

Polymer brushes – A versatile tool for surface modification

Gemischte Polymerbürsten besitzen als ultradünne funktionelle Schichten für die Oberflächenfunktionalisierung ein enormes Potential zur Herstellung einer Vielzahl von intelligenten, schaltbaren und multifunktionalen Oberflächen und dünnen Filmen.

Es wird gezeigt, wie Computersimulationen zu einem besseren Verständnis des Schaltverhaltens dieser Bürsten beitragen können. Außerdem wird beschrieben, dass Polymerbürsten zur Erzeugung von Oberflächen mit schaltbaren Ultrahydrophobie- und Benetzungsgradienten sowie von sogenannten "Janus"-Partikeln verwendet werden können. Die vielseitigen und multifunktionalen Bürstenschichten haben zahlreiche potentielle Anwendungsgebiete, z. B. in der Mikrofluidik oder im Bereich intelligente Textilien.

Introduction

The challenging aspect regarding polymer brushes originates from the fact that a nanoscopic thin layer at the surface can change the surface appearance and properties significantly keeping bulk properties virtually constant, and that this layer can be relatively tightly attached to most materials by the choice of suitable chemistry. In addition it is possible to provide switching or adaptive properties to the surface by the use of mixed brush layers, which offers further unique possibilities, and to introduce multifunctionality at the surface with different chains, nanoparticles and chemical functional groups [1-5].

The area has grown significantly over the last years, and polymer brush layers are used in many areas of application. This does include flat substrates, but also colloidal particles, fibres or rough surfaces for instance. A big area of application is without doubt bio-related interfaces, where blood interaction, cell growth or protein adsorption is investigated [6]. This happens in aqueous environment and usually water soluble or polyelectrolyte brushes are utilized. Other areas of application [4, 5] include coatings that control wetting, adhesion, friction or the emission of light. Some examples will be discussed below.

Before we start the further discussion we should define in more detail, what we mean with brushes. The more rigorous definition of Alexander and de Gennes [1] takes that brushes are end attached polymer chains, which are grafted to the surface at high grafting density that the chains are significantly stretched due to mutual interactions. There are much more than one chain in a volume which an unperturbed chain would adopt at the surface ($\Sigma \gg 1$). It has been shown theoretically and experimentally that those highly stretched chains show properties that are significantly different from unperturbed chains [2]. One example is the autophobicity of a so-called dry brush, where free chains cannot penetrate into the brush layer, which leads to dewetting of chains of the same kind on top of the brush layer.

We will not use this rigorous definition [1, 2], and call already chains with some stretching a brush layer [7]. So we only assume that there are more than one chain in a volume that an unperturbed chain would adopt at the surface ($\Sigma > 1$). The reason is that already this layer can shield the surface nearly completely, it is much easier to obtain experimentally, and there is sufficient chain mobility still

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left that mixed layers can switch and rearrange their conformation with external stimuli. In the following we will in particular discuss this aspect further and concentrate on mixed brush layers, which can exhibit switching and adaptive properties in response to external stimuli.

Switching of mixed brush layers

When two different polymers are grafted to a solid surface, this surface can adopt the properties of one or the other material depending on external stimuli [5, 8 and references therein]. Also intermediate and new properties can be achieved. The general scheme of switching is illustrated in Fig.1. The two polymers are covalently attached to the surface by grafting-to or grafting-from techniques. They are statistically distributed on the surface. Typically the one polymer is hydrophilic (e. g. poly(2vinylpyridine)) and the other polymer is hydrophobic (e. g. polystyrene). The two components are incompatible with each other, but similar to a copolymer they can only phase segregate at the scale of the molecular dimension. In a selective solvent for the hydrophilic polymer (e. g. acidic water) those chains are swollen, while the hydrophobic chains are collapsed at the surface. There will be a complex interplay of lateral and perpendicular phase segregation at molecular level [9], which causes on one hand a nanoscopic morphology in the surface plane, while the hydrophilic polymer will be enriched at the surface. When the film is dried after such a treatment, one can expect hydrophilic behavior, since wetting is determined by the outermost layer. A water drop on such a surface will show a low contact angle.

