Controlled Synthesis of Polymer Brushes by "Living" Free Radical Polymerization Techniques

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Received August 14, 1998; Revised Manuscript Received December 29, 1998

ABSTRACT: The preparation of a wide variety of unique polymer brush structures can be accomplished by "living" free radical polymerization of vinyl monomers from surface-tethered alkoxyamines or from tethered α-halo esters in the presence of $(PPh_3)_2NiBr_2$. The use of a "living" free radical process permits the molecular weight and polydispersity of the covalently attached polymer chains to be accurately controlled while also allowing the formation of block copolymers by the sequential growth of monomers from the surface. These block and random copolymer brushes have been used to control surface properties.

The control of surface properties is central to many areas of research and in numerous commercially important technologies ranging from biotechnology to advanced microelectronics.[1] One method that has been employed for controlling surface properties is the utilization of polymeric brushes. Traditionally, polymeric brushes are prepared from block copolymers where one block is strongly adsorbed to the surface with the other block forming the brush layer.[2] The noncovalent nature of this grafting strategy is a weakness, however, since desorption of the brush can subsequently occur. In addition, the demanding block copolymer synthesis limits the choice of functional groups for the block copolymer structure. To circumvent these deficiencies, an increasing amount of interest has been devoted to the covalent attachment of polymer chains to surfaces.[3] This can be accomplished in a number of ways, including a "grafting to" approach which involves the condensation of a functionalized polymer with the reactive surface groups of an appropriate substrate. While successful, this approach is inherently limited by the crowding of chains at the surface, which hinders the diffusion of chain ends to the surface for further attachment.[4] An alternative approach, pioneered by Sogah, involves the attachment of reactive units to the surface, followed by addition of an initiating moiety in one or more steps. While successful, this multistep approach has the complication of possible side reactions and ambiguities in the composition of the initiator layer.[5]

Perhaps the best approach to the synthesis of polymeric brushes is the recently reported strategy of Prucker and Rühe.[6] In this approach, a preformed monochlorosilyl functionalized azo initiator was synthesized and covalently attached to a variety of solid surfaces. Using normal free radical polymerization conditions, linear chains are then grown from the surface to give the covalently attached polymer brushes with high graft densities and molecular weights. The advantages of this approach are that the density of initiator groups at the surface can be easily varied, and functionalized polymer chains can be readily prepared. While this approach is extremely successful, the use of traditional free radical procedures precludes the formation of block copolymer brushes or accurate control of polymer structure. To build upon these promising results, "living" free radical procedures have been applied to the synthesis of well-defined and novel polymeric brushes.

"Living" free radical polymerizations have been a topic of considerable interest in recent years and have a number of advantages over traditional free radical procedures.[7,8] For this application, the potential advantages of a "living" free radical system are that the alkoxyamine or α-haloester initiating groups are more stable than the azo-based initiators of Rühe.[9] The controlled nature of the polymerization process also permits structural characteristics (MW, PD, branching, etc.) of the polymer brush to be readily varied. An added benefit is the ability to prepare block copolymers by the sequential activation of the dormant chain end in the presence of different monomers. In this report we detail the use of surface bound initiators and "living" free radical procedures for the preparation of a range of polymeric brushes with accurate control over the chain structure.[10] Preliminary reports detailing the use of ATRP procedures by Wirth and Tsujii for the generation of polymer brushes has recently appeared.[11]

Experimental Section

Commercial reagents were obtained from Aldrich and used without further purification. Analytical TLC was performed on commercial Merck plates coated with silica gel GF_{254} (0.25 mm thick). Silica gel for flash chromatography was Merck Kiselgel 60 (230−400 mesh). Nuclear magnetic resonance was performed on a Bruker AM 250 FT-NMR spectrometer using deuterated solvents with the solvent peak as a reference. Gel permeation chromatography was carried out on a Waters chromatograph connected to a Waters 410 differential refractometer with THF as the carrier solvent. X-ray photoelectron spectra were collected using a Perkin-Elmer Physical Electronics 5100 spectrometer using Mg Kα (200 W, 15 kV)

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10.1021/ma981290v CCC: $18.00
Published on Web 02/04/1999

(achromatic) excitation. Contact angle measurements were made with a Rame-Hart telescopic gonimeter using a Gilmont syringe with a 24-gauge flat-tipped needle. Water was used as the probe fluid. Dynamic advancing and receding angles were recorded while water was added to and withdrawn from the drop, respectively.

