaller quantities remained to be trapped. Upon pH increase, another 10−15% desorbed, about as much as the amount trapped. Hence, during sequential adsorption both rapid displacement and trapping occur but to different extents depending on the molar mass of the polymer supplied last.

Introduction

The exchange kinetics of adsorbed macromolecules by chemically or physically different chains from solution can provide insight into polymer behavior in the vicinity of a surface covered with an adsorption layer. The occurrence of time-dependent effects in this tiny interfacial region has been demonstrated experimentally[1−5] and discussed theoretically.[6−8]

An exchange process includes different steps beginning with the transport of the displacer (B) through the solution and its attachment to the surface, followed by conformation changes of the displacer and ending with the detachment of the preadsorbed molecules (A) and their transport away from the surface.[4] In general, weakly bound polymers are displaced by strongly adsorbing chains.[9] The overall driving force for this is the lowering of the surface energy by the formation of stronger bonds. However, short chains can also be displaced by chemically identical (or very similar) but longer chains, because this raises the entropy in the system. The central question with respect to such exchange processes is as follows: How do chains enter and leave the surface layer? Do entanglements play a role? Two scenarios have been proposed.

Granick[2,8] has held the view that the incoming polymer forms an overlayer over the preadsorbed chains, thereby pinning them to the surface. The desorbed chains have then to reptate out of the trapped state. A strong argument in favor of this view is the occurrence of topological effects, i.e., branching, which slow the exchange process considerably.[2] A problem with this picture is, however, the passive role of the overlayer; eventually, the segments of the overlayer must occupy the sites uncovered by the leaving chain. On a heterogeneous surface with two kinds of sites (X and Y), where polymer A has affinity for the X-sites only, and polymer B for the Y-sites, overlayer formation is quite conceivable. In this situation, however, removal of the trapped polymer (A) does not make new sites available (for B), so that displacement is not likely to occur because there is no driving force. Hence, the exchange process must also be considered at the level of individual segments competing for surface sites.

A different scenario favors a kind of “zipping” process, taking place at constant energy and thus diffusive in nature.[7] The displacer initially finds a small area on the surface (a “hole”) where it adsorbs in a coillike conformation. The preadsorbed chains are initially in a flattened conformation with a large number of contacts.[10] Displacement occurs by gradual enlargement of the area occupied by the displacer (spreading) at the expense of the surrounding chains.[11−13] This mechanism implies that spreading of the displacing chain is rate determining in a displacement process. This view does not account very clearly for the topological effect. Hence, it is still difficult to decide which process is occurring. It should be realized that in all cases studied so far the displaced polymer had attractive interactions with the surface which would affect the reptation and spreading processes. It has been shown that a weaker segment/surface interaction leads to faster exchange,[14] but this observation as such does not discriminate between the two proposed mechanisms.

Thus, the rates and the mechanisms of displacement and the mobility of polymers in the adsorbed or trapped state are still not understood. The present study aims at getting more insight in this issue.

To this end, we attempted to create a system where desorption is rate limited by pure diffusion (including topological effects) but not by energetics of surface detachment. In other words, we tried to trap nonadsorbed (A) chains by first forming a B-overlayer over adsorbed A and then switching the conditions such as to detach A’s polymer−surface bonds. The experimental approach was the following. Two chemically similar, flexible, water-soluble polymers, carboxylated pullulan and pullulan, are consecutively adsorbed on a polystyrene-coated silicon wafer. Provided fast and complete displacement can be ruled out, both polymers are present on the surface. When the pH of the solution is

S0024-9297(97)00762-6 CCC: $15.00

Table 1. Characteristics of Polymer Samples Used

polymer	M_w	M_w/M_n[a]	R_g (nm)[b]
Pu	48 000	1.09	5.9
Pu	100 000	1.1	8.9
Pu	186 000	1.13	12.5
Pu	380 000	1.12	18.6
Pu	853 000	1.14	29.2
Dx	500 000	<1.2	15.4
ox·Pu	105 000	1.3	9.1
PVP$^+$	120 000	1.03	10

[a] M_w and M_n are the weight-averaged and number-averaged molecular weights, respectively. [b] R_g, the radius of gyration, was calculated according to ref 18.

increased, the carboxylated pullulan charges up and desorbs, whereas the neutral pullulan is not influenced and remains adsorbed. If the two polymers would coexist at the surface separately without any entanglement, there should be no limitation for the detached polymer to leave the surface. In the case of overlayer formation, however, the diffusion away from the surface would be hindered due to the pullulan that pins the desorbed chains to the surface. It should be realized that, as a rule, polymers cannot be desorbed by a mere lowering of the concentration in solution; rinsing with pure solvent has hardly any effect. Hence, as long as the energy of the polymer—surface interaction is not affected, one may expect to have stable adsorption layers.

