Dynamic Microcontact Printing for Patterning Polymer-Brush Microstructures

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Microcontact printing (µCP), developed in the early 1990s by the Whitesides group[1] for the generation of patterned self-assembled monolayers (SAMs) of thiol molecules from a poly(dimethylsiloxane) (PDMS) stamp onto metallic substrate surfaces, has since become a simple, versatile, and inexpensive patterning approach for micro/nano fabrication.[2–5] In this field, patterning of polymer brushes is a rapidly developing direction[6–8] because the resulting polymer microstructures are potentially useful for surface-based technologies and for the study of stimuli-responsive phenomena.[9] While early examples of fabricating patterned polymer brushes using µCP involved printing an octadecyltrichlorosilane (OTS) pattern to direct the backfilling of the interspaces by an initiator, with a subsequent surface-initiated polymerization (SIP),[10,11] printed polymerization initiators have recently been used as alternative approaches.[12–14] At present, the development of µCP has exceeded the original aim of transferring a single-stamp feature pattern onto a surface. Some new patterns that do not exist on the original stamp could be achieved by extending µCP of a physical deformation via lateral compression or solvent swelling to a stamp[15,16] or of a plasma- or UV–ozone-treatment-induced chemical modification to a stamp feature surface.[17] Therefore, once the single stamp is available, not only multiple copies of the pattern can be produced using straightforward experimental techniques[2] but also a number of different transferred features could be obtained by extended µCP by varying the printing conditions. Obviously, they have the potential to be used in patterning polymer-brush microstructures with complex morphologies.

There is considerable demand to pattern complex polymer-brush microstructures because the properties of materials are highly dependent on the complexity of the structures in practical applications. These complex polymer brushes have been fabricated via several elegant patterning strategies, with expensive and complex instruments used, for example, electron-beam chemical lithography (EBCL)[18–21] or electron-beam-induced carbon deposition (EBCD).[22] Therefore, exploiting more simple strategies motivates several current endeavors as alternative approaches to fabricate complex polymer-brush morphologies, for example, by µCP via simply adjusting the printing conditions. Zhou et al.[14] described a general µCP route to pattern laterally distinctive multicomponent polymer brushes involving a repeated printing process following a deactivated step of previous polymer-brush activity, which enabled the "synthesis" of very complex polymer surfaces.[23] We have previously reported that egg-cup-shaped polymer-brush microstructures could be obtained using a circular cylindrical PDMS stamp with various printing conditions and multistep µCP.[24] More recently, we used the extended µCP strategies exploited by previous reports[15–17] and combined with subsequent SIP to fabricate further new polymer-brush microstructures that differ from the original stamp feature by varying the µCP conditions.[25]

In this Communication, we report the development of a PDMS stamp to be used under dynamic printing by moving or jumping the stamp during µCP, without physical deformation or chemical surface treatment. This new strategy, which we call "dynamic µCP", could be used to fabricate new complex (hierarchical and gradient) polymer-brush microstructures that do not exist on the original stamp, in combination with surface-initiated atom-transfer radical polymerization (SI-ATRP) of a monomer, for example, N-isopropylacrylamide (NIPAAM). Our advantage lies in extending a conventional printing process, which we call "static µCP", to a dynamic one for patterning complex and new polymer-brush microstructures by a simple approach without sophisticated instrumentation being necessary.

Our strategy for fabricating complex patterned polymer-brush microstructures is schematically shown in **Scheme 1**. A normal µCP, using a thiol-initiator-inked, dried PDMS stamp to contact conformally with the gold surface under a gentle force, was carried out to make a comparison with the extended moving and jumping µCP (Scheme 1A). The moving µCP is operated by gently placing an initiator-inked stamp on a gold surface and subsequently holding it with fingers to move it forward (Scheme 1B-1) by a defined distance and then pressing under the same force used in the normal µCP (Scheme 1B-2). The jumping µCP includes performing normal µCP two or three times with the additional need to raise and replace the stamp (Scheme 1C-2) on the gold surface after the first normal µCP (Scheme 1C-1). These transferred initiator patterns can subsequently be amplified into various polymer-brush microstructures via SI-ATRP. We demonstrate these series of patterning strategies using a

