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Molecular Engineering of Surfaces for Selective Separations

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ABSTRACT

A strategy is outlined for building designer adsorption-based separation materials. The strategy adopts a molecule-by-molecule approach to modify surfaces with polymer films that carry out selective separations. After describing the strategy, we focus this article on preparing the foundation for these materials using self-assembly and a type of surface-confined polymerization on model gold surfaces. Experimental ellipsometry data are presented that show polymer film thickness can be tuned with sub-nanometer precision. Also presented are x-ray photoelectron spectroscopy data that support the ability to control the areal density of growing polymer chains.

Key Words: Surface modification; Self assembly; Adsorption; Molecular imprinting; ATRP.

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INTRODUCTION

The modification of surfaces to enhance their performance as adsorptive separation agents has been the focus of numerous publications and patents. Generally speaking, methodologies fall into at least two broad categories: chemical class specific and chemical compound specific. Examples of the former include chemical treatments,[1–3] plasma treatments,[3,4] and thermal treatments.[1] These treatment methodologies produce separation materials that show performance improvements for adsorption of classes of compounds. Within classes of compounds, however, such treatments generally offer little to impart the selectivities necessary for compound specific separation. Examples of the compound-specific surface modification methodologies include ligand immobilization,[5] surface templating using plasma deposition of thin films,[6] and surface grafting of metal chelates.[7] These methodologies produce adsorbent materials that allow the separation of compounds that are highly similar in chemical reactivity, size, and structure (e.g., enantiomers).

We present here a new strategy for building "designer" adsorbent materials that can discriminate among similar molecules. As such, our approach belongs in the compound-specific surface modification category. After a brief discussion of the strategy and the motivation for it, we focus on how to build the foundation for these materials using self-assembly and a type of surface-confined polymerization.

Our primary objective is to design and synthesize separation materials that can perform molecular recognition, a process whereby an agent identifies a target molecule and interacts specifically and noncovalently with it. We consciously encounter molecular recognition processes every day. Our sense of taste, for example, is a recognition process. The basic tastes (sweet, sour, and bitter) are caused by different chemicals and are initiated by recognition reactions between these chemicals and receptors (taste buds) on the tongue.[8] One conceptual view suggests that the recognition properties of biological systems arise from a shape selective, 'lock and key' mechanism.[9] A receptor (the lock) interacts selectively with a particular chemical molecule (the key) that complements the receptor in size, shape, and functionalities. This same mechanism can be exploited to carry out difficult separations. To engineer separation materials that perform molecular recognition, we turn to molecular imprinting.

Molecular imprinting[7,10–16] is a templating technique that produces polymer materials in the presence of target, or print, molecules. Following polymer synthesis, the print molecule is removed from the polymer matrix by extraction. What remains is a polymer material that contains cavities with size and shape dimensions that match those of the print molecule. Furthermore, these cavities, or imprint sites, complement the print molecule in chemical functionalities.

Recent review articles[10−13] highlighted some successes of molecular imprinting; they also described the limitations that must be overcome for these materials to find commercial application. These limitations provide motivation for improvements; they include slow "apparent" binding kinetics; broad peaks during chromatography; and nonquantitative recovery of the print molecule, even with exhaustive extraction. This last limitation can be problematic for two reasons. For expensive print molecules, loss of even small masses is cost prohibitive. Also, it has also been shown[14] that "trapped" print molecules eventually leak out of the polymer over long time periods, interfering with the intended use of the printed polymer. Each of these limitations likely derives from a single source: the heterogeneous nature of the binding sites for materials prepared by conventional bulk or solution polymerization. For this reason, a new method is proposed for building ultrathin, surface-confined layers of molecularly imprinted polymers (MIPs) on uniform, solid support surfaces. Confining imprint sites to a thin outer layer ensures a more homogenous site distribution relative to the solid–solution interface, and should overcome the mass-transfer limitations experienced by conventional MIPs.