1-(4′-Oxa-2′-phenyl-11′-dodeceneoxy)-2,2,6,6-tetramethylpiperidine, 3. To a solution of the hydroxy functionalized alkoxyamine, **2**[12] (5.54 g, 20.0 mmol), in dry tetrahydrofuran (100 mL) was added sodium hydride (60% dispersion in oil, 1.0 g, 25.0 mmol), and the reaction mixture was stirred at room temperature under argon for 15 min. A solution of 1-bromooct-8-ene (5.0 g, 26.2 mmol) in dry tetrahydrofuran (10 mL) was then added dropwise, and the reaction mixture was heated at reflux for 16 h, cooled, and evaporated to dryness. The residue was partitioned between water (150 mL) and dichloromethane (150 mL), and the aqueous layer was extracted with dichloromethane (2 × 50 mL). The combined organic extracts were then dried and evaporated to dryness. The crude product was purified by flash chromatography eluting with 1:1 dichloromethane/hexane and gradually increasing to 4:1 dichloromethane/hexane to give the alkene, **3**, as a colorless oil (6.27 g, 81%). IR (neat) 3050, 2970, 1640, 1470, 1380, and 1140 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.60 and 1.00 (each br s, 6H, C*H*$_3$), 1.05−1.50 (complex m, 20H), 2.00 (q, J = 7 Hz, 2H, =CC*H*$_2$), 3.25 (ABq, 2H, C*H*), 3.55, 3.92, 4.77 (each ABq, 1H, C*H*), 4.92 (t of t, J = 1 and 7 Hz, 2H, =C*H*), 5.75 (ABq, 1H, =C*H*), and 7.20−7.33 (complex m, 5 H, Ar*H*); ^{13}C NMR ($CDCl_3$) δ 21.26, 23.39, 34.14, 34.45, 48.78, 48.88, 59.99, 60.20, 63.32, 83.30, 126.65, 126.95, 128.06, and 145.45; mass spectrum (FAB) 387.

4-(2′-Oxahept-6′-ene)styrene, 6. To a solution of pent-4-enol (17.2 g, 200 mmol) in dry tetrahydrofuran (200 mL) was added sodium hydride (60% dispersion in oil, 8.80 g, 220 mmol), and the reaction mixture was stirred at room temperature under argon for 15 min. A solution of (*p*-chloromethylstyrene, **5** (22.9 g, 150 mmol), in dry tetrahydrofuran (25 mL) was then added dropwise, and the reaction mixture was heated at reflux for 16 h, cooled, and evaporated to dryness. The residue was partitioned between water (300 mL) and dichloromethane (300 mL), and the aqueous layer was extracted with dichloromethane (2 × 150 mL). The combined organic extracts were then dried and evaporated to dryness. The crude product was purified by flash chromatography eluting with 1:9 dichloromethane/hexane and gradually increasing to 4:1 dichloromethane/hexane to give the alkene, **6**, as a colorless oil (26.4 g, 87%). IR (neat) 3050, 2970, 1640, 1470, 1380, and 1140 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.70 (quintet, 2H, C*H*$_2$), 2.13 (quartet, 2H, C*H*$_2$), 3.49 (t, 2H, C*H*$_2$), 4.56 (s, 2H, C*H*$_2$), 4.94−5.06 (complex m, 2H, alkene =C*H*$_2$), 5.25 (d, 1H, styrene =C*H*), 5.70−5.87 (complex m, 2H, styrene and alkene =C*H*), 6.67 and 6.74 (d or d, 1H, styrene =C*H*), and 7.29 and 7.38 (ABq, 4 H, Ar*H*); ^{13}C NMR ($CDCl_3$) δ 29.00, 30.37, 69.71, 72.62, 113.68, 114.75, 126.23, 127.82, 136.60, 136.91, 138.30; mass spectrum (FAB) 202.

1-(4-(2′-Oxahept-6′-ene)phenyl)-1-(2″,2″,6″,6″-tetramethyl-1-piperidinyloxy)ethyl, 4. To a solution of the styrene derivative, **6** (25.0 g, 124 mmol), and 2,2,6,6-tetramethylpiperidinyloxy (TEMPO) (19.3 g, 124 mmol) in 1:1 toluene/ethanol (750 mL) was added [*N*,*N*′-bis(3,5-di-*tert*-butylsalicylidene)-1,2-cyclohexanediaminato]manganese(III) chloride (11.8 g, 18.6 mmol), followed by di-*tert*-butyl peroxide (18.1 g, 124 mmol) and sodium borohydride (9.35 g, 248 mmol). The reaction mixture was then stirred at room temperature for 12 h, evaporated to dryness, and partitioned between dichloromethane (250 mL) and water (400 mL), and the aqueous layer was further extracted with dichloromethane (3 × 200 mL). The combined organic layers were then dried and evaporated to dryness, and the crude product was purified by flash chromatography eluting with 1:9 dichloromethane/hexane and gradually increasing to 2:1 dichloromethane/hexane. The desired alkene functionalized alkoxyamine, **4**, was obtained as a colorless oil. Yield 65%; ^1H NMR ($CDCl_3$) δ 0.65, 1.00, 1.14, 1.24 (each br s, 12H, C*H*$_3$), 1.28−1.58 (m, 6H, C*H*$_2$), 1.46 (d, J = 4 Hz, 3H, C*H*$_3$), 1.72 (quintet, 2H, C*H*$_2$), 2.14 (quartet, 2H, C*H*$_2$), 3.50 (t, 2H, C*H*$_2$), 4.48 (s, 2H, C*H*$_2$), 4.76 (quartet, 1H, C*H*), 4.92−5.03 (complex m, 2H, alkene =C*H*$_2$), 5.72−5.88 (complex m, 1H, alkene =C*H*), and 7.25−7.30 (m, 4 H, Ar*H*); ^{13}C NMR ($CDCl_3$) δ 17.23, 20.34, 23.60, 28.96, 30.36, 34.24, 40.36, 59.66, 69.66, 72.83, 82.90, 114.70, 126.57, 127.43, 136.97, 138.32, and 145.17; mass spectrum (EI) *m*/*z* 359; Anal. Calcd for $C_{23}H_{37}NO_2$: C, 76.8; H, 10.37; N, 3.90. Found: C, 77.0; H, 10.28; N, 4.01.

