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Rapid Synthesis of Functional Polymer Brushes by Surface-Initiated Atom Transfer Radical Polymerization of an Acidic Monomer

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ABSTRACT: The combination of a highly reactive monomer, 2-(methacryloyloxy)ethyl succinate (MES), and active catalyst systems, e.g., Cu(I) complexed with 1,1,4,7,10,10-hexamethyltriethylenetetramine (HMTETA), allows rapid formation of poly(carboxylic acid) brushes by atom transfer radical polymerization (ATRP) from a surface. ATRP from initiators immobilized on Au-coated Si wafers yields films with an ellipsometric thickness of 120 nm in less than 15 min. To the best of our knowledge, this is the first example of direct ATRP of protonated acidic monomers that is capable of yielding such thick films, and MES polymerizes much more rapidly than methacrylic acid both in solution and on a surface. The MES films are attractive for a number of applications, including immobilization of proteins. Assuming that a lysozyme monolayer has a thickness of 2 nm, a 55 nm poly(MES) brush binds ~70 monolayers of lysozyme via ion-exchange interactions. Additionally, when derivatized with nitrilotriacetate−Cu^{2+} complexes, poly(MES) films bind ~34 monolayers of BSA through metal-ion affinity interactions (assuming a BSA monolayer thickness of 4 nm). These binding capacities are similar to those of poly(acrylic acid) brushes prepared by polymerization of *tert*-butyl acrylate and subsequent hydrolysis, but the poly(MES) synthesis is a one-step, aqueous process.

Introduction

Poly(carboxylic acid) brushes, commonly known as polyacids, are an important class of polymers with potential applications in cell adhesion and growth,[1,2] immobilization of biomacromolecules,[3−5] synthesis of shell-cross-linked micelles,[6,7] and entrapment of nanoparticles and catalysts.[8] Synthesis of polyacid brushes frequently includes surface-initiated anionic polymerization[9−13] or ATRP[14−18] of an ester-containing monomer and subsequent hydrolysis. For instance, Boyes et al. synthesized polyacid brushes through growth and hydrolysis of poly(*tert*-butyl acrylate) and poly(methacrylate) films.[16] Unfortunately, these strategies require multiple steps including harsh acidic conditions for deprotection. Techniques such as photopolymerization are capable of directly forming acrylic acid (AA)[19,20] and methacrylic acid (MAA) films;[21] however, the use of irradiation or high temperatures for initiation might be incompatible with opaque or temperature-sensitive substrates. Additionally, conventional free radical techniques lead to extensive polymerization in solution and require exhaustive rinsing to remove physisorbed polymers. The use of controlled polymerization methods can potentially overcome these limitations.[22,23] Among the strategies for controlled polymerization, ATRP is attractive due to its mild reaction conditions (room temperature in many cases), tolerance to impurities, and use of readily available catalysts, initiators, and monomers.[24−26] Perhaps most importantly, surface-initiated ATRP results in minimal solution polymerization and allows control over polymer thickness by variation of polymerization time. Thus, ATRP is attractive for creating films in complex geometries such as the pores of membranes and for tailoring film architectures to maximize protein adsorption.

This article describes the rapid synthesis of carboxylic acid-containing polymer brushes using surface-initiated ATRP of an acidic monomer, 2-(methacryloyloxy)ethyl succinate (MES). The combination of this monomer and highly active ATRP catalysts yields 120 nm thick films in less than 15 min. Several papers reported growth of polymer brushes via surface-initiated ATRP of acid monomers in aqueous solution, but most polymerization rates and/or thicknesses were low.[27−31] Using ATRP from immobilized initiators, Sankhe et al. polymerized itaconic acid (IA) and methacrylic acid (MAA) from Au, but film growth ceased after the formation of 10 nm thick coatings.[32] The addition of salt to polymerization solutions allowed more controlled growth of poly(IA) and poly(MAA) films, but the growth rates were only 0.2 and 1 nm/h, respectively.[33] Other groups used a similar strategy to grow ~40 nm thick poly(AA) brushes.[31,34] Tugulu and co-workers reported that direct, aqueous polymerization of sodium methacrylate from initiators on Si can yield 300 nm thick poly(MAA) in 3 h.[35] Using the same conditions, we tried growing poly(MAA) brushes from Au surfaces that were modified by immersion in a solution containing a disulfide initiator, $(BrC(CH_3)_2COO(CH_2)_{11}S)_2$. These polymerizations yielded inhomogeneous films that were visibly rough and not smooth enough for ellipsometric characterization. Similar results occurred on Si modified with initiators. In contrast, the polymerization of MES in its protonated form provides visibly homogeneous films, and ellipsometry of these films yields data that are characteristic of smooth coatings.

Polyacid films are attractive as protein binders[3,20,36−38] for applications such as protein purification by affinity adsorption,[36,39−41] immunoassays,[42] enzymatic reactions,[3] and analyses with antibody arrays.[43−46] In these applications, the formation of thick polymer brushes is vital for achieving high binding capacities. Here we show that a 55 nm thick poly(MES) film absorbs the equivalent of ~70 monolayers ($14.4 \pm 0.3\ \mu g/cm^2$) of lysozyme, and derivatization of poly(MES) with metal-ion complexes allows binding of large amounts of protein via metal-affinity interactions.