Attempts to date to prepare surface layers of MIPs on solid substrates commonly have used silane chemistry[15,16] or surface "grafting to" approaches.[7] Our approach differs in that we tether and grow our materials from the substrate surface. Previous researchers[17,18] discussed the advantages that exist for using this so-called "grafting from" method to produce polymer-modified surfaces. Briefly, this approach allows the use of a wide range of monomer systems, prevents concurrent solution polymerization, produces higher polymer segment densities, and allows for molecular-level control over polymer structure.

Figure 1 illustrates the strategy for preparing our materials. The foundation is a solid support material (e.g., silica) that is capped with polymerization initiator molecules (★) off of which are grown the polymer chains. This initiator is anchored covalently to the support; subsequently, the growing polymer chains remain confined to the surface. Finally, in the presence of a template molecule and cross-linking agent(s), imprints can be formed at the polymer film periphery.

Here, we focus on how to prepare the foundation for these materials using self-assembly and a type of surface-confined polymerization on model gold surfaces. Using self-assembled monolayers on gold as a foundation has advantages for studying surface-confined polymerization: These systems have well-defined, uniform structures[19]; 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. Additionally, the use of gold substrate was adopted to allow us to use

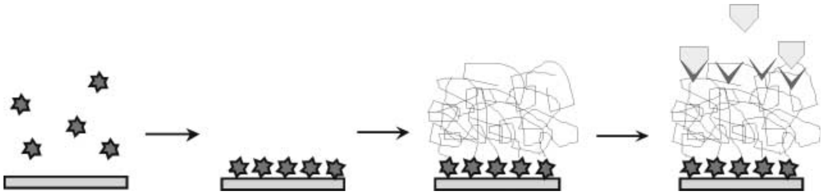

Figure 1. Schematic illustration of the strategy for preparing our materials. A polymerization initiator (★) is tethered covalently to a solid support. Polymer growth occurs from these initiator molecules. In the presence of a template molecule and cross-linking agent(s), imprints can be formed at the polymer film periphery.

a technique known as surface plasmon resonance (SPR) spectroscopy for surface adsorption studies that are in progress in our laboratory. SPR requires a substrate metal that has surface plasmons. Where appropriate, we note how our technology transfers to other substrate materials like silica.

EXPERIMENTAL MATERIALS AND METHODS

Materials

Chemical Reagent

The following reagents were used as purchased from Aldrich (Milwankee, WI, USA): 11-mercapto-1-undecanol (97%), absolute ethanol (99.5%; ACS), HPLC grade water, trichloro[4-(chloromethyl)-phenyl]silane (98%), (4-chloromethyl)benzoyl chloride (97%), anhydrous toluene (99.8%), tris-(2-aminoethyl)amine (96%), copper(I) chloride (99.995 + %), anhydrous tetrahydrofuran (99.9%; inhibitor-free), acrylamide (99 + %; electrophoresis grade), formaldehyde (37%; ACS), formic acid (97%; ACS). Other reagents were HCl (Fisher (Pittsburgh, PA, USA), 37.3%; ACS), potassium hydroxide (Fisher, 87.6%; ACS), sodium hydroxide (Sigma, (St. Louis, MO, USA) 98%), dimethylchloro((chloromethyl)phenylethyl) silane (Gelest, Morrisville, PA, USA).

Catalyst System

An organometallic catalyst system was used comprising the tridentate ligand, tris-[2-(dimethylamino)ethyl]amine (Me_6TREN), with copper(I) chloride. The organometallic catalyst was formed in a nitrogen atmosphere by adding Cu(I)Cl ($\sim 7\,\mu$mol) and Me_6TREN in a 1:2 molar ratio to 10 mL of tetrahydrofuran as solvent. The mixture was then sonicated for 1 to 2 hours to facilitate the formation of the Cu(I)Cl/Me_6TREN complexes. Me_6TREN was prepared according to the literature[20] from commercially available tris-(2-aminoethyl)amine (TREN). Product verification was done by ^{13}C NMR (300 MHz, $CDCl_3$ (t: 77.2, 77.6, 78.0): Experimental δ_C 57.4 (3×), 53.0 (3×), 45.8 (6×); predicted using ChemNMR Pro software (Cambridge Soft, Cambridge, MA, USA) δ_C 58.3 (3×), 52.7 (3×), 41.2 (6×).

