

Tapping the Potential of Polymer Brushes through Synthesis

Bin Li,^{†,‡} Bo Yu,[†] Qian Ye,[†] and Feng Zhou^{*,†}

[†]State Key Laboratory of Solid Lubrication, Lanzhou Institute of Chemical Physics, Chinese Academy of Sciences, Lanzhou, 730000 China

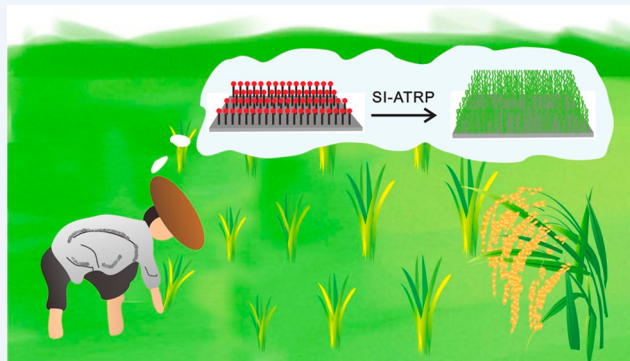
[‡]University of Chinese Academy of Sciences, Beijing 100049, China

CONSPECTUS: Polymer brushes are becoming increasingly popular in the chemical literature, because scientists can control their chemical configuration, density, architecture, and thickness down to nanoscale precision with even simple laboratory setups. A polymer brush is made up of a layer of polymers attached to a substrate surface at one end with the other end dangling into a solvent. In a suitable solvent, the polymer chains stretch away from the surface due to both steric and osmotic repulsion between the chain segments. In an inadequate solvent, however, the polymer chains collapse due to enough interior free space after desolvation. This unique class of materials exhibit interesting physicochemical properties at interfaces and have numerous applications from sensing to surface/interface property control.

Chemists have made recent advances in surface modification and specific application of polymer brushes, due to both profound mechanistic understanding and synthetic strategies. The commonly used synthetic strategies for generating polymer brushes are surface-initiated polymerizations (SIPs), which resemble planting rice. That is, the assembly of initiator on the surface is similar to transplanting rice seedlings, and the subsequent polymerizations are akin to rice growth. Among different SIP methods, researchers mostly use surface-initiated atom transfer radical polymerization (SI-ATRP) because it provides many advantages in the preparation of well-defined polymer brushes, including easy initiator synthesis, fair control over polymer growth, a “living” end for copolymer grafting, and polymerization in aqueous solution. However, chemists gradually realized that there still room for improvement in this method, since the conventional SI-ATRP method suffers several drawbacks. These include having limited availability on various materials surfaces, rigorous synthetic protocols, heavy consumption and waste of unreacted monomers, and limited ability to control a polymerization process. Moreover, applications of polymer brushes as model surfaces must benefit from the synergistic strategies and profound insights into the fundamental understanding of the polymerization. This is not only to optimize the SI-ATRP process but also to expand the range of monomers, simplify reaction setups, reduce the cost, and ultimately gain control of the synthesis of well-defined polymeric surfaces for material science and engineering.

In this Account, we provide an overview of our and others’ recent advances in the fabrication of polymer brushes by using SI-ATRP, to promote the widespread application of SI-ATRP and practical applications of the polymer brushes. We aim to provide fundamental mechanistic and synthetic features of SI-ATRP, while emphasizing the various externally applied stimuli mediated catalytic and initiation systems, including electrochemistry, chemical reducing agents, and photochemistry. In addition, we discuss how chemists can advantageously exploit these methods to synthesize functional polymeric surfaces in environmentally friendly media and facilitate *in situ* regulation of a dynamic polymerization process.

We also discuss structural polymer brushes, such as block copolymers and patterned and gradient structures. Finally, we provide examples that highlight some practical applications of polymer brushes using SI-ATRP, especially the emerging polymerization methods. Overall, recently developed SI-ATRP systems overcome many limitations that permit less rigorous synthetic protocols and facilitate scientific community-wide access to surface modifications. By using these methodologies, chemists are tapping the potential of polymer brushes in surface/interface research areas.



1. INTRODUCTION

Major recent advances have been made in the field of surface-initiated atom transfer radical polymerization (SI-ATRP) by using a variety of effective mediating approaches, allowing polymers to be synthesized with controlled composition and architecture; the development of SIP techniques has been largely facilitated by ATRP.^{1–5} Furthermore, the combination of bottom-up surface-initiated polymerizations (SIPs) with top-down lithography techniques enables the creation of complex

surface structures with novel applications. Overall, these advances in surface grafting of polymer brushes mainly focused on techniques that either facilitate the construction of completely new polymers or improve the existing approaches in terms of scope, controllability, and applications.

Received: August 30, 2014

Published: December 18, 2014

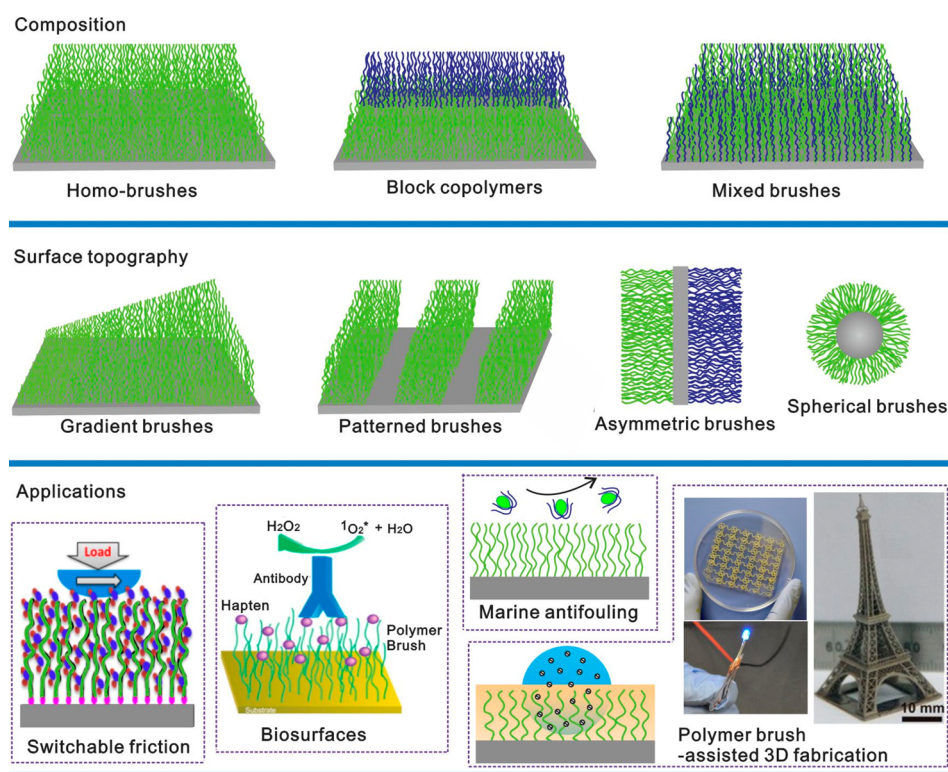


Figure 1. Overview of recent advances in manipulating the composition and surface topology of polymer brushes enabled by SI-ATRP, and some exemplified applications in controlled lubrication, biosurfaces, marine antifouling, and polymer brush assisted 3D fabrications. Adapted with permission from refs 10–13.

