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Expanding the Polymer Mechanochemistry Toolbox through Surface-Initiated Polymerization

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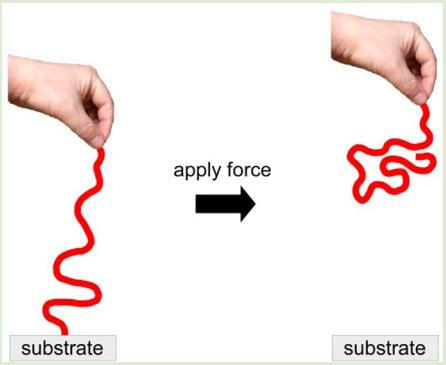
ABSTRACT: Surface-initiated polymerizations represent a versatile toolbox to generate densely grafted assemblies of chain end-tethered polymers. At sufficiently short interchain distances, surface-grafted polymers are forced into an extended chain conformation, which forms the basis of several unique properties, including their ability to withstand efficiently biofouling or to act as low friction coatings. While the effect on materials properties is well-established, only relatively recently first reports have appeared describing that chain stretching in surface-grafted polymer films also impacts chemical stability/reactivity. This Viewpoint presents surface-initiated polymerization as an alternative polymer mechanochemical tool. The absence of an external force field to induce chain elongation and the possibility to modulate chain stretching by varying brush molecular weight and grafting density, in conjunction with electrostatic interactions and nanoinclusions that may be present inside the polymeric grafts, make surface-initiated polymerization an attractive tool to both study and understand the effects of polymer chain conformation on the stability/reactivity of surface-grafted polymers.



Mechanical forces can alter reaction pathways of synthetic polymers.[1−7] For instance, mechanochemical activation of polymers in elongational flow fields has been used extensively to investigate chain scission and polymer degradation in solution. A major area of interest in modern polymer mechanochemistry includes the design of polymers that incorporate mechanically sensitive functional groups ("mechanophores"), which undergo site-specific bond cleavage.[8] With the improved understanding of the fundamental principles that govern mechanical activation of polymers in solution and the availability of an increasing variety of mechanophores, polymer mechanochemistry is no longer just a tool to study polymer degradation in solution, but offers unprecedented opportunities for the development of self-reporting and self-healing materials[9,10] as well as the creation of mechanocatalytic systems.[11]

A variety of techniques has been employed to induce chain stretching and mechanically activate polymers. These include, for example, turbulent and elongational flow fields as well as ultrasound[12,13] and single molecule force spectroscopy.[14] In this Viewpoint, surface-initiated polymerization (SIP) techniques are introduced as an alternative method that can be used to induce chain elongation and mechanochemically activate polymer chains. SIP techniques represent a largely unexplored toolbox to study and comprehend the effects of mechanical activation on the reactivity of surface-grafted polymers. This article consists of three parts. First, we briefly introduce SIP and highlight the main features of these techniques, which make them an attractive tool to induce chain stretching and mechanochemically activate polymers. We then briefly summarize the existing pertinent literature, which forms the basis for the fundamental ideas presented in this article. Finally, we present an outlook that discusses new possibilities SIP provides to both study and understand basic effects of chain stretching on polymer reactivity and the opportunities that arise in view of the generation of novel responsive surfaces.

Surface-Initiated Polymerization. SIP generates densely grafted assemblies of chain-end tethered polymer chains, which are often colloquially referred to as "polymer brushes" (Figure 1). During the past two decades numerous review articles have been published that provide an overview of the different synthetic approaches that can be used to fabricate such polymer assemblies.[15−28] In brief, polymer brushes can be prepared either by tethering appropriately chain-end functional polymers to a surface that presents complementary reactive groups ("*grafting-onto*"), or by polymerization of the monomer of interest from a surface that is modified with an appropriate initiator or chain transfer agent ("*grafting-from*"). The "*grafting-from*" approach generally allows to tether polymers at much shorter interchain distances (i.e., at higher grafting densities) and is also the technique that is most relevant to the ideas presented in this Viewpoint.

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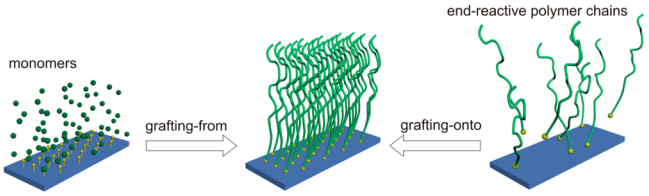

Figure 1. Cartoon illustrating the *"grafting-from"* and *"grafting-onto"* strategies for the preparation of polymer brushes. Note, for simplicity, the cartoons drawn here feature surface-tethered assemblies of polymer grafts with uniform lengths and grafting densities. In reality, the assemblies of polymer grafts will comprise chains with in-plane and length heterogeneities and spatially varying segment density distributions of the individual chains.

