Polymer Brushes Here, There, and Everywhere: Recent Advances in Their Practical Applications and Emerging Opportunities in Multiple Research Fields

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ABSTRACT: Bottom-up surface processing with well-defined polymeric structures becomes increasingly important in many current technologies. Polymer brushes, that is, assemblies of macromolecules tethered at one end to a substrate, provide an exemplary system of materials capable of achieving such a goal. While the focus in the past decades has been mostly on their synthetic aspects and the in-depth study of their interesting properties, from several years now the core area of research has already started to shift towards specific practical applications. Ample functional versatility and relative ease of preparation are special strengths of polymer brushes, lending them a strong interdisciplinary character. To this end, this work is entirely dedicated to bringing together the latest research on applications of polymer brushes in multiple research fields. The aim of this review are twofold: first, to give a critical discussion of the current status of development of application-oriented research on polymer brushes, and second, to inform the reader as to what can be done with polymer brushes in multiple research fields. It is therefore hoped that the juxtaposition of perspectives from different disciplines in one place will stimulate and contribute to the ongoing process of cross-fertilization that is driving this fascinating and emerging area of polymer science. © 2012 Wiley Periodicals, Inc. J Polym Sci Part A: Polym Chem 50: 3225–3258, 2012

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INTRODUCTION—ON THE WAY TOWARDS PRACTICAL APPLICATIONS OF POLYMER BRUSHES

Polymers at interfaces is a field which has fascinated physicists and chemists now for nearly half a century, with respect to both basic and applied research. Polymer brushes refer to polymeric assemblies tethered at one end to a solid substrate either through covalent attachment or physical adsorption.[1] From an historical perspective, much of the interest in polymer surfaces originated from their importance to different technologies, namely, wetting, corrosion or colloidal stabilization, among other examples. For several years now, innovative research in polymer brushes is no longer circumscribed to the realm of pure polymer science but has begun to enter the domain of materials science and engineering as well.[2,3] This tendency was accelerated with the advent of new polymerization techniques which introduced less demanding synthetic protocols (user-friendly chemistry) facilitating scientific community-wide access to a macromolecular design toolkit so far believed to be exclusive domain of polymer chemists.[4,5] During the 1990s the explosive surge of experimental information on polymer brushes prompted

an interest in how one could design polymer thin films with strict molecular control and how to exploit their properties in suitable applications. This in turn fostered the further development of macromolecular surface science with its concomitant expansion at the frontiers of polymer science with physics and biology.

While research in polymer brushes has been very active over the last 20 years,[6,7] these polymers have played, primarily, relatively limited roles as functional surface coatings exhibiting excellent long-term mechanical stability and chemical robustness. As we moved into the 21st century, the view of polymer brushes as surface-grafted architectures with only narrow applications changed at a rapid pace: it is now clear that polymer brushes can be considered as nanoscale "soft" building blocks capable of enabling practical nanotechnology by bestowing functions—from redox activity and photophysical properties to biocompatibility and capacity for energy storage—upon a broad range of materials with their concomitant practical benefits. The increasing popularity of polymer brushes is due to their flexibility to create highly tailored thin films in which chemical composition, thickness,

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grafting density and architecture of the macromolecular film can be controlled and even addressed with nanoscale precision using rather simple experimental settings, a concept often referred to as "nanoarchitectonics."[8,9] Furthermore, the combination of polymer brushes with lithographic techniques enables the creation of complex surfaces displaying compositionally controlled patterned domains.[10,11]

In most cases, covalent anchoring is the preferred choice due to its intrinsic stability in different solvent conditions. In essence there are two methods of tethering brushes: "grafting from" and "grafting to" (Fig. 1).[1] The *grafting to* technique employs a preformed polymer with a reactive end-group to attach the polymer chain onto the substrate (common reactive functional groups include thiols, silanes, amino
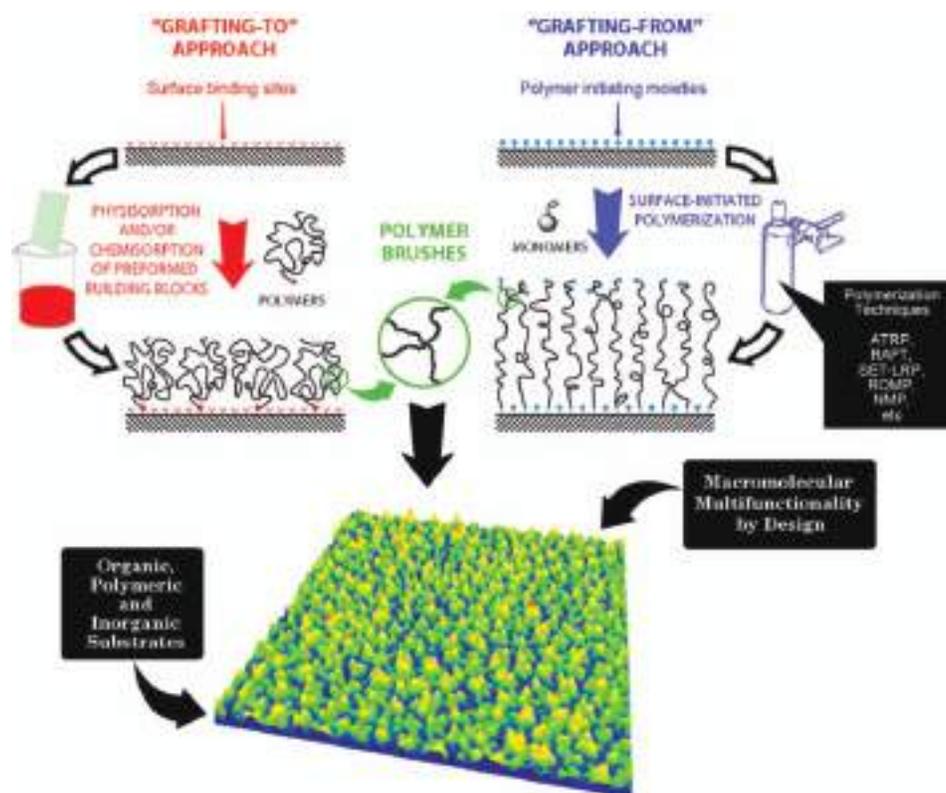
FIGURE 1 Conceptual illustration of the chemical strategies (*grafting-to* and *grafting-from* approaches) used to tether functional polymer brushes on a wide variety of substrates. The figure also includes an atomic force microscopy image (500×500 nm^2) of poly(2-(methacryloyloxy)-ethyl-trimethyl-ammonium chloride) brushes grown on silicon substrates via surface-initiated atom transfer radical polymerization (SI-ATRP).

or carboxylic groups). The *grafting to* technique usually involves low grafting densities due to steric repulsion between the already grafted chains and the incoming macromolecular units from solution that in turn preclude the access of new polymer chains to grafting sites on the surface. This effect is more pronounced when dealing with high molecular weight polymer chains. Conversely, in the *grafting from* strategy, polymer chains are straightforwardly synthesized from a substrate previously modified with polymerization initiators, the so-called "surface-initiated polymerization" in which polymerization occurs exclusively at the surface. This method introduces versatility, reliability, and controllability to the formation of dense polymer brushes and can be implemented with almost all available polymerization techniques: ring opening metathesis polymerization (ROMP),[12] nitroxide-mediated polymerization (NMP),[13] atom transfer radical polymerization (ATRP),[14] single-electron-transfer living radical polymerization (SET-LRP),[15] or reversible addition fragmentation chain transfer (RAFT) polymerization,[16] just to name some examples.

Another appealing aspect of tethered polymer films generated via *grafting-to* or *grafting-from* approaches is that they are fully compatible with a wide variety of technologically relevant substrates and nanomaterials, going far beyond the typical gold and silicon substrates used during the early days. Progress in molecular assembly and preparative chemistry during the last decade made possible to tether polymer brushes on an impressive wide variety of organic, polymeric and inorganic substrates including: cellulose,[17] chitosan,[18] poly(ethyleneterephthalate),[19] polyaniline,[20] poly(cyclopentadiene),[21] polystyrene,[22] poly(vinyl chloride),[23] poly(vinylidene fluoride),[24] nylon,[25] poly(divinylbenzene),[26] poly(tetrafluoroethylene),[27] poly(dimethylsiloxane),[28] poly(methylmethacrylate),[29] polyimide,[30] polyurethane,[31] polypropylene,[32] ITO,[33] Al_2O_3,[34] Fe_3O_4,[35] CuO_x,[36] γ-Fe_2O_3,[37] $MnFe_2O_4$,[38] $Mg(OH)_2$,[39] ZnO,[40] zirconium phosphonate,[41] halloysite,[42] montmorillonite,[43] steel,[44] sapphire,[45] CdSe,[46] CdS,[47] GaAs,[48] mica,[49] carbon black,[50] diamond,[51] single-walled carbon nanotubes,[52] multiwalled carbon nanotubes,[53] and nanographene.[54]

The fruitful synergies between polymer brushes and nanotechnology are becoming more evident in physics and engineering as we are able to integrate these polymeric assemblies in nanodevices and then trigger the emergence of novel and valuable properties. Similarly, the powerful combination of polymer brushes with inorganic nanomaterials opens up new opportunities in molecular materials science as has been demonstrated that they can interact together, self-organize and produce hierarchical structures without disrupting their own function. In very much the same way, the development of practical applications of biofunctional interfaces taking profit from the synergistic assembly of polymer brushes and biological entities is nowadays an amazing research line. However, when a field becomes fashionable, it is important to distinguish potential practical applications from "wishful thinking." Sometimes we feel that interesting scientific findings whose application was pushed too fast

were not able to reach the presumed technological impact as a consequence of lacking constructive feedback from complementary disciplines. The journey from basic science to technological applications has been compellingly described by Herbert Kroemer (Nobel Prize in Physics 2000):[55] "Even if the process from science and technology to applications is opportunistic rather than deterministic, we can speed up this process by better cross-discipline communication between scientists, technologists, and application engineers". In this regard, a non-negligible merit of polymer chemists has been their willingness to overcome the fences in which they have been traditionally confined and to promote collaboration with unrelated (in fact, complementary) research groups. Part of the appeal of doing research with polymer brushes is that they bring to bear a startling range of ideas from different research fields. This is one reason why the topic proves crucial to the whole field of nanoscience in which cross-fertilization between researchers from different disciplines is vital and necessary to address important challenges. Now the ever-growing field of polymer brushes encompasses a vast variety of quite different disciplines; which calls for more collaboration between researchers with different backgrounds and knowledge. In this era of exploding scientific information, it is difficult to keep abreast of scientific developments, even in a restricted discipline. In view of the recent progress in application-oriented research on polymer brushes, this review is specifically aimed at providing exposure of the most emerging practical applications of tethered polymer layers in multiple research fields and is focused on two key issues: new applications of polymer brushes and emerging technologies. Within this context, special emphasis has been devoted to very recent explorations (i.e., in the past five years) on prospective practical applications of polymer brushes. This is a chance for the polymer brush community—and also newcomers in the field of polymer thin films—to glimpse the future of their practical applications and help shape the evolution of this research area.

PRACTICAL APPLICATIONS OF POLYMER BRUSHES

Bioelectronic Systems Based on Polymer Brush–Enzyme Hybrid Interfacial Architectures

Bioelectronics is a rapidly progressing interdisciplinary research field that aims to integrate biomolecules and electronic elements into functional systems.[56] Devising new strategies to manipulate the electrical communication between redox enzymes and electrode surfaces is central to the ongoing development of a variety of bioelectronic devices. In essence, the creation of hybrid bio-macromolecular assemblies displaying 2D and 3D ordered structures on surfaces represents the key to afford systems in which (bio)chemical stimuli can trigger the generation of electronic signals. Minko and coworkers[57] developed an interesting concept to design enzyme-based logic gates assembled into polymer brushes that allow biochemical processing of complex information. The aim of these early attempts is the integration of biocomputing enzyme-based systems and signal responsive materials with bioelectronic devices like
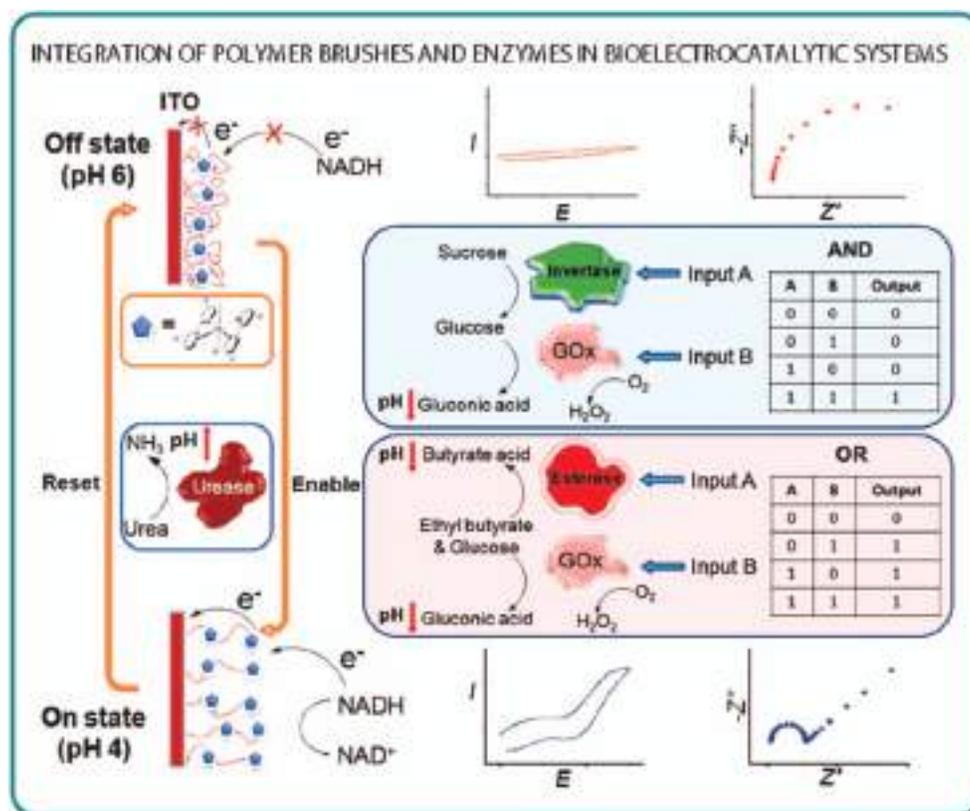
FIGURE 2 Logic operations AND/OR performed by the enzyme-based systems resulting in the ON and OFF states of the bioelectrocatalytic macromolecular interface. From Zhou et al., ACS Appl. Mater. Interfaces, 2009, 1, 144–149, © American Chemical Society, reproduced by permission.

biosensors, biofuel cells, or even bioactuating applications. These bioactive platforms were constituted of poly(4-vinylpyridine) (P4VP) brushes functionalized with redox-active Os complexes in the presence of a combination of enzymes: glucose oxidase, esterase, and urease. In very much the same way this group also used electroactive P4VP brushes for the electrocatalytic oxidation of NADH.[58] The operation of the pH-switchable redox-interface was controlled by logic operations performed by enzyme systems processing biochemical input signals (Fig. 2). Hence, the electrocatalytic oxidation of NADH was activated upon appropriate combinations of the signals processed by the AND/OR logic operations performed by the enzymes. The integration of redox enzymes into electroactive copolymer brushes was recently studied by Neoh and coworkers in order to develop amperometric biosensors prepared via successive surface-initiated atom-transfer radical polymerization (SI-ATRP) on ITO electrodes.[59] The copolymer brush was constituted of ferrocenylmethyl methacrylate (FMMA) and glycidyl methacrylate (GMA). Glucose oxidase (GOD) was subsequently immobilized on the modified ITO electrode surface via coupling reactions between the epoxide groups of GMA and the peripheral amine groups of GOD. The experimental results reveal that the spatial localization of the building blocks has an immediate impact on the chemo-responsiveness of the bio-macromolecular assembly. For example, the sensitivities of the ITO/P(GMA–

GOD)-*b*-P(FMMA) and ITO/P(FMMA)-*b*-P(GMA–GOD) electrodes are ∼3.6 and ∼10.9 μA mM^{-1} cm^{-2}, respectively. This indicates that the biocatalytic activity and sensitivity strongly depend on the spatial distribution of the redox mediator within the brush layer.

Controlling Bacterial and Cell Adhesion with Polymer Brushes

The development of strategies for controlling the interface between cells and materials is important in a wide range of settings. The Okano group has extensively studied the use of switchable surfaces based on thermoresponsive poly(*N*-isopropylacrylamide) (PNIPAM) brushes to control cell adhesion and detachment,[60] including the use of micropatterned thermoresponsive homo- and copolymer brush surfaces for fabricating cell sheets with well-controlled orientational structures[61] PNIPAM brushes change from an extended hydrophilic conformation to a collapsed state at its lower critical solution temperature (LCST), that takes place at ∼32 °C. In this way, this group was able to align normal human dermal fibroblasts onto patterned surfaces by simple one-pot cell seeding. Yu et al. synthesized poly(*N*-isopropylacrylamide)-*block*-polystyrene (PNIPAM-*b*-PS) brushes[62] with the aim of combing the thermosensitivity of PNIPAM and the hydrophobic characteristics conferred by the PS blocks in order to create surfaces responsive to both temperature and
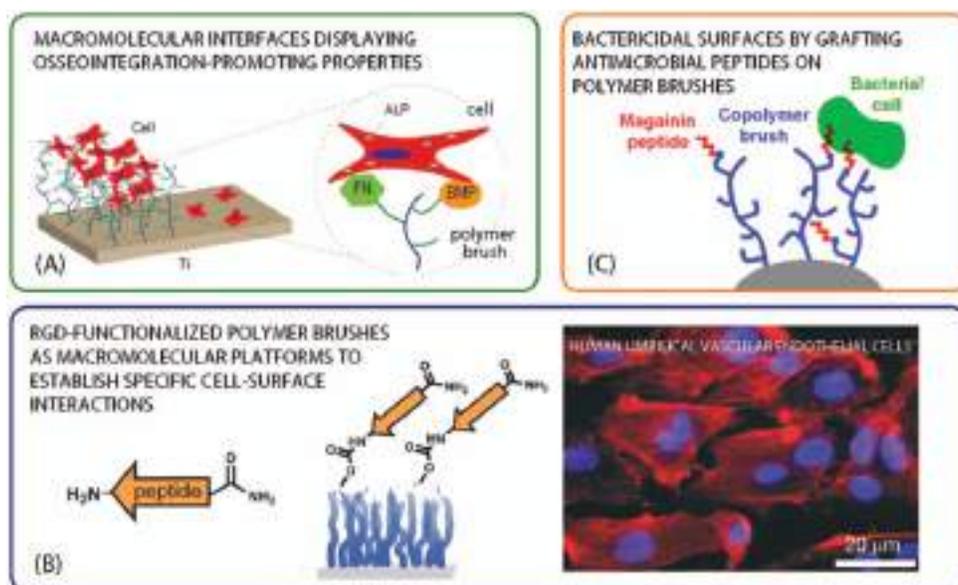
FIGURE 3 (A) Osteoblast attachment to poly(OEGMA-r-HEMA) brushes grafted from titanium surfaces. From Ren et al., Langmuir 2011, 27, 12069–12073, © American Chemical Society, reproduced by permission. (B) Simplified scheme of RGD functionalized polymer brushes and fluorescence micrograph of HUVECs immobilized on GGGRGDS functionalized polymer brushes 48 h post seeding and after application of fluid shear stress for additional 24 h. From Tugulu et al., Biomaterials, 2007, 28, 2536-2546, © Elsevier Science, reproduced by permission. (C) Silica particle modified with a magainin-functionalized copolymer brush interacting with a bacterial cell. From Blin et al., Biomacromolecules, 2011, 12, 1259–1264, © American Chemical Society, reproduced by permission.