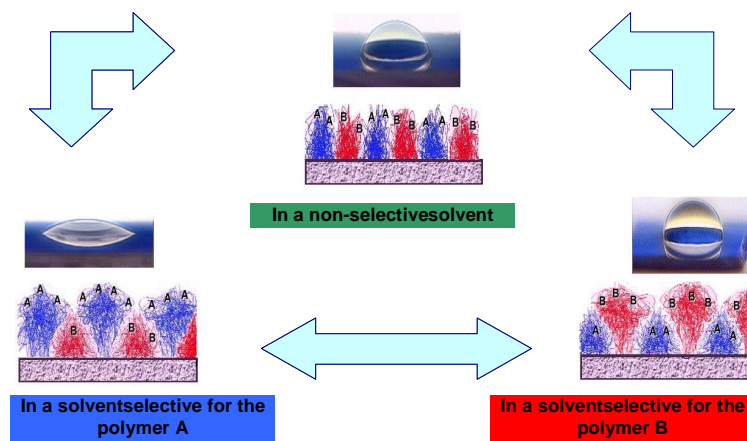


Fig. 1:
Scheme of the switching of physico-chemical surface properties of a binary polymer brush in solvents with different qualities for the brush components (Reproduced from reference [23] with permission by Elsevier)

When this surface is exposed to a non-polar solvent (e. g. toluene), which is selective for the red polymer, the situation just reverses. Now the hydrophobic polymer will be enriched at the surface, and the film will exhibit hydrophobic behavior. The contact angle of water will be high. This switching is achieved by a pure conformational change, and thus is completely reversible. Since the chains are covalently attached to the surface no long range changes are possible and the chains are not dissolved and removed, which would be the case for purely adsorbed molecules. Also intermediate states are possible in less selective solvents.

The situation is however not so trivial as it might appear at first glance. So there is some chain mobility necessary for the switching, chains should not be too short to be able to fill the upper layer, but should also not be too long to achieve reasonable switching times for conformational readjustment.

The solvent should be not a complete non-solvent for the other component, since then it might not penetrate the upper layer, which also is difficult, if the grafting density is too high. So there are several limitations and requirements to achieve switching at all and in a reasonable time.

So the timescales of response are crucial, and have to be adjusted depending on the application. If switching is relatively fast (e. g. in seconds), one can call the surface an adaptive surface. So the hydrophobic surface will immediately switch to hydrophobic behavior upon exposure to water – and vice versa. For a raincoat this would not be suitable, and the layer should be more stable upon exposure to water to keep the hydrophobic properties. This is achieved for instance, if the upper layer is relatively thick, quite immobile (e. g. in the glassy state), and if the layer is essentially impenetrable to water. Then switching times will be extremely large (can be days) and the coating will be quite stable. It is therefore very interesting to study the switching kinetics theoretically.

Computer simulations of switchable polymer brushes

To obtain a molecular understanding of the switching behavior of binary polymer brushes we have employed molecular dynamics simulation with implicit solvent interactions. Here, the polymers were created as a coarse-grained bead-spring model [10] first applied by Murat and Grest to polymer brushes, see Ref. [11]

The “spring” was a finite extensible nonlinear elastic (FENE) potential and the beads represent spherical Kuhn monomers which interact via a shifted Lennard-Jones (LJ) potential according to where d stands for the bead diameter and ϵ defines the strength of the interaction.

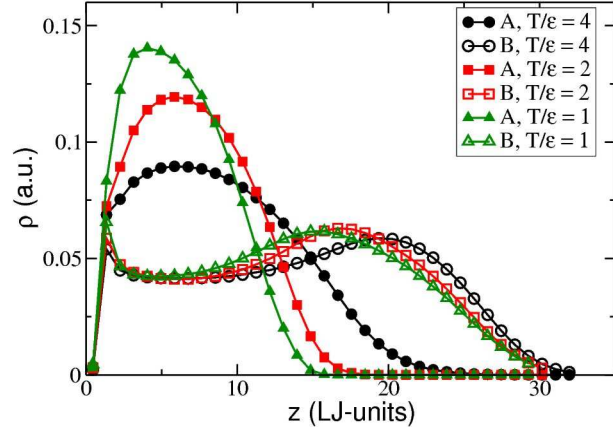
$$U(r) = 4\epsilon \left[\left(\frac{d}{r} \right)^{12} - \left(\frac{d}{r} \right)^6 - \left(\frac{d}{r_c} \right)^{12} + \left(\frac{d}{r_c} \right)^6 \right] \quad (1)$$

By setting the cut-off distance to the potential minimum an nearly athermal good solvent is simulated. By contrast, a far cut-off retains the attractive part of the potential and a poor solvent can be simulated at low temperatures. For an homogeneous solution of free chains the θ -temperature is located at about $3.18 \epsilon/k_B T$ [12]. Here a cut-off distance of $2.5d$ keeps the number of pair interactions within a manageable level.