1-(4-(2′-Oxahept-6′-ene)phenyl)-1-(2″,2″,6″,6″-tetramethyl-1-piperidinyloxy)ethyl, 4. To a solution of pent-4-enol (8.6 g, 100 mmol) in dry tetrahydrofuran (100 mL) was added sodium hydride (60% dispersion in oil, 4.40 g, 110 mmol), and the reaction mixture was stirred at room temperature under argon for 15 min. A solution of the chloromethyl-substituted alkoxyamine, **5** (15.5 g, 50 mmol), in dry tetrahydrofuran (25 mL) was then added dropwise, and the reaction mixture was heated at reflux for 16 h, cooled, and evaporated to dryness. The residue was partitioned between water (300 mL) and dichloromethane (300 mL), and the aqueous layer was extracted with dichloromethane (2 × 150 mL). The combined organic extracts were then dried and evaporated to dryness. The crude product was purified by flash chromatography eluting with 1:1 dichloromethane/hexane and gradually increasing to 3:1 dichloromethane/hexane to give the alkene, **4**, as a colorless oil (16.7 g, 93%). The spectroscopic date for this material were identical in all respects to those obtained above.

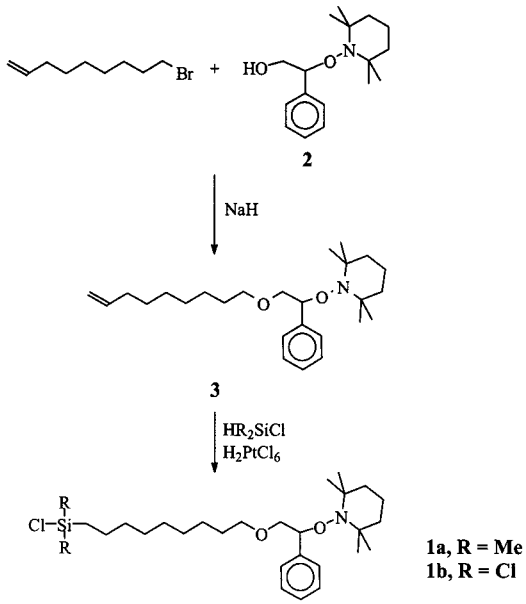
Pent-4′-enyl 2-bromo-2-methylpropionate, 9. 2-Bromo-2-methylpropionyl bromide (34.5 g, 150 mmol) was added in a dropwise fashion to a stirred solution of 5-hexen-1-ol (15.0 g, 150 mmol) and triethylamine (18.1 g, 179 mmol) in dry dichloromethane (80 mL). After stirring at 0 °C under argon for 1 h, the reaction mixture was allowed to warm to room temperature where it was stirred for an additional 2.5 h. The precipitated triethylamine hydrochloride was removed by filtration, and the solution was washed with aqueous ammonium chloride (saturated) and water. The dichloromethane was then removed, and the crude product was purified by vacuum distillation (78 °C/10 mm) to give **9** as a colorless oil. Yield 70%; ^1H NMR ($CDCl_3$) δ 1.44 (quintet, 2H, C*H*$_2$), 1.65 (quartet, 2H, C*H*$_2$), 1.93 (s, 3H, C*H*$_3$), 2.08 (q, 2H, C*H*$_2$), 4.16 (t, 2H, C*H*$_2$), 4.91−5.04 (complex m, 2H, alkene =C*H*$_2$), and 5.70−5.85 (complex m, 1H, alkene =C*H*); ^{13}C NMR ($CDCl_3$) δ 25.05, 27.77, 30.76, 33.17, 65.91, 114.90, 138.22, and 171.71; mass spectrum (EI) *m*/*z* 234/236 (1:1).

(5′-Trichlorosilylpentyl) 2-bromo-2-methylpropionate, 10, and General Procedure for Hydrosilylation. To a solution of the alkene, **9** (0.75 g, 3.20 mmol), in trichlorosilane (15.0 mL, 149 mmol) was added a 1:1 ethanol/dimethoxyethane solution of chloroplatinic acid, H_2PtCl_6 (15 mg, 2.5 mL), and the reaction mixture was stirred at room temperature under argon in the dark for 14 h. [If desired, the extent of reaction can be determined by ^1H NMR spectroscopy.] Dry toluene (5 mL) was then added and the excess trichlorosilane removed under reduced pressure; dry dichloromethane (15 mL) was then added and removed under reduced pressure. The crude product was then passed through a short column of dry sodium sulfate, the column was washed with dry dichloromethane (15 mL), and the dichloromethane was removed under reduced pressure. The toluene solution of the trichlorosilyl derivative was then used without further purification.

The same procedure was employed for the alkoxyamine derivatives **1**, as well as for reactions involving dimethylchlorosilane.

