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

Bin Li,† Bo Yu,† Wilhelm T. S. Huck,‡ Weimin Liu,† and Feng Zhou*†

†State Key Laboratory of Solid Lubrication, Lanzhou Institute of Chemical Physics, Chinese Academy of Sciences, Lanzhou 730000 China
‡Radboud University Nijmegen, Institute for Molecules and Materials, Heyendaalseweg 135, 6525 AJ Nijmegen, The Netherlands

ABSTRACT: Surface initiated atom transfer radical polymerization (SI-ATRP) was triggered after diffusion of a CuII activator generated at a working electrode. A stable [CuII]/[CuI] 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 [CuII]/[CuI] gradient.

Although generated 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, CuI catalyst was electrochemically generated from CuII 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 CuI 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 CuII to CuI on the working electrode; a CuI diffusion layer will instantaneously form with the highest CuI 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-CuII/L deactivator has the opposite distribution of the CuI 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 [CuII]/[CuI] 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 CuII/bipy complex exhibits a reversible peak couple and peak reduction potential (Ep) of −0.16 V vs SCE (Figure S1). In a typical experiment, a solution containing 3-sulfopropyl methacrylate potassium salt (SPMA) and CuII/bipy catalyst system in water/methanol (SI), gold substrate modified with the initiator ω-mercaptopundecyl bromoisobutyrate was placed in parallel to and 360 μm 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 reported16 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−CuII/L species was too

Received: November 28, 2012
Published: January 24, 2013
The measurement of molecular weight ($M_r$) and polydispersity index (PDI) of surface-initiated polyelectrolyte brushes is extremely challenging due to the small amount of material 

If a substrate is placed at a tilting angle with respect to the working electrode, the Cu$^{II}$/Cu$^{I}$ ratio will be different along the substrate surface. Therefore the polymerization rates will be different as well, leading to gradient brushes. 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 ($d\ h_{poly}/dx$) 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

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 1 h (no polymerization, ‘off’); sample 2 was placed for 1 h at 0.02 V and then 1 h at −0.16 V (polymerization ‘on’); sample 3: 0.02 V, 1 h (off); −0.16 V, 1 h (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 polynmers 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$^{II}$]/[Cu$^{I}$] 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$^{II}$], and therefore the reaction occurs more rapidly but with less control (Figure 1c, red). When eATRP was carried out 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 polyelectrolyte brushes is extremely challenging due to the small amount of material 

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 polyelectrolyte brushes is extremely challenging due to the small amount of material 

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 polyelectrolyte brushes is extremely challenging due to the small amount of material
increases with respect of the polymerization time, consistent with the fast brush growth kinetics found for small gap distances. If the tilting 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 bath28,29 or using lithographic approaches.30,31 The current approach of using the [CuII]/[CuI] 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 Cu1 diffusion from an electrode surface to initiate ATRP on nonconducting substrates. An adequate concentration of deactivator CuII 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.

■ AUTHOR INFORMATION

Corresponding Author
zhouf@licp.cas.cn

Notes
The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

NSFC (21125316, 51171202) and 973 project (2013CB632300) and the Key Research Program of the Chinese Academy of Sciences (grant no. KJZD-EW-M01).

■ REFERENCES