Rapid Growth of Polymer Brushes from Immobilized Initiators

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Abstract: This report describes the remarkably rapid synthesis of polymer brushes under mild conditions (50 °C) using surface-initiated polymerization. The highly active atom transfer radical polymerization catalyst Cu(I)−1,4,8,11-tetramethyl-1,4,8,11-tetraazacyclotetradecane allows synthesis of 100 nm thick poly(*tert*-butyl acrylate) brushes from initiator-modified Au surfaces in just 5 min. Using the same catalyst, polymerization of 2-hydroxyethyl methacrylate and methyl methacrylate yielded 100 nm thick films in 10 and 60 min, respectively. Such growth rates are an order of magnitude greater than those for traditional free-radical polymerizations initiated from surfaces. These polymerizations also retain some features of controlled radical polymerizations, such as the ability to form block copolymer brushes.

Introduction

Growth of polymers from surfaces using controlled polymerization schemes such as atom transfer radical polymerization (ATRP),[1,2] reversible addition−fragmentation transfer polymerization,[3] and nitroxide-mediated polymerization[4,5] has become a powerful strategy for anchoring well-defined polymers to substrates. These approaches to polymer brush synthesis limit the concentration of active chain ends (radicals) to minimize bimolecular termination reactions, thus providing control over the length of the chains and enabling the synthesis of block copolymers and other complex architectures. However, a consequence of gaining control is a substantial reduction in the polymerization rate, which can limit practical applications of polymer brushes. In this report we describe the unusually fast growth of polymer brushes using the highly active ATRP catalyst Cu(I)−1,4,8,11-tetramethyl-1,4,8,11-tetraazacyclotetradecane (Cu(I)−Me4Cyclam). Growth of 100 nm thick poly-(*tert*-butyl acrylate) (PtBA) brushes from initiator-modified Au surfaces occurs in just 5 min. Polymerization of 2-hydroxyethyl methacrylate (HEMA) in water and methyl methacrylate (MMA) in dimethylformamide/anisole mixtures using the same catalyst provided 100 nm thick films in 10 and 60 min, respectively.

Rapid growth of PtBA films has important technological implications, since these coatings are readily hydrolyzed to hydrophilic poly(acrylic acid) (PAA) films. The pendent carboxylic acids of PAA can chelate metals, induce changes in surface properties as a function of pH, and serve as scaffolds for anchoring chemical reagents, proteins, and other biomol-

ecules. An early approach to PAA-decorated surfaces employed grafting of hyperbranched PAA to substrates.[6] Although the graft-on-graft process is inherently slow, this technique yields relatively thick films for anchoring chemical reagents and biomolecules. Compared to "grafting to" strategies, direct growth of polymers from surfaces provides polymer brushes with greater thicknesses and chain densities. Allbritton et al. recently reported the rapid photoinitiated polymerization of acrylic acid from benzophenone adsorbed in poly(dimethylsiloxane) films.[7] The growth rates (100 μm/min) are remarkably fast and provide a direct route to PAA from polymer substrates. The methods presented in this work allow comparable films to be created on inorganic substrates and should be applicable to opaque supports with unusual geometries that are incompatible with photopolymerization techniques. Moreover, more complicated architectures such as block copolymers can be created.

Ideally, we would like to directly grow PAA brushes from surfaces using accelerated ATRP techniques. However, ATRP of acrylic acid is problematic, since carboxylic acids may react with the copper-amine catalysts typically used for ATRP. A partial solution is to polymerize tBA from a surface and then hydrolyze PtBA to PAA. While widely used for preparing block copolymers containing PAA,[8,9] application of this approach to surface-initiated polymerization is limited by slow polymerization rates (<5 nm/h) and low film thicknesses (<20 nm).[9−13]

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The process described here provides a uniquely rapid method for forming 100 nm thick films of PAA and other polymer brushes. Polymerization of HEMA, for example, provides another surface that can be readily derivatized to form functional coatings.[14]

