Functionalization of Surfaces by Water-Accelerated Atom-Transfer Radical Polymerization of Hydroxyethyl Methacrylate and Subsequent Derivatization

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ABSTRACT: We report the synthesis of unusually thick poly(2-hydroxyethyl methacrylate) (PHEMA) films on gold surfaces by surface-initiated atom transfer radical polymerization (ATRP). Polymerization from the surface occurs rapidly at room temperature in aqueous media, resulting in the formation of 700 nm thick polymer films in just 12 h. Control experiments using neat monomer and catalyst (no water) yield films with thicknesses of only 6 nm, demonstrating the accelerating effect of water on surface-initiated ATRP. Kinetic studies reveal a nearly linear increase in thickness with reaction time, indicating that chain growth from the surface is a controlled process with some "living" character. A second block can be grown from dormant initiators at the end of PHEMA chains, providing further evidence of "living" chain ends. Derivatization of the hydroxyl groups of grafted PHEMA with a variety of molecules allows dense functionalization of these films. Reflectance FTIR spectroscopy shows a virtually quantitative yield in derivatization reactions, and the increase in film thickness after surface derivatization correlates with the molecular mass of the newly formed repeat unit.

Introduction

Covalent attachment of polymer chains to solid substrates is an attractive method for tailoring interfacial properties and functionalizing surfaces.[1−3] The most common method for forming functional surfaces employs self-assembled monolayers (SAMs) terminated with a functional group amenable to subsequent derivatization.[4] While SAMs afford a high degree of molecular control over surface composition and architecture, they can only provide a limited density of functional groups on a substrate. To overcome this problem, several research groups developed grafting chemistry to attach polymeric films to surfaces and increase the areal density of functional groups. Bergbreiter and co-workers grafted hyperbranched poly(acrylic acid) (PAA) onto surfaces.[5,6] The layer-by-layer procedure allowed control over film thickness, and the carboxylic acid groups afforded facile derivatization. Ringsdorf and co-workers immobilized polymer chains on amino-silanized glass and utilized unreacted functional groups in the grafted polymer layers to build up polymer multilayers and to introduce different functionalities.[7] Löfås et al. coated gold surfaces with an active hydrogel matrix that then allowed further modification of the surface.[8]

Surface-initiated "living" polymerization techniques present new synthetic routes to dense, functional films. Polymerization from a surface is generally the preferred technique for preparing polymer brushes, as it leads to well-defined surfaces with higher grafting densities than can be obtained by chemical grafting of end-functionalized polymer chains onto a substrate.[9] Numerous recent reports describe the use of controlled polymerization techniques to grow polymer chains from surfaces in a well-defined manner.[10−27] Atom-transfer radical polymerization (ATRP) is especially useful because it is compatible with a variety of functionalized monomers that usually cannot undergo living ionic polymerization. The living/controlled character of the ATRP process results in polymers with relatively low polydispersity indices (PDI = M_w/M_n) and permits the preparation of block copolymers by activation of dormant chain ends in the presence of a second monomer. One drawback of ATRP is that control over the polymerization is gained at the cost of a decreased polymerization rate, and thus surface-initiated ATRP systems often provide films less than 100 nm thick, even for long reaction times and high polymerization temperatures.[28]

Several applications could benefit from the availability of thick (∼1 μm) polymer brushes, especially brushes that can be easily derivatized. Biologically active molecules tethered to brushes might serve as reservoirs that would provide near-constant concentrations of therapeutic agents in time-release applications. As the dimensions of microfluidic devices shrink, thick polymer brushes are likely to enable chromatographic separations of neutral molecules to augment the current electrophoretic schemes. Thick polymer brushes may also serve as films that enhance the selectivity of membranes and sensors.

Armes recently reported that ATRP of hydrophilic monomers can be greatly accelerated in aqueous media.[29,30] In this report, we extend the Armes method to grow thick (approaching 1 μm) films of poly(2-hydroxyethyl methacrylate) (PHEMA) from gold in just 12 h at room temperature.[31] Furthermore, we demonstrate the versatility of grafted PHEMA for surface functionalization by incorporating a variety of functional units into PHEMA in high yield via simple chemical reactions.

