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Polymers at Interfaces: Using Atom Transfer Radical Polymerization in the Controlled Growth of Homopolymers and Block Copolymers from Silicon Surfaces in the Absence of Untethered Sacrificial Initiator

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ABSTRACT: The atom transfer radical polymerization (ATRP) of styrene and acrylates from silicon wafers modified with an initiator layer composed of 2-bromoisobutyrate fragments is described. In the presence of the proper ratio of activating and deactivating transition-metal species, controlled radical polymerizations of styrene were observed such that the thickness of the layer consisting of chains grown from the surface increased linearly with the molecular weight of chains polymerized in solution in identical, yet separate, experiments. The layer thickness increased linearly with reaction time for ATRP of styrene and methyl acrylate due to both the extremely low initiator concentration relative to monomer and the low monomer conversion. Further evidence for control was observed by the polymerization of blocks of either methyl or *tert*-butyl acrylate from the polystyrene layer. Modification of the hydrophilicity of the surface layer was achieved by hydrolysis of the poly(styrene-*b*-*tert*-butyl acrylate) to poly(styrene-*b*-acrylic acid) and confirmed by decrease in water contact angle from 86° to 18°. The mechanistic aspects of ATRP in the polymerization process were confirmed by the growth of very thick polystyrene films in the presence of a pure copper(I) complex. Since no deactivator was present, the metal complex served only to facilitate initiation by a redox process. Attempts to extend chain with methyl acrylate under controlled conditions were unsuccessful in those films. The simulation of polymerization of surface layers suggests broader molecular weight and chain end distributions, confirming XPS results on the progressive decrease of Br absorption intensity.

Introduction

Increasing attention has been placed on the synthesis of dense films of polymer chains covalently bound to surfaces. Traditional methods have used coupling techniques between preformed chains and functional groups bonded to the substrate, but adsorption of the first fraction of chains has hindered diffusion of additional macromolecules, thereby limiting the formation of a dense brush. An alternative has been the use of self-assembly techniques to attach a monolayer of initiator molecules to the surface.[1] Since the chains grow from the interface, the only limit to propagation is diffusion of monomer to the chain ends. In the context of planar surfaces (i.e., silicon or gold wafers), the chlorosilane coupling of attachable initiators composed of azo moieties to oxidized silicon surfaces was used.[2] Initiation of the conventional radical polymerization of styrene showed that film thickness increased with reaction time. Consistent with polymerization in solution from an azo initiator, the rate of initiation from the surface was slower than propagation, resulting in poor control over the distribution of chain lengths as well as chain end functionality. Furthermore, due to the nature of the homolytic cleavage of the azo fragment, a proportional quantity of free chains in solution was formed with each chain generated at the surface. Following extraction of the adsorbed chains from the covalently bound polymer, a surface with a homogeneous, evenly distributed polystyrene layer was obtained.

Since disclosure of the above reaction, a number of research groups have explored the use of controlled/"living" polymerization techniques to propagate vinyl monomers in a well-defined manner. Cationic polymerization of 2-ethyloxazoline from a hydroxyl terminal thiolate self-assembled on a gold surface was reported.[3] Cationic polymerization of styrene from a silicon surface modified with a benzyl chloride monolayer has been described.[4] The polymer chains with phenylethyl chloride termini were then used to initiate the atom transfer radical polymerization (ATRP) of methyl methacrylate to make a block copolymer. For anionic polymerization, the versatility of the self-assembly of alkanethiol derivatives on gold surfaces[1] was exploited to facilitate the phenyllithium-initiated anionic polymerization of sty-

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rene.[5] Atomic force microscopy and polarized external reflectance FTIR spectroscopy revealed a smooth, homogeneous layer composed of stretched, oriented chains. In another study, silicon, platinum, and quartz surfaces were modified with phenylsilane or bromopropylsilane monolayers.[6] Substitution reactions at those groups were used to initiate polymerizations of methyl methacrylate, ethylene oxide, hexamethylcyclotrisiloxane, and acrylonitrile.[6] In the latter case, films thicker than 240 nm were obtained.

Of particular relevance to the current study is the controlled radical polymerization of vinyl monomers from silicon surfaces. The first of those utilized Langmuir−Blodgett techniques to attach a monolayer composed of arylsulfonyl chloride fragments to a silicon surface.[7] In the simultaneous ATRP of methyl methacrylate from the surface as well as from free (untethered) toluenesulfonyl chloride, a linear relation between the molecular weight of chains polymerized in solution and those grown from the surface was observed, indicating that controlled growth of the immobilized chains occurred. In another study, chlorosilane coupling reactions were used to attach initiators containing either alkoxyamines or 2-bromoisobutyrates to silicon substrates.[8] With the alkoxyamine, homopolymerization of styrene or copolymerization of styrene with 2-hydroxyethyl methacrylate was performed. In either case, excess (free) alkoxyamine had to be added to the reaction to provide a sufficiently high concentration of deactivator necessary for controlled polymerizations on the surface. Similar to the ATRP from the sulfonyl halides, polymerization of methyl methacrylate from the 2-bromoisobutyrate species in the presence of the small molecule initiator, ethyl 2-bromoisobutyrate, showed a linear correlation between free chain molecular weight and film thickness. The authors stated that polymerization in solution was necessary to ensure a sufficient concentration of deactivating copper(II) species, or control was not obtained.[8] In yet another study, a relationship between monomer concentration and film thickness was established in the ATRP of acrylamide from benzyl chloride-modified silicon surfaces.[9]

The goal of the current study was to demonstrate the versatility of ATRP in the preparation of high concentrations of surface bound polymers. Analogous to the control of polymer molecular weight for chains grown in solution, control over film thickness was maintained through a sufficient concentration of deactivator in the absence of untethered initiator. Verification of control over terminal chain functionality was obtained by block copolymerization. Finally, by choice of monomer or through postpolymerization functionalization reactions, the wettability of the surfaces was varied over a broad range.

