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# Electrochemically Mediated Atom Transfer Radical Polymerization on Nonconducting Substrates: Controlled Brush Growth through Catalyst Diffusion

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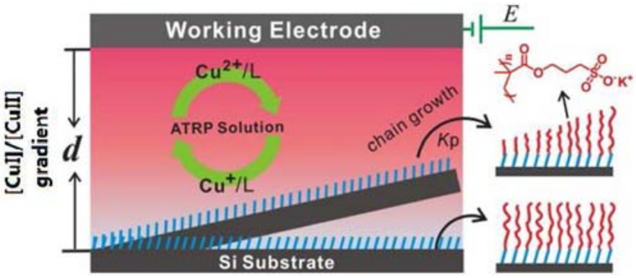
S *Supporting Information*

**ABSTRACT:** Surface initiated atom transfer radical polymerization (SI-ATRP) was triggered after diffusion of a $Cu^I/L$ activator generated at a working electrode. A stable $[Cu^{II}L]/[Cu^IL]$ ratio gradient was formed at the gap between the working electrode and the initiator terminated substrate due to ion diffusion. The size of the gap can be used to dictate polymer growth kinetics at different gap distances. Gradient polymer brushes were grafted when substrate was placed at a tilting angle along $[Cu^{II}L]/[Cu^IL]$ gradient.

Surface-initiated controlled radical polymerizations (SI-CRP) from initiator-modified surfaces lead to polymer brushes with well-defined compositions, architectures, and functionalities as well as complex (co)polymers and organic/inorganic hybrid materials.[1−3] Among the different controlled radical polymerization techniques, atom transfer radical polymerization (ATRP)[4−6] is widely used for tailoring the surface chemistry and topography, such as tuned physical and chemical properties,[7,8] pattern,[9,10] or responsivity, etc.[11,12] The past few years have witnessed the emergence of new strategies to regulate the ATRP process by using a wide range of external stimuli,[13−15] particularly the very recently developed eATRP.[13] SIP through eATRP on conducting electrode has been successfully demonstrated.[16] In this case, $Cu^I$ catalyst was electrochemically generated from $Cu^{II}$ at the vicinity of working electrode and locally initiated polymerization from electrode. Here we extend this technique to include the use of nonconducting substrates and to couple the growth rates to the distance between $Cu^I$ production and initiator surface.

As is shown in Scheme 1 (exact experiment data is given in Scheme S1), when a negative potential was applied to reduce $Cu^{II}$ to $Cu^I$ on the working electrode; a $Cu^I$ diffusion layer will instantaneously form with the highest $Cu^I$ concentration near the working electrode. If an initiator-modified substrate is placed in the vicinity of the electrode, polymerization will be triggered. The complementary $X\text{-}Cu^{II}/L$ deactivator has the opposite distribution of the $Cu^I$ activating species. By adjusting the magnitude of the applied potential $E$ or the gap $d$ between the working electrode and the sample allows control over the relative concentration of active and dormant species and consequently the rate and the controllability of polymerization.

**Scheme 1. Schematic Illustration of Using Diffusion to Control eATRP for Surface Modification**



Because of the presence of gradient $[Cu^I]/[Cu^{II}]$ distribution, different regions on the surface will experience different polymerization rates when the substrate is placed at a tilting angle. Our method thus opens up a new route to gradient polymer brushes.