Methods

Substrate Preparation

Gold substrates were prepared by thermal evaporation of gold (99.99%) at 7×10^{-6} torr from a tungsten holder onto polished silicon wafers (Silicon Quest International (Santa clara, CA, USA); 120 mm × 100 mm). A chrome adhesion layer of about 100 Å was evaporated onto the wafers prior to gold deposition.

Monolayer Preparation

Self-assembled monolayers of thiols were adsorbed spontaneously by immersing the fresh gold substrate into a freshly prepared 1-mM solution of the thiol [11-mercapto-1-undecanol ($HS(CH_2)_{11}OH$)] in ethanol at room temperature for 12 to 15 hours. After removal, the samples were rinsed extensively with ethanol and HPLC grade water using an ultrasonicator. This rinsing procedure was necessary to remove residual physisorbed thiol. Following the cleaning, the samples were blown dry using nitrogen.

Initiator Capping

Three initiator compounds were examined; Fig. 2 shows the structures of these initiators. To prepare an initiator-terminated layer, a surface bearing the SAM was immersed in a solution (< 1 mM) of initiator in anhydrous toluene for 18 to 24 hours. Various solution concentrations were used to examine the effect of solution initiator concentration on the resulting areal density of surface initiator molecules. Solid sodium hydroxide was used to scavenge the by-product HCl formed during reaction. The surface was then removed from

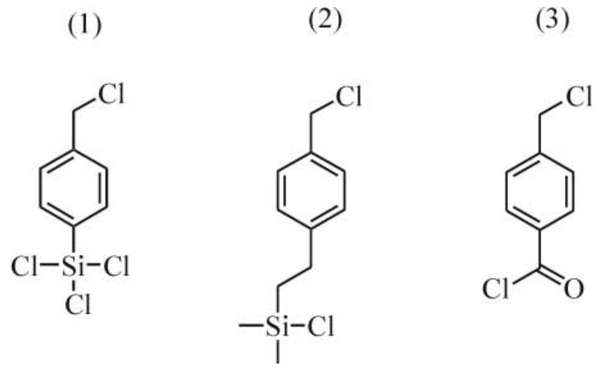

Figure 2. Initiator molecules used in this work.

the solution, rinsed thoroughly with toluene, and dried with nitrogen before exposure to the ambient atmosphere for characterization experiments.

Surface Polymerization

Acrylamide was added to the catalyst complex solution in a Schlenk flask; monomer concentrations that were used were 0.05 M, 0.10 M, and 0.20 M. A second Schlenk flask contained a surface with an initiator-terminated monolayer. Both flasks maintained a nitrogen atmosphere. Polymerization was carried out at room temperature (24 ± 1°C). 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 washed with tetrahydrofuran before characterization. The thickness of the polymer formed on the surface was determined using ellipsometry. Because the polymer chains remained "living," 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.

Characterization

Single-wavelength ellipsometry and reflection absorption FTIR were used to measure layer thicknesses and to infer SAM chain conformational order, while FTIR and liquid drop contact angle measurements with HPLC grade water were used to determine the chemical characteristics of the layers. X-ray photoelectron spectroscopy was used to measure atomic composition of the layers.

Film thickness was estimated using a Rudolph Research (Flanders, NJ, USA) AutoEL II Automatic Ellipsometer. Optical constants for the bare substrates were predetermined for 8 to 12 spots on the cleaned, uncoated surfaces for each sample immediately prior to immersion in the thiol solution. After removal from the thiol solution, with appropriate cleaning, the samples were again analyzed. The film thickness calculations were based on a three-phase ambient/film/gold model[21] in which the film is assumed to be isotropic and assigned a scalar refractive index value of $1.50 + 0i$.

