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Determination of the molar mass of surface-grafted weak polyelectrolyte brushes using force spectroscopy

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ABSTRACT

The molar mass and dispersity of a polycation, poly[2-(dimethyl amino)ethyl methacrylate] (PDMAEMA) grafted from a poly(methyl methacrylate) (PMMA) backbone, was measured by single-molecule force spectroscopy (SMFS) and shown to be consistent with results from gel permeation chromatography for the same comb polymer in aqueous solution. Comparison was then made between the comb polymer and PDMAEMA brushes that were grown from the substrate, as a function of the pH and ionic strength of the surrounding medium, and the limits of reliable characterization of the polymers are determined. A large discrepancy was observed between the responses of the comb and brush layer at low pH when the PDMAEMA molecules are extended from the supporting substrate. Here it is believed that the atomic force microscope (AFM) tip can penetrate the comb layer and selectively desorb side-chains of the comb. In the case of the well solvated PDMAEMA brushes at high pH, the tip preferentially selects larger chains, resulting in an over-estimate of the brush molar mass. The addition of salt also influenced the molar mass obtained by this technique. It is believed that salted brushes did not adhere well to the AFM tip, with subsequent desorption resulting in an underestimate of the molar mass. However, SMFS was shown to be capable of demonstrating the effect of salt on brush conformation, with greater swelling after the addition of a small amount of NaCl, but a significant decrease when 100 mM is added.

1. Introduction

Surface-grafted polymers, known as 'polymer brushes', play a significant role in controlling the chemical, mechanical, and physical properties of a surface [1]. They are used in a wide range of applications including colloidal stabilization [2], responsive surface coatings [3], flocculation [4], and superabsorbent gels [5]. Very often they are responsive to external and/or environmental stimuli, such as electric fields [6,7], temperature [5,8], pH [9,10], and salt [11,12]. In recent years, polymer brushes have been shown to be a useful class of materials for many medical and biological applications [13,14]. For example, custom synthetic polymers have great potential in drug delivery and molecular recognition [15], and tethering polymer chains onto surfaces can effectively reduce friction [16,17], and control adhesion [18–20].

The use of polyelectrolyte brushes enables control of the conformational behaviour of the brush layer, when the pH or ionic strength of the medium is changed. This is usually due to changes in the osmotic pressure caused by the presence of counterions within the brush layer [21]. The swelling behaviour of such systems exhibits some notable characteristics depending on the pH of the solvent, concentration and type of ions in the solution, and the grafting density of the brush. In particular, much attention has been paid to weak polyelectrolyte brushes, such as those considered in the present work, because their charge density is not fixed and can be tuned by varying the ionic strength of the surrounding medium [22,23].

In addition to a physisorption approach, chemical grafting can be achieved by two different routes: 'grafting-to', where the polymer chains are functionalized with end groups that can covalently bind to desired surfaces or interfaces, and 'grafting-from', where an initiator layer is used to grow polymer chains from a surface or interface. Forming polymer brushes via the 'grafting-to' method permits a pre-characterization of the polymers and a control of their

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molar mass and dispersity. However, brushes created via this method generally have a low grafting density due to entropic repulsion between the neighbouring chains. By contrast, a dense polymer brush layer can be achieved using 'grafting-from' techniques [1].

It is a considerable challenge to measure the molar mass of weak polyelectrolyte brushes prepared by the 'grafting-from' method. A simple but crude approach is to measure the height of fully stretched polymer brushes in a good solvent, and assume that this is the same as the chain length. The number averaged molar mass estimated by this method often exhibits the same order of magnitude as the values obtained by gel permeation chromatography (GPC) [24]. However, accurately determining the mass averaged and number averaged molar masses (respectively M_w and M_n), and therefore the dispersity ($D = M_w/M_n$) of the grafted chains is not trivial, given that many parameters, including grafting density, pH, and salt concentration, can affect the values obtained. In particular, due to the combination of hydrogen bonding, electrostatic interactions, and osmotic pressure from counterions, a determination of the molar mass of polyelectrolytes presents a challenge. A common method of estimating M_n and D for surface-grown polymers is to simultaneously carry out polymerization on the surface and in bulk solution under the same conditions. For this approach, one assumes that both the free and grafted polymer chains have similar molar mass and dispersity. Recently, it has been pointed out that polymers synthesized in bulk solution have a greater growth rate and a narrower molar mass distribution than those initiated from a flat substrate [25]. It has, however, been possible to characterize the molar mass from the growth of polymer from a 'free' initiator [26]. Another possibility is to remove the polymer from the surface and perform GPC on the degrafted polymer [25,27]. This technique is restricted to the growth of polymers on small colloidal surfaces because of the need for a large surface area to permit the retrieval of sufficient polymer for the subsequent GPC analysis. Nevertheless, a different approach to effectively characterize the molar mass of surface-anchored polymers is required.