The eATRP was carried out in an electrochemical cell equipped with platinum gauze working electrode, platinum wire counter electrode, and saturated calomel electrode (SCE) reference electrode, and initiator-modified substrate was placed opposite to the working electrode (Scheme S1). Cyclic voltammetry of $Cu^{II}$/bipy complex exhibits a reversible peak couple and peak reduction potential ($E_{pc}$) of −0.16 V vs SCE (Figure S1). In a typical experiment, a solution containing 3-sulfopropyl methacrylate potassium salt (SPMA) and $Cu^{II}$/bipy catalyst system in water/methanol (SI), gold substrate modified with the initiator $\omega$-mercaptoundecyl bromoisobutyrate was placed in parallel to and 360 $\mu$m away from electrodes. A potential was chosen such that no Cu(0) precipitation was observed; typically, polymerization was carried out for 7 h at −0.16 V, yielding a homogeneous film of around 250 nm thick (see SI for XPS and AFM measurements, Figure S2). As shown in Figure 1a, polymer growth exhibits linear first-order kinetic increase with time. Linear growth lasts up to 5 h. This is in contrast to what we have reported[16] previously on polymer grafting from initiator-modified gold working electrodes (Figure 1a, inset), where polymer growth leveled off after about 30 min. This is because in previous experiments the concentration of the deactivating $X\text{−}Cu^{II}/L$ species was too

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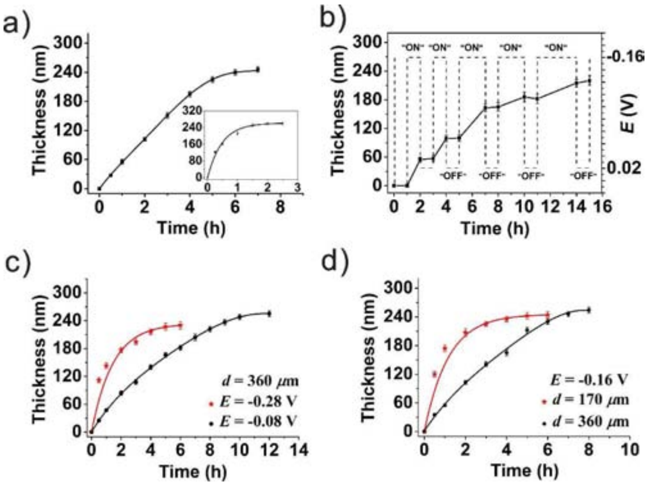

**Figure 1.** eATRP of SPMA on initiator covered surfaces with respect to time. (a) $d$ = 360 $\mu$m, $E$ = −0.16 V, gold substrate. Inset is the patterned PSPMA growth on gold (thiol ester initiator patterned gold slice as working electrode). (b) $d$ = 360 $\mu$m, PSPMA on gold, switching between active and dormant states is represented by changes of the applied potential values between −0.16 and 0.02 V (referenced SCE). (c) PSPMA on silicon substrate, $d$ = 360 $\mu$m, $E$ = −0.28 V (red), −0.08 V (dark). (d) PSPMA on silicon, $E$ = −0.16 V, $d$ = 170 $\mu$m (red), 360 $\mu$m (dark). Conditions: [SPMA] = 3.25 M, [BBAC] = 0.1 M; [SPMA]:[bipy]:[$CuCl_2$] = 100:2:1, monomer solution was reused.

low to deactivate polymerization,[17,18] especially in aqueous media, where the ATRP equilibrium constant is around $10^4$ times larger than in nonaqueous solvents.[19,20] The present methodology provides a robust way to maintain a constant $Cu^{II}/Cu^{I}$ ratio, independent of whether the initiator-modified substrate is conductive or not. Examples shown in Figure S2 include silicon, polydimethylsiloxane (PDMS), titanium, and gold, all modified with a suitable initiator (silane, catechol, or thiol-based, respectively, SI) and grafted with PSPMA brushes. After polymerization for 7h, only peaks of polymer brushes are detected by XPS, indicating homogeneous coverage of polymer brushes. It is worth noting that the diffusion layer is highly confined between the electrode and the substrate. Diffusion of $Cu^{I}$ to bulk solution is very limited, and no color change in bulk solution was observed even after 8h polymerization time (Figure S3).