A positively charged polyelectrolyte (quaternized polyvinylpyridine) was used as a probe for detecting the amount of trapped, negatively charged carboxylated pullulan remaining on the surface after the desorption step. Because the amount of adsorbed pullulan is known, this suffices to find, from a simple mass balance, the amounts of displaced, desorbable (nontrapped), and trapped carboxylated pullulan. We determined such distributions for different molecular weights of the displacer.

The adsorption and desorption was measured by reflectometry, a convenient tool for following the kinetics of these processes.

Experimental Section

Materials. The experiments were carried out with different polysaccharides: pullulan (Pu), carboxylated pullulan (ox·Pu), and dextran. Pullulan is a linear polysaccharide consisting of maltotriose as the repeating unit connected through α-1,4 and α-1,6 glycosidic linkages. It is a water-soluble polymer, and its solution properties have been studied by static and dynamic light scattering.[15]

In dextran approximately 95% of the glucose units are joined by α-1,6-linkages. The remaining 5% are connected via 1,4-, 1,3-, 1,2-linkages in side chains. Although the branches are mostly not very long, they have an influence on the solution properties.[16]

Pullulan with a narrow molecular weight distribution was purchased from PL-Polymer Standards and used without further purification. Dextran was a product of Pharmacia, Sweden. The characteristics of the samples are given in Table 1. Carboxylated pullulan (ox·Pu) was prepared from a commercial pullulan sample following the method described by De Nooy *et al.*[17] In the carboxylated pullulan the hydroxyl group at the C_6-atom was oxidized to get carboxylic groups. The approximate molecular weight was 105 kD ($M_w/M_n = 1.3$) with a degree of oxidation of 74% as was determined by specific colorimetry and ^{1}H NMR.

Quaternized poly(2-vinylpyridine) (PVP$^+$) with a molecular weight of 120 000 from Polymer Standards was used as a probe for the negatively charged ox·Pu remaining at the surface.

Table 2. Refractive Index Increments of Carboxylated Pullulan

pH	dn/dc (cm^3/g)
2	0.100
4	0.111
5.5	0.160
9.5	0.166

Weighed amounts of the polymer were dissolved in deionized water. A stock solution with a concentration of 100 ppm was prepared and diluted to 10 ppm prior to the measurement. The pH of the solutions was adjusted by adding 1 N HCl or NaOH. All adsorption experiments were performed at pH 2. Desorption was followed at pH 9.

Reflectometry. The adsorption measurements were carried out in a reflectometer equipped with a stagnation point flow cell as described by Dijt *et al.*[19] The relative change in the reflectometer signal ΔS upon adsorption with respect to the initial value S_0 on a bare surface is proportional to the adsorbed amount Γ:

$$\Gamma = \frac{1}{A_S}\frac{\Delta S}{S_0} \tag{1}$$

The sensitivity factor A_S was calculated by a method of Hansen.[20] In this method the reflection of the laserbeam is modeled as a reflection at flat parallel layers of uniform refractive index. Each layer is represented by a matrix containing the reflectivities at the phase boundary and the phase shift in the layer. Multiplication of the matrices yields A_S.

For the calculation of the adsorbed amount a model for the concentration profile in an adsorbed layer is required that can be converted into a refractive index profile. A single-step profile was proven to give reliable results for the adsorption of polymers.[19] The refractive index n_a of an adsorption layer of thickness d_a can be expressed as a function of the adsorbed amount

$$n_a = n_s + \left(\frac{dn}{dc}\right)\frac{\Gamma}{d_a} \tag{2}$$

where dn/dc is the refractive index increment of the adsorbing polymer in solution and n_s is the refractive index of the solution.

The refractive index increment (dn/dc) for pullulan and dextran in water is 0.148. This value is independent of molecular weight, temperature, and pH. The dn/dc of the carboxylated pullulan was found to depend strongly on the pH of the solution. In Table 2 the values as measured with a differential refractometer are listed.

The A_S values are 0.0266 m^2 mg^{-1} for both pullulan and dextran, and 0.0377 m^2 mg^{-1} for PVP$^+$. For the carboxylated pullulan, $A_S = 0.0179$ m^2 mg^{-1} and 0.0298 m^2 mg^{-1} were calculated for pH 2 and pH 9, respectively.

In adsorbed layers containing only one type of polymer, the adsorbed amount follows directly from eq 1. The results are then given in terms of Γ (mg/m^2).

In mixed adsorbed layers, as expected to appear in the present work, the signal $\Delta S/S_0$ contains contributions of different polymers with different sensitivity. Separation of these contributions is not possible, and therefore the adsorbed amount cannot be calculated unambiguously for mixed adsorbed layers. Therefore, the results of the adsorption measurements are given in terms of the signal $\Delta S/S_0$.