The natural topology and properties of polymer brushes depend on their chemical structures and synthetic strategies. In general, polymer brushes are prepared by grafting polymers to surfaces, either through covalent attachment or through physical adsorption. Physisorbed polymers utilize noncovalent interactions such as electrostatic interactions, hydrogen bond formation, or hydrophobic interactions to adhere to substrates; these kinds of films always suffer from solvent or thermal instabilities, especially when shear forces are involved. Covalent immobilization of polymers to surfaces is achieved through two techniques described as “grafting to” and “grafting from”. The *grafting to* method involves reactions of (end-)functionalized polymers with complementary surface functionalities; this method has been found to suffer from drawbacks like limited film thickness and low grafting densities due to the steric effect and unfavorable reactions between the surface anchors and functional groups. In the case of *grafting from* strategy, polymer chains straightforwardly grow from the substrate modified with a self-assembled monolayer of initiator; the grafting density can reach up to 1 chain/nm² and can be easily adjusted.

Various polymerization strategies have been explored to produce polymer brushes, for example, ATRP,⁶ reversible addition–fragmentation transfer (RAFT),⁷ ring-opening metathesis polymerization (ROMP),⁸ and nitroxide-mediated polymerization (NMP).⁹ However, ATRP is considered to be one of the most successful controlled radical polymerization (CRP) processes with significant commercial potential for producing functional materials. The recent successful application of SI-ATRP provides exquisite control of polymer brushes with more complex compositions and architectures (e.g., block, gradient, copolymer, inorganic/organic hybrid, bioconjugate, etc.). However, the original SI-ATRP suffers from disadvantages in terms of

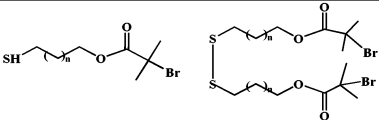
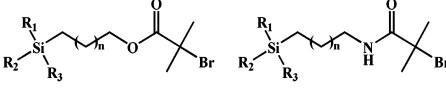
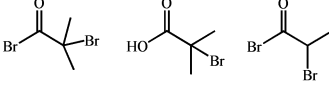
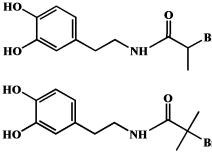
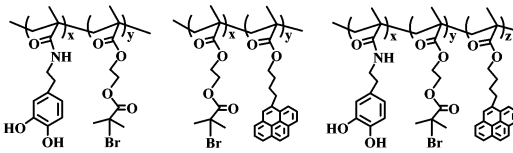
rigorous synthetic protocols, heavy consumption of monomers, limited controllability, and cost and environmental issues.

In this Account, a particular focus is given to the recent advances in SI-ATRP by using a wide range of external stimuli triggered polymerization, which allow polymerization with exquisite control that would otherwise be difficult to achieve. Next, we will show how this method can be advantageously used to create complex structures, specifically patterned and gradient surfaces. Finally, examples are provided that highlight some emerging applications in multiple research fields, which are mainly focused on applications of polymer brushes and emerging technologies.

2. SURFACE MODIFICATION BY SI-ATRP

SI-ATRP has become an indispensable tool for surface modifications. Compared with other CRPs, ATRP is chemically versatile and robust in manipulating a variety of important parameters of polymers and allows polymer brushes to be prepared with chains displaying unrivaled uniformity, predefined thickness, controlled architecture, and functionality. Figure 1 illustrates a variety of polymer brushes and structures prepared through SI-ATRP, such as homogeneous, patterned, and gradient polymer brushes. Mixed, copolymerized, branched, cross-linked, and free-standing or transferred brushes, as well as asymmetric or “Janus” and spherical brushes are also included.^{2,14,15} Similar to ATRP, SI-ATRP maintains all attributes of traditional ATRP. SI-ATRP is catalyzed by a redox-active transition metal complex (Mt/L, Mt = Cu, Fe, Ir, etc., L = ligand), most commonly a copper catalyst, at a lower oxidation state of Cu^I/L that reacts with initiator generating living radicals and starts the polymerization. The growing radicals can experience terminations and be deactivated with a higher

Table 1. Overview of the Commonly Used Substrates and the Corresponding ATRP (Macro)Initiators

Substrate	ATRP initiator
Noble metal (Au, Ag, Pt, etc.), Cu	
Si, SiO ₂ , glass, Ni, Cu, polymethylmethacrylate (PMMA), polydimethylsiloxane (PDMS), polyaniline (PANI), cellulose, chitosan	 R ₁ , R ₂ , R ₃ = Cl, OH, CH ₃ , OEt
Amine-, hydroxyl- or carboxylic acid functionalized surface	
Au, Ti, Si, Cu, Al, Zn; TiO ₂ , Fe ₂ O ₃ , Fe ₃ O ₄ , Al ₂ O ₃ , CdO, Nb ₂ O ₅ , SiO ₂ , ZrO ₂ , MnO ₂ ; steel, glass, mica, ceramics; polyimide, polystyrene, polycarbonate, PMMA	
Si, Ti, Au, Cu, stainless steel, Al ₂ O ₃ , PDMS, textile, wood, graphene and CNTs	

oxidation state $[\text{Cu}^{\text{II}}/\text{L}]$ deactivator. The polymerization rate depends on the propagation and deactivation rate constants and the concentration ratio of $[\text{Cu}^{\text{I}}]/[\text{Cu}^{\text{II}}]$.⁴

$$R_p = k_p[\text{P}^*][\text{M}] = k_p K_{\text{ATRP}} \left(\frac{[\text{P}_n\text{X}][\text{Cu}^{\text{I}}\text{L}^+]}{[\text{X} - \text{Cu}^{\text{II}}\text{L}^+]} \right) [\text{M}]$$

In a SI-ATRP system, chain growth starts with the attachment of ATRP initiator onto a surface that can be planar, curved, and irregular. Recent progress in molecular assembly techniques made it possible to tether ATRP initiator on an impressively wide range of inorganic and organic substrates, even biomolecules. The immobilization of initiators can be completed through noncovalent effects (e.g., π - π or electrostatic interaction) or chemical bond formation, for example, alkanethiols on noble metals and polydopamine coated surface,^{6,16} silanes on oxides,^{9,17} phosphate groups on metal oxides, catechol on almost “every” substrate,^{17,18} and initiator with a pyrene group can be assembled on carbon based materials such as graphene and carbon nanotubes (CNTs).^{19,20} Moreover, a mixture of dopamine and bromine-containing dopamine derivative could be a “universal” initiator to functionalize surfaces made of virtually all material chemistries.²¹ Table 1 lists the commonly used substrates (but not all available substrates) and the structures of the corresponding ATRP initiators.

SI-ATRP can be conducted in both aqueous and organic media. In particular, aqueous ATRP is attractive because most of solution polymerizations are conducted in aqueous conditions, especially for functionalization in biocompatible systems. However, the aqueous ATRP is challenging. First, aqueous ATRP has a relatively high K_{ATRP} , which consequently provides a high $[\text{R}^{\bullet}]$ and fast polymerization rate. Second, the $\text{Cu}^{\text{I}}/\text{L}$

complex should be stable enough to avoid disproportionation. Last, $\text{X}-\text{Cu}(\text{II})/\text{L}$ may undergo dissociation. Moreover, a high concentration of monomer is required to decrease the fraction of dead chains in pursuit of maximum brush growth. Other parameters, such as initiator, monomer, ligand, type of catalyst, and solvent conditions have strong effects on performance of SI-ATRP. However, these parameters offer opportunities to manipulate and optimize a polymerization process.

