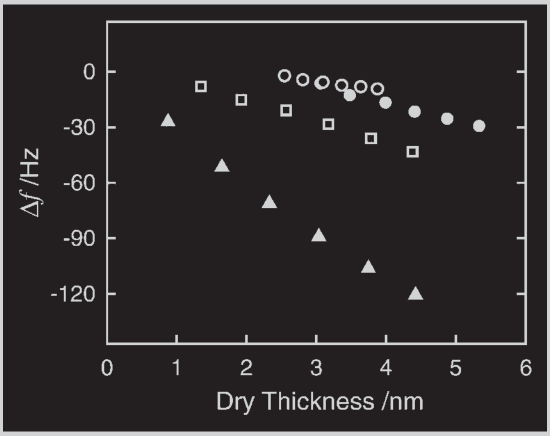
Summary: The atom transfer radical polymerization of [2-(methacryloyloxy)ethyl]trimethylammonium chloride (METAC) has been studied under different $[Cu^I]/[Cu^{II}]$ ratios. The reaction kinetics is followed by ellipsometry and quartz crystal microbalance and it was found that the reaction speed influences the grafting density of the polymer brushes. High $[Cu^I]/[Cu^{II}]$ ratios, i.e., fast polymerizations, lead to less dense polymer brushes.



Plot of the frequency change of wet brushes on a QCM crystal (Δf) versus the dry thickness of brushes synthesized at different $[Cu^I]/[Cu^{II}]$ ratios.

The Effect of $[Cu^I]/[Cu^{II}]$ Ratio on the Kinetics and Conformation of Polyelectrolyte Brushes by Atom Transfer Radical Polymerization

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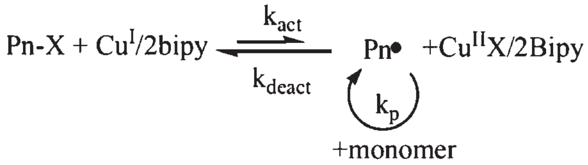
Introduction

Polymer brushes, both dry and swollen by solvents, are important in many areas of science and technology, which include colloid stabilization, lubrication,[1] and biocompatible interfaces.[2] Surface-initiated atom transfer radical polymerization (ATRP) is widely used for growing polymer brushes,[3] as it combines ease of preparation with good control over molecular weight, film thickness, and end functionality.[3,4] The mechanism[5] for the ATRP is presented in Scheme 1. The corresponding rate equation is:

$$R_p = k_{app}[M] = k_p[P][M] = k_p K_{eq}[In]\frac{[Cu^I]}{[Cu^{II}]}[M] \qquad (1)$$

where k_p is the rate constant for propagation, K_{eq} is the equilibrium constant ($K_{eq} = k_a/k_d$), [In] is the initiator concentration, and [M] is the monomer concentration. The dry thickness of polymer brush films prepared by ATRP is most easily controlled by varying the reaction time. However, a number of other factors need to be considered to control the polymerization reaction and thereby the architecture of the films. Matyjaszewski and co-workers have demonstrated how the rate of polymerization in bulk ATRP depends on the ratio of $[Cu^I]/[Cu^{II}]$.[6,7] To ensure a 'living' character, the reactivity of the catalyst,[8,9] and the amount of the deactivator (Cu^{II})[10] (added to the polymerization bath or formed from sacrificial initiator) need to be finely tuned. During the brush growth, unavoidable termination reactions,[11] loss of catalyst reactivity, and/or increasing



Scheme 1. Schematic of the atom transfer radical polymerization.

steric hindrance around the reactive chain ends, significantly affect the kinetics of polymerization and polymer brush structure. A simulation of the growth of polymer chains by surface-initiated ATRP[12] shows a progressive increase in polydispersity of the polymer chains and concomitant increase in disorder, with increasing polymerization time.