The simulations were carried out using the open source LAMMPS molecular dynamics package [13]. In the following the LJ system of units is used. It is defined using a model polymer with a LJ pair potential, featuring a bead size $d=1$ (one length unit), a potential depth $\epsilon=1$ (one energy unit), and a mass $m=1$ (one mass unit). The temperature is then normalized to that energy unit (using a Boltzmann constant $k_B=1$), and the time unit is the oscillation time of a monomer inside the LJ potential, at small amplitudes so that the harmonic approximation is valid. The grafting density σ of the polymer brush is defined as the (average) number of grafted monomers per unit area. Since in our case the bead size was fixed to $d=1$, a grafting density of $\sigma=1$ implies a closely packed system which would form a crystal [14]. The choice of the bond force parameters led to an average bond length of $0.97d$. The wall is implemented by a appropriately modified LJ-potential.

We simulate a fully symmetric binary polymer brush where both species, denoted as A and B in the following, belong to chains of the same length, and the same partial grafting density is implemented. In total 24×24 chains of various length and grafting densi-

Fig. 2:
Density profiles for chains of 64 monomers and a grafting density of $s = 0.116$. The B-species are exposed to athermal solvent and form the upper layer while the A-species are under thermal solvent conditions.



In Fig. 2 we display the density profiles for both species in the state where A is exposed to the good solvent. The upper layer displays a much lower density as compared to the lower layer. The two-layer system is not homogeneous as the snapshot of the two-phase system might suggest, see upper panel of Fig. 3. In fact, the good solvent fully penetrates the upper layer and, thus, the lower layer is exposed to unscreened thermal solvent, and it attains a collapsed, dense state. We note that $T/\epsilon = 4$ corresponds to a state above the θ -temperature of a free solution and the A-species are already partially swollen. Moreover, the lower layer shows a droplet-like pattern formation, which can be seen in the lower panel of Fig. 3. We have analyzed the pattern formation in detail [15], where we have shown that the pattern changes into a stripe-like morphology when increasing the grafting density or decreasing the solvent strength. In fact, it is reasonable to consider the lower layer as brush exposed to poor solvent decorated by a fluffy layer of the second species exposed to good solvent. Coupling of excluded volume interactions between the both species is responsible for deviations of the height scaling of the upper layer as compared with an athermal homogeneous brush. The two-phase behavior is also visible in the total density which displays a two-step-like profile in the strongly selective case.

To simulate the switching process we switch the local interaction properties for both species at once. This does not exactly correspond to the situation in the experiments where washing and replacement of the solvents takes addition time. When the solvent is switched the lower layer reacts immediately upon change of solvent. This is easy to understand because of the strong excluded volume repulsion stored in the collapsed state. For longer times, the height follows a single exponential behavior with a characteristic relaxation (switching time) τ_s . By analyzing the chain length and grafting density dependence of the switching time we arrived at the following empirical law:

$$\tau_s \sim N^2 \sigma^0 \quad (2)$$

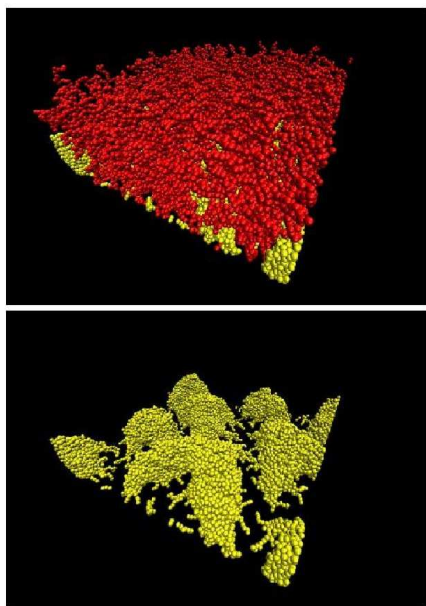


Fig. 3:
Snapshot of the binary brush of
grafting density $s=0.116$ and chain
length of $N=64$ at $T/e = 1$. The
lower layer displays pattern forma-
tion in the collapsed state [15].