Experimental Section

Materials Trichlorosilane was obtained from Gelest. 10-Undecen-1-ol and 2-bromoisobutyryl bromide were obtained from Aldrich. Styrene was distilled from calcium hydride. Methyl acrylate was washed three times with 5% sodium hydroxide solution and once with water. After drying with magnesium sulfate, the monomer was obtained in pure form by distillation twice from calcium chloride. 3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-Heptadecafluorodecyl acrylate (fluoro acrylate) was distilled at 90 °C and 4 mmHg. All of these monomers were stored in the drybox freezer immediately following distillation. *tert*-Butyl acrylate was purified in the same manner as methyl acrylate but was distilled only once from calcium chloride. The monomer was stored in the freezer outside of the drybox. Karstedt's catalyst was synthesized according to the method of Lewis et al.[10] Copper(I) bromide (CuBr) was stirred in glacial acetic acid overnight, filtered, and washed with absolute ethanol under an argon blanket. The compound was dried under vacuum at 60 °C overnight. *N*,*N*,*N*′,*N*″,*N*″-Pentamethyldiethylenetriamine (PMDETA) was distilled from calcium hydride and stored at room temperature in the drybox. The method of Griggs et al.[11] was adopted to the synthesis of 4-nonylpyridine which was used in a previously reported procedure[12] to produce 4,4′-di-*n*-nonyl-2,2′-bipyridine (dnNbpy). The complex copper(II) bromide bis(4,4′-di-*n*-nonyl-2,2′-bipyridine) ($CuBr_2(dnNbpy)_2$) was prepared by stirring 0.25 g (1.1 mmol) of $CuBr_2$ and 0.92 g (2.2 mmol) of dnNbpy in a 1:1 (v) mixture of THF and acetonitrile at room temperature until a homogeneous green solution formed. The solvents were removed by trap-to-trap distillation, and the green solid dried under vacuum (1 mmHg) overnight at room temperature. The complex copper(II) bromide−*N*,*N*,*N*′,*N*″,*N*″-pentamethyldiethylenetriamine ($CuBr_2$(PMDETA)) was prepared by stirring 0.52 g (2.4 mmol) of $CuBr_2$ and 0.41 g (2.4 mmol) of PMDETA in methanol at room temperature until a homogeneous green solution formed. The solvents were removed by trap-to-trap distillation, and the green solid dried under vacuum (1 mmHg) overnight at room temperature. Both compounds were henceforth stored in the drybox. Chloroform was distilled from calcium hydride and stored in the drybox. “Triple distillation” quality water for contact angle measurements was obtained from a Barnstead Nanopure II purification system.

Measurement. Film thickness was measured with a Gaertner model L116B ellipsometer operating with a 633 nm He/Ne laser at a 70° incident angle. The following refractive indices were used for the various layers: 3.865 for native silicon, 1.465 for silicon oxide, 1.527 for poly(acrylic acid),[13] 1.466 for poly(*tert*-butyl acrylate) (value from poly(*n*-butyl acrylate)),[13] 1.339 for poly(fluoro acrylate),[13] 1.5672 for poly(methyl acrylate),[13] and 1.59 for polystyrene.[13] Measurements were obtained at three spots on each wafer, 10 measurements per spot. The surface composition was measured using X-ray photoelectron spectroscopy (XPS) at 10^{-9} mmHg from a VG-Scientific Mg−Kα X-ray source ($h\nu = 12\,535.6$ eV). The energies of emitted electrons were measured using a Fissions Clam II hemispherical analyzer at a pass energy of 50 eV.

IR spectra of the polymer films grown on silicon substrates were measured in the external reflection mode using a Mattson RS1 FT-IR spectrometer coupled with a custom-made reflection optical system described in detail elsewhere.[14] P-polarized light was used at an incident angle of 80° with respect to the surface normal. A total of 1024 scans were co-added for each spectrum at 4 cm^{-1} spectral resolution from both the sample and a clean silicon reference.

Contact angle measurements using both the horizontal and tilting platform methods were obtained from a Panasonic GP-KR222 video camera connected to a Hitachi video copy processor model P71U. Angles from three different spots on each wafer were measured 10 times and statistically compiled. Molecular weights for free soluble polymers were measured in THF using a Waters 510 liquid chromatograph pump equipped with four Polymer Standards Service (PSS) columns (100 Å, 1000 Å, linear, and guard) in series with a Waters 410 differential refractometer. Molecular weights were calculated with PSS software; calibration was based on low-polydispersity polystyrene standards. Prior to injection, samples dissolved in either THF or chloroform were passed through a 2 cm column of alumina followed by a 0.2 μm syringe filter. When an air/moisture-free environment was required, a Vacuum Atmospheres HE-33 drybox was used. The concentrations of oxygen and water were both below 1 ppm in the nitrogen atmosphere.

Initiator Synthesis and Monolayer Self-Assembly. *10-Undecen-1-yl 2-Bromo-2-methylpropionate.* To a solution of 4.257 g (25 mmol) of ω-undecylenyl alcohol in 25 mL of dry tetrahydrofuran was added 2.1 mL of pyridine (26.5 mmol) followed by dropwise addition of 3.10 mL of 2-bromoisobutyryl bromide (25 mmol) over 5 min. The mixture was stirred at room temperature overnight and then diluted with hexane (50 mL) and washed with 2 N HCl and twice with water. The organic phase was dried over sodium sulfate and filtered. The solvent was removed from the filtrate under reduced pressure, and the colorless oily residue was purified by flash column chromatography (hexane/ethyl acetate 25/1 v/v) to give 7.34 g (92%) of the ester as a colorless oil. R_f (hexane/ethyl acetate 10/1 v/v): 0.68. MS (EI): 238, 168, 151, 123, 121, 109, 95, 69, 55. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 1.22−1.45 (br m, 12H); 1.62−1.75 (m, 2H); 1.94 (s 6H); 2.05 (q, 2H, $J = 6$ Hz); 4.17 (t, 2H, $J = 9$ Hz); 4.9−5.05 (m, 2H); 5.72−5.9 (m, 1H) ppm. ^{13}C NMR (300 MHz, $CDCl_3$) δ: 25.71, 28.27, 28.83, 29.01, 29.35, 30.71, 33.73, 55.88, 66.07, 114.09, 139.08, 171.65 ppm.

