

Surface grafted polymer brushes as ideal building blocks for “smart” surfaces†

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Polymer brushes are assemblies of macromolecules chemically tethered at one end to a substrate. They provide an alternative to self-assembled monolayers because of the intrinsically large size of the building blocks and the ensuing entropic contribution to the film morphology. In this article, an overview of a number of representative polymer brush systems will be presented and their potential application for surfaces with controlled wettability, smart surfaces and nanoactuators will be explored in some detail.

Introduction

Self-Assembled Monolayers (SAMs) have been used extensively as an extremely flexible route to modify and tailor surface chemistry of a wide range of metals, metal oxides, and semiconductors.^{1,2} SAMs are organic assemblies formed by the adsorption of molecular constituents having a chemical functionality, or “headgroup”, with special affinity for a substrate, a main chain organized by van der Waals interaction and a terminal group determining surface chemistry.³

In recent years, however, a number of limitations of SAMs have become apparent. First of all, due to the self-assembling nature of their formation, it is practically impossible to obtain large-area defect-free monolayers. Secondly, since monolayers are only several nm thick, they are mechanically and chemically fragile (and when used as etch resists, the processing window becomes very narrow). Thirdly, chemical groups can only be introduced at the surface, whereas in polymer brushes these groups can be carried all along the polymer backbone and, by fully exploiting ‘living’ polymerization conditions, can be placed in different pseudo-3D spatial arrangements when multiblock brushes are grown. Finally, SAMs can be used to introduce almost any functional group to the surface, but it is very difficult to introduce reversibly-changing chemical functionalities, without reverting to sequential chemical transformations. In light of these limitations, polymer brushes grown from initiator-terminated SAMs provide a conceptually simple route to robust, functional and switchable surfaces.^{4–6} In this article, we will briefly review some of the key characteristics of brushes and typical synthetic routes towards brushes, and then focus on the use of polymer brushes as smart or responsive surfaces.

The crucial difference between SAMs and polymer brushes is the size of the components: SAMs are assemblies of small molecules, whilst polymer brushes are monolayers of macromolecules. Therefore, the intrinsic difference lies in the size of

precursors to form monolayers and the size of the obtained assemblies. In SAMs, long chain aliphatic molecules are fully extended to maximize packing density and van der Waals interactions. However, the entropic cost for polymer brushes to stretch out to their maximum (contour) length would be very severe and, as a result, polymer brushes are disordered at the molecular level. At very low grafting density, the so-called mushroom regime, the polymers adopt a more or less random coil conformation (Fig. 1). In good solvents, the thickness of the anchored polymer, H , in the low grafting density mushroom regime scales as $H \propto N\sigma^0$, where N is the degree of polymerization of the polymer and σ the grafting density. At higher grafting densities, the polymers interact with each other and there will be a degree of distortion from the random coil. At sufficiently high grafting density, the so-called brush regime will be reached (Fig. 1). In this regime, the brush height scales as $H \propto N\sigma^{1/3}$.

Dense brushes are most easily prepared following a so-called grafting from or Surface Initiated Polymerization (SIP) method making use of the surface tethered initiators (see below Fig. 2).⁸ The amount of overlap between the chains, and hence the degree of stretching, is firmly dependent on the grafting density and chain length, and for any given polymer it is also dependent on the ‘solvent quality’. In good solvents, the chains will swell, thereby forcing them to stretch away from the surface. The conformation of polymer brushes is now a classical problem in polymer physics; the degree to which the chains are stretched away from the surface is determined by a competition between the entropic energy loss due to chain stretching and the excluded volume interactions between different segments of the brush. If the excluded volume interaction can be altered, then the conformation of the chains will, in turn, change. Since in good solvent conditions the brush height is predicted to vary linearly with the degree of polymerisation N , while in poor solvents the scaling is as $N^{1/3}$, the changes in conformation can be very large. This large response suggests a number of practical applications, including creating surfaces with switchable adhesion, creating selective and switchable membranes and pores, and creating synthetic molecular motors. The stretching of the polymer chains could also offer opportunities in the area of polymer electronics,

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† The HTML version of this article has been enhanced with colour images.

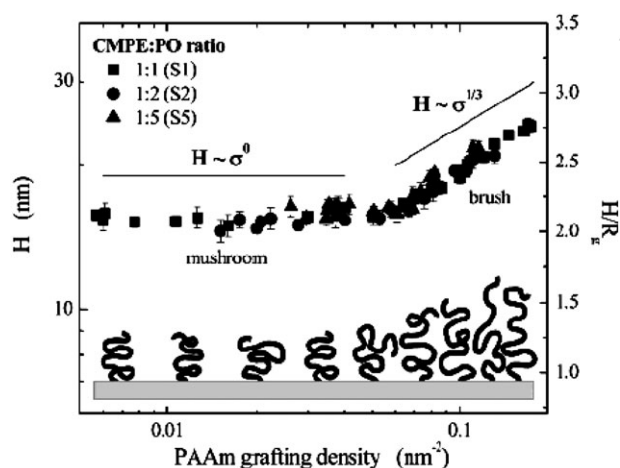


Fig. 1 Wet thickness of Polyacrylamide (PAAm) as a function of the PAAm grafting density for samples prepared on substrates containing the initiator gradients made of 1-trichlorosilyl-2-(*m/p*-chloromethyl phenyl) ethane : octadecyltrichlorosilane (CMPE : OTS) mixtures (w/w) 1 : 1 (■), 1 : 2 (●), and 1 : 5 (▲).⁷ The inset shows a cartoon illustrating different polymer states with increasing grafting density. Reprinted from ref. 7, with permission from the American Chemical Society.

where alignment of chains is highly desirable. In a recent work, we demonstrated that an 80 nm thick polytriphenylamine acrylate (PTPAA) brush film exhibited a current density three orders of magnitude higher than the spin-coated PTPAA film (2.2 A m^{-2} as opposed to $2.5 \times 10^{-3} \text{ A m}^{-2}$ at 3.5 V applied bias).⁹ The much-improved conductivity for the brush layers suggests that the different structure of the PTPAA brush film provides clearer pathways for charge transport than a spin-coated film. In the spin-coated films, the polymers are mostly disordered and do not present pathways where charges can travel from one electrode to the other along one polymer chain. Spin-coated films are in fact more likely to exhibit a certain degree of chain alignment in the plane of the film. Thus, the charges will need to hop between chains much more often than those in the brush system, which will significantly impede charge transport, and this effect will become amplified as the film thickness increases.

Synthesis

SIP from initiator SAMs provides a convenient way to form high density polymer brushes (Fig. 2).⁵ The Conventional Free

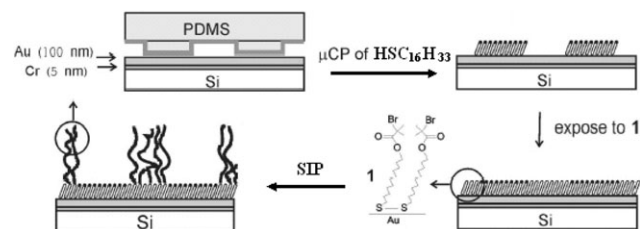


Fig. 2 General synthetic strategy for growing (patterned) polymer brushes from initiator-modified gold substrates via Atom Transfer Radical Polymerisation (ATRP).⁸ Reprinted from ref. 8, with permission from Wiley-VCH.