Reaction of 10 with Silicon Wafers—General Procedure for Formation of Surface Bound Initiators. Into a flame-dried reaction flask was placed a freshly cleaned silicon wafer, followed by dry toluene (5 mL) and the crude trichlorosilyl derivative **10** (1 mL of above toluene solution, ca. 0.6 mmol). The reaction flask was then placed under argon, triethylamine (1.0 mL) was added dropwise, and the reaction mixture was left to stand for 18 h. The silicon wafer was then removed and washed repeatedly with methanol followed by dichloromethane and then left to stand in dichloromethane for 18 h. This procedure was then repeated to give the functionalized wafers, which were either used immediately or stored

Scheme 1



under standard conditions. No loss of activity was observed on storage for several weeks.

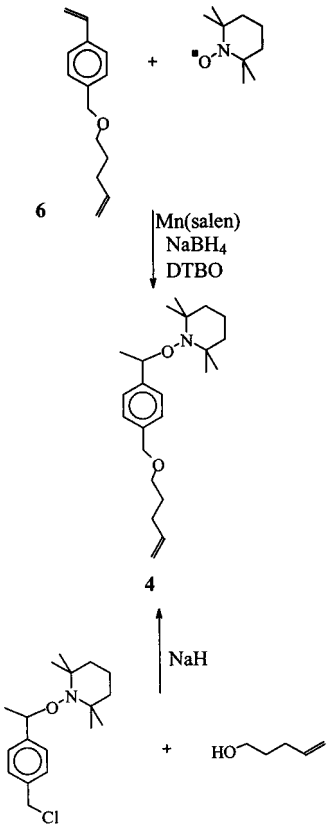
Formation of Polymer Brushes from Surface Grafted Alkoxyamine Initiators. To a reaction flask containing a functionalized silicon wafer was added a mixture of styrene (5.20 g, 50 mmol) and 1-phenyl-1-(2′,2′,6′,6′-tetramethyl-1′-piperidinyloxy)ethane, **8** (26.1 mg, 0.1 mmol). The flask was then purged with argon, heated at 125 °C for 24 h, and cooled, and the solidified reaction mixture was dissolved in dichloromethane; precipitation of this solution into methanol (500 mL) gave the polystyrene formed from the "added" initiator which was analyzed using standard techniques. The silicon wafer was then removed, continuously extracted with dichloromethane for 16 h, and dried. The polymer brush was then analyzed by XPS, contact angle measurements, IR, and ellipsometry.

Formation of Polymer Brushes from Surface Grafted α-Bromoester Initiators. To a reaction flask containing a functionalized silicon wafer was added a mixture of methyl methacrylate (6.90 g, 69 mmol), ethyl 2-bromoisobutyrate, **11** (29.5 mg, 0.15 mmol), and bis(triphenylphosphine)nickel(II) bromide (110 mg, 0.15 mmol). The flask was then purged with argon, heated at 100 °C for 3 h, and cooled, and the solidified reaction mixture was dissolved in dichloromethane; precipitation of this solution into methanol (500 mL) gave the poly(methyl methacrylate) formed from the "added" initiator which was analyzed using standard techniques. The silicon wafer was then removed, continuously extracted with dichloromethane for 16 h, and dried. The polymer brush was then analyzed by XPS, contact angle measurements, IR, and ellipsometry.

Results and Discussion

The surface active alkoxyamines **1**, were synthesized by reaction[13] of the hydroxy functionalized derivative, **2**, with 1-bromooct-8-ene in the presence of sodium hydride followed by hydrosilylation of the resulting alkene derivative, **3**, with either dimethylchlorosilane or trichlorosilane (Scheme 1). In the case where a more reactive linkage was required, the dialkyl ether of **3** was replaced with a benzyl ether to give **4**. The preparation of **4** was accomplished by two different synthetic procedures, either reaction of the chloromethyl-substituted alkoxyamine, **5**, with pent-4-enol in the presence of sodium hydride to give **4** in 93% yield after purification or, alternatively, the dialkene derivative, **6**, could be reacted with TEMPO in the presence of Jacobsen's

