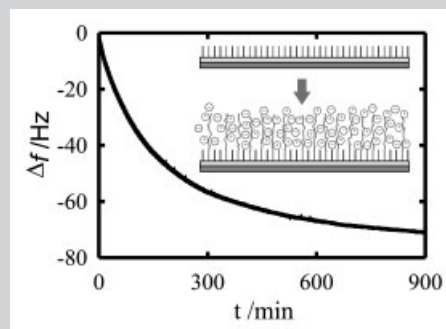


Summary: The growth of surface-initiated poly([2-(methacryloyloxy)ethyl]trimethylammonium chloride) (pMETAC) brushes by ATRP was monitored by the quartz crystal microbalance technique with dissipation (QCM-D). The change in mass of the quartz crystals starting from the adsorption of a thiol initiator monolayer through to the growth of the polymer brushes was determined. The use of QCM-D allowed determination of the kinetics of polymerization from the surface. The technique can be applied to other polymers synthesised from surfaces and allows the study of varying conditions on the polymerization kinetics.



Changes in frequency of a quartz crystal during polymerization.

Following Polymer Brush Growth Using the Quartz Crystal Microbalance Technique

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Introduction

Atom transfer radical polymerization (ATRP) is a simple and effective method of polymer synthesis that provides a narrow molecular weight distribution under easily controllable reaction conditions.^[1–3] Aqueous ATRP has the advantage of rapid polymerization (full conversion in minutes instead of hours or days) combined with a controlled character (reversible capping and activation of halogen-terminated growing polymer chains using a transition metal redox couple), which is retained to a large degree.^[4,5] When ATRP is applied to gold or silica surfaces modified with a thiol or a silane initiator, respectively, the polymerization leads to the growth of polymer brushes.^[6–11] Brushes consist of a dense monolayer of polymer molecules stretched out from the surface, not fully overlapping and swollen in the presence of solvent.^[12–14] By defining the initiator concentration and/or patterning the surface, many different surface morphologies can be produced.^[10]

Of particular interest are polymer brushes of charged monomers, such as [2-(methacryloyloxy)ethyl]trimethylammonium chloride (METAC) or methacrylic acid, since the resulting brushes will show an extended conformation in water, which can be affected by the ionic strength or pH of the environment.^[14–17] The extended conformation results from the internal repulsion of the polymer side-chains and the repulsion between the surrounding charged chains. Changing the ionic strength or pH (if the charged groups are pH sensitive) leads to screening of the charges and consequent collapse of the brush.

Although polymer brushes grown by ATRP have been well characterized post-synthesis, there is a lack of knowledge about the initiator adsorption on the surface and the kinetics of the polymerization process. One common way of measuring the kinetics of growth for brushes is to polymerize several samples simultaneously and stop them at different times to measure the thickness by either ellipsometry or atomic force microscopy (AFM), relying on

the assumption that the polymerization conditions and the amount of initiator are equal for all the samples. These measurements cannot be performed in real time on a single sample.

In this paper we will exploit the quartz crystal microbalance technique with dissipation (QCM-D)^[18–20] to monitor an ATRP reaction in real time, starting from the adsorption of a thiol initiator monolayer through to the growth of a polymer brush. Our main scope is to show that the QCM-D can be used as a tool for the study of polymerization reactions at surfaces providing information not available by any other technique.

Experimental Part

Chemicals

Mercaptoundecane (blank thiol), Cu^ICl, Cu^{II}Cl₂, 2,2'-dipyridyl (bipy), and [2-(methacryloyloxy)ethyl]trimethylammonium chloride (METAC) were purchased from Aldrich. The monomer was used as received. ω -Mercaptoundecyl bromoisobutyrate (thiol initiator) was synthesized following literature.^[11]

For the ATRP reaction a mixture of two parts solvent (80% methanol, 20% water) and one part of monomer was flushed with N₂ for one hour. Cu^ICl, Cu^{II}Cl₂, and bipy were then added to the solution in the following molar proportions: [METAC]/[Cu^ICl]/[Bipy]/[Cu^{II}Cl₂] = 100:2:5:0.1. The reaction is shown in Figure 1.