Substrate. Highly pure silicon wafers of the Czochralsky-type were cleaned with toluene, rinsed with alcohol, and dried with dust-free nitrogen gas. The clean strips were kept under a UV lamp and oxygen for 15 min to ozonize them.

Polystyrene films were prepared by spin coating on the clean and dust free silicon wafers from toluene solution (polystyrene of molecular weight 100 000, in HPLC grade toluene) at 2500 rpm. The samples were then annealed in an oven for 2 h at 100 °C.

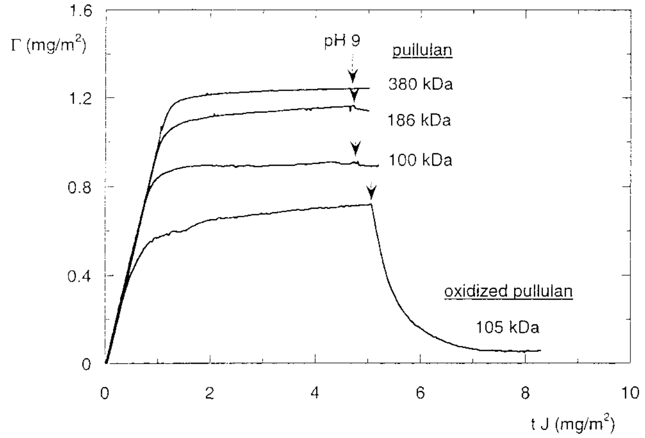

Figure 1. Adsorbed amount of pullulan and carboxylated pullulan on polystyrene-coated silica as a function of time for different molecular weights at pH 2. The time is given in reduced units t^*J (for explanation, see text). Indicated with an arrow is the moment of switching to pH 9. Polymer concentration: 10 ppm.

The resulting film thickness was found to be dependent on the concentration of the solution. With a concentration of 12 g/L a film thickness of 52−55 nm was found, as determined by ellipsometry. The homogeneity of the polystyrene film was checked by light microscopy and AFM. The films were very smooth and nearly defect free.

Results and Discussion

Polysaccharides (except as derivatives containing ether groups, such as ethyl(hydroxyethyl)cellulose) do not adsorb on oxidized silicon, but they readily adsorb onto a hydrophobic polystyrene surface. The adsorption of pullulan and carboxylated pullulan on a PS coated Si-wafer at pH 2 is shown in Figure 1. At $t = 0$ the supply of the polymer solution into the cell starts. First, the adsorbed amount, Γ, increases linearly with time. In this region the adsorption is transport-limited, and the initial adsorption rate $(d\Gamma/dt)_{t=0}$ equals the maximum mass transfer rate, J, toward the surface.[6] The adsorption rate is not reduced by previously deposited polymer until very close to saturation, when it falls abruptly. The adsorbed amount is given as a function of the rescaled time J^*t, leading to an initial slope of unity for all experiments.[21]

The shape of the adsorption curves is similar for all pullulans. Close to saturation the adsorption rate decreases, a plateau region is reached. The maximum adsorbed amounts, Γ_{max}, of the polysaccharides are different. It is the lowest for the carboxylated pullulan and increases with increasing molecular weight for pullulan. At pH 2 neither the adsorbing surface nor the carboxylated pullulan is charged. On comparing Γ_{max} of the carboxylated pullulan with that of pullulan of nearly the same molecular weight (Pu 100 000) a difference of the adsorbed amounts of about 0.1 mg/m² was found. This is an indication of a similar affinity for the surface, although the chemical structure of the polymers is slightly different (carboxylic group instead of hydroxyl group at the C_6-atom in the carboxylated pullulan). Apparently, pullulan and carboxylated pullulan adsorb by the same interaction with the surface. We note in passing that polydisperse polymers tend to show a somewhat more gradual increase in adsorbed amount, very likely due to exchange between short and long chains. This seems to be the case for oxypullulan, which is not a fractionated sample (see Table 1).

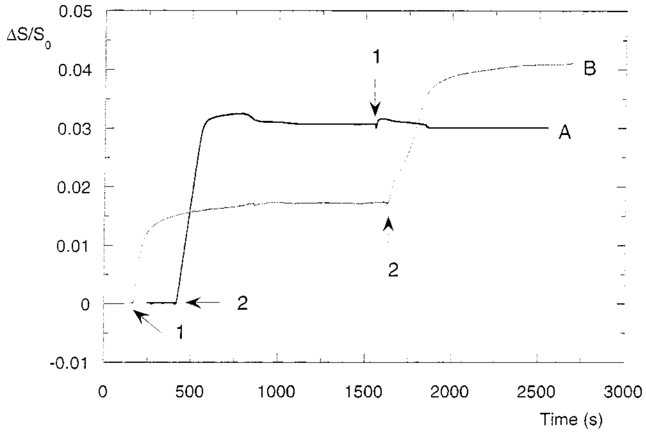

Figure 2. (a) Sequential adsorption of pullulan 380 kD (2) and carboxylated pullulan (1) on PS as a function of time. (b) Sequential adsorption of carboxylated pullulan (1) and pullulan 380 kD (2) on PS as a function of time.