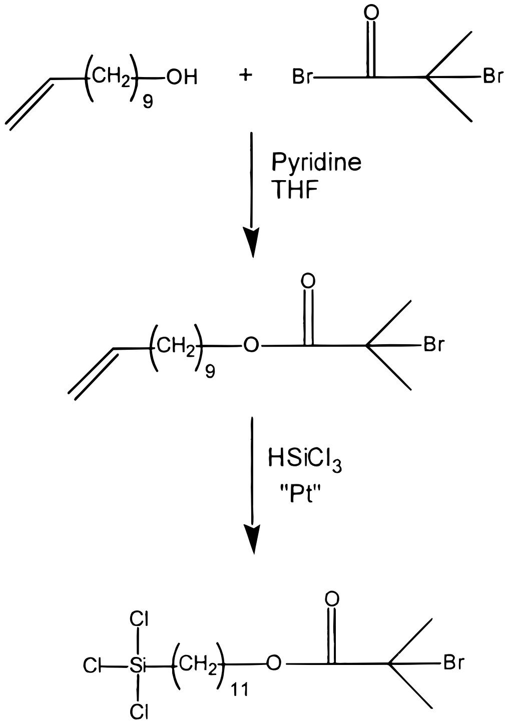
(11-(2-Bromo-2-methyl)propionyloxy)undecyltrichlorosilane. To a dry flask were added 1.35 g (4.23 mmol) of 10-undecen-1-yl 2-bromo-2-methylpropionate and 4.2 mL of trichlorosilane (42.6 mmol), followed by the addition of Karstedt catalyst (4 μL, 100 ppm Pt equivalents). The mixture was stirred at room temperature while the reaction was monitored by GC. The reaction was usually complete within 5 h. The solution was quickly filtered through a plug of silica gel to remove the catalyst. The excess reagent was removed under reduced pressure. The residue was found to be >95% pure by GC and was used as such. The compound can be further purified by vacuum distillation (80−85 °C at 2.0×10^{-2} mmHg). When not in use, the compound was stored in the drybox at 5 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 1.23−1.45 (br m, 16H); 1.54−1.75 (m, 4H); 1.93 (s 6H); 4.16 (t, 2H, $J = 9$ Hz) ppm. ^{13}C NMR (300 MHz, $CDCl_3$) δ: 22.16, 24.22, 25.69, 28.26, 29.07, 29.22, 29.38, 30.71, 55.88, 66.02 ppm.

Silicon (100) wafers, cut into 1 cm^2 pieces, were cleaned in a toluene bath under ultrasound for 5 min. The wafers were then rinsed with HPLC grade toluene, acetone, and absolute (water-free) ethanol and dried in a nitrogen stream. The samples were then oxidized in a UV/ozone chamber for 15 min; the thickness of the SiO_2 layer was 16.1 Å measured by ellipsometry. The wafers were transferred to the drybox and placed into a solution of 5 μL of the trichlorosilane in 10 mL of toluene (4 mM on wafer). The samples were allowed to stand in this solution for 18 h without stirring. The wafers were removed from the solution, cleaned by ultrasound in toluene for 1 min, rinsed again with toluene, acetone, and absolute ethanol, and again dried in a nitrogen stream. When not used in reactions, the wafers were stored at room temperature in the drybox.

Polymerizations. For polymerizations where samples were removed from a common reaction medium as a function of time, experiments were performed in glass jars with screw-top lids in a thermostated oil bath in the drybox. The purpose was to allow easy removal of individual wafers without prolonged exposure of the reaction to oxygen. A representative example is as follows: 4.5 g (43 mmol) of styrene and 36 mg (3.4×10^{-2} mmol) of $CuBr_2(dnNbpy)_2$ were placed into the reactor and stirred until a homogeneous purple solution formed. Then, 99 mg (0.69 mmol) of CuBr, 560 mg (1.4 mmol) of dnNbpy, and 2.7 g (26 mmol) of styrene were added and stirred until a homogeneous maroon solution formed. The wafers were then placed into the reactor, and the covered apparatus was held in a 100 °C oil bath. Periodically, wafers were removed from the reactor and rinsed with chloroform. At the conclusion of the reaction, any adsorbed polymer formed adventitiously in solution was removed from the wafers by Soxhlet extraction in toluene for 24−48 h. Upon removal from the extractor, the wafers were dried under a stream of argon or nitrogen and stored at room temperature under air.

For experiments examining the corresponding molecular weights of chains grown in solution, the above procedure was duplicated with the exception that, after all reagents had been combined and homogeneity reached, 11 μL (7.3×10^{-2} mmol) of ethyl 2-bromoisobutyrate was added *in the absence of wafers*. The reaction was conducted in such a way that solution samples were removed at times corresponding to removal of the wafers. The molecular weight of the polymer samples dissolved in THF was then determined.

Scheme 1. Chemical Diagram Describing the Synthesis of the Attachable Initiator 11-(2-Bromo-2-methyl)propionyloxyundecenyltrichlorosilane



When a polymerization from only one wafer was performed, a different procedure was adopted. Into a 10 mL round-bottom flask was placed 3.0 mg (1.3×10^{-2} mmol) of $CuBr_2$, 49 mg (0.34 mmol) of CuBr, and 290 mg (0.71 mmol) of dnNbpy. The solids were degassed under room-temperature vacuum for 20 min and backfilled with nitrogen. To this, 4.4 g (34 mmol) of *tert*-butyl acrylate, which was deoxygenated by a nitrogen bubble for 20 min, was added, and the mixture was stirred in a 60 °C oil bath under nitrogen for 30 min to promote formation of a homogeneous maroon solution. During the above process, a silicon wafer, with a preformed polystyrene layer, was placed into a 25 mL sidearm Erlenmeyer flask, covered with a rubber septum, and connected to the Schlenk line via rubber vacuum tubing. The flask was evacuated for 15 min and backfilled with nitrogen. The monomer/catalyst solution was then cannula transferred into the Erlenmeyer flask, and the reactor was placed into a 90 °C oil bath and stirred under nitrogen. After 4.5 h the wafer was removed from the flask and rinsed with chloroform. The wafer was then Soxhlet extracted with toluene for 20 h and dried under a nitrogen stream.

Results and Discussion

Initiator Synthesis and Self-Assembly The synthesis of an attachable initiator for self-assembly to a silicon surface is illustrated in Scheme 1 and is similar to that described by another group for the same purpose.[8] Esterification of 10-undecen-1-ol with 2-bromoisobutyryl bromide was followed by hydrosilylation with trichlorosilane to yield a compound with reactive species capable of bonding to the surface along with a latent α-halo ester which can later be used to initiate the ATRP of vinyl monomers. ^{1}H NMR of the attachable initiator showed the methyl protons for the species adjacent to the bromine carbon at 1.93 ppm along with the absence of any unsaturated hydrocarbon above 5 ppm, indicating that both reactions were effective in arriving at the desired product.