Radical Polymerization (CFRP) might be the primary choice to obtain polymer brushes when there are no requirements for multiblocks.⁶ Very thick polymer films can be obtained, and the grafting density can be controlled *via* judicious choice of initiator and polymerization conditions (slow decomposition of initiator leads to ever denser brushes due to polymerization of monomers diffusing into the brush film). Anionic polymerization may yield good control over thickness and formation of copolymer brushes, but suffers from the rigorous reaction conditions required, and as a consequence only a few examples have been reported in the literature. Cationic polymerization also requires a complex experimental procedure to form surface-bound initiators and only a few monomers can be polymerized. Grafting polymerization *via* the initiator proves to be efficient for a variety of monomers and demonstrates living characteristics. Nitroxide Mediated Polymerization (NMP) is usually carried out at high temperature, and is therefore not suitable for growing brushes on gold. NMP does yield control over brush architectures, and block copolymer brushes can be obtained. Ring Opening Metathesis Polymerization (ROMP) has thus far been restricted to norbornene-type monomers. Judging from the large number of recent papers appearing in the literature, Atom Transfer Radical Polymerisation (ATRP) appears to be the most widely adopted strategy, not only because it is potentially controlled but also because of the ease of initiator formation and relatively mild polymerization conditions.¹⁰ Especially attractive is room temperature ATRP in aqueous or methanolic solutions^{11,12} for a wide range of hydrophilic monomers like polyhydroxyethylmethacrylate (PHEMA), polyglycidyl methacrylate (PGMA) and polymethacryloyloxyethyltrimethylammonium chloride (PME-TAC), and even some more hydrophobic brushes such as polymethyl methacrylate (PMMA), and liquid crystalline polymers.^{13–16} Significant effort has gone into achieving controlled surface-initiated ATRP. In general, this can be achieved by either adding sacrificial initiator,¹⁷ or by adding a Cu(II) salt as deactivator.⁸ In the former case, the ‘persistent radical’ is created artificially because the active amount of conversion and living chains on the surface is too small to establish the standard equilibrium present in bulk ATRP. The disadvantage of adding sacrificial initiator is the formation of bulk polymers that are difficult to remove, and therefore the addition of Cu(II) can be a good alternative. However, adding very small amounts of both Cu(I) and Cu(II) salts in a precise ratio is difficult because of the oxygen sensitivity of Cu(I). Quenching the polymerization with Cu(II) species helps to preserve the initiation points and allows polymerization to be carried out for over six quenching and reinitiation cycles.¹⁸ It should be noted, though, that there is no universal recipe for ATRP, and many factors, including choice of solvents, ligands, monomers and reaction temperature, will affect the polymerization.

Micro- and nanopatterned polymer brushes

Patterned polymer brushes¹⁹ are useful for the study of responsive phenomena and can be directly obtained by carrying out polymerization from patterned initiator substrates, prepared by either soft lithography [microcontact printing

(Fig. 2)]²⁰ or photolithography.²¹ Nanopatterned initiator SAMs can be generated by nanocontact printing²² or dip-pen nanolithography²³ and amplified with ATRP.²⁴ Binary SAM patterns (*i.e.* patterns of SAMs terminating in one chemical functionality in a background of another) can be formed by contact printing one type of molecule and back-filling with another.²⁵ The synthesis of binary polymer brushes often needs multiple steps. R  he *et al.* described a step-and-repeat process for preparing binary polymer brushes.²⁶ Alternatively, binary brush patterns can be prepared by successive SIP from binary initiators adapted for ATRP and NMP, respectively.²⁷ Polymer brushes can be selectively etched away, exposing bare gold substrates that can be used to carry out a second ATRP step after depositing fresh initiator.²⁸ Binary polymer brushes allow direct comparison of the chemical and physical properties of two different polymers. Fig. 3(a) and 3(c) show the complementary binary PHEMA/PMMA structures (in Fig. 3(a), the circles are PMMA brushes and in Fig. 3(c) they are PHEMA), while Fig. 3(b) and 3(d) shows the etching contrast using binary brushes of PHEMA/PMMA in an aqueous etchant solution. It is clear that hydrophilic PHEMA covered areas were always etched more quickly than PMMA covered areas. When PHEMA was reacted with a hydrophobic silane, the etching resistance was greatly improved.²⁹

Gradient SAMs, with gradually altering grafting density, can be prepared by diffusion of silanes onto a silicon wafer.³⁰ SIP from gradient initiator SAMs generates gradient polymer brushes,^{31–33} and such brushes with orthogonal variation of molecular weight and grafting density enable the study of topography-related phenomena like fluid flow, and will facilitate multivariant studies of molecular and macromolecular adsorption, as well as phase diagrams in block copolymer brushes.

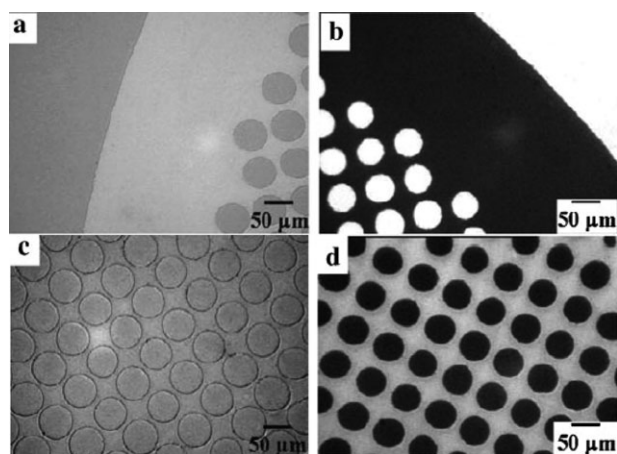


Fig. 3 Complementary binary PHEMA/PMMA brushes ((a) and (c)) and corresponding etching contrast image ((b) and (d)). The binary structure was prepared *via* two-step ATRP. The circled areas in (a) and (c) are PMMA and PHEMA, respectively. After etching with KI:I₂ aqueous etchant, PHEMA covered gold is always etched away first, indicating poorer etching resistance than PMMA.²⁸ Reprinted from ref. 28, with permission from Wiley-VCH.

Towards ‘smart’ surfaces: switchable surface energy

Surface wettability is an important parameter and is the first that will be controlled in almost all surface modification strategies. It is closely related to a series of other surface-relevant phenomena like absorption, nucleation, reactivity and even mechanical properties. Wettability mainly depends on surface chemical functionality, although surface roughness also plays an important role. SAMs provide a simple and convenient way to change surface wettability by altering the terminal groups.¹ However, SAMs have limitations in making surfaces with switchable wettability. A rare exception are electro-switchable SAMs based on terminal carboxyl groups, which can bend up and down when applying a potential to produce a wettability change. Mobility was introduced into the SAM by using a very bulky protecting group on the terminal group (preventing close-packing of the alkylthiolates), which was subsequently removed after assembly.³⁴ There are, however, several ways to modify surface wettability using polymer brushes, including grafting different types of polymer brushes, copolymer brushes, binary polymer brushes and using stimuli-responsive polymer brushes that change wettability upon an external trigger. Modification with different polymer brushes that have different affinity to different solvents represents the simplest way to change surface wettability.³⁵ Brushes incorporating neutral hydrophilic/hydrophobic polymers, charged polyelectrolytes and even extremely hydrophobic perfluorinated polymers have all been explored in this regard. Fluorinated polymers are very frequently utilized in creating low adhesion surfaces, but are often difficult to process due to low solubility in common organic solvents and weak adhesion to the substrate surface. The formation of surface-tethered fluorinated polymer brushes overcomes such problems.³⁶ Perfluorinated polymer brushes can retain hydrophobic properties for long periods of time even upon mechanical/thermal stress exposure.³⁷ Such surfaces show promise for the design of marine antifouling coatings for minimum adhesion and maximum bio-fouling release. Conversely, modification of low energy fluorinated materials with hydrophilic coatings is needed to improve compatibility with the aqueous environment. SIP from fluorinated materials can alter the wettability, for example, decrease the water contact angle from 115° for polytetrafluoroethylene (PTFE) to around 60° for PGMA and to 25° after grafting with PSSNa (polystyrene sulfonate sodium) brushes.³⁸ Random copolymer brushes with hydrophobic and hydrophilic gradients showed a gradual hydrophobic to hydrophilic change when increasing the volume fraction of one of the components.³⁹ By grafting copolymer brushes, it is possible to make surfaces that can reversibly switch wettability more dramatically. The principle lies in the distinct response of two immiscible blocks to different solvents or vapors. When copolymer brushes are treated with different solvents, compatible for the first block or the second block, the two blocks will alternately rise to the surface. The wettability changes reversibly as a result of co-operative action of both roughness and the brush type. Zhao *et al.* reported nanopattern formation during solvent treatment using a tethered polystyrene(PS)-*b*-PMMA brush.^{40,41} When this diblock copolymer brush