solvent. These diblock copolymer brushes exhibited both resistance to nonspecific protein adsorption and good cell interaction properties in adhesion and detachment studies performed on L929 cells. The use of PNIPAM brushes has also extended to the creation of surfaces displaying switchable protein adsorption.[63] However, PNIPAM is not a bioinert polymer and can induce cellular cytotoxicity[64] when switched from hydrophilic to hydrophobic states. This fact has been attributed to the presence of multiple secondary amide functions in the molecular structure of PNIPAM that may ultimately lead to the formation of cooperative hydrogen-bonding interactions with proteins.[65]

Recently, copolymer brushes of 2-(2-methoxyethoxy) ethyl methacrylate (MEO_2MA) and oligo(ethylene glycol) methacrylate (OEGMA) have been considered as an interesting biocompatible alternative to PNIPAM brushes. Jonas et al.[66] demonstrated that the LCST of poly(MEO_2MA-co-OEGMA) copolymer brushes can be adjusted by changing the comonomer compositions in order to obtain thermoresponsive properties close to physiological conditions. Along these lines, Laschewsky and coworkers demonstrated the attachment, proliferation and detachment of 3T3 mouse fibroblasts onto these biocompatible copolymer brushes, controlled by temperature cycling around the LCST of the macromolecular platform.[67] In a similar fashion, Dey et al. demonstrated the use of thermoresponsive poly(MEO_2MA-co-OEGMA) brushes as responsive platforms for culturing mouse embryonic stem cells (mESCs) and controlling their attachment/detachment to the substrate.[68] Wei and coworkers[69] described the modi-

fication of surfaces with poly(OEGMA-r-HEMA) brushes to confer an osteogenesis capacity. In principle, the modified surfaces were resistant to cell adhesion; however, after conjugating fibronectin (FN) and recombinant human bone morphogenetic protein-2 (rhBMP-2) to the polymer brushes the titanium surfaces were able to induce the adhesion MC3T3 cells [Fig. 3(A)]. Klok and his collaborators explored the functionalization of polymer brushes with short peptide ligands in order to promote endothelialization of blood-contacting biomaterials.[70] Poly(2-hydroxyethyl methacrylate) (PHEMA) or poly(poly(ethylene glycol) methacrylate) (PPEGMA), were used as macromolecular platforms suppressing nonspecific adhesion of proteins and cells and exposing hydroxyl groups for further conjugation of RGD containing peptide ligands. These authors found that human umbilical vascular endothelial cells (HUVECs) were able to adhere and spread rapidly on the RGD-bearing surface as well as to retain homeostasis when exposed to shear stresses that simulated arterial blood flow [Fig. 3(B)]. Interestingly, they observed differences in size and morphology of focal adhesions between HUVECs immobilized on PHEMA and PPEGMA brushes. These differences were attributed to the length of the ethylene glycol spacer and hydrophilicity of the PPEGMA brushes, which ultimately lead to increased ligand mobility and reduced ligand–integrin affinity.

Interesting results on cell adhesion have recently been described by Ober and coworkers.[71] These authors reported cell adhesion studies for RBL mast cells incubated on patterned poly(acrylic acid) (PAA) brushes grown on silicon

surfaces displaying different feature sizes. They observed that cell adhesion onto the patterned PAA brushes usually only occurred if the patterned features were small enough so that cells were exposed to the silicon surface. Their experimental evidence suggests this process is mediated by secreted fibronectin that adsorbs on the anionic brushes and then the cell membrane integrin receptors that bind fibronectin become localized in these regions, resulting in membrane accumulation. It is evident that the complex interplay between surface charge, hydrophilicity and topography in polymer brushes are key variables not only to understand but also to culture and maintain differentiated function of a wide variety of cells.[72]

On the other hand, polymer brushes have also been employed as substrates to control adhesion and proliferation of microorganisms on surfaces. The development of methods which localize the action of antimicrobial agents on the surface of biomaterials is very attractive. In this regard, antimicrobial peptides (AMPs) are an attractive choice due to their broad spectrum activity and relatively nontoxic nature toward host cells. Very recently, different groups started to explore the use of AMPs attached to polymer brushes in order to create surfaces with antibacterial properties. The challenge in this approach is to immobilize the peptide on the polymer brush while keeping its accessibility and its activity toward the surrounding bacterial cells. Gao et al. described the conjugation of antimicrobial peptide Tet213 on amine-functionalized copolymer brushes on Ti surface. They found that the composition and the brush properties, such as graft density and thickness, influence the peptide grafting onto the surface. Their experiments revealed that the interplay between grafting and peptide density determines the optimum antimicrobial properties of the peptide-modified polymer brush against *Pseudomonas aeruginosa*.[73,74] Glinel and coworkers[75] grafted magainin-I, a natural antimicrobial peptide, onto the hydroxyl groups of hydrophilic copolymer brushes based on biocompatible oligo(ethylene glycol) methacrylates. Magainin-functionalized polymer brush-coated surfaces were tested against Gram-positive *Listeria ivanovii* and *Bacillus cereus*. These studies corroborated the formation of efficient antibacterial surfaces and were then further extended to the formation of antibacterial silica particles [Fig. 3(C)].[76]

Polymeric materials bearing quarternary ammonium groups that are positively charged at physiological pH have been used widely as effective antibacterial agents. In principle, the lethal action of these polycationic disinfectants involves a sequence of steps that include a primary interaction with the bacterial cell surface (they are usually negatively charged) followed by diffusion through the cell wall. These processes lead to the binding to the cytoplasmic membrane which in turn promotes the disruption of the cytoplasmic membrane. In the case of polycationic polymer brushes, the interaction with the cell surface is expected to take place to a greater extent than that of monomeric cationic units because of the much higher charge density carried by the surface-grafted polymers. Within this framework, interesting

research has been undertaken by Matyjaszewski and Russell and coworkers to gain insight into the rational design of poly(quaternary ammonium) brushes to be used as antimicrobial polymeric coatings on inorganic surfaces.[77] To this end, poly2-(dimethylamino)ethyl methacrylate (PDMAEMA) brushes displaying precise control over molecular weight and the grafting density were quaternized with alkyl bromides to obtain polymer brushes bearing quaternary ammonium groups, a surface with antimicrobial activity. The experimental evidence indicates that surface charge density is a critical element for attaining macromolecular surfaces displaying maximum kill efficiency. In this context, they showed that short chains with high grafting density and long chains with low grafting density are equally effective against *E. coli*. In general terms, if the polycationic brushes expose surface charges greater than 5×10^{15} charges/cm^2, the surface would be able to kill at least a monolayer of *E. coli* cells before becoming susceptible to fouling and reduced bioactivity. Based on these results, the authors proposed an alternative to the widely accepted polycation-induced cell disruption mechanism[78] to explain the bioactivity of polycationic brushes. This mechanism essentially relies on the fact that a highly charged surface can induce an ion exchange between the positive charges on the surface and structurally critical mobile cations within the membrane.[79] Upon approaching a cationic surface, the structurally essential divalent cations of the membrane are relieved of their role in charge neutralization of the membrane components and consequently the loss of these structural cations results in a loss of membrane integrity.

More recently, Luzinov and coworkers explored the use of mixed polymer brushes to control the adsorption of bacteria on surfaces. Their approach was based on the modification of surfaces with bacteria-repelling PEG brushes and positively charged quaternized poly(vinylpyridine) brushes. These authors demonstrated that this simple and straightforward approach resulted in a 400-fold difference in the adsorption of *S. aureus*, thus allowing the design of substrates with tunable bacteria adsorption properties.[80]

Tunable Colloidal Systems Based on "Hairy" Particles

The ability to control the dispersion, aggregation, and assembly of colloidal systems is important for a number of applications including Pickering emulsions, drug delivery, control of fluid rheology, and the formation of colloidal crystal arrays, or even to devise new applications. For instance, recent work by Prud'homme and coworkers[81] demonstrated that nanoparticles grafted with polymer brushes can behave in close resemblance to surfactants due to the dislike between the nonpolar organic grafts and polar inorganic cores. Hence, brush-coated nanobuilding blocks in the 10-20 nm range display surface active properties and their surface activity and self-assembly can be tuned by changing the density of grafted chains or the solvent quality. In this context, surface modification of micro- and nanoparticles with functional polymer brushes[82,83] paved the way towards the creation of "smart" colloidal systems in which their dispersion behavior can be manipulated by environmental conditions like solvent

nature, temperature, pH, or even light. In some cases they are referred to as environmentally responsive "hairy" hybrid nanoparticles[84] due to the densely tethered polymer chains on the particle surface. Such colloidal materials are attractive in many practical applications since changes in material properties can be triggered on demand and provide an "ON/OFF" control of their collective properties as well as the formation self-organized structures. This in turn leads not only to the fine tuning of the three-dimensional organization of such materials but also facilitates the combination of different materials over several length scales.

Thermoresponsive poly(2-(N-morpholino)ethyl methacrylate) brushes grafted from silica particles were synthesized by Armes and coworkers using aqueous ATRP.[85] The hairy particles began to aggregate at ~34 °C, which is close to the cloud point of these polymers in water. PNIPAM brushes were also grown from functionalized anionic polystyrene latex particles by Kizhakkedathu et al. via surface-initiated ATRP.[86] Zhang et al. prepared poly(N,N-dimethylaminoethyl methacrylate) brushes on colloidal particles in order to create hairy assemblies that can respond to both pH and temperature variations under different environmental conditions.[87] Luo and coworkers prepared hybrid nanoparticles bearing PNIPAM brushes in the corona layer through a self-assembling approach[88] as well as double hydrophilic block copolymer monolayer protected hybrid gold nanoparticles via grafting to method.[89] From these results, it is evident that during the last decade the creativity of polymer chemists and materials scientists provided a means for developing a wide variety of colloidal materials with unprecedented functional properties.

More recently, Li and Zhao reported on the reversible temperature-induced transport of polymer brush-modified particles between aqueous and organic phases by exploiting the thermo-induced transitions of brushes between hydrated and dehydrates states.[90] Silica nanoparticles surface-derivatized with poly(methoxytri(ethylene glycol) methacrylate) brushes (thermosensitive water-soluble building blocks with a cloud point of ~48 °C in H_2O) were found to quantitatively transfer from aqueous to ethyl acetate phases upon heating at 60 °C under the stirring condition. Thereafter, cooling in an ice/water bath caused the particles to move from ethyl acetate to the aqueous layer. The reversible transfer of the particles between the aqueous and ethyl acetate phases could be repeated consecutively at least 10 times. The same colloidal materials can also be quantitatively transported from 1-butanol and toluene to H_2O by simply stirring in an ice/water bath. In a similar vein, Horton et al. explored the synthesis of thermo- and pH-sensitive hairy particles in order to control their phase-transfer behavior between water and a hydrophobic ionic liquid, 1-ethyl-3-methylimidazoliumbis(trifluoromethylsulfonyl)amide ([EMIM][TFSA]), in response to temperature and pH changes.[91] The hairy particles were synthesized via SI-ATRP of methoxytri(ethylene glycol) methacrylate (TEGMMA) and tert-butyl methacrylate with the subsequent removal of tert-butyl moieties to obtain carboxylic groups. The cloud points of the copolymer

brushes increased with the increase in pH and can be tuned over a wide temperature range. The hairy particles moved spontaneously from the aqueous phase to the [EMIM][TFSA] phase upon heating at 80 °C and returned to the aqueous layer upon cooling at 10 °C. In a similar way, pH-driven reversible transfer of the hairy particles at a fixed temperature by changing the pH of the aqueous phase was also demonstrated. Hairy colloids presenting triggered phase transfer ability between oil and water according to varied physicochemical parameters have also gained increasing attention recently because they are closely related with drug delivery transportation across amphiphilic biological membranes.

Matyjaszewski and coworkers studied the stabilization of Pickering emulsions by nanoparticles modified with thermally responsive polymer brushes.[92] Silica nanoparticles (20 nm in diameter) with PDMAEMA brushes grafted from their surfaces were able to form highly stable xylene-in-water and cyclohexane-in-water emulsions at extremely low particle concentrations. Particles with lower grafting densities proved to be the most robust and efficient emulsifiers stabilizing emulsions with as little as 0.05 wt %. The high emulsifying efficiency suggests that the nanoparticles have a high-affinity adsorption isotherm at the oil/water interface, requiring a low total particle content to stabilize large surface areas. Furthermore, these researchers showed that emulsions were thermally responsive, rapidly breaking upon increasing the temperature above the critical flocculation temperature of the SiO_2/PDMAEMA particles in water. Huck and his collaborators described the formation and manipulation of Pickering emulsions using ion-specific responsive hairy colloids.[93] They generated a responsive colloidal system based on cationic poly(2-(methacryloyloxy)-ethyl-trimethyl-ammonium chloride) (PMETAC) brushes grafted on silica nanoparticles and demonstrated that such a colloidal system can be used to produce stable oil-in-water Pickering emulsions. Owing to their counterion-specific properties, PMETAC brushes were able to tune the surface hydrophilicity of the colloidal particles. As a result, colloidal dispersion was shown to be responsive to ClO_4^- ions which triggered particle aggregation and enabled the generation of Pickering emulsions. The onset of aggregation was demonstrated to be dependent on the polymer chain length. These studies suggested that aggregation of charged hairy particles and the formation of stable Pickering emulsions are not simply due to brush collapse but gradual shielding of electrostatic repulsion must also be taken into account.

In 2007, Minko's group reported an interesting approach to achieve stimuli-responsive colloidal systems based on the use of mixed brush-coated nanoparticles.[94] They used mixed copolymer brushes constituted of P2VP-b-PEO and P2VP-b-PS macromolecular units to fabricate responsive nanoparticles and employed these particles to prepare responsive colloidal systems, which displayed drastic switching of material properties upon external stimuli [Fig. 4(A)]. The responsive polymer shell from mixed block copolymer brushes enabled them to attain reversible control over key interfacial processes, that is, segregation of particles at the liquid–liquid
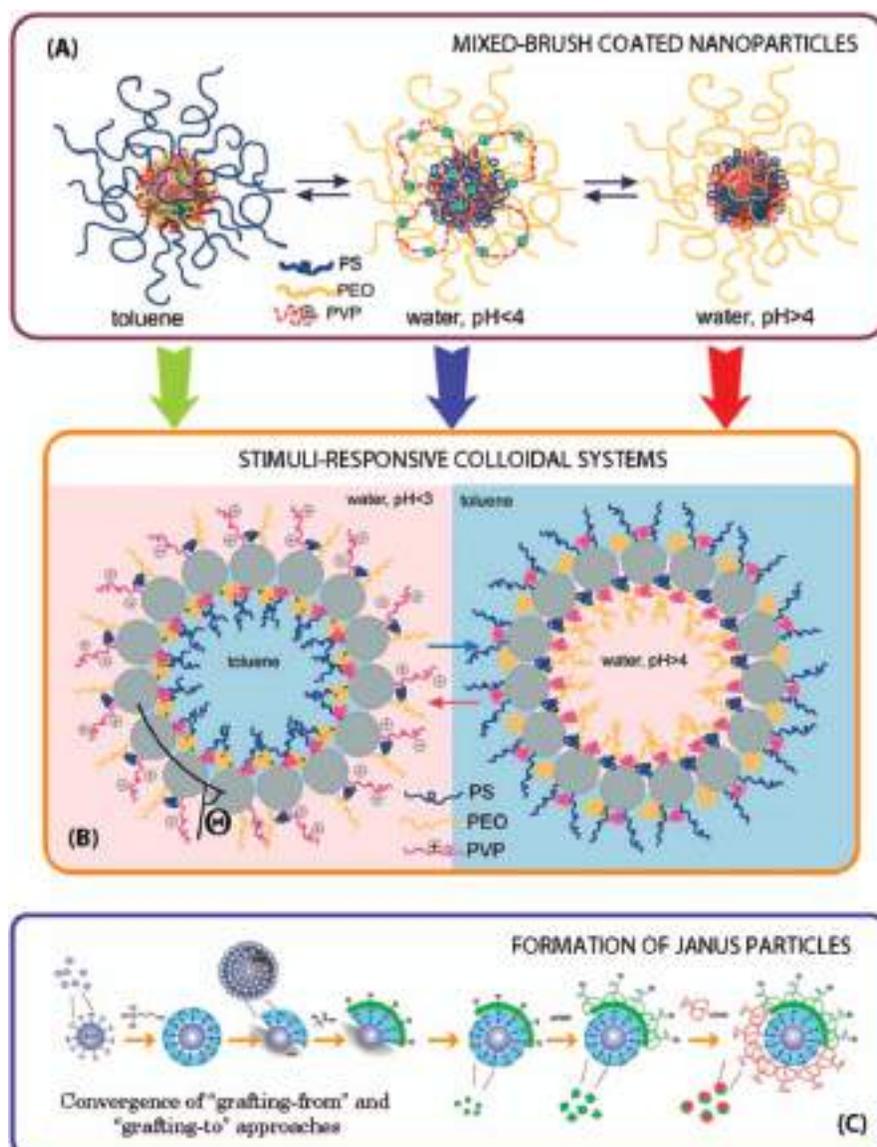
FIGURE 4 (A) Schematic representation of responsive particles generated through the grafting of mixed copolymer brushes on the surface of silica nanoparticles. (B) Cartoon describing the structure of oil-in-water and water-in-oil emulsions stabilized by responsive hairy nanoparticles. Panels (A) and (B) were From Motornov et al., Adv. Funct. Mater., 2007, 17, 2307-2314, © Wiley-VCH Verlag GmbH & Co. KGaA, reproduced by permission. (C) Scheme of the preparation of bicomponent Janus particles by grafting from and grafting to approaches. From Berger et al., Macromolecules, 2008, 41, 9669-9676, © American Chemical Society, reproduced by permission.

interface and aggregation of the particles through changes in the composition of the particle environment or external triggers. Applications of these responsive colloids were centered on the stabilization and switching of water-in-oil and oil-in-water emulsions [Fig. 4(B)], the regulation of the particle transport between immiscible liquids across the interface and the fabrication of ultrahydrophobic coatings with textured surfaces from aqueous dispersion. On the other hand, light-responsive hairy colloids were prepared by Wu et al. via grafting optically responsive spiropyran polymer brushes onto silica colloids.[95] Polyspyropyran brushes undergo a reversible change from a hydrophobic state to a hydrophilic state upon irradiation with UV light (or vice versa by visible light). In this way, the hairy colloids can be reversibly transferred between oil and water phases upon shining UV or visible light on the colloidal dispersion. Interestingly, at intermediate irradiation times, both hydrophobic and hydrophilic polymeric forms coexist, thus making the hairy colloids amphiphilic and capable of serving as particulate emulsifiers. Liu and coworkers described the fabrication of photoswitchable and thermotunable multicolor fluorescent hybrid silica nanoparticles modified with dye-labeled poly(N isopropylacrylamide) brushes.[96] Monodisperse fine particles grafted with concentrated polymer brush layers were used

as building blocks for the formation of a new family of colloidal crystals.[97] In these systems, the driving force of crystallization is the long-range repulsive (noninterpenetrating) interaction between the highly swollen concentrated brush layers. Consequently, the crystallization concentration is situated between those of typical soft and hard systems; that is why they are commonly referred to as "semisoft" systems. Advantages of semisoft colloidal crystal include controllability of interparticle distance and crystal structure by controlling the graft chain length and density. Using this approach Ohno et al. reported the formation of zwitterionic colloidal crystals with antibiofouling properties in aqueous media[98] as well as the construction of two-dimensional ordered arrays of monodisperse silica particles grafted with concentrated polymer brushes.[99]

Self-assembly of Janus colloids have attracted increasing attention recently due to their potential applications in many fields, including microrheological probes, functional surfactants, or the formation of complex superstructures. Recently, Li et al.[100] reported on the formation of Janus hairy colloids by simultaneous biphasic grafting of different polymer brushes onto the two parts of a Pickering colloid at a liquid/liquid emulsion interface by ATRP. These authors showed that the two parts of a colloid at a Pickering emulsion interface can be synchronously modified by ATRP in the two phases by a single-step approach. Hydrophilic/lipophilic interactions with the original Pickering colloid hinder colloid rotation and facilitate the formation of Janus hairy colloid. Stamm and coworkers described the preparation of bicomponent Janus nanoparticles decorated with poly(acrylic acid) and poly(2-vinylpyridine) brushes using an interesting combination of grafting from and grafting to approaches [Fig. 4(C)].[101] First, polymeric units were immobilized on one side of silica particles using a grafting from approach based on SI-ATRP. Then, the second polymer was immobilized using the *grafting to* procedure in melt by reaction of reactive terminating carboxylic group and functional groups on the other side of the particle surface. Owing to the contrasting proton-responsive nature of both macromolecular units, changes in proton concentration revealed responsive aggregation/disaggregation of the Janus particles as well as the formation of hierarchically structured aggregates.