Infrared spectra of the adsorbed films were obtained using a Nicolet (Madison, WI, USA) Nexus 870 FTIR spectrometer equipped with a nitrogen-purged sample chamber. All spectra were taken at 8-cm^{-1} resolution and 2000 scans. A reference spectrum was taken with clean substrate prior to thiol adsorption and was subtracted from the sample spectra during data processing.

XPS data were obtained using a Kratos (Chestnut Ridge, NY, USA) Axis ULTRA x-ray photoelectron spectrometer housed in the Center for Microanalysis of Materials at the University of Illinois, Urbana-Champaign. The data presented in this article were generated using a monochromatic Al $K\alpha$ x-ray source emitted at a 90° angle of incidence (normal to the surface). Four sweeps were performed per sample.

STRATEGY FOR BUILDING THE FOUNDATION

Figure 3 details the three-step process for building the foundation of our surface imprinted polymer films on model gold surfaces. Step 1 uses molecular self-assembly of hydroxyl-terminated alkanethiols. The sulfur end group of the alkanethiols reacts with the gold to form a gold thiolate bond.[22] This step produces a well-ordered underlayer that presents hydroxyl groups at its periphery. Step 2 reacts the surface initiator molecule with these hydroxyl groups to anchor the initiator to the surface covalently. For commercial applications, step 2 could be performed on any similar surface bearing hydroxyl functionality. An example is silica microspheres used commonly for chromatography stationary phases. A simple hydroxylation step[23] would make such a support accessible for reaction with the initiator molecule. Step 3 involves an organometallic catalyst system that activates the initiator molecule to form a surface radical. In the presence on monomer, polymer growth commences. By tuning the properties of the catalyst system, uniform