Experimental Section

Materials. Dimethylformamide (DMF, anhydrous, 99.8%), 11-mercaptoundecanol (97%), 2-bromoisobutyryl bromide (98%), CuBr (99.999%), $CuBr_2$ (99%), 2,2′-bipyridyl (bpy, 99%), 1,1,4,7,10,10-hexamethyltriethylenetetramine (HMTETA), 1,4,8,11-tetraaza-1,4,8,11-tetramethylcyclotetradecane (Me_4Cyclam), 4,4′-dinonyl-2,2′-bipyridyl (dnNbpy), 1-[3-(dimethylamino)propyl]-3-ethylcarbodiimide hydrochloride (EDC), *N*-hydroxysuccinimide (NHS),

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4-(bromomethyl)benzoic acid (97%), column packing for removing hydroquinone and monomethyl ether hydroquinone (cat. no. 311332), TWEEN-20 surfactant, bovine serum albumin (BSA), and lysozyme were used as received from Sigma-Aldrich. $CuSO_4 \cdot 5H_2O$ (CCI), NaOH (Spectrum), NaH_2PO_4 (CCI), Na_2HPO_4 (Aldrich), and N_α,N_α-bis(carboxymethyl)-L-lysine hydrate (aminobutyl NTA, Fluka) were also used without purification. 2-Hydroxyethyl methacrylate (HEMA, Aldrich, 97%, inhibited with 300 ppm hydroquinone monomethyl ether, MEHQ) was purified by passing it through a column of activated basic alumina (Aldrich). In most cases, 2-(methacryloyloxy)ethyl succinate (MES, Aldrich, inhibited with 750 ppm MEHQ), methacrylic acid (MAA, Aldrich, 99%, inhibited with 250 ppm MEHQ), and acrylic acid (AA, Aldrich, 99%, inhibited with 200 ppm MEHQ) were used as received, but where noted, the inhibitor was removed by passing the monomer through a column of inhibitor removal packing. The disulfide initiator, $(BrC(CH_3)_2COO(CH_2)_{11}S)_2$,[47] and tris[2-(dimethylamino)ethyl]amine (Me_6TREN)[48] were synthesized as described previously. Buffers were prepared using analytical grade chemicals and deionized water (Milli-Q, 18.2 MΩ cm).

Polymerization of 2-(Methacryloyloxy)ethyl Succinate (MES) on Au Substrates. Au-coated wafers (200 nm of sputtered Au on 20 nm of sputtered Cr on Si wafers) were cleaned with UV/ozone for 15 min, immersed in a 1 mM ethanolic solution of the disulfide initiator, $(BrC(CH_3)_2COO(CH_2)_{11}S)_2$, for 24 h, rinsed sequentially with ethanol and water, and dried under a stream of N_2. These initiator-modified substrates were then transferred to a N_2-filled glovebag where polymerization was carried out at ambient temperature.

To prepare most polymerization solutions, 10 mL of a mixture of neat monomer and 1 M aqueous NaOH (1:1, v/v) was first degassed with three freeze−pump−thaw cycles. A 1 mL solution of DMF containing CuBr, $CuBr_2$, and ligands was similarly degassed, and in a N_2-filled glovebag, this solution of catalyst was mixed with the monomer/NaOH solution. Finally, the initiator-coated substrate was immersed in the polymerization solution, and after the desired time, the coated wafers were removed from the glovebag, immediately sonicated in DMF for 10 min, rinsed sequentially with ethanol and water, and dried under a stream of N_2. Final concentrations of the different catalysts in the various polymerization solutions were CuBr (2 mM), $CuBr_2$ (1 mM), HMTETA (6 mM); CuBr (2 mM), $CuBr_2$ (1 mM), Me_4Cyclam (2 mM), dnNbpy (1 mM); and CuBr (2 mM), $CuBr_2$ (1 mM), Me_6TREN (6 mM).[14,49] In a few cases, we halved the concentrations of HMTETA and Me_6TREN ligands and achieved similar film thicknesses.[14,50] For the system containing bpy, the concentrations were CuBr (0.55 mM), $CuBr_2$ (0.16 mM), and bpy (1.56 mM). The use of a bpy system containing 6 mM bpy, 2 mM CuBr, and 1 mM $CuBr_2$ resulted in very thin (<25 nm) films after 2 h of polymerization. The pH of the polymerization solutions was ~5.0.

When examining polymerization rates as a function of the amount of NaOH added to the polymerization solution, the monomer and catalyst concentrations were kept constant. For these studies, neat monomer, aqueous solutions of 1 and 5 M NaOH, deionized water, and catalyst solution containing CuBr, $CuBr_2$, and HMTETA in DMF were degassed separately with three freeze−pump−thaw cycles and transferred to a N_2-filled glovebag. Solutions were prepared by mixing 5 mL of MES with varying amounts of NaOH solution and water in order to achieve the desired molar ratios of NaOH to MES. The total volume in each case was 10 mL. One milliliter of degassed catalyst solution was then mixed with the polymerization solution, and the initiator-coated films were immersed in this solution for 2 h. The polymer-coated wafers were removed from the glovebag, immediately sonicated in DMF for 10 min, rinsed sequentially with ethanol and water, and dried under a stream of N_2.