Reversible assembly of oppositely charged colloids in water can be obtained using polyelectrolyte brushes as building blocks to tune the interactions between dispersed particles.[102] Polystyrene colloids were modified by grafting of either positively charged poly(trimethylaminoethyl methacrylate) (PTMAEMA), or negatively charged poly(3-sulfopropyl methacrylate) (PSPMA). It has been observed that below a critical salt concentration oppositely charged colloids form clusters and gels with a fractal nature. These aggregated structures are fully reversible and can be redispersed by simply increasing the salt concentration above the critical concentration.

Manipulation of Surface Wettability with Stimulus-Responsive Polymer Brushes

The rational control of surface properties by external stimuli represents a topic of paramount relevance in materials science.[103] In recent years, the idea of designing polymer brushes displaying switchable wettability has raised broad scientific interest and, consequently, much of the research effort has been devoted to meet the challenges of developing new strategies to attain nonreversible and reversible control of wetting properties using surface-confined macromolecular architectures. Polymer brushes are capable of conformational and chemical changes on receiving environmental chemical or physical stimuli, such as temperature, solvent, counterion nature or light, among others. In some cases, these changes are accompanied by important variations in surface wettability. In this section we will discuss recent advances in manipulation of wetting properties using polymer brushes as stimuli-responsive building blocks.

Temperature-Driven Changes in Wettability

Depending on the nature of the monomer units, temperature variation can promote significant changes in the wetting properties of polymer brushes.[104] Poly(N-isopropylacrylamide) (PNIPAM), the quintessential thermoresponsive polymer with a lower critical solution temperature (LCST) of ~33°C, has been widely used to design polymer surfaces with controllable wettability.[105] Below the LCST, the intermolecular H-bonding interactions between PNIPAM grafted chains and the surrounding water promotes a swollen conformation in the polymer brush and contributes to the hydrophilicity of PNIPAM. Upon increasing temperature above the LCST, intramolecular hydrogen bonding between $C=O$ and $N-H$ groups in the PNIPAM brushes leads the macromolecular system to a compact and collapsed conformation of PNIPAM chains. The sharp conformational changes and the depletion of water result in an increase in hydrophobicity at high temperatures. The behavior of grafted PNIPAM brushes has been extensively studied using a wide range of experimental techniques including dynamic light scattering,[106] neutron reflectivity[107] and quartz crystal microbalance,[108] among others. These studies revealed that the grafting density and the molecular weight of the PNIPAM chains play a critical role in the thermally driven structural changes. Surface plasmon resonance studies performed by López and coworkers[109] revealed that the collapse transition for high-density PNIPAM brushes occurs over a broad range of temperatures across the LCST. Neutron reflectivity experiments reported by Yim et al.[110] indicated that the magnitude of chain conformational changes relies on a complex interplay among the grafting density and the molecular weight of the polymer. Recent in situ AFM imaging experiments performed by Ishida and Biggs also showed that the conformational transition PNIPAM brushes from a brush-like to a mushroom-like state is essentially dependent on the grafting density.[111] Despite the widespread use and interest in PNIPAM brushes as building blocks for designing thermoactive interfacial systems,[112] in recent years research community began explore new alternatives to achieve thermoresponsive polymer brushes. That is why the predominance of PNIPAM as a thermoresponsive polymer has been recently challenged by the discovery of random copolymers of 2-(2-methoxyethoxy)ethyl methacrylate (MEO_2MA) and oligo(ethylene glycol)
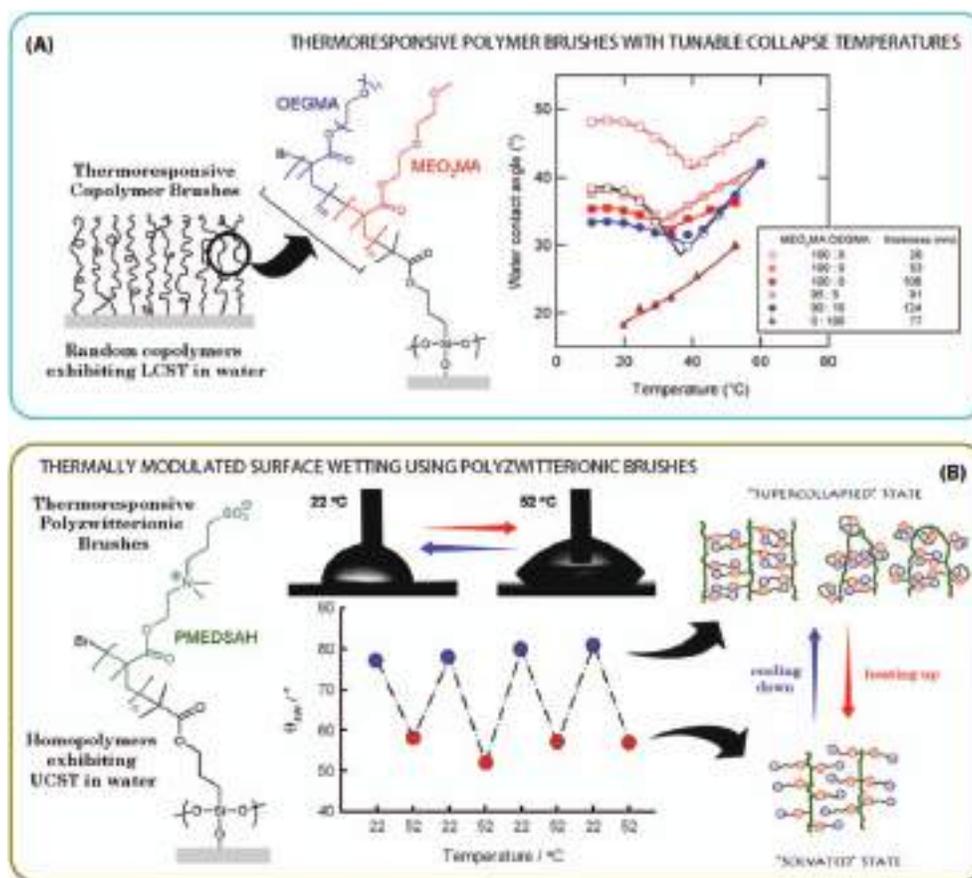
FIGURE 5 (A) (left) Simple schematic of copolymer brushes and chemical structure of P(MEO$_2$MA-*co*-OEGMA) brushes – (right) equilibrium water contact angles of P(MEO$_2$MA-*co*-OEGMA) brushes as a function of temperature. From Jonas et al., Macromolecules 2007, 40, 4403-4405, © American Chemical Society, reproduced by permission. (B) (left) Chemical structure of PMEDSAH brushes–(center) change of the wetting characteristics of thick, supercollapsed PMEDSAH brushes (thickness ∼180 nm) after increasing the temperature from 22°C to 52°C and the corresponding representation of the contact angle in water as a function of temperature—(right) simple schematic of the conformational states in different temperature regimes: "supercollapsed" state (interchain and intrachain associations) at T < UCST and "solvated" state (nonassociated brush) at T > UCST. From Azzaroni et al., Angew. Chem. Int. Ed. 2006, 45, 1770–1774, © Wiley-VCH Verlag GmbH & Co. KGaA, reproduced by permission.

methacrylate (OEGMA) exhibiting LCST behavior in water in a temperature rage comparable to PNIPAM.[113] For instance, the temperature range can be tuned between 26 and 90 °C depending on OEGMA content and, in contrast to PNIPAM, the LCST transition is almost independent of molar mass, concentration, and ionic strength.[114,115] Jonas et al. exploited the unique features of these copolymers to prepare novel thermoresponsive polymer brushes with finely tunable collapse temperatures located in the physiological range [Fig. 5(A)].[66]

On the other hand, polysulfobetaines exhibit an upper critical solution temperature (UCST).[116] In this context, Azzaroni et al. reported the first example of a thermoresponsive brush exploiting the UCST properties of these polyzwitterionic materials by translating the UCST characteristics of sulfobetaines to poly[2-(methacryloyloxy)ethyl]dimethyl(3-sulfopropyl)ammonium hydroxide (MEDSAH) brushes grown on gold and silicon substrates via surface-initiated ATRP [Fig. 5(B)].[117] In this way, PMEDSAH brushes granted access to

the creation of thermoresponsive brushes with a hydrophobic-to-hydrophilic transition when raising the temperature above the sulfobetaines' UCST (∼30 °C). Thick hydrophobic PMEDSAH brushes are in a self-associated state forming inter- and intrachain associations that contribute to the surface hydrophobicity. This self-associated state (also known as "supercollapsed" state) can be reversed by increasing the temperature, leading to a hydrophobic-to-hydrophilic switch that closely resembles the UCST characteristics observed for the same polyzwitterion in solution. PMEDSAH brushes typically show a variation in wetting properties from $\theta_{AW} \sim 79°$ to $\theta_{AW} \sim 58°$ when the temperature is increased from 22°C to 52°C.

Solvent-Induced Wetting Properties of Multicomponent Polymer Brushes

The behavior of multicomponent macromolecular systems at surfaces can differ significantly from that in the bulk because of preferential affinities of one or more components to the interface or the surrounding media.[118] For example, if we
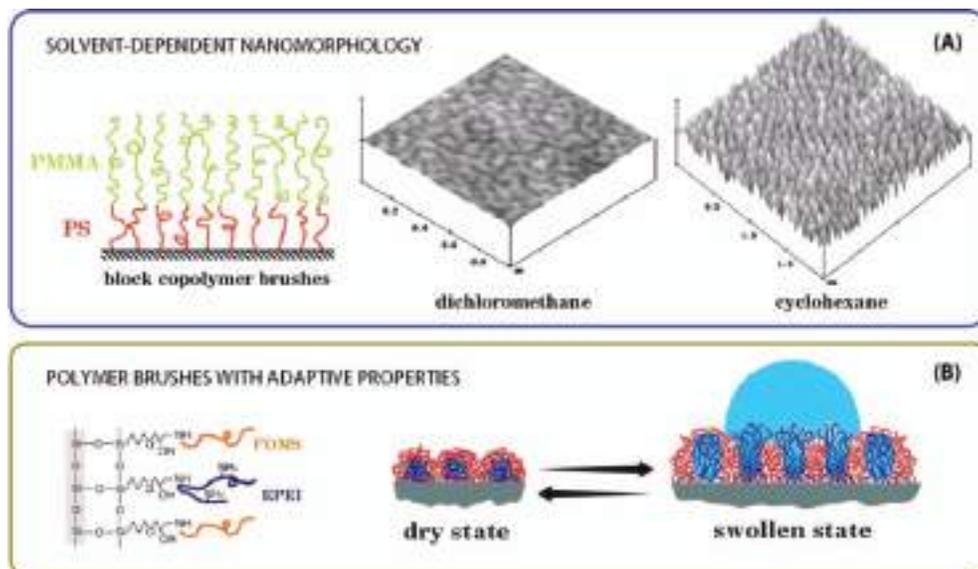
FIGURE 6 (A) Solvent-selective reorganization of poly(methyl methacrylate)/poly(styrene) block copolymer brushes (PMMA-*b*-PS) attached to surfaces through the PS chain end. After cyclohexane/dichloromethane treatment the PS blocks preferentially come to the surface due to favorable solvent-PS interactions. From Boyes et al., Surf. Sci. 2004, 570, 1-12, © Elsevier B.V., reproduced by permission. (B) Schematic depiction of the of the reversible film reorganization/segregation of hybrid polymer brushes constituted of highly branched ethoxylated polyethylenimine (EPEI) and poly(dimethylsiloxane) (PDMS) in air and under water conditions. From Motornov et al., Langmuir 2007, 23, 13–19, © American Chemical Society, reproduced by permission.

have a multicomponent polymer brush constituted of two distinct polymeric constituents of dramatically different surface energy characteristics, switching the interfacial organization of the polymer layer will lead to changes in wettability. Hence, by treating the surface with solvents selective to only one of the polymer types, rearrangement occurs revealing either the high or low surface energy constituent. This is the reason why a most common strategy for achieving solvent-responsive surfaces is the combination of two moieties with different solubility in the same polymer layer.[119] It is also important to note that by placing two incompatible polymer brushes in close proximity phase separation can occur when the surface is exposed to solvent.[120] For instance, a binary film containing poly(styrene) (PS) and poly(2-vinylpyridine) (PVP) becomes hydrophobic upon exposure to toluene, θ_{AW} ~90°. This can be attributed to phase separation of the polymer chains since PS preferentially swells in toluene increasing its fraction at the surface. Conversely, exposure of the film to acidic water, a good solvent for PVP, switches the surface into a hydrophilic state, θ_{AW} ~35°, since polymer rearrangement now brings the charged PVP to the surface.[121] Similarly, Lemieux et al. reported a film containing poly(methyl acrylate) (PMA) and poly(styrene-*co*-2,3,4,5,6-pentafluorostyrene) (PSF) brushes exhibiting switchable wettability when exposed to acetone (selective for PMA) or toluene (selective for PSF).[122] After treatment with toluene the surface becomes enriched with PFS and contact angles of 95°–100° are seen, in line with that for the homopolymer. However, after treatment with acetone the surface becomes enriched with PMA and excessive surface roughness is also observed, the resulting contact angles are therefore found

around 117–122° much higher than that seen for the corresponding PMA homopolymer. If two different polymers are covalently linked, as block copolymers, phase separation becomes more complicated and interesting topographic changes result when films containing these block copolymers are exposed to different solvents.[123] Poly(methyl methacrylate)/poly(styrene) block copolymers (PMMA-*b*-PS) have been attached to surfaces through the PS chain end. After cyclohexane/dichloromethane treatment the PS sections preferentially come to the surface due to favorable solvent-PS interactions [Fig. 6(A)]. However, since the PS block is attached to the surface at one end and attached to the collapsed PMMA block at the other its mobility is restricted. As a result, a regular ellipsoid surface morphology is seen composed of mostly PS. The high contact angle of PS combined with the increased surface roughness changes the contact angle of the copolymer film from ~ 74° (for a smooth PMMA outerlayer) to ~120°.[124] Similar experiments were performed with poly(methyl methacrylate)/poly(acrylamide) block copolymers (PMMA-*b*-PAAM) however little changes in contact angles were seen upon changes in solvent. The different behavior observed was attributed to the different hydrophilicity of the blocks involved. It was thought that any contact with water would rapidly rearrange the polymer bringing the PAAM to the surface making measurement of the hydrophobic state by aqueous contact angle goniometry difficult.[125]

Tsukruk and coworkers reported the use of Y-shaped block copolymers composed of PS and hydrophilic poly(acrylic acid) (PAA) grafted to a silicon surface as polymeric units

conferring solvent-responsive wetting properties to the substrate.[126] Upon exposure to toluene or cyclohexane, which are both good solvents for PS, the topmost surface layer becomes predominantly composed of PS arms, and the PAA arms collapse into cores in the inner environment of the brush. In this case, the θ_{AW} value reaches 79°. However, after treatment with water, which is a selective solvent for PAA, the θ_{AW} will decrease to 52° because PS is partially covered by PAA chains. Mixed brushes composed of polydimethylsiloxane (PDMS) and polyethyleneoxide (PEO) or ethoxylated polyethylenimine (EPEI) [Fig. 6(B)] revealed a selective layered segregation in air and water. Immersion of the substrate into an aqueous environment drove PEO or EPEI chains to the brush-water interface while upon drying the surface underwent reconstruction and was occupied with PDMS.[127] In this case, high values of advancing contact angles indicate the presence of PDMS chains in the top of the mixed brush. Brittain et al.[128] explored the potential of solvent-responsive multicomponent thin films by studying the wetting properties of ABA-type triblock copolymer brushes based on PMA-*b*-PS-*b*-PMA grafted from SiO$_2$/Si surfaces. In this surface-confined macromolecular system the middle block has different physicochemical properties from the end blocks. They observed that PMA-*b*-PS-*b*-PMA brushes when treated with dichloromethane (a good solvent for all the blocks), the films adopt an extended brush configuration, and hydrophilic PMA is at the topmost surface layer, displaying contact angles close to ∼ 69°; however, when the same films were exposed to cyclohexane (a good solvent for PS- the middle block) brushes exhibited a collapsed conformation and hydrophobic properties (contact angle ∼ 90°). More recently, Howarter and Youngblood[129] reported the use of highly responsive brush-type polymer layers to create self-cleaning and antifog surfaces. These authors used oligomeric amphiphiles of polyethylene glycol with short perfluorinated end caps (f-PEGs) to functionalize the surface via a *grafting-to* method. They found that surfaces with covalently grafted perfluorinated end-capped PEG layers were stimuli-responsive and simultaneously displayed PEG-like behavior to water and fluorinated behavior to hexadecane (oily environment). Intermediate brush densities were found to have optimum behavior, while denser brushes were detrimental to performance. This was attributed to fact that densely arranged brushes exhibit a slower response as the process of rearrangement is hindered by strong spatial confinement. However, polymer brushes grafted at the intermediate densities favor a rapid rearrangement and ease of motion of the oligomeric chains when the surface was exposed to water or hexadecane.