Surface grafting has important consequences on polymer chain conformation. If polymer chains are surface-grafted in sufficiently close proximity, steric repulsive interchain interactions will force the chains to stretch out and adopt an extended chain conformation, far away from the entropically more favored random coil conformation polymers adopt in a good solvent. The extended chain conformation is one of the key features that distinguishes densely grafted, chain end-tethered polymers from most other solution or solid state polymers, which generally adopt a more coil-like conformation. The extended chain conformation of polymer brushes also forms the basis for several unique physical and materials properties of these thin polymer films. These include the resistance of hydrophilic, water-swollen polymer brush films toward nonspecific adsorption of proteins, cells, and bacteria[29−32] as well as their ability to provide ultralow-friction surfaces and interfaces.[33−35] A number of recent reports has suggested that the extended chain conformation does not only influence the physical/materials properties of the surface-grafted polymer films, but also impacts their reactivity and stability. This Viewpoint aims to put these recent experimental findings in a conceptual framework and highlights the consequences and opportunities, which "mechanochemical" activation induced by chain stretching offers for the design of polymer brushes.

Degrafting of Polymer Brushes. The first reports that indicated that the stretched chain conformation of densely grafted polymer brushes can influence their chemical reactivity date back to 2007−2008. One of the first reports described the detachment of poly(poly(ethylene glycol) methacrylate) (PPEGMA) brushes upon incubating these films in cell culture medium.[36] These PPEGMA brushes were grown via surface-initiated atom transfer radical polymerization (SI-ATRP) from silicon substrates modified with a trimethoxysilane functionalized ATRP initiator. Scanning electron microscopy analysis of PPEGMA brushes that had been incubated for a period of 7 days in cell culture medium revealed the formation of wrinkled structures (Figure 2). The formation of these wrinkles was attributed to solvent-induced swelling of the PPEGMA brush and the concomitant stretching of the surface-grafted polymer chains, resulting in bond cleavage at the substrate−brush interface (Figure 3). Since SI-ATRP of PEGMA results in cross-linked films, bond cleavage at the anchoring site, after cleavage of a sufficient number of bonds, induces delamination of the brush film, which is visible in the form of wrinkles in scanning electron micrographs. The stability of the polymer brushes could be enhanced by decreasing the molecular weight and grafting density of the surface-tethered polymer chains,

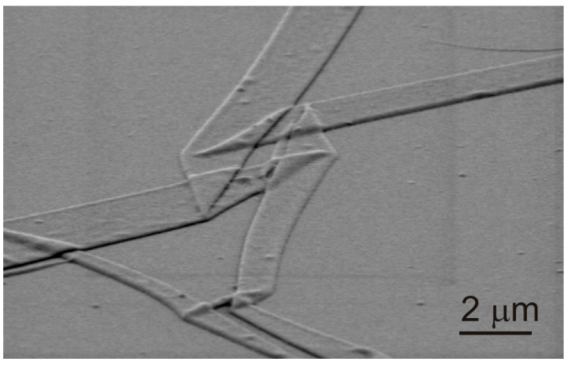

Figure 2. Scanning electron microscopy image of a densely grafted PPEGMA brush after 7 days of incubation in cell culture medium at 37 °C (reprinted/adapted with permission from ref 36. Copyright 2008 American Chemical Society).

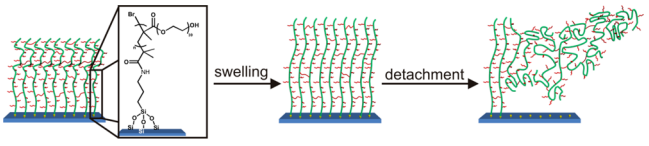

Figure 3. Swelling-induced detachment of cross-linked PPEGMA brushes grafted from silicon substrates.

which reduces the force acting on the bonds that anchor the polymer chains to the substrate.[36] A subsequent study reported that covering the ATRP initiator modified substrate with a thin layer of a hydrophobic polymer prior to reinitiating ATRP with methacrylic acid resulted in robust hydrophilic polymer brushes.[37] These results are consistent with hydrolytic bond cleavage at the brush−substrate interface (presumably the Si−O bond that links the organosilane modified ATRP initiator to the silicon substrate and/or the amide bond that connects the ATRP initiating group with the aminopropyl trialkoxysilane anchoring moiety), which is facilitated by the solvent-induced stretching of the surface-grafted polymer chains (and hence a "mechanochemical(ly-facilitated)" process). The findings discussed above were preceded by a paper by Deng and Zhu, who reported the degrafting of hyperbranched polyglycerols that were prepared via SIP from gold substrates.[38] Since 2010, a number of other studies has been published that describe the swelling-induced detachment of hydrophilic polymer brushes prepared via SIP, not only from silicon substrates,[39−41] but also from mica,[42] gold,[43−45] and polymer surfaces.[46]

