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Room Temperature Growth of Surface-Confined Poly(acrylamide) from Self-Assembled Monolayers Using Atom Transfer Radical Polymerization

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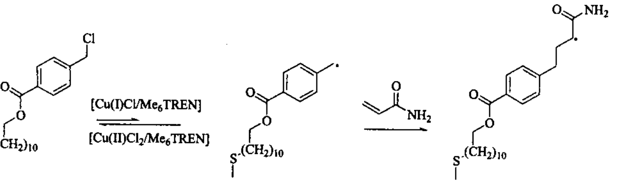
Introduction

Previous researchers[1−3] have discussed the advantages that exist for using the so-called "grafting from" method to produce polymer-modified surfaces. This method employs surface-confined polymerization initiators off of which are grown the polymer chains. The literature describes surface-confined polymerization schemes for many types of polymerization[4−6] primarily on silica[2,3,5,7,8] substrates and a few examples on gold.[1,4,6,9] Using SAMs on gold as a foundation has advantages for studying surface-confined polymerization: These systems have well-defined, uniform structures;[10] they provide opportunities to control areal surface initiator densities and hence polymer chain densities, and they facilitate characterization by analytical techniques commonly used for studying thin films. A limitation to using these systems has historically been their thermal instabilities at the temperatures needed for polymerization.[10,11] This limitation has been overcome in recent years by using cross-linked poly(siloxane) adhesion layers for initiator attachment[9] and also with the development[12] and use[4,12,13] of catalysts that promote room temperature polymerization. We have employed such a catalyst system to grow surface-confined poly(acrylamide) from SAMs on gold-coated silicon wafers.

The use of *flat* substrates in surface-confined polymerization inherently presents a challenge for controlled chain growth: The controlled nature of the ATRP reactions relies on a sufficient concentration (~10^{-3} M[8]) of deactivating species for the growing chain radicals. Typically, these persistent deactivating molecules form during the initial stages of polymerization via termination reactions and serve to control chain growth.[14] For surface-confined polymerization on flat surfaces, too few initiator molecules are available to generate a sufficient concentration of deactivator molecules under typical reaction conditions. (Our wafers have 1 cm^2 surface area; even if all of the SAM chains were capped with initiator, the molar amount of initiator would be ~7.9×10^{-10} mol based on known areal SAM chain densities.[15]) Prior to the work of Matyjaszewski et al.,[8] experiments to grow controlled polymers from flat surfaces required untethered "sacrificial" initiator to generate the deactivator. While successful, this strategy resulted in the formation of both surface-confined and solution-phase polymers. To overcome this limitation, Matyjaszewski et al.[8] devised a strategy that adds the deactivator species in sufficient concentration to the reaction mixture prior to the start of the reaction. However, in the case of acrylamide-based polymerization, low conversions are common for ATRP; this fact has been explained by a slow activation of the growing chain radicals in conjunction with fast deactivation, indicating an inadequate redox potential of the catalyst.[13] Addition of deactivator species increases the deactivation rate, resulting in very low or no polymerization. Preliminary studies confirmed this result; therefore, this initial study did not employ "sacrificial" initiator or preadded deactivator species. Data will be presented that support a first-order polymerization rate with respect to monomer concentration for the system studied. These data also indicate that polymer growth is not controlled.

Scheme 1. Polymerization Sequence



Experimental Methods

SAM Formation. Scheme 1 illustrates the polymerization reaction sequence used to prepare surface-confined poly(acrylamide). Self-assembled monolayers of hydroxyl-terminated thiols were formed by immersing a freshly prepared, gold-coated silicon substrate into a 1 mM solution of 11-mercapto-1-undecanol ($HS(CH_2)_{11}OH$) in absolute ethanol at room temperature for 12−15 h. After removal, the samples were rinsed extensively with ethanol and HPLC grade water using an ultrasonicator to remove residual physisorbed thiol. Sonication was done for less than 1 min to avoid the removal of chemisorbed thiol from the gold substrate. Single-wavelength ellipsometry and external reflection (ER)−FTIR were used to measure the monolayer thickness and to infer the chain conformational order, while ER−FTIR and liquid drop contact angle measurements with HPLC grade water were used to determine the chemical characteristics of the SAM. Ellipsometry showed the monolayer thickness to be 9.6 ± 1 Å. Static liquid drop contact angle measurements with water gave contact angles of <15°. FTIR showed wavenumbers of 2919−2920 cm^{-1} for the asymmetric methylene stretching vibration. All of these measurements are consistent with a fairly well-ordered, hydroxyl-terminated SAM of $HS(CH_2)_{11}OH$.[15]