Ion and pH-Controlled Wettability of Polymer Brushes

Surface-tethered polyelectrolytes are another common interface with tunable wettability. In general, their surface properties are determined by the nature of the ions to which they are exposed; and in cases involving protons, the pH. The conformation of the polymer chains is governed by three effects: electrostatic interaction, solvation and excluded volume effects. The interplay of these three effects can have a drastic effect on the surface wettability of a polyelectrolyte substrate. A well studied system is that of the cationic polyelectrolyte poly(2-(methacryloyloxy) ethyl)trimethylammonium chloride) (PMETAC). In the absence of electrolyte, charge repulsion of the chains and excluded volume effects from solvation dominate, causing the surface to be hydrophilic. When in electrolyte solutions however, electrostatic screening of the cationic charges takes place and the polymer chains collapse into a more entropically favorable coiled conformation.[130] Azzaroni et al. demonstrated that the wetting behavior is however more complex and highly dependent on the anions present at the interface.[131] Cationic polyelectrolyte brushes bearing quaternary ammonium groups may undergo strong 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 polymer brush. This unique feature has been used to tune the wettability of polyelectrolyte brush-modified substrates simply by using a set of different counterions. It has been shown that the hydrophobicity of these collapsed PMETAC surfaces in water follows the lipophilic scale of anions: $ClO_4^- > SCN^- > I^- > Br^- > Cl^- > PO_4^{3-}$. Among a broad variety of counterions studied, perfluorinated bis(trifluoromethane) sulfonimide anions (TFSI), showed the highest hydrophobicity, $\theta_{AW} \sim 90°$, whereas polyphosphate (PP) displayed the lowest contact angle angle, $\theta_{AW} \sim 15°$ (Fig. 7) In this way, these authors demonstrated that a dynamic regulation of wettability for the same polymer brush system can easily be achieved. Using the same approach Pein et al.[132] manipulated the wetting properties of surfaces using poly(ionic liquid) brushes. [PVBIm][PF6] ([1-(4-vinylbenzyl)- 3-butylimidazolium hexafluorophosphate]) brushes were grafted from silicon surfaces via a surface-initiated ATRP displaying a rather hydrophobic behavior ($\theta_{AW} \sim 95°$). Thereafter, immersion in 0.2 M NaCl aqueous solution for 1 h led to the to PF_6^- exchange with Cl^- anions, thus promoting a drastic change in the wetting properties of the substrate ($\theta_{AW} \sim 40°$).

On the other hand, polymers containing acidic or basic functional groups usually exhibit pH-responsive wetting behavior because their morphologies and/or charges are dramatically influenced by the pH of solution. Zhou and Huck[133] synthesized polymer brushes bearing phosphate side groups that were used to reversibly switch wettability between three different states. This strategy was based on the presence of two well-defined ionization states, $pK_1 \sim 4.5$ and $pK_2 \sim 7.7$, that leads to different conformational configurations and, consequently, to different physicochemical states depending on the pH: (i) high pH values—fully ionized brushes—hydrophilic surface ($\theta_{WA} \sim 13°$); (ii) low pH values—fully protonated brushes—hydrophobic surface ($\theta_{WA} \sim 65°$); (iii) intermediate pH values—intermediate hydrophobicity ($\theta_{WA} \sim 49°$). Yu et al.[134] synthesized diblock polyampholyte brushes with different block sequences, PAA-*b*-P2VP and P2VP-*b*-PAA, and different block lengths through SI-ATRP. These
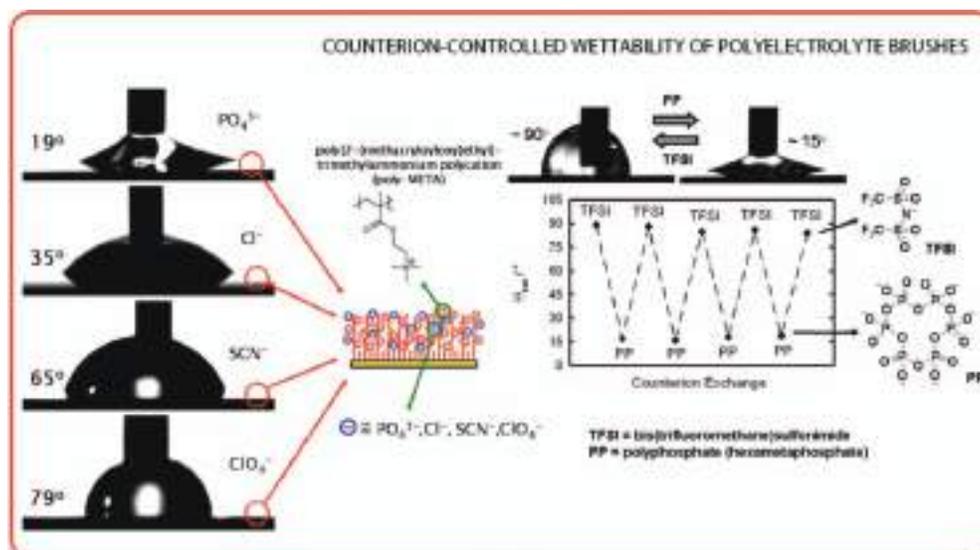
FIGURE 7 (Left) Wetting modulation of PMETA brushes grown on Au surfaces (thickness ~20 nm) in the presence of different counterions. (Right) Change in the wetting characteristics of PMETA brushes after exchanging the two contrasting counterions: TFSI and PP. From Azzaroni et al., Adv. Mater. 2007, 19, 151–154, © Wiley-VCH Verlag GmbH & Co. KGaA, reproduced by permission.

polyampholyte brushes display very unique pH-responsive behavior. In the intermediate pH region, these brushes exhibit a less hydrophilic wetting behavior and a rougher surface morphology due to the formation of polyelectrolyte complexes arising from electrostatic interactions between oppositely charged blocks. In the low pH and high pH regions, the experimental evidence revealed that the rearrangement of polyampholyte brushes is highly dependent on the block sequence and block length. Polyampholyte brushes with P2VP-b-PAA sequence underwent rearrangement during sequential exposure to acidic and basic aqueous solutions. However, similar brushes presenting the PAA-b-P2VP sequence did not evidence any significant rearrangement. In this case, upon increasing the length of the inner PAA block in the low pH region hydrogen-bonding interactions between blocks became stronger and, consequently, reorganization of the inner PAA at the polymer–air interface took place.

Light-Induced Changes in Wettability

Light is one of the least invasive stimuli available in order to elicit responsive behavior. Polymer brushes utilizing direct physicochemical modification upon exposure to light became an area of particular interest because the cumulative effect of changes on each monomeric unit within a surface tethered polymer film can bring forth significant changes in wetting properties. Locklin and coworkers[135,136] described the use of spiropyran-containing polymer brushes as reversible, photoswitchable optical platforms showing selectivity for different metal ions and drastic changes in surface wettability. Spiropyrans are photoswitchable functional groups displaying light-induced cleavage of the spiro C—O bond. The photoinduced geometry change between the ring closed spiropyran (SP) and the ring-opened merocyanine form is accompanied by a large change in dipole moment that, in turns, affects the

surface free energy and consequently promotes a switch in wettability. These authors also found that metal ion bonding further amplifies the wettability changes due to the stabilization of the phenolate tautomer of the merocyanine.

Minko and coworkers reported the very interesting use of poly(2-vinylpyridine) (P2VP) and poly(isoprene) (PI) independently tethered to a surface in a random array in order to exhibit solvent dependent wettability.[137] However, this switching behavior could be neutralized if the surface was irradiated with UV light due to cross-linking of the PI units. Polymer brushes bearing photolabile protecting groups have been exploited as building blocks to create hydrophilic surfaces. Utilizing the mild photochemistry of o-nitrobenzyl groups, the synthesis of polymer brushes bearing monomeric NVOCMA units facilitated the creation of hydrophobic protected brushes that transform into hydrophilic PMAA chains upon exposure to UV light. Controlled cleavage and removal of the protecting group liberates the hydrophilic polymer,[138] thereby switching the surface wettability from hydrophobic to hydrophilic. This switch can be augmented by increasing the surface roughness [Fig. 8(A)]. Exposure of PNVOCMA brushes through a TEM grid, with subsequent pattern visualization by condensation imaging, demonstrated the ability to locally switch the surface on the micron scale, and to reproduce this switch over a large area [Fig. 8(A)].[139] Another interesting strategy relies on the synthesis of a "self-contained polymer brush resist," combining the chemistries of surface initiated atom transfer radical polymerization (SI-ATRP) and photoacid generators (PAGs), in order to create substrates with light-responsive wettability. Brown et al. demonstrated that the incorporation of PAGs as light-activatable functional blocks into block copolymer brushes provides a latent acid poised for activation by an external light
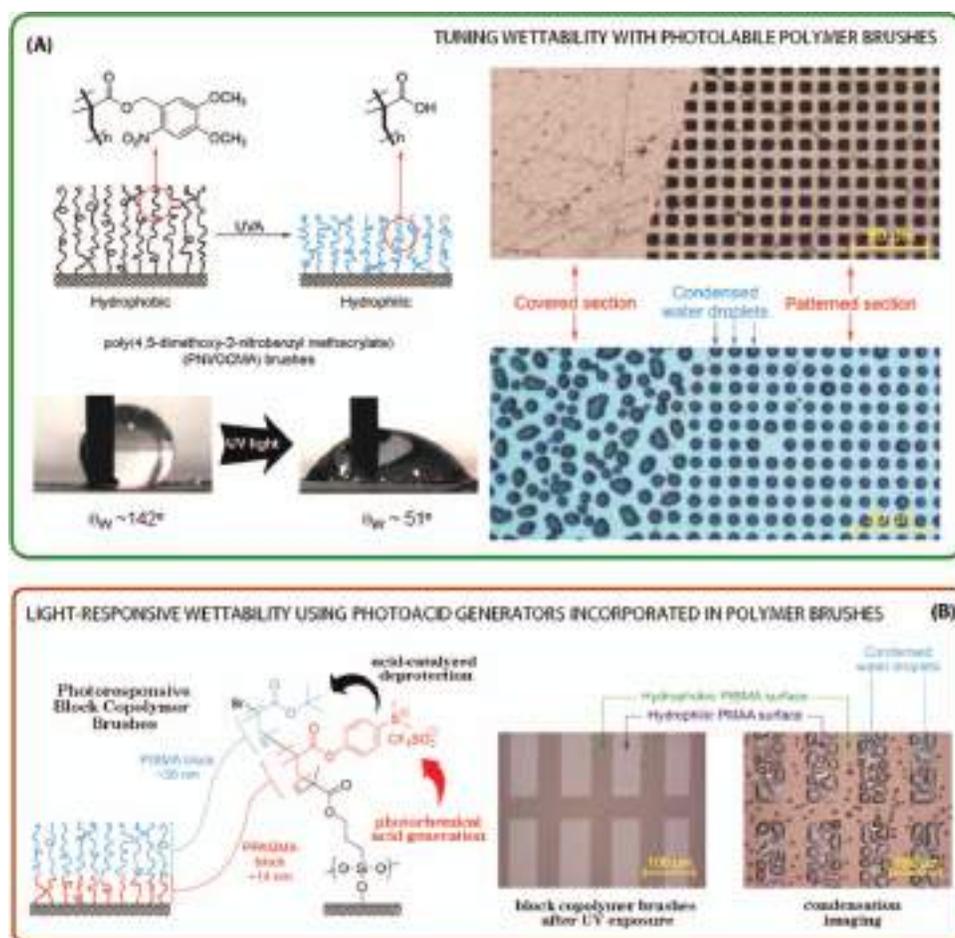
FIGURE 8 (A) Chemical and wettability changes occurring when PNVOCMA brushes are converted to PMAA brushes upon exposure to UV light. The figure also depicts a condensation picture, taken by optical microscopy, of a PNVOCMA brush after patterned deprotection. From Brown et al., Langmuir 2009, 25, 1744, © American Chemical Society, reproduced by permission. (B) (Left) Simple schematic of PPAGMA-b-PtBMA brush. (Right) PPAGMA-b-PtBMA polymer brush after patterned UV exposure and the subsequent condensation imaging of the same sample revealing the hydrophilicity of the exposed regions. From Brown et al., Soft Matter 2009, 5, 2738, © Royal Society of Chemistry, reproduced by permission.

source.[140] Activation of the acid results in the conversion of PtBMA blocks into poly(methacrylic acid) (PMAA) domains, thus resulting in a wettability switch provided that the hydrophobic PtBMA blocks should in principle switch to a hydrophilic state when converted to PMAA [Fig. 8(B)]. Inducing this switch by using a PAG can be thought of as an indirect photo-responsive surface, since light is used as the triggering stimulus but it is the photolytically generated acid which performs the chemical modification/deprotection of the PtBMA blocks. These authors also demonstrated that spatially addressable patterning was feasible, allowing for the formation of polymer brushes with regions of different wettabilities [Fig. 8(B)].

Polymer Brushes in Organic Electronic Devices

For organic (opto)electronic devices such as light-emitting diodes (LEDs), photovoltaic (PV) cells and field-effect transistors (FETs), the processes of charge (hole/electron) injection, charge transport, charge recombination (exciton formation), charge separation (exciton diffusion and dissociation) and

charge collection on electrode supports are critical to enhance their performance.[141] The magnitude of these processes relies on nanoscale interfacial phenomena in which the integration of polymer thin films on electrode supports plays a major part. Here is when polymer brushes come into the picture as valuable tools to enginner electronic properties of surfaces with macromolecular assemblies. In contrast to spin-coated thin films that provide little control over film structure, polymer brushes offer a broad variety of resources to gain nanoscale control over the size, sequence, conformation, and spatial distribution of functional building blocks. For example, the conventional method for preparing hole-transport polymer layers typically involves spin-coating processing. However, integration of the electroluminescent active polymer layer also by spin-coating on top of the hole-transport layer results in dissolution of the underlying film. In this regard, surface-tethered polymer brushes exhibit a higher degree of control over the arrangement and morphology of the polymer interface, an essential feature to afford highly efficient electronic materials and devices.
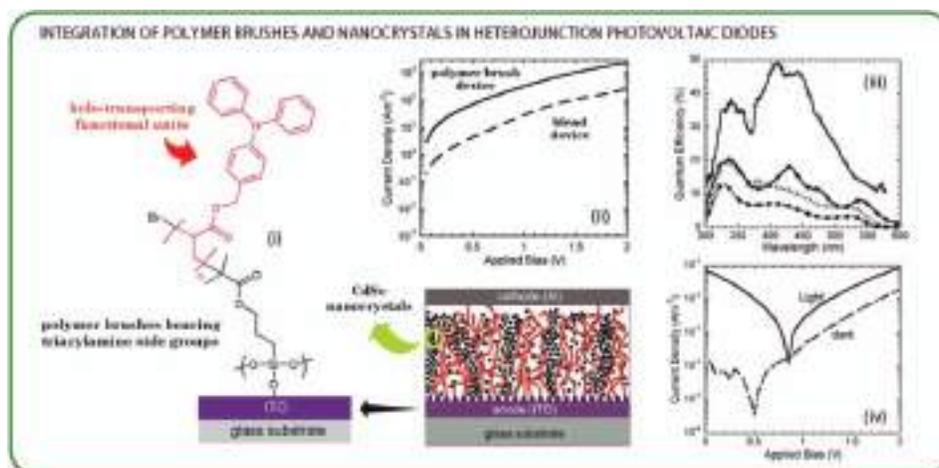
FIGURE 9 (A) (i) Chemical structure poly(triphenylamine acrylate) (PTPAA) brushes grafted from ITO electrodes. The figure also includes a simplified cartoon describing the inferred structure for CdSe nanocrystal infiltrated polymer brush photovoltaic device. (ii) Current-voltage characteristics for diodes fabricated with ITO anodes and Al cathodes with active layers of PTPAA brushes (45 nm) infiltrated with 2.6 nm diameter CdSe nanocrystals (solid line), PTPAA/CdSe nanocrystals blend 1:8 by weight (70 nm thick) (dashed line). (iii) Photovoltaic action spectra for a CdSe nanocrystal (2.6 nm diameter) infiltrated PTPAA brush (45 nm thick) device (open diamonds) and for PTPAA/CdSe nanocrystal blend device 1:8 by weight (solid circles), with external quantum efficiency (dotted lines) and internal quantum efficiency (solid lines). (iv) Current-voltage characteristics for a device comprising a 20 nm thick PTPAA brush film grown from a modified PEDOT:PSS coated ITO slide, infiltrated with 2.8 nm diameter CdSe nanocrystals and capped with an aluminum cathode, in the dark (dashed line) and under 400 nm incident illumination (solid line). From Snaith et al., Nano Lett. 2005, 5, 1653-1657, © American Chemical Society, reproduced by permission.

Seminal work by Huck, Friend and coworkers demonstrated the valuable contribution of polymer brushes to the design of photovoltaic devices.[142] They introduced a new concept to achieving order in molecular semiconductors via alignment of polymer chains using surface-initiated polymerization. Polyacrylate brushes bearing triarylamine side groups as hole-transporting components grown from transparent conducting electrodes showed characteristics of high mobilities for hole transport and were then employed in composite diodes integrating CdSe nanocrystals. As the polymer chains exhibiting high degree of alignment perpendicular to the substrate were tethered to the anode, any hole generated within the device had a direct path to the collection electrode. Experimental evidence also demonstrated that the transport in the nanocrystal phase was dramatically improved as compared to that of a spincoated polymer/nanocrystal blend film (Fig. 9). The same authors also showed that charge-transporting polymer brushes exhibit up to a 3 orders of magnitude increase in current density normal to the substrate as compared with a spin-coated film.[143] These facts eloquently illustrate that controlled polymer architecture and morphology results in better charge carrier transport properties in organic devices.

Electrochemically crosslinked surface-grafted poly(N-vinyl-carbazole) (PVK) brushes as hole transport layers on a photovoltaic devices have been demonstrated using SI-RAFT polymerization.[144] Drawing on electrodeposited chain transfer agents Advincula and coworkers used these macroprecursors to grow polymer brushes from ITO electrode surfaces thus providing a well-defined and selective anchoring point

from where the polymer brush can grow. In contrast to typical approaches based on self-assembled silane initiators that modify not only the conducting side of the ITO but also the glass side, the electropolymerization route facilitates the selective surface-initiated polymerization of the conducting region of the electrode support and ensures an efficient way to yield a good control over the film thickness and a good surface coverage due to the high grafting densities. Furthermore, the covalent anchoring of the PVK brush allowed for a direct electroluminescent device preparation on SIP modified ITO in which PVK acted as the hole-transporting layer. Polyfluorene copolymer was easily spin-casted on top of the grafted PVK without dissolution problems resulting in an improved polymer light-emitting diode (PLED) device.[145] Gopalan et al.[146] developed a *grafting-to* approach based on "click" chemistry to anchor poly(3-hexylthiophene) (P3HT) brushes on substrates bearing azide groups under mild conditions resulting in fairly high grafting densities. The saturation hole mobility for "clicked" P3HT brushes measured in an field-effect transistor was comparable to hole mobilities in FETs constituted of monolayer thick dip-coated P3HT. This approach to anchoring of conjugated polymers brushes directly onto the acceptor surfaces could provide new means for controlling the conjugated polymer/inorganic semiconductor interface.