Derivatization of Carboxylic Acid Groups and Protein Immobilization. The carboxylic acid groups of poly(MES) were activated by immersing the films in a solution containing NHS (0.1 M) and EDC (0.1 M) in water for 30 min, and the films were rinsed sequentially with water and ethanol (20 mL each) and dried with N_2. The NHS-modified films were immersed for 1 h in an aqueous solution of aminobutyl NTA (0.1 M, pH 10.2), rinsed with 20 mL of water, and dried with N_2. Finally, the NTA−Cu^{2+} complex was formed by immersing the coated wafer in 50 mM $CuSO_4$ for 2 h, rinsing the substrate sequentially with water and ethanol (20 mL each), and drying with N_2. To immobilize BSA, the poly(MES)−NTA−Cu^{2+} films were immersed in a solution of 1.0 mg/mL BSA in 20 mM phosphate buffer (pH 7.2) (referred to as buffer from now on) for 18 h. The films were then rinsed with 20 mL of washing buffer (buffer containing 150 mM NaCl and 0.1% Tween-20, pH 7.2) followed by 20 mL of buffer and 20 mL of ethanol. Films were dried under a stream of N_2.

For lysozyme-binding studies, poly(MES) wafers were immersed in a 1 mg/mL solution of lysozyme in buffer for 3 h. The films were then rinsed with 20 mL of washing buffer followed by 20 mL of buffer and 20 mL of ethanol. Films were dried under a stream of N_2. Before characterizing the poly(MES)−NTA−Cu^{2+} and poly(MES)−NTA−Cu^{2+}−protein films by reflectance FTIR spectroscopy and ellipsometry, the films were immersed in buffer for 15 min followed by rinsing with 20 mL of ethanol and drying under a stream of N_2.

Quantification of Protein Binding. To quantify the amount of protein bound to poly(MES) brushes on Au-coated Si wafers, the method reported previously by Dai and co-workers was employed.[4] Briefly, a calibration curve was obtained by plotting the ellipsometric thickness of spin-coated BSA or lysozyme films against the reflectance FTIR absorbance of their amide I band. The amide absorbance of lysozyme or BSA adsorbed to poly(MES) or poly(MES)−NTA−Cu^{2+} films was then compared to the calibration curve to obtain the thickness added due to protein adsorption. These results were confirmed by ellipsometric studies.

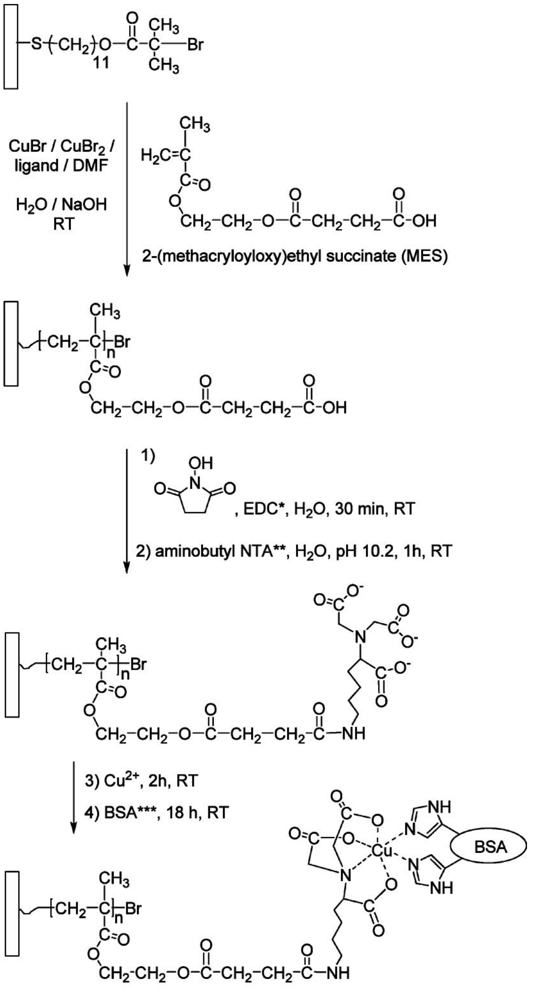
Kinetics of Solution Polymerization of MES, MAA, and HEMA. Solution polymerizations of MES and MAA were performed using 4-(bromomethyl)benzoic acid as the initiator.[30] For these studies, neat monomer (with or without inhibitor), 1 M aqueous NaOH, and catalyst solution in DMF were degassed separately using three freeze−pump−thaw cycles and transferred to a N_2-filled glovebag. Initiator (20 mM) was dissolved in 1 mL of 1 M NaOH. In another vial, neat monomer (5 mL) was mixed with 4 mL of 1 M NaOH, and 1 mL of degassed catalyst solution containing CuBr (2 mM), $CuBr_2$ (1 mM), and HMTETA (6 mM) in DMF was added. The initiator and monomer solutions were mixed together, and a 0.5 mL aliquot of this mixture was transferred to an NMR tube containing 50 μL of D_2O. (Before adding the polymerization solution, the NMR tube was purged with N_2 for 30 min and then kept in a N_2-filled glovebag for at least 3 h to remove oxygen.) The time difference between the start of polymerization and the start of NMR data acquisition was 8 min.