Experimental Section

Materials. CuCl (99.999%), CuBr (99.999%), $CuBr_2$ (99%), 2,2′-bipyridine (bpy, 99%), 1,1,4,7,10,10-hexamethyltriethylenetetramine (HMTETA, 97%), acetyl chloride (99+%), cinnamoyl chloride (98%), 1,1′-carbonyldiimidazole (CDI, 98%), and *N*,*N*-dimethylethylenediamine (DMEDA, 95%) were used as received from Aldrich. Dimethylformamide (DMF, anhy-

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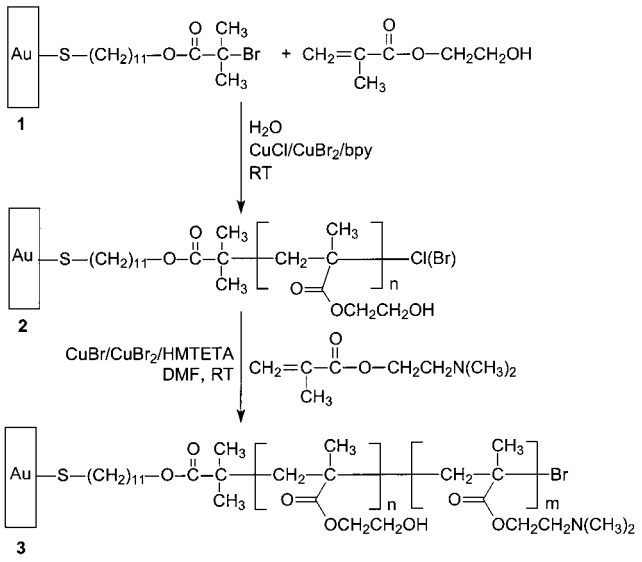
Scheme 1



drous, Aldrich, 99.8%) and Milli-Q water (18 MΩ cm) were used as solvents for polymerizations. Gold-coated wafers (electron beam evaporation of 200 nm of gold on 20 nm of Ti on Si(100) wafers or sputter coating of 200 nm of gold on 20 nm of Cr on Si(100) wafers) were cleaned in a UV/O_3 chamber for 15 min just before use. 2-Hydroxyethyl methacrylate (HEMA, Aldrich, 98%) was purified by washing an aqueous solution of 25 vol % monomer with hexanes (8 × 200 mL), salting the monomer out of the aqueous phase by addition of NaCl, drying over $MgSO_4$, passing through a column of basic alumina, and distilling under reduced pressure. 2-(Dimethylamino)ethyl methacrylate (DMAEMA, Aldrich, 98%) was purified by passing through a column of basic alumina and distilling over CaH_2 under reduced pressure just before polymerization.

The disulfide initiator, $(BrC(CH_3)_2COO(CH_2)_{11}S)_2$, was synthesized according to a literature procedure.[22] To form monolayers of this initiator, clean gold slides were immersed in a 1 mM ethanolic solution of the disulfide initiator for 24 h. Slides were then rinsed with ethanol and dried with nitrogen. The initiator packing density is about 0.21 nm^2/per molecule.[4]