On the other hand, the inclusion of a polymer brush as a dielectric element has been demonstrated to be a significant step toward optimizing the nanostructures of organic semiconductors through the engineering of the OFET interface. Huck, Sirringhaus and coworkers developed organic thin film

transistors with polymer brush gate dielectrics synthesized by SI-ATRP.[147] In this way, polymer brush dielectrics based on PMMA allowed fabrication of low voltage OFETs with both evaporated pentacene and solution deposited poly(3-hexylthiophene). The semiconductor-dielectric interfaces were studied with a variety of methods that highlighted key differences between similar systems created with surfaces of polymer brushes and spin-coated films. Similarly Chi et al.[148,149] reported the use of polymer brush-inorganic oxide hybrid nanodielectrics exhibiting smooth surface topography, high capacitance values and low leakage current densities for the fabrication of high performance organic transistors. Park et al. investigated the crystalline nanostructures and film morphologies of pentacene films deposited onto a polystyrene brush interlayer in high performance organic field-effect transistors (OFETs).[150] Pentacene FETs fabricated on top of the polymer brushes showed excellent device performance, and these properties were superior to those of devices using typical surface modification techniques, such as octadecyltrichlorosilane (ODTS) and hexamethyldisilazane (HMDS). These improvements in the device performance were ascribed to the critical role of the polystyrene brush in tailoring the surface energy and morphology that in turn has a profound impact on the crystalline structure and grain interconnectivity of the pentacene layer. In the same context, triethylsilylethynyl anthradithiophene (TES-ADT) FETs fabricated on top of PS brushes showed dramatically improved device performance.[151] Polymer brushes with high grafting densities conferred excellent electrical and environmental stability to these devices due to minimal presence of pinholes and defects. Poly(9-(2-(4-vinyl(benzyloxy)ethyl)-9H-carbazole)) (PVBEC) brushes, have been successfully prepared on silicon surfaces via SI-ATRP.[152] Integration of PVBEC brushes into memory devices showed that ON/OFF current ratios as high as 10^5 are feasible, being this value comparable to those of contemporary single layer molecular switching devices and the switching performance is superior to that of the conventional spin-coated devices. These breakthroughs in interface design have enabled the emergence of polymer brushes as versatile building blocks for the fabrication of polymer devices.[153]

Metal and Semiconducting Nanoparticles Confined in Polymer Brushes: Polymer-Inorganic Hybrid Interfaces by Design

Synthesis and self-organization of nanoparticles confined in thin polymer films are central topics in contemporary nanomaterials science and technology owing to major interests in optical, nonlinear optical, and sensor applications,[154] especially those requiring large area coating.[155] Inorganic nanoparticle–polymer brush thin film nanocomposites[156] offer the interesting possibility of merging the unique properties of two classes of building blocks: inorganic particles enabling exquisite control over a myriad of functional features emanating from their collective behavior and polymer brushes displaying well-defined physicochemical changes in response to environmental stimuli. Embedding and/or confining inside polymer brushes facilitates immobilization and organization of the metal nanoparticles and tuning of their electronic and optical responses by the dielectric environment. The embedded metal nanoparticles in turn can impact upon the various material attributes of the polymer brush layer. Within this framework, seminal work by Minko's group demonstrated the realization of nanosensors based on gold nanoparticle enhanced transmission surface plasmon resonance spectroscopy using poly(2-vinylpyridine) (P2VP) polymer brushes as pH-responsive functional units [Fig. 10(A)].[157] Tokarev et al.[158] exploited the combination of the swelling-shrinking transition in poly(N,N′-dimethylaminoethyl methacrylate) brushes and the localized surface plasmon resonance of metal nanoparticles to facilitate the transduction of pH variations into optical signals [Fig. 10(B)]. Miyashita and co-workers[159] described the fabrication of hybrid nanoassemblies combining thermoresponsive PNIPAM brushes and gold nanoparticles independently and selectively assembled on substrates, thus enabling detection of nanoscale optical changes based on localized surface plasmon resonance. A rather similar concept to create thermosensitive plasmonic nanosensors was explored by Gupta et al.[160] using PNIPAM-gold nanoassemblies on macroscopic surfaces. In their study, carboxyl-terminated PNIPAM chains were attached to the substrate in a brush conformation followed by the immobilization of carboxy-capped Au NPs through hydrogen bonding interactions. Ionov et al.[161] grafted solvent-responsive poly(2-vinyl pyridine) (P2VP) brushes onto a reflecting surface and immobilized CdSeS nanocrystals on top of the polymer layer [Fig. 10(C)]. The fluorescence intensity of the quantum dots (QDs) was found to be strongly dependent on the surrounding medium, which influenced the thickness of the polymer layer, and thus the distance of the QDs to the surface. QD immobilization on polymer brushes can be also achieved through covalent anchoring on macroscopic surfaces using poly(acrylic acid) brushes.[162] This approach offers the possibility of irreversible bonding and homogeneous distribution on underlying substrates. Temperature-modulated quenching of quantum dots covalently coupled to chain ends of poly(N-isopropyl acrylamide) brushes on gold was also reported by Vancso and coworkers.[163] PNIPAM chains grafted from gold surfaces end-functionalized with amine groups were conjugated to COOH-functionalized core/shell CdSe/ZnS QDs. Upon increasing the temperature above the lower critical solution temperature (LCST) of PNIPAM the QD luminescence is quenched owing to the temperature-modulated thickness changes of the PNIPAM layer and the concomitant quenching of the QDs by the gold surface via nonradiative energy transfer. Using electrochemical impedance spectroscopy of Zhou and coworkers[164] showed that poly (1-ethyl 3-(2-methacryloyloxy ethyl) imidazolium chloride) (PEMEIm-Cl) brushes with locally generated Pd nanoparticles exhibits high electrocatalytic activity for the reduction of oxygen, a functional feature, that is, not observed in nanoparticle-free PEMEIm-Cl brushes. In addition, these researchers observed that the electrocatalytic activity of brush nanocomposite for oxygen reduction was highly tunable by changing the thickness of the composite film.
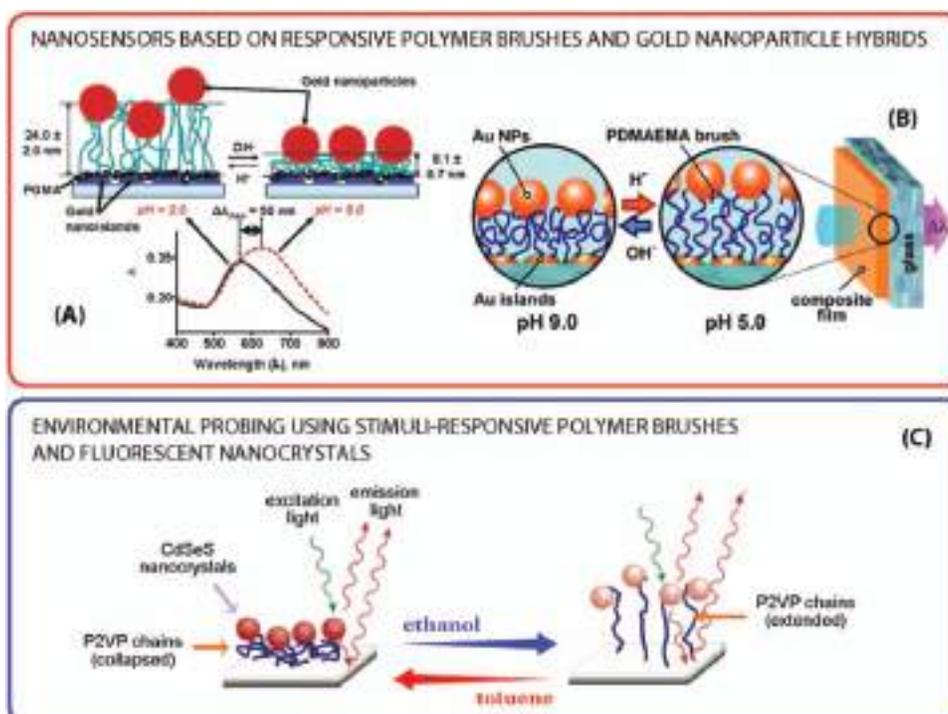
FIGURE 10 (A) Simplified scheme of the reversible pH change-induced swelling of gold nanoparticle-coated poly(2-vinylpyridine) (P2VP) polymer brushes and the corresponding SPR spectra AuNP/P2VP brushes at pH 2.0 and 5.0. From Tokareva et al., J. Am. Chem. Soc., 2004, 126, 15950, © American Chemical Society, reproduced by permission. (B) Plasmonic sensing platform constituted of responsive ultrathin PDMAEMA brushes, Au nanoislands and Au NPs. From Tokarev et al., ACS Appl. Mater. Interfaces, 2011, 3, 143, © American Chemical Society, reproduced by permission. (C) Schematic of the polymeric sensor. Hydrophobic nanocrystals are adsorbed on a stimuli-responsive polymer layer that was previously grafted onto a reflecting substrate. The nanocrystal– surface distance depends on the conformation of the polymer chains and changes in different solvents. The change in height is then reported by a variation in the detected fluorescence intensity. From Ionov et al., Adv. Mater. 2006, 18, 1453, © Wiley-VCH Verlag GmbH & Co. KGaA, reproduced by permission.

Ag NP-conjugated poly(L-lysine) (PLL) brushes has been used for the fabrication of biocompatible 3D soft substrates in order to accomplish surface-enhanced Raman scattering (SERS) measurements with high sensitivity.[165] Negatively charged citrate-stabilized Ag NPs were conjugated to the exposed amine groups of PLL brush via strong electrostatic interactions. Stamm and coworkers similarly developed a SERS active sensing layer using Ag NPs incorporated in poly(2-(dimethylamino)ethyl methacrylate) brushes.[166] Ag NPs embedded in PDMAEMA brushes were obtained by incubating the brush surface with an aqueous solution of the $AgNO_3$, followed by the reduction of coordinated Ag^+ ions in aqueous $NaBH_4$ solution. In situ reduction of trapped or coordinated ions into polyelectrolyte brushes is a strategy that has proved very successful for homogeneously immobilizing nanoparticles in the inner environment of polymer brush. In this regard, Azzaroni et al.[167] observed that in situ synthesized nanoparticles are not only uniform in size and fully stabilized by the surrounding polyelectrolyte chains but XRR analysis also revealed that the metal NPs are fully confined within the ultrathin polymer layer.

An increasing number of recent studies demonstrate that polymer brushes serve as versatile platforms for the prepa-

ration, stabilization, and application of hybrid-polymer thin films owing to their nanometer dimensions, a broad variety of functional groups, well-defined structure, and their intrinsic ability to control assembly of NPs over multiple length scales. Within this framework, an ongoing challenge in this field is the direct organization of nanoparticles within the polymer environment; for instance, to localize nanoparticles in particular regions of the brush due to preference or affinity for that chemical surrounding.[168] Recently, Huck and coworkers devoted considerable research efforts to control the organization of nanoparticles in polymer brushes.[169] These authors explored the use of polymer brushes to direct organization of nanoparticles on surfaces. The key aspect of these experiments relied on a macromolecular system in which the polymer and particles prefer to phase separate, that is, PS-coated Au NPs infiltrated into poly(4-vinylpyridine-b-styrene) (P4VP-b-PS) block copolymer brushes. Control over the extent of phase separation was obtained by variation of brush thickness leading to strong suppression of the growth of particle-rich domains in the case of thickness values comparable to the diameter of the particles. This effect was ascribed to the chain stretching penalties that arise due to perturbation of inner brush structure by the growing particle

aggregates. Experimental evidence indicates that after solvent annealing polymer-covered NPs are either sequestered into the corresponding block copolymer domain or expulsed from the brush, depending on the shell density of the NPs. This in turn leads to a situation, in which metal nanoparticles are locally addressed into predefined inner regions of the polymer brush, that is, spatial organization of NPs within the polymer layer.

Hybrid Architectures Combining Mesoporous Materials and Responsive Polymer Brushes: Gated Molecular Transport Systems and Controlled Delivery Vehicles

Interest in and thereby also development of ordered mesoporous silica as controlled delivery systems has grown immensely over the past few years. Due to its nontoxic nature, high surface area, large pore volume, tunable pore size, and chemically modifiable surfaces, mesoporous silica has been used as a promising carrier system for drug delivery.[170] In view of this situation, their surface functionalization with polymeric assemblies became a major topic of research because it offers a further possibility to tailor the chemical properties of the porous materials. In principle, surface modification involves homogeneous derivatization of inner and outer surfaces using conventional *grafting-to* and *grafting-from* approaches. However, using simple but effective experimental protocols selective molecular engineering of the outer and inner mesoporous environment is also feasible. The basis of this method developed by de Juan and Ruiz-Hitzky[171] consists of gradual functionalization which includes grafting of selected organic groups on the external surface of the silica containing the template species necessary to conform the mesophase, extraction of the template agent; and grafting of new organic groups in the interior of pores. In this way, the resulting materials preserve the characteristic structural organization of mesoporous silica, but the introduced chemical anisotropy makes them unique materials for applications in controlled delivery systems. One of the first attempts to control transport properties of mesoporous materials using responsive polymer brushes was reported by López et al.[172] SI-ATRP was employed to graft PNIPAM brushes onto the inner and outer surfaces of mesoporous silica particles. By employing fluorescein as the tracer and flow cytometry as the detection method, these authors were able to show how the transport of the fluorescent guest could be controlled by a variation in the temperature. Below LCST swollen, hydrated PNIPAM brushes inhibit the transport of solutes through the mesopores, whereas at higher temperatures (above LCST) brushes collapse at the pore walls, thus making the pores permeable to solutes. Similarly, SI-RAFT was also used to prepare PNIPAM-coated mesoporous silica nanospheres.[173] According to Oupicky and coworkers[174] selective modification of the outer surface of silica nanoparticles with PNIPAM brushes via a *grafting-to* strategy improves the thermo-triggered "on/off" properties of the composite nanomaterial, thus exhibiting a low level of leakage upon switching the conformational state of the grafted chains. This mode of operation is opposite to that observed for systems in which the PNIPAM is grown from the porous silica surface, that is,

diffusion occurs when the brush is swollen and retarded when it is collapsed, and is accompanied by a greater than 10-fold improvement in fluorescein retention in the "pore-closed" conformation.

Martínez-Máñez and coworkers reported the first gated hybrid system operating in aqueous solution and controlled ionically by pH modulation.[175] This was achieved through the grafting of polyamines on the external surface of mesoporous silica scaffolds. In this system, the opening/closing mechanism arises from hydrogen-bonding interactions between unprotonated amines (open pores) and Coulombic repulsions between protonated amino groups (closed pores). The inner pores of the material were funtionalized with thiol groups, which are known to react with a blue squaraine dye to give a colorless derivative, to enable the opening and closing to be monitored. At acidic pH values the amines are fully protonated, the gate is closed, and access to the inner pores is inhibited; thus the solution remains blue. In contrast, in the neutral pH region the amines are unprotonated, the gate is open, and the dye can enter the pores, thus leading to a bleaching of the dye solution. Interestingly, an anion-controlled effect was also observed. In the neutral pH region the gate is only open in the presence of small anions such as Cl^-, while bulky anions such as adenosine 5'-triphosphate (ATP) close the gate through formation of strong complexes with the amines at the pore outlets. Thereafter, several groups explored similar strategies to synthesize pH-activatable brush-coated mesoporous particles. SI-ATRP has been employed to prepare poly(2-(diethylamino)ethyl methacrylate)-coated mesoporous silica nanoparticles resulting in hybrid nanoparticles with a pH-sensitive polymer shell and a mesoporous core.[176] PDEAEMA brushes act as a good gatekeeper to control access to the pores via a pH-dependent open-close mechanism, which was confirmed by the well-controlled release of rhodamine B from the mesopores through adjusting pH of the solution. Release studies of guest molecules were conducted at different pHs, and the results showed a rapid release in acidic aqueous solution but very little leakage in alkaline solution. Hence, by adjusting the pH of the solution repeatedly, the release of encapsulated molecules was switched "on" and "off" at will. Poly(acrylic acid) brushes grafted onto the exterior surface of mesoporous silica by reversible addition fragmentation chain-transfer (RAFT) polymerization also display gating properties similar to "smart" nanovalve sensitive to pH changes.[177] Feng and coworkers used a *grafting to* method to tether PVP brushes onto mesoporous silica surfaces in order to create a proton-gated macromolecular barrier to control the molecular transport from the mesopore.[178] Under neutral or slightly alkaline conditions PVP brushes are collapsed on the pore entrance, thus blocking the passage of species trapped in the interior of the mesoporous particle. Then, upon lowering the pH conditions the protonated brushes become swollen and permeable to the trapped molecule. On the other hand, the use of cross-linked polymer brushes as "gatekeepers" on the surface of mesoporous silica-based materials enables the gating operation in the

presence of redox stimuli.[179] Poly(N-acryloxysuccinimide) brushes were grafted at the pore entrance of mesoporous particles. After loading the dye molecules into the particles, the openings are blocked by the addition of cystamine, a disulfide-based bifunctional primary amine, which allows polymer chains to be cross-linked through the reaction between cystamine and N-oxysuccinimide groups along the polymer chain. The cross-linked macromolecular barrier formed around the pore opening can be reopened by cleaving the disulfide bond of cystamine in the presence of dithiothreitol (DTT), a disulfide reducing agent. In this configuration, the gate operation is based on redox reactions in which the cross-linked polymer brush works as an off-on switch in response to redox signals. Integration of polymer brushes into mesoporous matrices has not been solely focused on the modification of nanoparticles, mesoporous thin films have also been the object of several investigations related to gated molecular transport in hybrid interfacial architectures. Modification of mesoporous silica thin films with polyelectrolyte brushes, for example, poly(styrene sulfonate) brushes, greatly facilitates the manipulation of the permselective properties of the membrane-like interface.[180] Essentially, the solvent and the mobile ionic species are taken up and confined into the nano-dimensional domains of the polyelectrolyte brushes hosted in the mesoporous matrix, which in turn determine (to a certain extent) whether diffusion through the pore is feasible or not. Other example include the integration of poly[2- (methacryloyloxy) ethyl phosphate] (PMEP) brushes into and onto mesoporous silica thin films to create mesostructured interfaces with reversible gate-like transport properties that can be controlled not only by protons but also by calcium ions.[181] Pore-confined PMEP brushes responded to the external triggering chemical signals by switching the transport properties of the mesoporous film [Fig. 11(A)]. The ion-gate response/operation was based on the protonation and/or chelation of phosphate monomer units in which the polymer brush works as an off-on switch in response to the presence of protons or Ca^{2+} ions. The combination of "caged" poly2-[(4,5-dimethoxy-2-nitrobenzoxy) carbonyl] aminoethyl methacrylate (PNVO-CAMA) brushes and mesoporous oxide thin films enables the creation of photoactive hybrid polymer–inorganic assemblies displaying light-activated gating and permselective transport of ionic species through 3D nanoscopic scaffoldings [Fig. 11(B)].[182] Interestingly, owing to the hydrophobic and bulky nature of the monomers that precludes their free diffusion into the hydrophilic inner environment of the nanoporous framework, SI-ATRP of NVOCAMA on initiator functionalized mesoporous films leads to the selective growth of the photolabile brush atop the mesoporous film. Selective tailoring of the "outer" chemistry of the hybrid mesostructured assembly is the key to control the gating properties. The marked hydrophobic nature of the outer PNVOCAMA layer precludes hydrated ions from entering into the nanoscopic channels and diffusing across the interfacial architecture. This scenario leads to the "hydrophobic gating" or "capping" of the mesopores that hinders the transport of solvated ionic species through the nanostructured interface. Light exposure cleaves the chromophore from the polymer layer and generates poly(2-aminoethyl methacrylate) (PAMA) brushes that upon protonation, that is, formation of NH_3^+ in acidic solutions, introduce permselective properties to the hybrid mesoporous film.