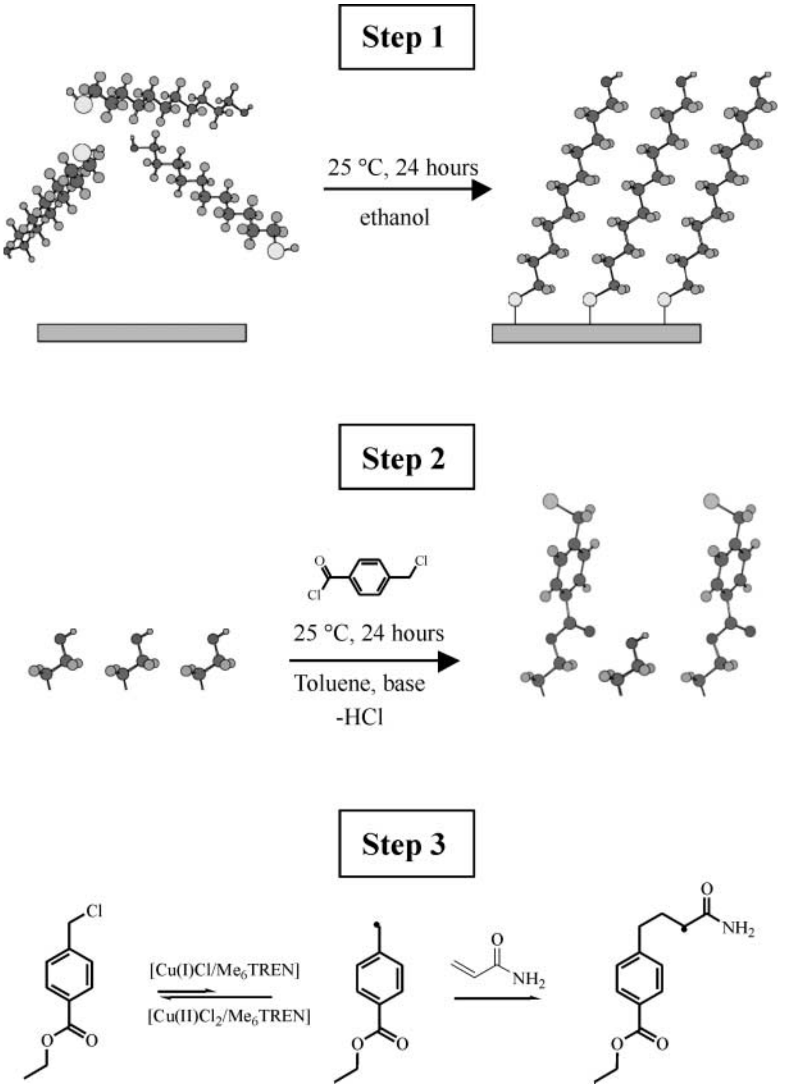

Figure 3. Three-step procedure for growing surface-confined poly(acrylamide) from a gold substrate. Step 1 involves molecular self-assembly of 11-mercapto-1-undecanol. Step 2 attaches the initiator, (4-chloromethyl)benzoyl chloride. Step 3 uses an organometallic catalyst to carry out atom-transfer radical polymerization.

and "living" growth of the polymer chains can be achieved (see, e.g., Refs.[24,25]). By tuning the solution concentration of initiator in step 2, the areal density of growing polymer chains can be altered. Finally, by altering the monomer concentration and growth time in step 3, the polymer film thickness, can be controlled with molecular-level precision. We now expand on these effects with experimental results.

RESULTS AND DISCUSSION

Monolayer Formation

A fully extended chain of $HS(CH_2)_{11}OH$ should give a thickness of 12.3 Å, as calculated using molecular modeling simulations and previous measurements of chain tilt angles[22]; an actual thickness of 9.6 ± 1Å was observed. Static liquid drop contact angle measurements with water gave contact angles of $<15°$. Table 1 shows the major vibrational wavenumbers seen in the FTIR spectrum along with their assignments. Wavenumbers of 2919 to 2920 cm^{-1} were seen for the asymmetric methylene stretching vibration. All of these measurements are consistent with a fairly well-ordered, hydroxyl-terminated SAM of $HS(CH_2)_{11}OH$.[22]

Initiator Studies

Three types of initiator systems were evaluated as candidates for surface polymerization; they are shown in Fig. 2. Initial studies focused on

Table 1. Major reflectance FTIR peak assignments for surface layers.

Monolayer	Initiator (**3**)	Polymer film	Assignment
2919.6, 2849.5	2920.4, 2850.5	2930.7, 2865.1	CH_2 (a), (s)
3400 (broad)	—	—	Intermolecular H-bonding
1061	—	—	C—O stretch (CH_2OH)
—	1728.9	1728.0	C═O
—	1263.8	—	CH_2 deformation (CH_2Cl)
—	1123.3	1121.9	C—O stretch (ester linkage)
—	—	1676.7	Amide 1
—	—	1598.7	Amide 2
—	—	3352.9	N—H stretch (primary amide)

the trichlorosilane initiator (**1**), because it has been shown to be effective for surface-confined polymerization,[24] and because it is commercially available. After capping our SAM layer with (**1**), layer thickness was measured by ellipsometry. The average initiator layer thickness across the dimensions of an individual sample was on the order of 75 ± 2Å. By comparison, a thickness of 7.9 Å was estimated (Cerius2 molecular modeling software), using standard bond lengths, for a complete monolayer of (**1**) grown perpendicular to the SAM surface. The following scenario describes a likely cause for this discrepancy. Due to steric factors, less than 2 equivalents of Cl-functionality per mole of silane can react with OH groups on the substrate surface,[23] leaving unreacted, or residual Cl groups on the silane. In the presence of water or moist air, these residual Cl groups on the silane hydrolyze to produce acidic SiOH groups; these groups might react further with additional molecules of (**1**) to form a polymerized layer on the surface. This "initiator polymerization" might account for the high values of thickness obtained from ellipsometry. Since we envision molecular-level control of film structural properties, uncontrolled initiator polymerization is unacceptable.