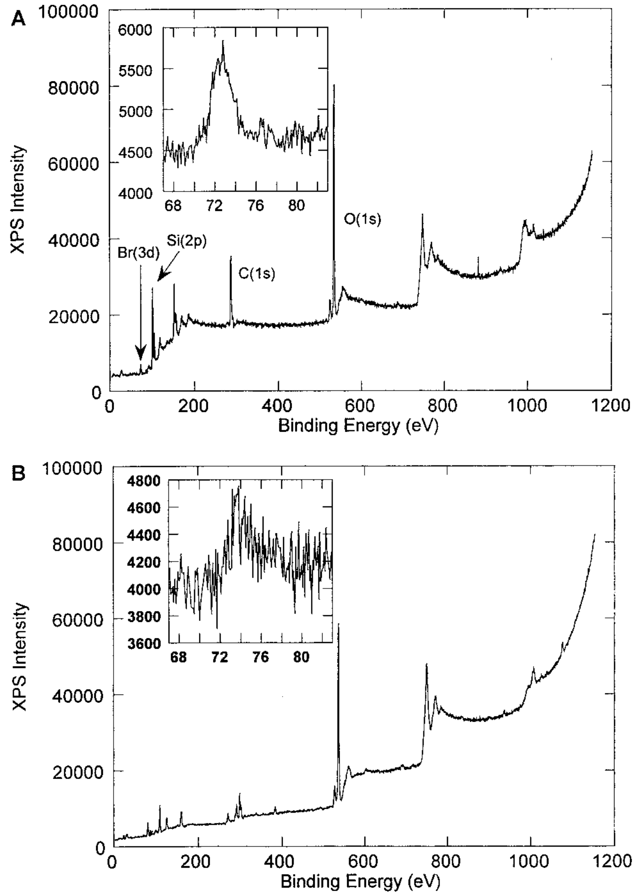


Figure 1. XPS spectra for (A) the self-assembled initiator layer and (B) a 7 nm thick polystyrene layer grown from that initiator surface. Insets: region associated with the peak derived from bromine.

Formation of densely covered monolayers of initiator on silicon wafers was performed using well-established techniques.[15] The wafers were immersed in a dilute solution of the trichlorosilane in toluene for 18 h and rinsed with toluene, acetone, and absolute ethanol to remove free attachable initiator from the monolayer. Trace A of Figure 1 displays the XPS spectrum of the initiator layer. The spectrum shows the carbon signal at 286 eV associated with the organic portion of the attachable initiator along with the bromine signal at 73 eV. In the absence of impurities deposited on the wafers during preparation, the only sources of carbon and bromine should be from the initiator layer.

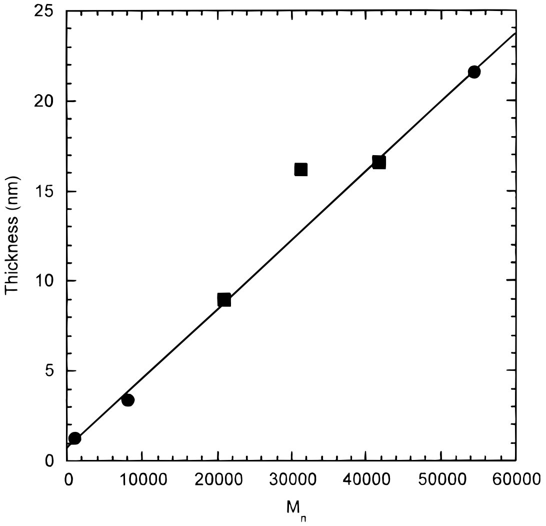


Figure 2. Plot of evolution of polystyrene layer thickness from a modified silicon surface as a function of molecular weight of chains polymerized in solution. Conditions: surface reaction—1% $CuBr(dnNbpy)_2$, 0.05% $CuBr_2(dnNbpy)_2$, 100 °C, bulk, drybox; solution reaction—initiator = ethyl 2-bromoisobutyrate, $[M]_0/[I]_0/[CuBr(dnNbpy)_2]_0/[CuBr_2(dnNbpy)_2]_0 = 960{:}1{:}9.6{:}0.48$, 100 °C, bulk, drybox. Circles and squares represent results from separate, yet identical, experiments. Line: linear curve fit of data points excluding the square at thickness = 16 nm, $M_n = 30\,000$.

Homopolymerizations. The ATRP of styrene from the modified silicon wafers was conducted first. Typical of many standard polymerizations from free (untethered) initiators, 1 mol % of $CuBr(dnNbpy)_2$ relative to monomer was used. However, in those reactions, deactivator was formed spontaneously by radical termination early in the reaction until the nearly steady-state concentration of copper(II) was achieved according to the persistent radical effect.[16] Since the concentration of initiator was extremely low and, in contrast to previous studies,[7,8] no free initiator was added to the reaction, the deactivator was added at the beginning of the reaction (vide infra). For styrene, 5 mol % $CuBr_2$ relative to copper(I) was chosen on the basis of EPR measurements of the deactivator concentration during the bulk ATRP of styrene for metal complexes ligated by the dnNbpy system.[17] The relationship between the thickness of the polymer layer grown from the surface and the molecular weight of chains which would have propagated in solution is plotted in Figure 2. The experiment synthesizing polymer in solution was conducted using identical components except the silicon wafers were substituted with ethyl 2-bromoisobutyrate at a molar monomer-to-initiator ratio of 960. Similar to the studies of the simultaneous growth of chains of poly(methyl methacrylate) in solution and at interfaces,[7,8] a linear increase in thickness with chain length was observed, indicating some control over the propagation of polymer bound to the silicon substrate.

The XPS spectrum B of Figure 1 illustrates the composition of the wafer composed of a 7 nm thick polystyrene layer. The decrease of the intensity of the silicon (101 eV) and oxygen (533 eV) peaks relative to the carbon signal (286 eV) indicates the addition of the organic polymer to the surface. A small signal remains for the bromine at 73 eV (inset). Estimation of the peak heights of that signal for the initiator and this sample indicates (qualitatively) a 50% reduction in the bromine signal. The data indicate that the bromine could be either lost through some termination/elimination event[18] or still present at the termini of the majority of the chains which are, however, not fully extended with some of the terminal alkyl halides not readily detectable by the XPS technique. Chains growing from the surface may be less uniform than under homogeneous conditions due to limited access of the catalyst and monomer to the areas close to the interface. The nonuniformity of chain ends should lead to a broader distribution of Br atoms and a less intense XPS signal.