Initiator Capping. The SAM was functionalized with the initiator, (4-chloromethyl)benzoyl chloride; the (4-chloromethyl)benzyl structure has been used previously[16] to initiate ATRP of acrylamide. To prepare this initiator-functionalized SAM, a surface bearing the SAM was immersed in a 1 mM solution of (4-chloromethyl)benzoyl chloride in anhydrous toluene for 18−24 h. The surface was then removed from the solution, rinsed thoroughly with toluene, and dried with nitrogen before exposure to the ambient atmosphere for characterization experiments. Because of the susceptibility of the acid chloride group of the initiator to hydrolysis, anhydrous toluene was used as solvent, and the coupling reactions were performed in a glovebox filled with dry nitrogen. Solid anhydrous sodium hydroxide was used to scavenge the byproduct HCl formed during reaction using a packed column above the reaction mixture. Characterization was done on the initiator-functionalized surface by ellipsometry, contact angle goniometry, and FTIR. Ellipsometry showed the initiator thickness to be 6.7 ± 1 Å. Static liquid drop contact angle measurements with water gave contact angles of 68 ± 2°. Figure 1 compares ER−FTIR spectra for the SAM and the initiator-functionalized surface in the wavenumber region used to identify the initiator. The vibrational wavenumbers at 1730 and 1265 cm^{-1} correspond to the carbonyl group (C═O) of aromatic ester and the CH_2

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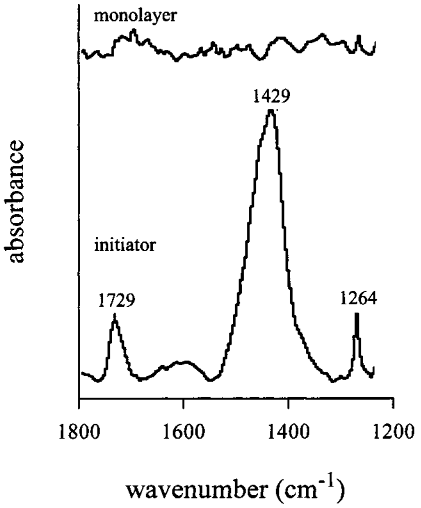

Figure 1. Comparison of the ER−FTIR spectra for the SAM and the (4-chloromethyl)benzoyl chloride initiator-functionalized surface in the wavenumber region used to identify the initiator.

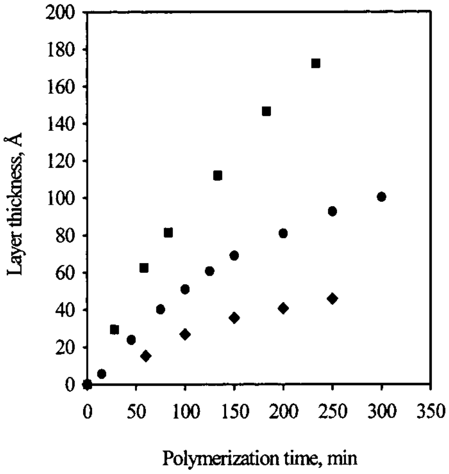

Figure 2. Growth of surface-confined poly(acrylamide) at 25 °C on SAM surfaces functionalized with (4-chloromethyl)-benzoyl chloride initiator. Cu(I)Cl/Me$_6$TREN was used as catalyst. Acrylamide concentrations in solutions of THF were (◆) 0.05, (●) 0.10, and (■) 0.20 M.

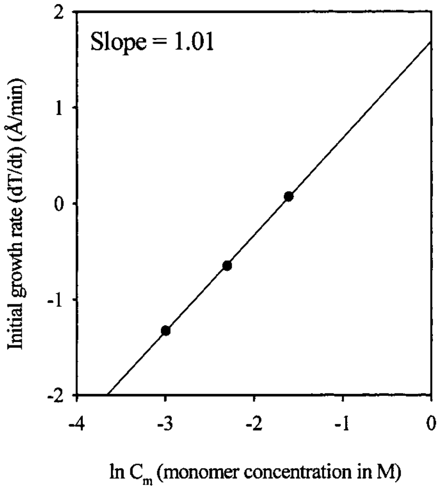

Figure 3. Elucidation of the rate order for growth of surface-confined poly(acrylamide) at 25 °C on SAM surfaces functionalized with (4-chloromethyl)benzoyl chloride initiator. Cu(I)Cl/Me$_6$TREN was used as catalyst.

deformation (CH_2−Cl), respectively. The peak at 1429 cm^{-1} is due to aromatic ring C=C stretching.