Instrumentation. ^1H NMR spectra were collected on a Varian Inova-300 spectrometer, and reflectance FTIR spectra of films on Au-coated wafers were obtained with a Nicolet Magna-IR 560 spectrophotometer containing a PIKE grazing angle (80°) accessory. A UV/ozone-cleaned Au-coated wafer was used to obtain a background spectrum. Film thicknesses were determined using a rotating analyzer ellipsometer (model M-44; J.A. Woollam) at an incident angle of 75°, assuming a film refractive index of 1.5. Ellipsometric measurements were performed on at least three spots on a film.

Results and Discussion

Kinetics of Surface-Initiated MES Polymerization. Scheme 1 outlines the synthesis of poly(MES) brushes on Au-coated Si wafers and the derivatization of these brushes with metal-ion complexes that bind proteins. The reflectance FTIR spectra in the Supporting Information are consistent with the synthetic scheme. We examined the kinetics of room temperature, surface-initiated MES polymerization using several catalyst systems (Figure 1). Usually, ATRP maintains a low concentration of active radicals to provide control over molecular mass and polydispersities, and the rate of ATRP is low. However, the use of HMTETA or Me_4Cyclam/dnNbpy as ligands for the Cu catalyst systems yields unusually rapid film growth and high

Scheme 1. Synthesis of Protein-Binding Poly(MES) Brushes on Au Surfaces



* 1-[3-(Dimethylamino)propyl]-3-ethylcarbodiimide hydrochloride

** *Nα, Nα–Bis*(carboxymethyl)-L-lysine Hydrate

*** Bovine Serum Albumin

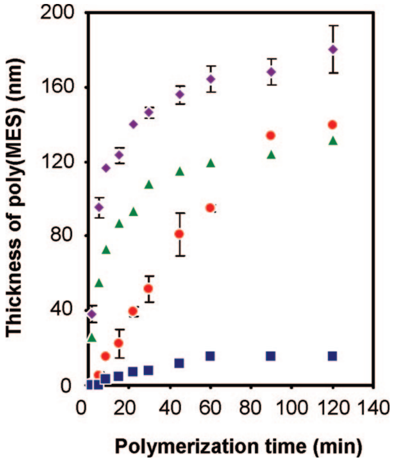


Figure 1. Evolution of ellipsometric thickness with time for surface-initiated polymerization of 2-(methacryloyloxy)ethyl succinate (MES) using 1,1,4,7,10,10-hexamethyltriethylenetetramine (HMTETA, purple diamonds), 1,4,8,11-tetraaza-1,4,8,11-tetramethylcyclotetradecane (Me_4Cy-clam)/4,4′-dinonyl-2,2′-bipyridyl (dnNbpy) (green triangles), tris[2-(dimethylamino)ethyl]amine (Me_6TREN, red circles), and 2,2′-bipyridyl (bpy, blue squares) catalyst systems. The room temperature, aqueous polymerizations occurred on Au-coated Si, and each point represents a different film. The purple diamonds and red circles show the average of three independent runs, and the error bars correspond to the standard deviation.

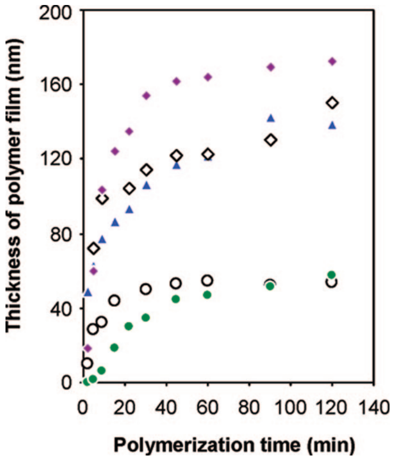


Figure 2. Evolution of ellipsometric film thickness with time for surface-initiated polymerization of (a) 2-(methacryloyloxy)ethyl succinate (MES) inhibited with 750 ppm of hydroquinone monomethyl ether (MEHQ) (purple diamonds), (b) MES without inhibitor (hollow diamonds), (c) 2-hydroxyethyl methacrylate (HEMA) without inhibitor (blue triangles), (d) methacrylic acid (MAA) inhibited with 250 ppm of MEHQ (green circles), and (e) MAA without inhibitor (hollow circles). Polymerizations were performed at room temperature on initiator-modified Au substrates in aqueous solutions using $CuBr/CuBr_2$/1,1,4,7,10,10-hexamethyltriethylenetetramine (HMTETA) as a catalyst. Each point represents a different film.