When the adsorption had stopped increasing, the flow was switched to pure solvent (pH 2). It was checked that no desorption took place, even after prolonged rinsing (data not shown). This is commonly observed for adsorbed flexible polymers and is evidence for a strong attachment of the polymers to the surface with a large number of segments.

Marked with an arrow in Figure 1 is a pH-change from pH 2 to pH 9. While no desorption occurred in the case of pullulan, the carboxylated pullulan desorbed almost entirely within 100 s. At high pH the carboxylic groups are negatively charged. The charges repel each other, leading to the desorption of the macromolecules due to the lateral electrostatic repulsion. In addition, the counterions around each polyion tend to move way from the surface (for entropic reasons) thereby inducing desorption, too.

In Figure 2 the results of sequential adsorption measurements at pH 2 are plotted. In Figure 2a pullulan (380 000) was first allowed to adsorb. After the plateau value was reached, the flow was switched to carboxylated pullulan. In Figure 2b the order of addition of the two polymers was reversed. The adsorption curves show a qualitatively different behavior. For the case where the PS-surface was first covered with pullulan no additional adsorption of carboxylated pullulan occurred. The reflectometer signal remained constant and no change in the adsorbed amount took place. This indicates that attractive interactions between pullulan and carboxylated pullulan are absent or negigible and rules out the possibility that there is a propensity to form mixed layers for thermodynamic reasons. On the contrary, it is the sample history which determines the layer structure and composition.

If carboxylated pullulan was preadsorbed and pullulan was consecutively added, the signal increased sharply (Figure 2b). The final signal was more than twice as high as for carboxylated pullulan alone and even exceeded the value for pullulan 380 000 on an initially bare surface (see Figure 2a). Although it was not possible to distinguish directly between the adsorbed polymers, because the signal contained contributions of both of them, the absolute height of the signal clearly indicated that both polymers were adsorbed. On the other hand, some displacement of the carboxylated pullulan by the pullulan 380 000 cannot be ruled out.

Similar measurements were carried out with all pullulans, and with dextran, as listed in Table 1. The

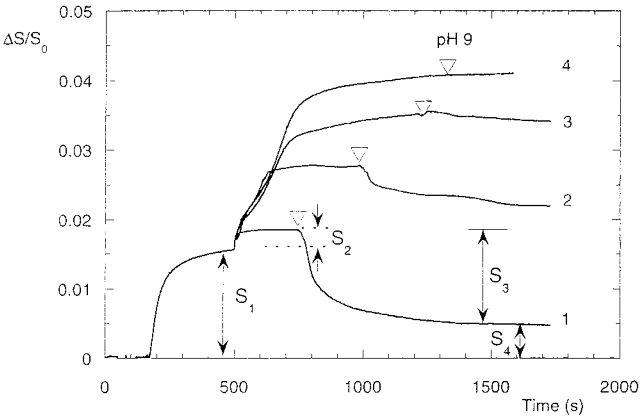

Figure 3. Sequential adsorption of carboxylated pullulan and different amounts of Pu 380 kD (curves 1–4). Marked with a triangle on every curve is the change to pH 9 and the following desorption of carboxylated pullulan. S_1, signal change due to the adsorption of carboxylated pullulan; S_2, adsorption of Pu 380; S_3, desorbed amount carboxylated pullulan; S_4, final adsorbed amount.

qualitative behavior was the same for all polysaccharides. The sequence pullulan–carboxylated pullulan did not show an increase in the adsorbed amount, whereas the reversed order resulted in a remarkable increase of adsorbed polymer in all cases.

When the pH was increased, the carboxylic groups charge up and the carboxylated pullulan chains are no longer attached to the surface and may desorb. As we have seen above from the reverse sequence experiments, carboxylated pullulan and native pullulan do not attract each other so that at pH 9 it seems unlikely that potential wells hold the desorbing polymer.