Many of the exciting and unique responsive properties of polymer brushes (e.g., increased charge transport in hole-transporting brushes,[13] and collapse transitions in polyelectrolyte brushes[14]) result from the high grafting density of the polymer chains, and therefore, a thorough study of the reaction conditions that influence the grafting density is required. It has previously been shown that the grafting density can be controlled by the density of initiator groups on the surface,[15,16] and in some cases, also by the quality of the solvent.[17] However, any attempt to control the grafting density of polymer brushes should also consider the 'speed' of polymerization. The rationale for this consideration is the hypothesis that very rapid brush growth will inevitably lead to more termination reactions during the initial stages of the polymerization and hence to lower grafting densities of the remaining 'living' chain ends. The 'speed' of polymerization is easily varied by adjusting the [Cu^I]/[Cu^{II}] ratio (Scheme 1) while keeping all other parameters constant. In this paper, ellipsometry, quartz crystal microbalance (QCM), and atomic force microscopy (AFM) under water combined with compression/tip penetration experiments, are used to probe the relationship between growth rate and grafting density.

Experimental Part

Chemicals

[2-(Methacryloyloxy)ethyl]trimethylammonium chloride (METAC) was purchased from Aldrich and treated with aluminium oxide to remove the inhibitor. 2,2′-bipyridyl (bipy), $CuCl_2$, and CuCl were purchased from Aldrich and used as received. ω-Mercaptoundecyl bromoisobutyrate (thiol initiator) was synthesized following a literature procedure.[18]

Growth of Cationic METAC Polyelectrolyte Brushes

METAC monomer (46.33 g, 0.223 mol) and bipy (2.411 g, 15.4 mmol) were dissolved in methanol (46 mL). $CuCl_2$ was added to the solution and the mixture was degassed for 20 min. CuCl (611 mg, 6.17 mol) was then added, and the solution was degassed for a further 30 min. Different [Cu^I]/[Cu^{II}] ratios were obtained by varying the amount of $CuCl_2$. Initiator-coated wafers were sealed in Schlenck tubes and degassed by three vacuum-refilling cycles with N_2 gas. The polymerization solution was added by a syringe into the tubes and left at room temperature (20 °C) under N_2. Samples were taken at different times and washed several times with water and methanol.

In-Situ Observation of Polymer Growth by QCM

QCM measurements were performed using a Q-sense Microbalance (Sweden). All QCM chips (QXS-301, Q-Sense) were coated with a thiol initiator self-assembled monolayer before being placed inside the QCM chamber. The polymer solution was prepared in two parts, the first contained just monomer solution without catalyst and the second contained both monomer and catalyst. The first (part one) solution was initially flowed into the chamber to remove all oxygen and to obtain a reference change in frequency and dissipation. When the frequency stabilized, the second solution was added and allowed to flow over the sample. The reaction was stopped by the inlet of water, and the chamber was washed with ethanol and water several times to remove all excess chemicals.

Atomic Force Microscopy

A patterned initator thiol monolayer was prepared by microcontact printing[19] (μCP) on a clean gold surface. The patterned gold surface was used for brush growth in the same polymerization solution as described above, and samples were taken out at predetermined times and measured by AFM (PicoScan^{TM} 2100, Molecular Imaging). The thickness of the patterned polymer brushes was measured in the dry state and under water following a previously described procedure.[20]

Results and Discussion

The thickness of the polymer brushes is related to the molecular weight of the polymer chains and the grafting density. The thickness (as measured by ellipsometry on dry films) versus time plot (Figure 1a) shows a close to linear relationship during the initial polymerization process (first 100 min) for all [Cu^I]/[Cu^{II}] ratios, which indicates a controlled reaction. The rate of the polymerization is expected to be proportional to the [Cu^I]/[Cu^{II}] ratio according to Equation (1), but clearly the rates seem comparable for all [Cu^I]/[Cu^{II}] ratios. This apparent insensitivity is attributed to the fact that these numbers are the dry thicknesses as measured by ellipsometry, and since the polymer chains are collapsed, differences between the grafting density and chain length of the brushes are obscured. However, higher [Cu^I]/[Cu^{II}] ratios should lead to more polydisperse brushes as termination reactions are more likely at high radical concentrations. Termination reactions would result in an overall lower grafting density and hence, brushes grown for