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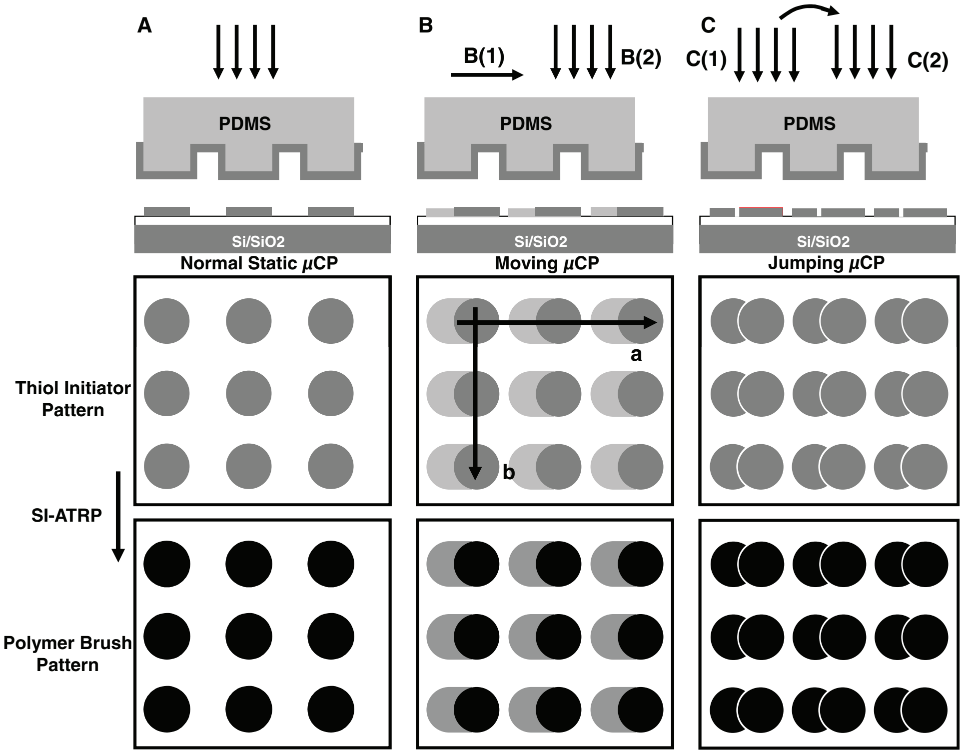

Scheme 1. Schematic illustrations showing the main steps involved in various µCP of initiator patterns and their subsequent amplification into patterned polymer-brush microstructures by SI-ATRP. A) Normal µCP: printing an inked stamp with a gentle force. B) Moving µCP: placing an inked stamp on gold surface with subsequent moving (B-1) and printing under normal µCP conditions (B-2). C) Jumping µCP: normal printing (C-2) following a normal printing (C-1) after a raised and replaced stamp on the surface.

single conventional circular cylindrical PDMS stamp that was utilized under dynamic µCP conditions.

The static µCP, without moving during this process, was carried out to pattern polymer-brush microstructures under a gentle printing force at ≈50 g in a perpendicular direction, combined with SI-ATRP of NIPAAM. Under this mild printing condition, the feature size and shape could be transferred from a thiol-initiator-inked stamp after µCP. The atomic force microscopy (AFM) height images, selected height profiles, and corresponding 3D images of the grafted polymer brushes are shown in **Figure 1**. The resulting patterned brush microstructure has a height of ≈100 nm, a feature diameter of 6.6±0.2 µm, and ≈15-µm feature space, which is consistent with the size of the original stamp feature.

