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Surface-Initiated Atom Transfer Radical Polymerization on Gold at Ambient Temperature

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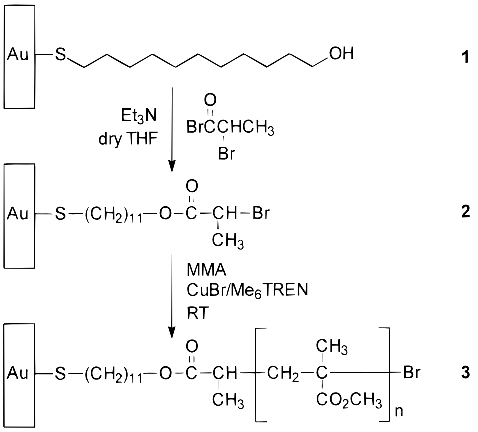
In this work, we report surface-confined atom transfer radical polymerization (ATRP) of methyl methacylate (MMA) on gold surfaces at room temperature (RT). To our knowledge, the polymerization temperature in this report is the lowest reported for surface-initiated radical polymerizations, and it is the first report of the direct measurement of the molecular weight of polymer brushes grown on a flat surface. The molecular weight of the polymer brushes suggests a high grafting density of PMMA on gold surfaces. No polymer forms in solution, and a simple solvent rinse can clean the polymer brushes on the surface.

Growth of polymer brushes is an attractive method to modify and control interface properties.[1−5] Strategies for attaching polymer brushes to surfaces include the “grafting to”[6] technique, tethering preformed polymer chains from solution onto a surface, and the “grafting from”[7−24] technique, polymerizing from surface-anchored initiators. The latter results in a higher density of polymer brushes on a surface because the “grafting to” technique eventually faces serious steric hindrance that prevents incoming polymer chains from diffusing through the film to surface reaction sites.

Several research groups used radical,[7−10] cationic,[11,12] anionic,[13,14] ring-opening,[15] ring-opening metathesis,[16−18] and ATRP[19−24] to grow polymer chains from a surface. Among these approaches, ATRP is especially attractive because it is a living process that gives a low polydispersity index (PDI = M_w/M_n). To prepare well-organized polymer brushes, the PDI should be close to 1. Because ATRP is a living process, initiating sites that are dormant after removal of monomer can be used to prepare block[12,23] copolymers.

Scheme 1



Research on surface-initiated polymerization has focused on silicon substrates, and studies on gold[15,24] are rare. Since the Au−S bond is unstable above 60 °C,[24−27] growing well-ordered polymer brushes from thiols on gold is a challenge. Shah et al. showed that the thermal stability of the self-assembled monolayer (SAM) affects the overall thickness of the polymer brushes.[24] To have more thermally stable SAMs, they intentionally prepared the SAM at the polymerization temperature. Polymerization at RT will thus be beneficial for preparing grafted polymer layers from thiol monolayers on gold. Recently, Matyjaszewski prepared polyacrylates by ATRP at RT.[28] We apply this polymerization scheme to grow polymer brushes from thiol monolayers on gold.

One challenge in surface-initiated polymerization is the characterization of polymer chains grown on surfaces.[14,23] So far, two research groups published direct measurements of the molecular weight of polymer chains detached from a curved surface.[7,19] To have measurable amounts of detached polymers, they grew polymer chains on silica gel with a large surface area. As Jordan et al. pointed out, polymer growth on a flat surface might be quite different from growing polymers on a curved surface, because these sterically different systems might have different kinetics and different polymer brush conformations.[14] Here we report direct measurement of the molecular weight of polymer chains grown from a flat surface.

Scheme 1 outlines the synthetic pathway for the preparation of grafted PMMA chains. Substrate-**1** was prepared by immersing a gold-coated Si substrate in a 1 mM 11-mercaptoundecanol (MUD) solution for 1 day. The ellipsometric thickness of the MUD layer was 12 ± 1 Å. To produce the anchored initiator, **2**, substrate−**1** was treated with 2-bromopropionyl bromide in the presence of triethylamine.[29]

Initiator immobilization is apparent from the appearance of a carbonyl peak at 1743 cm^{-1} in the reflectance FTIR spectrum

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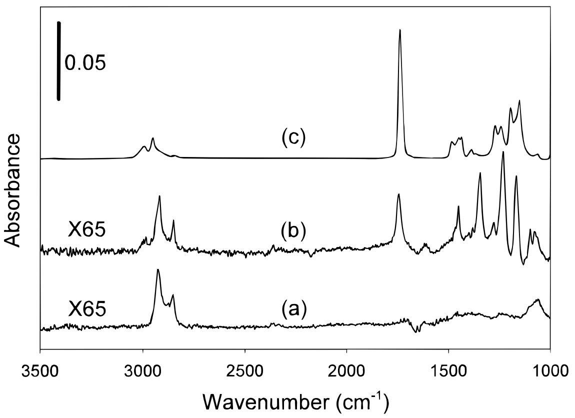


Figure 1. Reflectance FTIR spectra of (a) a SAM of MUD (**1**), (b) a layer of initiator immobilized on a MUD SAM (**2**), and (c) a grafted PMMA layer (340 Å-thick) on the initiator surface (**3**).