Perspectives and Outlook. While the examples presented above provide first evidence that chain stretching in densely grafted polymer brushes alters the chemical reactivity of the constituent polymer chains, there are still many open questions. The specific nature of the bond (or bonds) that is (or are) responsible for the degrafting of polymer brushes from silicon substrates is one example. According to Rubinstein and co-workers, the largest tension in the brush takes place in the linker point (i.e., the bond where the polymeric graft attaches to the substrate).[47,48] It needs to be established whether the breakage occurs at the interface between the initiator and the substrate, for example, via the Si−O bond that anchors brushes grown from silicon surfaces, or within the initiator itself via the bond that connects the actual ATRP active group to the surface-anchoring moiety. Since many ATRP initiators contain either ester or amide bonds, those can be the source of breakage. While a variety of polymer brushes and different

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substrates has been investigated, systematic work pertaining to investigating the influence of brush composition, molecular weight and grafting density on the degrafting process is still missing. Degrafting of polymer chains from surfaces involves osmotic swelling of the grafted chains. While exposing grafted polymer assemblies to good solvents alone may not cause degrafting, there are instances that may lead to chain degrafting from the surfaces. Those include strong or weak electrolyte brushes with a high degree of charging, impregnation of brushes with salt or nonpolymeric inclusions (e.g., metallic or inorganic/oxide nanoparticles), attaching side-branches to the polymeric chains, or simply "squeezing" the polymer grafts on the substrate by an external force (Figure 4).

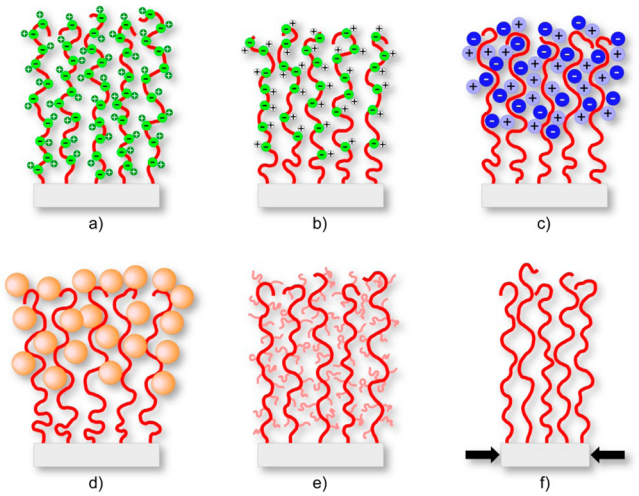

Figure 4. Examples of surface-grafted polymer brush assemblies that may be susceptible to swelling-induced degrafting: (a) strong polyelectrolytes; (b) weak polyelectrolytes; (c) brushes impregnated with salts; (d) brushes impregnated with nanoinclusions; (e) branched brushes; and (f) brushes prepared on flexible substrates exposed to lateral stresses.

Most work that has been carried out so far has been qualitative and there is a need for more quantitative approaches to describe and understand these phenomena. This includes, for example, investigation of the kinetics of the degrafting reaction as well as (semi)quantitative guidelines for the design of polymer brushes with predictable degrafting properties, systematic studies of the effects of the aforementioned parameters, determination of the locus of degrafting, and so on. Degrafting polymer brushes can offer new important insight into the structure of polyelectrolyte grafts. For instance, while strong polyelectrolyte brushes have their charges fixed, the distribution of charges in weak polyelectrolyte brushes depends not only on the solution pH and concentration of external salt but also on the brush grafting density; these properties collectively govern the charge distribution within the brush.[49] To this end, due to charge regulation close to the substrate, where the degree of charging is lower than that close to the free end of the brush, weak polyelectrolyte brushes may be more stable than their strong polyelectrolyte counterparts. While initial work on this topic has begun, more systematic investigation is needed.[40] These are just a few examples of fundamental questions, which are not only exciting, but also important to address. Answering these queries will not only help to develop more stable, robust polymer brush films, but is also essential in order to explore these mechanochemical phenomena for the development of novel responsive surfaces.

Conclusions. The aim of this Viewpoint has been to convey the idea that SIP is not only a powerful method to generate densely grafted polymers with intriguing materials properties, but can also be used to modulate the chemical reactivity of these surface-grafted polymer films. Compared to other methods that can be employed to generate molecular forces, SIP techniques are characterized by a number of unique features that make them very attractive for polymer mechanochemistry. These include, among others (i) the absence of a need for an external force field to induce chain elongation and (ii) the ability to investigate systematically the influence of chain stretching on chemical reactivity by varying independently the brush molecular weight and grafting density.

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Notes

The authors declare no competing financial interest.

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