3. MANIPULATING SI-ATRP THROUGH EXTERNAL STIMULI

3.1. Electrochemistry

Electrochemistry emerges as a powerful tool in polymer science; electrochemical parameters that relate to an ATRP process can be used to determine equilibrium constant K_{ATRP} , redox behavior of catalyst, and ligand binding.^{22–24} Electrochemically mediated ATRP (eATRP) has a number of attractive features, including tolerance of functional groups, easily adjustable parameters (e.g., applied potential, current, and total charge passed), and the compatibility with automation in an electrochemical cell in potentiostatic or galvanostatic mode (Figure 2a).^{25,26} We reported aqueous electrochemically induced SI-ATRP of 3-sulfopropyl methacrylate potassium salt (SPMA) and 2-hydroxyethyl methacrylate (HEMA) from an initiator-functionalized conductive substrate (i.e., Au), which acted as working electrode with tunable grafting densities (Figure 2b).^{24,27} An application of a cathodic current reduced the air-stable $\text{Cu}(\text{II})$ to $\text{Cu}(\text{I})$ *in situ* in the vicinity of the initiator layer, reacted with initiator $\text{R}-\text{X}$ generating radicals, and started the polymerization. Reoxidation of the $\text{Cu}(\text{I})$ activators was achieved via an anodic current yielding inactive $\text{Cu}(\text{II})$ species for cessation of

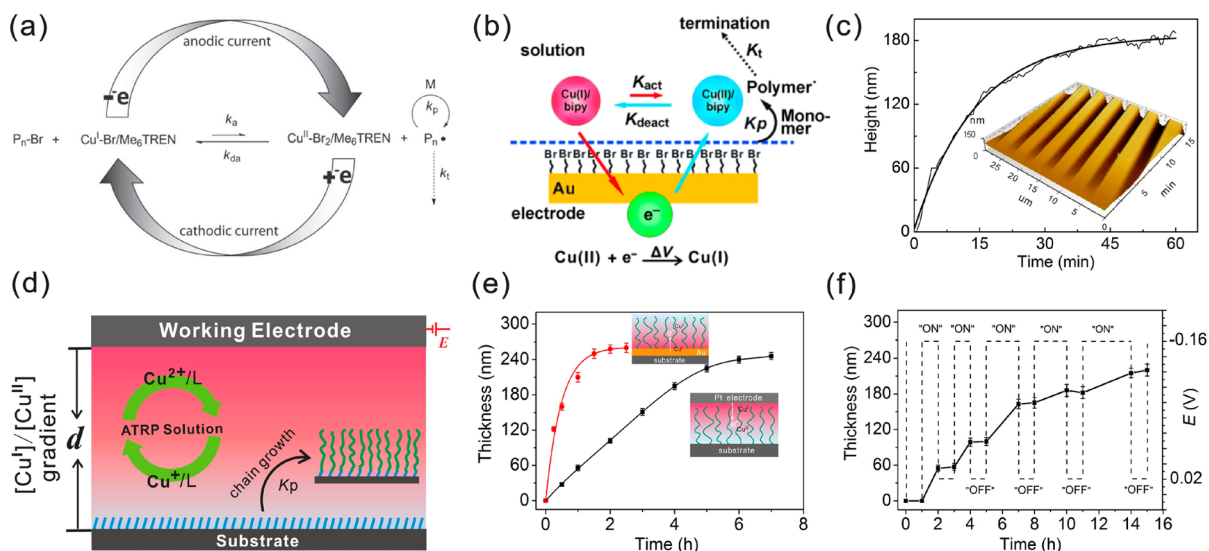


Figure 2. (a) Mechanism of eATRP. Reproduced from ref 25. Copyright 2011 American Association for the Advancement of Science. (b) eATRP for surface polymerization on gold and (c) *in situ* AFM investigation of SI-eATRP of SPMA. Reproduced from refs 24 and 27. Copyright 2013 and 2012 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim, respectively. (d) Controlled eATRP on nonconductive substrates through catalyst diffusion. (e,f) Electrochemically controlled brush growth. Adapted from ref 28. Copyright 2013 American Chemical Society.

polymerization; activator regeneration was accomplished by electrons supplied by the cathode.

We have demonstrated that the applied potentials strongly affected the outcome of polymerization, in which they would dictate the concentration of $[\text{Cu}^{\text{I}}]/[\text{Cu}^{\text{II}}]$, a more negative potential value produced a corresponding higher current value accompanied by a faster reduction rate of $\text{Cu}^{\text{II}}\text{X}_2/\text{L}$ and provided a higher concentration of $\text{Cu}^{\text{I}}\text{X}/\text{L}$ and a fast polymerization rate. The controlled, living nature of eATRP and the preserved chain end functionality were exemplified by the block copolymer formation (PHEMA-*b*-PSPMA).²⁷ This may offer the possibility of postmodification of polymer brushes via further electrochemically induced reactions. Though effective, a higher concentration of Cu^{I} near the initiator layer resulted in a fast polymerization rate; the brush growth leveled off quickly after ca. 30 min, and further quite limited control over polymerization was poor (Figure 2c,e, red curve). Matyjaszewski et al. demonstrated that a more negative potential equals a higher current value and R_p and thus more terminations.²⁹

The utility of eATRP was further extended to a nonconductive substrate system where the ATRP initiator modified substrate was positioned close to the working electrode, which broadened the scope of eATRP in general (Figure 2d).²⁸ The concentration ratio of $[\text{Cu}^{\text{I}}]/[\text{Cu}^{\text{II}}]$ can be adjusted and retained electrochemically throughout the polymerization, and the living chain growth was maintained for longer durations (Figure 2e, black curve). Thus, a higher ratio of $[\text{Cu}^{\text{I}}\text{X}_2/\text{L}]/[\text{Cu}^{\text{II}}\text{X}_2/\text{L}]$ should produce polymers with lower M_w/M_n values from an increased rate of deactivation within each activation–deactivation cycle and, thereby, suppress unwanted terminations and significantly enhance levels of control.^{26,29}

Since the electrochemistry permits a dynamic equilibrium between the two oxidation states of Cu^{I} and Cu^{II} , the polymerization can be reversibly switched “on” and “off” between the activated and deactivated states in a highly responsive manner by application of multistep intermittent potentials (Figure 2f). Furthermore, the electrochemical reduction/oxidation cycle can be employed to eliminate oxygen, and hence, the polymerization can be carried out without deoxygenation, which was previously

only possible for activators regenerated by electron transfer (ARGET) ATRP.³⁰ Meanwhile, the polymerization mixture can be reused many times without any degradation of the brush growth. The ability to dynamically control the polymerization makes this system almost ideal. However, the SI-eATRP process is restricted to work in an electrochemical cell and requires sufficient conductivity of the reaction mixtures.

3.2. Chemical Reducing Agent

Redox-active systems have the ability to be reversibly switched between two oxidation states that have different catalytic activities and were the first systems to be exploited as a means to manipulate an ATRP process. The polymerization process and the level of control are similar to ARGET ATRP or single electron transfer–living radical polymerization (SET-LRP) ATRP. ATRP is started by addition of a more reducing agent (e.g., tin(II) 2-ethylhexanoate ($\text{Sn}(\text{EH})_2$), glucose, ascorbic acid, zerovalent metals ($\text{Zn}(0)$, $\text{Cu}(0)$), etc.) for $\text{Cu}^{\text{II}}/\text{L}$ species, which were then converted to active $\text{Cu}^{\text{I}}/\text{L}$ *in situ* (Figure 3). This exploit permits starting ATRP with oxidatively stable complexes, allows ppm levels of catalyst loading, and is distinguished from the earlier ATRP system, in which a sacrificial initiator or an additional deactivator is necessary for a well-controlled polymerization.