In previous examples describing the combined use of polymer brushes and mesoporous matrices, the inorganic material has been mostly relegated to mere scaffolds to create nanoscopic channels. Interestingly, Calvo et al.[183] have recently demonstrated that the interplay between the intrinsic acid-base properties of silica mesoporous frameworks and the pH-responsive character of the zwitterionic brushes can gave rise to new proton-gated cation-selective membranes with properties observed neither in mesoporous films nor in brushes, so far. In close resemblance to biological acid-sensing ion channels, mesoporous silica thin films modified with zwitterionic poly(-methacryloyl-L-lysine) brushes can act as gateable ionic filters discriminating and modulating the transport of cations while inhibiting the passage of anions over a wide pH range. A "bipolar" Donnan exclusion phenomenon is responsible for building up, in a reversible manner, a chemically actuated ionic barrier at pH < 5. This distinctive feature is exclusively due to the synergy between the electrostatic characteristics of the brush layer and the silica scaffold. It is clear that the combination of "hard" and "soft" building blocks to yield hybrid materials exhibiting functional domains ordered in space offers a wide range of opportunities for materials nanoarchitectonics[184] as well as the design of delivery systems.[185] For instance, bringing polymer brushes into the game opens a new dimension: the possibility to create phase separated regions (functional domains) within the pores that can behave as gatekeepers of nanoscale size, with highly controlled chemistry and interactions within restricted volumes.

Polymer Brushes for Efficient Heterogeneous Catalysis and Biocatalysis in Microreactors

Microreactors represent a huge potential for chemical industry in terms of process flexibility, capacity and viability. This is the reason why the advantages of using microreactors to enhance the efficiency of chemical reactions are increasingly harnessed in different types of chemical industries. Recently, Verboom and coworkers reported a novel use of polymer brushes as supports for the catalytic coating of the inner wall of microreactors.[186] Polyglycidylmethacrylate (PGMA) brushes bearing a large number of epoxy groups was used for attaching 1,5,7-triazabicyclo[4.4.0]dec-5-ene, an organic catalyst, via nucleophilic attack to the inner wall of a silicon-glass microreactor. By varying the thickness of the polymer brush the amount of catalyst was easily tuned and the Knoevenagel condensation reaction between benzaldehyde and malononitrile to give 2-benzylidene malononitrile was studied to monitor the performance of these catalytic microreactors. The macromolecular layer turned out to be highly effective in the catalysis. In all experiments carried out in the presence of the catalytic coating the reaction was complete in a few minutes. No reaction was observed when the reagents were flowed into a microreactor coated with
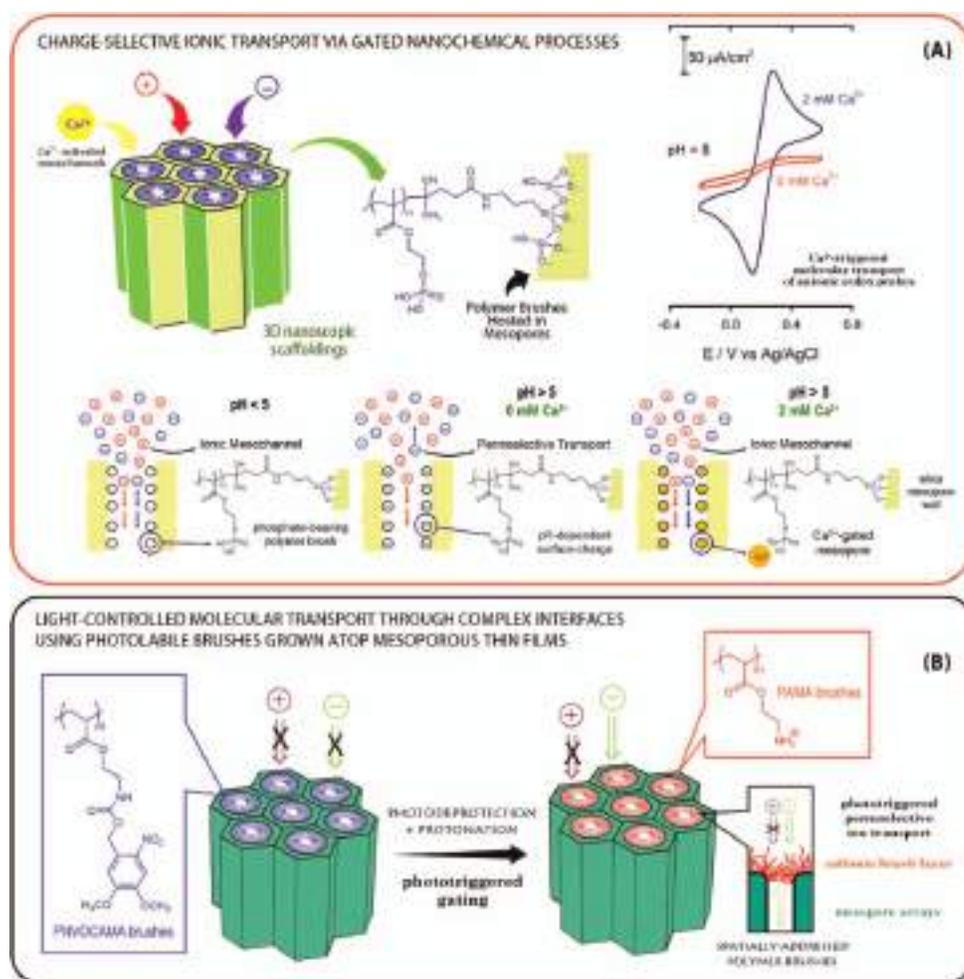
FIGURE 11 (A) Schematic depiction of the ionic transport processes taking place in mesoporous thin films modified with phosphate-bearing polymer brushes (PMEP) under different pH conditions and in the presence or in the absence of Ca^{2+} ions. Cyclic voltammograms (on the right) describe the molecular transport through PMEP-modified mesoporous thin films in the absence and in the presence of Ca^{2+} using $Fe(CN)_6^{3-}$ as a redox probe. From Brunsen et al., Langmuir, 2012, 28, 3583, © American Chemical Society, reproduced by permission. (B) Schematic representation describing the modification of mesoporous silica films with photolabile polymer brushes and their subsequent "uncaging" to build up a permselective polycationic barrier in the outer region of the film. From Brunsen et al., Chem Commun., 2012, 48, 1422, © Royal Society of Chemistry, reproduced by permission.

unmodified PGMA brushes for 2 h, thus suggesting the anchoring of the organic catalyst on the polymer brush did not affect their intrinsic catalytic properties. A rather similar approach was used to build up a polymer brush-metal nanoparticle hybrid film as an efficient supported catalyst in glass microreactors.[187] The inner walls of the microreactors were modified poly(hydroxyethyl methacrylate) (HEMA) brushes cross-linked with tetraethylene glycol dimethacrylate. Then, treatment with succinic anhydride enabled the introduction of carboxylic groups in the PHEMA-PEG brush layers. Subsequent incubation of the substrate in aqueous solutions of Ag^+ or Pd^{2+} ions followed by reduction with $NaBH_4$ promoted the homogeneous formation of Ag and Pd NPs, respectively, on the microreactor walls. Control over the polymer film thickness permits the tuning of the density of nanoparticles formed on the channel walls that, ultimately, defines the catalytic activity of the microdevice. The wide

applicability of the catalytic devices was demonstrated for the reduction of 4-nitrophenol and for the Heck reaction. The silver and palladium catalytic devices exhibited no leaching and could be reused for at least four months, without showing a decrease of catalytic activity. The same group also extended this concept to the design of microreactors exhibiting tunable biocatalytic activity using enzyme-functionalized polymer brush films[188] The lipase from *Candida rugosa* was immobilized on poly(methacrylic acid) brushes using typical *N*-hydroxysuccinimide coupling protocols. The amount of bound lipase was controlled by changing the brush thickness whereas the biocatalytic activity of the microreactor was monitored using the hydrolysis of 4-nitrophenyl acetate as a model reaction. Estimation of the Michaelis–Menten constants for brush-confined and free lipase revealed that both are similar. This indicates that the activity of lipase is not seriously affected upon immobilization to the polymer brush
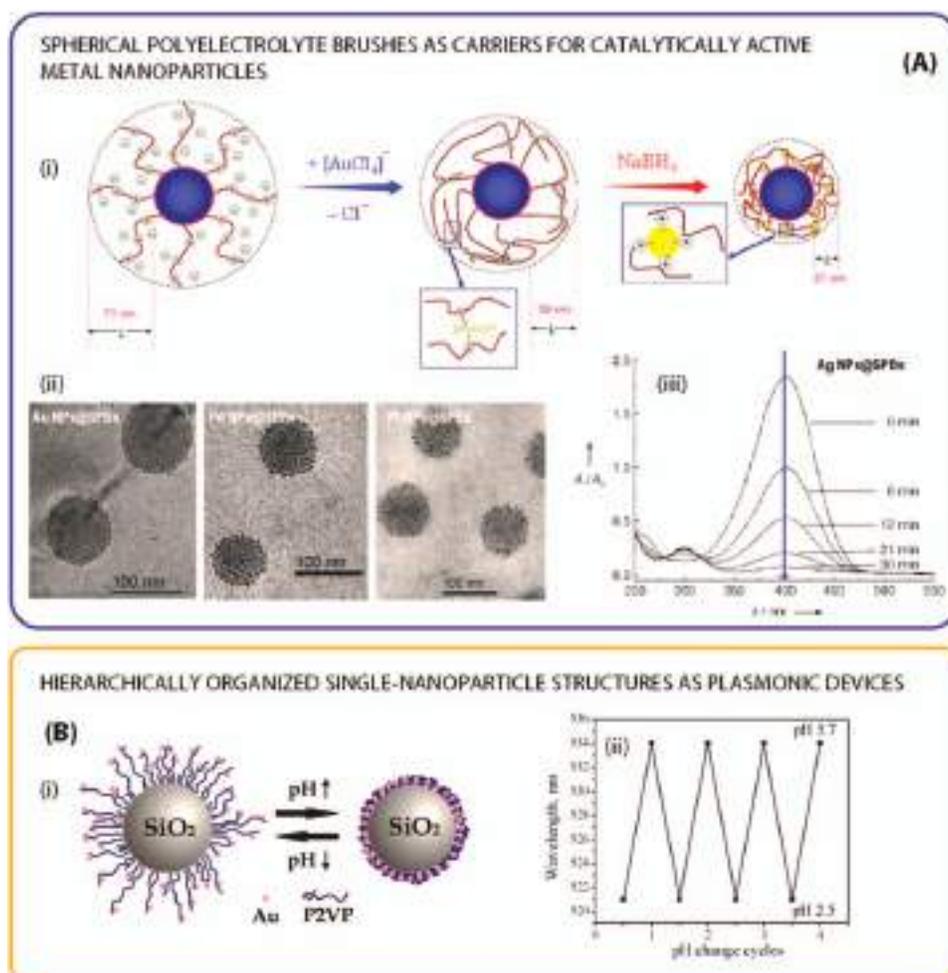
FIGURE 12 (A) (i) Schematic representation of the generation of gold nanoparticles inside spherical brushes (SPBs). (ii) Cryo-TEM images of different metal NPs encapsulated in spherical polyelectrolyte brush particles. From Ballauff et al., Macromol. Rapid Commun., 2009, 30, 806 and Macromol. Symp. 2007, 254, 42, © Wiley-VCH Verlag GmbH & Co. KGaA, reproduced by permission. (iii) Reduction of 4-nitrophenol by $NaBH_4$ in the presence of AgNPs@SPB. UV/Vis spectra of solutions of 4-nitrophenol measured at different times. From Ballauff et al., Angew. Chem. Int. Ed., 2006, 45, 813, © Wiley-VCH Verlag GmbH & Co. KGaA, reproduced by permission. (B) (i) Schematic representation of the pH-responsive behavior of a AuNPs@P2VP-SiO_2. (ii) Maximum wavelength of the surface plasmon peak as a function of pH change in the cycle between 2.5 and 5.7. From Minko et al., Langmuir, 2008, 24, 8976, © American Chemical Society, reproduced by permission.

in the microchannel wall. One attracting feature of this strategy is the facile control over the catalytic sites by simple changing the thickness of the brush layer which might be very useful in a wide variety of biocatalytic microreactors.

Nanoparticles at Spherical Polymer Brushes for Catalytic Purposes and Optical Transduction of Environmental Stimuli

Ballauff's group has extensively studied the construction of supramolecular hierarchical structures for catalytic purposes by means of spherical polyelectrolyte brushes incorporating different nanomaterials on their surface.[189] Typically, spherical polymer brushes consist of a solid core with dimensions in the 100 nm range onto which long polymer brushes are densely grafted. In the case of polyelectrolyte brushes constituting the soft shell the confinement/complexation of the counterions can be used to generate metal nanoparticles on

the surface of the colloidal core [Fig. 12(A)]. One of the striking advantages of these hierarchical systems is their ease of handling and filtering off that make them excellent carrier systems for applications in catalysis.[190,191] Along these lines, Ballauff and coworkers were able to develop spherical polyelectrolyte brushes as carriers for platinum nanoparticles in heterogeneous hydrogenation reactions[192] or bimetallic Au–Pt nanoparticles for the oxidation of alcohols.[193] Interestingly, this approach combining different chemistries in different length scales enabled the preparation of composites of metal nanoparticles and TiO_2 immobilized in spherical polyelectrolyte brushes[194] These composite particles have been synthesized by reduction of the respective metal (Au, Pt, Pd) ions adsorbed on the surface of as-prepared TiO_2 nanoparticles that are confined into poly(styrene sodium sulfonate) brushes grafted on a polystyrene core.

HIGHLIGHT

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Metal nanoparticles are only generated on the surface of the anatase particles having a size of ~10 nm. The combination of materials in the form of a very stable colloidal system has proven to be an excellent heterogeneous photocatalyst for the degradation of rhodamine B under UV irradiation. For instance, the photocatalytic activity of the hierarchical hybrid particles was 2-5 times higher than that of the pure TiO_2 particles. This finding was ascribed to the enhanced adsorption of the dye at the metal $NP@TiO_2@$polyelectrolyte brush hierarchical interface. A similar concept was also developed by Minko and coworkers[195] to fabricate hierarchically organized single-nanoparticle structures employing 200 nm silica cores modified with pH-responsive poly(2-vinylpyridine) brushes, into which 15 nm gold nanoparticles were synthesized. Swelling and collapse of the polymer brush driven by pH changes in the range of 3-6 resulted in the modulation of the interparticle distance and the concomitant shift in the maximum wavelength of the surface plasmon absorption peak [Fig. 12(B)]. Such hierarchically assembled nanostructures present potential capabilities to be used as free-standing single-particle sensors in various miniaturized analytical systems.

Macromolecular Design of Chemically-Modified Electrodes with Polymer Brushes

Deliberate control of reactivity at the electrode/solution interface plays a pivotal in modern electrochemistry. Such control has a profound impact on many applications including electrocatalysis, corrosion, electroanalysis, electrochromics, etc. Chemical modification of electrode surfaces with polymer layers has been studied for many decades,[196] yet it remains challenging to devise simple protocols to control at a molecular level the nanoscale engineering of such functional assemblies formed on the conducting supports.[197] In this context, polymer brushes grafted on electrode surfaces have recently emerged as invaluable building blocks for such nanoengineered architectures in which a broad variety of design parameters such as porosity/permeability, tunable environmental sensitivity, hydrophobicity, charge, thickness or spatial localization of functional groups can be controlled at will.

The synthesis and electrochemical characterization of ferrocene-containing methacrylate (FcMA) brushes on indium tin oxide (ITO) electrodes using SI-ATRP was recently reported by Pyun and coworkers.[198] Cyclic voltammetric studies revealed significant solvent effects in the electrochemical response of the polymer brushes being attributed to the interplay between hindered counterion diffusion across the film and differences in electron transfer rates between electroactive groups. Electrochemical studies on block copolymers of PFcMA and PMMA with varied sequences and distances between PFcMA segments and the ITO electrode eloquently confirmed that the block sequence directly has an immediate impact on the electrochemistry of these films. Nitroxide polymer brushes grafted onto silica nanoparticles[199] and ITO planar surfaces[200] via SI-ATRP have been investigated as cathodes for organic radical batteries [Fig. 13(A)]. The covalent bonding of nitroxide polymer brushes

to the ITO surface prevents their dissolution by solvents and thus improves the cycle-life performance of batteries. In addition, due to the rapid electron-transfer process and a high diffusion coefficient of nitroxide it is expected that these polymer brush-based systems display high rate charge and discharge performance. The formation of electroactive conjugated polymer brushes of poly(thiophene) and poly(phenylene) have been prepared via a surface-initiated Kumada-type polycondensation reaction, yielding films with a thickness up to 42 nm.[201] Poly(3-alkylthiophenes) brushes were also grown via surface-initiated polycondensation of 2-bromo-5-chloromagnesio-3-alkylthiophene.[202] End-tethered poly-(p-phenylene) (PPP) brushes having high molecular weight and low polydispersity can be obtained by aromatization of poly(1,3-cyclohexadiene) (PCHD).[203] The synthesis of grafted homopolymer and block copolymer films can be accomplished using SI-RAFT polymerization from electropolymerized polythiophene macro-RAFT agents on flat electrode substrates.[204] SI-RAFT polymerization of different monomers like styrene, pentafluorostyrene, methyl methacrylate, tertbutyl acrylate or carbazole ethyl methacrylate from conjugated polymer films (such as polythiophene) offers immense opportunities to construct layered films integrating and locally addressing different functionalities on the electrode surface.

