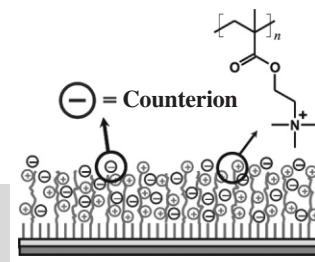


DOI: 10.1002/adma.200601257

Tunable Wettability by Clicking Counterions Into Polyelectrolyte Brushes**

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Polymer brushes have recently emerged as an extremely versatile way to modify surface properties in a robust and controlled way. The introduction of responsive polymers and block copolymers in polymer-brush systems has also opened up new routes to 'smart' surfaces with switchable surface properties. Here, the use of polyelectrolyte brushes as a supramolecular platform for the immobilization of a wide range of species, leading to a tunable wettability of substrates, is presented.



1. Introduction

Organic thin films provide a versatile platform for introducing those chemical functionalities that will ultimately determine the overall characteristics of a substrate.^[1] However, a more ambitious challenge in materials science is the design of smart surfaces with dynamically controllable properties.^[2] Such surfaces have characteristics that can be changed or tuned in an accurate and predictable manner by using an external stimulus. The classical framework is focused on triggering conformational and/or chemical changes in the organic film upon environmental variations. These stimuli-induced transformations are commonly a result of changes in electrochemical potential,^[3] pH,^[4] solvent,^[5] or irradiation.^[6] In previous years, many different and innovative approaches have been explored using these stimuli as tools. Katz et al. demonstrated the reversible change of wettability by using an electrochemically driven translocation of cyclophanes on molecular strings.^[7] Others have used thin organic films containing pyrimidine-terminated molecules as photoresponsive surfaces that can undergo dimerization, with concomitant changes in wetting upon irradiation with UV light.^[8]

However, a completely different, and potentially much more versatile, route to tailored surface properties based on surface-based supramolecular chemistry has recently emerged.

A number of different research groups have demonstrated that the wettability of charged organic films can be tuned by choosing the proper counterions.^[9–11] Choi and co-workers showed, by using imidazolium ion-terminated self-assembled monolayers, the dependence of the wettability on the nature of the counterion.^[10] In this case, contact angles varied from 25° to 65° upon coordination with Br⁻ or bis(trifluoromethane)sulfonimide anions (TFSI), respectively. We have shown that the wetting properties of substrates modified with cationic polyelectrolyte brushes are strongly dependent on the nature of the counterion. Coordination of polyelectrolyte brushes bearing quaternary ammonium groups (QA⁺) with sulfate anions resulted in creation of highly hydrophilic surfaces.^[12] Moreover, we also observed that coordination of similar brushes with ClO₄⁻ rendered the surface hydrophobic.^[13] Our previous work on studying the strong impact of counterions on the overall properties of polyelectrolyte brushes paved the way for the idea of creating surfaces with easily tunable wetting properties.

This Research News article attempts to give an overview of the recent developments in the field and explores how supramolecular chemistry based on ion pairing can be used to tune the wettability in a rational manner. In order to give the reader a full picture of this interesting approach we have complemented our previous results with new examples from our lab. This has been done with the aim of supporting and demonstrating the idea that a simple, rational, and predictable design

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[**] This research was financially supported by the EPSRC (GR/T11555/01), a Marie Curie Research Fellowship (O. A.), and Faraday Partnership-Unipath Ltd. (A. A. B.).

of wetting properties based on ion-pairing interaction into polyelectrolyte brushes is achievable.

