

Polymer Communication

Extending micro-contact printing for patterning complex polymer brush microstructures

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ARTICLE INFO

Article history:

Received 25 January 2011

Received in revised form

28 February 2011

Accepted 5 April 2011

Available online 12 April 2011

Keywords:

Soft lithography

Patterning

SI-ATRP

ABSTRACT

As a fast developing soft lithographic technique, the development of micro-contact printing (μ CP) has exceeded the original aim of replicating poly(dimethylsiloxane) (PDMS) stamp patterns. Here we exploited several extended μ CP strategies with various printing conditions (over-force or swelling induced physical deformation, and UV-Ozone treated chemical surface modification to a PDMS stamp), combining with surface initiated atom transfer radical polymerization (SI-ATRP), to pattern complex poly(N-isopropylacrylamide) (PNIPAAm) brush microstructures. These series of μ CP strategies avoid the need for expensive and sophisticated instrumentation in patterning complex polymer brush microstructures that do not exist on the original PDMS stamp.

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1. Introduction

Micro-contact printing (μ CP) was first exploited in 1993 by Whitesides et al. for depositing patterned self-assembled monolayers (SAMs) from an elastomeric poly(dimethylsiloxane) (PDMS) stamp feature onto Au substrate surfaces [1]. As a simple and cost-effective patterning approach, this technique has been used by a large number of researchers in the preparation of micro/nanomaterials [2–5]. Specifically, patterning of polymer brushes is a rapidly developing direction [6–8], because of their potentially useful for protein-resistant coatings, switchable sensors, and for the study of stimuli-responsive phenomena [9]. While early examples, reported by Jeon [10] and Husemann et al. [11] of fabricating patterned polymer brush microstructures using μ CP involved printing an octadecyltrichlorosilane (OTS) pattern to direct the backfilling of the interspaces with an initiator and a subsequent surface initiated polymerization (SIP), more recent, alternative approaches, printed polymerization initiators directly [12–14]. To date, the development of μ CP has exceeded the original

aim of replicating PDMS stamp patterns. Much complex microstructures were extended to achieve easily by physical alternation of the elastomeric stamps via lateral compression or solvent swelling of a stamp during μ CP [15,16]. Recently, edge transfer lithography (ETL), combined with μ CP was exploited to pattern ring-shaped SAMs when treating a cylindrical PDMS stamp surface by plasma or UV-Ozone that allows to deposit SAMs onto a substrate selectively along the feature edges of the stamp [17].

In practical applications, the properties of materials are highly dependent on the complexity of structures that render the necessity for the fabrication of complex polymer brush microstructures. They have been fabricated via several patterning strategies combining with SIP, e.g. electron-beam chemical lithography (EBCL) [18,19], or electron-beam induced carbon deposition (EBCD) [20]. These elegant patterning strategies remain inaccessible to a large number of researchers due to the instrumental expensive complexity required. This motivates one endeavor to exploit new simple patterning strategies. There are several current efforts, as alternative approaches, of fabricating complex polymer brush morphologies by μ CP via adjusting printing conditions. For examples, Zhou et al. described a general μ CP route to pattern laterally distinctive multi-component polymer brushes involving repeated printing process following a deactivated step of previous polymer brush activity, which enabled the “synthesis” of very complex polymer surfaces [14]. Wang et al. recently prepared hierarchically structured polymer brushes with well-defined geometries via

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multiple step μ CP that using inks containing different ratios of initiator thiols and non-reactive thiols [21]. We have previously reported egg-cup shaped polymer brush microstructures could be obtained using a circular cylindrical PDMS stamp with a various printing conditions and multi step μ CP [22].

In this communication, we exploited several extended μ CP approaches [15,17], and combined surface initiated atom transfer radical polymerization (SI-ATRP) of N-isopropylacrylamide (NIPAAM) for patterning complex (feature size or morphology) poly(N-isopropylacrylamide) (PNIPAAM) brush microstructures. We demonstrated these series of patterning strategies using a conventional circular cylindrical PDMS stamp that was utilized under various μ CP conditions including physical deformation, or UV-Ozone treatment induced chemical modification, to a PDMS stamp feature. Our work not only develop a strategy to fabricate new polymer brush microstructures that do not exist on the original PDMS stamp by μ CP, but also provide an alternative simple approach without sophisticated instrumentation necessary to pattern complex brush morphologies.