was treated with dichloromethane—a good solvent for both PS and PMMA—water contact angle measurements indicated a characteristic advancing contact angle of PMMA of 74° , and the brush surface was smooth. When the same sample is treated with mixed solvents of dichloromethane and cyclohexane, and the percentage of cyclohexane—a good solvent for PS—is gradually increased, the advancing water contact of the brush increased to 120° , and the tethered diblock brush was seen to reorganize, resulting in the formation of a regular nanopattern on the surface. Polymer brush layers reversibly rearrange to form either a hydrocarbon polymer-enriched or a fluoropolymer-enriched air–polymer interface, depending on the nature of the solvent⁴² and also the temperature at which the sample is annealed.⁴³

The molecular organization of binary heterogeneous polymer brushes also leads to reversible wettability change. When binary polymer brushes of end functionalized PS and poly(2-vinylpyridine) (P2VP) chains were exposed to selective solvents for PS (toluene) and for P2VP (acidic water), it resulted in reversible switching of adhesive and wetting properties.⁴⁴ Binary polymer brushes of PMMA/PS brushes were prepared with a Y-type initiator carrying ATRP and NMP initiation moieties.⁴⁵ For a series of mixed brushes with a fixed PMMA molecular weight and systematically changed PS molecular weight, a transition in water advancing contact angle from 74° —the value for a flat PMMA surface—to 91° —the value for a flat PS film—was observed with increasing PS molecular weight after treatment with CHCl_3 . Intriguing surface morphologies composed of relatively ordered nanoscale domains were found in mixed brushes with PS molecular weight slightly smaller than or similar to that of PMMA after treatment with acetic acid, a selective solvent for PMMA. Incompatible polymers, polymethyl acrylate (PMA) and polystyrene-co-2,3,4,5,6-pentafluorostyrene (PSF), were randomly grafted one after another onto a silicon wafer.⁴⁶ The resulting layers possessed a nanostructured surface exhibiting either complete vertical or a combination of vertical and lateral microphase separation of the two components. The lateral and vertical reorganization of the mixed brush layer was observed to be reversible for at least 100 “switches” between good and bad solvent states for each component. Since PSF and PMA are mechanically dissimilar (glassy and rubbery, respectively) at room temperature, the bimodal response of the mechanically heterogeneous surface, with elastic modulus and adhesion distributions was very different for the “glassy state” and the “rubbery state”. The dramatic mechanical contrast of the surface as a function of solvent conditions decisively revealed the modes of phase segregation in a binary polymer brush.

Wettability/solubility also affects mass/electron transport through polymeric layers. Derivation of PHEMA cannot only increase the hydrophobicity but also greatly increase the resistance. Modification of a surface by a 250 nm thick PHEMA film can lead to a dramatic increase in surface resistance by four or five orders of magnitude and reduction of capacitance by two or three orders as probed with electrochemical impedance spectroscopy (EIS).^{47–49} Resistance measurements of polyelectrolyte brushes showed further refined adjustable properties. A pH-sensitive polymer brush

[polydimethylaminoethylmethacrylate (PDMAEMA)] was grafted onto gold, and electron transport was enhanced in the protonated state as compared to the deprotonated state, corresponding to a swollen/collapse transition.⁵⁰ Polymer brushes show an increased fidelity in guiding electrodeposition. Using patterned SAM as the template, conducting polymers preferably deposit on SAM-covered areas, due to the dominance of hydrophobic–hydrophobic interactions over electro-polymerization speed, ultimately resulting in resistance failure.^{51,52} On the other hand, on the patterned surfaces of polymer brushes, only the non-brush areas were covered with electrodeposited polymer.⁵³

In all cases discussed above, switching is based on immersion in different solvents, whereas ideally, the trigger should be light, salt, pH *etc.*, which allows *in situ* altering of the surface wettability. A more convenient way to reversibly change the wettability can be achieved by exploiting changes in the conformation of polymer chains in contact with different external environments (*i.e.* stimuli-responsive polymers). The most widely studied system is poly(*N*-isopropyl)acrylamide (PNIPAm), a thermo-responsive polymer that has a Low Critical Solution Temperature (LCST) around 32°C , below which it is hydrophilic due to H-bonding with water, and above which it is hydrophobic due to intra-molecular H-bonding. As a result, polymer brush-coated surfaces show contact angles of around 30° at room temperature and up to 70° at 45°C . The wettability change can also be seen from the adhesion change between an AFM tip and PNIPAm brushes, which increased twofold due to the increased hydrophobic–hydrophobic interactions above the LCST.⁵⁴ Brushes grafted on (micro)structured surfaces exhibited increased changes in reversible wettability from superhydrophobic to superhydrophilic.⁵⁵ The reverse situation, *i.e.* hydrophobic at low temperature and hydrophobic at high temperature is observed when polymer brushes exhibiting Upper Critical Solution Temperature (UCST) behavior are studied. Polysulfobetaines are zwitterionic polymers containing sulfonate anions and ammonium cations, and brushes made thereof indeed showed thickness- and temperature-dependent changes in wettability caused by UCST behaviour.⁵⁶ This is evidenced by a transition from hydrophilic at low thickness to hydrophobic at large thickness, due to formation of a completely collapsed self-associated state that can be reversed by increasing the temperature, leading to a hydrophobic-to-hydrophilic switch.