Polymerizations. Most polymerizations of HEMA and all polymerizations of DMAEMA were performed in a glovebox. Polymerizations of HEMA also were run outside of the glovebox using a procedure described previously.[32] Monomers and solvents were degassed through three freeze−pump−thaw cycles before being introduced into the glovebox. For homopolymerization of HEMA from a surface, 55 mg (0.55 mmol) of CuCl, 36 mg (0.16 mmol) of $CuBr_2$, and 244 mg (1.56 mmol) of bpy were added to 8 mL of an aqueous solution of monomer (HEMA/H_2O, 1:1 v:v), and the mixture was stirred until a homogeneous dark brown solution formed. The solution was then transferred into a vial containing substrate **1** (Scheme 1), and the vial was covered with a rubber septum and kept at room temperature for polymerization. After polymerization for times ranging from 30 min to 12 h, the substrates were removed from the vial and rinsed with Milli-Q water and then sonicated in DMF and dried under a flow of nitrogen. To prepare PHEMA-coated substrates for use as macroinitiators for the block copolymerizations, the polymerizations were quenched by injection of 2.5 mL of an aqueous solution containing $CuBr_2$ and bpy (1:2, molar ratio, 0.05 M $CuBr_2$) into the vial to ensure a high retention of the end group functionality of the polymer chains. For room-temperature polymerization of DMAEMA, substrate **1** or PHEMA-coated substrates were added to 8 mL of a monomer/DMF solution (DMAEMA/DMF, 1:1 v:v) containing 50 mg (0.35 mmol) of CuBr, 8 mg (0.03 mmol) of $CuBr_2$, and 88 mg (0.38 mmol) of HMTETA. After 4 h of polymerization, the substrates were cleaned with DMF and dried with a flow of nitrogen.

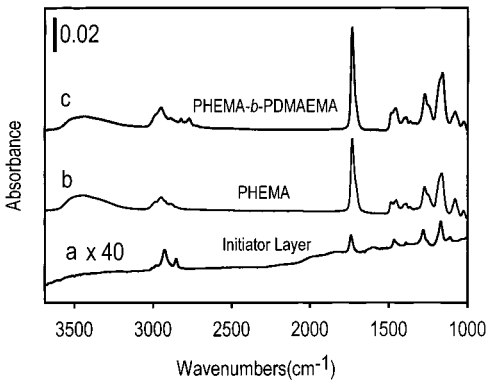


Figure 1. Reflectance FTIR spectra of (a) an initiator monolayer, (b) a grafted PHEMA layer (39 nm), and (c) a grafted PHEMA-*b*-PDMAEMA layer (39 nm for PHEMA, 40 nm for PDMAEMA).

To detach PHEMA films from substrates, we either immersed the films into a 2 mM solution of I_2 in anhydrous DMF for 8 h and subsequently sonicated for 5 min[23] or subjected the coated gold slides to a potential scan between −1.0 and 1.0 V (0.1 M tetraethylammonium chloride in DMF, Ag/AgCl reference electrode) for 10 cycles at a scan rate of 50 mV/s. After the electrochemical cycling, the slides were rinsed with ethanol, and the films were removed by sonication in DMF for 20 min.

Derivatization of PHEMA films. To acylate PHEMA films, the coated substrate was immersed in 10 mL of a DMF solution containing the appropriate acid chloride (0.08 M) and pyridine (0.1 M). After a 20 min immersion for acetyl chloride or a 3 h immersion for cinnamoyl chloride, the films were removed from the solution, rinsed with DMF and then ethanol, and dried with a flow of nitrogen. To couple CDI to PHEMA, the film was immersed into a 0.2 M solution of CDI in DMF for 12 h. Coupling of DMEDA to CDI-functionalized PHEMA films was achieved by immersing the coated substrate into a 0.2 M solution of DMEDA in a 1:1 mixture (v:v) of DMF and H_2O for 4 h. The substrates were then cleaned with DMF and dried under a nitrogen flow.

Characterization Methods. Ellipsometric measurements were obtained with a rotating analyzer ellipsometer (model M-44; J.A. Woollam) using WVASE32 software at an incident angle of 75°. The refractive index of the films at all wavelengths was assumed to be 1.5. Thickness measurements were taken on at least three spots on each substrate. Reflectance FTIR spectroscopy was performed using a Nicolet Magna-IR 560 spectrometer containing a PIKE grazing angle (80°) attachment. The spectra were typically collected with 256 scans using a MCT detector. NMR spectra were collected in $CDCl_3$ on a Varian Gemini-300 spectrometer. The chemical shifts were calibrated using residual $CHCl_3$ and are reported relative to tetramethylsilane. Atomic force microscopy (AFM) images were obtained in the tapping mode with a Nanoscope IIIa instrument (Digital Instruments). A cantilever having a nominal spring constant of 20−100 N/m was used along with etched silicon tips. The tips have a nominal radius of curvature of 20−60 nm.