film thicknesses. The decline in film growth rate with time for these systems suggests a relatively high radical concentration that leads to rapid polymerization as well as some termination. Compared to HMTETA and $Me_4Cyclam$/dnNbpy catalyst systems, polymerizations using Me_6TREN as the Cu ligand were more controlled, as evidenced by a nearly linear increase in thickness with time for the first hour of polymerization. Even with the Me_6TREN catalyst system, however, the brush thickness was >120 nm after 90 min of polymerization. In contrast, polymerizations using bpy as the catalyst ligand yielded <25 nm thick poly(MES) films. As proposed by Matyjaszewski,[51] multidentate ligands like $Me_4Cyclam$, Me_6TREN, and HMTETA may complex the cupric species more efficiently than bpy, shifting the equilibrium toward the Cu(II) species and providing a higher radical concentration and faster polymerization than bpy−Cu catalysis. Previous studies demonstrated that $Me_4Cyclam$, Me_6TREN, and HMTETA Cu complexes are highly active catalysts for solution ATRP at ambient temperature;[52,53] however, Me_6TREN provides better control over polymerizations due to a higher deactivation rate.[51,53,54]

Comparison of ATRP of MES, MAA, and AA. To determine whether the high rates of film growth are partly due to the relatively high reactivity of MES, we grew films of poly(AA) and poly(MAA) using the $CuBr/CuBr_2$/HMTETA catalyst system. After 2 h of polymerization, poly(AA) and poly(MAA) brush thicknesses were <15 and 60 nm, respectively, while the poly(MES) thickness was >170 nm. Notably the rates of polymerization of MES and HEMA are similar (Figure 2), suggesting that the methacrylates have an inherently faster polymerization rate than methacrylic and acrylic acid. Unfortunately, methyl methacrylate and ethyl methacrylate are not soluble in water, so we could not investigate the polymerization of these monomers under similar conditions.

We should note that during most polymerizations of MES and MAA the inhibitor (MEHQ) was still present. As shown in Figure 2, the initial rate of MAA polymerization increased in

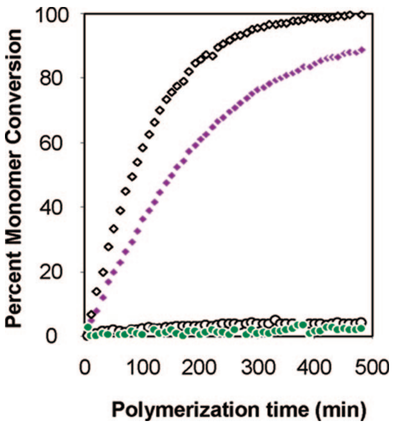


Figure 3. Percent monomer conversion as a function of time for solution polymerization of 2-(methacryloyloxy)ethyl succinate (MES) without inhibitor (hollow diamonds), MES inhibited with 750 ppm of hydroquinone monomethyl ether (MEHQ) (purple diamonds), methacrylic acid (MAA) without inhibitor (hollow circles), and (d) MAA inhibited with 250 ppm of MEHQ (green circles). Polymerizations were studied using NMR at room temperature.

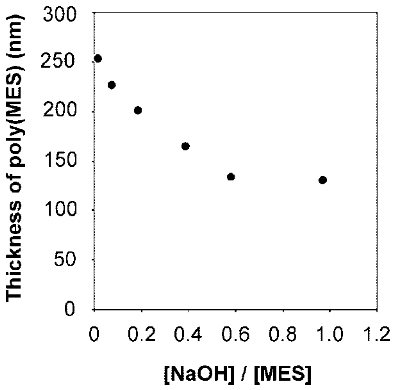


Figure 4. Thickness of poly(2-(methacryloyloxy)ethyl succinate) (poly(MES)) brushes as a function of the molar ratio of NaOH to MES added to the polymerization solution. The brushes were grown using a 2 h, room temperature polymerization with a CuBr/CuBr$_2$/1,1,4,7,10,10-hexamethyltriethylenetetramine (HMTETA) catalyst system.

the absence of inhibitor, but film growth stopped after 30 min so the overall MAA film thickness (<60 nm) was the same as that obtained in the presence of inhibitor. MES, on the other hand, gave films that were ~15% thicker when polymerized in the presence of inhibitor. Lower initial radical concentrations in the presence of inhibitor could lead to less termination and thicker films with MES. In any case, in the presence or absence of inhibitor, poly(MES) films are much thicker than poly(MAA) films.

To test whether the observed kinetic behavior during film growth is specific to surface-initiated polymerization, we examined solution-phase ATRP of MES and MAA under similar conditions. Figure 3 shows that in both the presence and absence of inhibitor MES polymerizes much more rapidly than MAA. Polymerization of inhibitor-free MAA resulted in only 4.2% conversion to poly(MAA) (Figure 3, hollow circles), and no detectable MAA polymerization occurred in the presence of inhibitor (Figure 3, green circles). In contrast, polymerization of inhibitor-free MES reached >99.5% conversion in about 7 h. Thus, the faster growth of poly(MES) than poly(MAA) from surfaces is likely a direct result of the different reactivities of the two monomers.