Visual inspection of the switching process reveals a cooperative behavior (movement of domains) of the chains during the switching process; the penetration of individual chains through the respective incompatible layer remains an exception. This might explain the deviation of the switching time from the equilibrium diffusion time of chains in a homopolymer brush, where $\tau \sim N^3$ is expected [16, 17]. The chain length dependence of the switching time resembles that of the longitudinal breathing modes suggested by Halperin [18]. The switching process is fully reversible and entanglement effects are not expected.

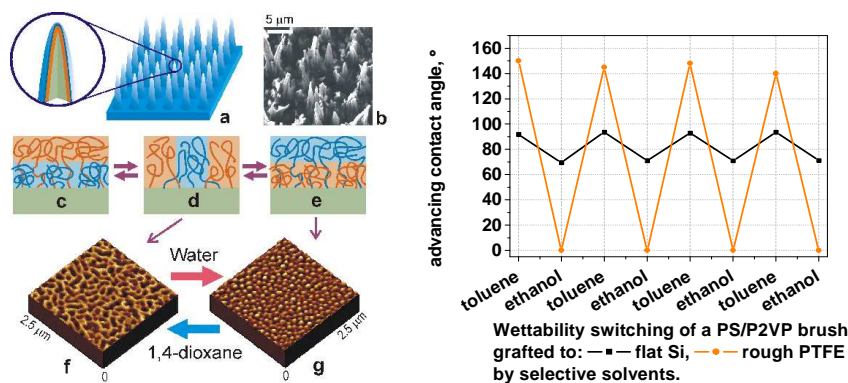
Ultrahydrophobic brushes, wettability gradients and microfluidics

The switching effect can be significantly enhanced by a combination of surface chemistry with surface topography. This amplification effect comes from the well known ultrahydrophobicity effect, which is achieved at a particular surface roughness. If we combine our binary brushes with a given surface roughness, the water contact angle can be switched between virtually zero and 150 degrees [19]. This is simply achieved by attaching the brushes to a surface with appropriate roughness. In a typical experiment a PTFE surface is etched by plasma treatment. Roughness values have to reach a sufficient level which is in the micrometer range. The plasma treatment has the additional effect that generates functional groups at the surface so that it is easy to attach the mixed polymer brush chains by grafting-to technique to it. In this way one can prepare a rough surface which contains mixed PS and P2VP grafted chains symbolizing a surface hierarchically structured at two lengths scales: at the micron scale by plasma etching and at the nanometer scale by the morphology of the polymer brush. Exposure to acidic water produces a contact angle close to zero, while exposure to 1,4-dioxane or toluene provides a contact angle of 150 degrees (Fig. 4). Again we emphasize that the contact angles of corresponding smooth surfaces only switch between 70 and 90 degrees, and the roughness provides the significant amplification in both directions, to smaller and larger contact angles, respectively [19, 20]. In the ultrahydrophobic state of the brush the contact angle hysteresis disappears, which is an ultimate criterium of ultrahydrophobicity.

Fig. 4:

a) Creation of switchable ultrahydrophobicity: schematic of the needle like surface morphology of PTFE (a), SEM graph of PTFE after 600s of plasma etching (b), grafting of a binary brush (hydrophilic and hydrophobic polymer) on the structured PTFE surface (c-e), switching of the binary brush in a selective solvent (c, d) and a non-selective solvent (d), AFM images of the brush on smooth model substrates after treatment with different solvents (f, g). (Reproduced with permission by Elsevier)

b) Advancing contact angles of water after treatment of a polystyrene/ poly(2-vinylpyridine)-brush on a smooth (silicon wafer, squares) and a rough surface (etched PTFE, circles) (Reproduced from reference [21] with permission by the American Chemical Society)



a)

b)