One goal of the current study was to probe the conformation of the chains grown from the surface which, however, appeared rather difficult. In a situation where each graft initiates and propagates at the same time, the limited geometric constraints imposed on a chain by its neighbors could force the macromolecule to adopt an extended conformation. Given the molecular weights of chains grown in solution and a repeat unit distance of 2.51 Å, comparisons between the measured film thickness and this theoretical length can be drawn. The results from this study show that the measured thickness is less than the values calculated for the contour length. For instance, according to Figure 2, when a polymer grown in solution has reached M_n = 60 000, the thickness of the film is ~24 nm. The contour length of the untethered chain is ~150 nm, approximately 6 times larger than our measured value. However, the root-mean-square end-to-end distance for a random coil would be ~15 nm.[19] The difference between the thickness expected for fully extended chains of the average size reach at the particular moment in solution and the observed thickness can be explained by either slower growth at the surface or enhanced polydispersity and consequently broader chain end distribution of macromolecules grown from the surface. The growth at the surface may be slower than in solution due to the geometric constraints resulting from high surface density of the chains. This can additionally influence growth rates of individual chains, resulting in a broadening of the chain length distribution with respect to that observed for polymerization occurring under normal, i.e., nonconstrained conditions. At a sufficiently high surface density of the initiator, the crowded chains can relax through a differentiation of growth rates of individual chains rather than exclusively through the chain extension. The observed disappearance of the XPS signal related to Br in thicker layers seems to confirm the above conjecture. This would mean that the surface-initiated polymerization would not be able to solve the problem of preparation of thick brushes with high grafting density of uniform long chains.

Kinetics. A difference between the studies conducted using "free" (untethered) initiator in solution[7,8] in conjunction with surface bound alkyl halides and the experiments using strictly covalently attached 2-bromoisobutyrates is the kinetic behavior of the polymerizations. At a typical free initiator concentration of 0.1 M, the consumption of monomer is dictated by the chains propagating in solution and, as a result, first-order kinetics is commonly observed in ATRP. However, at the approximate initiator concentration of 10^{-9} mol/cm^2 (i.e., 10^{-7} mol/L) when the alkyl halide is attached to the wafers, virtually no consumption of monomer occurs. Therefore, when the thickness data of the styrene polymerization is plotted versus reaction time, a linear plot is obtained in Figure 3. Such a situation is not unique to controlled radical polymerizations—a linear increase in film thickness versus time was observed in the conventional radical polymerization of styrene from a modified silicon surface containing azo initiating fragments.[2] It should be stressed that the amount of the polymer grafted from the flat surface is extremely small; e.g., only 0.01 mg of the polymer corresponds to 100 nm thick film grown from a flat surface of 1 cm^2. This does not allow for the analysis of molecular weight and molecular weight distribution of the obtained polymers by cleaving from them from the surface.

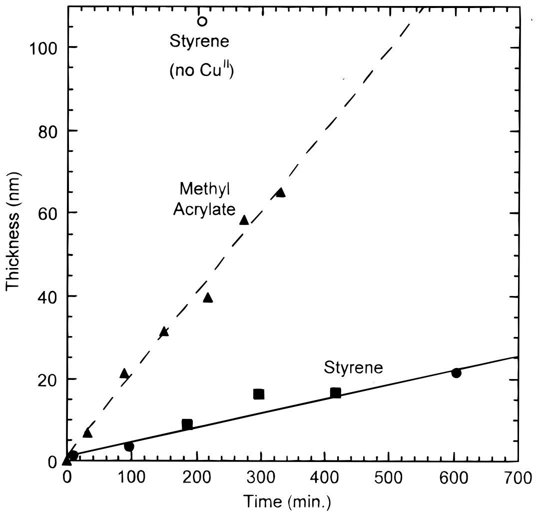


Figure 3. Plot of evolution of polymer layer thickness from a modified silicon surface as a function of reaction time. Conditions: closed circles and squares, styrene, 1% CuBr(dnNbpy)$_2$, 0.05% CuBr$_2$(dnNbpy)$_2$, 100 °C, bulk, drybox; open circle, styrene, 1% CuBr(dnNbpy)$_2$, 100 °C, bulk, drybox; triangles, methyl acrylate, 1% CuBr(PMDETA), 0.03% CuBr2(PMDETA), 70 °C, bulk, drybox. Solid line: linear curve fit of data points for the styrene polymerization excluding the square at thickness = 16 nm, M_n = 30 000. Dashed line: linear curve fit of data points for the methyl acrylate polymerization.

The persistent radical effect, applied to controlled radical polymerizations,[16] suggests that a sufficient concentration of deactivator be present to provide reversible deactivation of chains during propagation. In a typical ATRP process, a few percent of chains terminate and spontaneously form deactivating Cu(II) species. As detected by EPR, the concentration of Cu(II) is in the range 10^{-3} mol/L, and such a concentration is needed for a sufficiently controlled process. In the previous controlled radical polymerization experiments growing dense polymer films from the surface, the "sacrificial" initiator was present in solution. The "free" (untethered) chains terminated in solution, thereby spontaneously forming a sufficient amount of the deactivator. It was reported that the presence of the sacrificial initiator was required for polymerization control. In our experiments, we did not use the sacrificial initiator but added a sufficient amount of the deactivator at the beginning of the reaction. Otherwise, no control can be observed, and the process would resemble a redox-initiated conventional radical system. Since under typical conditions of self-assembly the concentration of initiator can be no larger than ~5 × 10^{14} molecules/cm^2 [20] (i.e., 10^{-9} mol/cm^2 or 10^{-7} mol/L), even the termination of all alkyl halide fragments would provide a concentration of CuBr$_2$ that is 10 000 times lower than that observed and required for a well-controlled ATRP. To verify this hypothesis, a polymerization of styrene was performed using 1 mol % pure CuBr(dnNbpy)$_2$ with no added CuBr$_2$. The solution was stirred over four wafers at 100 °C for 205 min. The mean thicknesses of the wafers was 106 ± 5 nm (open circle in Figure 3). According to the reaction run with CuBr$_2$, the height above the surface should have been 12 nm. The surfaces were blue, indicating that very thick polymer layers had been grown. Attempts to chain extend the bound chains with methyl acrylate under ATRP conditions (1% CuBr(dnNbpy)$_2$, 0.03% CuBr$_2$(dnNbpy)$_2$ relative to monomer, 80 °C, bulk) resulted in no change in film thickness (106 ± 5 nm for samples removed at various times), confirming the conventional free radical mechanism and a loss of chain end functionalities. This series of experiments demonstrates that to control the growth of chains from the silicon surface, accessible deactivator must be present whether it is derived from the simultaneous polymerization of chains