(Figure 1, spectrum b). To perform ATRP, substrate-**2** was immersed in MMA containing 0.1 mol % CuBr and 0.1 mol % tris[2-(dimethylamino)ethyl]amine (Me$_6$TREN)[30] at 25 °C for 12 h.[31] After polymerization, the newly formed film was washed with dry THF. A large increase in the carbonyl peak, $\nu_{C=O}$ at 1745 cm^{-1} in the external reflection FTIR spectrum confirmed the formation of PMMA brushes (Figure 1, spectrum c). The ellipsometric thickness of the polymer film measured at five different spots on a 75 cm^2 wafer was 370 ± 5 Å; this implies that the polymer film is remarkably uniform.

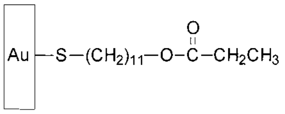
To determine the molecular weight and polydispersity of the grafted brushes, we removed the PMMA from the surface using I$_2$,[32] and characterized the polymer by GPC. For the 370 Å-thick film, GPC yields a M_n value of 44 500 and a PDI of 1.30. Since the detached PMMA brushes should exist as disulfides,[33] we cleaved the S−S bond using NaBH$_4$[34] and repeated the GPC measurements. The same M_n value and PDI were obtained, which implies that the disulfides (R$_1$S−SR$_2$), if formed, are likely unsymmetrical disulfides formed from the PMMA chain and a MUD molecule that was buried by the growing PMMA brushes during polymerization. Thus, M_n only depends on the length of the PMMA brush since the molecular weight of the short chain thiolate is negligible compared to that of the PMMA brush. We estimate that 10% of the surface bound initiators actually initiate PMMA chains, and thus each PMMA brush is surrounded by nine short chain thiolates. Thus it is natural that a polymer brush desorbs as an unsymmetrical disulfide.

Using the M_n value from GPC analysis, the calculated average cross-sectional area[35] of each polymer chain is ~180 Å^2. This result suggests a high grafting density, and is consistent with results (~200 Å^2/chain) of Shah et al.[24] which were calculated on the basis of the M_n of polymer formed in solution. AFM and ellipsometry show that these films are both macroscopically and microscopically uniform. After grafting of PMMA, the surface roughness decreased from 1.92 nm (bare gold) to 0.54 nm (gold with grafted PMMA). As shown in Table 1, these polymerizations are very repeatable.

Table 1. Molecular Weight of PMMA Brushes

surface thickness (Å)	M_n	PDI
331	33 100	1.29
370	44 500	1.30
402	68 900	1.45

To show that MMA polymerization only occurs on surfaces with immobilized initiators, substrate-**4** was prepared.[36] Thus, the only difference between the initiator-immobilized surface (substrate-**2**) and the control surface (substrate-**4**) is the existence of the α-bromocarbonyl functionality which acts as a radical initiator for ATRP. The evidence for the synthesis of **4** is again based on the appearance of an ester carbonyl peak at 1746 cm^{-1}. A control polymerization was carried out on substrate-**4** under the same polymerization conditions used with substrate-**2**. Ellipsometry and FTIR confirm that no polymerization occurs on this surface. There was no change in the thickness of the organic layer or in the IR intensity of the carbonyl peak after the polymerization.



$$\text{Au}-S-(CH_2)_{11}-O-\overset{O}{\overset{\|}{C}}-CH_2CH_3$$

4

There are several advantages to using room-temperature ATRP for "grafting from" surfaces. First, the process is compatible with substrates that are sensitive to high polymerization temperatures. Second, a simple washing step *without* Soxhlet extraction gives clean polymeric thin films because polymer chains grow only on the surface. There should be no polymerization in solution as long as there is no chain transfer from surface propagating sites to solution. Thus, thermal polymerization will be negligible at RT. NMR analysis showed no signs of polymerization in solution. This implies that the monomer could be recovered from solution and reused. Perhaps the biggest advantage of this technique is the high grafting density of polymer brushes, which results in films that are uniform at the Å level.

In conclusion, ambient temperature ATRP using Me$_6$TREN allows successful synthesis of dense chemically bound PMMA brushes on gold surfaces. The polymer films are uniform over large areas and grow only on the surface without parallel formation of polymer in solution. The polymerization kinetics are under investigation, as well as the surface-confined ATRP of other monomers for the facile synthesis of block copolymers on gold.

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(29) To achieve near-quantitative initiator immobilization, we used a concentrated 2-bromopropionyl bromide solution (0.1 M). Since a thiol SAM could be unstable in the acid bromide, substrate-**1** was dipped in acid bromide solution for only 2 min. This reaction was done in a drybox because the acid bromides are moisture sensitive, especially in the presence of an organic base.

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(31) Since ligated Cu(I) is sensitive to O$_2$, all the polymerizations were carried out in a drybox filled with helium.

(32) PMMA chains were removed from the surface by immersing the PMMA films in a 4 mM I$_2$ in CH$_2$Cl$_2$ solution for 10 h. The PMMA was isolated by removal of CH$_2$Cl$_2$ and I$_2$ by evaporation and sublimation, respectively. Detachment of the polymers was confirmed by IR and the collected PMMA was identified by NMR. A model study with PMMA GPC standards showed that PMMA is stable under the I$_2$ treatment conditions.

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(35) For the calculation, $A_x = M/\rho t N_A$ was used, where A_x is the average cross-sectional area of polymer chain, M is the molecular weight of the chain, ρ is the density of PMMA (1.1 g/cm^3), t is the polymer thickness, and N_A is Avogadro's number.

(36) Substrate-**4** was prepared by the immersion of substrate-**1** in a solution of 0.1 M propionyl chloride and pyridine for 2 min.