Transport properties of homopolymer brushes tethered on electrode surfaces have been recently investigated using Faradaic impedance spectroscopy demonstrating that polyelectrolyte brushes have switchable electron-transfer resistance.[205,206] The swollen poly(methacryloyloxy)-ethyl-trimethyl-ammonium chloride brush was shown to have good ion permeability, while high resistance was observed for the collapsed brush in the presence of counterions forming ions pairs with the charged monomer units. Electrochemically driven stimuli can be exploited to achieve reversible "closing" of electrode interface modified with polymer brushes.[207] In one example, ITO electrodes modified with poly(4-vinyl pyridine) (P4VP) brushes were used to switch reversibly the interfacial activity by the electrochemical signal. Electrochemical reduction of O_2 promotes a pH increase at the electrode interface that concomitantly triggers the collapse of the P4VP brush on the electrode surface. As a result, the initially swollen protonated brush which was permeable to the anionic $[Fe(CN)_6]^{4-}$ redox species, turned into a deprotonated hydrophobic collapsed layer, that is, impermeable to anionic redox species. Motornov et al.[208] described a novel approach to create gate-like macromolecular systems using mixed poly(dimethylsiloxane) (PDMS) and poly(2-vinylpyridine) (P2VP) brushes anchored on ITO electrodes. They showed that mixed polymer brushes are able to regulate the transport of ions and gate electrochemical processes thus offering remarkable and versatile opportunities for chemical gating in complex solid–liquid interfaces. The gating properties are based on the regulation of ion transport through nanoscopic domains that are reversibly formed in the nanostructured thin film in response to pH variations. The same group also investigated the use of ITO electrodes modified
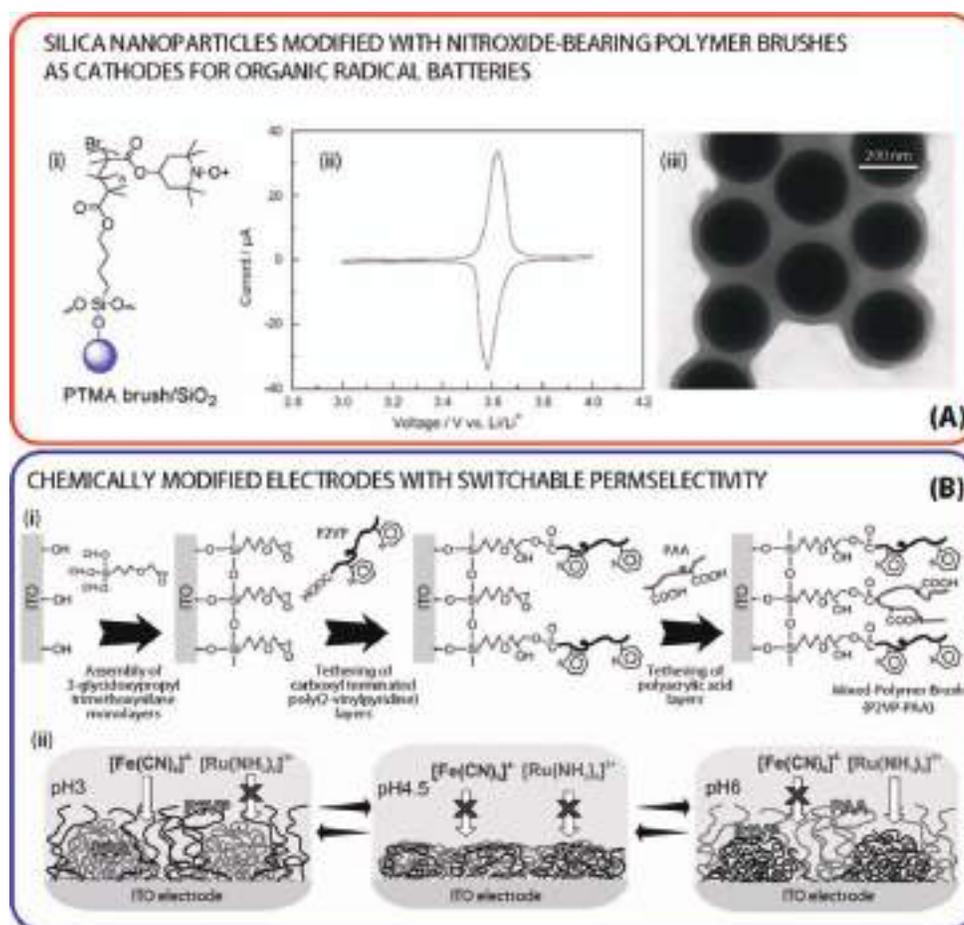
FIGURE 13 (A) Scheme of poly(2,2,6,6-tetramethylpiperidin-1-oxyl-4-yl methacrylate), (PTMA) brush on silica nanoparticles. (ii) Cyclic voltammogram for the PTMA brush/silica nanoparticles composite electrode in 1.0 M LiClO$_4$. (iii) TEM micrographs of PTMA brush/silica nanoparticles. From Lee et al., J. Power Sources, 2011, 196, 8098, © Elsevier B.V., reproduced by permission. (B) (i) Stepwise modification of the ITO electrodes to yield the mixed polymer brush composed of P2VP and PAA. (B) Simplified scheme describing the polymer brush permeability for the differently charged redox probes controlled by the solution pH value: (a) the positively charged protonated P2VP domains allow the electrode access for the negatively charged redox species; (b) the neutral hydrophobic polymer thin-film inhibits the electrode access for all ionic species; (c) the negatively charged dissociated PAA domains allow the electrode access for the positively charged redox species. From Katz et al., Electroanalysis 2010, 22, 35, © Wiley-VCH Verlag GmbH & Co. KGaA, reproduced by permission.

with mixed polymer brushes composed of poly(2-vinylpyridine) and polyacrylic acid (PAA) to create switchable interfacial properties discriminating negatively and positively charged redox species [Fig. 13(B)].[209,210] This binary macromolecular interface allowed effective discrimination of the cationic and anionic redox species, separating their electrochemical responses by the application of different pH values. The cationic redox species reached the electrode surface through the anionic PAA domains and revealed their electrochemical activity at pH > 5.5, while the electrochemical process of the anionic redox species was inhibited. On the other hand, the anionic redox species were electrochemically active at pH < 3.5, when the protonated P2VP brush domains allowed their passage to the electrode surface while transport of the cationic redox species was effectively inhibited. This kind of interfacial configurations allows the develop-

ment of electrochemical multiplexers converting chemical signals to switchable electronic outputs.

Opal Nanopores Modified with Polymer Brushes: Towards Rational Design of "Smart" Colloidal Nanomembranes

Artificial opals having a periodic and tailored structure attracted great attention in the past decade due to their novel properties and potential applications in condensed-matter physics. For example, opals were used as templates to fabricate complex topographies which may present different optical properties. Noteworthy, despite the growing importance of opals in optical applications, one interesting feature of these structures is closely related to membrane technology. Opals contain highly ordered arrays of 3D interconnected nanopores whose size can be controlled by
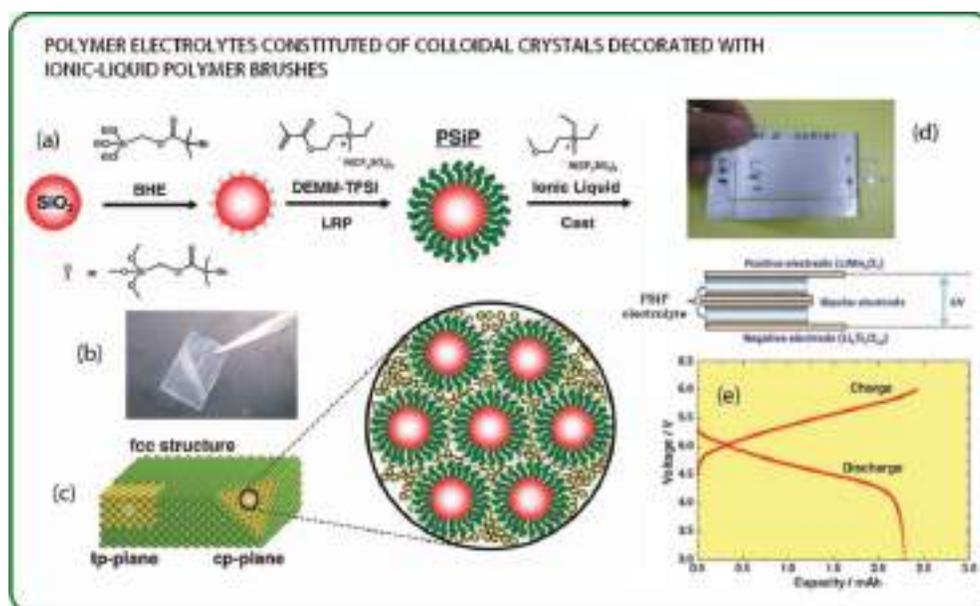
FIGURE 14 (a) Preparation process for novel PSiP/IL-solid electrolyte with three-dimensionally assembling PSiPs. (b) Photograph of produced solid film. (c) Analyzed structure of PSiP array in the solid state. (d) Photograph and illustrated bipolar-cell structure. (e) charge/discharge curve of a lithium-ion battery using PSiP/IL solid electrolyte. From Sato et al., Adv. Mater., 2011, 23, 4868, © Wiley-VCH Verlag GmbH & Co. KGaA, reproduced by permission.

changing the size of the silica spheres used to assemble the structure. In 2006, Zharov's group demonstrated for the first time that surface-initiated polymerization of polymer brushes can be conducted inside opal nanopores without perturbing the opal lattice structure[211] which in turn facilitated the formation of uniform polymeric layers inside the opal nanopores. In this way, they were able to control not only the chemical nature of the opal inner environment but the effective size of the modified nanopore by simply adjusting the polymerization time, that is, brush thickness. This early attempt to control the chemical properties of the opal structures with polymer brushes opened the way to the modification of opal nanopores with stimuli-responsive polymers with the aim of generating tailor-made "smart" nanomembranes. Modification of colloidal films assembled from silica spheres with PNIPAM brushes exhibited a positive or negative gating behavior depending on the thickness of the polymer brush.[212] When thin PNIPAM brushes were grown on the nanopores, transport through the opal structure occurs in the polymer-free volume available. Increasing the temperature leads to the brush collapse on the pore walls, providing a larger volume for diffusion (positive gating). On the other hand, when polymerization is conducted for a sufficiently long time and thick PNIPAM were grown, polymer chains growing from the opposite nanopore walls become long enough to interpenetrate and form a gel-like environment. This hybrid structure is in principle highly porous and does not hinder the molecular transport through the opal; however, above LCST the gel-like polymer dehydrates and becomes impermeable to aqueous, solvated probes (negative gating). Exploiting this strategy centered on the design of responsive colloidal membranes with polymer membranes, the

same group was able to fabricate proton conducting membranes using poly(3 sulfopropylmethacrylate) and poly(stryrenesulfonic acid) brushes,[213] pH-responsive opal-like membranes using poly(2- (dimethylamino)ethyl methacrylate) (PDMAEMA)[214] brushes and dual (thermo-pH) responsive platforms using colloidal films modified with poly(L-alanine) brushes.[215]

Solid-State Polymer Electrolytes Based on Hybrid Colloidal Crystals: Polymer Brushes as Building Blocks in Lithium-Ion Rechargeable Batteries

For many years now, polymer electrolytes have been considered as key materials for the development of high energy density rechargeable batteries. Solid electrolytes can be considered as a new class of solid state ionic materials which exhibit an exceptionally high ionic conduction at room temperature close to that in the range of liquid/aqueous electrolytes. In fact, these solid state ionic materials attracted tremendous technological attention worldwide due to potential to eliminate and/or minimize the shortcomings of liquid/aqueous electrolytes.[216] Very recently, Sato and coworkers[217] developed a groundbreaking concept for fabricating a leak- and vapor-free, nonflammable, solid electrolytes with highly ion-conductive network channels. This interesting approach is based on the three-dimensional self-assembly of silica particles modified with ionic liquid-type polymer brushes. In this way, polymer brush domains are continuously connected forming network channels on the nanometer scale that in turn enhance the ion conduction through the structural hybrid assembly (Fig. 14). Then, the solid-state polymer electrolyte was integrated into a bipolar lithium-ion rechargeable battery and connected with a bipolar electrode of $Li_4Ti_5O_{12}$

(anode) and $LiMn_2O_4$ (cathode) layers, thus giving a $Li_4Ti_5O_{12}$/hybrid solid electrolyte/$LiMn_2O_4$ unit cell. The discharge specific capacity and Coulombic efficiency of the hybrid assembly were 2.3 mAh and 95%, respectively, at the fifth charge and discharge operation cycle. Coulombic efficiency after 50 cycles was 98%. This work clearly demonstrates that the molecular design of ion conducting pathways using polymer brushes can improve the performance of lithium-ion rechargeable batteries, thus making it possibly applicable to practical use.

Development of Novel Proton-Conducting Membranes with Enhanced Properties Using Polymer Brushes

Proton exchange membranes (PEMs) are key constituting elements in different industrial applications and particularly in energy conversion technologies.[218] To date, the PEMs are typically constituted of perfluorinated polyelectrolytes, like Nafion. This material is characterized by forming nanoscopic hydrophilic channels suitable for the conduction of protons across the membrane, even if 60% of the hydrophilic domains at the surface of an operating Nafion membrane remain inactive.[219] On this basis, Azzaroni and coworkers developed a new approach to the facile large-scale fabrication of robust silicon membranes with artificial proton conducting channels based on the molecular design of well-oriented hydrophilic domains using polymer brushes.[220] In principle, ordered two-dimensional macroporous silicon membranes were rendered proton conducting by growing thick uniform polyelectrolyte brushes using pore-confined SI-ATRP throughout the porous matrix.[221] The fabricated silicon-poly(sulfopropyl methacrylate) hybrid membranes were evaluated for their proton conductivity, ion exchange capacity, and water uptake revealing a temperature- and humidity-dependent functional behavior similar to that exhibited by Nafion. These hybrid membranes displayed proton conductivities in the range of 10^{-2} S/cm. The very possibility of fabricating proton exchange membranes in which the polyelectrolyte environment is deliberately created into a robust, rigid scaffold marks a profound conceptual difference from typical approaches relying on phase-segregated all-polymer membranes. Polyelectrolyte domains bearing sulfonate groups have been used extensively to create hydrophilic channels in PEMs; however, dehydration at low relative humidity promotes a pronounced decrease in the proton conductivity. To overcome this problem these authors introduced comonomers into the molecular design of the proton channel to improve the hydration of the polyelectrolyte bearing sulfonate groups (Fig. 15). Poly(ethylene glycol) (PEG) derivatives are known to have excellent hydroscopic properties, hence, in the presence of PEGylated macromolecular architectures, water molecules are able to hydrogen bond with the ethylene oxide units of the polymer chains, thereby leading to the formation of large clusters and dynamic hydrogen-bonded networks. Note that this modification at the molecular cannot be easily achieved in typical phase-segregated membranes; otherwise it will affect the equilibrium configuration of the segregated domains. Interestingly, the incorporation of a small fraction of MeOEGMA monomer

units in the polyelectrolyte brush architecture promoted a five orders of magnitude increase in the proton conductivity measured at low relative humidities (Fig. 15).[222] More importantly, these platforms displayed high conductivity values ($\sim 10^{-2}$ S cm^{-1}) regardless of the humidity, thus surpassing the performance of Nafion. These experiments highlight a promising alternative for fabricating tailorable proton conducting membranes with highly optimized physical and chemical characteristics that could lead to new methods for the production of PEMs meeting current industrial requirements.

Polymer Brushes Confined in Single Solid-State Nanopores: Biomimetic Nanofluidic Elements with Enhanced Properties

The creation of synthetic devices that mimic functionality of biological systems has attracted a lot of scientific interest due to their application as biomimetic systems. Among a wide variety of bio-inspired devices, designed nanopores and nanochannels with an embedded functionality are of particular interest because of their potential applications in nanofluidic electronics, biosensing, separation, synthetic biology, and single-molecule manipulation. In this respect, the development of nanopores derivatized with "active" macromolecular units leading to the modulation of their physicochemical properties provides an exciting new approach to gain control over the ion transport through the nanopores. On this basis, Azzaroni et al. developed pH-tunable nanofluidic elements capable of rectifying the transmembrane ion transport using pH-responsive polymer brushes integrated on the inner walls of ion-track etched single nanochannels. It has been demonstrated, both theoretically[223] and experimentally,[224] that the rectifying characteristics of the nanopores emerge due to a synergy of the entropic driving force caused by the channel asymmetry and the electrostatic effects due to the fixed charges on the pore wall. As a consequence, finding new avenues to manipulate the surface charges of conical nanopores is of paramount importance to further expand the potentialities of these nanosized systems. The growth of zwitterionic (poly(methacryloyl-L-lysine) brushes provides a useful approach to finely tune the ionic rectification characteristics of the nanochannels.[225] By simply varying the environmental pH above or below the isoelectric point of the zwitterionic moieties the magnitude and the nature of the charge can be finely tuned. At low pH values, protonated amino groups render the nanochannel selective to anions displaying the rectification properties characteristic of the conical channel with positive fixed charges. On the contrary, at high pH values, the presence of anionic carboxylate groups reverses the permselective behavior of the nanochannel and their concomitant rectification properties. In a similar vein, the rectifying properties of pH responsive conical nanochannnels can be enhanced by using polyprotic polymer brushes as highly tunable building blocks.[226] Functionalization of asymmetric ion-track etched nanochannels poly2-(methacryloyloxy) ethyl phosphate enabled the creation of rectifying nanofluidic devices whose transport properties bear a close resemblance to a pH-actuated "electrostatic nanovalve" [Fig. 16(A)]. Jiang's group also developed a very interesting concept to
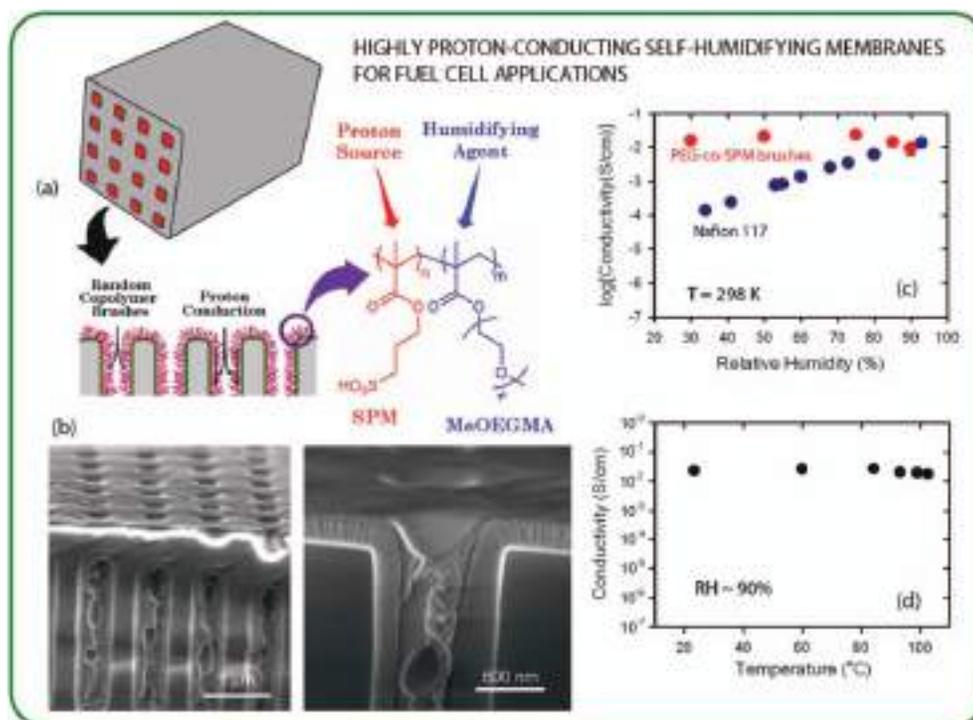
FIGURE 15 (a) Chemical structure of the random copolymer brush and simplified illustration of the ordered two-dimensional macroporous silicon membrane modified with the polymer brushes. (b) Scanning electron micrographs corresponding to the silicon membrane modified with polySPM-co-MeOEGMA brushes. (c) Conductivity versus relative humidity plots corresponding to the silicon membrane modified with polySPM-co-MeOEGMA brushes and Nafion 117 membrane. (d) Conductivity versus temperature plot corresponding to the silicon membrane modified with polySPM-co-MeOEGMA brushes. From Azzaroni et al., Angew. Chem. Int. Ed., 2009, 48, 3124, © Wiley-VCH Verlag GmbH & Co. KGaA, reproduced by permission.

create nanodevices with pH-triggered rectification properties through the asymmetric modification of single nanochannels with pH-responsive brush-like architectures.[227]

In addition to the asymmetric single nanochannels, cylindrical polymer nanochannel modified with weak polyelectrolyte brushes[228] also exhibit pH-modulated ionic transport; however, owing to the symmetric chemical and physical characteristics of the nanochannel, they do not display rectifying properties. The creation of the pH switchable and tunable single nanochannels displaying ionic transport properties similar to the typical behavior observed in many biological channels was accomplished through the modification iontrack etched nanopores with polyvinylpyridine (PVP) brushes. These nanochannels can be switched from an "off" state to an "on" state in response to a pH drop [Fig. 16(B)]. Current-voltage curves of these single nanochannels modified with polyvinylpyridine (PVP) brushes eloquently show the dramatic effect of pH on the transport properties. By increasing the pH from 2 to 4, and finally to 10, a significant decrease in the transmembrane ionic current was observed under the same applied bias. The "on/off" switching was based on the manipulation of the surface charges of the channel walls via the protonation of the brush layer, which in turn control the channel conductivity.[229]