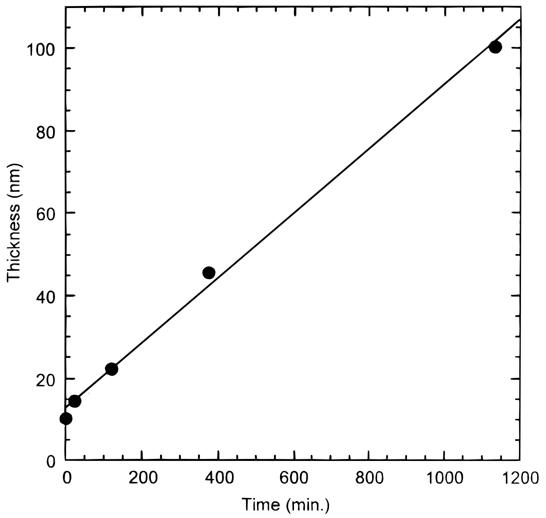


Figure 4. Plot of evolution of block copolymer layer thickness from a silicon surface composed of a 12 nm thick polystyrene layer as a function of reaction time. Conditions: methyl acrylate, 1% CuBr(dnNbpy)$_2$, 0.03% CuBr$_2$(dnNbpy)$_2$, 80 °C, bulk, drybox. Line: linear curve fit of data points.

in solution[7,8] or by the addition of the persistent radical prior to the commencement of the reaction.

Also shown in Figure 3 is the bulk ATRP of methyl acrylate from the same 2-bromoisobutyrate-modified silicon wafers. The ligand in the transition-metal complex was PMDETA.[21] Again, 1 mol % CuBr and 0.03% CuBr$_2$ both relative to monomer were used; the deactivator concentration was again determined from EPR measurements.[22,23] It was found that even after stirring in monomer for 30 min at 70 °C, the CuBr$_2$(PMDETA) complex was not entirely soluble. However, a linear increase in film thickness with time indicated that there was sufficient deactivator in solution to provide control over the growth of the brush chains.

Block Copolymers. An additional method toward verifying the functionality of a polymer prepared by ATRP is its use as a macroinitiator for the ATRP of the same or another monomer. Since XPS was not conclusive in determining the concentration of bromine, a chain extension of methyl acrylate from a surface composed of a polystyrene layer was performed. The polymerization was initiated from a 10 nm thick macroinitiator layer using 1 mol % CuBr(dnNbpy)$_2$ and 0.03 mol % CuBr$_2$(dnNbpy)$_2$ dissolved in the bulk monomer. Similar to polymerizations from the initiator bound to the surface, Figure 4 shows that a linear relationship was established between the increase in layer thickness and reaction time. The increase in thickness upon addition of the second block demonstrated that some fraction of the chains contained terminal bromine groups capable of participating in ATRP. Similar to the polystyrene-modified surfaces prepared by redox initiated polymerization, the final sample, more than 100 nm thick, had a blue appearance.

In another example, a 26 nm thick polystyrene layer was grown from two 2 × 3 cm silicon wafers primed with initiator. One of those substrates was then chain extended with *tert*-butyl acrylate using 1% CuBr(dnNbpy)$_2$ and 0.03% CuBr$_2$(dnNbpy)$_2$ at 90 °C. An increase in film thickness to 37 nm was measured by ellipsometry after a 4.5 h reaction time. IR reflection spectra of the two wafers are shown in Figure 5. Vibrational assignments and peak frequencies of the major absorptions in these spectra are listed in Table 1. The polystyrene spectrum (A) shows most of the stronger absorption peaks of reference transmission spectra of polystyrene films[24] at essentially unchanged peak wavenumbers. In addition, a weak absorption at 1244 cm^{-1} is assigned to the Si−O stretching absorption of the initiator bound to the silicon substrate via cross-polymerized siloxane headgroups.[25] The polystyrene/poly(*tert*-butyl-acrylate) sample (spectrum B) shows, in addition to the polystyrene peaks, some characteristic and intense absorptions of poly(acrylic acid) esters[24] (ν(C=O) at 1733 cm^{-1} and ν(C−O) at 1254/1159 cm^{-1}) and of the *tert*-butyl group[24,26] (ν_{as}(CH$_3$) at 2979 cm^{-1} and a doublet at 1393/1368 cm^{-1} from the symmetric methyl deformation mode). Note that the spectra in Figure 5 are plotted in the conventional absorbance scale; i.e., all absorption bands are inverted and point downward. As shown previously, IR absorptions on dielectric substrates undergo a band inversion as a function of the transition dipole moment tilt angle on the surface.[27] Under the current measurement conditions (p-polarized radiation at 80° incidence), negative (downward-pointing) absorptions are in conjunction with essentially unchanged, relative peak intensities in comparison to transmission spectra of isotropic reference samples,[24] a clear indication of a disordered, random orientation of the polymer chains in these films.

Tuning Surface Properties A benefit of radical polymerization over other techniques such as ionic or metathesis processes is the wide variety of monomers amenable to the process. Therefore, by choice of monomer one can tune the physical properties of the surface. One such property is hydrophilicity. Table 2 shows the water contact angles of a series of polymers prepared by ATRP from identically modified silicon wafers. In the first entry, a polystyrene layer 10 nm thick showed a contact angle of 90°. When that surface was chain extended with an additional 12 nm of poly(*tert*-butyl acrylate), the surface became slightly less hydrophilic (86°). The polyacrylate was then hydrolyzed to poly(acrylic acid) by refluxing a solution of 10% aqueous HCl over the wafer overnight. Ellipsometry showed that the thickness decreased to 16 nm most likely due to relaxation of the chains upon removal of the bulky *tert*-butyl groups.[28] The presence of the acid was confirmed by the significant decrease of the water contact angle from 86° to 18°. Finally, in a separate experiment a very hydrophobic surface composed of a poly(fluoro acrylate) was constructed. The large contact angle of 119° is typical of surfaces containing high fluorine contents. All of the above examples demonstrate the versatility of the ATRP technique to polymerize a variety of monomers from the surfaces.

