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Polymer Brushes

Ultradense Polymer Brushes by Adsorption

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In 1979, De Gennes[1] coined the term "brushes" for dense layers of end-attached polymer chains on surfaces. Brushes are an intriguing class of matter: the molecules in a (solvent-swollen) brush are forced by their neighbors into a permanent state of stretching, a state they would never adopt in a three-dimensional solution. For this stretching to occur, the number of end-attached chains per unit area (the so-called grafting density) has to reach values in the range of at least 0.1 nm^{-2}, preferably even ten times as high. Brush layers have been investigated intensively, not only to fundamentally understand their peculiar properties, but also because they give a surface very useful properties, such as ultralow friction and repellence towards proteins, bacteria, and cells (antifouling).

Making dense brushes is quite a challenge, though. The various techniques have been extensively debated in a number of good reviews.[2–5] Essentially, there are three methods: the first is to grow polymer molecules from the attachment point outward ("grafting from"), the second is to chemically graft an existing polymer chain (with a reactive chain end) to a surface ("grafting to"), and the third is to attach a polymer to the surface physically, using an anchor block ("adsorption"). Again it was De Gennes who pointed out that it would be impossible to achieve the required grafting densities with the "adsorption" method. The argument is that in order to bring its sticky end in contact with the surface, each new chain has to make its way through a "forest" of previously attached chains by which it is strongly repelled. The strength of the repulsion for a chain consisting of N monomers would be of order $kTN\nu(\sigma L^2)^{2/3}$, where σ is the grafting density, L the typical length of a monomer, ν the (scaled) excluded volume of a monomer, and kT the thermal energy. For a poly(ethylene oxide) (PEO) brush of 400 monomers in a good solvent like water at a grafting density of 0.1 nm^{-2}, the barrier would be roughly $20\,kT$. Since the grafting rate is exponentially lowered by this barrier, it can be estimated that the rate of attachment would sink down to something like 0.1 chain per nm^2 per two weeks, which clearly precludes getting near 1 nm^{-2}.

We might assume that De Gennes' argument also applies to the "grafting to" technique, as in that case polymer chains also need to reach the interface. This problem, however, is circumvented by producing such brushes from a polymer melt. Without solvent the repulsive barrier is much lower, and high grafting densities can be reached. For PEO brushes, Zdyrko et al.[6] reached a grafting density of about 1.5 nm^{-2} using the "grafting to" approach. Obviously, De Gennes' argument does not apply to the "grafting from" approach, as when growing the chains from the surface, the separate monomers do not experience such a high barrier. This approach has been taken by many a polymer chemist, and dense brushes have indeed been reported.[5] However, for both approaches the price paid for these high grafting densities is that the density is very hard to control and that both approaches, compared to the "adsorption" approach, are relatively difficult and time-consuming.

From the above discussion, it may be concluded that adsorption is a poor approach to make dense brushes of polymer chains in a good solvent. Herein, we show that this is not always true: we report a new method to produce very dense brushes (well over 1 nm^{-2}) using adsorption and thus "sneak" around De Gennes' argument.

We aimed at a very strong attraction between the anchor block and the surface. Such strong attraction is generally hard to achieve in a solvent in which both blocks are soluble, but in water electrostatic attraction can be exploited by adsorbing a diblock copolymer comprising a charged anchor block and a neutral block to an oppositely charged surface. However, as a flat solid surface can only accommodate a limited number of charges, this approach would not ensure obtaining high grafting densities. We therefore decided to employ as substrate a surface covered with attached polyelectrolyte, for example, a polyelectrolyte brush, which can accommodate many more charges. A large amount of the diblock copolymer can potentially adsorb onto such a surface, so the resulting neutral brush may have a very high grafting density. The principle is depicted in Figure 1. The typical nature of electrostatic interactions would imply that the density of the new brush, σ_{brush}, is determined by a charge-compensation rule, that is, the charge on the adsorbing chains (the anchor blocks with length N_{anch}) should equal that of the polyelectrolyte brush ($\sigma_0 N_0$, where σ_0 is the density of this brush and

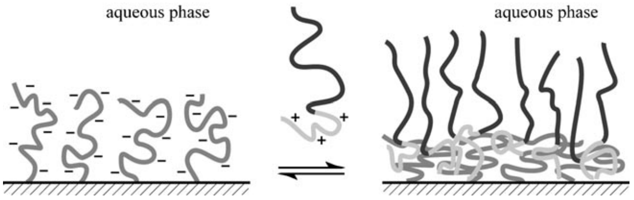

Figure 1. Schematic representation of the formation of "zipper brushes", that is, dense neutral brushes by adsorption of a diblock copolymer to a polyelectrolyte brush layer. In this picture, the polyelectrolyte block has half the degree of polymerization of the polyelectrolytes in the brush. Thus, the grafting density of the formed neutral brush is twice that of the original polyelectrolyte.