To avoid this initiator polymerization, we used structurally similar monochlorosilane (**2**) as our initiator. This monochlorosilane will not allow for the polymerization reaction that we speculated to be occurring with (**1**). The measured layer thickness of initiator (**2**) was 6.5 ± 1Å. A thickness of 9.2 Å was estimated, using standard bond lengths, for a fully extended monolayer of (**2**). The slightly lower value could possibly be due to the slight tilting or bending of the initiator chain due to packing inefficiencies. Nevertheless, use of a monochlorosilane avoids unwanted initiator polymerization.

Examination of initiator (**2**) suggests that we might avoid packing inefficiencies by using an initiator with a more rigid chain. Initiator (**3**) was tested. The measured layer thickness of initiator (**3**) was 6.9 ± 1 Å. A thickness of 6.7 Å was estimated for a monolayer of (**3**). For the purpose of molecular-level control of film thickness, the monochlorosilane and the acid chloride initiator molecule are acceptable candidates. The polymerization work employed initiator (**3**).

In addition to control of layer thickness, we would like to have control over the areal density of growing polymer chains. Figure 4 illustrates data from x-ray photoelectron spectroscopy (XPS) studies on several initiator layers prepared from solutions differing in initial initiator concentration. (Moles of SAM chains in the abscissa were used from the work of Dubois and Nuzzo.[22]) Figure 4a shows qualitatively that increases in solution initiator concentration result in a higher intensity for the Cl 2p photoelectrons ejected from the resulting surface layer. Figure 4b quantifies this effect; plotted is

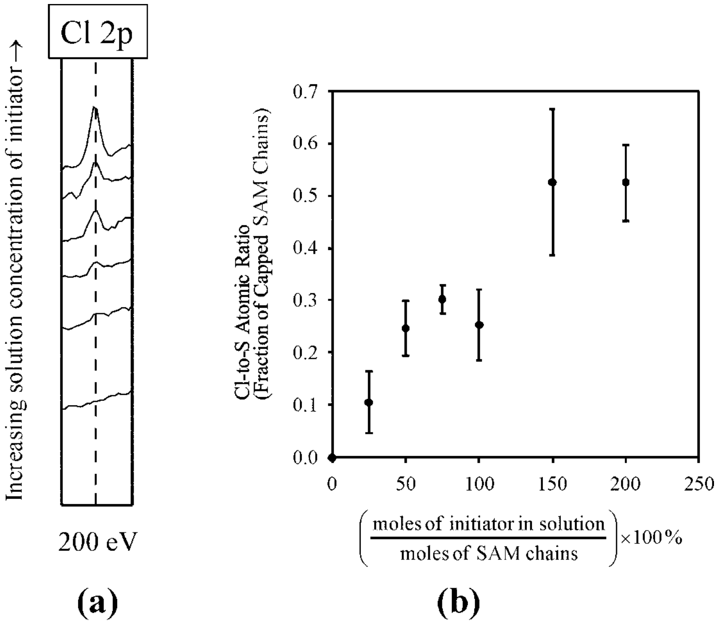

Figure 4. Qualitative (a) and quantitative (b) XPS data that show the relationship between solution and surface molar amounts of initiator, (4-chloromethyl)benzoyl chloride. Solution number of moles in (b) refers to initial moles prior to contact with SAM-terminated surfaces.

the ratio of Cl-to-S atomic concentration versus initial moles of initiator. This ratio is equivalent to the fraction of SAM chains that is capped with initiator. The error bars result from measurements made on at least two different samples. It appears, therefore, that areal density of growing chains can be manipulated easily via solution initiator concentration.

Surface-Confined Polymerization

Previous investigators[25,26] examined the solution polymerization of (meth)acrylamides with the catalyst system that we used. Because polymer molecular weight in solution polymerization is proportional to monomer concentration, the film thickness on the surface was expected also to be proportional to monomer concentration. Mathematically,

$$-\left(\frac{dC_m}{dt}\right) \propto \left(\frac{dT}{dt}\right) = k \cdot C_m^{\alpha} \cdot C_{chains}^{\beta}$$

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

Figures 5 and 6 show the growth rates for surface-polymerization of acrylamide using this catalyst system. Figure 6 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, confirming that the reaction is first-order in monomer concentration. The nonlinear growth at longer times has been described previously,[25–27] and is believed to result from catalyst deactivation[25,26] or bimolecular termination[27] for the system studied.