The catalyst diffusion related to a solution ATRP process makes eATRP and ARGET ATRP particularly suitable for surface polymerization in a confined environment. We used a zinc slice as a reducing resource to catalyze SI-ATRP in a confined space using microliter volumes of ATRP solution; a difference in electrochemical potential allowed Cu^{I} to be continuously generated and diffused to the initiator layer, resulting in a locally dynamic concentration of $[\text{Cu}^{\text{I}}]/[\text{Cu}^{\text{II}}]$ species as a function of the distance to the Zn substrate. Zinc acted as a supplemental activator for alkyl halides and an efficient reducing agent for Cu^{II} species.³¹ The overall rate of this process and the control over the polymerization can be tuned by the type and the amount of the reducing agent in the reaction mixture. The versatility of this method was demonstrated by polymerizing various monomers, including: neutral *N*-isopropylacrylamide (NIPAm), HEMA, and

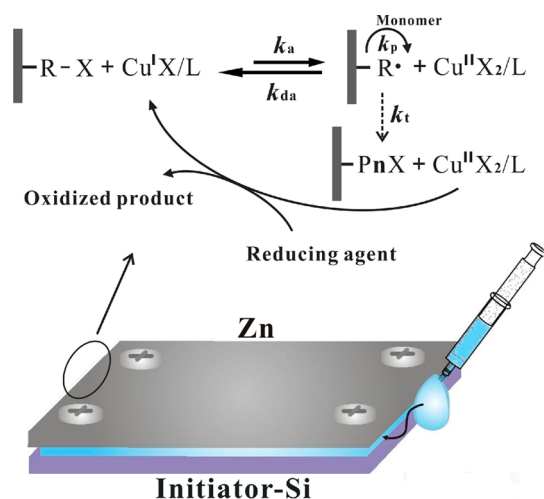


Figure 3. Principle of chemical reducing agent induced SI-ATRP (top) and Zn mediated surface confined polymerization (bottom). Adapted with permission from ref 31. Copyright (2013) WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim.

oligo(ethylene glycol) methacrylate (OEGMA), anionic SPMA and sodium methacrylate (MAA-Na), and cationic methacrylo-choline chloride (METAC), which substantially expanded the scope of monomers, promising novel polymer synthesis for a wider range of applications.

The rate of polymerization is primarily required for a well-controlled SI-ATRP process, in which a fast initiation and rapid, reversible deactivation should be assured. In comparison of polymer brushes with similar dry thickness that were prepared at different reaction rates, brushes obtained at fast polymerization rate had a higher degree of polymerization but lower grafting density than those obtained at slow rate. Thus, for the same polymerizable monomer, a catalyst that deactivated the growing chains faster would result in fewer termination reactions and produce polymers with a lower M_w/M_n value and maximum retention of the chain end functionality.^{28,32} Another system composed of Cu(0) to (re)generate Cu(I) from Cu(II) via a single-electron-transfer process in the presence of a suitable polar solvent and *N*-donor ligand Me₆-Tren, leading to a self-regulated disproportionation/comproportionation of Cu(I)X generating Cu(0) powder and Cu(II) deactivator, resulted in a controlled polymerization of various vinyl monomers with retention of polymer chain-end functionality.³³ However, the reducing agent should be carefully selected to avoid its reactivity toward the reaction mixture components. An ideal process should have a constant and high Cu^{II}/Cu^I ratio, which can hardly be achieved by a single addition of reducing agent, and the reducing agent is oxidized after the polymerization generating undesirable by-products, which represents a major disadvantage of such reactions. Therefore, it would be of interest to avoid using chemicals such as reducing agents and replace them by environmentally friendly mediating agents.

3.3. Photochemistry

Photoinduced reactions have successfully catalyzed a broad range of synthetically valuable reactions such as ATRP. The current explored methodology is mainly focused on the manipulation of light sources to activate a monomer, initiator, or catalyst. The latter is particularly attractive. It utilizes a photosensitizer³⁴ or a photoredox metal catalyst (Figure 4),^{35,36} providing several distinct advantages, including the minimized formation of bulk

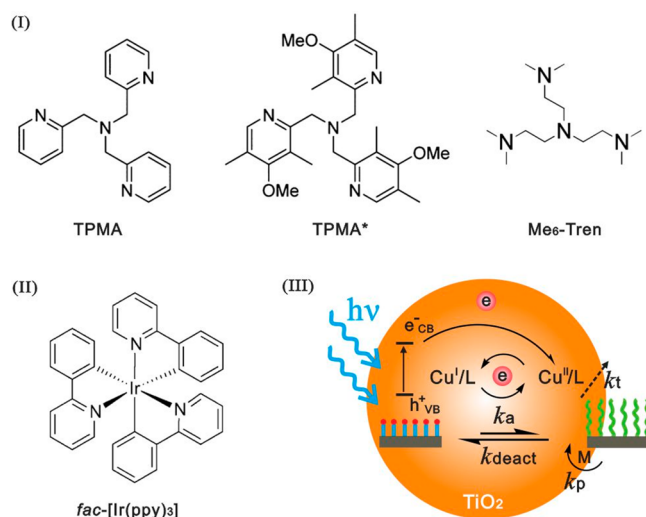


Figure 4. Three representative types of photosensitive materials utilized for ATRP. (I) Photosensitive pyridine-based ligands (TPMA, TPMA*) and tertiary amine Me₆-Tren.^{35,36} (II) Ir based photoredox catalyst.³⁹ (III) TiO₂ used to trigger SI-ATRP.^{34,38}

polymers and enhanced controllability and properties of the produced polymers. Our groups, along with others, have exploited photoinduced SI-ATRP by utilizing semiconductor such as TiO₂ or ZnO as a photocatalyst.^{34,37} Upon UV irradiation, these photosensitive materials are capable of absorbing photons and consequently promoting electrons from the valence bands to the conduction bands and releasing electrons. The excited electrons can spontaneously reduce Cu^{II}/L to Cu^I/L *in situ* by a one-electron transfer process. The growth of polymer brushes is sensitive to the content of photoactive materials and light intensity; in this manner, Cu^I species are continuously (re)generated to maintain a targeted concentration ratio of [Cu^{II}/L]/[Cu^I/L].³⁴ However, UV assisted surface grafting techniques may denature materials such as bioconjugates or degrade chain functionality. Recently, dye sensitized TiO₂ was used as a photocatalyst for SI-ATRP. The light absorption of TiO₂ can be shifted into visible regimes by doping with dye molecules, and the polymerization is well-controlled under “sunlight”.³⁸

Many photosensitive Mtⁿ/L complexes can undergo photoredox reactions during light irradiation, for example, Cu^{II}/TPMA*, Cu^{II}Br₂/Me₆-Tren, fac-[Ir(ppy)₃] (Figure 4),^{35,36,39} Cu^{II}/PMDETA (PMDETA = *N,N,N',N',N''*-pentamethyldiethylenetriamine) and a cyclometalated ruthenium(II) complex.^{40,41} In their proposed mechanism, photoexcited Mtⁿ⁺¹ was reduced to Mtⁿ directly upon absorption of light and subsequently triggered the polymerization. The polymerization preceded in a well-controlled manner of high monomer conversion and narrow dispersities with ppm amounts of catalyst without adding any conventional photoinitiators or dye sensitizers. The reversible chain activation/deactivation was demonstrated by repeatedly switching the light “on” and “off”, and block copolymerization of different kinds of monomers further illustrated that minimal termination was occurring during the polymerization.³⁹