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N_0 the length of its chains). Such a charge-compensation rule is also seen in the formation of so-called complex coacervate core micelles (C3Ms) as described by Voets et al.,[7] in which oppositely charged polyelectrolyte blocks form a relatively dense core with the neutral chains sticking out into the solution. In our case, the polyelectrolyte coacervate phase forms a relatively dense layer at the substrate surface with the neutral brush on top of it. Since each adsorbing diblock carries one neutral chain, we can use Equation (1) to describe the density of the resulting brush:

$$\sigma_{\text{brush}} = \frac{N_0\sigma_0}{N_{\text{anch}}} \qquad (1)$$

Note that if $N_0/N_{\text{anch}} > 1$, the original density is amplified, potentially by a significant factor (e.g., 5–10).

A further advantage of this method is that the complexes of oppositely charged polyelectrolyte chains can be broken by adding salt or changing the pH value of the solution, thus restoring the original polyelectrolyte brush. We therefore introduce the term "zipper brush" for this kind of brush layers.

Does this idea work? We investigated the adsorption of poly(*N*-methyl-2-vinyl pyridinium)-*block*-poly(ethylene oxide) (P2MVP-PEO) and poly(*N*,*N*-dimethyl amino ethyl methacrylate)-*block*-poly(ethylene oxide) (PDMAEMA-PEO) to a poly(acrylic acid) (PAA) brush. We prepared PAA brush layers on polystyrene-coated silicon wafers by means of the Langmuir–Blodgett (LB) technique described by Currie et al.[8] This technique is a variation of the "adsorption" approach, in which the polymer brush is first produced on an air–water interface. By compression of the air–water interface, the grafting density of the brush can be controlled, and the brush can be attached to a solid interface by LB transfer. The technique, however, can only be used to produce brushes of relatively low density. For this system, complete transfer is obtained and the material is evenly spread over the surface.[9] Adsorption of the diblock copolymers onto the PAA brush layers was monitored with fixed-angle optical reflectometry.[10]

In Figure 2 the adsorption is given as a function of pH value. At low pH values, the PAA brush is almost uncharged and both P2MVP-PEO (Figure 2a) and PDMAEMA-PEO (Figure 2b) hardly adsorb. The small adsorbed amounts at pH 2 are most probably due to hydrogen bonding between PEO and the uncharged PAA, as reported by several authors (see, e.g., reference [11]). With increasing pH value, the PAA becomes increasingly charged, and more diblock copolymer is adsorbed until a plateau is reached at about pH 6. The quaternized P2MVP block has a constant charge, but PDMAEMA is a weak polycation and becomes uncharged at high pH values. Therefore, at high pH values the adsorbed amount of P2MVP-PEO hardly changes anymore, but the adsorption of PDMAEMA-PEO drops to zero. For both polymers, equilibrium adsorption is reached within 5 to 10 min ($C_{\text{polymer}} = 0.1\ \text{g L}^{-1}$).

Both P2MVP-PEO and PDMAEMA-PEO can be desorbed completely by increasing the salt concentration to about 1 M. Partial desorption is obtained by lowering the pH value; a combination of low pH value and nonionic surfactants also gives complete desorption. Moreover, PDMAEMA-PEO is completely removed by rinsing with a solution of pH 10 or higher. These desorption steps are fairly quick; complete desorption can be reached within one minute.

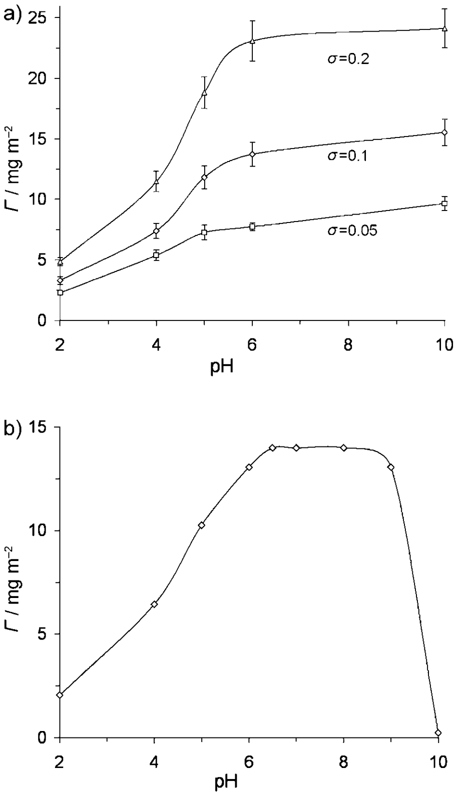

Figure 2. Adsorption Γ of the diblock copolymers on a PAA brush as a function of pH value. Length of the PAA chains is 270 monomers, solvent is aqueous 10 mM KNO_3. a) Amount of $P2MVP_{42}$-PEO_{205} adsorbed to PAA brushes of different grafting density σ as indicated (in nm^{-2}). Points are averages based on a minimum of three experiments, error bars show the standard deviation in the average. b) Amount of $PDMAEMA_{35}$-PEO_{120} adsorbed to a PAA brush with $\sigma = 0.2\ nm^{-2}$. Lines are drawn to guide the eyes.