2. Experimental section

2.1. Chemical materials

General chemicals were analytical reagent grade and were used as received from Sigma Aldrich, or Acros Organics. NIPAAM (99%), Sodium Acrylate (97%), Copper(I) Bromide (CuBr, 99.9%), Toluene (anhydrous, 99.8%), Sodium Azide (NaN_3) and Methanol (MeOH, 99.9%) were obtained from Sigma–Aldrich (Milwaukee, WI). Milli-Q (Millipore, Billerica, MA) water (18 M Ω /cm) and methanol were used as polymerization solvents. N,N,N,N,N-Pentamethyldiethylenetriamine (PMDETA) was used as received from Acros Organics (Hampton, NH). PDMS stamp were fabricated from Sylgard 184 (the ratio between component A and B was 1:10, Dow Corning, Midland, MI). The thiol initiator, ω -Mercaptoundecyl Bromoisobutyrate ($\text{BrC}(\text{CH}_3)_2\text{COO}(\text{CH}_2)_{11}\text{SH}$) was synthesized as reported [23,24]. To immobilize the initiators for surface-initiated polymerization, gold substrates were prepared by thermal evaporation under a vacuum of 4×10^{-7} Torr. For this purpose an adhesion layer of chromium (50 Å) followed by a layer of gold (450 Å) was evaporated onto silicon wafers. Before deposition,

silicon wafers were cleaned in a mixture of $\text{H}_2\text{O}_2/\text{H}_2\text{SO}_4$ (1:3, v/v) at 80 °C (“piranha solution”) for 10 min and washed thoroughly with Milli-Q-grade water. (Caution: Piranha solution reacts violently with organic matter!).

2.2. Micro-contact printing (μ CP)

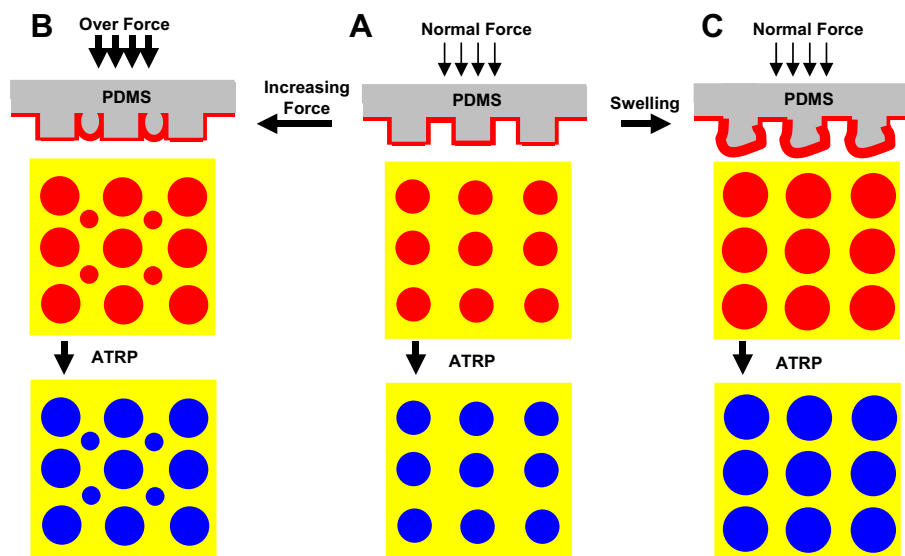
The PDMS stamp was inked by exposing the stamp features to an ethanol solution of thiol initiator (~ 2 mM) for 3 min, and dried with nitrogen, then brought into contact with gold substrate for 20 s. Normal μ CP: print stamp on gold surface at perpendicular direction with gentle force at ~ 50 g; Swelling PDMS stamp induced μ CP: print swelled stamp on gold surface at perpendicular direction with print force at ~ 50 g. The stamp was swelled in toluene for 20 min before conducting μ CP. Over-force induced μ CP: print stamp on gold surface at perpendicular direction with print force at ~ 1000 g.

2.3. Surface initiated atom transfer radical polymerization (SI-ATRP)

The polymer brushes were synthesized according to our previous report [22]. Briefly, the polymerization solution was prepared by adding a water solution of NIPAAM monomer to an organometallic catalyst. The organometallic catalyst was formed in a nitrogen atmosphere by adding CuBr (1.8 mg, 0.013 mmol) and PMDETA (14 μ L, 0.064 mmol) in a 1:5 M ratio to 1.0 mL of MeOH as solvent. The mixture was then sonicated for 2 min to facilitate the formation of the CuBr/PMDETA complex. Next, 1.5 g (17 mmol) of NIPAAM monomer was dissolved in 5 mL of water. The polymerization solution was then transferred into flasks containing the sample substrates with immobilized patterned initiator. The flasks were sealed with rubber septa and kept at room temperature under nitrogen. After the desired reaction time, substrates were removed from the polymerization solution, exhaustively rinsed with DI-water to remove all traces of the polymerization solution, and subsequently dried in a stream of nitrogen.