Based on the above successful growth of polymer brushes under the normal static µCP, we extended µCP to a dynamic printing. The elastomeric property of PDMS allows the stamp to be widely used in replicating 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 stamp being used in dynamic printing. An early example was reported by Xia and co-workers,[26] who described a dynamic µCP approach of using a rolling PDMS stamp to generate patterned SAMs on a metallic surface over a large area. This remarkable procedure showed by its simplicity and speed that the inked stamp could be used to make ≈4–5 cycle printings with a single inking, without any measurable reduction in quality before requiring more ink.[26] This inspired us that a normal stamp could also be used to make

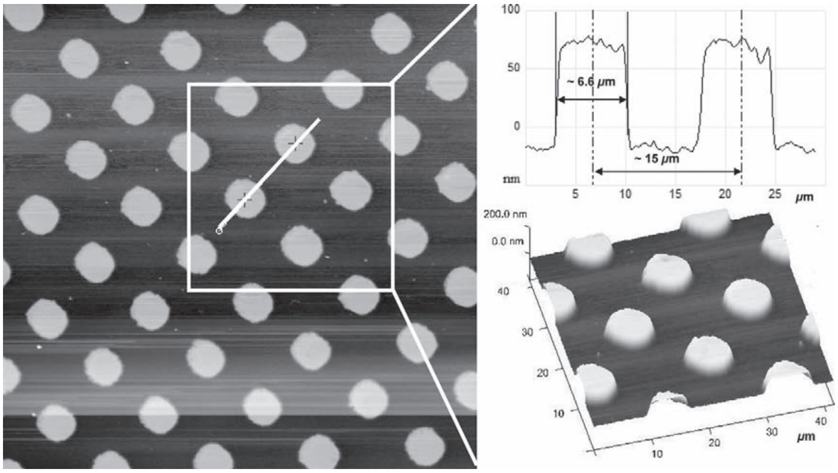

Figure 1. Contact-mode AFM height images (90 µm × 90 µm) of patterned polymer-brush microstructures prepared by normal µCP on a gold surface with a force at ≈50 g and a contact time of 20 s, imaged at room temperature (RT) in air, the selected corresponding height profiles, and 3D images. The PDMS stamp has a circular cylindrical pattern with a feature size of ≈7 µm and feature spacing (center to center) of ≈15 µm. All the printing in this paper used the same PDMS stamp.

repeated printings several times without further ink, which improves µCP for bringing forth a spectacular increase in versatility of SAMs by dynamic printing and the subsequent potential possibility of fabricating complex polymer-brush microstructures. We demonstrate the moving printing by two different approaches for fabricating hierarchical and gradient polymer brushes, respectively.

By using the conventional stamp under dynamic printing conditions, the first moving µCP was operated by placing an initiator-inked, dried stamp gently on a gold surface and subsequently holding it with fingers to move it forward without applied force on the stamp at a defined distance, before stopping it with a press under the same gentle force used in the normal µCP. The AFM images of resulting hierarchically patterned polymer-brush microstructures are shown in **Figure 2**. The moving direction could be defined easily upon making sure of the stamp feature pattern.[14] Control of the movement distance is more difficult than when the moving is operated by hand but still could be achieved by gentle and careful operation. For example, upon printing without applied force during the moving (direction a or b, in Scheme 1B) and with a normal printing force when moving stops. Figure 2A shows an AFM image of the resulting patterned brushes by moving µCP with a distance of ≈3 µm along the fixed movement direction. The polymer brushes grafted from the moving area and from the ended area had a diameter at 6.5 ± 0.2 µm and a height of ≈40 and ≈110 nm, respectively. The different brush height results from the graft density of the initiator transferred from the stamp during this process.[27] During the moving process, ink diffusion transfer played an important role in a short time (≈1–2 s), which produced a low initiator grafting density. In contrast, ink contact transfer resulted in a high initiator graft density during the normal static printing (under an applied force for 20 s) performed at the end of moving. Similar hierarchically structured polymer brushes have been prepared by Wang et al.,[23] who used multiple-step µCP of inks containing different ratios (by concentration) of initiator thiols and nonreactive thiols. In their approach, a PDMS stamp inked with a high concentration of initiator was used to print the first pattern, followed by printing a second low concentration using a different stamp. Polymer brushes with different thicknesses, resulting from different initiator densities, were then grown in a single step via SI-ATRP.[23] Our approach simplifies the preparation process that needs only one-step printing with a single initiator concentration.