2. Counterion-Dependent Wettability of Cationic Polyelectrolyte Brushes

Facile changes in surface properties by chemical means have been demonstrated with polyelectrolyte brushes, which are ideal building blocks for engineering surfaces at the molecular level. Polyelectrolyte brushes refer to charged polymer chains that are tethered at one end to a substrate, forming a brushlike layer.^[14] Environmental changes in ionic strength, pH, or solvent properties can promote sharp changes in surface characteristics due to transitions between the stretched and collapsed states of the polymer chains. The conformation of polyelectrolyte brushes is mainly governed by three factors: electrostatic interactions, solvation forces, and excluded volume effects. Polyelectrolyte chains will show a strongly stretched conformation in pure water, due to both the electrostatic repulsion between neighboring chargelike chains and the excluded volume effects of the solvated chain side groups.^[15] Conversely, in concentrated electrolyte solutions, the charges of the pendant groups in the polymer chains are screened; this minimization of the electrostatic repulsions leads to an entropically more favorable collapsed conformation. This conformational transition into a collapsed state is analogous to the well-known extended-to-coil-like transition commonly observed for polyelectrolytes in solution. However, the nature of the counterion greatly influences the characteristics of this collapsed state. This has been studied in detail by R uhe and co-workers for cases of anionic and cationic brushes in different environments.^[16–19] They reported how important the chemical nature of the counterion is in order to determine the coordination geometry^[17] or the degree of swelling^[18] of the polyelectrolyte brush.

In addition to the electrostatic screening of charges, supramolecular chemistry has shown that noncovalent interactions, such as ion-pairing interactions, can be used to create stable materials with well-defined properties.^[20]

Extending well-established supramolecular surface chemistry^[21–24] to polyelectrolyte brushes has greatly expanded the potential of these systems for surface modification. Rather than relying on the well-known salt-induced collapse we can exploit ion-pairing interactions to create completely new monomer units using only a standard polyelectrolyte brush, which acts as a matrix. This is a technique that we termed “clicking” due to the ease with which the ion-paired counterions can be attached and removed.

Our system is based on “work-horse” quaternary ammonium polyelectrolyte brushes, synthesized

via atom transfer radical polymerization (ATRP) on different surfaces.^[25,26] The as-synthesized poly[2-(methacryloyloxy)ethyl-trimethylammonium chloride] (PMETAC) brushes (20 nm in thickness) contain Cl[−] anions as counterions. These substrates show a rather hydrophilic behavior, as determined by using contact-angle goniometry (ca. 35°).^[13] Exchange of the counterions simply requires immersion of the PMETAC-modified substrates in a 0.1 M solution of the required counterions for a few minutes. Replacing the Cl[−] with ClO₄[−] promotes a drastic change in the wetting properties of the substrate from approximately 35° to 79° (Fig. 1).

The interaction between the QA⁺ groups in the PMETAC brushes and the surrounding counterions plays a major role in determining this change in the wetting characteristics. In contrast to hydrated Cl[−] anions, ClO₄[−] anions are poorly hydrated, large, and highly polarizable. They can interact very strongly with the quaternary ammonium pendant groups through ion pairing.^[27,28] This means that the two ionic entities are held together by strong Coulombic forces. As a result, ion pairing introduces significant changes in the physicochemical properties of the brush layer. In addition, not only the wetting properties are modified: significant changes in the nanomechanical properties of the organic film were also observed.^[29]

Counterion-dependent properties of quaternary ammonium salts have been observed by chemists for many years. In the case of QA⁺-containing cationic-exchange resins, different anions lead to significant differences in affinities or retention times. Another interesting example is in solvent extraction, where anion characteristics such as radius, charge, and hydra-