One of the most attractive features of electrostimulus is the possibility for reversibly modulating the polymerization. Figure 1b shows the thickness values of 11 samples, where sample 1 was placed at 0.02 V for 1hr (so no polymerization, 'off'); sample 2 was placed for 1hr at 0.02 V and then 1hr at −0.16 V (polymerization 'on'); sample 3: 0.02 V, 1hr (off); −0.16 V, 1hr (on); 0.02 V, 1 h (off) and so on for all samples to build the curve shown in Figure S4. It is seen that the growth of polymers can be started or stopped by switching the redox states of the copper catalyst by applying an alternating potential of −0.16 and 0.02 V. Growth kinetics depend on the $[Cu^{I}]/[Cu^{II}]$ ratio, which can be adjusted by varying the applied potentials or the gap $d$ between the platinum working electrode and the sample surface. When eATRP is carried out at −0.28 V (much lower than $E_{pc}$), the more negative potential leads to a higher $[Cu^{I}]$, and therefore the reaction occurs more rapidly but with less control (Figure 1c, red). When eATRP brush growth was performed at −0.08 V (higher than $E_{pc}$) with the same electrode−substrate gap, "living" character up to 10 h (Figure 1c, dark) was observed because of the smaller $Cu^{I}/Cu^{II}$ ratio. The same result can be observed when eATRP was carried out at a smaller electrode−substrate gap ($d$ = 170 $\mu$m) compared to 360 $\mu$m (Figure 1d). An enhanced polymerization rate was observed at the smaller gap ($d$) but poorer polymer growth controllability because of higher local $Cu^{I}/Cu^{II}$ ratio than that at 360 $\mu$m distance. Figure S5 shows plot of PSPMA brushes thickness vs the sample−electrode gap ($d$) after 3 h polymerization at the applied potential of −0.16 V. It is seen that the larger the gap distance, the smaller the final brush thickness and so the slower growth rates.

The measurement of molecular weight ($M_r$) and polydispersity index (PDI) of surface-initiated polyelectolyte brushes is extremely challenging due to the small amount of material grafted.[21,22] Alternatively, the conformational changes of the surface-tethered polymer chains (swelling−collapse) in good solvent are useful tools for estimating the chain length and density of the brushes. PSPMA brushes prepared via eATRP at faster reaction rates were found to exhibit a higher swelling factor $f$ ($f = h_{swollen}/h_{dry}$) than those prepared at a slower rate (Figure S6). For example, 80 nm dry patterned PSPMA brushes obtained in 0.5 h ($E$ = −0.14 V, $d$ = 170 $\mu$m) have a swelling factor of 3.44, while the same thickness brushes obtained in 1.5 h ($E$ = −0.16 V, $d$ = 360 $\mu$m) have a swelling factor of 2.75. From Pincus theory,[23] the average swollen height of the polyelectrolyte brushes scales in salt-free solutions (water) almost linearly with the length of the attached polymer and is independent of the grafting density. Therefore, brushes obtained under fast polymerization ($h$) have higher molecular weights and degree of polymerization but lower grafting density $\sigma$ ($\sigma = h_{dry}\rho N_A/M_r$, where $\rho$ is the density of the polymer) than those obtained via slow polymerization.[24,25]

If a substrate is placed at a titling angle with respect to the working electrode, the $Cu^{I}/Cu^{II}$ ratio will be different along the substrate surface. Therefore the polymerization rates will be different as well, leading to gradient brushes.[26,27] The steepness of the gradient can be easily controlled by changing the tilt angle between electrode and substrate. Figure 2 displays a linear continuous increase in polymer layer thickness gradient ($dh_{dry}/dx$) along one direction (i.e., $x$-axis). Thickness gradients with slopes of 11.2 and 16.7 were obtained in 0.5 and 1 h, respectively (Figure 2a). The slope of gradient brushes