As a special structured polymer brush, gradient brushes with gradients in graft density, chemical composition, or molecular weight allow a systematic variation of surface properties across the substrate.[28] In addition to several traditional preparation methods to obtain gradient-brush layers at the macroscopic scale,[29,30] they were recently structured by EBCL, EBCD, or UV-interference lithography at a micro/

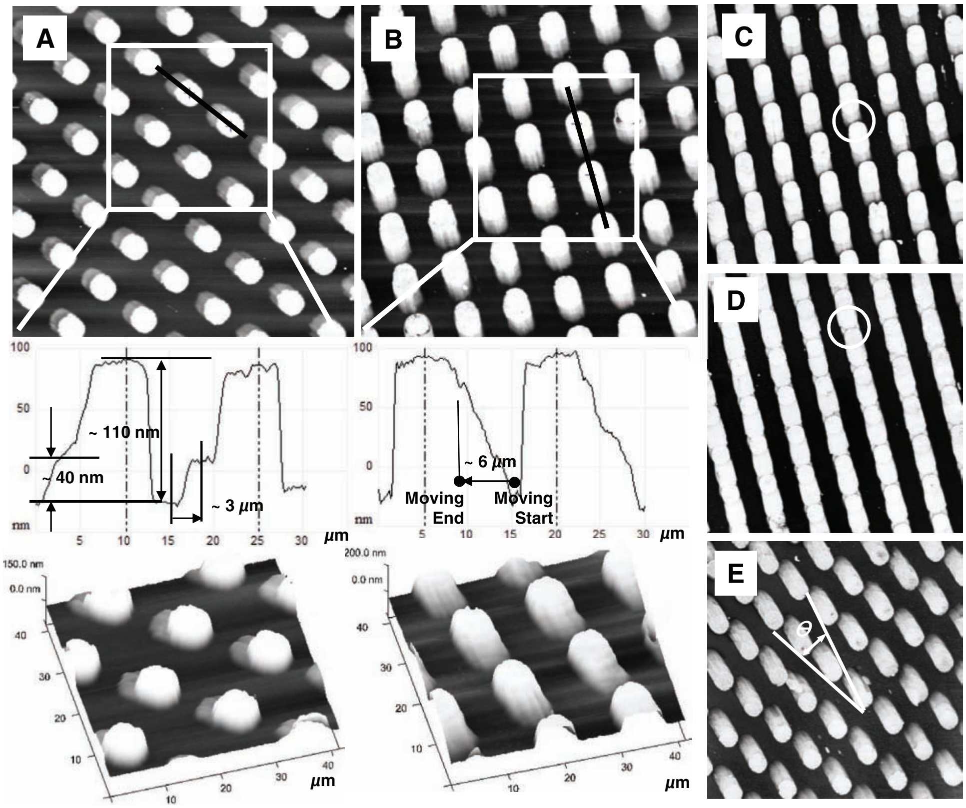

Figure 2. Contact-mode AFM height images (90 µm × 90 µm) of various morphology-adjustable patterned polymer-brush microstructures created by moving µCP, imaged at room temperature in air, the corresponding height profiles, and 3D images: A) without print force during moving and normal printing upon stopping; B,C) with print force during moving for different moving distances; D) a returned moving printing; E) moving printing with a changed angle compared to (A–D). In (A–D), the movement direction is along the closely neighbored feature pattern that was shown in direction a or b in Scheme 1B. The print force in each case is ≈50 g, print time is 20 s, and moving time is ≈1–2 s.