Figure 2a further illustrates that the adsorption of diblock copolymer strongly increases with the grafting density of the PAA brush. Calculation of the fraction of charges of the PAA brush that have been compensated by the adsorption of P2MVP-PEO at pH 6 (Table 1) shows that the adsorbed amounts correspond fairly well to full charge compensation.

Table 1: Amounts of $P2MVP_{41}$-PEO_{205} adsorbed to PAA brushes with different grafting densities as well as the corresponding charge compensation and the resulting PEO grafting densities.[a]

σ_{PAA} [nm^{-2}]	Γ [$mg\,m^{-2}$]	Charge comp.[b]	σ_{PEO} [nm^{-2}]	$\sigma_{PEO}/\sigma_{PAA}$
0.05	7.73	1.02	0.34	6.8
0.1	13.70	0.90	0.60	6.0
0.2	23.09	0.76	1.01	5.1
0.3	36.13	0.79	1.59	5.3

[a] $N_{PAA} = 270$, pH 6, 10 mM KNO_3. [b] The total amount of positive charge divided by the total amount of negative charge, assuming complete dissociation.

For this calculation, we assumed complete dissociation of PAA, although the small increase in adsorption between pH 6 and pH 10 in Figure 2a suggests that at pH 6 PAA complexed with P2MVP may not yet be completely deprotonated.

The PEO grafting density that results from the adsorption reflects a strong enhancement of the grafting density of the PAA brush. From Table 1, a multiplication factor of about six is found, in line with Equation (1) ($N_{PAA}/N_{P2MVP} = 270/41 = 6.6$). Choosing shorter PAA brush chains ($N = 120$ instead of 270, results not shown) gives a large reduction in the amount of adsorbed block copolymer and the PEO grafting density, as expected. The maximum PEO grafting density that is reached with $N = 270$ is 1.59 nm^{-2}. This grafting density is much higher than any reported result on brushes of long polymer chains prepared by adsorption. It is even slightly higher than the maximum grafting density reported for PEO brushes prepared by the "grafting to" approach.[6]

The applicability of Equation (1) was further tested by adsorption measurements for copolymers with other block lengths (Table 2). Generally, the results are in line with Equation (1), implying that the adsorbed amounts and densities of the resulting brushes are controlled by full charge compensation. We also observe a few trends that indicate that there are limits to multiplication of the grafting density of the PAA brush by diblock copolymer adsorption. Most obviously, for the highest PEO length (450) the degree of charge compensation is significantly lower than 1. In this case, the very high pressure in the thick and dense neutral polymer brush is the likely reason that adsorption of diblock copolymer stops before all charges in the PAA brush have been compensated. This effect can be partially compensated by employing a longer anchor block (cf. $P2MVP_{42}$-PEO_{450} and $P2MVP_{72}$-PEO_{450}). The results in Table 1 suggest that high grafting densities of the PAA brush also lead to termination of adsorption before full charge compensation is reached, owing to volume effects. However, this trend is hardly beyond experimental error.

Table 2: Amount Γ of diblock copolymer adsorbed to PAA brushes ($N = 270$, $\sigma = 0.2$ nm^{-2}) and the resulting PEO grafting density and charge. Results are averages of several measurements on two PAA brush surfaces.

	Γ [$mg\,m^{-2}$]	Charge comp.	σ_{PEO} [nm^{-2}]	N_{PAA}/N_{anch}	$\sigma_{PEO}/\sigma_{PAA}$
$P2MVP_{42}$-PEO_{205}	25.9	0.90	1.16	6.4	5.8
$P2MVP_{42}$-PEO_{450}	33.0	0.63	0.81	6.4	4.1
$P2MVP_{72}$-PEO_{450}	26.2	0.74	0.56	3.8	2.8
$PDAEMA_{35}$-PEO_{120}	26.4	0.98	1.51	7.7	7.6
$PDAEMA_{77}$-PEO_{120}	21.6	1.09	0.76	3.5	3.8

In conclusion, we have presented herein a new approach to produce dense neutral polymer brushes by adsorption: the zipper brush approach. This new method has the large advantage over approaches such as "grafting to" and "grafting from" that the grafting density can be controlled and that the brush can also be desorbed again by changing the solution conditions. We stress that this approach is not limited to the polymers used in the experiments described herein. By using a different neutral polymer block, poly(acrylamide), poly(vinyl alcohol), or poly(*N*-isopropylacrylamide) brushes could be produced, for instance. By using different polyelectrolyte chains, the pH values at which the brush is stable and at which the brush can be desorbed could be influenced. We believe that even only strong polyelectrolytes could be used to produce a zipper brush stable at all but the most extreme pH values (although such a brush would have to be produced at high ionic strength to prevent irreversible complexation that would prevent the system from reaching equilibrium).

Finally, what do our findings imply for the kinetic barrier argument that ruled out high densities by adsorption? It might be naively concluded that the supposed barrier is elusive. However, the case may in fact be more subtle; adsorbing chains do not have to go all the way through the brush before they can attach, because the bare PAA chains themselves stand out from the surface so that they are able to capture incoming chains at the periphery of the brush, a mechanism not taken into account by De Gennes.

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