The power of photochemical SI-ATRP is most apparent in its local and temporal control; this means, by generating the active catalyst *in situ*, the brush growth can be controlled both temporally and spatially through the modulation of light. Given these accomplishments, photomediated SI-ATRP is an excellent

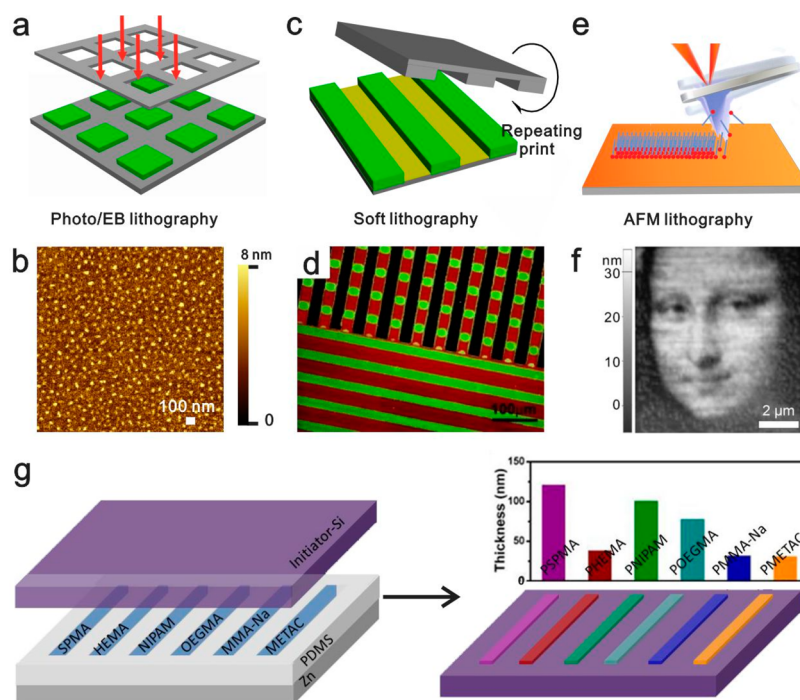


Figure 5. Schematic view of typical strategies and the corresponding examples of patterned polymer brushes. (a, b) Nanopatterned PSPMA brushes prepared through photolithography. Adapted with permission from ref 38. Copyright 2014 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim. (c, d) Multicomponent brushes enabled by μ CP and SI-ATRP. Adapted from ref 6. Copyright 2006 American Chemical Society. (e, f) AFM image of the Mona Lisa obtained from PMETAC brushes prepared by DPN, and (g) grafting multiple patterned polymer brushes. Reproduced from refs 46 and 31. Copyright 2011 and 2013 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim, respectively.

approach that has added new knowledge in surface grafting. It is believed that the “green” surface polymerization techniques will undoubtedly play a major role in future polymer synthesis in the way that plants do, using photosynthesis to construct complex molecule structures.

3.4. Others

Other strategies involve manipulating temperature or pressure, surface confinement, charge repulsion, complexation, etc. Recently, bioinspired polymerizations are particularly fascinating and can be used for surface modifications. For example, the successful ATRP of oligo(ethylene oxide) methyl ether methacrylate was catalyzed by an iron-based hemin complex in aqueous media with ascorbic acid as a reducing agent.⁴² Some enzymes or modified enzymes such as horseradish peroxidase can be used to catalyze ATRP.⁴³ The environmentally friendly redox process is a breakthrough in the level of control over the ATRP process, because of its low toxicity and biocompatibility, especially for biologically relevant systems.

4. TOPOLOGICAL AND CHEMICAL CONTROL WITH POLYMER BRUSHES

4.1. Pattern

Patterned surfaces offer a number of unique advantages, including precisely confined chemicals and topographical features, strict arrangement and control of interfacial properties and functionalities at the micro- or nanometer scale, introducing a new route for achieving novel properties suitable for specific applications where homogeneous films are unnecessary. The straightforward synthetic strategies are lithographic techniques, ranging from photo or electron beam lithography, scanning probe lithography, and photolithography to soft lithography, nanoimprinting, and capillary force or colloidal lithography.^{15,44}

Mixed brushes that consist of at least two types of polymers, are also used for patterning due to their different responsive properties in a selective solvent.⁴⁵ In particular, the combination of top-down lithography techniques and bottom-up strategies allows patterned polymer brushes with high fidelity and high reproducibility on various substrates (Figure 5).

Soft lithographic techniques, such as microcontact printing (μ CP) and dip-pen nanolithography (DPN), have been found versatile and technologically attractive for micro- and nanopatterning. μ CP utilizes an initiator inked stamp to deposit initiator at well-defined regions, subsequent polymerization yields intricate arrays of polymer patterns (Figure 5c, 5d).^{6,47} More complex patterns can be achieved by repeating print steps and be finished by backfilling the unmodified surface with initiator and subsequent polymerization. Nanocontact printing is capable of fabricating patterns at submicron resolution. In particular, scanning probe lithography such as DPN allows patterns with nanometer resolution by coating a SAM of initiator from an AFM tip.^{46,48} Figure 5f shows an arbitrary 3D microscale portrait of the Mona Lisa obtained from arrays of PMETAC brushes nanodots via DPN. We have demonstrated that a Zn slice can be used as a “printer” to “paint” polymer brushes with different shapes (cross, triangle, letters, and Y shape) by simply changing its shape (Figure 5g). Theoretically, “infinite” components of patterned brushes can be prepared in a single polymerization step by rationally designed surface chemistry and topology. Very recently, patterned polymers were prepared directly from a uniform initiator layer by photomediated SI-ATRP through traditional photomasks; the brush growth only occurred in regions where the initiator was exposed to the sunlight irradiation and resulted in patterns with size matching the transparent areas of the masks.^{38,49} By choosing appropriate spatial and temporal patterning parameters, nanoscale patterns

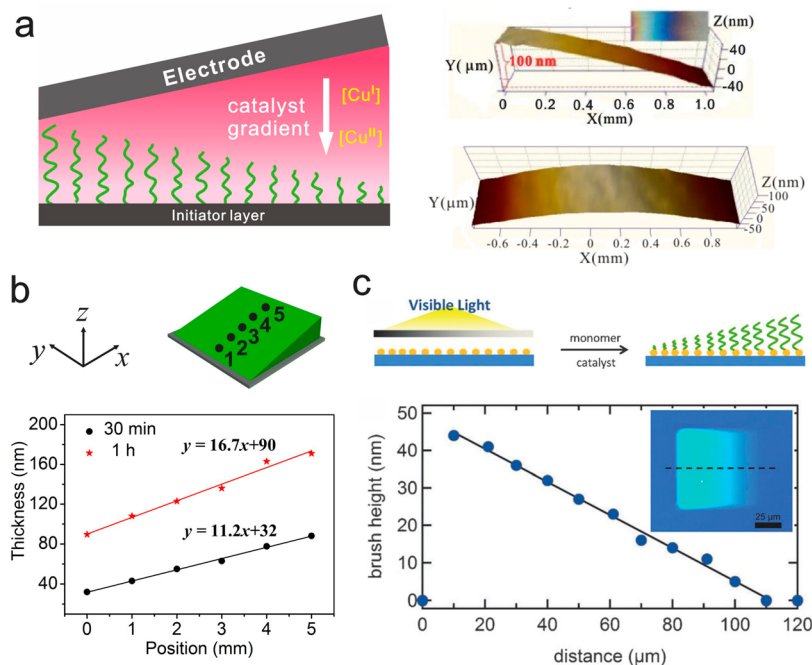


Figure 6. (a) Synthesis of complex gradient surfaces by a $\text{Cu}^{\text{I}}/\text{Cu}^{\text{II}}$ concentration gradient. Adapted from ref 31. Copyright 2013 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim. (b) Thickness gradient of brushes prepared by SI-eATRP through catalyst diffusion. Adapted from ref 28. Copyright 2013 American Chemical Society. (c) Nanoscale-inclined gradient 3D polymer brush and the corresponding height profiles by using a neutral density filter. Adapted from ref 49. Copyright 2013 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim.

were also obtained using a nanoporous alumina oxide membrane as a photomask (Figure 5a,b).