Interestingly, unlike polymerization from a surface, the solution phase polymerization of MES is faster without inhibitor. This difference between solution and surface polymerization of MES presumably occurs because there are many more initiators in solution than on the substrate, so termination by radical recombination is less important in solution.[26] Additionally, radicals are likely in closer proximity on the surface than in solution. The Supporting Information contains NMR spectra of the polymerization solutions.

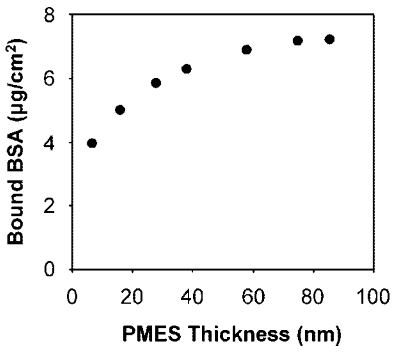


Figure 5. Bovine serum albumin (BSA) binding capacity as a function of poly(2-(methacryloyloxy)ethyl succinate) (poly(MES)) film thickness. The poly(MES) films were derivatized with NTA−Cu^{2+} complexes, and the amount of bound BSA was determined using reflectance FTIR spectroscopy.

Effect of NaOH on MES Polymerization. We also examined film growth as a function of the amount of NaOH added to the polymerization solution. Figure 4 shows that film thicknesses are highest when most of the MES in solution is in the protonated form (little NaOH is added), but even with a 1:1 ratio of NaOH to MES, films with thicknesses >100 nm can form. Thus, both protonated and deprotonated MES can polymerize, but the protonated form polymerizes faster. This is in agreement with some previous reports that showed that the rate of polymerization of acidic monomers decreases with increasing pH.[55,56] The decrease in rate at high pH presumably occurs because the electrostatic repulsion between growing chains and deprotonated monomers decreases the rate at which monomers can reach confined radicals.

At NaOH to MES ratios <0.08, the polymerization solution is turbid, and when no NaOH is added, the solution consists of two phases, the denser of which contains MES and most of the catalyst, as discerned by its blue color. Even two-phase polymerizations, when no NaOH is added to the reaction mixture, give film thicknesses similar to those obtained when adding small amounts of NaOH to the solution. (The substrate sits in the MES-rich phase during polymerization.) However, some water in the MES phase is necessary for rapid brush growth,[57] as polymerization from a solution containing only monomer and catalyst gives film thicknesses of 25 nm after 2 h of polymerization.

Protein Binding to Poly(MES) Brushes and Their Derivatives. To demonstrate the utility of poly(MES) brushes, we examined their ability to bind proteins. Initially, we immersed poly(MES) films on Au-coated Si in 1 mg/mL solutions of lysozyme in 20 mM phosphate buffer (pH 7.2) for 3 h. After removal of the film from solution and rinsing, reflectance FTIR spectroscopy allowed determination of the amount of bound lysozyme using a procedure we developed previously (see Supporting Information).[4] Remarkably, a 55 nm poly(MES) film binds 14.4 ± 0.3 μg lysozyme/cm^2, which is equivalent to ~70 monolayers of lysozyme in the brushes (assuming a monolayer thickness of 2 nm).[58] Ellipsometric measurements also show that the film thickness increases from 55 to 205 nm after lysozyme adsorption. This binding capacity is higher than the 38 monolayers of lysozyme reported to bind to sulfonated poly(glycidyl methacrylate) coatings[36] and is comparable to the

~80 lysozyme monolayers found to bind to poly(AA) brushes prepared by hydrolysis of poly(*tert*-butyl acrylate).[4]

Building on these promising results, we investigated the adsorption of BSA in poly(MES) brushes modified with NTA−Cu^{2+} complexes (Scheme 1). This adsorption occurs through a metal-affinity interaction between BSA and the Cu(II) complex. We immersed poly(MES)−NTA−Cu^{2+} films overnight in a solution containing 1 mg/mL BSA and then thoroughly rinsed these films with buffers and solvent. As seen in Figure 5, 55 and 85 nm poly(MES) films derivatized with NTA−Cu^{2+} had BSA binding capacities of 6.8 and 7.2 μg/cm^2, respectively, which is equivalent to 34 and 36 monolayers of BSA in poly(MES) brushes (assuming a monolayer thickness of 4 nm).[59] These high binding capacities and the fact that BSA binding initially increases with brush thickness suggest that binding occurs both at the film−solution interface and inside the brushes. However, steric hindrance to binding may result in the plateau in adsorption capacity at thicknesses >60 nm (Figure 5). The poly(MES) binding capacity is similar to that reported previously for poly(AA), but the poly(MES) can be synthesized in a rapid, one-step procedure.

Conclusions

Surface-initiated aqueous ATRP enables rapid growth of poly(MES) brushes under gentle conditions that should allow formation of films on a wide range of substrates. Both on a surface and in solution, polymerization of MES occurs much faster than polymerization of MAA, presumably because methacrylates are more reactive than MAA or AA. HEMA, another water-soluble methacrylate, shows brush growth rates similar to those of MES. Poly(MES) brushes and their derivatives are capable of binding many monolayers of BSA as well as lysozyme, and we are currently investigating the growth of poly(MES) brushes inside membranes to form protein absorbers.