Results and Discussion

Surface-Initiated Polymerization. Scheme 1 outlines the synthetic pathway for the preparation of PHEMA and PHEMA-*block*-poly(DMAEMA) (PHEMA-*b*-PDMAEMA) films from gold surfaces. Immersion of gold-coated wafers in a 1 mM solution of $(BrC(CH_3)_2COO(CH_2)_{10}S)_2$ in ethanol for 24 h leads to the formation of a monolayer film **1**, with an ellipsometric thickness of 1.7 ± 0.1 nm.[22] Reflectance FTIR spectra show the appearance of a carbonyl peak at 1739 cm^{-1} (Figure 1, spectrum a), confirming the attachment of the initiator layer. Immersion of substrate **1** in an aqueous solution

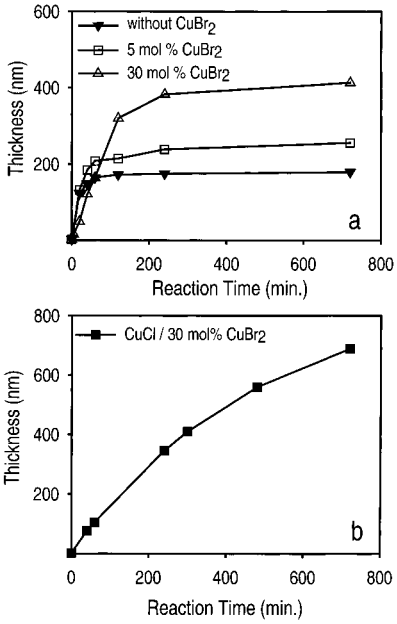


Figure 2. Dependence of PHEMA film thickness on polymerization time for water accelerated room temperature ATRP (a) using varying concentrations of $CuBr_2$ combined with CuBr/bpy and (b) using a mixed halide catalyst system ($CuCl:CuBr_2$:bpy = 1:0.3:2.9, molar ratio). The mol % of $CuBr_2$ is given with respect to Cu(I) species. The molar ratio of HEMA to Cu(I) was fixed at 56:1 in all the polymerizations. Each data point represents a measurement on a different substrate. The lines in the plot simply connect points.

of HEMA containing the CuBr/bpy catalyst initiates the polymerization.

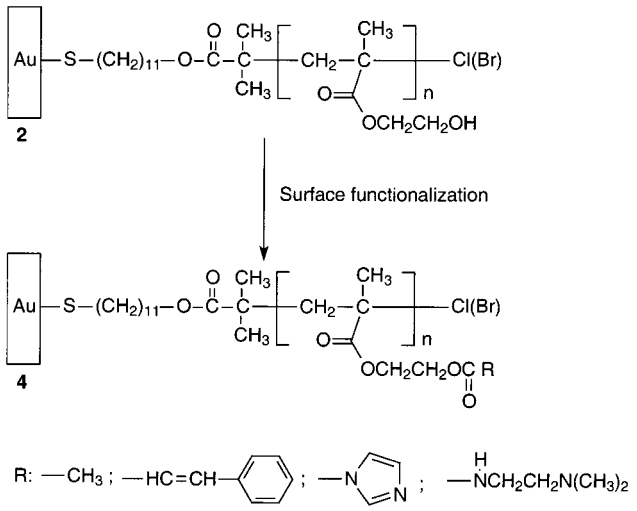
A high concentration of a deactivating Cu(II) complex is necessary for control of ATRP.[21] In solution ATRP, the reaction of Cu(I) with initiator produces the corresponding Cu(II) complex, but for ATRP from a surface, the small amount of initiator tethered to the substrate provides too low a concentration of Cu(II) to control the polymerization. One solution to this problem is to add free initiator to the solution,[16,19,20,22] but this strategy failed for polymerization of HEMA from substrates. When we added ethyl 2-bromoisobutyrate (0.02 M) as a free initiator, polymerization of HEMA in solution resulted in gelation of the mixture in 8 min. After sonicating the substrate in fresh DMF, ellipsometric measurements showed that only 5 nm of PHEMA was on the surface. To ensure a sufficient concentration of deactivating Cu(II) species while limiting initiation of polymerization to the surface, we added $CuBr_2$ to the solution.[21] During these polymerizations, the solution remained fluid and homogeneous in appearance. After polymerization, the substrate was rinsed with DMF and dried under a flow of nitrogen. A broad hydroxyl peak at 3500−3300 cm^{-1} and a large increase in the carbonyl peak at 1734 cm^{-1} in the reflectance FTIR spectra of these films reflect the formation of a PHEMA layer (Figure 1, spectrum b). Ellipsometric measurements show large increases in film thickness after growth of the polymer layer (vide infra).