Quartz Crystal Microbalance with Dissipation

Monitoring reactions using a quartz crystal microbalance with dissipation (QCM-D) allows changes in both frequency and dissipation of an excited quartz crystal to be followed as a function of time.^[18–24] A QCM crystal consists of a thin layer of quartz between two electrodes; the crystal is excited by applying an RF voltage across the electrodes near the resonance frequency. The frequency of oscillation is related to the mass of the crystal, additions of mass to the surface of the crystal will decrease the frequency. The dissipation of the crystal is measured by recording the response of the freely oscillating crystal that has been vibrated at its resonant frequency. The values of the dissipation are related to the viscoelasticity of the film. All measurements were performed on a quartz microbalance from Q-Sense, Gothenburg, Sweden. The dissipation is defined as $\Delta D = E_{\text{dissipated}}/2E_{\text{stored}}$. The equipment has a chamber with an 80 μL volume, which is closed at one side by the quartz crystal. The cell can be filled and the fluid exchanged using the standard Q-Sense flow system. The quartz crystals, purchased from Q-sense, have a main resonance frequency of 5 MHz.

Results and Discussion

Figure 1 shows the two stages in the surface polymerization of METAC and the idealized resulting brush structure. The first stage corresponds to the adsorption of a 5×10^{-3} M

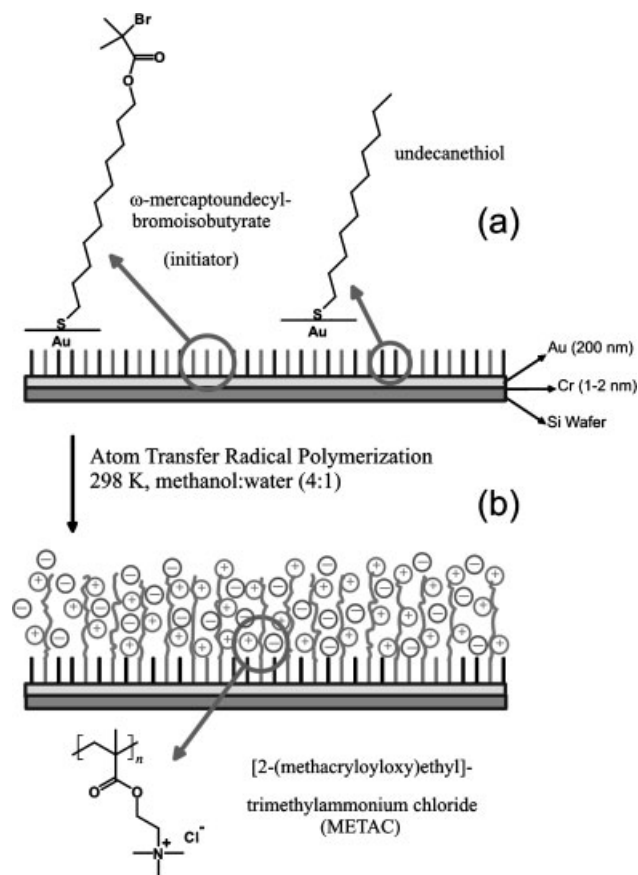


Figure 1. Schematic of a) a mixed initiator and blank thiol monolayer, and b) surface-initiated polymerization of p(METAC).

solution of ω -mercaptoundecyl bromoisobutyrate and mercaptoundecane from an ethanolic solution; we assume here that the thiols assemble randomly since they have similar sizes. The mercaptoundecane is used as a spacer to vary the density of the initiator in the thiol monolayer. The second stage is the polymerization of METAC by ATRP from the thiol monolayer.