It must be remembered that for efficient block copolymer formation it is necessary to obey a certain order of monomer addition, unless halogen exchange is employed.[29] Thus, styrene and acrylates can be used in any order, but addition of methyl methacrylate to polystyrene chain ends has low efficiency in ATRP systems. It would be interesting to verify whether the same rules apply to the chains grafted to the surface as previously reported.[4]

Simulation of Surface-Initiated Polymerization. Polymer layers obtained by surface-initiated polymerization constitute a specific case of polymer brushes. The brushes have been extensively studied theoretically as model systems; however, the most detailed information about the structure of brushes and the conformation of

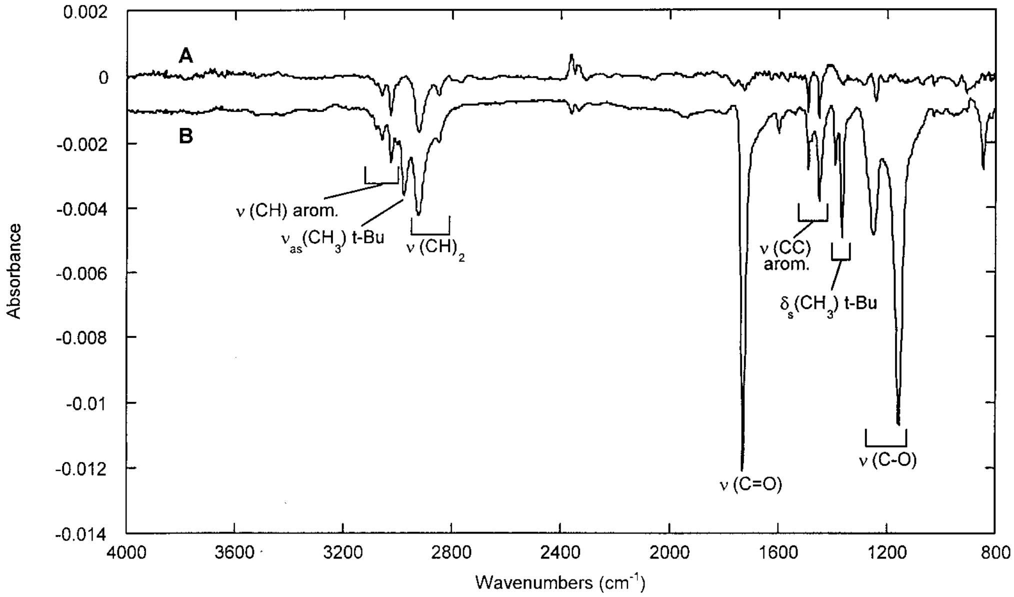


Figure 5. External reflection infrared spectra of (A) a film of polystyrene ($d = 26$ nm) on a silicon substrate primed with initiator ($d = 2.6$ nm) and (B) of the same sample with an additional layer of poly(*tert*-butyl-acrylate) ($d = 11$ nm) adsorbed on top.

Table 1. Peak Assignments and Wavenumbers (in cm^{-1}) for Infrared Reflection Spectra of a Polystyrene (PS) Film (Spectrum A of Figure 5) and a Polystyrene/Poly(*tert*-butyl acrylate) (PS + PA) Film (Spectrum B of Figure 5) on a Silicon Substrate

	sample	
vibration	PS	PS + PA
$\nu(CH)_{aromat.}$	3083	3083
	3061	
	3062	
$\nu_{as}(CH_3)_{t-butyl}$		2979
$\nu_{as}(CH_2)$	2924	2925
$\nu_s(CH_2)$	2850	2850
$\nu(C{=}O)$		1733
$\nu(CC)_{aromat}$	1493	1493
	1453	1453
$\delta_s(CH_3)_{t-butyl}$		1393
		1368
$\nu_{as}(SiO)$	1244	
$\nu(C{-}O)$		1254
		1159

Table 2. Composition, Thickness, and Water Contact Angles for Films Grown from Silicon Surfaces by ATRP

polymer	thickness (nm)	contact angle (deg)[a]
polystyrene	12.4	90 ± 1
poly(styrene-*b*-*tert*-butyl acrylate)	24.3	86 ± 4
poly(styrene-*b*-acrylic acid)	18.8	18 ± 2
poly(fluoro acrylate)[b]	7.7	119 ± 2

[a] Determined by the horizontal plane method immediately after application of the water droplet. [b] Poly(heptadecylfluorodecyl acrylate).

chains has been obtained from computer simulations.[30] The "cooperative motion algorithm" (CMA),[31] which is particularly suitable for simulation of dense polymer systems, has appeared very successful for simulation of both dry and wet layers of polymers consisting of chains grafted by one end at a surface.[32,33] Various specific features of the layers such as orientation and extension of chains, concentration profiles, and free end distributions have been established as mainly dependent on the length of chains, the density of grafting, and the interaction with the surrounding medium.

We would like to demonstrate here that the same methods as these used for simulation of model brushes can be applied for spatial simulations of the surface-initiated polymerization and for an analysis of the resultant structures in the layers. To represent the initial reaction medium, we start with a 3D model system of a lattice liquid considered between two parallel walls and artificially unlimited in two other directions due to the periodic boundary conditions. The liquid consists of beads occupying lattice sites and representing monomers that can polymerize to chains starting from initiators located at one of the walls. Chain growth is realized by bounding the initiator or an already existing free chain end with a neighboring free monomer. The bounding is considered to be irreversible and taking place with a certain probability which can be related to the reactivity. Both the bound and nonbound monomers remain mobile all the time so that the created structures can relax to equilibrium states. The simulation allows an analysis of the kinetics of polymerization which can be performed under various conditions given by a number of parameters such as reactivity and mobility of elements, concentrations of the monomer and initiator, and so on. A break of the reaction at any stage is possible which allows a detailed analysis of system structure relaxed to an equilibrium condensed state which would correspond to states analyzed usually for real systems. A simulation describes a moderately dense packing of the initiating sites at the surface ($\sigma = 0.25$, where $\sigma = 1$ corresponds to a fully packed surface). The polymerization does not include the activation/deactivation equilibria (like in real ATRP) but is represented by one type of active chain ends, like for example in anionic polymerization.