2.4. Binary polymer brush fabrication

The PNIPAAM brush was deactivated by immersing it into a 0.36 M NaN_3 /water solution for two days [25]. It was then



Scheme 1. Schematic illustrations of our first strategies showing the main steps involved in various μ CP of initiator patterns and their subsequent amplification into patterned polymer brush microstructures by SI-ATRP. (A) Normal μ CP: printing stamp with a gentle force. (B) Over-force μ CP: printing stamp with an over-force. (C) Swelling μ CP: print swelled stamp with a gentle force. μ CP was carried out at perpendicular direction on gold surface.

ultrasonically rinsed with de-ionized water. The deactivated brush grafted substrates were used to backfill the thiol initiator and for growing second polymer brushes of poly(sodium acrylate) (PNaAc) [26,27].

2.5. Edge transfer lithography (ETL)

PDMS stamp was treated by UV-Ozone for 2 min before using as an ETL tools. The oxidized PDMS stamp was then inked by exposing the stamp features to an ethanol solution of thiol initiator (~ 2 mM) for 3 min, and dried with nitrogen, then brought into contact with gold substrate for 20 s.

2.6. Characterization

Polymer brush grafted substrates were rinsed with DI water, dried under a stream of nitrogen, and mounted on steel sample disks prior to AFM measurements. AFM topographic images were collected in contact mode using V-shaped silicon nitride cantilevers (Nanoprobe, Veeco, spring constant 0.12 N/m; tip radius 20–60 nm) using a Multi-Mode atomic force microscope (Digital Instruments, Santa Barbara, CA). Topographic imaging was performed in air at room temperature, and were obtained under low

applied normal forces (< 1 nN) to minimize compression and lateral damage of the polymer microstructures.

3. Results and discussion

Our first strategy that lies on physical deforming a PDMS stamp for patterning complex polymer brush microstructures for was schematically shown in Scheme 1. A normal μ CP (Scheme 1A), using a thiol initiator inked and then dried PDMS stamp to contact conformal with gold surface under a gentle force, was carried out to make a comparison with over-force and swelling induced μ CP. The over-force μ CP (Scheme 1B) was operated by applying an over-force on an initiator inked PDMS stamp under the perpendicular direction compels collapsed stamp roof contact with gold surface which results in initiator, both on roof and on feature surface, being transferred onto gold surface. Cross-linked PDMS can be swelled in a number of solvents, such as toluene or hexane [28]. An initiator inked such swelled PDMS stamp could be used to transfer bigger thiol initiator pattern feature during μ CP (Scheme 1C). These transferred initiator pattern can subsequently be amplified into various polymer brush microstructures via SI-ATRP. We demonstrate these series of patterning strategies using a conventional circular cylindrical PDMS stamp without particular design of their structure parameter.