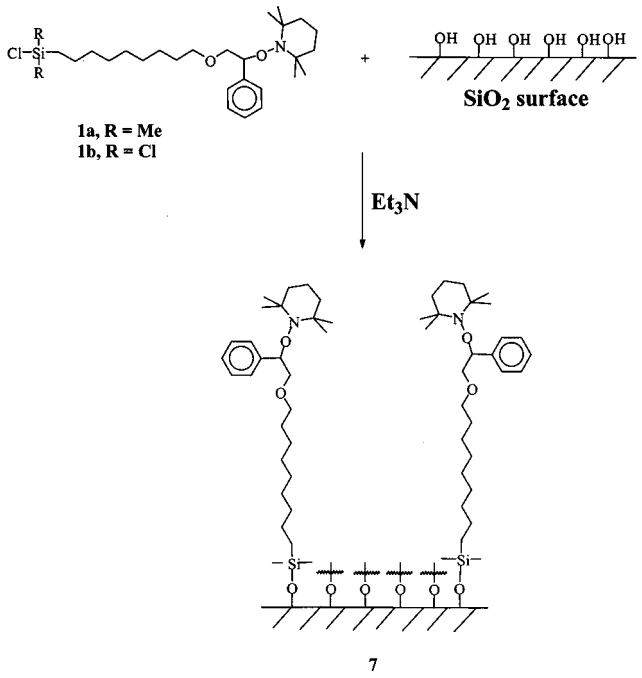
Scheme 2



catalyst {[*N*,*N*′-bis(3,5-di-*tert*-butylsalicylidene)-1,2-cyclohexanediaminato]manganese(III) chloride} under mild reaction conditions to give **4** in 65% yield. The notable feature of this second procedure is that the addition of the nitroxide occurs exclusively at the styrenic double bond (Scheme 2). This high degree of regioselectivity demonstrates the usefulness of this manganese-catalyzed procedure for the formation of functionalized alkoxyamines.[14] Formation of the trichloro- and monochlorosilyl derivatives **1a** and **1b** was then accomplished under standard conditions from the corresponding silyl hydride and chloroplatinic acid. The disappearance of the alkene resonances could be conveniently monitored by ^{1}H NMR spectroscopy, and after complete reaction, the crude product was filtered through sodium sulfate and used without further purification. Reaction of **1** with the surface silanol groups of silicon wafers or silica gel particles was catalyzed by triethylamine to give the desired surface bound alkoxyamine groups, **7** (Scheme 3). The covalent attachment of the alkoxyamine groups was demonstrated by a number of analytical techniques such as XPS, ellipsometry, and grazing angle incidence infrared spectroscopy.

Initial attempts to control polymer growth from the surface bound initiators under standard "living" free radical conditions was unsuccessful due to the extremely low concentration of initiating sites with respect to the monomer concentration. Attempts to dilute the concentration of monomer units in the polymerization mixture were also unsuccessful due to the severe reduction in the rate of polymerization at monomer concentrations of less than 25 wt %. To overcome these problems and to control the surface-initiated polymerization, it was necessary to add predetermined amounts of "free" alkoxyamine initiator to the reaction mixture. As shown previously,[15] the mediating radicals are not associated

Scheme 3



with a single chain end and are free to diffuse throughout the polymerization mixture. The addition of "free" alkoxyamine, therefore, creates an overall concentration of nitroxide in the polymerization mixture, which controls the chain growth of both the immobilized and soluble initiators. The polymer chains formed from the addition of "free" alkoxyamine are, however, soluble and can be easily separated from the covalently bound polymer brushes by washing with the appropriate solvent. For example, the functionalized silicon wafers prepared from the trichloro derivative **1b** were heated at 125 °C in a 500:1 molar mixture of styrene and the unimolecular initiator, **8**, for 18 h under an inert atmosphere. Exhaustive extraction of the wafer with refluxing dichloromethane[16] was shown to remove any noncovalently bound polymer chains completely. Analysis of the grafted polymer brush by XPS, FTIR, and contact angle measurements revealed a covalently attached polystyrene layer which was shown by ellipsometry to have a thickness of 47 nm. Assuming that the molecular weight of the covalently bound polymer chains is related to the molecular weight of the "bulk" polymer, control of the brush thickness should be afforded by varying the ratio of added initiator to monomer. Growing longer polymer chains in solution should, therefore, lead to thicker polymer brushes. As can be seen in Figure 1, this is observed experimentally with an almost linear relationship between brush thickness and molecular weight of "bulk" polymer being obtained. These results demonstrate that chain growth from the surface is a controlled process with a degree of "living" character to it and that the brush thickness, which corresponds to the chain length, can be easily manipulated. The "living" nature was further probed by examining the relation between conversion and brush thickness for the polymerization of a 1000:1 molar mixture of styrene and the unimolecular initiator, **8**, in the presence of functionalized silicon wafers prepared from the trichloro derivative **1b**, at 125 °C. As expected for a nitroxide mediated "living" free radical, the molecular weight, M_n, of the "bulk" chains increased in a linear fashion with conversion. Interestingly, the thickness of the dried polymer brush also varies in a linear fashion with conversion (Figure 2). These two observations demonstrate that the growth of the polymer chains in the bulk and from the surface is a "living" or controlled process. The degree of similarity also suggests that significant exchange of mediating nitroxide radicals between the surface bound chains and "bulk" chains is also occurring which is consistent with results in solution for mixtures of functionalized initiators.[15] Matching results were obtained with the monochloro derivative **1a**, though the degree of control was lower than for the trichloro derivative **1b**. This slight difference in behavior may actually be due to the stability of the respective initiator layers, rather than actual differences in the polymerization process.