Ion transport through solid-state ion channels can be also activated by temperature changes that transduce this stimulus into molecular conformational changes that, in turn, lead to the opening and closing of the nanogates. Azzaroni et al.[230] reported the modification of conical single nanochannels with thermoresponsive PNIPAM brushes in order to build up molecular gates nanoactuated by temperaturedriven conformational transitions. At room temperature (below the LCST transition) PNIPAM brushes remain in a swollen conformation, thus decreasing the effective cross section of the nanochannel which is associated with a low conductance state of the nanochannel. Upon increasing the working temperature above LCST brushes experience a transition into a collapsed state, leading to an increase of the effective cross-section of the nanochannel. The temperatureinduced widening of the nanochannel leads to an effective increasing in the nanochannel conductance. As a result, the thermoresponsive brush can act as thermally driven macromolecular gate controlling the ionic flow through the nanochannel. Moreover, this thermoresponsive nanochannel is completely reversible, due to the reversibility of conformational states of the PNIPAM brushes. Jiang's group[231] gave an interesting twist to this concept through the "grafting-to" of thiol-terminated PNIPAM brushes into gold-coated conical nanochannels. This brush assembly strategy enables the facile adsorption of anions on the bare gold domains around the grafted polymer chains, thus conferring negative charges to the nanoconfined system. Hence, these channels not only display thermoresponsive transport properties but also they
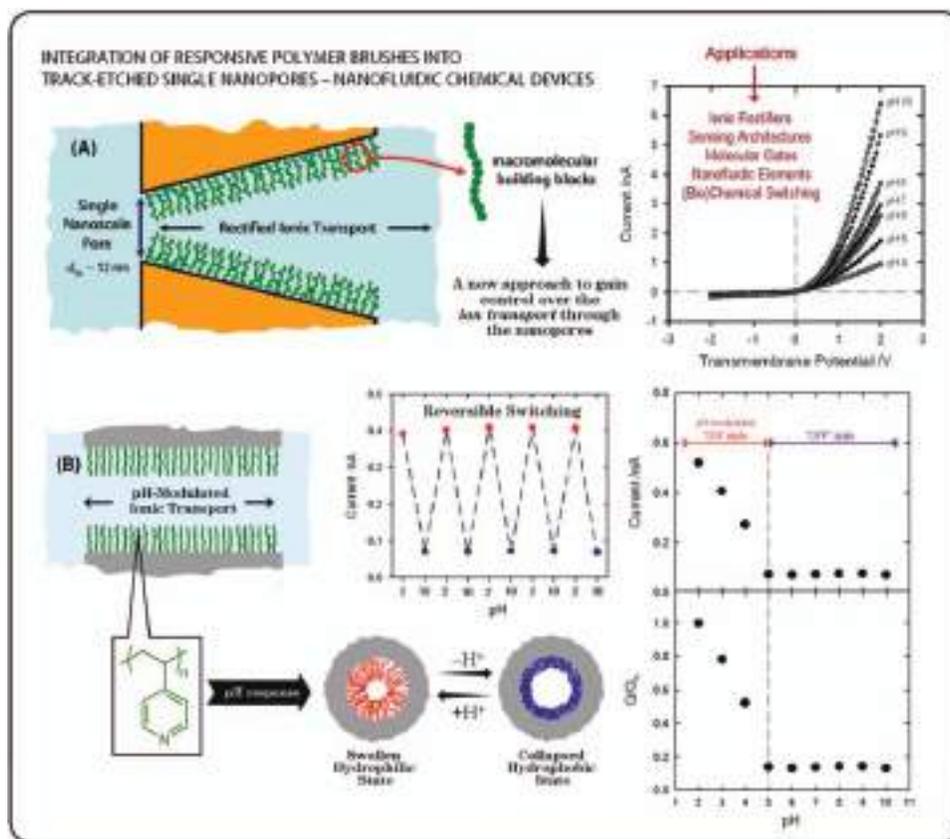
FIGURE 16 (A) (left) Schematic depiction of a conical nanopore modified with polymer brushes—(right) I–V curves corresponding to a single conical nanopore modified with poly 2-(methacryloyloxy) ethyl phosphate brushes measured at different pH values (using 0.1 M KCl as electrolyte). From Azzaroni et al., Chem Comm. 2010, 46, 1908, © Royal Society of Chemistry, reproduced by permission. (B) Simplified description of the cylindrical nanochannel.modified with poly(4-vinyl pyridine) brushes, reversible variation of the transmembrane ionic current passing through the PVP brush-modified nanochannel upon alternating the environmental pH between 2 and 10, and representation of the transmembrane ionic current and the normalized nanochannel conductance as a function of the environmental pH for a PVP brush-modified cylindrical nanochannel. From Azzaroni et al., Nano Lett. 2009, 9, 2788, © American Chemical Society, reproduced by permission.

are able to rectify the ionic current. At temperatures lower than ∼34 C, the nanochannel rectifies the ionic current. The degree of the rectification can be enhanced upon rising the working temperature. While at temperatures higher than 38 °C, the nanochannel no longer rectifies the ionic current, showing linear and ohmic ionic transport behavior. Creating macromolecular assemblies into conical nanopores through surface-initiated polymerization approaches represents a very versatile means of fabricating multiresponsive nanopores by simply using copolymer brushes presenting different predefined functionalities. In this way, Jiang et al.[232] developed solid state nanopores integrating ionic gating and rectifying functions into the same nanosystem. Dual-functional nanofluidic devices were afforded by synthesizing temperature- and pH-responsive (PNIPAM-co-PAA) brushes onto the walls of conical nanopores. At room temperature the nanopore operates on a low ion conducting state. Then, upon increasing the temperature to 40 °C, the nanopore switches to a high conduction state. Independently, the rectifying properties can be tuned by varying the pH of the work-

ing solution. In neutral or alkaline solutions, carboxylate groups are ionized and the nanopore rectifies the ionic current. On the other hand, in acidic solutions nanopores display no rectifying properties. Dual responsive nanopores can be also accomplished through the integration of homopolymer brushes displaying multistimuli response. One example is poly[2-(dimethylamino) ethyl methacrylate] (PDMAEMA) exhibiting a LCST 40–50 °C and ionizable tertiary amine moieties on the polymer backbone (pK_a ∼ 7.0). Very recently, Zhang et al.[233] demonstrated that conical nanopores modified with PDMAEMA brushes be reversibly switched between high (on) and low (off) conducting states with high gating efficiency due to the conformational changes of the homopolymer brush effected by varying the pH and temperature of the working electrolyte solution. The versatility of these fluidic nanosystems illustrate the capabilites of polymer brushes to achieve an accurate and reversible control of the physical and chemical characteristics of nanoconfined environments with dimensions comparable to biological channels.
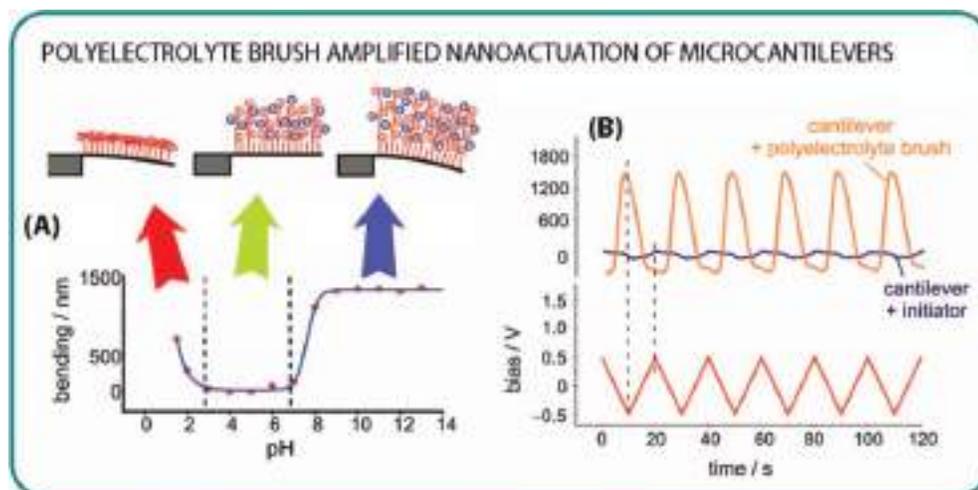
FIGURE 17 (A) Observed bending of single-side PMEP brush-modified cantilever with changing pH and schematic illustration of brush conformation in different regimes. From Zhou et al., J. Am. Chem. Soc. 2006, 128, 5326, © American Chemical Society, reproduced by permission. (B) Actuation of PMETAC brush-modified cantilever in response to the applied bias. The actuation directly follows the applied bias without apparent lag; initiator-only cantilevers show a very small response to changes in electric field. From Zhou et al., Nano Lett., 2008, 8, 725, © American Chemical Society, reproduced by permission.

Integration of Polymer Brushes into Micromechanical Devices: Mechanical Transduction of Chemical Stimuli

For several years, researchers engaged in nanotechnology have been interested in the idea of building nanosystems capable of transducing chemical inputs into mechanical forces. In this respect, microcantilever devices have demonstrated to be versatile sensor platforms with straightforward sensing mechanisms. Physicochemical changes onto the sensing element, that is, cantilever, shift its resonance frequency and changes its surface forces (surface stress). On the other hand, molecular changes on a sensing element composed of two chemically different surfaces produce a differential stress between the two surfaces and induces bending.[234] Polymer brushes are attractive building blocks for mechanosensitive systems based on microcantilever devices because their conformation and chemical state are highly sensitive to the environment and their synthesis is flexible enough to permit selective modification of the cantilever surface. The nanoactuation of cantilevers using responsive polymer brushes has attracted considerable interest due to their potential as "soft" nanoactuators.[235,236]

Huck's group reported the integration of responsive polyelectrolyte brushes and microcantilever devices with the aim of attaining reversible nanoactuation arising from large conformational changes in response to pH and electrolyte concentration.[237] Polymethacryloyl ethylene phosphate (PMEP) brushes selectively grown on one side of the cantilever via SI-ATRP enabled the highly reversible actuation of cantilevers as well as the possibility to control the magnitude of cantilever bending by placing the brushes in different ionic strength solutions [Fig. 17(A)]. The versatility of the chemical strategy based on the use of polyelectrolyte brushes allowed the manipulation of a wide range of parameters which govern the bending behavior, including grafting density, chain length, nature of the monomer units or even the nature of the electrolyte. This strategy was further extended by the same group to the electroactuation of microcantilevers coated on one side with cationic polyelectrolyte brushes [Fig. 17(B)].[238] By applying an alternating positive and negative bias to a polyelectrolyte brush-covered cantilever, significant surface stresses were generated. According to these authors this phenomenon is governed by a correlation between the conformational changes of the polymer chains and the reorganization of ions due to the applied potential. In a similar vein, Gutmann, Berger and coworkers demonstrated that the strain produced in poly(methyl methacrylate) brushes on cantilevers could be used as an analytical tool to determine solvent composition.[239] Depending on the solvent conditions polymer brushes can stretch away from the surface creating significant surface stresses due to interchain repulsion. Zauscher and collaborators[240] also showed that cantilevers coated with poly[(N-isopropylacrylamide)-co-(N-vinylimidazole)] copolymer brushes were responsive not only to the solvent nature (water and methanol mixtures) but also to the pH. The NIPAM monomer units provided solvent-responsive characteristics whereas the vinylimidazole monomer introduced pH responsiveness to the polymer brush. They showed that the cantilever bending response increases with increasing brush height, but the relative change in cantilever deflection, when cycled between good and poor solvent, remains independent of brush height. This suggests that already thin polymer brush layers are sufficient to elicit the full sensing potential of a cantilever.

Mechanochromic Polymer Thin Films Based on Dye-Loaded Polyelectrolyte Brushes

Mechanochromic polymers, that is, polymers that exhibit a color change on the application of mechanical stress, have been investigated due to their possible use in materials applications.[241,242] Azzaroni et al.[243] exploited the richness of strong polyelectrolyte brushes as mechanotransduction
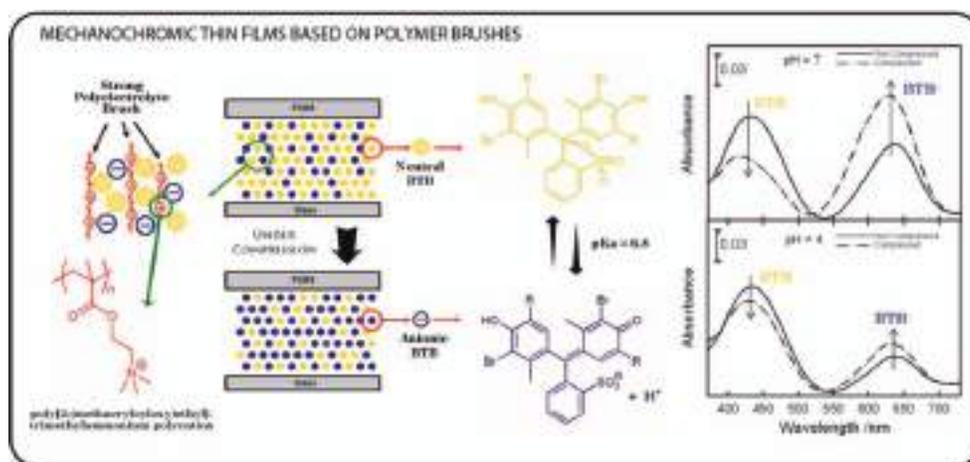
FIGURE 18 (Left) Simplified depiction of the variation in the population of neutral and anionic bromothymol blue (BTB) species inside PMETAC brush films upon compression. Also depicted in the schematic representation are the chemical structures corresponding to the cationic polyelectrolyte brush and the neutral and anionic form of the BTB dye. (Right) UV/Vis spectra corresponding to the compression experiments for BTB-loaded PMETAC brushes in a hydrated environment at different pH values: (a) pH 7 and (b) pH 4. Dotted and solid lines refer to spectra taken under compression and with no compression, respectively. The arrows indicate the direction of changes upon compression. From Azzaroni et al., Angew. Chem. Int. Ed., 2006, 45, 7440, © Wiley-VCH Verlag GmbH & Co. KGaA, reproduced by permission.

units to create mechanosensitive macromolecular systems capable of converting physical forces into chemical information, thus leading to "smart" thin films whose response can be triggered upon mechanical solicitation. Strong polyelectrolyte brushes densely grafted onto a surface exhibit interesting "mechanoacid" behavior when subjected to strong confinement. Charged polymer chains bearing like charge monomers in a wet environment experience repulsive Coulombic forces, causing the chains to stretch from the surface (extended conformation).[244] The presence of electrolytes screening these Coulombic forces may cause a pronounced conformational change causing the collapse of the chains (collapsed conformation). When strong poly[(2-methacroyloxy)ethyl]trimethylammonium chloride (PMETAC) brushes are compressed by external mechanical force, an unfavorable environment of high ionic strength is created due to the mechanically induced confinement and the intrinsic resistance of brushes to collapse under mechanical pressure.[245] However, when brushes are loaded with easily ionizable molecules, such as bromothymol blue (a pH sensitive dye), they can act as a hidden source of counterions that emerges when the brushes are subjected to mechanical forces (Fig. 18). Bromothymol blue (BTB) molecules loaded into the PMETAC brushes dissociate according to the equilibrium between the neutral (yellow) and anionic (blue) forms due to the charged environment. Compression of the dye/brush film with polydimethylsiloxane (PDMS) slides caused a large increase in absorbance for the anionic form (at $\lambda = 625$ nm) and an irreversible compression of the material (Fig. 18). This experimental evidence indicated that repulsive Coulombic forces arising from the mechanical compression were balanced by dissociation of BTB to locally produce counterions, which in turn leads to a color change in the brush layer. These results demonstrate the interesting use of polymer

brushes as mechanotransduction elements suitable for the fabrication of very sensitive and low-cost pressure-sensing thin film devices.

SUMMARY AND OUTLOOK—LOOKING BACK AND LEAPING FORWARD

During the past decades, polymer brushes emerged as a new class of building blocks offering a new dimension in the design of advanced materials with controlled interfacial properties. Polymer brushes have now come a long way and borne many fruits. They have outpaced other polymer thin film technologies in terms of topological and functional versatility owing to their exquisite control over grafting density, chemical composition, film architecture and thickness, which can be easily manipulated through straightforward preparative procedures. Thin films are very simple to construct and allow the formation of conformal thin film films on planar, concave or convex substrates holding impressive potential in a wide range of applications.

The unique characteristics of polymer brushes offer a myriad of possibilities for playing with the chemistry of the monomer units and their supramolecular organization in different environments for the fabrication of stimuli-responsive surfaces. Surface-grafted polymer films have been integral to control the interactions of materials with biological entities, generate arrays of ligands at an interface and manipulate the adhesion of cells. The combination of nanoparticles and polymer brushes offers synthetic routes to nanostructured materials and composites that can be used in catalysis, plasmonics, or nanomedicine. Considerable interest and data is presently being generated on the potential health and environmental implications of nanoparticles and how they can be controlled using polymer brushes as capping agents.

HIGHLIGHT

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Integration of polymer brushes and porous materials in fuel cells and lithium battery electrodes can produce composite nanostructures with enhanced properties leading to cells with increased capacity and extended operation life. These experimental findings eloquently illustrate a new role of polymer brushes in energy-related areas. Bioelectrochemical devices based on polymer brushes are also true demonstrations of the potential feasibility of integration between biology, electronics and polymer chemistry to devise nanosystems with potential benefits for health, environment, defense, agro, food and other industrial applications. In a similar way, the development of nanoengineered optoelectronic devices using polymer brushes as structural and functional units holds a mid-term promise for building up light-emitting diodes, photovoltaic cells and field-effect transistors with improved performance.

In the light of the above discussion it is clear that polymer brushes have provided an entirely new way of doing chemistry, physics and even biology at surfaces with the aid of polymer science. Our understanding of polymer brushes at the nanoscale and our ability to control their function and structure granted access to a range of "soft" interfaces with novel characteristics, functions and potential applications that could lead, in a not too distant future, to interesting commercial technologies. It may be that some of the potential applications that were identified are never realized on a large scale, whereas others that are currently unforeseen could have a major impact in industry. Nanomanufacturing with polymer brushes is still in the conceptual stage of development and will probably have to face many challenging technical and cultural barriers. In this respect, reproducibility and repeatability of nanomanufacturing protocols will be essential. Another important aspect of developing nanomanufacturing technologies for the production of materials and devices based on polymer brushes is the necessity of gathering expertise and services from a multidisciplinary force of engineers and scientists. By nature, the subject of polymer brushes is diverse and interdisciplinary and, as such, chemists, biologists, physicists, materials scientists and engineers can make valuable contributions to the field.

Today, research into polymer brushes is an important and well-established subject in polymer science. They are on the brink of being able to provide almost unlimited alternatives to molecularly design thin polymer films and already became one of the core areas in the development of macromolecular surfaces. But what is more enthralling is how much there is still waiting to be done. This is particularly exciting considering the number of nanotechnological applications relying on the use of thin polymer films. Undoubtedly, the success of these endeavors will depend on a convergence between polymer brush capabilities and application requirements. Hence, to bridge this gap and attain new applications this field should evolve within an interdisciplinary framework in which polymer chemistry should play a leading role. This is particularly true, considering that innovative work in polymer synthesis during the last decade has given a decisive impetus to the current development of polymer brushes.

In summary, this review has provided a broad description of relevant examples of new applications and potential uses of polymer brushes in multiple research fields. Hopefully, this work will trigger a cascade of new, refreshing ideas in macromolecular surface science as well as engender interest in resorting to polymer brushes as a vehicle to carry out interdisciplinary work between different areas of science and technology.

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