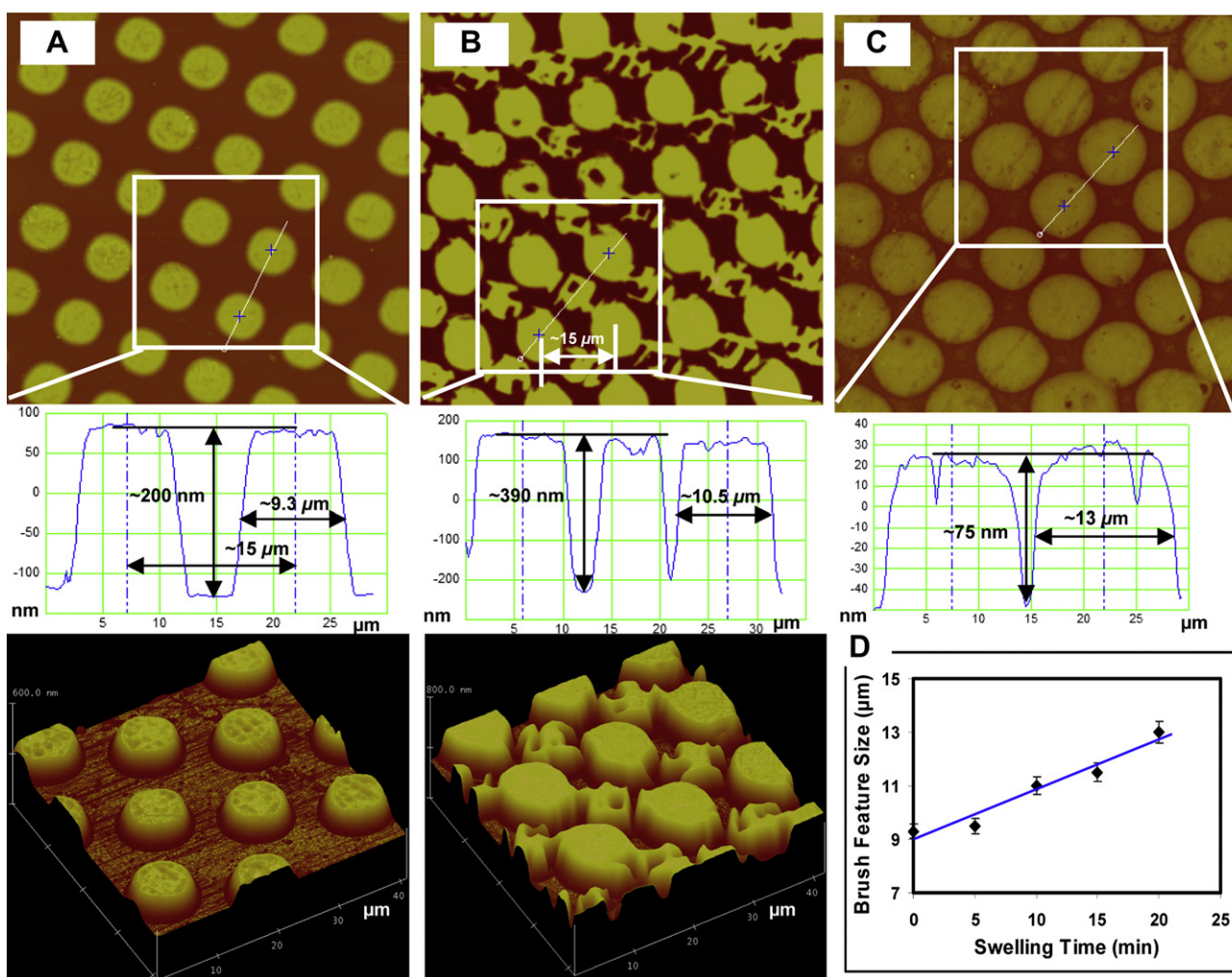


Fig. 1. Contact mode AFM height images ($80 \mu\text{m} \times 80 \mu\text{m}$) of various morphology adjustable patterned polymer brush microstructure by μ CP under different printing conditions, imaged at RT in air and the corresponding height profiles and 3D images, (A) Normal μ CP, ~ 50 g. (B) Over-force μ CP, ~ 1000 g. (C) Swelling μ CP, PDMS stamp was swelled in toluene for ~ 20 min before conducting μ CP, ~ 50 g. All the contact time is 20 s. (D) Plot of brush feature diameter versus swelling time. The polymerization conditions were maintained unchanged in all three examples. The PDMS stamp had a circular cylindrical pattern with a feature size of $\sim 10 \mu\text{m}$ and feature spacing (center-to-center) of $\sim 15 \mu\text{m}$.

The normal μ CP was firstly carried out to pattern a regular polymer brush microstructures by a gentle print force at ~ 50 g under perpendicular direction, combining with SI-ATRP of NIPAAm. Under this general mild printing condition, feature size and shape could be transferred from thiol initiator inked stamp after μ CP. The AFM height images and selected corresponding height profiles and 3D images of the grafted polymer brushes were shown in Fig. 1A. The resulting brush microstructure has a height of ~ 200 nm, a feature diameter of $9.3 \pm 0.2 \mu\text{m}$ and $\sim 15 \mu\text{m}$ feature space, which is consistent with the size of original stamp feature.

Based on the above successful growth of polymer brushes under the normal μ CP, we extended μ CP to use the same PDMS stamp that was handled under various printing conditions. The elastomeric property of PDMS allows stamp to be widely used in replicating contact feature patterns with high fidelity through the conformal contact between the substrate and the inked stamp feature surfaces [2]. This unique property is also applicable to a deformed stamp [15,16]. Xia and coworkers [15] gave us early examples to demonstrate a number of approaches of extending μ CP for fabricating new patterns that do not exist on the original PDMS stamp via controlling the stamp physical structures by force or solvent induced mechanical deformation. Yang et al. [16] recently focused on overpressure contact printing (oCP) during μ CP to pattern micro/nano structured materials, in which the feature shape differed with the original one. These efforts improve μ CP for bringing forth a spectacular increase in versatility of SAM and subsequent potential possibility of fabricating complex polymer brush microstructures. In their approaches, the structure or chemical composition of the PDMS stamp was particularly designed for specified μ CP. We demonstrated here that

a conventional PDMS stamp without particular design could also be used to pattern various morphologies.