To study the degree of desorption the following experiment was carried out. First, carboxylated pullulan (**1**) was flowed into the cell until the surface was saturated; i.e., the adsorption curve reached its plateau region. After rinses with pure solvent, different amounts of the second polymer, pullulan (**2**), were added. This was done by varying the time of injection of polymer **2**. The flow was switched for several seconds to pullulan and then back to the solvent. The signal raised with the addition time of pullulan. After switching back to the solvent the signal remained constant at that value, indicating that no desorption, either of polymer **1** or of polymer **2**, occurred in pure solvent flow. The results are shown in Figure 3 for four different addition times of pullulan 380 000. Curve 1 corresponds to the shortest time, and curve 4 to an uninterrupted flow of polymer **2**, i.e., to a complete adsorption curve (see also Figure 2b).

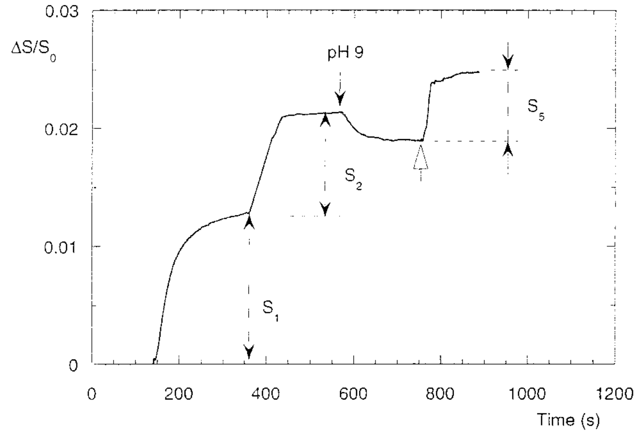

Figure 4. Sequential adsorption of carboxylated pullulan, Pu 380, and PVP$^+$. Key: S_1, signal change due to the adsorption of carboxylated pullulan; S_2, adsorption of Pu 380; S_5, signal change due to the adsorption of PVP$^+$. Marked with an arrow is the switch to pH9.

For the purpose of interpretation, we distinguish various levels of adsorption in Figure 3. For the interpretation of the results for mixed layers we use the reflectometer signals as such; we do not calculate the corresponding adsorbed amounts for the reason explained in the Experimental Section. S_1 corresponds to the change in the reflectometer signal due to the adsorption of carboxylated pullulan (polymer 1). S_2 is the additional signal change which occurs upon the adsorption of the second polymer, the pullulan. S_3 and S_4 correspond to the desorbed amount and the remaining signal, respectively. The latter contains contributions from the trapped carboxylated pullulan and the pullulan, whereas S_3 can be attributed to the desorbed carboxylated pullulan alone. The moment of switching between pH 2 and pH 9 is marked with a triangle at every curve. After the pH-change the adsorbed amount began to decrease, being most pronounced in curve 1. It is important that the steepness of decrease is less than for carboxylated pullulan alone (Figure 1): the pullulan chains slow the desorption of the carboxylated pullulan despite the repulsion between the two. This must be due to topological effects. Even a small adsorbed amount of pullulan ($S_2 << (S_2)_{max}$), influences the desorption rate of ox· Pu. We further note the large decrease in S_3 upon an increase in the adsorbed amount of pullulan (S_2). The more pullulan was adsorbed the less carboxylated pullulan seems to desorb. In curve 4 only a small remaining change in the signal was observed.

What scenarios could one think of to explain these observations?

As was shown before, *complete* displacement of the carboxylated pullulan did not occur. On the other hand, some displacement seems to be likely especially for pullulans with a higher molecular weight than ox·Pu. Nevertheless, some carboxylated pullulan remains at the surface. This finding was proven by measuring the adsorption of the positively charged polyelectrolyte PVP$^+$. If there is negatively charged ox·Pu trapped at the surface, one should expect an increase in the reflectometer signal due to the binding of the oppositely charged macromolecules. The measurements were carried out in a salt-free solution so that electrostatic interactions are not screened. A rapid increase of the signal was found. For an unambiguous interpretation of the results additional measurements have been done to establish the adsorption behavior of PVP$^+$ at the polystyrene surface as well as at a neutral pullulan adsorption layer. A small and very slow increase of the adsorbed amount PVP$^+$ occurred at the naked PS-surface at pH 9. No adsorption of PVP$^+$ occurred at a pullulan-coated surface.

In Figure 4 we give, by way of example, a full adsorption curve for the sequential adsorption of carboxylated pullulan and pullulan 380 000, together with the signal change due to the addition of PVP$^+$. The addition of PVP$^+$ after the desorption step at pH 9 is marked with an open arrow. The signal increases sharply upon the addition of PVP$^+$ (S_5), indicating the presence of carboxylated pullulan on the surface.