Among the few techniques that were used to characterize the molar mass of grafted polyelectrolytes, atomic force microscope-based single molecule force spectroscopy (SMFS) has been demonstrated to possess good potential [28–31]. By stretching single molecules between an atomic force microscope (AFM) tip and a supporting substrate, not only will intermolecular interactions be revealed, but also the contour length of the chain, and the conformation of the molecules on the surface or interface [10,32–36]. The number of repeat units of each individual chain can then be estimated by dividing the calculated contour length with the length of monomer units. With the data acquisition over a large number of molecules, statistical analysis can reveal the molar mass as well its distribution. An SMFS study was carried out on grafted layers of poly(*N*,*N*-dimethylacrylamide), a hydrogen bonding non-electrolyte [37], where it was demonstrated that SMFS can be effective in characterizing the molar mass of grafted polymer chains of various densities. In that study it was reported that the M_n measured using SMFS agreed quite well with the GPC result, although the molar mass could be significantly underestimated when the grafting density was low. It was explained that when the distance between grafting points is greater than the radius of gyration, the polymer chains tend to form mushroom structures on the surface, increasing the probability of the AFM tip contacting points along the chain rather than contacting the chain end. In this study it was also showed that the M_w (and thus the dispersity) obtained by SMFS was considerably larger than that measured using GPC (~24%) because the AFM tip would preferentially select high molar mass chains.

The purpose of the present study is to first evaluate the effectiveness of single molecule force spectroscopy (SMFS) in characterizing the molar mass of polyelectrolyte brushes. SMFS was also used to examine the effects of salt and pH on the observed average contour length (proportional to average M_n) of films formed from a pre-characterized polymer comb [38], which also provides an effective control sample for the measurements to determine the molar mass. The comb, composed of a hydrophobic poly(methyl methacrylate) (PMMA) backbone with responsive poly[2-(dimethyl amino)ethyl methacrylate] (PDMAEMA) side-chains, is self assembled into a brush conformation via the Langmuir-Schaefer (LS) method and deposited onto hydrophobized silicon surfaces. A homogeneous PDMAEMA brush is grafted from silicon surfaces using atom transfer radical polymerization (ATRP) [13]. For convenience, the comb refers to the polymer prepared by 'grafting-to' method, whilst brush refers to those prepared by the 'grafting-from' method, even though both methods do, in fact, produce brush surfaces. The conformational behaviour of the two materials on the supporting substrate was also revealed by SMFS. The results presented here indicate that the comb and the brush both behave differently as a function of pH and salt concentration, and successfully demonstrate that SMFS is an effective method for characterizing the molar mass of surface-anchored polymers.

2. Experimental

2.1. Materials

Silicon wafers (<100> orientation, boron doped, resistivity 0–100 Ω cm; the dopant is present at very low concentration and does not influence the brush density) were purchased from Compart Technology (Peterborough, UK). 2-(Dimethyl amino)ethyl methacrylate (DMAEMA, 98% purity, Aldrich), methyl methacrylate (MMA, 99%, Aldrich), copper(II) chloride [$Cu(II)Cl_2$, >99%], 4-(dimethyl amino)pyridine (DMAP, 99%, Aldrich), triethylamine (TEA, 99%, Aldrich), anhydrous diethyl ether (Fisher), 2-Bromoisobutyryl bromide (BIBB, 98%, Aldrich) were all used as received. Copper(I) chloride (CuCl, 99%, Aldrich) was rinsed with 10% aqueous HCl, methanol, and diethyl ether in sequence, before drying in vacuum.

2.2. Preparation of PDMAEMA-coated silicon substrate

PDMAEMA chains grafted to a PMMA backbone were synthesized as described previously [38] and a PDMAEMA brush layer was formed by controlled deposition on a silicon surface, as shown in Fig. 1. The PMMA, with a molar mass of approximately 7 kDa per molecule, was used as a hydrophobic initiator backbone and then the PDMAEMA chains, with molar mass of approximately 20 kDa per chain, were grown as side-chains to form a copolymer comb. This method produced typically 2 or 3 side-chains per backbone [38]. Polymer combs were synthesized via the 'grafting-to' technique using the LS method on a silicon surface at 15 and 30 mN/m deposition pressures. The thicknesses of the resulting comb layers in this case were 1.9 nm and 3.3 nm in air as measured by ellipsometry.

As well as these comb layers, PDMAEMA brushes were grown from a silicon surface using ATRP. UV-ozone treated silicon wafers immersed overnight in a dilute anhydrous toluene solution held at −10 °C of (11-(2-bromo-2-methyl)propionyloxy) undecyltrichlorosilane (the initiator for surface ATRP). The solution for surface ATRP of PDMAEMA was prepared by adding 24.1 mg CuCl, 54 µl *N*,*N*,*N*′,*N*′,*N*″-pentamethyldiethylenetriamine, 2.14 ml ethanol, and 2.14 ml DMAEMA to a small flask after each was sparged with nitrogen for 10 min. The treated silicon wafers were added to the solution and left at room temperature for 24 h. Afterwards, the