4.2. Gradient

Gradient brushes have complex and gradual variation in grafting density, chain length, and chemical composition, as well as physicochemical properties, along one or more directions on a substrate.^{50,51} The use of polymer brushes to fabricate patterned and gradient structures are complementary and related. Usually, gradient formation relies on selective physical or chemical treatment of surfaces before or during the growth of polymer brushes, including gradient deposition of initiator in density, manipulation the contact time of the initiator layer with the polymerization solution, regulation of the radiation intensity or time during UV exposure, or variation of the reaction conditions, for example, concentration of catalyst or temperature. Consequently, an ultrathin initiator layer can be directly amplified into a 3D brush gradient via SI-ATRP. Here, we only focus on gradients fabricated by the newly developed SI-ATRP methods.

Among these well-established techniques, diffusion-based systems combined with other lithography techniques are popular in generating gradient surfaces. Recently, our group used an electrochemical method to create complex gradients in a confined space, in which a spatiotemporal concentration gradient of $[\text{Cu}^{\text{I}}\text{X}/\text{L}]/[\text{Cu}^{\text{II}}\text{X}_2/\text{L}]$ was formed as a function of the distance to the electrode and reaction time. By simply adjusting the arrangement of the initiator covered substrate in combination with the variation of the applied potentials, gradients of different slopes were formed. This setup was extended to the fabrication of various compositional and topological brush gradients by a chemically formed $\text{Cu}^{\text{I}}/\text{L}$, because a locally dynamic catalyst gradient can be used to dictate the growth kinetics. Gradients of both homogeneous and patterned brushes can be fabricated (Figure 6a,b).³¹ Furthermore, the intensity of incident light can be applied in a gradient manner, therefore, changing the

polymerization rate. For example, by using a neutral density filter with varying optical densities, arbitrary 3D structures with nanoscale features in the height were obtained in a single step from a uniform initiator layer (Figure 6c).⁴⁹

5. APPLICATIONS OF POLYMER BRUSHES

ATRP has been used industrially for several years with commercial products. However, for years, polymer brushes have been studied for their unique physicochemical properties and used as functional surfaces or interfacial materials. Now the focus has already started to shift to practical applications. The very precise control of the composition and architecture has enabled the development of numerous advanced materials with specific properties that are suitable for targeted applications, ranging from areas of chemistry and surface science to materials science, nanotechnology, and biomedical engineering, such as wettability, adhesion, separations (chromatography and membrane), corrosion resistance, and friction, as well as microelectronics, microfluidics, drug delivery, cell growth control, etc., which have been well studied and reviewed in the literature and will thus not be repeated here; we will only include a few emerging examples.

Polymer brushes on flat surfaces are known for their excellent self-lubricating properties in their swollen state; now we can use responsive polyelectrolyte brushes to tailor their lubricating performances. The friction coefficients were progressively tuned from $\sim 10^{-3}$ to ~ 1 by clicking different counterions into polyelectrolyte brushes, due to the conformation and surface chemistry changes.¹⁰ Polymer brushes are of particular interest in medical applications such as biomaterial implants and medical devices, as well as diagnostics, packaging, and blood contact materials.⁵² Functional polymer brushes especially the patterned and gradient surfaces are employed extensively for biological applications, such as biosensing and biomolecule immobilization.^{11,53} Furthermore, it is envisioned that micro- or nanosized gradients could be used to control the locomotion of object such

as cells and even nanoparticles. Polymer brush coatings have been also designed as antimarine fouling or fouling release coatings through incorporation or inclusion of multiple functionalities with much less environmental impact than traditional biocides.⁵⁴ Polymer brush-assisted metal electroless deposition of metals (e.g., Cu, Ni, Ag, or Au) on various substrates combined with lithography or printing techniques allows one to prepare inorganic/organic hybrid materials, which have great potential applications in flexible electronics.^{12,55} Similarly, the polymer-based 3D-printing resin integrated with polymer brushes and subsequently followed by electroless plating of metals allows one to create sophisticated and customized objects.¹³ Novel applications in biological, solar cell, memory storage, sensors and electronic circuit fields are also indicated.

6. CONCLUSION

In this Account, we have described recent advances in the field of SI-ATRP for preparation of well-defined polymer brushes. The emerging externally regulated SI-ATRP strategies provide a robust means to manipulate the initiation and activation/deactivation steps and enhance the controllability, which have revolutionized the fields of surface polymerization. The attractive features include adaptability to virtually any substrates, mild stimuli with ppm levels of catalyst loading, multiple microliter volume usage of monomer solutions, tolerance to oxygen and functional groups, and environmentally benign reaction processes, which are especially well-suited for large scale grafting. The marriage of polymer brushes with nanotechnology is becoming more evident in material science and has valuable applications. Profound mechanistic understanding of SI-ATRP is prerequisite to develop rational synthetic strategies and design new structures and functionalities for novel applications. Further challenges include comprehensive understanding of structure–reactivity–property correlations, exploring multifunctional polymer brushes, seeking multiple surface functionalizations by recycling or reusing “healable” initiating surfaces, and tailoring specific structure and composition for target applications. It is expected these new synthetic strategies will continue to promote the prosperity of surface modifications.

AUTHOR INFORMATION

Corresponding Author

*E-mail: zhouf@licp.cas.cn.

Funding

This work was financially supported by NSFC (Grants 21125316, 21434009, and 51335010) and Key Research Program of CAS (Grant KJZD-EW-M01).

Notes

The authors declare no competing financial interest.

Biographies

Bin Li received his B.S. in chemistry from Lanzhou University in 2009, China. He is currently a Ph.D. candidate in the group of Prof. Feng Zhou at the Lanzhou Institute of Chemical Physics, Chinese Academy of Sciences. His research interests are in the fields of SI-ATRP and responsive polymers at surfaces and interfaces.

Bo Yu got her Ph.D. in chemistry at the Lanzhou Institute of Chemical Physics in 2007. She is currently an associate researcher. Her research interests are in the areas of polymer brushes and their applications.

Qian Ye got his Ph.D. in chemistry in 2010 from Lanzhou University. He is currently an assistant Professor in the group of Prof. Feng Zhou.

His research interests are antifouling surfaces and polymer brushes for surface modifications.

Feng Zhou earned his Ph.D. in physical chemistry at the Lanzhou Institute of Chemical Physics in 2004. He spent three years for postdoctoral research with Prof. Wilhelm T. S. Huck at the University of Cambridge. He is currently Professor in Lanzhou Institute of Chemical Physics. His research interests are in the areas of polymer science, surfaces and interfaces of soft matter, marine antibiofouling, and biolubrication.