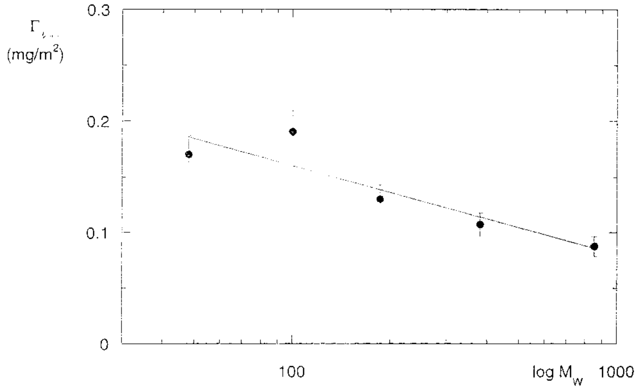

Figure 5. Adsorbed amount PVP$^+$ on an adsorption layer of carboxylated pullulan and pullulan with different molecular weights.

Having established the presence of retained ox•Pu in a qualitative sense, we would like to proceed to a more quantitaive approach. To this end, systematic measurements of the dependence of the adsorbed amount PVP$^+$ on the molecular weight and the adsorbed quantity (S_2) of pullulan have been performed. In Figure 5 we plot results of these experiments, namely the adsorbed amounts of PVP$^+$ as a function of the molecular weight of the five pullulan samples used as displacers. An clear overall tendency of decreasing adsorbed amounts of PVP$^+$ with increasing molecular weight of the pullulans is found.

Does this decrease in Γ_{PVP} really correspond to a decrease in the amount of retained ox•Pu or is it due to some other effect? It might be that the adsorption of PVP$^+$ becomes more and more hindered for sterical reasons. Pullulans with increasing molecular weights form thicker adsorption layers and might screen the remaining carboxylated pullulan. However, because of the absence of electrolyte this is unlikely. We therefore conclude that the amount of ox•Pu really decreased and that this was due to the fact that Pu becomes a more effective displacer when its molecular weight increases. This interpretation was corroborated by our observation that PVP$^+$-adsorption was also decreased when, for one pullulan, S_2 was increased.

All this implies that we can, by using a simple mass balance, get a more quantitative idea of the fractions of carboxylated pullulan that are displaced, desorbed, and trapped. First, we assume that the stoichiometry of binding of positive charges in PVP$^+$ and negative charges in ox•Pu can be described by the following ratio:

$$f = \frac{\Gamma_+ M_-}{\alpha \Gamma_- M_+} \tag{3}$$

Γ_+ and Γ_- are the adsorbed amounts and M_+ and M_- are the molar monomeric masses of the cationic and anionic polymer, respectively, and $\alpha = 74\%$ is the degree of carboxylation of ox•Pu.

It was found, that any signal change, i.e., decrease upon switching to pH 9 and increase upon addition of PVP$^+$, occurred *only* on adsorbed and dissociated carboxylated pullulan. Thus, from the experiments, the desorbed (S_3) and trapped (S_5) amounts of carboxylated pullulan can be found, and subsequently the amount of displaced ox•Pu can be calculated according to

$$S_{\mathrm{displ}} = S_1 - (S_3 + S_5)$$

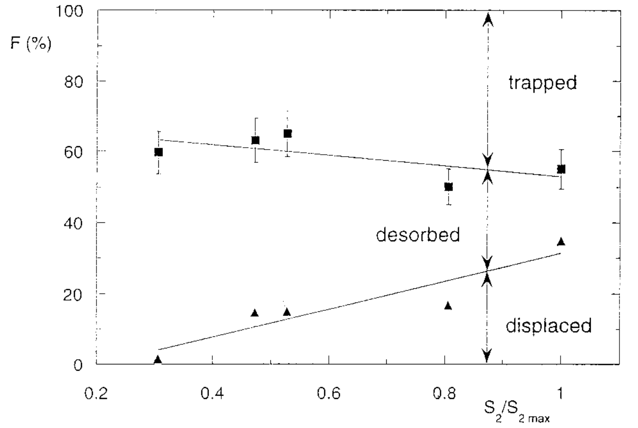

Figure 6. Trapped (S_5/S_1), desorbed (S_3/S_1) and displaced ($S_1 - (S_5 + S_3)$) fractions of preadsorbed carboxylated pullulan (in %) as a function of consecutively adsorbed pullulan 100 K (S_2). $(S_2)_{\max}$ corresponds to full and uninterrupted adsorption of pullulan. The error bars give an indication of the experimental uncertainty. Key: triangles, displaced fraction; squares, displaced + desorbed fraction ox•Pu.