An example of results obtained according to the method described above is illustrated in Figures 6 and 7. Figure 6 shows concentration profiles and distributions of chain ends of the growing macromolecules at various times after activation of the initiator fixed at one wall. An increase of the layer thickness and density with time as well as considerable changes in distribution of chain ends is well seen. With the progress of the reaction, the chains grow but not necessarily uniformly

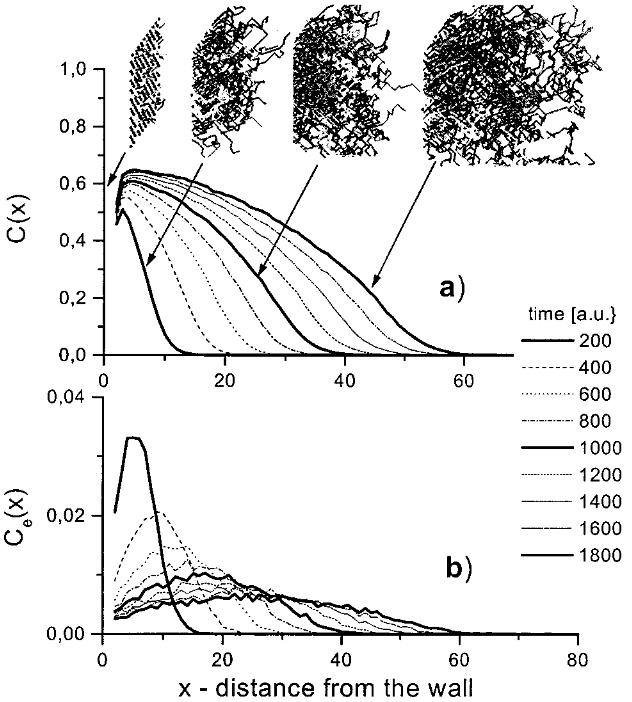


Figure 6. Evolution of polymer concentration distributions (a) and distributions of free chain ends (b) with time in a simulated system of polymers growing from the initiator attached to the wall (at $x = 1$, where x represents the distance from the wall). The insets in (a) illustrate the polymers in the simulated system at certain stages of the layer growth which corresponds to distributions shown in both (a) and (b) as thick solid lines. The distance from the surface is normalized by the lattice constant of the free lattice used to discrete the space for the simulated system.

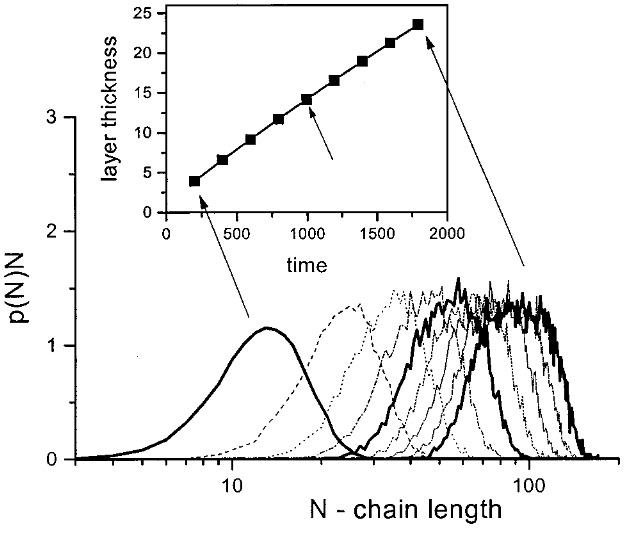


Figure 7. Evolution of chain length distributions with time in the simulated growth of the polymer layer by surface initiated polymerization. The inset shows the thickness of the dry layer vs time. Distributions presented by thick lines correspond to layer states in Figure 6 marked in the same way. Layer thickness is normalized by the lattice constant of the fcc lattice used to discrete the simulated system.

which can lead to changes of the chain length distributions, as illustrated in Figure 7 for the considered case. The highlighted stages correspond to $DP_n = 12$, 54, and 92. The polydispersities of chains grown from solution are $M_w/M_n = 1.11$, 1.06, and 1.06 and are larger than for unperturbed chains grown in solution (1.08, 1.02, and 1.01, respectively). Nevertheless, under such conditions, an almost linear dependence of the dry layer thickness on time has been observed, as in the reported experimental observations. For other conditions of the layer growth, e.g., with a higher density of the initiator at the surface ($\sigma > 0.5$), a much broader chain length distribution and a nonlinear conversion versus time dependence have been simulated. These effects will be discussed in detail in another publication. The simple example has been shown in order to illustrate that the films obtained by the surface-initiated polymerization should exhibit a distribution of chain lengths, which can considerably change the layer structure in comparison with the structure of brushes consisting of monodisperse polymers, as usually considered.[30,32,33] Distributions may become even broader for systems with additional bimolecular activation/deactivation equilibria which require diffusion of the activator and the deactivator to the chain end, as in ATRP systems.

Conclusions

Controlled radical polymerization techniques such as ATRP can be very effective tools in synthesizing dense, homogeneous polymer layers from initiators attached to the surface. This work and previous studies have shown that in controlled radical polymerizations the persistent radical effect must be considered when designing well-defined materials at interfaces. In other words, a sufficient concentration of deactivator must be available to provide control over chain lengths and distributions. The copper(II) can be supplied by termination of initiator molecules in the early stages of the polymerization or by addition of the transition metal complex prior to commencement of the reaction—no significant differences should be observed between the two techniques in terms of providing a monomodal distribution in molecular weight. The only factor affected is the kinetics of the reaction. In the former case, first-order consumption of monomer is dictated by the chains generated from the free initiator while in the latter, due to the extremely low concentration of alkyl halide bound to the surface and low monomer conversion, growth of polymer chains scales linearly with reaction time. Confirmation of the effectiveness of the ATRP process was obtained through chain extension of prepurified polymer layers with other monomers. Under ATRP conditions, linear increases in thickness with time were derived, demonstrating the preservation of chain functionality in an environment where termination is limited to very low levels.

It should be stressed that, in the design of such complex structures whether in solution or at an interface, understanding of the relative rates of chain propagation, equilibrium constants, and the influences of the end group, metal, and ligand in crossover reactions is important. Factors such as (macro)initiator functionality and blocking efficiency can have a profound influence on the physical properties of the resulting material. In the context of the current and related studies, understanding these parameters is important in the drive to specifically tune the properties of a surface. XPS results on the progressive decrease of Br absorption intensity may be correlated with the simulation of polymerization of surface layers which suggests broader molecular weight and chain end distributions. The simulation, when performed under various conditions and for various polymerization mechanisms, may become a useful tool for an estimation of relationships between the layer preparation method and the resulting structure.

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