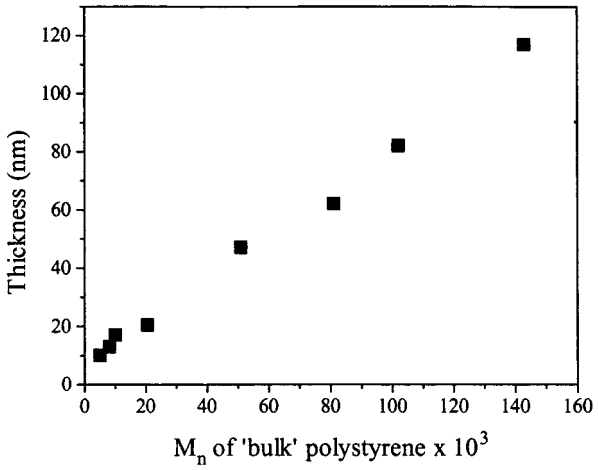


Figure 1. Variation in thickness of polymer brush with molecular weight, M_n, of "bulk" polystyrene.

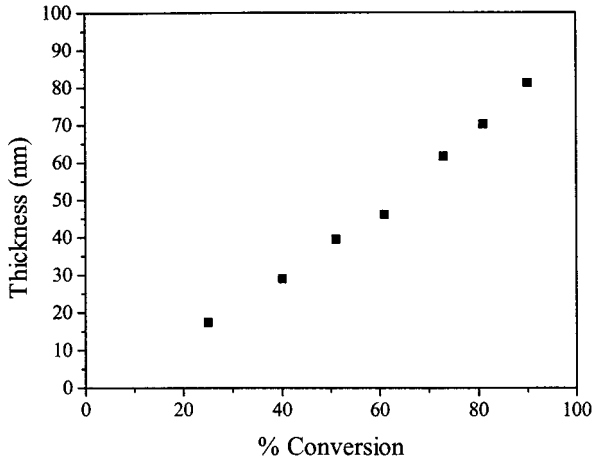


Figure 2. Variation in thickness of polystyrene brush with conversion for the polymerization of styrene (1000 equiv) in the presence of **8** (1 equiv) and an alkoxyamine functionalized silicon wafer.

From the data in Figure 1, a cross-sectional area per chain, A_x, can be determined from the molecular weight of the chain, M, and the corresponding film thickness, t, by

$$A_x = \frac{M}{t\rho N_A}$$

where ρ is the mass density (1.05 g/cm^3 for polystyrene) and N_A is Avogadro's number. Above a molecular weight of $\sim$ 20 000 amu, an average value of A_x of ca. 200 Å^2 is found. If we compare this to the cross-sectional area of

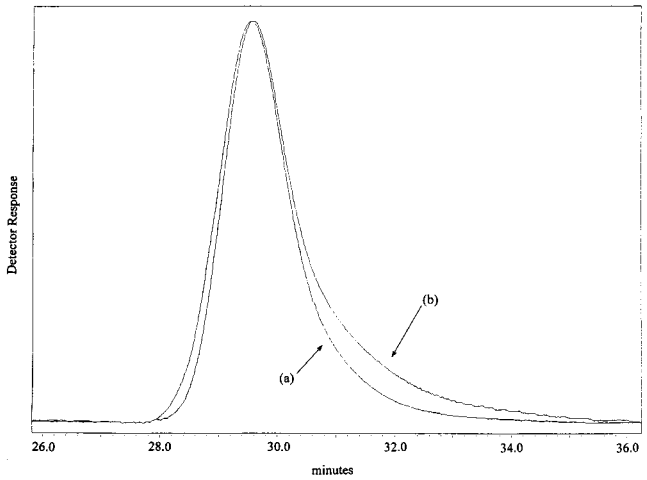


Figure 3. Comparison of the GPC traces for (a) the "cleaved" polystyrene and (b) the "bulk" polystyrene obtained from the polymerization of a 500:1 mixture of styrene and **8** in the presence of alkoxyamine functionalized silica gel.

a polystyrene chain anchored to the interface in a lamellar block copolymer microdomain structures where A_x is ca. 900 Å^2, it is seen that the chains grown from the solid substrate are quite stretched. This is consistent with the findings of Rühe et al.[6] Such a high packing density, i.e., low cross-sectional area, is most difficult, if not impossible, to achieve by the "grafting to" technique. It should be noted that when M_n is less than 20 000 amu, a slight curvature in the data is found. In these cases, $A_x \sim 100$ Å^2; i.e., the chains are very highly extended from the surface. This is a highly unfavorable condition since the elastic energy required to maintain this amount of extension is quite high. With increasing molecular weight there is a decrease in the number of chains growing from the surface, suggesting possible termination reactions are occurring at higher molecular weights.