Catalyst System. To overcome difficulties associated with growing polymers from SAMs on gold at elevated temperatures,[10,11] we carried out the polymerization reaction at room temperature (24 ± 3 °C). To accommodate room temperature polymerization, we used an organometallic catalyst that comprised tris[2-(dimethylamino)ethyl]amine (Me$_6$TREN) as the complexing ligand with copper(I) chloride. Other researchers[4,12] have shown the Cu(I)Cl/Me$_6$TREN catalyst system can be used for room temperature ATRP. It initiates radical formation by abstracting a chlorine atom from the surface-confined (4-chloromethyl)benzoyl chloride (initiator) to form a surface radical and Cu(II)Cl$_2$. Reaction of this surface radical with acrylamide monomer in solution leads to polymer growth. Me$_6$TREN [$N(C(1)H_2C(2)H_2N(C(3)H_3)_2)_3$] was prepared by a one-step synthesis procedure[17] from commercially available tris(2-aminoethyl)amine (TREN). The product was verified by ^{13}C NMR (75 MHz, CDCl$_3$): Experimental: δ 57.4 (C(2)), 53.0 (C(1)), 45.8 (C(3)). Predicted using ChemNMR Pro software (Cambridge Soft): δ 58.3 (C(2)), 52.7 (C(1)), 41.2 (C(3)).

Polymerization. The organometallic catalyst was formed in a nitrogen atmosphere by adding Cu(I)Cl and Me$_6$TREN in a 1:2 molar ratio to 10 mL of tetrahydrofuran as solvent.[18] The mixture was then sonicated for 1−2 h to facilitate the formation of the Cu(I)Cl/Me$_6$TREN complexes. Next, acrylamide was added to the catalyst complex solution; monomer concentrations that were used were 0.05, 0.10, and 0.20 M. The pale green mixture was mixed thoroughly and then transferred to a Schlenk flask. A second Schlenk flask contained a surface with an initiator-functionalized SAM. Both flasks were evacuated and purged with nitrogen to remove oxygen. To begin polymerization, the monomer/catalyst solution was transferred via cannula to the flask containing the surface. At regular time intervals, the solution was cannula transferred back to the starting flask, and the surface was removed and cleaned with tetrahydrofuran before characterization. The thickness of the polymer formed on the surface was determined using ellipsometry. Recontacting the surface with the monomer/catalyst solution led to continued growth, thereby allowing us to monitor polymer growth rate via ex-situ ellipsometric thickness measurements.

Results and Discussion

ATRP studies by other groups show that the polymerization is a first-order reaction with respect to monomer concentration. (See Qiu et al.[19] for a review.) Because polymer molecular weight in solution polymerization is proportional to monomer concentration, the film thickness on the surface should also to be proportional to monomer concentration. Mathematically,

$$-\left(\frac{\mathrm{d}C_{\mathrm{m}}}{\mathrm{d}t}\right) \propto \left(\frac{\mathrm{d}T}{\mathrm{d}t}\right) = k_1 C_{\mathrm{m}}{}^{\alpha} C_{\mathrm{chains}}{}^{\beta} \qquad (1)$$

where C_m and C_{chains} represent the monomer concentration in solution and the areal surface concentration of growing polymer chains, respectively.

To test this hypothesis, reactions were performed at three different monomer concentrations. Figure 2 shows a plot of the layer thickness of poly(acrylamide) vs time for the conditions studied. Figure 3 uses the initial slopes from the growth rate data to determine the rate order (α) by a linear, least-squares regression; it is 1.01. This result confirms that the reaction is first-order in monomer concentration.