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Supporting Information Available: Reflectance FTIR spectra of poly(MES) brushes on Au-coated Si wafers before and after the derivatization steps; ^{1}H NMR spectra before and after 8 h of solution polymerization of MES and MAA; reflectance FTIR spectra of lysozyme binding to poly(MES) films. This material is available free of charge via the Internet at http:/pubs.acs.org.

References and Notes

(1) Singh, N.; Cui, X.; Boland, T.; Husson, S. M. *Biomaterials* **2006**, *28*, 763–771.
(2) Ghosh, P.; Amirpour, M. L.; Lackowski, W. M.; Pishko, M. V.; Crooks, R. M. *Angew. Chem., Int. Ed.* **1999**, *38*, 1592–1595.
(3) Cullen, S. P.; Liu, X.; Mandel, I. C.; Himpsel, F. J.; Gopalan, P. *Langmuir* **2008**, *24*, 913–920.
(4) Dai, J.; Bao, Z.; Sun, L.; Hong, S. U.; Baker, G. L.; Bruening, M. L. *Langmuir* **2006**, *22*, 4274–4281.
(5) Tsarevsky, N. V.; Braunecker, W. A.; Vacca, A.; Gans, P.; Matyjaszewski, K. *Macromol. Symp.* **2007**, *248*, 60–70.
(6) Buetuen, V.; Lowe, A. B.; Billingham, N. C.; Armes, S. P. *J. Am. Chem. Soc.* **1999**, *121*, 4288–4289.
(7) Zhang, Q.; Remsen, E. E.; Wooley, K. L. *J. Am. Chem. Soc.* **2000**, *122*, 3642–3651.
(8) Xu, J.; Bhattacharyya, D. *Ind. Eng. Chem. Res.* **2007**, *46*, 2348–2359.
(9) Balastre, M.; Li, F.; Schorr, P.; Yang, J. C.; Mays, J. W.; Tirrell, M. V. *Macromolecules* **2002**, *35*, 9480–9486.
(10) Mykytiuk, J.; Armes, S. P.; Billingham, N. C. *Polym. Bull.* **1992**, *29*, 139–145.
(11) Zhang, H.; Rühe, J. *Macromol. Rapid Commun.* **2003**, *24*, 576–579.
(12) Haddleton, D. M.; Crossman, M. C.; Dana, B. H.; Duncalf, D. J.; Heming, A. M.; Kukulj, D.; Shooter, A. J. *Macromolecules* **1999**, *32*, 2110–2119.
(13) Rannard, S. P.; Billingham, N. C.; Armes, S. P.; Mykytiuk, J. *Eur. Polym. J.* **1993**, *29*, 407–414.
(14) Bao, Z.; Bruening, M. L.; Baker, G. L. *J. Am. Chem. Soc.* **2006**, *128*, 9056–9060.
(15) Matyjaszewski, K.; Miller, P. J.; Shukla, N.; Immaraporn, B.; Gelman, A.; Luokala, B. B.; Siclovan, T. M.; Kickelbick, G.; Vallant, T.; Hoffmann, H.; Pakula, T. *Macromolecules* **1999**, *32*, 8716–8724.
(16) Boyes, S. G.; Akgun, B.; Brittain, W. J.; Foster, M. D. *Macromolecules* **2003**, *36*, 9539–9548.
(17) Treat, N. D.; Ayres, N.; Boyes, S. G.; Brittain, W. J. *Macromolecules* **2006**, *39*, 26–29.
(18) Biesalski, M.; Rühe, J. *Macromolecules* **2003**, *36*, 1222–1227.
(19) Hu, S.; Ren, X.; Bachman, M.; Sims, C. E.; Li, G. P.; Allbritton, N. L. *Anal. Chem.* **2004**, *76*, 1865–1870.
(20) Ulbricht, M.; Yang, H. *Chem. Mater.* **2005**, *17*, 2622–2631.
(21) Rahane, S. B.; Floyd, J. A.; Metters, A. T.; Kilbey, S. M., II. *Adv. Funct. Mater.* **2008**, *18*, 1232–1240.
(22) Matyjaszewski, K. *ACS Symp. Ser.* **1998**, *685*, 2–30.
(23) Matyjaszewski, K. *ACS Symp. Ser.* **2000**, *768*, 2–26.
(24) Chung, I.-D.; Britt, P.; Xie, D.; Harth, E.; Mays, J. *Chem. Commun.* **2005**, 1046–1048.
(25) Tsarevsky, N. V.; Pintauer, T.; Matyjaszewski, K. *Macromolecules* **2004**, *37*, 9768–9778.
(26) Kim, J.-B.; Huang, W.; Miller, M. D.; Baker, G. L.; Bruening, M. L. *J. Polym. Sci., Part A: Polym. Chem.* **2003**, *41*, 386–394.
(27) Keoshkerian, B.; Georges, M. K.; Boils-Boissier, D. *Macromolecules* **1995**, *28*, 6381–6382.