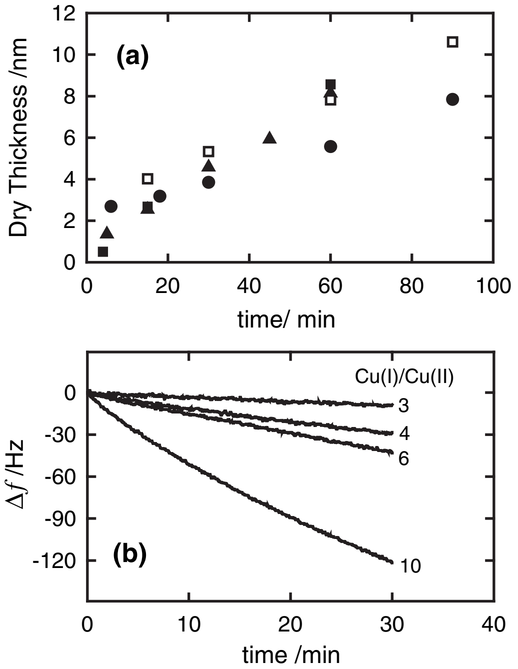


Figure 1. a) Dry thickness (ellipsometry) of METAC polymer brushes as a function of time, for different $[Cu^{I}]/[Cu^{II}]$ ratios: ●$[Cu^{I}]/[Cu^{II}] = 3$, □$[Cu^{I}]/[Cu^{II}] = 4$, ▲$[Cu^{I}]/[Cu^{II}] = 6$, and ■$[Cu^{I}]/[Cu^{II}] = 10$. $[M] = 3$ M. b) Changes in frequency of a quartz crystal during polymerization with different $[Cu^{I}]/[Cu^{II}]$ ratios. The brushes are grown under identical conditions as those used to study dry thickness in (a).

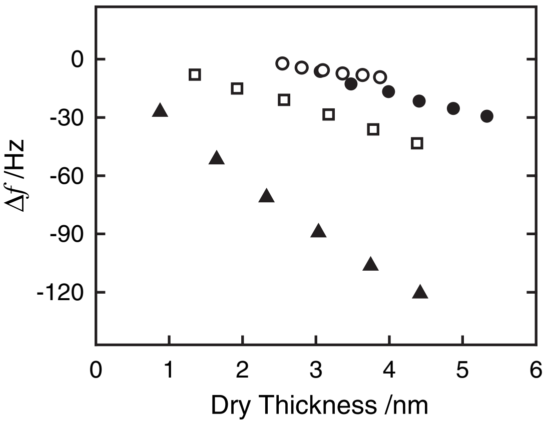


Figure 2. Plot of Δf versus thickness at the same polymerization time with different $[Cu^{I}]/[Cu^{II}]$ ratios. ○ $[Cu^{I}]/[Cu^{II}] = 3$, ◆$[Cu^{I}]/[Cu^{II}] = 4$, □ $[Cu^{I}]/[Cu^{II}] = 6$, and ▲$[Cu^{I}]/[Cu^{II}] = 10$.

the same amount of time should exhibit higher molecular weights, but less dense architectures. To obtain more detailed information, the polymer brush growth has been followed using QCM, which has recently been used to study the surface-initiated polymerization in real time.[21] In QCM, an increase in mass on the surface will decrease the frequency according to the Sauerbrey equation:[22]

$$\Delta m = \Delta f \times 17.7\,\mathrm{ng \cdot cm^{-2}} \qquad (2)$$

where Δm is the change in mass and Δf is the change in frequency. As shown in Figure 1b, a strong dependency of frequency versus time is observed for all polymerizations as the reaction proceeds. In all cases, this dependency is negative, which indicates an increase in mass of the crystal, as expected. The higher the $[Cu^{I}]/[Cu^{II}]$ ratio, the faster the reaction, and indeed the slope of Δf versus time is largest for the highest ratio. However, these data need to be studied more closely, since there are no such obvious differences in dry thickness, and hence the difference in mass on the surface cannot be solely attributed to the growth of polymer brushes.