An important result is illustrated in Fig. 5; polymer layer thickness can be controlled with sub-nanometer precision by tuning the monomer and catalyst concentrations and the reaction time. Thus, we have illustrated a strategy for

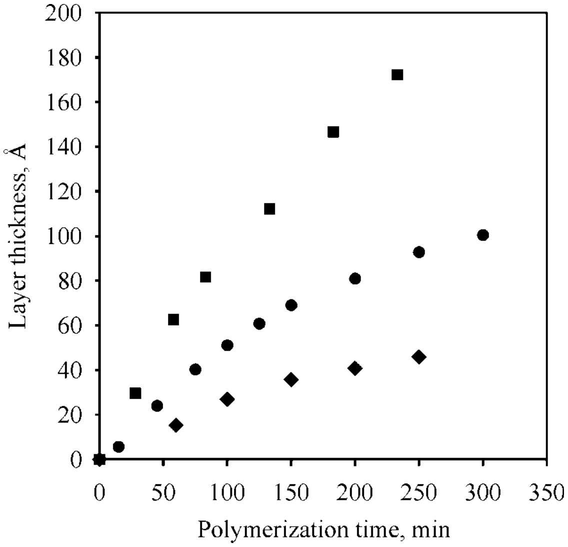

Figure 5. Growth of surface-confined poly(acrylamide) at 25°C on SAM surfaces functionalized with (4-chloromethyl)benzoyl chloride initiator. Cu(I)Cl/Me6TREN was used as catalyst. Acrylamide concentrations in solutions of THF were (◆) 0.05 M; (●) 0.10 M; (■) 0.20 M. Reproduced with permission from Ref.[27] Copyright 2002 Am. Chem. Soc.

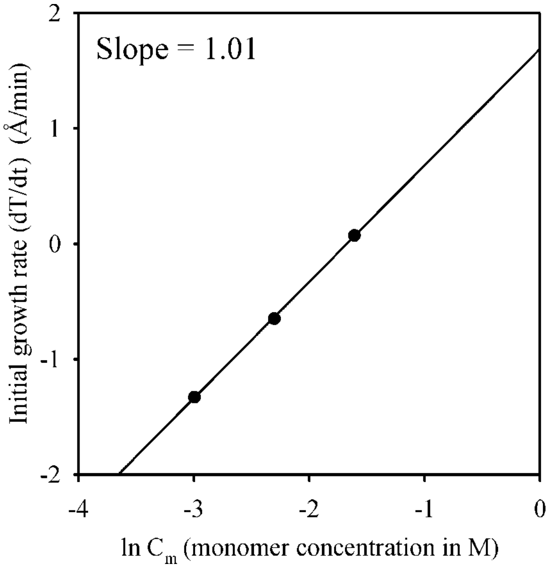

Figure 6. Elucidation of the rate order and apparent reaction rate constant for growth of surface-confined poly(acrylamide) at 25°C on SAM surfaces functionalized with (4-chloromethyl)benzoyl chloride initiator. Cu(I)Cl/Me6TREN was used as catalyst. Reproduced with permission from Ref.[27] Copyright © 2002 Am. Chem. Soc.

engineering surfaces to provide a well-defined foundation for growing ultrathin imprinted polymer films.

CONCLUSION

A molecule-by-molecule approach was described to engineer surfaces for selective separations. Surface modification by confined polymerization allowed for sub-nanometer precision control of film thickness, as measured by ellipsometry. Film growth was found to be first-order with respect to monomer concentration for acrylamide using $Me_6TREN \cdot CuCl(I)$ as catalyst at 25°C. This work represents a foundation for producing designer separation materials by surface imprinting. Work is under way in our laboratories to build these printed materials; it will be the focus of subsequent publications.

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