To further understand the growth characteristics of the surface initiated polymerization, it was necessary to cleave these chains from the surface at their point of attachment. The detached polymer chains could then be analyzed by standard techniques, i.e., GPC, ^{1}H NMR, etc., to give molecular weight, polydispersity, and other structural information. To accomplish this, the benzylic alkoxyamine precursor, **4**, was used since cleavage of the benzyl ether is much more facile than the dialkyl ether present in **3**. In addition, silica gel particles were used instead of silicon wafers to increase the surface area for functionalization and, therefore, the amount of polymer prepared by the surface initiated polymerization. The procedure used for derivitization of dried silica gel with the chlorosilyl derivatives **1** was the same as detailed above, and the initiator functionalized silica gels could be stored for extended periods without significant loss of initiator efficiency. To effect polymerization, the functionalized particles were added to various mixtures of styrene and **8** and heated at 125 °C for 16 h. A series of extraction and centrifugation steps were then performed to separate the grafted silica particles from nongrafted polystyrene chains. As in our previous work with graft and star copolymers,[17] the presence of a cleavable ether linkage permits the grafted polymer chains to be cleaved from the silica particles by reaction with an excess of trimethylsilyl iodide. For example, reaction of grafted silica particles, prepared from a 500:1 mixture of styrene and **8**, with trimethylsilyl iodide afforded a linear polystyrene derivative with a molecular weight, M_n, of 51 000 and a polydispersity of 1.14. Note that this corresponds very closely to the observed M_n for the "bulk" polystyrene of 48 000, while the polydispersity, PD = 1.20, is slightly higher than for the surface grafted case. It is also important to note that the GPC peak shape for the grafted material was almost symmetrical, which is in contrast to the peak shape for the material grown in the bulk which shows a low molecular weight tail, characteristic of TEMPO mediated "living" free radical polymerizations (Figure 3). The greater degree of control observed for the grafted material is primarily due to the removal of polymer chains formed by autopolymerization, which contribute

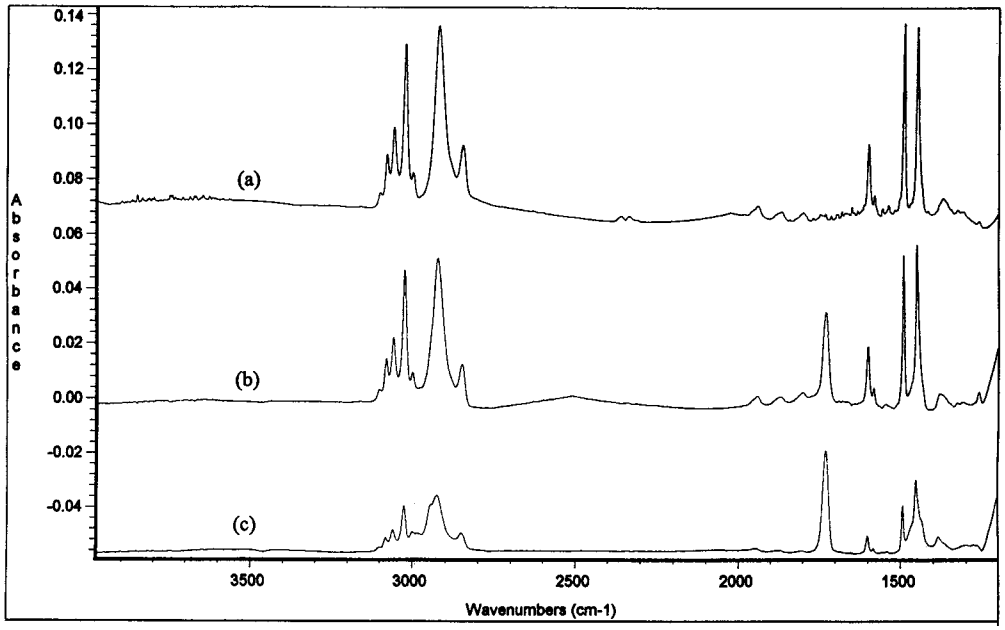
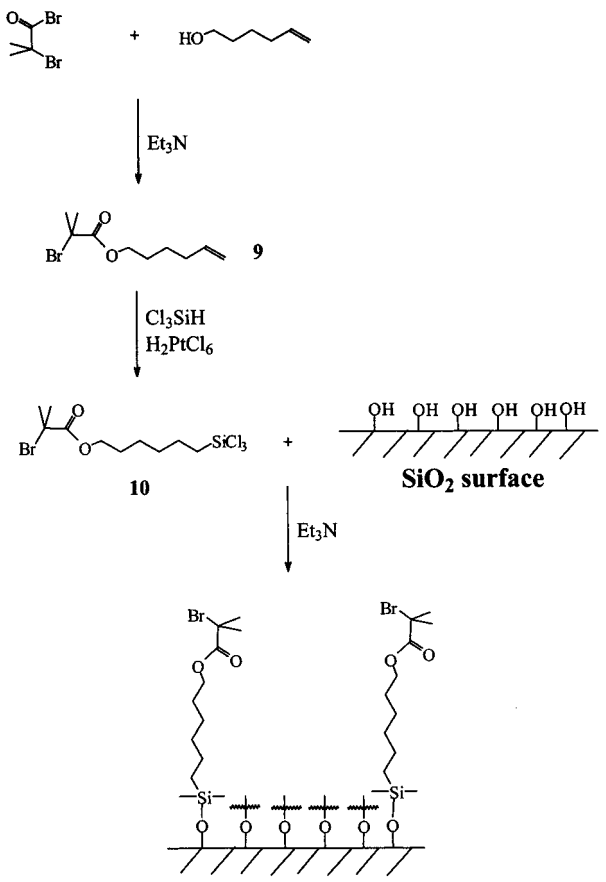


Figure 4. Comparison of IR spectra for (a) polystyrene brush, 27 nm, and (b) block copolymer brush composed of an initial polystyrene block, 102 nm, and a second block of 1:1 styrene/methyl methacrylate, 26 nm, and (c) block copolymer brush composed of an initial polystyrene block, 27 nm, and a second block of 1:1 styrene/methyl methacrylate, 26 nm.