The combination of Figure 2a and b allows the magnitude of Δf to be plotted versus the nanometer thickness of the dry polymer brush, and hence is independent of reaction time (Figure 3). In all cases, a linear relationship between the frequency decrease and the corresponding dry thickness is observed, but the magnitude of the relationship is different for all polymerization speeds. As mentioned above, the decrease in frequency is a result of an increase in the oscillating mass, and since the polymer brushes are all solvated, this increased mass includes not only the polymer brushes but also the solvent trapped inside the brush (methanol in this case). In other words, the slope of the Δf vs. dry thickness plot (Figure 2) indicates the actual amount of solvent and monomers required to obtain a 1 nm dry thickness brush. Since the total weight of polymer required per nanometer of dry brush is the same (assuming that the bulk density of the film is the same in every case), the differences in the slopes of the different $[Cu^{I}]/[Cu^{II}]$ ratios are a result of the different amounts of solvent molecules incorporated inside the brushes. Therefore, it is concluded that the volume fraction of polymer in the hydrated brush layers is different for different polymerization speeds.

Table 1 illustrates the different amounts of solvent present in brush layers grown at different $[Cu^{I}]/[Cu^{II}]$ ratios. The values cannot be interpreted quantitatively since the Sauerbrey equation is not accurate for 'wet' polymer films because of the slightly different viscoelastic properties of the brushes. Therefore, a realistic value for the brushes grown at the 'slowest' $[Cu^{I}]/[Cu^{II}]$ ratio also cannot be obtained. For entry 1, the mass on the surface is similar but slightly less than the monomer mass required for the growth of 1 nm thick dry brushes. This either illustrates the problems with using the Sauerbrey equation for these films, or (and more likely) it could mean that the sample used to measure the dry thickness is not completely dry. Polyelectrolyte brushes are very hygroscopic and it is likely that the charged polymer chains absorb water from the air. Increasing the ratio of $[Cu^{I}]/[Cu^{II}]$ clearly leads to more and more solvent incorporated inside the brushes, and hence, to less dense brushes. Because the ratio of $[Cu^{I}]/[Cu^{II}]$ is proportional to the rate of polymerization, it is concluded that the

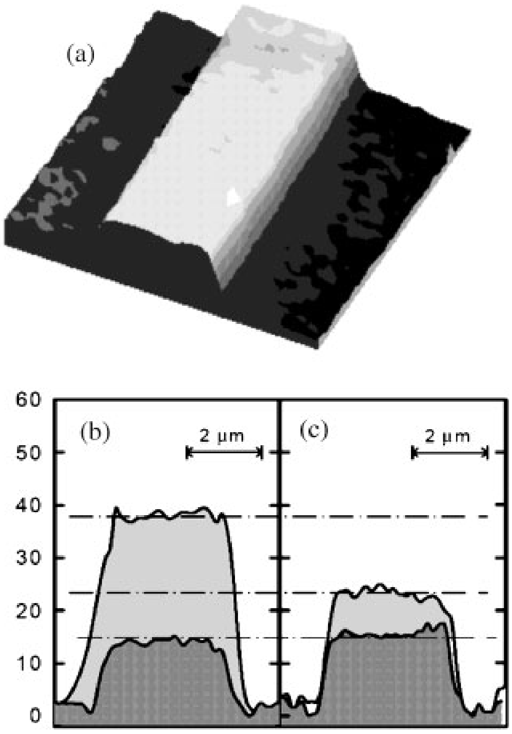


Figure 3. a) AFM topographic image of polymer brushes. b) Cross-sectional analysis of [Cu^{I}]/[Cu^{II}] = 10 polyelectrolyte brushes, derived from AFM imaging in a dry state and in water. c) Cross-sectional analysis of [Cu^{I}]/[Cu^{II}] = 3 polyelectrolyte brushes, derived from AFM imaging in a dry state and in water.

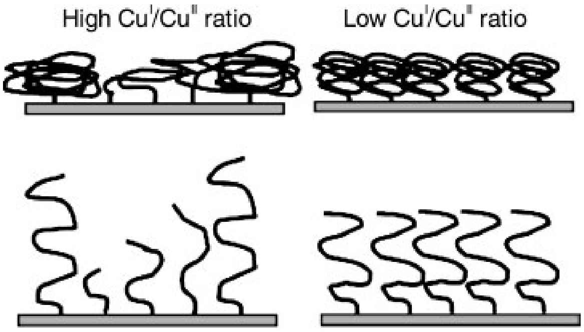


Figure 4. Schematic illustration of the effect on brush growth for different rates of polymerization. At high [Cu^{I}]/[Cu^{II}] ratios, less dense, but higher-molecular-weight polymer brushes are formed, which swell to a higher degree when placed in a good solvent.

polymerization speed influences the polymer brush conformation: the faster the reaction, the less dense the brushes grown.

