



Desorption of bottle-brush polyelectrolytes from silica by addition of linear polyelectrolytes studied by QCM-D and reflectometry

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ABSTRACT

The possibility of exchanging adsorbed layers of PEO₄₅MEMA:METAC-X brush polyelectrolytes (with two different charge densities, 10 and 75 mol%, denoted by X), with poly(MAPTAC), a highly charged linear polyelectrolyte, was investigated by quartz crystal microbalance with dissipation and reflectometry. The studies were conducted on a silica substrate at pH 10, conditions under which only electrostatic interactions are effective in the adsorption process. Based on the results, it was concluded that PEO₄₅MEMA:METAC-10 forms an inhomogeneous layer at the interface through which poly(MAPTAC) chains can easily diffuse to reach the surface. On the other hand, the PEO₄₅MEMA:METAC-75 layer was not affected when exposed to a poly(MAPTAC) solution. We argue that the observed effect for PEO₄₅MEMA:METAC-75 is due to the formation of a homogeneous protective brush layer, in combination with the small difference in surface affinity between the bottle-brush polyelectrolyte and poly(MAPTAC), together with the difficulty of displacing highly charged polyelectrolyte chains once they are adsorbed on the oppositely charged surface. We also use the combination of QCM-D and reflectometry data to calculate the water content and layer thickness of the adsorbed layers.

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1. Introduction

The in-solution performance of polymeric coatings is highly dependent on the stability of the layers at the adsorbing interface. It is understood that a decrease in the mass, thickness, and surface coverage of the polymer layers will have a negative impact in, e.g., applications where the polymer coating has a protective roll. Bottle-brush (also known as brush or comb) polyelectrolytes are a subclass of polymeric systems, which due to, e.g., their very promising protective [1,2] ability, have been extensively studied in recent years. However, very little is known about the stability of such preadsorbed layers in environments in which they are envisaged to perform. An attempt to fill some of this gap was made by our group in a recent publication [3] where the effects of the ionic strength and the presence of an oppositely charged surfactant (sodium dodecyl sulfate, SDS) on the stability of preadsorbed

comb polyelectrolyte layers were reported. It was shown that comb polyelectrolytes with grafted poly(ethylene oxide), PEO, side chains desorb more readily in electrolyte solutions than linear equivalents. This was attributed to the weaker anchoring (smaller number of interaction points between the polyelectrolyte and the surface) of brush polyelectrolytes to the surface because of the steric repulsion between the PEO side chains and to the entropic penalty that is involved when the side chains are confined at an interface. However, contrary to what might be expected, the brush polyelectrolytes showed [3] a comparable, or even higher, resistance (compared to the linear equivalents) against desorption in SDS solutions, when the charge density of the brush polyelectrolyte exceeded 10% (on molar basis). It was argued that this feature is due to the protective PEO side chains of the polyelectrolytes, which make it difficult for SDS to reach the cationic polymer segments bound to the surface.

There are other routes to achieve desorption, e.g., through competition for the adsorption sites at the surface – competitive adsorption. There are several experimental studies [4] on systems in which the polyelectrolyte competes with a similarly charged sur-

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factant for the adsorption sites on an oppositely charged surface. However, competitive adsorption studies [5–9] between (linear) polyelectrolytes, in which polyelectrolytes with different surface affinity compete, are rather few, and to our knowledge there are no reports describing the surface exchange of bottle-brush polyelectrolytes with linear polyelectrolytes. However, there are contributions [10,11] in which surface exchange in brush layers, formed through the adsorption of amphiphilic polymers, has been studied.

In this report, the resilience of preadsorbed brush polyelectrolyte layers against competing linear polyelectrolytes was investigated by means of QCM-D (quartz crystal microbalance with dissipation monitoring ability) and reflectometry. QCM-D enables real-time study of changes in the (sensed) mass and viscoelastic properties of the polymer layer, allowing close monitoring of the surface exchange process. However, QCM-D cannot provide the actual adsorbed mass (dry mass) of the adsorbent; rather, it registers the mass of the adsorbent together with the solvent that couples with the formed layer. Hence, to obtain the dry mass, optical reflectometry was employed. As a model substrate we chose silica, which at pH 10 (the condition under which the investigations were performed) is highly charged; as a model competing species, poly(MAPTAC) was chosen. This polyelectrolyte contains one positive charge per segment. The reasons for these choices are as follows: Studies [12,13] on the brush polyelectrolytes used in this report have revealed that the PEO₄₅ chains of the polyelectrolytes do not adsorb on silica at pH 10. Adsorption of the brush polyelectrolytes under this condition therefore occurs solely through the interaction between the charged groups of the polyelectrolyte backbone and those on the substrate. Furthermore, poly(MAPTAC) has been characterized both with SFA [14,15] (when adsorbed on mica) and with QCM-D [7] (on gold surfaces). These studies showed that poly(MAPTAC) adsorbs in a flat conformation on highly charged surfaces, giving rise to very low dissipation and sensed mass values. These parameters are expected to be significantly larger in magnitude for the brush polyelectrolyte layers, which have protruding and highly hydrated PEO side chains. The scientific question we attempt to answer is if the PEO₄₅ chains counteract the surface exchange reaction with linear polyelectrolytes (as was found to be the case for desorption by surfactants [3]), or if the PEO₄₅ side chains do not offer protection (as was the case [3] for simple salts). This information is technologically important for application of bottle-brush polymer coatings in contact with complex liquids (e.g., paints, blood, and nonfouling surfaces).