Experimental Section

Unless otherwise noted, all chemicals were obtained from Aldrich. 11-Mercapto-1-undecanol (MUD, 97%), 2-bromopropionyl bromide (2-BPB) (97%), anisole (99.7%), *N,N*-dimethylformamide (DMF, 99.8%), Cu(I)Br (99.999%), Cu(II)Br$_2$ (99.999%), Me$_4$Cyclam (99%), 4,4′-dinonyl-2,2′-bipyridyl (dnNbpy, 97%), and 1,1,4,7,10,10-hexamethyl-triethylenetetramine (HMTETA) (97%) were used as received. Tris[2-(dimethylamino)ethyl]amine (Me$_6$TREN) was synthesized as previously described.[15] (11-(2-Bromo-2-methyl)propionyloxy)undecyldimethyl-chlorosilane was prepared using the procedure described for its trichloro analogue.[19] 2,2′-Bipyridine (bpy, 99%) was recrystallized from hexane and then sublimed. Triethylamine was distilled from calcium hydride under an argon atmosphere under reduced pressure. *tert*-Butyl acrylate (tBA) (98%), MMA (99%), styrene (99%), 4-vinylpyridine (4-VP) (95%), and HEMA (97%) were passed through a 10 cm column of basic alumina to remove inhibitors. After purification, the monomers and solvents were transferred to Schlenk flasks, degassed using three freeze−pump−thaw cycles, and then transferred into a drybox. *Note: For best results, solvents and monomers must be scrupulously purified and deoxygenated.*

Preparation of Immobilized Initiators on Gold Substrates. Au-coated Si wafers (200 nm of Au sputtered on 20 nm of Cr on Si(100) wafers) were UV/O$_3$-cleaned for 15 min before use and transferred into a N$_2$-filled glovebag. Hydroxy-terminated SAMs were formed by immersing the Au-coated substrates in a vial containing a 1 mM ethanolic solution of MUD for 24 h. After removing the vial from the glovebag, the substrates were rinsed sequentially with ethanol and water and dried under a stream of N$_2$. The ellipsometric thickness of the MUD layer was 10−15 Å. MUD-coated substrates were transferred to a drybox filled with N$_2$ and were dipped in a 10 mL solution of 0.12 M triethylamine in anhydrous THF at ∼0 °C. After 1 min, 10 mL of a solution of 2-BPB in anhydrous THF (0.1 M) was added dropwise to the solution to form the immobilized initiator layer. The reaction time was limited to 2−3 min, since thiol-terminated SAMs could be unstable in the presence of acid bromides. After rinsing with THF in the drybox, the Au substrates were removed from the drybox; rinsed with ethyl acetate, ethanol and deionized water (Milli-Q, 18 MΩ cm) sequentially; and dried under a stream of N$_2$.

Preparation of Immobilized Initiators on Si Substrates. UV/O$_3$-cleaned Si wafers with an ellipsometrically determined oxide thickness of 16 Å were transferred to a drybox filled with N$_2$ and immersed in a toluene solution (20 mL) containing triethylamine (150 μL) and 30 μL of (11-(2-bromo-2-methyl)propionyloxy)undecyldimethylchlorosilane. (Initiator layers give thicker polymer brushes when they are prepared in solutions containing triethylamine.) After 48 h without stirring, the samples were removed from the solution, placed in fresh toluene, and sonicated for 1 min. Following additional rinsing with toluene, acetone, and ethanol, the substrates were dried under a stream of N$_2$. The ellipsometric thickness of the initiator layer was ∼10 Å.

Polymerization of tBA, MMA, Styrene, and 4-VP from Initiators Immobilized on Au and Si Substrates. In a N$_2$-filled drybox, 5.74 mg (0.04 mmol) of CuBr, 4.47 mg (0.02 mmol) of CuBr$_2$, 10.26 mg (0.04 mmol) of Me$_4$Cyclam, and 16.35 mg (0.04 mmol) of dnNbpy were added to a round-bottom flask containing 20 mL of a degassed solution of monomer in DMF/anisole (tBA/DMF/anisole = 2:1:1 v:v:v, [tBA] = 3.5 M). The mixture was well-stirred and heated with an

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Scheme 1. Preparation of PAA Brushes via Surface-Initiated Polymerization of *t*BA and Subsequent Hydrolysis
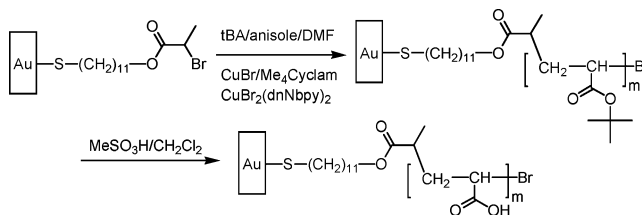
oil bath to 50 °C until a transparent, light green solution formed. The prepared solution was then transferred into a small vial containing an initiator-modified Au or Si substrate to start the surface-initiated polymerization. After a set reaction time at 50 °C, the substrate was removed from the vial, washed with ethyl acetate and THF sequentially, and then was dried under a flow of N$_2$ in the drybox. The same conditions were used for polymerization of methyl methacrylate ([MMA] = 4 M), styrene ([styrene] = 4.6 M), and 4-vinylpyridine ([4-VP] = 4.5 M).