Initial experiments using a $CuBr/CuBr_2$ catalyst system for polymerization from a surface did not afford a controlled process, as evidenced by initial rapid growth of the polymer film followed by a large decrease in this rate. Figure 2a shows plots of film thickness as a function of reaction time for various $CuBr/CuBr_2$ molar ratios. We varied the concentration of added $CuBr_2$ in an attempt to regulate the polymerization process because the concentration of the deactivating Cu(II) species affects both the rate of polymerization and the "living" character of ATRP. Without added $CuBr_2$, the film thickness increased rapidly at the beginning of the reaction but leveled off after 1 h, reflecting a mechanism similar to conventional redox-initiated polymerizations. With 5 mol % $CuBr_2$ (relative to CuBr), we observed similar results but with a higher limiting film thickness. Adding 30 mol % $CuBr_2$ to the solution resulted in a decrease in the initial rate of the polymerization but also yielded a substantial increase in film thickness. The thickness vs time plot for this polymerization still plateaus, indicating that the concentration of the propagating species decreases as the film grows. The most likely cause of this is the loss of terminal C−Br bonds, presumably through radical coupling and disproportionation reactions.[33]

Matyjaszewski and co-workers reported that mixed halide initiation systems provide better control of ATRP because C−Cl bonds are more stable than C−Br bonds.[33] When we changed the catalyst system to CuCl/30 mol % $CuBr_2$, we observed a more linear increase in thickness with reaction time (Figure 2b), indicating better control over polymer growth and some degree of "living" character at early stages of polymerization. This aqueous ATRP system enables controlled growth of polymer films as thick as 700 nm in a 12 h period and was used for all subsequent experiments. We stopped polymerization at 12 h, as longer reaction times generally resulted in a viscous solution, which suggests chain transfer from surface propagating sites to solution. To our knowledge, this is the thickest polymer film synthesized by surface-initiated ATRP. Another important aspect of the polymerization is that while HEMA is water-soluble, the polymer is not. Nevertheless, the polymerization of HEMA is a controlled process in aqueous media, indicating that solubility of the grafted polymer in the reaction medium is not a requirement for control over polymerization from a surface.[32]

Surface-initiated polymerization of neat HEMA using the CuCl/30 mol % $CuBr_2$ initiation system in the absence of water gave a 6 nm PHEMA film in 12 h, compared to a 700 nm thick film for the same polymerization in an aqueous medium. This dramatic difference in film thickness clearly shows that water acts as an accelerator of ATRP, rather than merely as a diluent. Recently, Matyjaszewski and co-workers showed that the use of polar solvents for ATRP resulted in an increase in the activation rate constant as well as a decrease in the deactivation rate constant.[33] Obviously, biasing the ATRP system toward activated chain ends increases the rate of polymerization. The unique properties of HEMA also aid in the formation of thick PHEMA films. The propagation rate constants k_p, for methacrylate monomers have been measured by pulsed laser polymerization experiments, and the results show that k_p increases as the size of the ester increases.[34,35] Making the ester hydrophilic, as in the case of HEMA, leads to a further increase in k_p to ∼15 times that of methyl methacrylate. In addition, a recent study showed that k_p is approximately the same for the polymerization of HEMA in acetonitrile or water, but the overall rate of polymerization in water is faster because the rate of termination is suppressed in water.[36] The rapid growth of PHEMA brushes from surfaces and the nearly linear

Scheme 2



thickness vs growth curves seen for PHEMA films are consistent with these studies.