Figure 2 shows the changes in frequency and dissipation on a quartz crystal during the polymerization process in the chamber. The QCM trace begins with the adsorption of the thiol initiator on the gold-coated surface, through to the addition and removal of the polymerization solution and ends with surface washings of the sample. The first part of the graphs corresponds to the adsorption of an ω -mercaptoundecyl bromoisobutyrate thiol initiator monolayer from a 5×10^{-3} M ethanolic solution. The process of thiol adsorption was followed for over 3 h, and the sample was then washed with ethanol, water, and 1 M NaCl (aq).^a

^a Mixed monolayers provide, in principle, good control over the grafting density of the brush, although the composition of the monolayer does not necessarily correspond to that of the mixture in solution. This particular point and the kinetics of adsorption of mixtures of initiator and blank can be studied in detail with the QCM-D and is the subject of another paper.

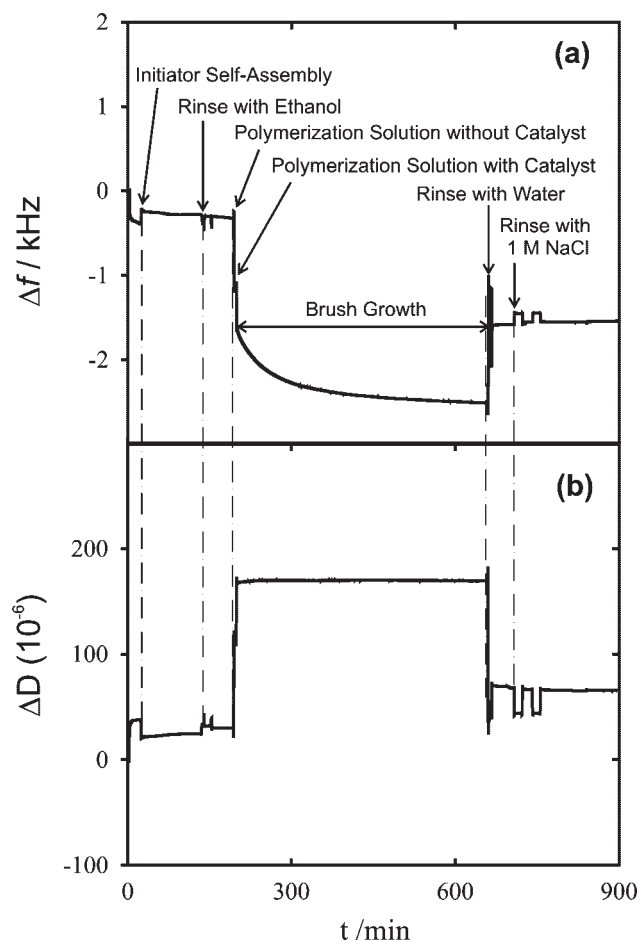


Figure 2. Changes in a) frequency and b) dissipation of a quartz crystal during assembly of a monolayer of 100% thiol initiator and the subsequent METAC polymerization and rinsing.

For the polymerization reaction, the chamber was filled with a mixture of 2 parts solvent (methanol/water, 80:20) and 1 part monomer solution (see Experimental Part). The mixture had been deoxygenated by flushing with nitrogen for one hour. This stage was followed by the addition of the same deoxygenated mixture of solvents and monomer but with the catalyst ($\text{Cu}^{\text{I}}\text{Cl}$, $\text{Cu}^{\text{II}}\text{Cl}_2$) and ligand (bipy) added. The initial addition of monomer and solvent without any

catalyst has two functions; firstly, to obtain a reference for the changes in frequency and dissipation due to the exchange of water for the mixture of solvents and monomer, and secondly, to remove all the oxygen present in the chamber before the actual polymerization starts. The polymerization reaction was left to run to completion, which occurs when the frequency and dissipation reach a plateau. The chamber was then washed with methanol, water, and finally with 0.1 M NaCl (aq). The three different washings are to assure that the brush is free from ligand, catalyst, and excess monomers.

The METAC polymerization shows an initial rapid increase as can be seen by the steep changes in frequency and dissipation. This stage is followed by a slower increase in rate for the frequency and an almost immediate plateau for the dissipation. The apparent mass increase after the polymerization, calculated using the Sauerbrey equation,^[18] is of the order of $4400 \text{ ng} \cdot \text{cm}^{-2}$. This mass is not only associated with the polymer brushes grown from the substrate, but also the mass of the water retained in the film.

