Physicochemical behaviour of cationic polyelectrolyte brushes

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ARTICLE INFO

ABSTRACT

Water soluble cationic polyelectrolytes, composed of chargeable basic monomers, make up one major subclass of stimuli-responsive polymer brushes. They have displayed potential in bio-sensing, antimicrobial and drug delivery applications, and in micro-electromechanical devices. However optimising these polybasic brushes for such promising practical applications requires the nanoscale structure and interfacial chemistry to be well-understood. Herein we discuss recent theoretical and experimental work concerning the behaviour of cationic polybasic brushes. Particular attention is focussed towards ionisable polybasic brushes whose degree of charge is variable and solution behaviour is dependent on environmental pH, temperature or ionic strength, as well as the specific nature of the dissolved electrolyte or the presence of applied electrical fields. Polybasic brushes are complex systems that behave in ways far beyond extant theoretical predictions. As discussed herein, these brushes exhibit diverse hydrophobicity modulated salt- and pH-responsive behaviour and structures, tuneable interfacial friction, adhesion and wettability, and specific ion effects that follow the Hofmeister series.

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1. Introduction

Stimuli-responsive polymer coated surfaces are important in many scientific fields including colloidal stabilisation, antifouling surfaces, nano-actuation and nano-sensing devices [1–8]. One robust approach to their production has been the deployment of polymer brushes. Brushes, densely packed assemblies of surface tethered polymer chains, can now be synthesised with low chain dispersity and control over polymer molecular weight by making use of advances in controlled polymerisation

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techniques [9–12], including reversible addition—fragmentation chain-transfer (RAFT) polymerisation and atom transfer radical polymerisation (ATRP). Brushes are advantageous because of their ability to impart desired physical and chemical properties to an interface. This can be achieved by controlling the length of the polymer, the surface coverage and, most significantly, the chemical nature of the constituent monomer groups [13].

Brushes composed of polyelectrolytes are of particular interest. This is in part because of their relevance to biology and medicine [8], for example their chemical similarity to proteins (e.g. amino acid-containing [14] and hyaluronic acid brushes [15]), but also because they are capable of interacting and responding to the surrounding environment. However the ionisable nature, and corresponding charge regulation mechanisms, as well as the hydrophobicity of the polymer backbone impart a considerable deal of complexity to the behaviour of polyelectrolyte brushes. For these reasons polyelectrolyte brushes offer broad opportunities for creating responsive surfaces and nano-devices. Moreover, polymer brushes are important models of biological systems. This is because brush behaviour can be used to assist in understanding how environmental conditions such as pH, temperature, ionic strength and ion identity dictate characteristics such as polymer charge, solvation, chain conformation and the interactions with other molecules like surfactants, proteins and colloidal particles [16–19]. In turn these affect interfacial behaviour, for example, their lubricating or adhesive properties.

A number of review articles comprehensively discuss the behaviour of neutral and charged polymer brushes [13,20], as well as recent advances in brush synthesis [9–12], the emerging practical applications of brushes [6–8,10], and the behaviour and applications of spherical polyelectrolyte brushes [21]. From these foundations, herein we aim to use selected recent studies to demonstrate how the theoretical and experimental understanding of polyelectrolyte brushes has progressed. As previous reviews are dominated by acidic polymer brushes, our discussion focusses on the behaviour of polybasic brushes, which are cationic polyelectrolyte brushes that consist of monomers containing basic functional groups. Much of this focus is on weak polybasic brushes. Weak polyelectrolyte brushes are of specific interest because the fraction of charged monomer units (degree of ionisation) varies with solution pH and ionic strength; the degree of charge is fixed for strong polyelectrolyte brushes. This complex interaction offers an additional mechanism for controlling brush behaviour.