Copolymer brushes with two responsive blocks allow adjustable wettability using multiple environmental triggers. Copolymer brushes of polyacrylic acid (PAA)–PNIPAm with a pH-sensitive PAA block and thermo-sensitive PNIPAm block have been prepared and exhibit complex wettability changes. Fig. 4 shows the contact angle of PAA-co-NIPAm brushes on flat and microstructured surfaces. By altering the pH and the temperature, surface wettability changes as a result of both conformational change and compositional change of the outermost layer (PAA and PNIPAm respectively). The most hydrophobic surface was formed with protonated PAA blocks, and above the LCST of PNIPAm and in both PAA–PNIPAM blocks as well as random copolymers, a continuous change of contact angles can be accessed using different pH and temperature combinations. Structured

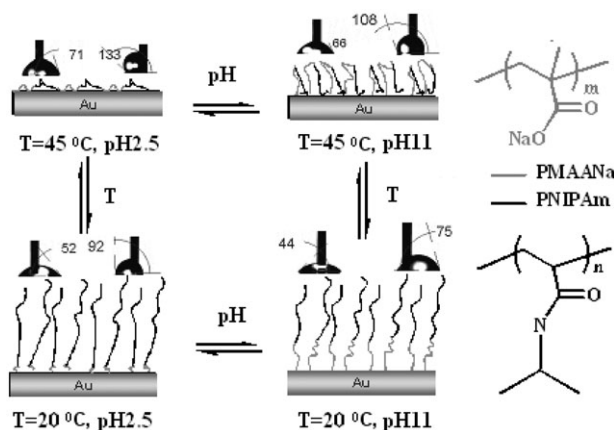


Fig. 4 Schematic drawings of conformational change of PMAA–PNIPAM block copolymer brushes in response to multiple external triggers, and corresponding contact angle images on flat surfaces (left) and on microstructured surfaces (right). The wettability changes are caused by both conformational and compositional change of the outmost layer. At low pH, the PAA is in its acid form, insoluble in water and remains underneath the two blocks. At high pH, anionic PAA migrates to the surface.

surfaces were again used to enhance wettability differences between different states.⁵⁷

Polyelectrolyte brushes for nanoactuator use

Polymer brushes experience swelling and collapse transitions in good and poor solvents, associated with large conformational changes of the polymer backbones. When charges are introduced along the polymer backbone (*i.e.* polyelectrolyte brushes), a much richer behaviour can be expected. Seminal work by Pincus and Zhulina^{58–60} has indicated the existence of different regimes for polyelectrolyte brushes. Scaling theories explain the relation between brush height and salt concentration, length of the polymer chains, grafting density and degree of charging. Despite a large amount of theoretical work, there has been little experimental evidence in this direction, mainly because of the synthetic difficulties in preparing well-defined brushes. In the so-called *osmotic* regime, the height h of strong, dense polyelectrolyte brushes is independent of salt concentration (eqn (1)).

$$h \approx N\alpha^{1/2} \quad (1)$$

$$h \approx 2\pi l_B \frac{a^2}{D^2} \alpha^2 N^3 \quad (2)$$

$$h \approx Na(2aD^2C_s)^{-1/3} \quad (3)$$

where N is the number of monomers in the chain, α the degree of ionization, a the size of the monomers and C_s is the salt concentration. For less dense strong polyelectrolytes (*Pincus* regime), we expect a dependency on the grafting density (a^2/D^2), and the length of the polymer chains (eqn (2)), where l_B is the Bjerrum length (a measure for the separation of charges; in water at 24 °C, l_B is 0.714 nm).

In the presence of salt, the situation is much more complex and is strongly influenced by the chemical nature of the

brushes. Strong polyelectrolytes carry charges regardless of the osmotic strength or pH of the solution, whereas weak polyelectrolytes have pH-dependent charge distribution along the chains. For both strong and weak polyelectrolyte brushes, the thickness scales with $(C_s)^{-1/3}$ at sufficiently high concentration due to charge screening (eqn (3)). However, at low salt concentrations, salt has little effect on strong polyelectrolyte brushes, but increases the height of weak polyelectrolyte brushes because of the exchange of added ions with protons within the brush layer. When large amounts of salts are added, the brushes will collapse regardless of charge and grafting density due to the very large osmotic pressure exerted on the films as well as ion pairing/charge condensation events, which reduce the effective charge density along the backbone (hydrophobic collapse).

Polyelectrolyte brushes can be prepared either using free radical polymerization of neutral monomers and subsequent post-functionalization of the brushes to introduce charges or using controlled radical polymerization of charged monomers. Anionic PMAA and PSSNa brushes on a spherical surface and cationic PVP brushes were synthesized by free radical polymerization and studied mainly by multi-angle null ellipsometry in solution.⁶¹ The experimental results were almost consistent with theoretical predictions. PSSNa brushes showed little pH dependence, while PMAA brushes are pH dependent. For weak PMAA brushes, at pH values between 4 and 10, the brush thickness initially increased and then decreased with increasing concentration of added salt; *i.e.*, a maximum of brush thickness appears at a medium salt concentration. The chemical nature of the polymers also has a profound impact on the swelling/collapse behavior of the brushes.⁶²

There are two different ways to induce conformational changes in polyelectrolyte brushes: charge screening at high salt concentration and hydrophobically-induced collapse due to ion pairing of counterions with the charges on the brushes. The former usually occurs at high concentration (although different salts have different capacity for charge screening), while the latter usually occurs at low concentration and with specific salts. In our group, we have exploited both solution AFM and QCM-D as tools to probe both the swelling/collapse transition and the changes in the viscoelastic properties of the brushes in real time.^{55,63,64} Interestingly, collapsed 2-poly[(methacryloyloxy)ethyl] trimethylammonium chloride (PME-TAC) brushes show intrinsically different mechanical properties depending on the nature of the collapse transition. Charge-screened PMETAC still remains in a hydrated state and relatively soft, as can be deduced from the tip penetration in AFM experiments at high applied loads (Fig. 5(a)), while hydrophobically collapsed brushes become much more rigid and show little height change with increasing applied load during AFM measurement (Fig. 5(b)). A strong ion-pairing effect can also be translated into wettability changes: collapsed PMETAC brushes show more hydrophobic contact angles after strong coordination with perchlorate anions. Strongly coordinated brushes did not return to their original conformation when flushed with water, and only after exchange with a NaCl solution the brush was ‘free’ to swell again. Such properties potentially offer the feasibility of brushes being used in actuation.

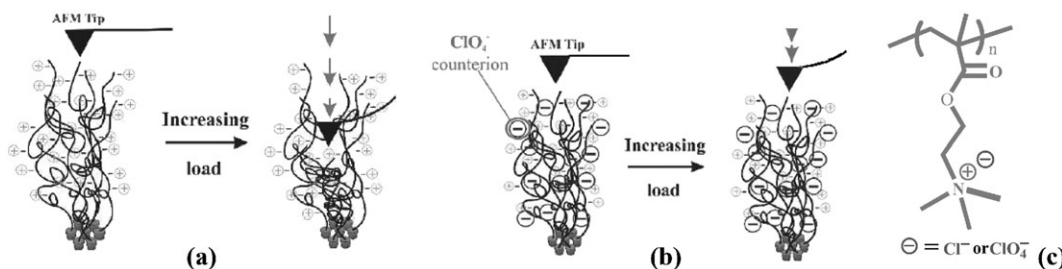


Fig. 5 Schematic drawing of the elastic properties of polycationic brushes as probed with AFM.⁶³ (a) The counterions within the PMETAC brush are Cl^- , and the brushes are highly hydrated and soluble in water. Therefore, they are soft and the height dramatically decreases with increasing applied loads, indicating the AFM tip penetrates into the brush. (b) When Cl^- is replaced with perchlorate anions the polymer brushes became extremely rigid due to diminished solubility in water, and the AFM tip cannot penetrate into brush. (c) Structure of PMETAC. Reprinted from ref. 63, with permission from the Royal Society of Chemistry.

The apparent swelling/collapse caused by conformational changes reflects an energy re-distribution within polymer brushes. On a sufficiently rigid substrate, energy will lead to an internal rearrangement of the brush conformation. However, if the substrate is soft and flexible, the conformational changes will lead to surface stresses and to bending of the substrate. As a result, chemical energy will be translated into mechanical movement.