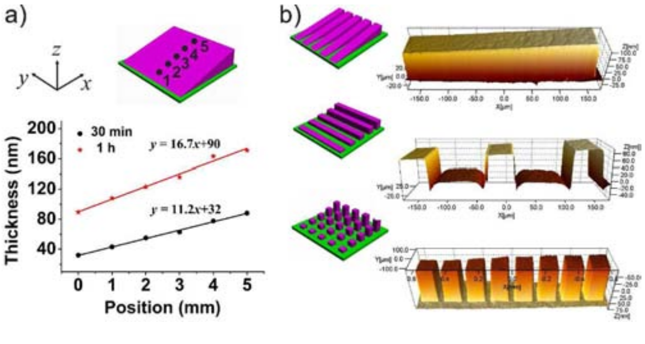

**Figure 2.** Thickness gradient brushes on homogeneous and patterned surfaces. (a) Ellipsometry thickness gradients vs position and time (silicon) of two separate samples, the substrate−electrode distance is 170 and 360 $\mu$m at each end, $E_{pc}$ = −0.16 V. The 'zero' point is arbitrarily selected. (b) Optical image of a part of patterned gradients grown on gold surfaces. The substrate−electrode distance is 85 and 360 $\mu$m at each end (top and middle), 170 and 360 $\mu$m (bottom). $E_{pc}$ = −0.16 V, the reaction time was 30 min.

increases with respect of the polymerization time, consistent with the fast brush growth kinetics found for small gap distances. If the titling angle was changed, the slope of brush gradient was changed accordingly (Figure S7). It is noticed that the change in slope at longer polymerization times is smaller than expected. This implies that polymerization at the smaller gap distance is less controlled and exhibits termination and that the density of the brushes will show a gradient as well (both along the surface and within the brush layer).

By prepatterning the initiator areas, a "wedge" or "stair" shaped gradient pattern can be formed (Figure 2b). Gradients are generally prepared by using initiators with gradient densities or by slowly immersing substrates into a polymerization bath[28,29] or using lithographic approaches.[30,31] The current approach of using the [$Cu^{II}$]/[$Cu^{I}$] concentration gradients for tailored gradient slopes can be potentially used to prepare very complex surface topographies in a straightforward way. In order to get more insights into the gradient structure, we have measured the thickness gradient of (patterned) gradient PSPMA brush swollen in water by AFM from the patterned PSPMA (Figure S8). The slope of the thickness of the dry brush is smaller than that of the swollen brush; this can be attributed to the decrease in grafting density. Where the polymerization rate is very fast, less control and lower (re-)initiation efficiency lead to thicker but also less dense brushes.

In conclusion, we have successfully exploited concentration gradients originating from $Cu^{I}$ diffusion from an electrode surface to initiate ATRP on nonconducting substrates. An adequate concentration of deactivator $Cu^{II}$ in the polymerization can be rationally adjusted by the applied potentials or the gap $d$ between the two electrodes to ensure a fast rate of deactivation, thereby suppressing unwanted termination reactions for many hours and brush growth with significantly enhanced control. The approach can not only give more insights into surface initiated ATRP kinetics but also provide the easiest way for forming surface gradients by simply changing the sample conformation.

## ■ ASSOCIATED CONTENT

### Ⓢ Supporting Information

Experimental details and additional data. This material is available free of charge via the Internet at http://pubs.acs.org.

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### Notes

The authors declare no competing financial interest.

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## ■ REFERENCES

(1) Barbey, R.; Lavanant, L.; Paripovic, D.; Schüwer, N.; Sugnaux, C.; Tugulu, S.; Klok, H.-A. *Chem. Rev.* **2009**, *109*, 5437.

(2) Edmondson, S.; Osborne, V. L.; Huck, W. T. S. *Chem. Soc. Rev.* **2004**, *33*, 14.

(3) Tsujii, Y.; Ohno, K.; Yamamoto, S.; Goto, A.; Fukuda, T. *Adv. Polym. Sci.* **2006**, *197*, 1.

(4) Pyun, J.; Kowalewski, T.; Matyjaszewski, K. *Macromol. Rapid Commun.* **2003**, *24*, 1043.

(5) Siegwart, D. J.; Oh, J. K.; Matyjaszewski, K. *Prog. Polym. Sci.* **2012**, *37*, 18.

(6) Zhou, F.; Huck, W. T. S. *Phys. Chem. Chem. Phys.* **2006**, *8*, 3815.