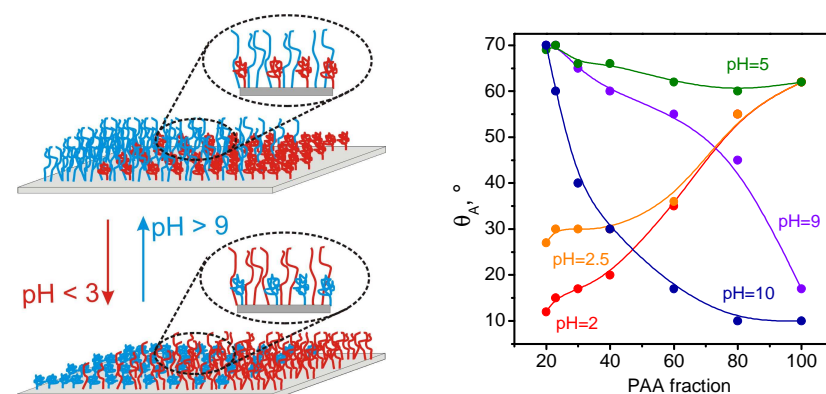
Mixed polymer brushes were also shown to be suitable to produce layers having a wettability gradient in one direction. These brushes were made by transferring a temperature gradient on a stage into a grafting density gradient. The applied stage is providing a linear temperature trend and was used to graft the first homo polymer, the second polymer was then grafted so that it “filled” the remaining reactive sites at the substrate. Those gradient brushes were created with polystyrene and with two incompatible polyelectrolytes (poly(acrylic acid), PAA, and poly(2-vinyl pyridine)) [21-23]. For the preparation of the polyelectrolyte brushes poly(butyl acrylate), PBA was annealed on the mentioned temperature gradient stage. In a second step poly(2-vinylpyridine) was spin-coated on top of the gradient PBA layer. After annealing the PBA was transformed into PAA by hydrolyzation. The obtained binary gradient brush is able to switch the direction of the gradient of wettability by treatment with aqueous solutions of different pH values (Fig. 8). In an acidic medium (pH=2) the wettability gradient goes along with the increase of the poly(2-vinylpyridine) content in the brush. An increase of pH to 2.5 is decreasing the switching amplitude by 10° due to the decrease of the degree of protonation of poly(2-vinylpyridine). In neutral media the gradient is almost “switched off”, whereas it appears again in basic media (pH=9-10), but in the opposite direction, along with the increasing PAA fraction of the brush. That means that the direction and the amplitude of the wettability gradient of a binary polyelectrolyte brush can be tuned by pH (Fig. 5, for details see Ref. 22). These properties are very interesting for micro and nano fluidics and for the transport of liquids and particles.

We investigated the separation of binary liquid mixtures on gradient surfaces. In the first step

Fig. 5:

a) Polyelectrolyte gradient mixed brush (P2VP-mix-PAA): Advancing contact angles of water in dependence on PAA fraction of the brush and pH (right)

b) Scheme of the switching of the wettability gradient by pH (Reproduced from reference [22] with permission by the American Chemical Society)



a)

b)

fundamental process steps were defined and shown that the separation of fluid mixtures is a highly complex multiscale phenomenon which we tried to understand by using a combined top-down- and bottom-up approach. Firstly we experimentally identified that the dynamics of single water droplets in flow and not the liquid bulk motion is critical for conducting the separation process (top-down). Secondly the critical processes namely droplet coalescence, droplet movement on the wettability gradient and liquid flow within droplets were studied in detail by mesoscopic computer simulations and corresponding experiments (bottom-up). Based on the results of these studies we succeeded in the development of a lab on a chip [24] device with integrated FET sensors for the separation of fluid mixtures (compare Fig. 6).

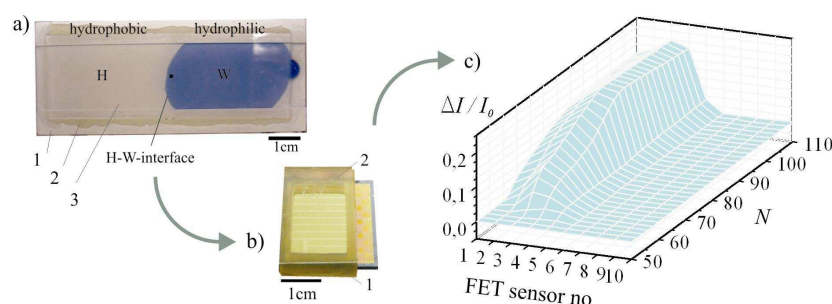


Fig. 6:
Development of microfluidic separation cells.

- a) Perfect separation in a closed separation cell (W=Water, H=Hexane, 1=aluminum channel, 2=glass cover, 3=epoxy resin).
- b) Lab on a chip separation device with integrated FET sensor array (1=epoxy resin frame, 2=glass cover).
- c) During lab on a chip separation the FET sensor signals $\Delta I/I_0$ indicate the water surface coverage on the hydrophilic side (FET sensors no. 1 to 5) and the presence of the solvent on the hydrophobic side (FET sensors no. 6 to 10). N indicates the number of measurements.

