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Sub-Micron Patterning of Polymer Brushes by Controllable Deposition of Polyelectrolyte Monolayers

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Abstract

The controlled deposition of polyelectrolyte macroinitiators for polymer brush growth is investigated. High resolution patterns are created for periodic array gratings towards responsive polymer brush sensors. Further, controlling the segregation of the macroinitiator to the droplet edge by careful manipulation of the constituent solutes leads to sub-micron patterning of polymer brushes.

Introduction

Thin films formed of polymer chains densely end-grafted to a surface are known as *polymer brushes*[1]. The excellent solvent-resistance conferred by grafting, the vast range of applicable polymers, including stimulus-responsive and multiblock, along with fundamental differences in physical properties compared to free polymers due to the steric constraint, has led to emerging applications in diverse fields such as biomedicine, microelectronics, photovoltaics and sensing[2]–[8]. High resolution patterning of polymer brushes is further expanding their utility, for example in biomedical applications; the manipulating of cell culture microenvironments, patterning cell growth and sensors based on photonic effects[9]–[12].

Brushes can be created by direct attachment of a preformed polymer to a surface, known as *grafting-to.* Aternatively, an initiator monolayer is first deposited on the surface from which a polymerization can be initiated, growing the polymer directly. This technique is known as *grafting-from* and often offers more flexibility than the *grafting-to* process.

A range of high resolution techniques has been considered for polymer brush patterning. For example, microcontact printing (μCP), in which a topographically patterned rubber stamp is 'inked' with an initiator monolayer-forming reagent and applied to the surface, allows for rapid and complex brush patterning. However, the initial stamp fabrication can be costly and is not compatible with rapid pattern iteration[13], [14]. Further, the generation of sub-micron features by this technique requires even more specialized procedures. Equally, direct photolithographic monolayer patterning, such as the destruction or activation of a pre-formed monolayer, by exposing directly through a mask or via photoresist processes, suffers from the same barrier to rapid pattern iteration of lengthy mask fabrication[15]–[17]. Techniques are available which can generate monolayer patterns *on-the-fly* such as dip-pen nanolithography and e-beam lithography but are typically used for the production of extremely high resolution patterns, require long processing times and cover only small areas[18], [19]. To the best of our knowledge there is currently no universal technique capable for the rapid iteration of high resolution polymer brush initiator patterns.

In contrast, direct additive printing is fast becoming a tool for high throughput tool for materials patterning. It possesses a number of potential benefits, including good material usage efficiency, the avoidance of expensive process steps such as photo-lithography, etching and vacuum deposition, and the ability to rapidly change designs in real time in a highly cost effective fashion. Here we focus on the use of inkjet because of its ability to accurately dispense variable volumes of material per drop, 0.5 fL – 100 pL, with high resolution. Feature sizes currently down to 15 μm are achievable for piezo drop on demand and ca. 1 μm utilizing an electrohydrodynamic based firing mechanism, all in the absence of complimentary small feature patterning strategies.

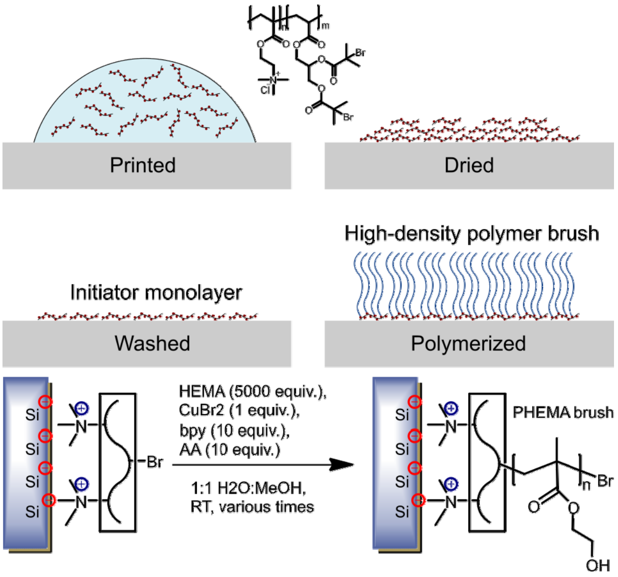

Figure 1*. Schematic of the printing a polymerization process of creating macroinitiator patterns and growing pHEMA polymer brushes by SI-ARGET-ATRP.*

The patterning of initiator monolayers by inkjet is a technological challenge and as such there are only a few examples in the literature. Sankhe *et al*[20] used drop-on-demand printing of self-assembled monolayers (SAMs) with thiol-terminated ATRP initiators to produce millimeter-scale patterns on gold using a consumer inkjet printer. Although this is an easily-accessible process, due to both the inherently large drop-size and monolayer spreading after jetting, using consumer technology such as this is unlikely to be applicable to *micro*patterning. Emmerling *et al*[21] also produced large scale brush patterns (> 50 μm feature size) using inkjet printing with a drop-on-demand microarray system. In this instance a pre-formed homogeneous monolayer was patterned by jetting sulphuric acid causing the acid-sensitive initiator to be destroyed in the printed regions. This approach required extended acid contact times and careful control of conditions to properly destroy the initiator, but does allow tunable grafting density. Finally, polymer brushes have been formed directly by jetting reactive end-functional polymers from an electrohydrodynamic printer on silica substrates at sub-micrometer resolution, which were then used to control block copolymer phase separation[22]. However, it is extremely difficult to access high grafting densities and thick brush layers with such *grafting-to* strategies, hence a *grafting-from* procedure (i.e. polymerisation from immobilised initiators) was chosen for our work.

Herein we create polyelectrolyte macroinitiator (MI) based inks to functionalize a surface. Polymer brushes are grown from this MI monolayer using a surface initiated atom transfer radical polymerization with activator regenerated by electron transfer (SI-ARGET-ATRP) in a *grafting-from* procedure (**Figure 1**).

Using functional polyelectrolytes for surface functionalization has several benefits: being large molecules, spreading on the surface by diffusion (as observed with small-molecule thiols) is negligible, allowing excellent pattern fidelity[20]. Polyelectrolyte deposition can be generalized to any charged surface, avoiding surface-specific and reactive chemical groups[23] and, unlike silane and thiol self-assembled monolayers, polyelectrolytes can be processed from water. Furthermore, these polymers can be synthesized on a large scale, the grafting density (number of initiator sites per unit area) can be tuned through varying monomer ratios and further functionality can be introduced through copolymerization.

We go on to explore how control over the precipitation of the cationic polyelectrolyte MI during the print drying process the can be further harnessed for ultra-fine patterning whereby feature size is in part decoupled from the limitations of the droplet size. These patterns are then amplified by SI-ARGET-ATRP of polymer brushes, producing robust surface-grafted topographic patterns of sub-micron size. Further, we believe that this has the potential to be applied to many other polyelectrolyte based systems.

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