AFM measurements have been performed under water to gain additional insight into the grafting density/mechanical properties of these brushes. Commercially available type II MAClevers with a nominal force constant of 2.8 N · m^{-1} are used at a driving frequency of 19 Hz in the liquid environment. Two patterned polymer brushes with the same dry thickness (15 nm) have been prepared by µCP followed by brush growth using [Cu^{I}]/[Cu^{II}] = 3 and [Cu^{I}]/[Cu^{II}] = 10 polymerization conditions. Measurements taken under water reveal that the [Cu^{I}]/[Cu^{II}] = 10 brushes swell to a larger degree (≈39 nm) than the [Cu^{I}]/[Cu^{II}] = 3 brushes, which swell to about 24 nm (Figure 3). The swelling of polyelectrolyte brushes in a good solvent is strongly dependent on the repulsive polymer–polymer interactions as a result of steric hindrance and the electrostatic osmotic pressure of the counter-ions within the polymer layer and in the aqueous environment.[23] According to the scaling theories for charged brushes,[24–26] in the *osmotic regime* for relatively dense and strongly charged brushes, the thickness should be independent of the grafting density:[27]

$$h \approx Na\,\alpha^{1/2} \tag{3}$$

where h is the thickness of the brushes, N is the number of monomers per chain (molecular weight of polymer), a is the monomer size, and α is the fraction of charged monomers.

Considering Equation (3) and the differences in height when the brushes are swollen, the ratio between the number of monomers in the brushes grown at [Cu^{I}]/[Cu^{II}] = 10 and 3, $h_{10}/h_3 \sim N_{10}/N_3$ is approximately 1.63. Assuming that the brushes are close to fully stretched, i.e., $\alpha = 1$ (fully charged), and that the size of the monomers is approx. 0.25 nm, N_{10} is estimated to be around 150. In dry brushes, $h \sim N\sigma$[28] and $h_{10} = h_3$. Therefore, $h_{10}/h_3 \sim \sigma_3/\sigma_{10}$, i.e., the most rapidly grown brushes are 1.6 times less dense. This further confirms that different [Cu^{I}]/[Cu^{II}] ratios lead to brushes with different internal structures as illustrated in Figure 4.

Table 1. Mass increases for 1 nm thick, 1 cm^2 surface area brush films as determined from QCM and ellipsometry data.

[Cu^{I}]/[Cu^{II}]	Mass (QCM) monomer + solvent$^{a)}$	Monomer mass required$^{b)}$	Solvent ‘coupled to’ brushes
	ng	ng	ng
3	100	111	–
4	179	111	68
6	206	111	95
10	467	111	256

$^{a)}$ Calculated using Equation (2).
$^{b)}$ Density of METAC monomer = 1.105 g · cm^{-3}.

Conclusion

The polymerization conditions for surface-initiated polymer brushes are directly relevant for controlling the kinetics of brush growth and to allow the formation of block copolymer brushes. However, these conditions are also of crucial importance for controlling the internal architecture (in this case grafting density) of the polymer brushes. The grafting density plays a major role in some of the highly desirable properties of polymer brushes. In addition to all the other parameters that need to be optimized for efficient brush growth, the overall rate of polymerization is very important to ensure dense polymer brushes. Here, evidence is found for much lower grafting densities in polyelectrolyte brushes grown with higher $[Cu^I]/[Cu^{II}]$ ratios, even though the evolution of the dry thickness vs. time looks reasonably well controlled. This dependence of brush density versus rate of polymerization is currently being investigated in more detail using a number of different monomers, to evaluate how great a role this effect plays for monomers of different reactivity. In any case, the present findings might have important implications when comparing literature reports on polymer brushes, which appear at first sight identical, but have been grown under different conditions.

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