Polymerization of HEMA from Initiators Immobilized on Gold Substrates. HEMA was polymerized in a N$_2$-filled glovebag. For polymerization using Me$_4$Cyclam as the ligand, an 18 mL solution of monomer (HEMA/H$_2$O, 5:4, v:v) was stirred in a Schlenk flask until homogeneous, degassed using three freeze−pump−thaw cycles, and then transferred into a glovebag filled with N$_2$. At the same time, a 2 mL DMF solution containing 5.74 mg (0.04 mmol) of CuBr, 4.47 mg (0.02 mmol) of CuBr$_2$, 10.26 mg (0.04 mmol) of Me$_4$Cyclam, and 16.35 mg (0.04 mmol) of dnNbpy was prepared in a N$_2$-filled drybox and transferred into the glovebag with the monomer solution. After mixing the monomer and catalyst solution and stirring for half an hour in the glovebag, the solution ([HEMA] = 4 M) was poured into a second vial containing an initiator-covered Au substrate. The polymerization was allowed to proceed at room temperature for a set reaction time, and the vial was removed from the glovebag. The substrate was removed from the vial; washed sequentially with water, ethyl acetate, ethanol, and water; and dried under a stream of N$_2$. For polymerization using bpy as the ligand, 244 mg (1.56 mmol) of bpy was added to a Schlenk flask containing 20 mL of an aqueous monomer solution (HEMA/H$_2$O, 1:1 v:v). The mixture was stirred until homogeneous and then was degassed using three freeze−pump−thaw cycles. CuCl (55 mg, 0.55 mmol) and CuBr$_2$ (36 mg, 0.16 mmol) were quickly added to the flask under Ar, and the mixture ([HEMA] = 4 M) was sonicated for 1 min and transferred into a glovebag filled with N$_2$. After stirring the catalyst mixture for an hour in the glovebag, the solution was poured into a second vial containing an initiator-covered Au or Si substrate. The polymerization was allowed to proceed at room temperature for a set reaction time of 0.5−8 h, and then the vial was removed from the glovebag. The substrate was removed from the vial; washed sequentially with water, ethyl acetate, ethanol, and water; and dried under a stream of N$_2$.

Characterization Methods. Film thicknesses were measured using a rotating analyzer ellipsometer (model M-44, J. A. Woollam) at an incident angle of 75°. The data were analyzed using WVASE32 software, and thickness and refractive index determinations were performed on at least three spots on each substrate. The refractive index of the films was assumed to be 1.5 and then fitted with the film thickness. Reflectance FTIR spectroscopy was performed using a Nicolet Magna-IR 560 spectrometer containing a PIKE grazing angle (80°) attachment.

Results and Discussion

Scheme 1 shows the synthetic route to thick PAA films on Au. (Analogous work on other surfaces is also possible, and data for polymerization from silicon are presented in the Supporting Information). Formation of a mercaptoundecanol
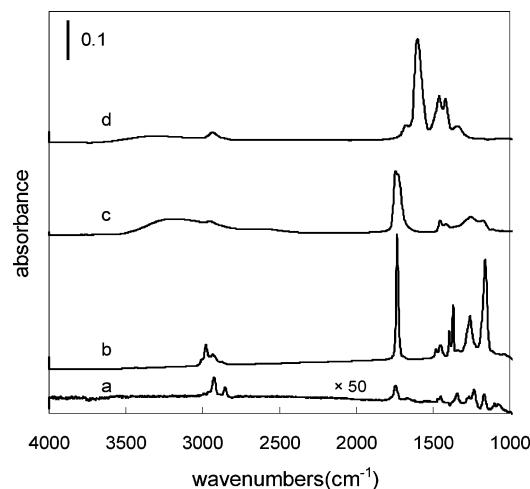
Figure 1. Reflectance FTIR spectra of gold substrates coated with (a) an immobilized initiator layer, (b) 150 nm PtBA brushes grown from the initiator layer, (c) 60 nm PAA brushes prepared by a 10-min hydrolysis of the PtBA film in a 150 mM solution of CH_3SO_3H in CH_2Cl_2, and (d) PAA brushes after immersion in a pH 10 buffer solution for 10 min and rinsing with ethanol. A UV/O_3-cleaned gold slide was used as a background.