(7) Zhou, F.; Shu, W.; Welland, M. E.; Huck, W. T. S. *J. Am. Chem. Soc.* **2006**, *128*, 5326.

(8) Cao, Z.; Brault, N.; Xue, H.; Keefe, A.; Jiang, S. *Angew. Chem., Int. Ed.* **2011**, *50*, 6102.

(9) Zhou, F.; Zheng, Z.; Yu, B.; Liu, W.; Huck, W. T. S. *J. Am. Chem. Soc.* **2006**, *128*, 16253.

(10) Nie, Z.; Kumacheva, E. *Nat. Mater.* **2008**, *7*, 277.

(11) Chen, T.; Ferris, R.; Zhang, J.; Ducker, R.; Zauscher, S. *Prog. Polym. Sci.* **2010**, *35*, 94.

(12) Stuart, M. A. C.; Huck, W. T. S.; Genzer, J.; Müller, M.; Ober, C.; Stamm, M.; Sukhorukov, G. B.; Szleifer, I.; Tsukruk, V. V.; Urban, M.; Winnik, F.; Zauscher, S.; Luzinov, I.; Minko, S. *Nat. Mater.* **2010**, *9*, 101.

(13) Magenau, A. J. D.; Strandwitz, N. C.; Gennaro, A.; Matyjaszewski, K. *Science* **2011**, *332*, 81.

(14) Simakova, A.; Averick, S. E.; Konkolewicz, D.; Matyjaszewski, K. *Macromolecules* **2012**, *45*, 6371.

(15) Fors, B. P.; Hawker, C. J. *Angew. Chem., Int. Ed.* **2012**, *51*, 8850.

(16) Li, B.; Yu, B.; Huck, W. T. S.; Zhou, F.; Liu, W. *Angew. Chem., Int. Ed.* **2012**, *51*, 5092.

(17) Matyjaszewski, K.; Coca, S.; Gaynor, S. G.; Wei, M.; Woodworth, B. E. *Macromolecules* **1997**, *30*, 7348.

(18) Ramstedt, M.; Cheng, N.; Azzaroni, O.; Mossialos, D.; Mathieu, H. J.; Huck, W. T. S. *Langmuir* **2007**, *23*, 3314.

(19) Bortolamei, N.; Isse, A. A.; Magenau, A. J. D.; Gennaro, A.; Matyjaszewski, K. *Angew. Chem., Int. Ed.* **2011**, *50*, 11391.

(20) Matyjaszewski, K.; Xia, J. *Chem. Rev.* **2001**, *101*, 2921.

(21) Turgman-Cohen, S.; Genzer, J. *J. Am. Chem. Soc.* **2011**, *133*, 17567.

(22) Turgman-Cohen, S.; Genzer, J. *Macromolecules* **2012**, *45*, 2128.

(23) Tran, Y.; Auroy, P.; Lee, L.-T. *Macromolecules* **1999**, *32*, 8952.

(24) Jordan, R.; Ulman, A.; Kang, J. F.; Rafailovich, M. H.; Sokolov, J. *J. Am. Chem. Soc.* **1999**, *121*, 1016.

(25) Sanjuan, S.; Tran, Y. *Macromolecules* **2008**, *41*, 8721.

(26) Genzer, J.; Bhat, R. R. *Langmuir* **2008**, *24*, 2294.

(27) Luzinov, I.; Minko, S.; Tsukruk, V. V. *Soft Matter* **2008**, *4*, 714.

(28) Morgenthaler, S.; Lee, S.; Zürcher, S.; Spencer, N. D. *Langmuir* **2003**, *19*, 10459.

(29) Ionov, L.; Zdyrko, B.; Sidorenko, A.; Minko, S.; Klep, V.; Luzinov, I.; Stamm, M. *Macromol. Rapid Commun.* **2004**, *25*, 360.

(30) Lin, X.; He, Q.; Li, J. *Chem. Soc. Rev.* **2012**, *41*, 3584.

(31) Chen, T.; Amin, I.; Jordan, R. *Chem. Soc. Rev.* **2012**, *41*, 3280.