Ellipsometry and AFM showed that the grafted PHEMA films were macroscopically and microscopically uniform. The variation in the ellipsometrically measured thickness across a 6 × 6 mm surface area was 1 nm for a 193 nm thick film, while AFM images of the same film yielded an rms roughness of 1 nm. In an attempt to characterize the surface-initiated polymerization at the molecular level, we detached grafted polymer films from their substrates. Dissolution of these films would allow direct analysis of polymer chains by GPC and ^{1}H NMR to obtain molecular weights, molecular weight distributions, and chemical structure information. PHEMA films (400 nm thick) were detached using I_2 or potential cycling, and reflectance FTIR spectra and ellipsometry confirmed that both methods completely removed the polymer films from the surface. Unfortunately, the detached film was insoluble in all solvents that we examined (DMSO, DMF, 70:30 methyl ethyl ketone/1-propanol). The insolubility of the grafted PHEMA film is not unexpected as Armes et al. also reported an insoluble product when HEMA was polymerized in pure water.[30] Since PHEMA prepared in alcohol/water mixtures is soluble, the most reasonable explanation for PHEMA's insolubility is intermolecular cross-linking via transesterification. Consistent with this view is that complete esterification of PHEMA films by reaction with various reagents (vide infra) failed to yield a soluble polymer. Previous studies showed that soluble PHEMA derivatives can be prepared from monomers that have protected hydroxy groups,[30,37,38] further suggesting that the insolubility is due to transesterification. We also attempted to hydrolyze the insoluble polymer film to poly(methacrylic acid), but we were unable to recover material suitable for GPC measurement.

Dormant sites at the termini of polymer chains can be used for further elaboration of the polymer films. To confirm the presence of these sites, we prepared a block copolymer film by immersing a PHEMA-coated (39 nm) wafer into a room temperature DMF solution containing DMAEMA and the Cu catalyst system (Scheme 1).[39] After 4 h, the substrates were removed, washed with DMF, and analyzed by IR spectroscopy (Figure 1, spectrum c). Peaks at 2821 and 2771 cm^{-1}, attributed to the asymmetric and symmetric stretches of the methyl group in the $N(CH_3)_2$ moiety, and an increase in the carbonyl peak at 1733 cm^{-1} confirmed formation of a PHEMA-*b*-PDMAEMA copolymer. Ellipsometric measurements showed a 40 nm increase in film thickness after 4 h of DMAEMA polymerization at room temperature. The 40 nm increase is comparable to that observed for a DMAEMA homopolymer layer grown from substrate **1** under identical polymerization conditions. Thus, most grafted polymer chains in the films retain a dormant site at the chain end, allowing reactivation of the polymerization and formation of block copolymer films.

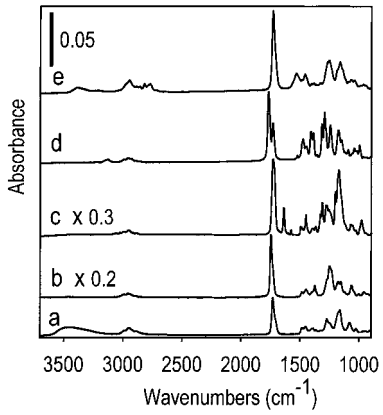


Figure 3. Reflectance FTIR spectra of (a) an unmodified PHEMA film (22 nm) and PHEMA films derivatized with (b) acetyl chloride (145 nm), (c) cinnamoyl chloride (358 nm), (d) CDI (35 nm), and (e) CDI followed by DMEDA (38 nm). The value in parentheses represents the thickness of the films after all modifications.