Conformational change-induced nanomechanical motion seems attractive because, at some level, it resembles the way muscles function.^{65,66} R  he *et al.* proposed a system to exploit changes in surface topography of microphase-separated PMMA-*b*-GMA diblock copolymer brushes and PMMA-PGMA mixed brushes for the motion of nano-objects adsorbed to the brush surface.⁶⁷ The idea is illustrated in Fig. 6. Different topographical and chemical configurations of the polymer brushes, together with dramatic changes in the surface energy potential landscape during a phase transition, can cause the polymer chains to grasp or release a nano-object successively, moving it across a surface. In this way, chemical

energy was transferred to mechanical movement of nano-objects. Silica particles adsorbed on top of the diblock copolymer brushes did move and organize into islands during periodic switching of the topography. Motion is shown to occur independently of the solvents or their vapors to induce topography switching. In analogous experiments, the silica particles on homopolymer brushes were found not to move, further proving that the changing topography is actually responsible for the motion. Unfortunately, directional motion of the particles has not yet been demonstrated.

Another way to translate conformational energy (entropic energy) into nanoscale motion is to utilize materials with low Young's modulus and small dimensions. AFM cantilevers (Fig. 7(a), left) can be actuated by differential surface stress changes acting on the two sides. Assembly of SAMs on one side of cantilevers results in tensile stresses, forcing bending towards the SAM-modified side.⁷⁷ Modification of cantilevers with SAMs of biomolecules takes advantage of specific interactions (antigen–antibody, hybridization of DNA strands, *etc.*^{68–71}) for highly sensitive detection. However, most systems suffer from a small amplitude and/or poor reversibility, which limits their application in actuation. Polymer brushes seem more promising than SAMs because both conformational changes in normal polymers and charging/discharging in PELs can result in potentially large surface stresses and, importantly, the conformational changes in polymer brushes are completely reversible.

Bumbu *et al.* demonstrated how surface grafted brushes could be harnessed as a sensitive sensor to a common solvent.⁷² Reproducible bending of the cantilever was achieved by cycling the brushes from the swollen to dry state by changing the cantilever environment from a solvent-saturated to a nitrogen-flushed atmosphere. Stimulus-responsive polymer brush-coated cantilevers can be used to sense and transduce changes in solvent conditions.⁷³ Cantilevers modified with thermoresponsive pNIPAm brushes responded to changes in temperature due to the collapse of the brushes. The deflection was proportional to the brush height and the conformational state. Although the cantilever deflections were largely reversible, there were slight variations from one cycle to the next. The cantilever response increases with increasing brush height, but the relative changes in cantilever deflection, when cycled between good and poor solvent, remained independent of brush height.

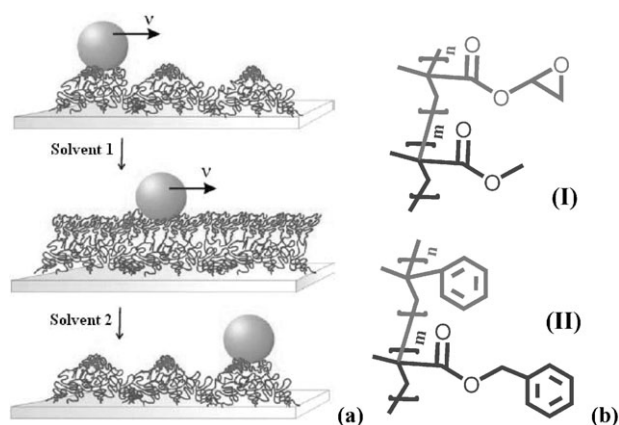


Fig. 6 (a) Mechanism, proposed by R  he *et al.*,⁶⁷ describing how responsive polymer brushes move nano-objects on their upper surface when subject to alternating, different solvents or solvent vapors. When a structural element forms, the local, inhomogeneous chemical composition might attract or repel the object away from the element's center of mass. In this way, the nano-object is subject to fluctuating force fields on a nano-scale during topography switching. (b) Structure of diblock-copolymer brushes used. Reprinted from ref. 67, with permission from Elsevier.

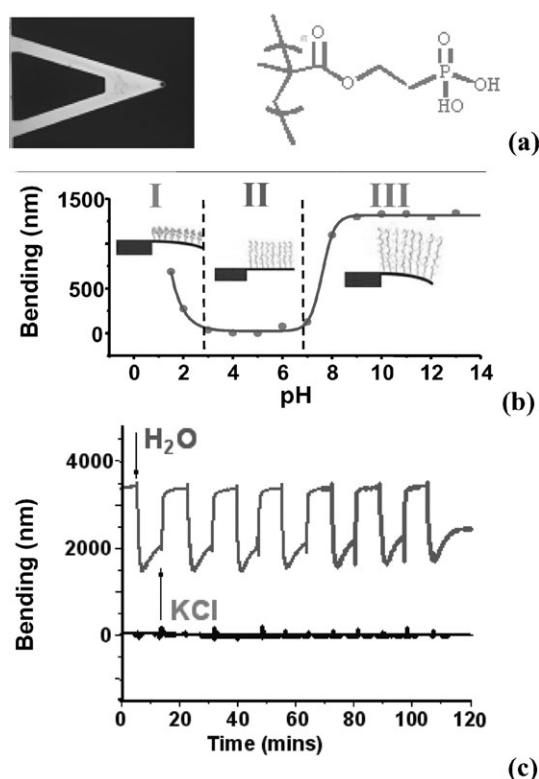


Fig. 7 (a) Shape of triangle silicon cantilever and the structure of PMEP brushes. The cantilever was coated on both sides with a ~ 20 nm gold film and the top of the cantilever was modified with ~ 20 nm PMEP brush and the bottom modified with inert thiol. (b) Response of cantilever at different pH values. (c) The reversible response of cantilever to alternate switching between water and 0.1 M KCl solution.⁷⁴ Reprinted from ref. 74, with permission from the American Chemical Society.

Cantilevers modified on one side with phosphate-containing PEL brushes (Fig. 7(a)) exhibited highly reversible and multi-stage cantilever actuation in response to the pH and electrolyte concentration.⁷⁴ Polymethacryloyloxyethyl-phosphate (PMEP) brushes showed multistep changes in wettability, corresponding to three different protonation states (doubly-, mono- and un-protonated).⁷⁵ Two transition points were found in the cantilever deflection (Fig. 7(a)), consistent with wettability measurements. Collapse of the polymer brushes at low pH resulted in compressive stress and the cantilever bent away from the brush-modified side to create more space to accommodate collapsed polymer chains. At high pH, more compressive stress was observed probably due to strong charge repulsion. The magnitude of cantilever bending could be tuned by placing the brushes in solutions of different ionic strength. When switching between water and 0.1M KCl solution, cantilever actuation was highly reversible (Fig. 7b). This polymer brush driven nanomechanical motion holds promise for applications in microfluidic devices, sensors and actuators. Importantly, the highly sensitive and time-resolved measurements of cantilever bending can also be used as a means to probe the internal structure of the brushes and to reveal some of the processes occurring during brush collapse and stretching. The versatility of the chemical strategy used to obtain these brushes allows the study of a wide range of parameters

that could govern allbending behavior, including grafting density, chain length, nature of the polyelectrolyte brushes, salts used to collapse the brushes and patterning of the brush layer to create non-biaxial stresses. Further work is required to fully understand the origin of the surface stress, and the effect of grafting density and thickness on actuation and power generation.