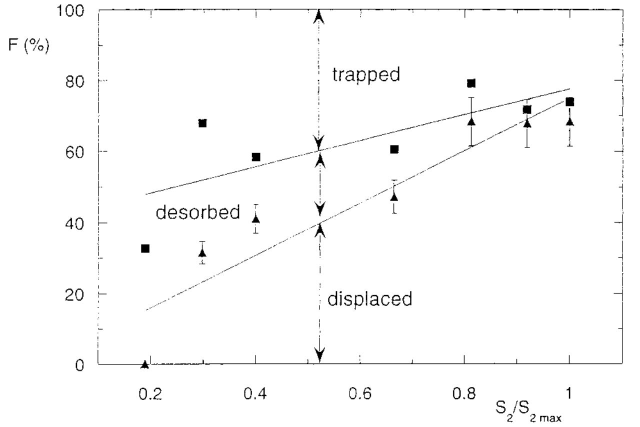

Figure 7. Trapped, desorbed, and displaced fractions of preadsorbed carboxylated pullulan (in %) as a function of consecutively adsorbed pullulan 380 K (S_2). $(S_2)_{\max}$ corresponds to full and uninterrupted adsorption of pullulan. Key: triangles, displaced fraction; squares, displaced + desorbed fraction ox•Pu.

First, let us give an estimation for the stoichiometric factor *f*. For this purpose we inspect the results for Pu 48 000. The sum of the signal changes on desorption of ox•Pu ($S_3 = 9.3$ mV) and on adsorption of PVP$^+$ ($S_5 = 6.4$ mV) equals the signal change on adsorption of carboxylated pullulan S_1 (15.7 mV). That means, that there cannot be displacement of ox•Pu by Pu 48 000. We can rewrite eq 3 in terms of signals, and by taking into account that $S_+ = S_-$, we find

$$f = \frac{S_+ A_S^+ M_-}{S_- A_S^- M_+ \alpha} = 1.7 \tag{4}$$

This stoichiometric ratio implies that roughly every second positive charge compensates a negative one. Thereby we might rather underestimate the trapped amount ox•Pu at the surface. We note in passing that *overcompensation* is a recurrent feature of charged polymers binding to charged surfaces.

In Figures 6 and 7 the dependence of the trapped and desorbed carboxylated pullulan as a function of pullulan adsorption, as found experimentally, is given for Pu 100 000 and 380 K, respectively. The displaced fraction

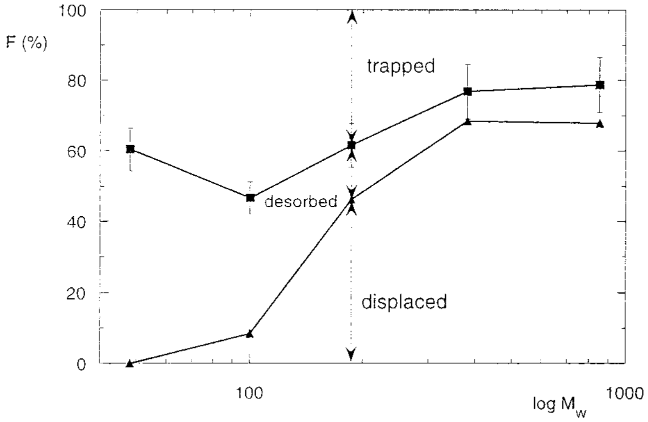

Figure 8. Trapped, desorbed and displaced fractions of preadsorbed carboxylated pullulan (in %) for different consecutively adsorbed pullulans and for dextran 500 K. Key: triangles, displaced fraction; squares, displaced + desorbed fraction ox·Pu.

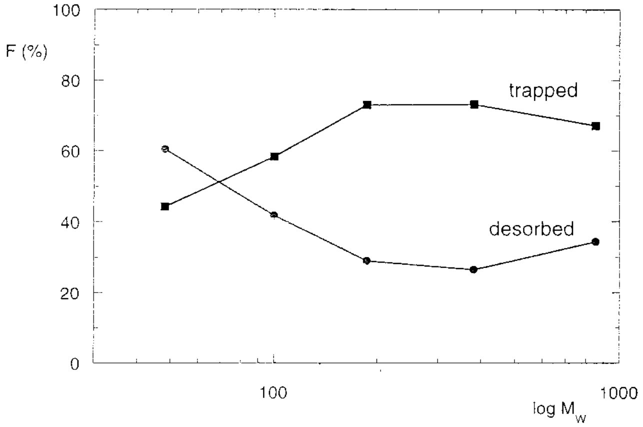

Figure 9. Distribution of the desorbed and trapped fraction of remaining carboxylated pullulan after displacement as a function of pullulan molecular weight. Key: circles, desorbed fraction; squares, trapped fraction.

was calculated and plotted in the same figure. The amounts are given as fractions of the preadsorbed ox·Pu (S_1). On the x-axis S_2 is given as $S_2/(S_2)_{\max}$, where $(S_2)_{\max}$ corresponds to an uninterrupted adsorption of pullulan onto the surface with preadsorbed carboxylated pullulan at pH 2.