By applying an over force (~ 1000 g) to the PDMS stamp, a thiol initiator pattern is transferred both from roof and features to gold substrate [16,29]. Subsequent amplification produced complex polymer brush patterns including the “original” feature pattern (feature diameter of $\sim 10.5 \pm 0.5 \mu\text{m}$, height ~ 390 nm, and $\sim 15 \mu\text{m}$ feature space), and the new produced pattern ($\sim 4.0 \pm 0.5 \mu\text{m}$ with a similar height and feature space) located in the center of original features (Fig. 1B). Although the over-force induced μ CP could be used to generate new patterned brush microstructures, there is still some difficulty to reach an expected feature size. This could be advanced by a future improvement of designing a smart machine to program over-force μ CP. A swelled PDMS stamp still has good mechanical properties and could be used for μ CP under normal printing conditions. Subsequent amplification of the transferred initiator pattern template yielded PNIPAAm brush microstructures possessing a bigger feature size with a diameter of $13.0 \pm 0.3 \mu\text{m}$ and a height of ~ 75 nm without feature space change (Fig. 1C). The feature diameter of the resulted polymer brush microstructure highly depended on the swelling time to a PDMS stamp. An approximate linear increasing relation could be obtained upon swelling the stamp with increased times (Fig. 1D).

It was noted that the brush height in different type of μ CP showed a various value even the all the polymerization condition was kept similar. The reason resulted from the different initiator grafting density [23] generated during various μ CP. Compared with the normal μ CP, a higher applied printing force during over-force μ CP promoted the thiol initiator transfer from stamp to the gold