Also lattice Boltzmann computer simulation indicates that a water drop on a gradient layer has the tendency, and a driving force, to move onto the favorable side of the gradient surface. In an emulsion of two separate liquids (e. g. water and toluene) the two liquids may be separated by the interaction with a gradient surface (e.g. PS and P2VP). The geometry of the experiment plays an important role, and slit geometry is favored over open channel geometry. It was found out that the surface energy hysteresis is the key phenomenon to understand the different droplet coalescence dynamics on open surfaces and inside the gap [25].

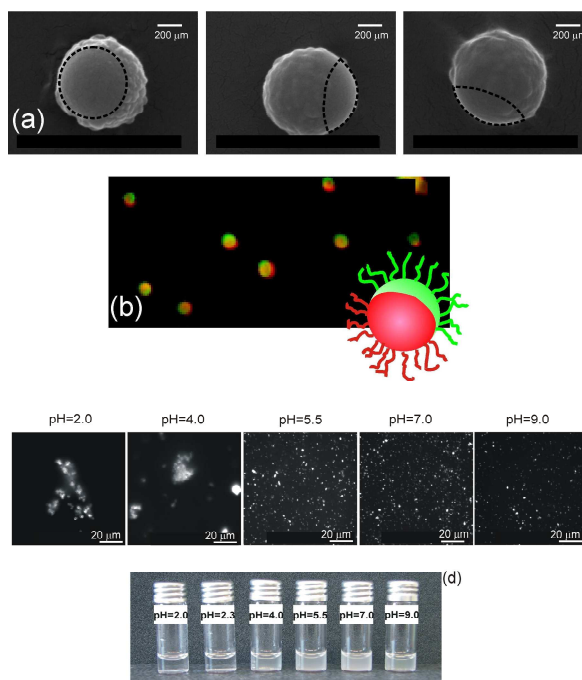
Stimuli-responsive Janus particles decorated with polymer brushes

Apparently, modification of colloidal particles with smart polymer brushes of different sensitivities can lead to design of novel switchable functional surfaces and interfaces. The design of uniformly coated responsive hybrid particles with polymer brushes is of great interest because of their diverse applicability.

Particularly interesting properties, however, can be expected from asymmetrically coated particles i.e. the ones whose surface chemical composition differs on two opposite sides. These particles are often called “Janus” particles (JPs) and were introduced by de Gennes for the first time. Due to anisotropy or properties, the JPs are unique among other micro- and nanoparticles. Recently, JPs demonstrated enormous potential as emulsion stabilizers, micro-rheological probes and functional elements for design of electronic paper devices. Stimuli-responsive JPs are expected to be particular promising as elements of smart systems, which can assemble and disassemble in response to change of environmental conditions.

We presented a new versatile concept for design stimuli-responsive bicomponent Janus particles decorated by polymer brushes with different polarity and charge [27-28]. The responsive Janus particles were synthesized by sequential grafting of two sorts of polymers on silica core using a combination of “grafting-from” and “grafting-to” approaches. In particular, we have grafted poly-

Fig. 7:
Representative
a) ESEM images (P2VP - modified area is enclosed by dashed line and PtBA area possesses raspberry morphology)
b) Fluorescence microscopy image of bifunctional PtBA-P2VP decorated Janus particles
c) Fluorescence microscopy and
d) Optical microscopy images for PAA/P2VP JPs
(Reproduced from references [27-28] with permission by the American Chemical Society)



In particular, JPs decorated by two oppositely charged polyelectrolytes – polyacrylic acid (PAA) and poly(2-vinylpyridine) (P2VP) – demonstrated reversible aggregation/ stabilization behavior depending on pH which are caused by electrostatic repulsions/attractions between the parts of the particles (Fig. 7c, d) [27-28]. We believe that switchable Janus particles decorated with two sorts of responsive polymers can be used for controlled stabilization of emulsions and regulation of the molecular transport at interface between immiscible liquids.

Conclusions

The ability of mixed brushes for switching was shown, where by external stimuli wettability, charge, salt content etc. can be changed. Computer simulation helps to understand the switching process and density distribution in the brush. A combination of brush layers with surface roughness can amplify the effects and ultra-hydrophobicity is achieved. Applications of the brush layers are discussed. Those include the control of flow of liquids on surfaces, which is utilized in microfluidics and separation of emulsion components. Smart Janus particles decorated with polymer brushes can lead to design of novel switchable surfaces and interfaces. The examples shown only represent a small fraction of possible applications, and we have left out for instance bio-related applications in this review. So we believe that polymer brushes will be used in the future in many areas and that their multi-talented properties will help to solve many problems in our everyday applications.

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