An unanticipated result was the nonlinear growth seen in Figure 2. On the basis of previous work by Huang and Wirth,[16] we anticipated "apparent" zero-order kinetics stemming from the fact that monomer concentration remains nearly constant during the polymerization, together with their claim of “living” acrylamide polymerization. Low monomer conversion can be attributed to the low number of polymer chains (~10^{14} chains/cm^2) on the surface. Looking at eq 1, it appears then that the nonlinear growth results from nonconstant concentrations of growing chains. Chain concentration appears to be a decreasing function with time, which suggests that polymerization is not “living” for our system. This observation is consistent with previous works on (meth)acrylamides and could be due to chain−chain termination[13,20] or loss of catalyst activity.[13] The idea of termination suggests that the chains are not experiencing controlled growth; this is consistent with the observation of Matyjaszewski et al.[8] that an insufficient concentration of deactivator is generated with flat surfaces and with the belief of Brittain et al.[20] that copper halide salts complex to the amide group of the chain ends, thereby promoting radical stability. On the basis of one study[13] of (meth)acrylamide polymerization, however, catalyst deactivation may also be a culprit to the slowing of growth rate. In that work, it was shown that addition of new initiator to the reaction led to practically no continued growth, whereas addition of new catalyst led to continued growth, confirming the persistence of active chains in the polymerization mixture.

To examine whether bimolecular termination might account for the nonconstant concentrations of growing chains, we introduced a second kinetic expression that describes loss of active chains:

$$\frac{\mathrm{d}C_{\mathrm{chains}}}{\mathrm{d}t} = -k_2 C_{\mathrm{chains}}^2 \tag{2}$$

Integration of eq 2 gives a time-dependent expression for the concentration of active chains.

$$C_{\mathrm{chains}} = \frac{C_{\mathrm{chains}}^0}{1 + k_2 t C_{\mathrm{chains}}^0} \tag{3}$$

where the superscript 0 indicates the initial value. Substitution of eq 3 into eq 1, with the assumptions of constant monomer concentration and first-order growth dependence on chain concentration, yields the following expression for film growth rate:

$$\frac{\mathrm{d}T}{\mathrm{d}t} = k_1' \frac{C_{\mathrm{chains}}^0}{1 + k_2 t C_{\mathrm{chains}}^0} \tag{4}$$

Normalization of the growth rate by the initial growth rate (i.e., as $t \rightarrow 0$) yields

$$\frac{\mathrm{d}T/\mathrm{d}t}{(\mathrm{d}T/\mathrm{d}t)_{\mathrm{initial}}} = \frac{1}{1 + k_2 t C_{\mathrm{chains}}^0} \cong 1 - k_2 t C_{\mathrm{chains}}^0 \tag{5}$$

The linear approximation results from a Taylor series expansion; it is appropriate for short times. Figure 4 shows the time dependence of the growth rate, normalized by the initial growth rate. This figure illustrates that the decrease in growth rate is linear with time (at the short times investigated) and independent of the monomer concentration, as expected from eq 5. This result supports a bimolecular termination mechanism as the cause for nonlinear growth in this system.

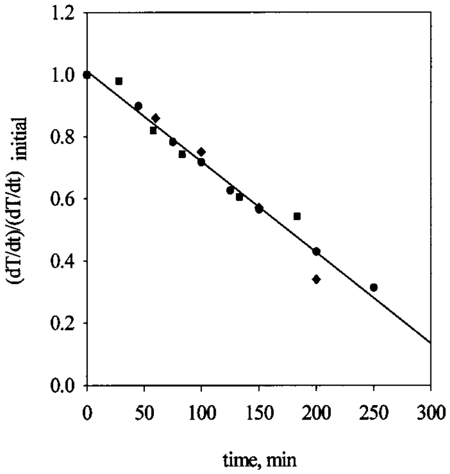

Figure 4. Time dependence of the growth rate for growth of surface-confined poly(acrylamide) at 25 °C on SAM surfaces functionalized with (4-chloromethyl)benzoyl chloride initiator. Cu(I)Cl/Me$_6$TREN was used as catalyst. Acrylamide concentrations in solutions of THF were (◆) 0.05, (●) 0.10, and (■) 0.20 M.

Conclusions

SAMs of 11-mercapto-1-undecanol can be functionalized with (4-chloromethyl)benzoyl chloride for growing surface-confined poly(acrylamide). Growth rates determined by ex-situ layer thickness measurements indicated that polymerization kinetics are first-order with respect to monomer concentration. Nonlinear growth rates were observed for the system studied; this result is consistent with previous studies using (meth)acrylamide monomers and appears to be caused by bimolecular termination. No attempts were made in this preliminary work to control growth by preaddition of catalyst deactivator or to elucidate the percentage of SAM chains that are functionalized with initiator molecules; such work is under way in our laboratory.

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