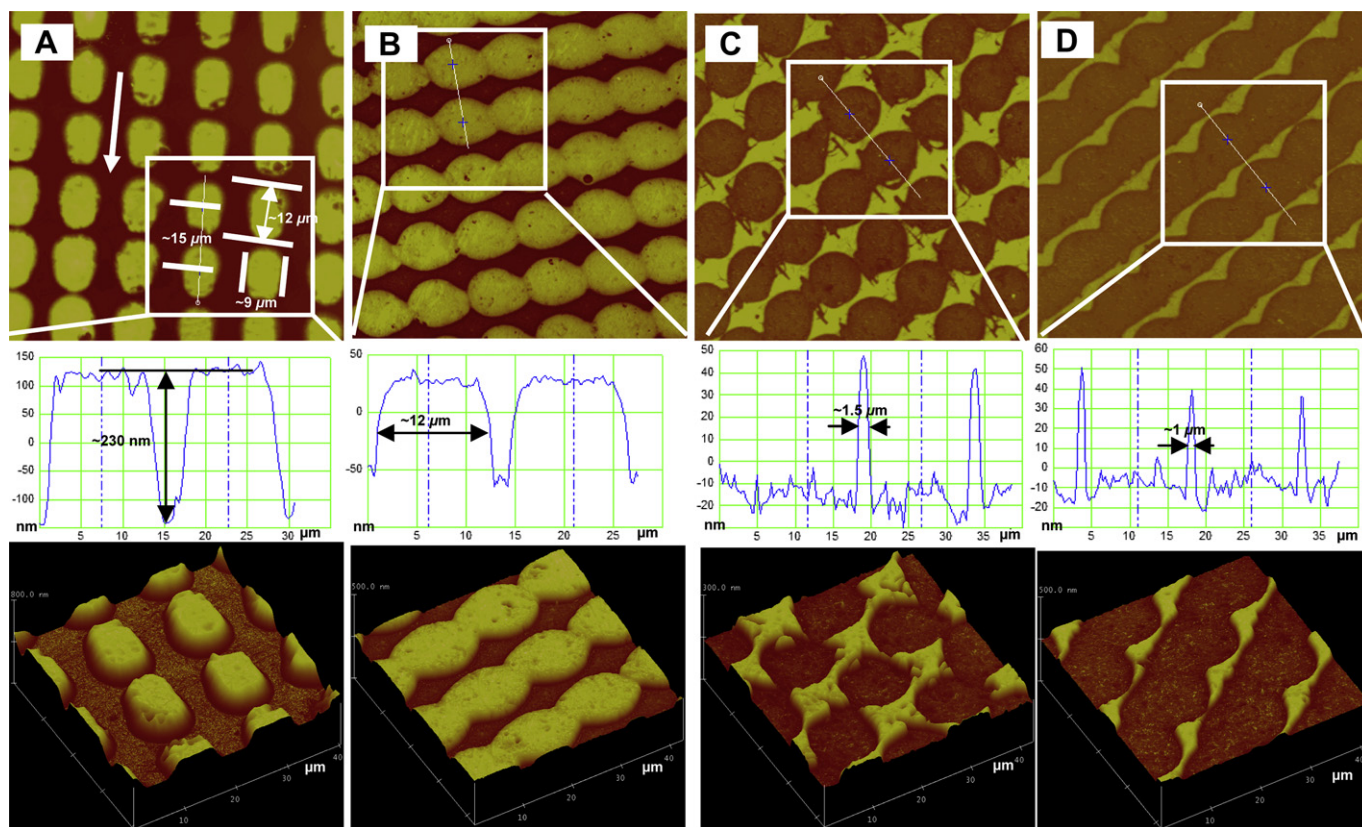


Fig. 2. Contact mode AFM height images ($80 \mu\text{m} \times 80 \mu\text{m}$) of patterning complex polymer brush microstructure under the combination of various printing conditions, imaged at RT in air and the corresponding average-height profiles. (A) Combining force direction and higher force induced μ CP, ~ 500 g. (B) Combining swelling and force direction induced μ CP, ~ 500 g. (C) Binary polymer brush obtained after swelling induced μ CP, ~ 50 g. (D) Binary polymer brush obtained after swelling and force direction induced μ CP, ~ 500 g. All the contact time is 20 s. For swelling μ CP, PDMS stamp was swelled in toluene for ~ 20 min before conducting μ CP.

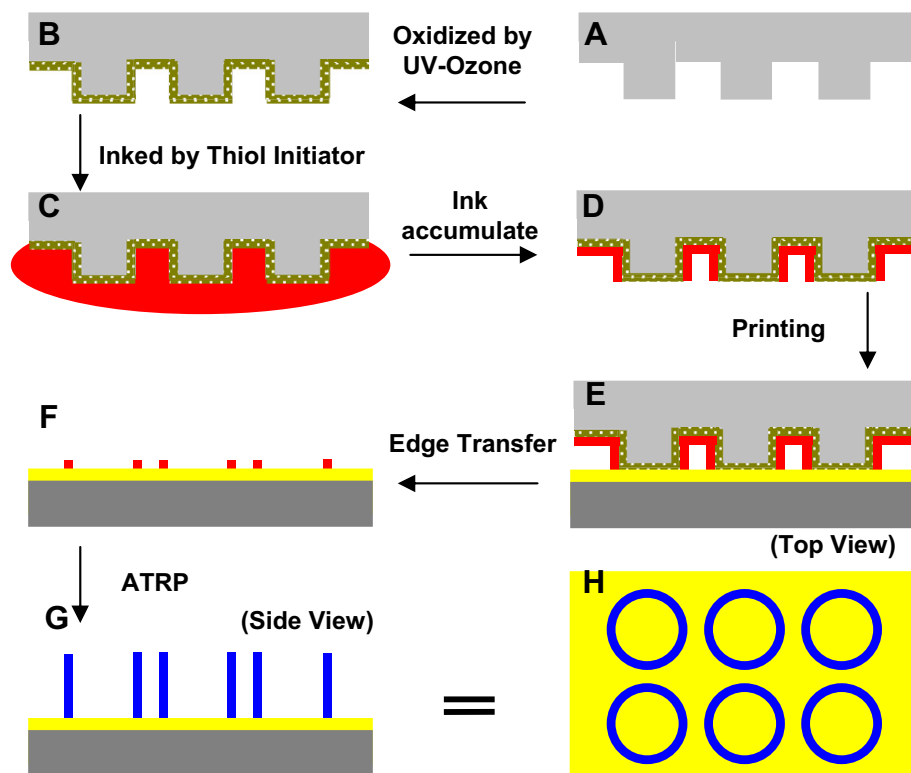
surface for forming a higher initiator graft density. An increased feature size diluted the distribution of thiol initiator on stamp surface, which produced low grafting density of initiator SAMs. We noted that both over-force and swelling induced printing process were reversible once removing the over force or evaporating all the solvents [15]. The former took a significantly faster than the latter as PDMS stamp may return easily to its original shape and feature size after taking off the over-force. Nevertheless, it took normally one week to recover a swelling stamp under a room condition, a few hours under vacuum condition. The AFM images, showing a decreased feature diameter of the resulted polymer brush microstructure upon using the stamp dried with increasing time under room conditions, were shown in the Supporting Information (SI, Fig. S1).