Whereas the trapped amounts in Figure 6 are nearly constant, the desorption of ox·Pu is decreasing with increasing Pu 100 000 adsorption. According to the mass balance that means increasing displacement of preadsorbed ox·Pu upon addition of Pu 100. Finally, nearly half of the carboxylated pullulan remains trapped at the surface; 20% can desorb, and 30% must have been displaced.

In Figure 7 the results are given for Pu 380 000. The molecular weight of this polymer is three times as high as that of the carboxylated pullulan. One would expect a more effective displacement, because entropically it is more favorable for the pullulan to adsorb at the surface. Indeed, we could find about 70% displacement of ox·Pu for an uninterrupted, full adsorption of pullulan. This is almost twice as much as for Pu 100 000. Both the trapped and the desorbed fractions of ox·Pu decrease upon addition of pullulan. Over the whole range of added pullulan the trapped fractions are higher than the desorbed ones. Finally, all remaining ox·Pu is trapped, and no desorption takes place at $S_2/(S_2)_{\max} = 1$.

In Figure 8 we compare the results for the five different pullulans at $S_2/(S_2)_{\max} = 1$. The trapped, desorbed and displaced fractions of carboxylated pullulan are plotted for each polysaccharide. With increasing molecular weight of the pullulans the displacement of carboxylated pullulan during the sequential adsorption increases. Remarkable is the shape of the displacement curve. Similar S-shaped curves have been found earlier [24] for increasing molecular weights of the displacer, although they usually reach 100% displacement. In our experiments we found that the displacement is not complete even for the highest measured molecular weight pullulan (Pu 853 000). A small amount of carboxylated pullulan remains always at the surface. Those macromolecules which are not (or only loosely) pinned to the surface by the consecutively adsorbed pullulan can leave the surface when switching to pH 9. This amount was found to be lower than that of trapped chains for Pu 100 000-853 000. Only for Pu 48 000 and dextran 500 000 this order is reversed. Pu 48 000 appears to be a bad displacer for ox·Pu (105 000) but a good trapper, whereas Pu 853 000 displaces about 70% of the preadsorbed ox·Pu and traps about 10%. This tendency is also illustrated in Figure 9. It shows the fractions of desorbed and trapped ox·Pu that remain after displacement by the pullulans. The fraction of trapped ox·Pu is always higher than the desorbed one except for Pu 48 000 and is nearly constant for M_w >100 000.

The behavior of dextran differs from that of the pullulans. Dextran 500 000 displaces less ox·Pu upon adsorption than one would expect when taking into account the molecular weight. The fraction of desorbed ox·Pu at pH 9 is higher than for Pu 380 or 853 000. Dextran seems to form more easily mixed layers without displacing big amounts of ox·Pu. On the other hand, the trapped amounts are comparable to those of pullulan. Structural constraints are important factors in the kinetics of displacement, and most likely the branched structure of dextran is the reason for this behavior.

Conclusions

The consecutive adsorption of carboxylated pullulan (ox·Pu) and pullulan (five different molecular weights) has been studied by reflectometry. It could be shown that both polymers are present at the surface. When the incoming pullulan is of low molecular weight (Pu 48 000), it adsorbs but it does not displace the carboxylated pullulan. Higher molecular weight pullulans can displace ox·Pu; the displaced amount increaes with molecular weight up to a maximum of about 70%. In no case does complete displacement occur. When the pH is increased to 9, the surface is no longer attractive for the carboxylated pullulan. As a result, part of the remaining carboxylated pullulan desorbs, *but not all*; part is retained by the pullulan overlayer. As there is no attractive interaction left, we conclude that these "trapped" chains are held *purely* by entanglements (pinning). Weak dependencies on molecular weight of the pullulan are found for the trapped and desorbed amounts. Roughly 60% of the remaining carboxylated pullulans were found to be in a trapped state, and 40% can still desorb. The constancy of this ratio despite the variations in molecular weight of the adsorbed pullulan suggests that the chances for a molecule to escape from under an overlayer are determined by some kind of local structure, for which the length of the chains is irrelevant. It thus seems that the effectiveness of the longer pullulan chains in displacing ox•Pu molecules is not related to the overlayer structure but instead to their having a better chance to find a "hole" and start displacing ox•Pu by the spreading process. Clearly, a complete description of the exchange process should involve both spreading and reptation processes.

Acknowledgment. This work was supported financially by the Eu-HCM program under contract no. CHRX-CT94-0655. We thank E. Paris for making useful suggestions concerning the pullulan polymers. Several suggestions from the reviewer to improve the discussion and presentation of the paper are also gratefully acknowledged.

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MA970762N