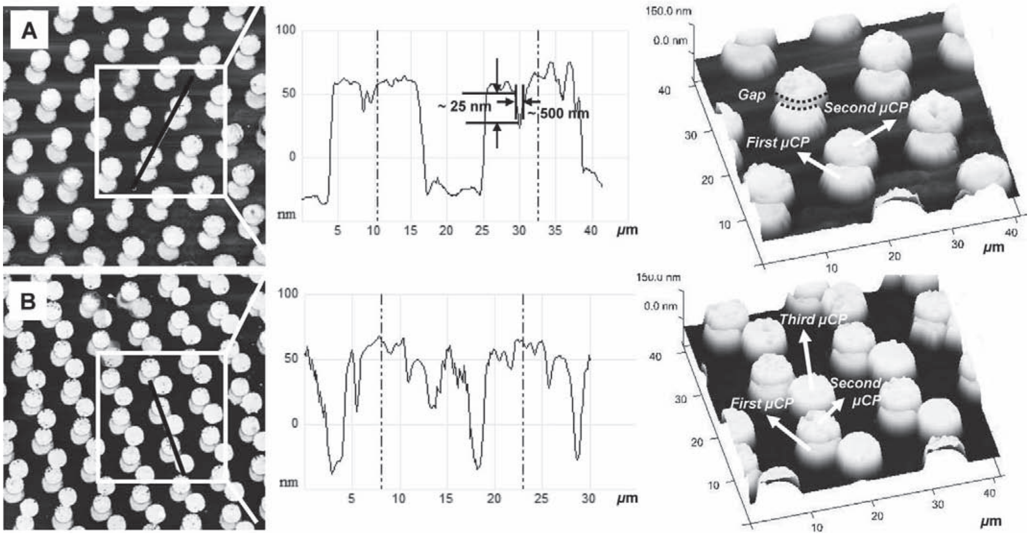

Figure 3. Contact-mode AFM height images (90 μm × 90 μm) of various morphology-adjustable patterned polymer-brush microstructures by jumping μCP, imaged at room temperature in air, the corresponding height profiles, and 3D images: A) jumping two-time μCP and B) jumping three-time μCP. Each print force is ≈50 g and print time is 20 s.

nanoscale resolution.[21,22,31] Here, our approach of moving μCP provides an alternative simple way to obtain gradient polymer brushes. When moving a stamp (for example, in direction a or b in Scheme 1B) with an applied force at a distance of ≈6 or ≈9 μm, a patterned polymer brush with a gradient height is obtained (Figure 2B and C). During the moving process under an applied force, ink transferred from both the ink diffusion and contact transfer formed gradient initiator SAMs from the moving start point to the moving end point. The gradient SAMs resulted from the contact-time difference between the moving start area and moving end area during moving μCP, where the latter having a longer time formed a higher initiator density. We noted that moving with a longer distance or returned moving creates the possibility of connecting two neighbored features (see marked circle in Figure 2C and D) for producing a line pattern only using a circular cylindrically patterned stamp. When slightly changing the movement direction, it is clear to see from Figure 2E that the direction of gradient brushes of each feature (the changed angle θ shown in Figure 2E) has been adjusted correspondingly.

Furthermore, the alternative printing approach of jumping μCP was handled via raising a stamp and reprinting in a closely neighboring area after first printing under a normal μCP. **Figure 3**A shows AFM images of the resulting polymer brushes with two-time printing. The height of the two-polymer-brush pillar is similar (≈100 nm), showing that the thiol initiator transferred from the stamp during these two times has the same amount as needed to form a similar initiator density and a corresponding polymer-brush height by subsequent amplification of SI-ATRP.[27] Upon jumping three times, the polymer brush still maintained a similar height (Figure 3B). The results are consistent with a previous report by Xia et al. of using a rolling stamp to make repeated printings without any measurable reduction in quality before requiring more ink.[26] It was noted that there is an obvious rim or gap of ≈500-nm width and ≈25-nm depth (dashed line marked in Figure 3) between consecutive brush dots amplified from initiator SAMs produced by both two- and three-time printing. We suggest that this undesirable possibility resulted from the extrusion of the PDMS stamp during the second printing on the previous existing initiator SAMs and thus slightly affected the initiator distribution and subsequent polymer-chain stretching direction in the boundary area. A similar gap was also found in the moving printing.

In conclusion, we have demonstrated a prototype of a dynamic μCP for patterning complex polymer brushes by operating a conventional circular cylindrical PDMS stamp under a dynamic printing condition via moving/jumping the stamp during μCP. This new strategy, combined with SI-ATRP, not only provides an alternative but simple approach to obtain complex (hierarchical and gradient) polymer brushes but also the resulting brush microstructures do not exist on the original stamp and can be adjusted by various printing conditions. Although the present dynamic μCP is operated by hand, it is already shown to be a powerful tool for patterning polymer brushes with complex morphologies. This simple approach could be advanced by the future improvement of designing a smart machine to program the movement of the stamp. Our work thus provides the point of departure to more systematically establish the connections among various printing conditions for the transfer of thiols onto metallic surfaces and further micro/nanofabrication. This strategy could also be used in other surface-fabrication fields, for example, selective wet etching or deposition of other materials.