By mixing ω -mercaptoundecyl bromoisobutyrate with a blank thiol (non-initiating), it is possible to change the density of the initiating molecules on the surface and consequently the density of the surface-initiated polymer brushes. In our experiments we have assembled monolayers with percentages of ω -mercaptoundecyl bromoisobutyrate ranging from 0.5 to 100%. The same protocol for thiol adsorption and polymer synthesis has been followed for the different thiol ratios.

In this present work we will only consider three cases: a low fraction of initiator (0.5%), the 50% case, and the 100% initiator monolayer. In Table 1 we have listed the apparent mass increase after polymerization for each of the three systems, and the thickness of the films measured in the dry state with ellipsometry. Ellipsometry measurements were performed on the quartz crystal after the synthesis of the brushes to obtain a reference for the polymer film thickness.

At low initiator concentration, 0.5%, the growth is almost linear for the time measured leading to a mass of the brush of around $1000 \text{ ng} \cdot \text{cm}^{-2}$ after 4 h polymerization. The dry brush has a thickness of 4 nm, as obtained by ellipsometry (this value includes the thiol monolayer: 1.5 nm thick).

Table 1. Mass increase after polymerization measured with QCM-D for p(METAC) grown from thiol monolayers with different percentages of initiator and the corresponding dry thickness measured by ellipsometry.

ω -Mercaptoundecyl bromoisobutyrate ^{a)}	Mass increase after polymerization ^{b)}	Thickness of polymer brushes ^{c)}	Polymerization time
%	$\text{ng} \cdot \text{cm}^{-2}$	nm	h
0.5	1000 ± 100	4 ± 2	4
50	4000 ± 200	14 ± 5	5
100	4400 ± 100	27 ± 2	5

^{a)} Percentage of ω -mercaptoundecyl bromoisobutyrate in the adsorbed thiol monolayer.

^{b)} Measured with QCM-D in water.

^{c)} Calculated in the dry state with ellipsometry.

For the case of the 50% initiator the plateau in the frequency is reached more slowly compared to the 100% case. After 5 h of polymerization the mass is of the order of $4000 \text{ ng} \cdot \text{cm}^{-2}$, with a measured thickness in the dry state of 14 nm. Although the mass increase is similar to the monolayer with 100% initiator, the thickness increase is around half. Before drawing too many conclusions from this experiment, we should realize that the mass measured is not only that of the brush but also of the water present in the film. The collapse of the brushes in the presence of NaCl varies for each initiator-to-blank ratio indicating that the content of water in the brushes must be different for each initiator-to-blank ratio.^[25–27] The similar mass increases under water but different dry ellipsometric thicknesses observed between the 50 and 100% initiator samples supports this hypothesis. The difference in ellipsometric thickness of 13 nm is almost half the thickness of the 100% initiator brush, even though the brushes are of similar masses in a water environment. The reason for this difference may have two explanations which are not mutually exclusive: firstly, it can be attributed to the difference in water content for the two brushes, and secondly, the free space for each polymer chain could be higher for the 50% initiator brush, which then leads to a less densely packed, thinner film.

The rates of polymerization observed for the various thiol mixtures reflect, to our understanding, the accessibility of the monomers to the growing chain, which is in a collapsed state in the methanol/water solvent mixture.^[28] The more diluted the thiol monolayer the fewer initiating chains are formed. A low chain density increases the accessibility and minimizes quenching of the radical chains, which translates to a “longer life” of the polymerization (i.e., it takes longer to reach the plateau values).

Besides studying the polymerization reactions for monolayers of different compositions, it is possible to follow changes in other reaction parameters, such as catalyst concentration or ligand type, which will give us a more detailed view of the kinetics of the ATRP on surfaces.

In Figure 3 we have plotted the changes in frequency for two concentrations of initiator in the thiol monolayer, 100% and 5%, for different amounts of $\text{Cu}^{\text{I}}\text{Cl}$ in the reaction. In the case of 100% initiator (Figure 3a) and 100% catalyst the reaction occurs rapidly within the first 300 min, beyond which only a slight change in frequency is observed. In contrast to this, a four-fold decrease in catalyst concentration shows a less rapid variation in frequency indicating a slower brush growth. For the 5% initiator monolayer (Figure 3b) the amount of $\text{Cu}^{\text{I}}\text{Cl}$ was tested at 100% and 50%. For both Cu concentrations the increase in frequency is slow with respect to the 100% initiator experiments, and the reaction starts terminating after around 750 min.