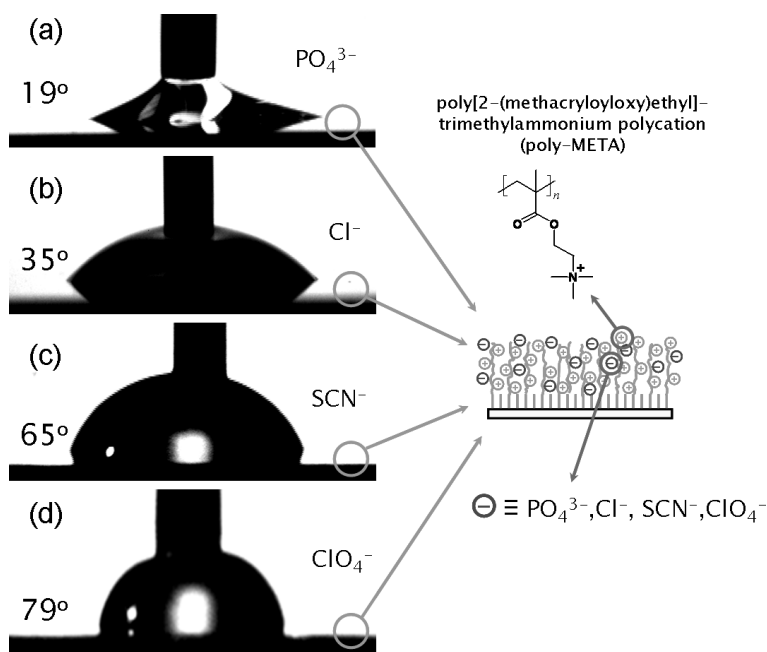


Figure 1. Changes in wettability corresponding to a Au surface modified with PMETAC brushes ($h=20$ nm) when their corresponding counterions are: a) PO₄³⁻, Cl[−], b) SCN[−], and c) ClO₄[−]. The schematic depicts the structure of the cationic polyelectrolyte brush.

tion govern the selectivity. Based on the immense influence of anions on the extraction performance of quaternary ammonium salts, Clifford and Irving constructed a scale of lipophilicity of anions.^[28] This scale was based on the order of extractability for the chloroform/water system, ranging from the most lipophilic anion, ClO_4^- , to the most hydrophilic, PO_4^{3-} . For anion selectivity using quaternary ammonium compounds the trend shown is an increasing affinity with decreasing hydration energy. Large anions with low hydration energies preferentially coordinate large, hydrophobic cations over smaller anions with higher hydration energies. This is something that we observed in QA^+ -bearing polyelectrolyte brushes when comparing affinity to Cl^- with respect to ClO_4^- ^[13] or PdCl_4^{2-} .^[30,31] More importantly, the lipophilicity of anions (A^-) indicates the affinity of the QA^+-A^- pair for an organic or aqueous environment. In other words, the anion plays a key role in determining the hydrophobic/hydrophilic character of the ion pair. Hence, when a situation arises such that a considerable number of ion pairs are exposed on a surface (as is the case for polymer brushes), the nature of the anion (counterion) tunes the wettability of the surface. This is the origin of the sharp change in wettability upon coordination of ClO_4^- with the brushes, where the anion confers its hydrophobic characteristics to the brush layer.^[13,29]

Within the traditional picture of polyelectrolyte brushes, the presence of counterions is mostly associated with the electrostatic screening of pendant charges by means of highly mobile counterions. However, in the case of strongly ion-paired species the brush experiences not only an electrostatic change, but also a drastic chemical change (hydrophilic–hydrophobic). As a consequence of this change, the brush suffers what we call “hydrophobic collapse” instead of the traditional “electrostatic-driven collapse”.^[15] Ion-pairing interactions are strong enough, and sufficiently selective, to tune the wetting of PMETAC brushes in such a manner that they cannot be reversed even when the inner ionic environment of the brush is diluted.^[12,13] This has been demonstrated for counterions promoting either hydrophilic^[12] or hydrophobic characteristics.^[13] In accordance with the lipophilicity scale, the hydrophobic character follows the trend: $\text{ClO}_4^- > \text{SCN}^- > \text{I}^- > \text{Br}^- > \text{Cl}^- > \text{PO}_4^{3-}$.

In order to demonstrate the applicability of the lipophilicity series we measured the contact angle of PMETAC brushes when coordinated with other anions. In agreement with the series, PMETAC brushes evidence a hydrophilic character (Fig. 1) when coordinated with PO_4^{3-} anions. Further, when coordinated with SCN^- anions they show a rather hydrophobic character (advancing contact angle in water, $\theta_{\text{AW}} \sim 65^\circ$), but not as pronounced as that in the case of ClO_4^- . Figure 1 clearly indicates how sensitive the wetting properties of brushes are to the presence of different counterions. The remaining question relevant to the materials science audience is: How pronounced can the change in wettability be between two different counterions? The possibility of achieving significant changes in wettability simply by using different counterions would facilitate the design of smart tunable surfaces.

