Synthesis and Characterization of Hydrogels Grown on Surfaces by ATRP

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Statement of Purpose: Biocompatible polymer networks with specific structure and orientation have tremendous potential in the biomedical field (e.g., diagnostic and therapeutic applications). The spatial control over the growth on surfaces plays a vital role, since it allows specific regions (e.g., sensing elements) of the device to be functionalized. Herein, atom transfer radical polymerization (ATRP) was applied for the controlled synthesis of hydrogel systems on Au and Si substrates. Patterning using microcontact printing (μCP, XY control) followed by ATRP (Z control) and optimization of process variables for the synthesis of novel hydrogels (e.g., temperature responsive) on gold and silicon surfaces was completed.

Methods: μCP of a hydrophobic thiol or silane was performed over Au and Si surfaces respectively using a PDMS stamp prepared by the replica molding method of soft lithography technique. The PDMS pattern was obtained by using a suitable Si master stamp, prepared initially by UV photolithography. Then the surface was made to adsorb a second self assembled monolayer, SAM of a hydrophilic thiol or silane which eventually filled the zones not occupied by the first thiol or silane. After modifying the terminal end group of the hydrophilic SAM with the initiator molecule, ATRP was carried out at 60°C and under N_2 atmosphere. Various sets of monomers, crosslinkers, ligand, and monomer to crosslinker ratios were used. Figure 1 shows a scheme of the ATRP reaction carried out over a gold surface. Also a similar scheme is applied in the case of Si.

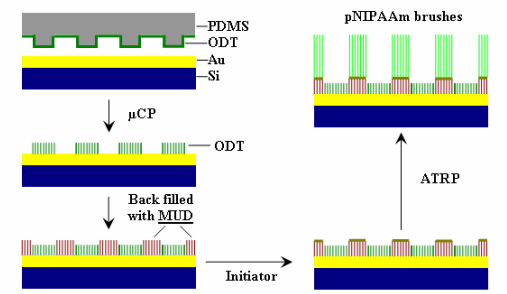

Figure 1. Scheme of μCP and ATRP over gold substrate

Results/Discussion: Characterization was done using FTIR and AFM imaging. Swelling studies were carried out in the liquid cell. From figure 2a and b it is clear that the photolithography step of making master stamps is precise and a similar kind of microstructure is easy to replicate using PDMS. The thickness of the microstructures in the PDMS was confirmed using AFM as 1.5 μm.

The polymer growth and patterns were verified for their thickness using the AFM. As it can be seen from Figure 3 precise patterns were obtained using μCP and that the growth of the polymeric film was found to be in tens of nanometers. The growth increased gradually with increased reaction time. In the case of silicon clear patterns were not obtained because oxygen inhibited the attachments of SAMs. Nitrogen was used to rectify this problem and clear patterns were formed.

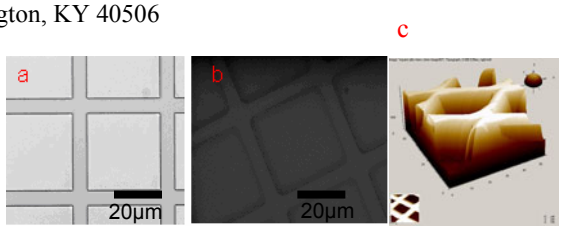

Figure 2. a) Nikon Microscope image of master stamp showing squares (pits) of 25 μm and b) PDMS stamp of squares (elevated portions) 25 μm width and c) is the contact mode AFM 3D image of master stamps of thickness 1.4 μm

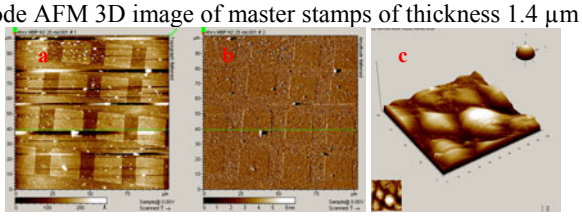

Figure 3. Non contact mode AFM image showing a) the flattened topography and b) deflection (2-D) buffers of an ATRP sample carried for 24 hours over gold surface. c) the 3-D image of polymer brush over squares over a silicon surface.

FTIR was used to verify the extent of reaction and is being used to correlate with the thickness of polymer grown over surfaces (figure 4.)

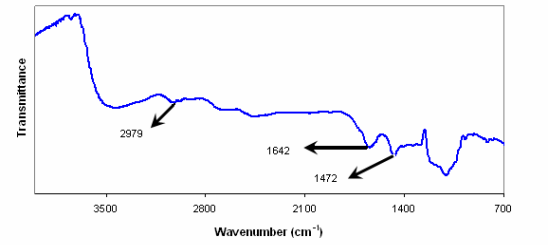

Figure 4. FTIR absorbance profile of a Si sample confirming the presence of NIPPAm and crosslinker TEGDMA over the surface.

Conclusions: We have successfully demonstrated a route for forming patterned polymeric chains on surfaces by using μCP and ATRP techniques. We have also showed that by using an inert atmosphere, better micropatterns can be achieved over Si surfaces. We have produced clear and precise micropatterns over Si master stamps using photolithography which were reproduced successfully as PDMS stamps. Results show that the thickness of polymer networks over surfaces can be controlled by varying the reaction conditions. It is easy to produce intelligent polymer networks such as temperature responsive hydrogels using suitable crosslinkers. Characterization and analysis using AFM and FTIR can be employed to study the response behavior of hydrogel networks when stimulated environmentally. These methods will be applied to integrate intelligent polymer networks into various biomedical devices.