Bio-compatible brushes

Both SAMs and polymer brushes can serve as model surfaces for studies in nanotechnology, molecular biology, and biomedical sciences.⁷⁶ So far, SAMs have received extensive exploration in biology, including: protein adsorption/resistance, biocompatible surfaces, and covalent attachment of biomolecules.^{1,77} Of particular interest is the fabrication of non-fouling surfaces to minimize the non-specific adsorption that hampers detection limits in diagnostic tools like ELISA assays, protein microarrays, biosensors, and single molecule detection. Polyethylene glycol (PEG) is the most widely used non-fouling material and shows a high capacity to suppress protein adsorption.^{78,79} However, SAMs of linear (non-overlapping) PEG surfaces might not be sufficiently robust to significantly prevent protein adsorption in real-life applications. Star polymers incorporating PEG chains show high protein resistance, but are difficult to synthesize.^{80,81} Polymer brushes can introduce high density PEG moieties through side chains [poly (oligoethylene glycol) methacrylate (POEGMA)] and are exceptionally resistant to absorption of even very sticky proteins such as fibronectin (FN), and the adsorption of complex and concentrated protein mixtures.⁸² Most importantly, POEGMA brushes have prolonged stability (more than 10 d) as well as superior surface coverage (no pinholes) compared to SAMs. A systematic study of the growth kinetics of POEGMA brushes *via* ATRP has been reported.⁸³ These brushes, with precisely controlled thicknesses over 100 nm, are readily obtained at room temperature and can be modified further to introduce specific binding sites. PEG-containing brushes have been grown on a range of substrates, including silicon surfaces,⁸⁴ a variety of conducting substrates including engineering materials,⁸⁵ carbon black,⁸⁶ and titanium.⁸⁷ This will greatly expand the applications of these materials *in vivo*. The grafting density of the brushes significantly affects the amount of adsorbed proteins.⁸⁸ For example, the amount of FN adsorbed is correlated with the coverage of brushes on the substrate; the amount decreases with increasing brush coverage. On the other hand, the density of adsorbed cells and their spreading on the substrate increased with increasing FN coverage.⁸⁹ Hydroxyl group-capped PEG-containing polymer brushes can be used to chemically attach biomolecules for subsequent detection through specific interactions. Protein-modified non-fouling polymer brushes are attractive candidates for the development of protein microarrays.⁹⁰ Another polymer of interest for biomedical applications is zwitterionic poly[(2-methacryloyloxy)ethyl phosphorylcholine] (PMPC). A detailed synthetic study using SI-ATRP and up to 100 nm thick brushes was recently reported.⁹¹ Protein adsorption decreased with increasing thickness of the PMPC grafts. Grafts of chain length 200 gave adsorption levels of 7 and

2 ng cm⁻² for fibrinogen and lysozyme at 1 mg mL⁻¹ protein concentration, respectively, corresponding to reductions of greater than 98% compared to the unmodified silicon.⁹² Iwata *et al.* showed that when the thickness of the PMPC brush layer was greater than 5.5 nm, serum protein adsorption and fibroblast adhesion were effectively reduced.⁹³ A variety of other polymers can be selected for targeted biological studies. For example, cationic polymer brushes (quaternized PDMAEMA) showed substantial antimicrobial activity against *Escherichia coli* and *Bacillus subtilis*. The permanence of the antimicrobial activity was demonstrated through repeated use of the modified substrate without significant loss of activity.⁹⁴

Reversible interactions between biomolecules and interfaces are extremely attractive and can be achieved by incorporating the responsive polymer brushes discussed above. The adsorption of BSA and *Streptococcus mutans* on thermoresponsive PNIPAm brushes was LCST-dependent in hydrophobic related adhesion.^{95,96} The change in the pattern of *S. mutans* attachment following 'cycling' of PNIPAm brushes above and below the LCST was correlated with changes in the surface properties as a result of the phase transitions. Polyelectrolyte brushes can also act as nanocontainers. The amount captured in the brushes depends on the solution conditions and can be tuned by changing the conformation of the polymer chains, and thereby the effective free volume within the brush layer. Ballauff *et al.*⁹⁷ used confocal fluorescence microscopy with single molecule sensitivity to characterize uptake and release of fluorescent protein molecules by individual Spherical Polyelectrolyte Brush (SPB)-modified nanoparticles. They demonstrated that SPBs could be loaded with up to 30 000 mEosFP molecules in a solvent of low ionic strength. Essentially, complete release of the bound proteins was observed after increasing the ionic strength by adding 250 mM NaCl to the solvent. Their high storage density, good retention, and controlled uptake and release of the proteins make these colloidal nanoparticles promising candidates for applications in drug delivery systems, biosensors, immunoassays, and biocatalysts. Similarly, it is possible to release the included small molecules by external triggers in a controllable manner. From these initial studies it seems that polymer brushes provide a versatile platform for biological studies.

Concluding remarks and perspectives

Polymer brushes amplify the structures of SAMs. They offer more flexibility for surface modifications and, more importantly, open up opportunities for creating smart or responsive surfaces. The large dimensions of the molecular building blocks immediately lead to mechanically and chemically more robust films than their monolayer counterparts. More importantly, the large size of the building blocks also introduces entropic factors to the film, and hence many of the reported surface characteristics are a result of the interplay between entropic penalties resulting from stretching of chains, and enthalpic gains resulting from bond formation at the surface and interchain van der Waals forces or other non-covalent interactions. As a result, polymer brushes exhibit large conformational changes in different solvents, which has been exploited in many 'smart' systems, where surface properties

change in response to environmental triggers. Associated with this is the reversible switchable wettability, and "on and off" states that can be used for site selective deposition/nucleation/adsorption/attachment, controlled uptake and release, and transduction of chemical energy into mechanical work. Unlike SAMs, polymer brushes are able to introduce adjustable amounts of desirable functionalities on surfaces through copolymerisation. Polyelectrolyte brushes are now beginning to be explored in a wide range of different applications, ranging from sensors to nanoactuators, and it is clear that the fundamental properties of the collapse transition can be exploited as an 'energy' source in nanoactuating systems. Design of polymeric systems, especially polyelectrolyte brushes that can mimic structures in biology, will be of immediate interest and relevance. In future, questions related to the confinement of the polymers at the surface will also need to be addressed. For example, what are the fundamental differences in chemical and physical properties in brushes and bulk polymers? To make these comparisons, polymer brushes with precisely controlled thickness and composition will be required. Full control over the surface-initiated polymerization is thus needed and many of the recent developments in controlled polymerization techniques will need to be adapted for surface-initiated growth. With the current momentum in both synthetic and physical chemical efforts towards ever more complex brush systems, we envisage polymer brushes to emerge as key components in soft nanotechnology.