2. Aqueous solution chemistry of polyelectrolyte brushes

The physical and chemical properties of surfaces bearing charged macromolecules are fundamentally different to those of surfaces with neutral polymers in aqueous solution. Polyelectrolytes can be composed of entirely anionic (polyacid) or cationic (polybase) monomer groups, or a combination: polyampholytes for unbalanced charges, or zwitterionic polymers when the number of anionic and cationic groups is equal. Polyelectrolytes are ubiquitous in soft matter and biological systems with, for example, DNA, actin, polypeptides and polysaccharides all being polyelectrolytes. Their charged nature means that electrostatic interactions come into play resulting in rich behaviours not seen for neutral brushes [20]. Importantly, brush charge is compensated by the adsorption of oppositely charged counterions with the spatial range of the electrostatic interactions directed by the Debye screening length, κ^{-1}. Herein we focus on homopolymer basic (cationic) brushes, however, examples exist of polyampholyte (mixed anionic and cationic copolymer) brushes [22–26]. For polybases an important distinction exists; strong (quenched) polybases possess a permanent charge irrespective of the aqueous solution environment. In contrast, the degree of charge of a weak (annealed) polybase varies with solution conditions including pH and ionic strength.

2.1. Strong polyelectrolyte brushes

For strong polyelectrolyte brushes (both polybases and polyacids), several theoretical behavioural and scaling regimes in aqueous solution have been identified [27,28]. Two of these are readily accessible through experiment: the so-called osmotic and salted brush regimes. The distinction between the two regimes arises from the impact of solution ionic strength. For a strong polyelectrolyte brush in the osmotic regime, salt counterions are predominantly localised within the brush, where they screen the polymer charge [29]. This creates a significant osmotic pressure difference inside and outside the brush and results in chain extension and brush swelling. The overall swelling of the brush is a balance of three contributions: the osmotic pressure of the confined counterions (and associated water molecules as well as direct solvation of the polymer chains by the solvent), the excluded volume interactions and the opposing elastic chain restoring force. In most cases the osmotic pressure of confined counterions is at least several orders of magnitude greater than the excluded volume effects and hence it is solely the balance between the osmotic pressure of the counterions and the chain elasticity that determines brush thickness [29,30]. In this regime, brush thickness was initially predicted to be independent of grafting density (number of chains·nm^{-2}) [29]. However, by accounting for lateral inhomogeneity and excluded volume effects, Seidel and co-workers predict that brush thickness actually increases slightly with increasing grafting density (known as the nonlinear osmotic brush regime) [31,32]. This has been confirmed experimentally for a strongly charged poly(styrenesulfonate) brush through X-ray reflectometry measurements [32]. Significantly, because the location and number of charged monomer units is fixed for strong polyelectrolyte brushes, brush thickness is predicted to remain constant as a function of solution ionic strength in the osmotic brush regime [29]. However, in a few studies brush collapse has been observed experimentally at very low salt concentrations [33–35].

As the amount of added salt is increased further, the extent of brush swelling becomes increasingly controlled by the excluded volume interactions between polymer segments. This is because the influence of repulsive electrostatic interactions diminishes since κ^{-1} tends to smaller values at higher salt concentrations; the salted brush regime. Consequently, more collapsed brush conformations are favoured. The extent of brush collapse is dependent on the hydrophobicity of polymer and the quality of the surrounding solvent. Seminal theoretical work identified a simple scaling power law dependency for the expected decrease in brush thickness, h, with increasing inert salt concentration, C_s; $h \sim C_s^{-0.33}$ [27–29,36,37]. Since then, by accounting for lateral inhomogeneity across the brush surface, excluded volume effects and finite chain extension, molecular dynamics simulations have revealed a weaker dependency with $h \sim C_s^{-0.15}$ [38–41]. Fig. 1a presents a subset of the molecular dynamics simulation results from Guptha and Hsiao for the behaviour of strong polyelectrolyte brushes as a function of grafting density and solution ionic strength [41]. At increased ionic strengths brush collapse is predicted, which follows the −0.15 scaling exponent. The effect of grafting density on this transition is minimal with the brush being slightly more collapsed at higher densities. Grafting density is considered in terms of the dimensionless parameter called the reduced grafting density, Σ. Theoretically, a Σ value of 1 corresponds to the start of the brush regime where neighbouring chains begin to sterically interact and are forced to stretch away from the grafting surface [42]. $\Sigma < 1$ are sparsely grafted chains (pancake and mushroom conformations), while $\Sigma > 1$ are densely grafted chains. Note that in real