Figure 2. Evolution of the ellipsometric brush thickness with time for the polymerization of tBA from initiator monolayers on Au substrates at 50 °C. The polymerizations were carried out using a mixture of CuBr/Me$_4$-Cyclam (2 mM) and CuBr$_2$(dnNbpy)$_2$ (1 mM) in 20 mL of a 2:1:1 (v:v:v) tBA/DMF/anisole solution ([tBA] = 3.5 M). The filled squares show the average of three independent runs, and the error bars correspond to the standard deviation. The inset shows data from 0 to 10 min. The open squares are data from the polymerization of tBA from initiators anchored on SiO$_2$ using the same polymerization conditions.

self-assembled monolayer on a Au-coated silicon wafer followed by reaction with α-bromopropionyl bromide yielded a dense initiator monolayer.[16] Immersion of the initiator-coated substrate in a mixture of monomer, Cu(I)−Me$_4$Cyclam, and Cu(II)-dnNbpy$_2$ dissolved in a 1:1 mixture of DMF and anisole initiated rapid polymerization of tBA at 50 °C. At predetermined times, the substrates were removed from the solution, and after washing with solvent to remove residual catalyst and monomer and drying with N$_2$, the films were characterized by FTIR spectroscopy and ellipsometry. Growth of PtBA brushes was apparent in the reflectance FTIR spectrum of the film from the appearance of a large carbonyl peak at 1740 cm^{-1} and *tert*-butyl ester peaks at 1390 and 1180 cm^{-1} (Figure 1, spectrum b). No film was detected on a control substrate (no initiator anchored on the surface) placed in the same polymerization solution.

Hydrolysis of a 150 nm thick film of PtBA using 150 mM methanesulfonic acid in CH_2Cl_2 for 10 min yielded a 60 nm thick PAA film.[17] The formation of PAA was apparent from a broad carboxylic acid peak at 3000−3500 cm^{-1} and the disappearance of the *tert*-butyl ester peaks (Figure 1, spectrum c). To prove an essentially quantitative conversion of the *tert*-butyl ester to the corresponding acid, we treated the film with a pH 10 sodium diphosphate solution followed by rinsing with ethanol. The resulting FTIR spectrum showed the loss of the OH band at 3000−3500 cm^{-1} and the disappearance of the acid carbonyl peak at 1740 cm^{-1}, as well as the growth of characteristic carboxylate peaks at 1610 and 1450 cm^{-1} (Figure 1, spectrum d). The disappearance of the acid carbonyl peak upon deprotonation did not reveal an underlying ester carbonyl peak, confirming complete hydrolysis.

Figure 2 shows the evolution of film thickness with time for polymerization of tBA. The high polymerization rate and thicknesses for PtBA are unusual for ATRP systems, which generally provide control over molecular weight and polydispersity by maintaining a low concentration of active (radical)
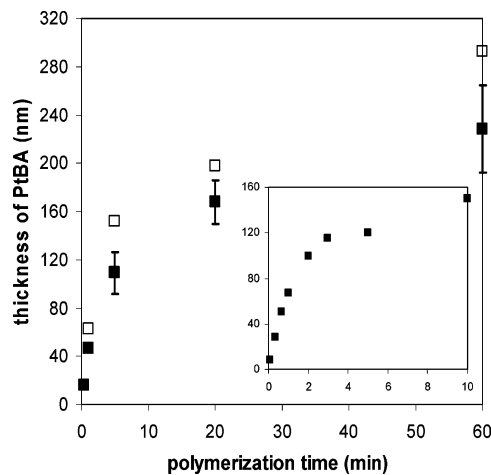
chain ends. The nonlinear relationship between film thickness and time for PtBA (Figure 2) suggests that in this case a relatively high concentration of radicals leads to both termination and a high polymerization rate, especially early in the polymerization (see inset to Figure 2). However, the loss of some control in this polymerization system is more than compensated by the possibility of growing thick films in a few minutes. The data for polymerization from SiO$_2$ surfaces (Figure 2) show that the accelerated polymerization rates are not limited to Au substrates.