More significant here are the actual values for the increases in frequency for the first three hundred minutes after the addition of the polymerization solution (Figure 3b):

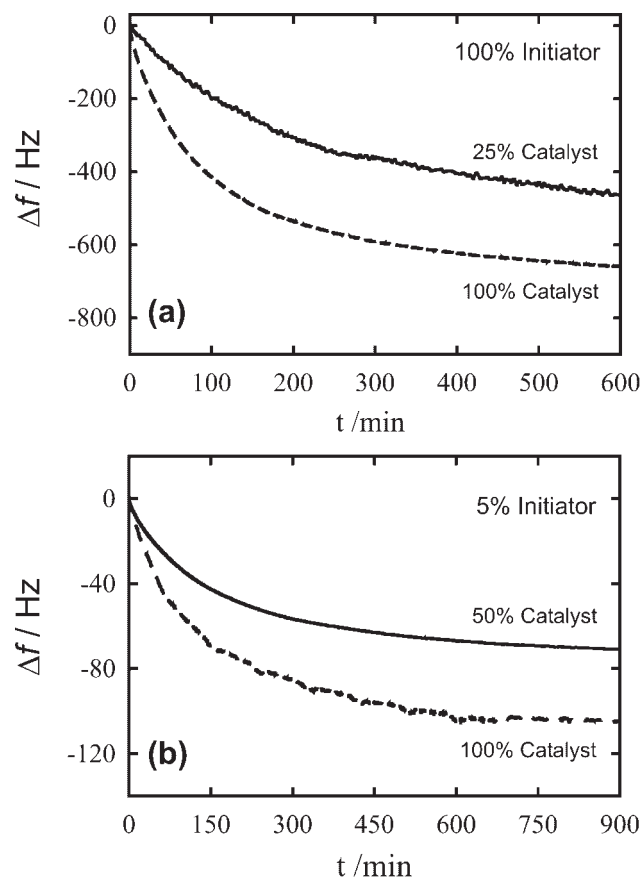


Figure 3. Changes in frequency of a quartz crystal during polymerization a) from 100% ω -mercaptoundecyl bromoisobutyrate at 100% $\text{Cu}^{\text{I}}\text{Cl}$ (dotted line) and 25% $\text{Cu}^{\text{I}}\text{Cl}$ (solid line), b) from 5% ω -mercaptoundecyl bromoisobutyrate in the thiol monolayer at 100% (dotted line) and 50% (solid line) $\text{Cu}^{\text{I}}\text{Cl}$.

80 Hz for the 100% (or “standard”) Cu concentration and 60 Hz for the 50% Cu concentration. It must be pointed out that there is a fast change in frequencies when the polymerization is started, both because of the reaction and the change in the composition of the solution as the monomer is used up.

In all cases we can say that decreasing the Cu catalyst concentration in the reaction leads to a slower polymerization, as expected since activation of the dormant halogen-terminated chain ends depends on the concentration of the Cu^{I} species.

These initial data show that it is possible to study the kinetics of p(METAC) brush growth using the QCM-D. A more detailed study of the effects of catalyst concentration, ligand type, and quality of solvent for different dilutions of initiator is in progress.

Conclusion

We have presented here, for the first time, the monitoring of the growth of surface-initiated polymer brushes by the

quartz crystal microbalance technique. The ability to record changes in mass on the surface of a gold-coated quartz crystal throughout the polymerization is very useful from a fundamental point of view and will allow a deeper understanding of the kinetics of polymerization from surfaces. The technique can be applied to other polymers synthesized from surfaces and it is also possible to vary the polymerization conditions, such as solvent quality, mole fraction of initiator, or catalyst and ligand type as well as concentration, which can aid in the elucidation of the reaction kinetics.

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