REFERENCES

- (1) Edmondson, S.; Osborne, V. L.; Huck, W. T. S. Polymer Brushes via Surface-Initiated Polymerizations. *Chem. Soc. Rev.* **2004**, *33*, 14–22.
- (2) Barbey, R.; Lavanant, L.; Paripovic, D.; Schüwer, N.; Sugnaux, C.; Tugulu, S.; Klok, H.-A. Polymer Brushes via Surface-Initiated Controlled Radical Polymerization: Synthesis, Characterization, Properties, and Applications. *Chem. Rev.* **2009**, *109*, 5437–5527.
- (3) Azzaroni, O. Polymer Brushes Here, There, And Everywhere: Recent Advances in Their Practical Applications and Emerging Opportunities in Multiple Research Fields. *J. Polym. Sci., Part A: Polym. Chem.* **2012**, *50*, 3225–3258.
- (4) Matyjaszewski, K.; Tsarevsky, N. V. Macromolecular Engineering by Atom Transfer Radical Polymerization. *J. Am. Chem. Soc.* **2014**, *136*, 6513–6533.
- (5) Hui, C. M.; Pietrasik, J.; Schmitt, M.; Mahoney, C.; Choi, J.; Bockstaller, M. R.; Matyjaszewski, K. Surface-Initiated Polymerization as an Enabling Tool for Multifunctional (Nano-)Engineered Hybrid Materials. *Chem. Mater.* **2014**, *26*, 745–762.
- (6) Zhou, F.; Zheng, Z.; Yu, B.; Liu, W.; Huck, W. T. S. Multicomponent Polymer Brushes. *J. Am. Chem. Soc.* **2006**, *128*, 16253–16258.
- (7) Baum, M.; Brittain, W. J. Synthesis of Polymer Brushes on Silicate Substrates via Reversible Addition Fragmentation Chain Transfer Technique. *Macromolecules* **2002**, *35*, 610–615.
- (8) Ye, Q.; Wang, X.; Li, S.; Zhou, F. Surface-Initiated Ring-Opening Metathesis Polymerization of Pentadecafluorooctyl-5-norbornene-2-carboxylate from Variable Substrates Modified with Sticky Biomimic Initiator. *Macromolecules* **2010**, *43*, 5554–5560.
- (9) Husseman, M.; Malmstro, E. E.; McNamara, M.; Mate, M.; Mecerreyes, D.; Benoit, D. G.; Hedrick, J. L.; Mansky, P.; Huang, E.; Russell, T. P.; Hawker, C. J. Controlled Synthesis of Polymer Brushes by “Living” Free Radical Polymerization Techniques. *Macromolecules* **1999**, *32*, 1424–1431.
- (10) Wei, Q.; Cai, M.; Zhou, F.; Liu, W. Dramatically Tuning Friction Using Responsive Polyelectrolyte Brushes. *Macromolecules* **2013**, *46*, 9368–9379.
- (11) Welch, M. E.; Ritzert, N. L.; Chen, H.; Smith, N. L.; Tague, M. E.; Xu, Y.; Baird, B. A.; Abruna, H. D.; Ober, C. K. Generalized Platform for Antibody Detection using the Antibody Catalyzed Water Oxidation Pathway. *J. Am. Chem. Soc.* **2014**, *136*, 1879–1883.
- (12) Guo, R.; Yu, Y.; Xie, Z.; Liu, X.; Zhou, X.; Gao, Y.; Liu, Z.; Zhou, F.; Yang, Y.; Zheng, Z. Matrix-Assisted Catalytic Printing for the Fabrication of Multiscale, Flexible, Foldable, and Stretchable Metal Conductors. *Adv. Mater.* **2013**, *25*, 3343–3350.
- (13) Wang, X.; Guo, Q.; Cai, X.; Zhou, S.; Kobe, B.; Yang, J. Initiator-Integrated 3D Printing Enables the Formation of Complex Metallic Architectures. *ACS Appl. Mater. Interfaces* **2014**, *6*, 2583–2587.
- (14) Advincula, R. C.; Brittain, W. J.; Caster, K. C.; Rühle, J. *Polymer Brushes: Synthesis, Characterization, Applications*; Wiley-VCH Verlag GmbH & Co. KGaA: Weinheim, Germany, 2004.
- (15) Welch, M. E.; Ober, C. K. Responsive and Patterned Polymer Brushes. *J. Polym. Sci., Part B: Polym. Phys.* **2013**, *51*, 1457–1472.
- (16) Hu, H.; Yu, B.; Ye, Q.; Gu, Y.; Zhou, F. Modification of Carbon Nanotubes with a Nanothin Polydopamine Layer and Polydimethylamino-ethyl Methacrylate Brushes. *Carbon* **2010**, *48*, 2347–2353.