Experimental Section

Chemical Materials: General chemicals were analytical reagent grade and were used as received from Sigma Aldrich, or Acros Organics. NIPAAM (99%), copper(I) bromide (CuBr, 99.9%), and methanol (MeOH, 99.9%) were obtained from Sigma-Aldrich (Milwaukee, WI). Milli-Q (Millipore, Billerica, MA) water (18 MΩ cm^{-1}) and methanol were used as polymerization solvents. ***N,N,N,N,N***-pentamethyldiethylenetriamine (PMDETA) was used as received from Acros Organics (Hampton, NH). PDMS stamps with circular cylindrical relief structures were fabricated from Sylgard 184 (the ratio between component A and B was 1:10, Dow Corning, Midland, MI) on a master. The thiol initiator, ω-mercaptoundecyl bromoisobutyrate ($BrC(CH_3)_2COO(CH_2)_{11}SH$) was synthesized according to the literature.[27] To immobilize the initiators for surface-initiated polymerization, gold substrates with an average grain diameter of 45 nm 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 H_2O_2/H_2SO_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!).

µCP: The PDMS stamp was inked by exposing the stamp features to an ethanol solution of thiol initiator (≈2 mM) for 3 min and drying with nitrogen, before being brought into contact with a gold substrate for 20 s. Normal µCP: printing inked stamp with a gentle force of ≈50 g. Moving µCP: an initiator inked, dried stamp was gently placed on a gold surface and subsequently held by fingers to move it forward before being pressed under normal µCP conditions; Jumping µCP: jumping µCP including two- or three-times normal µCP needed raising and replacing in order to print on the gold surface after the first normal µCP.

SI-ATRP: The polymer brushes were synthesized according to our previous report with a slight modification.[24] Briefly, the polymerization solution was prepared by adding a water (with a little amount of MeOH for speeding the dissolution of monomer) 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 µL, 0.064 mmol) in a 1:5 molar ratio to 0.8 mL of MeOH as solvent. The mixture was then sonicated for 1 min to facilitate the formation of the CuBr/PMDETA complex. Next, 0.2 mL MeOH was first poured into 3.0 g (≈34 mmol) of NIPAAM monomer with a subsequent being added into with 5 mL of water for dissolution. The polymerization solution was then transferred into flasks containing the sample substrates with immobilized patterned initiator via µCP. The flasks were sealed with rubber septa and kept at room temperature under nitrogen atmosphere. After the desired reaction time, substrates were removed from the polymerization solution, exhaustively rinsed with deionized water with a sonication to remove all traces of the polymerization solution, and subsequently dried in a stream of nitrogen.

Characterization: Polymer-brush-grafted substrates were rinsed with deionized water, dried under a stream of nitrogen, and mounted on steel sample disks prior to AFM measurements. AFM topography images were collected in contact mode using V-shaped silicon nitride cantilevers (Nanoprobe, Veeco; spring constant: 0.12 N m^{-1}; tip radius: 20–60 nm) using a multimode AFM system (Digital Instruments, Santa Barbara, CA). Topographic imaging was performed in air at room temperature and was obtained under low applied normal forces to minimize compression and lateral damage of the polymer microstructures.