Our PMETAC brushes can be considered as organic thin platforms with a considerable number of QA^+ groups confined to a ca. 20 nm thick film. The chemistry governing the characteristics of these brushes is mostly associated with the chemical features of QA^+-A^- ion pair. It is well known from studies of ionic liquids based on QA^+ species that there is a strong correlation between hydrophobicity and the number of coordinating fluorine atoms located on the anion.^[9,10,32] The most-common species used to fulfill these requirements are hexafluorophosphate or tetrafluoroborate anions. However, these species can undergo decomposition in water to form HF. As an interesting alternative, one highly fluorinated species that is more stable and soluble in water is TFSI, which is commercially available as a lithium salt.^[10]

In agreement with results observed by Choi and co-workers^[10,11] using imidazolium-terminated SAMs, PMETAC brushes coordinated with TFSI anions also show a marked increase in hydrophobicity ($\theta_{\text{AW}} \sim 90^\circ$). Brushes ion-paired with TFSI anions behave like polymer chains in a poor solvent. The “electrostatically perfluorinated” pendant groups try to exclude the polar solvent (water) and attract one another so as to minimize the interaction between the perfluorinated monomers and the polar aqueous surroundings.

Once a net hydrophobic substrate is obtained, the wettability can be easily reversed and tuned by simply following the trend of the lipophilic scale. Replacing the TFSI anions with highly hydrophilic polyphosphate (hexametaphosphate) anions^[33] clearly leads to a change in the contact angle from 90° to 15° (Fig. 2a and b). This fact indicates that completely dissimilar counterions such as TFSI and polyphosphate can lead to changes in wettability of up to 75° . More importantly, if the same anions are sequentially replaced via consecutive counterion exchanges the tunability of the wetting properties is reversible (Fig. 2c).

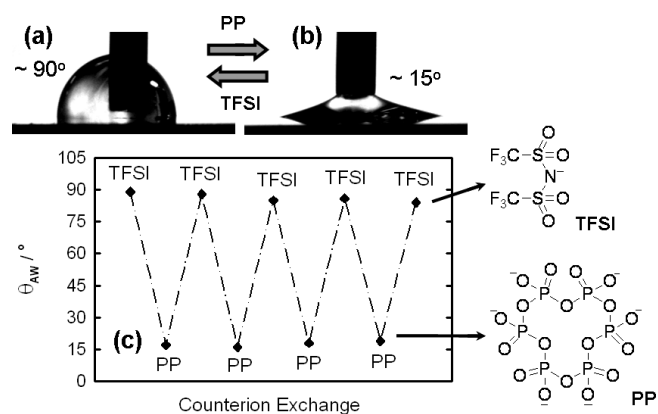


Figure 2. Change in the wetting characteristics of PMETAC brushes (height, $h \sim 20$ nm) after exchanging the two contrasting counterions: TFSI (a) and polyphosphate (PP) (b). c) Representation of θ_{AW} as a function of counterion (PP and TFSI). The plot depicts the reversible behavior of PMETAC brushes over repeated cycles of TFSI and PP counterion exchange. On the right the chemical structures of both counterions are represented.

3. Summary and Outlook

Cationic polyelectrolyte brushes bearing quaternary ammonium groups undergo ion-pairing interactions in the presence of scarcely hydrated anions. The characteristics of the ion-paired state are extremely sensitive to the nature of the counterion. This fact reflects the critical role of the counterion in determining the degree of hydration, and as a consequence, the overall properties of the organic thin film. This unique feature has been used to tune the wettability of polyelectrolyte-brush-modified substrates simply by using a set of different counterions. Introducing predictable changes at the molecular level with the aid of the "lipophilic scale of anions", a dynamic regulation of wettability for the same substrate can easily be achieved. These findings are a result of the sensitive, reversible modification of the properties of surface-tethered polyelectrolytes by flushing or placing them into contact with an aqueous solution of the chosen counterion. Using aqueous solutions of perfluorinated counterions, it is possible to reversibly obtain contact-angle values as high as those seen for substrates modified with (chemisorbed) methyl-terminated self-assembled monolayers.

Published online: December 5, 2006

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