Table 1. Thicknesses of Surface-Grafted PHEMA Films before and after Derivatization with a Variety of Molecules

derivatization reagent	surf. thickness (nm)		percent increase	
	before	after	measd	calcd[a]
acetyl chloride	114	145	27	32
cinnamoyl chloride	146	285	96	100
cinnamoyl chloride	176	358	110	100
CDI	22	35	62	72
CDI	74	115	55	72
CDI/DMEDA[b]	22	38	73	88

[a] Calculated values are the increases in the molecular weights of the polymer repeat units after the coupling reactions. [b] PHEMA film was first activated with CDI and then reacted with DMEDA.

Surface Functionalization. An important feature of PHEMA films is that their hydroxyl groups can serve as reactive sites for insertion of a variety of functional groups (Scheme 2). The room temperature reaction of acetyl chloride, cinnamoyl chloride, or CDI with PHEMA films results in nearly quantitative conversion of hydroxyl groups to the corresponding esters, as indicated by the complete disappearance of the hydroxyl peak (3500−3300 cm^{-1}) in reflectance FTIR spectra (Figure 3). This high level of conversion was achieved even in thick (>100 nm) surface-grafted PHEMA films (Table 1), showing that despite the thickness of the films, the hydroxyl groups are very accessible and reactive. Reflectance FTIR spectra of derivatized films show the characteristic bands for the esters. For example, we observed a large increase in the carbonyl peak at 1747 cm^{-1} when a PHEMA film was reacted with acetyl chloride (Figure 3b). After treating a PHEMA film with cinnamoyl chloride, a C=C stretching band appears at 1639 cm^{-1}, and there is a strong

increase in the carbonyl peak at 1732 cm^{-1} (Figure 3c). In the reaction of the hydroxyl groups with CDI, a strong carbonyl peak at 1771 cm^{-1} signals formation of the expected imidazole carboxylic ester intermediate (Figure 3d). The high degree of conversion with CDI is important, as the imidazole groups can be displaced by nucleophiles such as amines and alcohols.[40] For example, immersion of CDI-functionalized PHEMA films into a solution of DMEDA in a mixture of DMF/H_2O for 4 h resulted in quantitative conversion of the imidazole carboxylic esters into the corresponding carbamates. This is revealed by the complete disappearance of the carbonyl peak at 1771 cm^{-1}, the appearance of a new amide II peak at 1535 cm^{-1}, and a large increase in the carbonyl peak at 1735 cm^{-1} (Figure 3e). Since the activated ester is reactive toward amines in aqueous environments, CDI-functionalized PHEMA films are attractive platforms for the immobilization of biological molecules. In addition, although CDI-activated films are very reactive, storage of these substrates in air for 1 month led to no detectable loss in their activity.

Table 1 summarizes the changes in the thickness of PHEMA films after surface derivatization. After the coupling reaction, all films show an increase in thickness due to the increased volume of the repeat unit. As shown in Table 1, the percent increase in film thickness after derivatization correlates reasonably well with the change in the molecular weight of the repeat unit, which is consistent with the high conversion of these reactions. Assuming there is no change in the density of the PHEMA film, these results suggest that little surface-bound polymer is lost during derivatization.

The significant change in film thickness and the high yields seen in derivatization reactions points to loose packing of the polymer chains tethered to the surface. Previously, we determined the molecular weight of poly(methyl methacrylate) chains grown from surface-bound ATRP initiators and estimated a cross-sectional area of 1.8 nm^2 per chain.[23] This suggests that only 10% of the initiators led to high molecular weight polymer, while the remainder were either lost via termination reactions or never initiated polymerization. While the details of the methyl methacrylate and HEMA systems are different, the PHEMA data are in accord with a similar picture: loosely packed brushlike chains that become increasingly extended as the hydroxyl groups are derivatized as esters, carbamates, and similar groups.

Conclusions

Water-accelerated ATRP is an efficient procedure for growth of thick PHEMA films on gold. This method yields polymer films with controlled thicknesses up to 700 nm within a 12 h period, and the living character of grafting polymerization allows the growth of a second polymer block. Moreover, the grafted PHEMA films can be further functionalized in high yield via reaction of their hydroxyl groups. This provides opportunities for tailoring the surface properties of polymer brushes to satisfy possible applications in separations and controlled release applications.

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