2. Materials

The brush polyelectrolytes employed in this work, see Table 1, are abbreviated as PEO₄₅MEMA:METAC-*X*. They were synthesized by radical polymerization [13,16] of poly(ethylene oxide)-methyl ether methacrylate (PEO₄₅MEMA) and methacryloxyethyl trimethylammonium chloride (METAC) monomers, Fig. 1. In the polyelectrolyte representation *X* stands for the molar percentage of METAC segments, which constitute the permanently charged segments of the copolymer. Each of the remaining segments con-

Table 1
List of the polyelectrolytes used in this study

Polyelectrolyte	METAC (mol%)	M_w (kg mol ⁻¹)	$\frac{dn}{dc} \times 10^4$ (cm ³ g ⁻¹)
PEO ₄₅ MEMA:METAC-10	10	760 ^a	0.137 ^b
PEO ₄₅ MEMA:METAC-75	75	520 ^a	0.147 ^b
Poly(MAPTAC)	–	240	0.158 ^{a,b}

Note. M_w denotes weight average molecular weight, while dn/dc refers to refractive index increment.

^a Data obtained through the measurements conducted in Ref. [16].

^b The dn/dc of poly(MAPTAC) was assumed to be the same as for poly(METAC), due to the structural similarity of the polyelectrolytes.

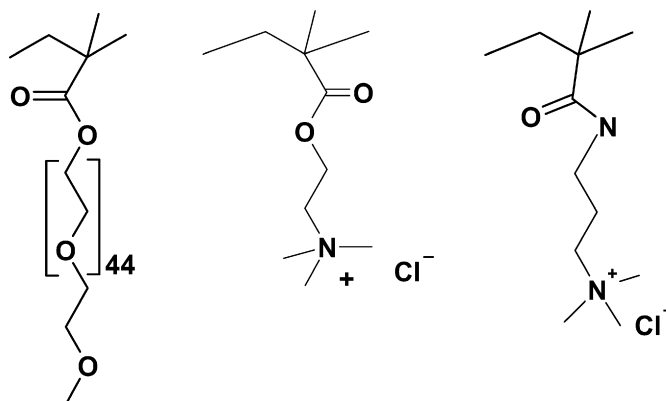


Fig. 1. Molecular structures of PEO₄₅MEMA (left), METAC (center), and MAPTAC (right).

tains a PEO₄₅ side chain. The poly(ethylene oxide) component has a molecular weight of 2000 g/mol (ca. 45 repeating units) and a polydispersity index of less than 1.1. The synthesized brush polyelectrolytes are, however, polydisperse, with typical polydispersity indices of 2–3 (as determined by GPC for selected [13] samples).

The poly(MAPTAC) used in the desorption experiments was received as a gift from the Laboratoire de PhysicoChimie Macromoléculaire, Université Pierre et Marie Curie, Paris. This polyelectrolyte (Fig. 1) has a weight-average molecular weight of 240 kg/mol, and potentiometry and elemental analysis investigations have indicated that the polyelectrolyte is made of 100% MAPTAC monomers. The water used in all experiments was first pretreated by a Milli-RO Plus unit and then purified further by a Milli-Q Plus185 system. The resistivity after the treatment was 18 MΩ-cm, and the total organic carbon content of the water did not exceed 2 ppb. NaOH (purum grade) from Sigma-Aldrich was used as received to adjust the pH in the experiments. The (thermally oxidized) silicon wafers used in the reflectometry measurements were purchased from Wafer Net, Germany.

3. Methods

3.1. QCM-D (quartz crystal microbalance with dissipation monitoring ability)

A commercially available QCM-D apparatus, D300 (Q-Sense AB), and silica-coated quartz sensors (crystals) with a fundamental frequency of 5 MHz (also supplied by Q-Sense AB) were used in our investigations. A detailed description of the principles of the instrument can be found elsewhere [17]. In brief, the instrument allows the simultaneous determination of changes in resonance frequency (Δf) and energy dissipation (ΔD) that occur as a result of adsorption. A negative Δf denotes accumulation of mass (dry weight of the adsorbing species together with solvent that couples to the oscillating crystal), while the absolute value of ΔD provides some information on layer properties; for example, a large ΔD value is indicative of the formation of a highly viscoelastic layer, while a small value is associated to a rigid layer.

There are different theories [18–20] for calculation of the sensed mass, which take into account the change in frequency registered by the sensor. In this work we make use of the Johannsmann [20] relation (1), which has been derived for viscoelastic layers:

$$m^* = m^0 \left(1 + \hat{J}(f) \frac{\rho_q (2\pi f)^2 d^2}{3} \right), \quad (1)$$

$$m^* = -\frac{C \Delta f}{n}. \quad (2)$$

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