Furthermore, the combination of the various printing conditions could also be used to fabricate new polymer brush microstructures. For example, during a higher force (~ 500 g) μ CP, changing the applied force direction from perpendicular to tilted one and along the marked direction (see white arrow in Fig. 2A) results the contact or ink diffusion from feature surface to both feature surface and side feature with gold surface. The resulting elongated PNIPAAm brush pattern was achieved to have a feature size at wide side of 12.0 ± 0.3 μ m and narrow side of 9.0 ± 0.2 μ m, with a height at ~ 230 nm (Fig. 2A). While a swelled cylindrical PDMS stamp was used in the above printing condition, a pearl-liked pattern was generated because of the swelled stamp feature resulting in the connection of neighbored feature. The resultant polymer brush microstructures with a size 15.0 ± 0.2 μ m and ~ 85 nm at height were shown in Fig. 2B.

The above patterning strategies of generating polymer brush microstructure using swelling or further combination with force direction induced μ CP, produced a bigger feature size, leaving

a smaller blank space that could be used to fabricate binary polymer brushes with a size-reduced even sub-micrometer feature. There is considerable interest to pattern binary polymer brushes because of their wide applications as the model surfaces for the investigation of interfacial phenomena, protein adsorption and separation, molecular recognition, and as the templates in the pattern formation of bio-specie array [14,25,30]. To confine the second brush to only the backfilled initiator areas, the bromo-initiator at the end of PNIPAAm brush was deactivated. This was realized by transforming the Br end-group to an azide end-group by immersing it into a 0.36 M NaN_3 /water solution for two days, followed by an ultrasonic rinse with de-ionized water [25]. After backfilling a thiol initiator and a subsequent amplification by second SI-ATRP of sodium acrylate, a binary polymer brushes of poly(sodium acrylate)(PNaAc)/PNIPAAm was fabricated after a swelling induced μ CP (Fig. 2C). The feature size of the second polymer brush of PNaAc was reduced to ~ 1.5 μ m. When the binary polymer brush of PNaAc was grown after first PNIPAAm brushes that was fabricated under a force direction and swelling induced μ CP, the feature of PNaAc was changed to a line pattern with a even more smaller size (Fig. 2D). The success and advantage of this approach lie in the flexibility and generality without the use of any complex instruments and rigorous experimental conditions.

Our second strategy that lies on UV-Ozone treatment to a PDMS stamp for patterning ring-shaped polymer brush microstructures using a cylindrical PDMS stamp was schematically shown in Scheme 2. As a fast developing soft lithographic technique, μ CP was extended to be combined with other techniques, such as ETL [17], for patterning more complex microstructures. Edge lithographic patterning techniques are based on the utilization of the edges of micrometer-sized features for the generation of sub-micrometer structures. When combined with μ CP, ETL permits a local surface modification in a single step by transferring SAMs onto a metal



Scheme 2. Outline procedure for fabricating patterned ring-shaped polymer brush microstructures by stamp based ETL combining with SI-ATRP. The surface of a PDMS stamp (A) was treated by UV-ozone (B) to form a surface oxidized silica layer; upon inked by thiol initiator (C), the ink was accumulated in the recessed areas of the stamp feature (D) and are transferred after dry to the gold surface via the edges of the elevated stamp features (E, F). After subsequent amplification by SI-ATRP, a ring-shaped polymer brushes was obtained (G, H).