(28) Vo, C.-D.; Iddon, P. D.; Armes, S. P. *Polymer* **2007**, *48*, 1193–1202.
(29) Ashford, E. J.; Naldi, V.; O'Dell, R.; Billingham, N. C.; Armes, S. P. *Chem. Commun.* **1999**, 1285–1286.
(30) Wang, X. S.; Jackson, R. A.; Armes, S. P. *Macromolecules* **2000**, *33*, 255–257.
(31) Singh, N.; Wang, J.; Ulbricht, M.; Wickramasinghe, S. R.; Husson, S. M. *J. Membr. Sci.* **2008**, *309*, 64–72.
(32) Sankhe, A. Y.; Husson, S. M.; Kilbey, S. M., II. *Macromolecules* **2006**, *39*, 1376–1383.
(33) Sankhe, A. Y.; Husson, S. M.; Kilbey, S. M., II. *J. Polym. Sci., Part A: Polym. Chem.* **2007**, *45*, 566–575.
(34) Dong, R.; Krishnan, S.; Baird, B. A.; Lindau, M.; Ober, C. K. *Biomacromolecules* **2007**, *8*, 3082–3092.
(35) Tugulu, S.; Barbey, R.; Harms, M.; Fricke, M.; Volkmer, D.; Rossi, A.; Klok, H.-A. *Macromolecules* **2007**, *40*, 168–177.
(36) Kawai, T.; Saito, K.; Lee, W. *J. Chromatogr. B* **2003**, *790*, 131–142.
(37) Singh, N.; Husson, S. M.; Zdyrko, B.; Luzinov, I. *J. Membr. Sci.* **2005**, *262*, 81–90.
(38) Kurosawa, S.; Aizawa, H.; Talib, Z. A.; Atthoff, B.; Hilborn, J. *Biosens. Bioelectron.* **2004**, *20*, 1165–1176.
(39) Jain, P.; Sun, L.; Dai, J. H.; Baker, G. L.; Bruening, M. L. *Biomacromolecules* **2007**, *8*, 3102–3107.
(40) Roper, D. K.; Lightfoot, E. N. *J. Chromatogr. A* **1995**, *702*, 3–26.
(41) Lee, W. C.; Lee, K. H. *Anal. Biochem.* **2004**, *324*, 1–10.
(42) Arenkov, P.; Kukhtin, A.; Gemmell, A.; Voloshchuk, S.; Chupeeva, V.; Mirzabekov, A. *Anal. Biochem.* **2000**, *278*, 123–131.
(43) MacBeath, G.; Schreiber, S. L. *Science* **2000**, *289*, 1760–1763.
(44) Phizicky, E.; Bastiaens, P. I. H.; Zhu, H.; Snyder, M.; Fields, S. *Nature (London)* **2003**, *422*, 208–215.
(45) Zhu, H.; Bilgin, M.; Bangham, R.; Hall, D.; Casamayor, A.; Bertone, P.; Lan, N.; Jansen, R.; Bidlingmaier, S.; Houfek, T.; Mitchell, T.; Miller, P.; Dean, R. A.; Gerstein, M.; Snyder, M. *Science* **2001**, *293*, 2101–2105.
(46) Dai, J. H.; Baker, G. L.; Bruening, M. L. *Anal. Chem.* **2006**, *78*, 135–140.
(47) Shah, R. R.; Merreceyes, D.; Husemann, M.; Rees, I.; Abbott, N. L.; Hawker, C. J.; Hedrick, J. L. *Macromolecules* **2000**, *33*, 597–605.
(48) Ciampoli., M.; Nardi, N. *Inorg. Chem.* **1966**, *5*, 1150.
(49) Huang, W. X.; Kim, J. B.; Bruening, M. L.; Baker, G. L. *Macromolecules* **2002**, *35*, 1175–1179.
(50) Zheng, Y. Ph.D. Dissertation, Michigan State University, **2007**.
(51) Matyjaszewski, K. *Curr. Org. Chem.* **2002**, *6*, 67–82.
(52) Pintauer, T.; Matyjaszewski, K. *Coord. Chem. Rev.* **2005**, *249*, 1155–1184.
(53) Tsarevsky, N. V.; Matyjaszewski, K. *J. Polym. Sci., Polym. Chem.* **2006**, *44*, 5098–5112.
(54) Xia, J. H.; Gaynor, S. G.; Matyjaszewski, K. *Macromolecules* **1998**, *31*, 5958–5959.
(55) Niwa, M.; Date, M.; Higashi, N. *Macromolecules* **1996**, *29*, 3681–3685.
(56) Matyjaszewski, K.; Xia, J. H. *Chem. Rev.* **2001**, *101*, 2921–2990.
(57) Wang, X.-S.; Lascelles, S. F.; Jackson, R. A.; Armes, S. P. *Chem. Commun.* **1999**, 1817–1818.
(58) Tsuneda, S.; Shinano, H.; Saito, K.; Furusaki, S.; Sugo, T. *Biotechnol. Prog.* **1994**, *10*, 76–813.
(59) Carter, D. C.; He, X. M.; Munson, S. H.; Twigg, P. D.; Gernert, K. M.; Broom, M. B.; Miller, T. Y. *Science* **1989**, *244*, 1195–1198.

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