Polymerizations using the structurally related Me$_6$TREN and HMTETA ligands under the same conditions were not accelerated and yielded <20 nm films in 60 min (see Figure S1, Supporting Information). While the Me$_4$Cyclam/CuBr system seems to be unique, other combinations of ligands and polymerization conditions also may yield ultrafast polymerizations. To examine to what extent the polymerization exhibits features of a controlled polymerization, we used CuBr$_2$(Me$_4$Cyclam)$_2$ as the Cu(II) source. Prior research showed that the use of Me$_4$-Cyclam/CuBr for the solution ATRP of dimethylacrylamide[18,19] and 2-vinyl-4,4-dimethyl-5-oxazolone[20] provides marginal control over the molecular weight, most likely due to an inefficient back-reaction (R• + CuX$_2$ → RX + CuX) and, hence, insufficient deactivation of chain ends.[21] When CuBr$_2$(Me$_4$-Cyclam)$_2$ was used as the Cu(II) source in tBA polymerizations, the initial polymerization rate increased as expected for an uncontrolled polymerization and ultimately yielded thinner films due to a rapid decrease in polymerization rate after initiation (Figure 3). Using CuBr$_2$(dnNbpy)$_2$, the initial polymerization rate is slower, but the polymerization yields thicker films,

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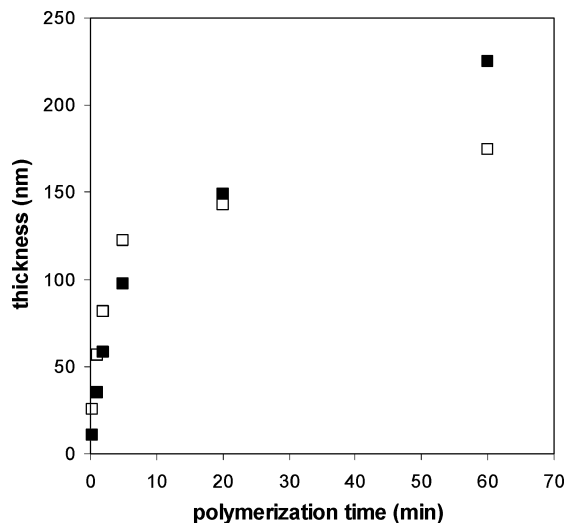
Figure 3. Evolution of the ellipsometric brush thickness with time for the polymerization of tBA from initiator monolayers on Au substrates using Me$_4$Cyclam and dnNbpy as the Cu(II) source. ■, [CuBr/Me$_4$Cyclam] = 2 mM, [CuBr$_2$(dnNbpy)$_2$] = 1 mM, in 20 mL of a 2:1:1 (v:v:v) tBA/DMF/anisole solution ([tBA] = 3.5 M); □, [CuBr/Me$_4$Cyclam] = 2 mM, [CuBr$_2$(Me$_4$Cyclam)$_2$] = 1 mM, in 20 mL of a 2:1:1 (v:v:v) tBA/DMF/anisole solution ([tBA] = 3.5 M). The polymerizations were performed in a N$_2$-filled drybox at 50 °C.
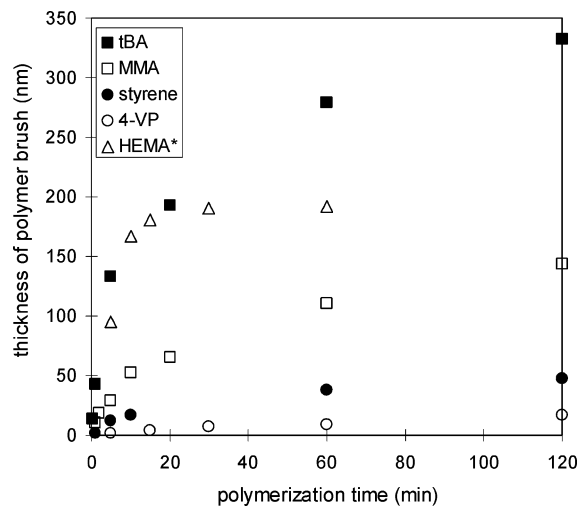

Figure 4. Evolution of the ellipsometric brush thickness with time for the polymerization of tBA, MMA, styrene, 4-vinylpyridine (4-VP), and HEMA from initiator-coated Au substrates. HEMA was polymerized from aqueous solution (see Experimental Section for details), whereas the other brushes were prepared as shown in Scheme 1.

indicating some level of control in polymerizations using CuBr$_2$-(dnNbpy)$_2$.