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[1] A. Kumar, G. M. Whitesides, *Appl. Phys. Lett.* **1993**, *63*, 2002.
[2] Y. N. Xia, G. M. Whitesides, *Angew. Chem. Int. Ed.* **1998**, *37*, 551.
[3] S. A. Ruiz, C. S. Chen, *Soft Matter* **2007**, *3*, 168.
[4] T. Kaufmann, B. J. Ravoo, *Polym. Chem.* **2010**, *1*, 371.
[5] A. Perl, D. N. Reinhoudt, J. Huskens, *Adv. Mater.* **2009**, *21*, 2257.
[6] B. Zhao, W. J. Brittain, *Prog. Poly. Sci.* **2000**, *25*, 677.
[7] W. Senaratne, L. Andruzzi, C. K. Ober, *Biomacromolecules* **2005**, *6*, 2427.
[8] T. Chen, R. Ferris, J. M. Zhang, R. Ducker, S. Zauscher, *Prog. Polym. Sci.* **2010**, *35*, 94.
[9] R. Ducker, A. Garcia, J. M. Zhang, T. Chen, S. Zauscher, *Soft Matter* **2008**, *4*, 1774.
[10] N. L. Jeon, I. S. Choi, G. M. Whitesides, N. Y. Kim, P. E. Laibinis, Y. Harada, K. R. Finnie, G. S. Girolami, R. G. Nuzzo, *Appl. Phys. Lett.* **1999**, *75*, 4201.
[11] M. Husemann, D. Mecerreyes, C. J. Hawker, J. L. Hedrick, R. Shah, N. L. Abbott, *Angew. Chem. Int. Ed.* **1999**, *38*, 647.
[12] J. Hyun, A. Chilkoti, *Macromolecules* **2001**, *34*, 5644.
[13] P. Xu, H. Uyama, J. E. Whitten, S. Kobayashi, D. L. Kaplan, *J. Am. Chem. Soc.* **2005**, *127*, 11745.
[14] F. Zhou, Z. J. Zheng, B. Yu, W. M. Liu, W. T. S. Huck, *J. Am. Chem. Soc.* **2006**, *128*, 16253.
[15] Y. N. Xia, G. M. Whitesides, *Langmuir* **1997**, *13*, 2059.
[16] Q. J. Guo, X. W. Teng, H. Yang, *Nano Lett.* **2004**, *4*, 1657.
[17] R. B. A. Sharpe, B. J. F. Titulaer, E. Peeters, D. Burdinski, J. Huskens, H. J. W. Zandvliet, D. N. Reinhoudt, B. Poelsema, *Nano Lett.* **2006**, *6*, 1235.
[18] N. Ballay, S. Schilp, M. Zharnikov, *Angew. Chem. Int. Ed.* **2008**, *47*, 1421.
[19] U. Schmelmer, R. Jordan, W. Geyer, W. Eck, A. Golzhauser, M. Grunze, A. Ulman, *Angew. Chem. Int. Ed.* **2003**, *42*, 559.
[20] U. Schmelmer, A. Paul, A. Kuller, M. Steenackers, A. Ulman, M. Grunze, A. Golzhauser, R. Jordan, *Small* **2007**, *3*, 459.
[21] M. Steenackers, A. Kueller, N. Ballav, M. Zharnikov, M. Grunze, R. Jordan, *Small* **2007**, *3*, 1764.
[22] M. Steenackers, R. Jordan, A. Kuller, M. Grunze, *Adv. Mater.* **2009**, *21*, 2921.
[23] M. Wang, J. E. Comrie, Y. P. Bai, X. M. He, S. Y. Guo, W. T. S. Huck, *Adv. Funct. Mat.* **2009**, *19*, 2236.
[24] T. Chen, J. M. Zhong, D. P. Chang, A. Carcia, S. Zauscher, *Adv. Mater.* **2009**, *21*, 1825.
[25] T. Chen, R. Jordan, S. Zauscher, *Polymer* **2011**, DOI: 10.1016/j.polymer.2011.04.008.
[26] Y. N. Xia, D. Qin, G. M. Whitesides, *Adv. Mater.* **1996**, *8*, 1015.
[27] D. M. Jones, A. A. Brown, W. T. S. Huck, *Langmuir* **2002**, *18*, 1265.
[28] R. R. Bhat, M. R. Tomlinson, T. Wu, J. Genzer, *Adv. Polym. Sci.* **2006**, *198*, 51.
[29] L. Ionov, B. Zdyrko, A. Sidorenko, S. Minko, V. Klep, I. Luzinov, M. Stamm, *Macromol. Rapid Commun.* **2004**, *25*, 360.
[30] T. Wu, K. Efimenko, P. Vlcek, V. Subr, J. Genzer, *Macromolecules* **2003**, *36*, 2448.
[31] C. Schuh, S. Santer, O. Prucker, J. Ruhe, *Adv. Mater.* **2009**, *21*, 4706.

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