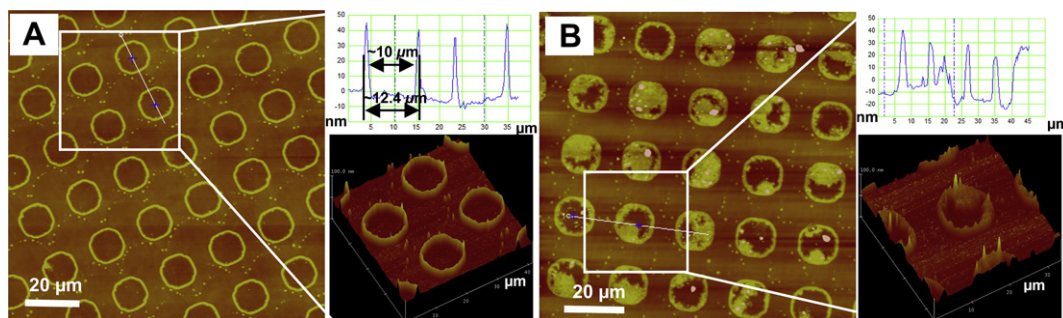


Fig. 3. Contact mode AFM height images ($100\ \mu\text{m} \times 100\ \mu\text{m}$) of polymer brush microstructure by ETL using a fresh (in 30 min, A) and non-fresh (after 4 h, B) UV-ozone treated PDMS stamp by combining SI-ATRP, imaged at RT in air and the corresponding average-height profiles. A cylindrical PDMS stamp with a feature size of $\sim 10\ \mu\text{m}$ and feature spacing (center-to-center) of $\sim 20\ \mu\text{m}$. Force, $\sim 50\ \text{g}$, contact time 20 s.

surface selectively along the feature edges of a PDMS stamp. Burdinski and coworkers [17] reported a successful approach to extend the use of ETL to thiol inks without the loss of the inherent advantages of μCP . By exchanging simply the thiol molecules with thiol initiator, a ring-shaped polymer brushes microstructures could be fabricated. In the first step, PDMS stamp was firstly oxidized by UV-Ozone for 2 min to form a hydrophilic barrier layer (Scheme 2A and B), which renders it impermeable and repellent to the applied ink molecules [17]. Thiol initiator was used to ink the stamp and thus could be accumulated in the recessed area of the oxidized stamp pattern (Scheme 2C and D). Upon contact between the dried inked stamp and a gold substrate, the ink was transferred to the gold surface exclusively via the vertical edges of the elevated stamp features, and was amplified into ring-shaped polymer brush microstructures via SI-ATRP (Scheme 2E and H).

Fig. 3 showed the AFM images of ring-shaped polymer brush microstructures fabricated by ETL combining SI-ATRP. Edge structures were obtained over a large surface area ($\sim 0.5\ \text{cm}^2$) gold substrates and could be varied for different shapes and sizes that depended on designed stamp used. When a cylindrical patterned PDMS stamp was used as edge lithographic tools, a ring-shaped polymer brush microstructures with an inside diameter of $10.0 \pm 0.1\ \mu\text{m}$, outside diameter of $12.4 \pm 0.1\ \mu\text{m}$ and the wall thickness of $\sim 1.2\ \mu\text{m}$ were obtained (Fig. 3A). The widths of the edge features could be controlled by varying the contact times between stamp and substrate (results not shown here), which is consistent with the previous report [17]. A double line patterned polymer brush microstructures could be obtained (see Fig. S2 in SI) when a line patterned PDMS stamp was used. Because of spontaneous hydrophobic recovery, the oxidized PDMS stamp could not be further as edge lithographic tools after several hours later. When the treated stamp, existing in air after 4 h, was carried out by stamp based ETL, the existing of ring-shaped and cylindrical patterned polymer brushes were achieved (Fig. 3).

4. Conclusions

In summary, we have fabricated a series of complex patterned PNIPAAm brush microstructures that do not exist on the original stamp via extending μCP with various printing condition of physical deformation by over force or solvent swelling to a PDMS stamp, or UV-Ozone induced chemical surface treatment to the stamp surface, and combining surface initiated atom transfer radical polymerization. The size and shape of the polymer brush microstructures can be adjusted by varying the μCP condition, especially the feature pattern parameters of a stamp. Our simple approach could be advanced by a future improvement of designing a smart machine to program the printing. The generic nature of ATRP could mostly

likely be used to be extended to include a wide range of vinyl monomers or mixtures of different vinyl monomers for designing different polymer brush with a number of stimulus responsive properties. Using a simple μCP technique without sophisticated instrumentation necessary to fabricate complex polymer brush microstructures open a windows of using micro-sized stamp to obtain sub-micrometer's feature. Beyond the original aim of replicating PDMS stamp patterns, it is believed that with the development of μCP and the combination with other modern micro/nanofabrication techniques, more and more complex polymer brush microstructures will be prepared, and can be used in practical applications of array-based diagnostic platforms, protein-resistant coatings, switchable sensors, and molecular recognition etc.

Acknowledgments

TC and RJ thank the Alexander von Humboldt Foundation for support of TC by an Alexander von Humboldt Research Fellowship. SZ thanks the National Science Foundation for support through grants NSF DMR-0502953 and NSF NIRT CBET-0609265.

Appendix. Supplementary data

Supplementary data related to this article can be found online at doi:10.1016/j.polymer.2011.04.008.

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