A more rigorous test for control of polymerization was the successful formation of block copolymers. A 97 nm PtBA film was grown in 5 min, rinsed with solvent, and dried under N$_2$. The sample was removed from the drybox and characterized by ellipsometry and FTIR spectroscopy. After 24 h, the substrate was returned to the drybox, and a PMMA film with a thickness of 210 nm was grown from the PtBA film in 1 h using the Me$_4$Cyclam-based catalyst. Interestingly, the PMMA block is comparable in thickness to a PMMA film grown directly from surface anchored initiators, suggesting that a substantial fraction of the chains were active after polymerization of the initial PtBA block.

The unusually high growth rates for PtBA films prompted us to examine other monomers to see if they too could be polymerized rapidly to provide thick films. As shown in Figure 4, polymerization rates for styrene, methyl methacrylate, and vinylpyridine were slower than for tBA, and the limiting film thicknesses were also lower. However, the polymerization rates were still significantly higher than those described to date. For example, Huck et al. reported the growth of 35 nm thick PMMA films from Au in 2 h,[22] whereas the Me$_4$Cyclam/CuBr system gave a 100 nm thick PMMA film in just 1 h. Husson et al. grew a 40 nm thick polystyrene film in 25 h from a silicon substrate at 50 °C,[23] compared to a 30 nm film from Au in just 1 h at 50 °C with the Me$_4$Cyclam/CuBr system. Despite the potential utility of poly(4-vinylpyridine) brushes, we are aware of only one example of the polymerization of 4-vinylpyridine from a surface: Rühe's growth of 430 nm thick films from surface anchored azo initiators in 14 h.[24] However, Husson et al. reported very slow growth rates for poly(2-vinylpyridine)

(6 nm in 5 h).[25] In the case of PHEMA (Figure 4), polymerization occurred in aqueous solution, and the initial rate of polymerization was approximately 70 times faster than when using a bipyridine catalyst under similar conditions. Thus, PHEMA provides a second polymer system that can be rapidly polymerized and readily derivatized to control functionality.

Comparison of the polymerization rates of tBA, MMA, styrene, and 4-vinylpyridine in DMF/anisole suggests that the unusually rapid growth of PtBA films stems from a combination of tBA's fast propagation rate and reduced bimolecular coupling due to the steric bulk of the monomer. Neglecting chain transfer processes, the degree of polymerization realized in a chain-growth polymerization is defined by the relative probabilities of a growing chain by adding a monomer or terminating. Since most syntheses of polymer brushes from surfaces are carried out at high monomer concentrations that are approximately constant during the polymerization, the ratio of k_p to k_t, the rate constants for propagation and termination, serves as an indicator of the likelihood that a reaction will reach high degrees of polymerization before termination. The order of the limiting film thicknesses shown in Figure 4 is consistent with the relative values of k_p/k_t for the monomers.[26] Moreover, preliminary data show that tBA polymerizations show a strong dependence on monomer concentration (Figure S2, Supporting Information), which should alter the ratio of polymerization and termination rates.

In summary, the use of the Me$_4$Cyclam/CuBr catalyst system allows rapid polymerization of a variety of monomers. Such rapid polymerization from a surface will be very important in potential applications of polymer brushes as skin layers in separation membranes and as substrate coatings for probe immobilization in gene and protein chips. It is important to note that while these rapid polymerizations from surfaces are not "living", they do allow formation of block copolymers and their high growth rates are very attractive for forming functional films.

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Supporting Information Available: Polymerization data for tBA using Me_4Cyclam, HMTETA, and Me_6TREN as ligands; polymerization data for tBA at different monomer concentrations, in different solvents, and at different temperatures; and FTIR spectra of PMMA, PS, and PVP grown from Au and SiO_2 substrates. This material is available free of charge via the Internet at http://pubs.acs.org.

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