References

- 1 J. C. Love, L. A. Estroff, J. K. Kriebel, R. G. Nuzzo and G. M. Whitesides, *Chem. Rev.*, 2005, **105**, 1103.
- 2 C. Vericat, M. E. Vela and R. C. Salvarezza, *Phys. Chem. Chem. Phys.*, 2005, **7**, 3258.
- 3 F. Schreiber, *Prog. Surf. Sci.*, 2000, **65**, 151.
- 4 O. Prucker and J. Rühe, *Macromolecules*, 1998, **31**, 592.
- 5 S. Edmondson, V. L. Osborne and W. T. S. Huck, *Chem. Soc. Rev.*, 2004, **33**, 14.
- 6 R. C. Advincula, W. J. Brittain, K. C. Caster and J. Ruehe, *Polymer Brushes: Synthesis, Characterization, Applications*, Wiley-VCH Verlag GmbH & Co KGaA, Weinheim, Germany, 2004.
- 7 T. Wu, K. Efimenko, P. Vlček, V. Šubr and J. Genzer, *Macromolecules*, 2003, **36**, 2448.
- 8 D. M. Jones and W. T. S. Huck, *Adv. Mater.*, 2001, **13**, 1256.
- 9 G. L. Whiting, H. J. Snaith, S. Khodabakhsh, J. W. Andreasen, D. W. Breiby, M. M. Nielsen, N. C. Greenham, R. H. Friend and W. T. S. Huck, *Nano Lett.*, 2006, **6**, 573.
- 10 J. Pyun, T. Kowalewski and K. Matyjaszewski, *Macromol. Rapid Commun.*, 2003, **24**, 1043.
- 11 J. B. Kim, M. L. Bruening and G. L. Baker, *J. Am. Chem. Soc.*, 2000, **122**, 7616.
- 12 V. L. Osborne, D. M. Jones and W. T. S. Huck, *Chem. Commun.*, 2002, 1838.
- 13 S. E. Moya, A. A. Brown, O. Azzaroni and W. T. S. Huck, *Macromol. Rapid Commun.*, 2005, **26**, 1117.
- 14 D. M. Jones, A. A. Brown and W. T. S. Huck, *Langmuir*, 2002, **18**, 1265.
- 15 P. J. Hamelinck and W. T. S. Huck, *J. Mater. Chem.*, 2005, **15**, 381.
- 16 S. Edmondson and W. T. S. Huck, *Adv. Mater.*, 2004, **16**, 1327.
- 17 M. Husseman, E. E. Malmstrom, M. McNamara, M. Mate, D. Mecerreyes, D. G. Benoit, J. L. Hedrick, P. Mansky, E. Huang, T. P. Russell and C. J. Hawker, *Macromolecules*, 1999, **32**, 1424.
- 18 J. B. Kim, W. Huang, M. L. Bruening and G. L. Baker, *Macromolecules*, 2002, **35**, 5410.
- 19 D. J. Dyer, *Adv. Funct. Mater.*, 2003, **13**, 667.
- 20 M. Husemann, D. Mecerreyes, C. J. Hawker, J. L. Hedrick, R. Shah and N. L. Abbott, *Angew. Chem., Int. Ed.*, 1999, **38**, 647.