- (17) Sugnaux, C.; Lavanant, L.; Klok, H. A. Aqueous Fabrication of pH-Gated, Polymer-Brush-Modified Alumina Hybrid Membranes. *Langmuir* **2013**, *29*, 7325–7333.
- (18) Ye, Q.; Zhou, F.; Liu, W. Bioinspired Catecholic Chemistry for Surface Modification. *Chem. Soc. Rev.* **2011**, *40*, 4244–4258.
- (19) Wei, Q.; Wang, X.; Zhou, F. A Versatile Macro-Initiator with Dual Functional Anchoring Groups for Surface-Initiated Atom Transfer Radical Polymerization on Various Substrates. *Polym. Chem.* **2012**, *3*, 2129–2137.
- (20) Gao, T.; Wang, X.; Yu, B.; Wei, Q.; Xia, Y.; Zhou, F. Noncovalent Microcontact Printing for Grafting Patterned Polymer Brushes on Graphene Films. *Langmuir* **2013**, *29*, 1054–1060.
- (21) Hong, S.; Na, Y. S.; Choi, S.; Song, I. T.; Kim, W. Y.; Lee, H. Non-covalent Self-Assembly and Covalent Polymerization Co-contribute to Polydopamine Formation. *Adv. Funct. Mater.* **2012**, *22*, 4711–4717.
- (22) Qiu, J.; Matyjaszewski, K.; Thouin, L.; Amatore, C. Cyclic Voltammetric Studies of Copper Complexes Catalyzing Atom Transfer Radical Polymerization. *Macromol. Chem. Phys.* **2000**, *201*, 1625–1631.
- (23) Bell, C. A.; Bernhardt, P. V.; Monteiro, M. J. A Rapid Electrochemical Method for Determining Rate Coefficients for Copper-Catalyzed Polymerizations. *J. Am. Chem. Soc.* **2011**, *133*, 11944–11947.
- (24) Li, B.; Yu, B.; Zhou, F. In Situ AFM Investigation of Electrochemically Induced Surface-Initiated Atom-Transfer Radical Polymerization. *Macromol. Rapid Commun.* **2013**, *34*, 246–250.
- (25) Magenau, A. J. D.; Strandwitz, N. C.; Gennaro, A.; Matyjaszewski, K. Electrochemically Mediated Atom Transfer Radical Polymerization. *Science* **2011**, *332*, 81–84.
- (26) Bortolamei, N.; Isse, A. A.; Magenau, A. J. D.; Gennaro, A.; Matyjaszewski, K. Controlled Aqueous Atom Transfer Radical Polymerization with Electrochemical Generation of the Active Catalyst. *Angew. Chem., Int. Ed.* **2011**, *50*, 11391–11394.
- (27) Li, B.; Yu, B.; Huck, W. T. S.; Zhou, F.; Liu, W. Electrochemically Induced Surface-Initiated Atom-Transfer Radical Polymerization. *Angew. Chem., Int. Ed.* **2012**, *51*, 5092–5095.
- (28) Li, B.; Yu, B.; Huck, W. T. S.; Liu, W.; Zhou, F. Electrochemically Mediated Atom Transfer Radical Polymerization on Nonconducting Substrates: Controlled Brush Growth through Catalyst Diffusion. *J. Am. Chem. Soc.* **2013**, *135*, 1708–1710.
- (29) Magenau, A. J. D.; Bortolamei, N.; Frick, E.; Park, S.; Gennaro, A.; Matyjaszewski, K. Investigation of Electrochemically Mediated Atom Transfer Radical Polymerization. *Macromolecules* **2013**, *46*, 4346–4353.
- (30) Matyjaszewski, K.; Dong, H.; Jakubowski, W.; Pietrasik, J.; Kusumo, A. Grafting from Surfaces for “Everyone”: ARGET ATRP in the Presence of Air. *Langmuir* **2007**, *23*, 4528–4531.
- (31) Yan, J.; Li, B.; Yu, B.; Huck, W. T. S.; Liu, W.; Zhou, F. Controlled Polymer-Brush Growth from Microliter Volumes using Sacrificial-Anode Atom-Transfer Radical Polymerization. *Angew. Chem., Int. Ed.* **2013**, *52*, 9125–9129.
- (32) Matyjaszewski, K. Atom Transfer Radical Polymerization (ATRP): Current Status and Future Perspectives. *Macromolecules* **2012**, *45*, 4015–4039.
- (33) Zhang, Q.; Wilson, P.; Li, Z.; McHale, R.; Godfrey, J.; Anastasaki, A.; Waldron, C.; Haddleton, D. M. Aqueous Copper-Mediated Living Polymerization: Exploiting Rapid Disproportionation of CuBr with Me₆TREN. *J. Am. Chem. Soc.* **2013**, *135*, 7355–7363.
- (34) Yan, J.; Li, B.; Zhou, F.; Liu, W. Ultraviolet Light-Induced Surface-Initiated Atom-Transfer Radical Polymerization. *ACS Macro Lett.* **2013**, *2*, 592–596.
- (35) Anastasaki, A.; Nikolaou, V.; Zhang, Q.; Burns, J.; Samanta, S. R.; Waldron, C.; Haddleton, A. J.; McHale, R.; Fox, D.; Percec, V.; Wilson, P.; Haddleton, D. M. Copper(II)/Tertiary Amine Synergy in Photo-induced Living Radical Polymerization: Accelerated Synthesis of ω -Functional and α,ω -Heterofunctional Poly(acrylates). *J. Am. Chem. Soc.* **2014**, *136*, 1141–1149.
- (36) Konkolewicz, D.; Schröder, K.; Buback, J.; Bernhard, S.; Matyjaszewski, K. Visible Light and Sunlight Photoinduced ATRP with ppm of Cu Catalyst. *ACS Macro Lett.* **2012**, *1*, 1219–1223.
- (37) Dadashi-Silab, S.; Atilla Tasdelen, M.; Yagci, Y. Photoinitiated Atom Transfer Radical Polymerization: Current Status and Future Perspectives. *J. Polym. Sci., Part A: Polym. Chem.* **2014**, *52*, 2878–2888.
- (38) Li, B.; Yu, B.; Zhou, F. Spatial Control over Brush Growth through Sunlight-Induced Atom Transfer Radical Polymerization Using Dye-Sensitized TiO₂ as a Photocatalyst. *Macromol. Rapid Commun.* **2014**, *35*, 1287–1292.
- (39) Fors, B. P.; Hawker, C. J. Control of a Living Radical Polymerization of Methacrylates by Light. *Angew. Chem., Int. Ed.* **2012**, *51*, 8850–8853.
- (40) Mosnáček, J.; Ilčíková, M. Photochemically Mediated Atom Transfer Radical Polymerization of Methyl Methacrylate Using ppm Amounts of Catalyst. *Macromolecules* **2012**, *45*, 5859–5865.
- (41) Alfredo, N. V.; Jalapa, N. E.; Morales, S. L.; Ryabov, A. D.; Le Lagadec, R.; Alexandrova, L. Light-Driven Living/Controlled Radical Polymerization of Hydrophobic Monomers Catalyzed by Ruthenium(II) Metalacycles. *Macromolecules* **2012**, *45*, 8135–8146.
- (42) Simakova, A.; Mackenzie, M.; Averick, S. E.; Park, S.; Matyjaszewski, K. Bioinspired Iron-Based Catalyst for Atom Transfer Radical Polymerization. *Angew. Chem., Int. Ed.* **2013**, *52*, 12148–12151.
- (43) Sigg, S. J.; Seidi, F.; Renggli, K.; Silva, T. B.; Kali, G.; Bruns, N. Horseradish Peroxidase as a Catalyst for Atom Transfer Radical Polymerization. *Macromol. Rapid Commun.* **2011**, *32*, 1710–1715.
- (44) Chen, T.; Amin, I.; Jordan, R. Patterned Polymer Brushes. *Chem. Soc. Rev.* **2012**, *41*, 3280–3296.
- (45) Ionov, L.; Minko, S.; Stamm, M.; Gohy, J.-F.; Jérôme, R.; Scholl, A. Reversible Chemical Patterning on Stimuli-Responsive Polymer Film: Environment-Responsive Lithography. *J. Am. Chem. Soc.* **2003**, *125*, 8302–8306.
- (46) Zhou, X.; Wang, X.; Shen, Y.; Xie, Z.; Zheng, Z. Fabrication of Arbitrary Three-Dimensional Polymer Structures by Rational Control of the Spacing Between Nanobrushes. *Angew. Chem., Int. Ed.* **2011**, *50*, 6506–6510.
- (47) Liu, J.; Ye, Q.; Yu, B.; Wang, X.; Zhou, F. Contact Printing a Biomimetic Catecholic Monolayer on a Variety of Surfaces and Derivation Reaction. *Chem. Commun.* **2012**, *48*, 398–400.
- (48) Piner, R. D.; Zhu, J.; Xu, F.; Hong, S.; Mirkin, C. A. “Dip-Pen” Nanolithography. *Science* **1999**, *283*, 661–663.
- (49) Poelma, J. E.; Fors, B. P.; Meyers, G. F.; Kramer, J. W.; Hawker, C. J. Fabrication of Complex Three-Dimensional Polymer Brush Nanostructures through Light-Mediated Living Radical Polymerization. *Angew. Chem., Int. Ed.* **2013**, *125*, 6982–6986.
- (50) Coad, B. R.; Bilgic, T.; Klok, H. A. Polymer Brush Gradients Grafted from Plasma-Polymerized Surfaces. *Langmuir* **2014**, *30*, 8357–8365.
- (51) Krabbenborg, S. O.; Huskens, J. Electrochemically Generated Gradients. *Angew. Chem., Int. Ed.* **2014**, *53*, 2–18.
- (52) Wei, Q.; Becherer, T.; Angioletti-Uberti, S.; Dzubiel, J.; Wischke, C.; Neffe, A. T.; Lendlein, A.; Ballauff, M.; Haag, R. Protein Interactions with Polymer Coatings and Biomaterials. *Angew. Chem., Int. Ed.* **2014**, *53*, 8004–8031.
- (53) Jiang, H.; Xu, F. J. Biomolecule-Functionalized Polymer Brushes. *Chem. Soc. Rev.* **2013**, *42*, 3394–3426.
- (54) Yang, W. J.; Neoh, K.-G.; Kang, E.-T.; Teo, S. L.-M.; Rittschof, D. Polymer Brush Coatings for Combating Marine Biofouling. *Prog. Polym. Sci.* **2014**, *39*, 1017–1042.
- (55) Paripovic, D.; Klok, H.-A. Polymer Brush Guided Formation of Thin Gold and Palladium/Gold Bimetallic Films. *ACS Appl. Mater. Interfaces* **2011**, *3*, 910–917.