- 21 U. Schmelter, R. Jordan, W. Geyer, W. Eck, A. Golzhauser, M. Grunze and A. Ulman, *Angew. Chem., Int. Ed.*, 2003, **42**, 559.
- 22 H. W. Li, B. V. O. Muir, G. Fichet and W. T. S. Huck, *Langmuir*, 2003, **19**, 1963.
- 23 R. D. Piner, J. Zhu, F. Xu, S. H. Hong and C. A. Markin, *Science*, 1999, **283**, 661.
- 24 M. Kaholek, W. K. Lee, S. J. Ahn, H. Ma, K. C. Caster and S. Zauscher, *Nano Lett.*, 2004, **4**, 373.
- 25 Y. Xia and G. M. Whitesides, *Angew. Chem., Int. Ed.*, 1998, **37**, 550.
- 26 O. Prucker, J. Habicht, I. J. Park and J. Rühe, *Mater. Sci. Eng., C*, 1999, **8**, 291.
- 27 F. J. Xu, Y. Song, Z. P. Cheng, X. L. Zhu, C. X. Zhu, E. T. Kang and K. G. Neoh, *Macromolecules*, 2005, **38**, 6254.
- 28 F. Zhou, L. Jiang, W. M. Liu and Q. J. Xue, *Macromol. Rapid Commun.*, 2004, **25**, 1979.
- 29 F. Zhou, W. M. Liu, J. C. Hao, T. Xu, M. Chen and Q. J. Xue, *Adv. Funct. Mater.*, 2003, **13**, 938.
- 30 M. K. Chaudhury and G. M. Whitesides, *Science*, 1992, **256**, 1539.
- 31 T. Wu, K. Efimenko, P. Vlček, V. Šubr and J. Genzer, *Macromolecules*, 2003, **36**, 2448.
- 32 X. Wang, H. Tu, P. V. Braun and P. W. Bohn, *Langmuir*, 2006, **22**, 817.
- 33 C. Xu, T. Wu, C. M. Drain, J. D. Batteas and K. L. Beers, *Macromolecules*, 2005, **38**, 6.
- 34 J. Lahann, S. Mitragotri, T. N. Tran, H. Kaido, J. Sundaram, I. S. Choi, S. Hoffer, G. A. Somorjai and R. Langer, *Science*, 2003, **299**, 371.
- 35 R. R. Shah, D. Merceyces, M. Husemann, I. Rees N. L. Abbott, C. J. Hawker and J. L. Hedrick, *Macromolecules*, 2000, **33**, 597.
- 36 D. H. Jung, I. J. Park, Y. K. Choi, S. B. Lee, H. S. Park and J. Rühe, *Langmuir*, 2002, **18**, 6133.
- 37 L. Andruzzi, A. Hexemer, X. Li, C. K. Ober, E. J. Kramer, G. Galli, E. Chiellini and D. A. Fischer, *Langmuir*, 2004, **20**, 10498.
- 38 W. H. Yu, E. T. Kang and K. G. Neoh, *Langmuir*, 2005, **21**, 450.
- 39 F. Zhou, W. Liu, M. Chen and D. C. Sun, *Chem. Commun.*, 2001, 2446.
- 40 B. Zhao, W. J. Brittain, W. Zhou and S. Z. D. Cheng, *J. Am. Chem. Soc.*, 2000, **122**, 2407.
- 41 S. G. Boyes, A. M. Granville, M. Baum, B. Akgun, B. K. Mirous and W. J. Brittain, *Surf. Sci.*, 2004, **570**, 1.
- 42 A. M. Granville, S. G. Boyes, B. Akgun, M. D. Foster and W. J. Brittain, *Macromolecules*, 2004, **37**, 2790.
- 43 A. M. Granville, S. G. Boyes, B. Akgun, M. D. Foster and W. J. Brittain, *Macromolecules*, 2005, **38**, 3263.
- 44 H. Retos, G. Gorodyska, A. Kiriy, M. Stamm and C. Creton, *Langmuir*, 2005, **21**, 7722.
- 45 B. Zhao, R. T. Haasch and S. MacLaren, *J. Am. Chem. Soc.*, 2004, **126**, 6124.
- 46 M. Lemieux, D. Usov, S. Minko, M. Stamm, H. Shulha and V. V. Tsukruk, *Macromolecules*, 2003, **36**, 7244.
- 47 E. L. Brantley and G. K. Jennings, *Macromolecules*, 2004, **37**, 1476.
- 48 G. K. Jennings and E. L. Brantley, *Adv. Mater.*, 2004, **16**, 1983.
- 49 E. L. Brantley, T. C. Holmes and G. Kane Jennings, *J. Phys. Chem. B*, 2004, **108**, 16077.
- 50 F. Zhou, H. Y. Hu, B. Yu, V. L. Osborne, W. T. S. Huck and W. M. Liu, in preparation.
- 51 F. Zhou, M. Chen, W. M. Liu, J. X. Liu, Z. L. Liu and Z. G. Mu, *Adv. Mater.*, 2003, **15**, 1367.
- 52 F. Zhou, Z. L. Liu, B. Yu, M. Chen, J. C. Hao, W. M. Liu and Q. J. Xue, *Surf. Sci.*, 2004, **561**, 1.
- 53 F. Zhou, Z. L. Liu, W. N. Li, J. C. Hao, M. Chen, W. M. Liu and D. C. Sun, *Chem. Lett.*, 2004, **33**, 602.
- 54 D. M. Jones, J. R. Smith, W. T. S. Huck and C. Alexander, *Adv. Mater.*, 2002, **14**, 1130.
- 55 T. Sun, G. Wang, L. Feng, B. Liu, Y. Ma, L. Jiang and D. Zhu, *Angew. Chem., Int. Ed.*, 2004, **43**, 357.
- 56 O. Azzaroni, A. A. Brown and W. T. S. Huck, *Angew. Chem., Int. Ed.*, 2006, **45**, 1770.
- 57 F. Xia, L. Feng, S. Wang, T. Sun, W. Song, W. Jiang and L. Jiang, *Adv. Mater.*, 2006, **18**, 432.
- 58 P. Pincus, *Macromolecules*, 1991, **24**, 2912.
- 59 E. B. Zhulina, T. M. Birshtein and O. V. Borisov, *Macromolecules*, 1995, **28**, 1491.
- 60 E. B. Zhulina and O. V. Borisov, *J. Chem. Phys.*, 1997, **107**, 5952.
- 61 J. Rühe, M. Ballauff, M. Biesalski, P. Dziezok, F. Grohn, D. Johannsmann, N. Houbenov, N. Hugenberg, R. Konradi, S. Minko, M. Motornov, R. R. Netz, M. Schmidt, C. Seidel, M. Stamm, T. Stephen, D. Usov and H. Zhang, *Adv. Polym. Sci.*, 2004, **165**, 79.
- 62 H. Zhang and J. Rühe, *Macromolecules*, 2005, **38**, 4855.
- 63 T. Farhan, O. Azzaroni and W. T. S. Huck, *Soft Matter*, 2005, **1**, 66.
- 64 O. Azzaroni, S. Moya, T. Farhan, A. A. Brown and W. T. S. Huck, *Macromolecules*, 2005, **38**, 101947.
- 65 M. O. Magnasco, *Phys. Rev. Lett.*, 1994, **72**, 2656.
- 66 T. Duke, T. E. Holy and S. Leibler, *Phys. Rev. Lett.*, 1995, **74**, 330.
- 67 S. Santer and J. Ruehe, *Polymer*, 2004, **45**, 8279.
- 68 R. Berger, E. Delamarche, H. P. Lang, C. Gerber, J. K. Gimzewski, E. Meyer and H. J. Güntherodt, *Science*, 1997, **276**, 2021.
- 69 G. Wu, H. Ji, K. Hansen, T. Thundat, R. Datar, R. Cote, M. F. Hagan, A. K. Chakraborty and A. Majumdar, *Proc. Natl. Acad. Sci. U. S. A.*, 2001, **98**, 1560.
- 70 J. Fritz, M. K. Baller, H. P. Lang, H. Rothuizen, P. Vettiger, E. Meyer, H. J. Güntherodt, C. Gerber and J. K. Gimzewski, *Science*, 2000, **288**, 316.
- 71 W. Shu, D. Liu, M. Watari, C. K. Riener, T. Strunz, M. E. Welland, S. Balasubramanian and R. McKendry, *J. Am. Chem. Soc.*, 2005, **48**, 17054.
- 72 G. G. Bumb, G. Kircher, M. Wolkenhauer, R. Berger and J. S. Gutmann, *Macromol. Chem. Phys.*, 2004, **205**, 1713.
- 73 N. I. Abu-Lail, M. Kaholek, B. LaMattina, R. L. Clark and S. Zauscher, *Sens. Actuators, B*, 2006, **114**, 371.
- 74 F. Zhou, W. Shu, M. E. Welland and W. T. S. Huck, *J. Am. Chem. Soc.*, 2006, **128**, 5326.
- 75 F. Zhou and W. T. S. Huck, *Chem. Commun.*, 2005, 5999.
- 76 W. Senaratne, L. Andruzzi and C. K. Ober, *Biomacromolecules*, 2005, **6**, 2427.
- 77 M. Mrksich, *Chem. Soc. Rev.*, 2000, **29**, 267.
- 78 K. L. Prime and G. M. Whitesides, *J. Am. Chem. Soc.*, 1993, **115**, 10714.
- 79 M. Mrksich, G. B. Sigal and G. M. Whitesides, *Langmuir*, 1995, **11**, 4383.
- 80 S. W. Lee and P. E. Laibinis, *Biomaterials*, 1998, **19**, 1669.
- 81 S. J. Sofia, V. Premnath and E. W. Merrill, *Macromolecules*, 1998, **31**, 5059.
- 82 H. Ma, J. Hyun, P. Stiller and A. Chilkoti, *Adv. Mater.*, 2004, **16**, 338.
- 83 A. A. Brown, N. S. Khan, L. Steinbock and W. T. S. Huck, *Eur. Polym. J.*, 2005, **41**, 1757.
- 84 L. Andruzzi, W. Senaratne, A. Hexemer, E. D. Sheets, B. Ilic, E. J. Kramer, B. Baird and C. K. Ober, *Langmuir*, 2005, **21**, 2495.
- 85 S. Gabriel, P. Dubruel, E. Schacht, A. M. Jonas, B. Gilbert, R. Jerome and C. Jerome, *Angew. Chem., Int. Ed.*, 2005, **44**, 5505.
- 86 M. Ignatova, S. Voccia, B. Gilbert, N. Markova, D. Cossement, R. Gouttebaron, R. Jerome and C. Jerome, *Langmuir*, 2006, **22**, 255.
- 87 X. Fan, L. Lin, J. L. Dalsin and P. B. Messersmith, *J. Am. Chem. Soc.*, 2005, **127**, 15843.
- 88 R. R. Bhat, B. N. Chaney, J. Rowley, A. Liebmann-Vinson and J. Genzer, *Adv. Mater.*, 2005, **17**, 2802.
- 89 H. Ma, M. Wells, T. P. Beebe and A. Chilkoti, *Adv. Funct. Mater.*, 2006, **16**, 640.
- 90 S. Tugulu, A. Arnold, I. Sielaff, K. Johnsson and H. A. Klok, *Biomacromolecules*, 2005, **6**, 1602.
- 91 W. Feng, J. Brash and S. Zhu, *J. Polym. Sci., Part A*, 2004, **42**, 2931.
- 92 W. Feng, S. Zhu, K. Ishihara and J. L. Brash, *Langmuir*, 2005, **21**, 5980.
- 93 R. Iwata, P. Suk-In, V. P. Hoven, A. Takahara, K. Akiyoshi and Y. Iwasaki, *Biomacromolecules*, 2004, **5**, 2308.
- 94 S. B. Lee, R. R. Koepsel, S. W. Morley, K. Matyjaszewski, Y. Sun and A. J. Russell, *Biomacromolecules*, 2004, **5**, 877.
- 95 D. L. Huber, R. P. Manginell, M. A. Samara, B. Kim and B. C. Bunker, *Science*, 2003, **301**, 352.
- 96 C. de las Heras Alarcón, T. Farhan, V. L. Osborne, W. T. S. Huck and C. Alexander, *J. Mater. Chem.*, 2005, **15**, 2089.
- 97 K. Anik, C. Rolcker, A. Wittmann, J. Wiedenmann, M. Ballauff and G. U. Nienhaus, *J. Phys. Chem. B*, 2005, **109**, 5418.