Scheme 4



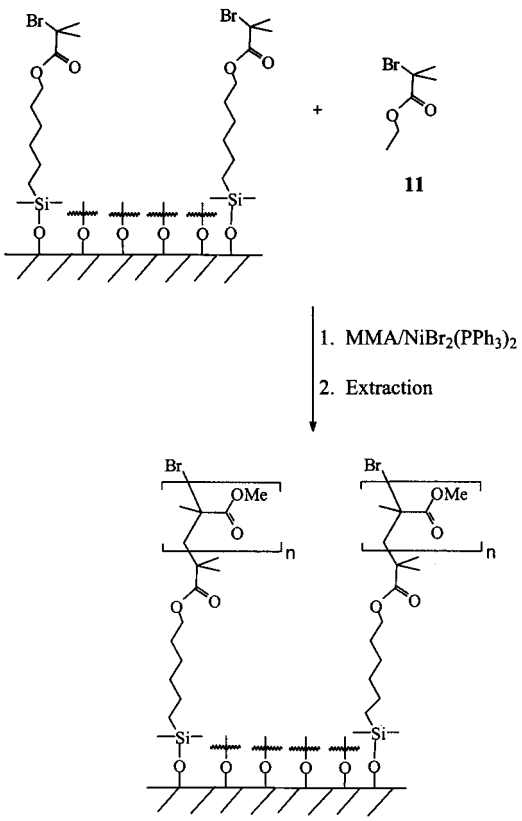
significantly to the lower molecular weight tail and asymmetric peak shape, being soluble and therefore removed by solvent washing. It should also be noted that the curvature of the silica particles promotes easy access of the monomer to the growing chain end since the segmental density decreases with increasing molecular weight or distance from the surface of the particle. This alleviates any crowding issues that would tend to retard growth of the chains and lead to a broader molecular weight distribution, skewed toward lower molecular weights. This, for example, is one possible origin for the initial nonlinearity observed in Figure 1. Nonetheless, these results demonstrate that the covalent attachment of alkoxyamine initiators to a surface does not inhibit or affect the polymerization to any detectable degree, and polymer brushes with low polydispersity and controlled molecular weight are obtained.

One of the unique features of "living" free radical processes is the presence of a dormant alkoxyamine groups at the chain end(s) of the isolated polymer which permits reactivation of the polymerization and leads to block copolymer formation. To investigate whether such chemistry is still applicable to grafted polymer brushes, alkoxyamine functionalized silicon wafers were initially heated at 120 °C in the presence of various mixtures of styrene and **8** for 16 h. The wafers were then exhaustively washed with dichloromethane to remove any nonbonded polymer brushes, dried, and stored at room temperature. Analysis of the wafers showed polystyrene brushes with thicknesses of 27, 76, and 102 ± 3 nm. The wafers were then heated separately at 120 °C in the presence of a 1:1 mixture of methyl methacrylate and styrene, and in each case the total ratio of monomer to "added" initiator, **8**, was 250:1. After removal and washing of the wafers, a significant increase in the thickness of the polymer brush was observed with the increase being 26 ± 3 nm in each case. This increase of 26 nm correlates closely with that expected for a polymer brush grown from a well-defined initiator layer in the presence of a 250:1 mixture of monomer and **8**. This indicates that a high percentage of the ends of the attached chains are active alkoxyamine groups capable of further initiation, which can be used for the preparation of block copolymers. Further evidence for block formation comes from infrared analysis of the polymer brushes. As can be seen in Figure 4, the initial brush reveals absorbencies at 3100−2800, 1601 cm^{-1}, etc., which is characteristic of a polystyrene brush. Reinitiation of the polymer brush in a mixture of methyl methacrylate and styrene leads to block copolymer brushes, for example, the block copolymer brush (b) composed of an initial polystyrene block, 102 nm, and a second block of 1:1 styrene/methyl methacrylate, 26 nm, and the block copolymer brush (c) composed of an initial polystyrene block, 27 nm, and a second block of 1:1 styrene/methyl methacrylate, 26 nm. Both block copolymer brushes show the characteristic polystyrene absorbance at 1601 cm^{-1}; however, a new absorbance at 1725 cm^{-1} is clearly visible and is characteristic of the methyl methacrylate units in the second block. As expected, the ratio of these two absorbances changes on going from (b) to (c) since the length of the second PMMA/PSt block remains constant while the initial polystyrene block in (b) is significantly longer than in (c). The relative ratio of methyl methacrylate is therefore greater in (c) than in (b) and is in agreement with the observed infrared spectra.

Additional evidence was also gained from reflectivity experiments on a functionalized wafer which was initially polymerized in the presence of styrene followed by washing and a second subsequent polymerization in the presence of deuterated d_8-styrene. Analysis of the wafer by ellipsometry showed an increase in thickness of 20 nm, which correlates closely with the reflectivity data. These results add further support to the concept that tethering alkoxyamine initiators to a solid support does not change their polymerization behavior and that well-defined block copolymer brushes can be readily prepared.

The ability to form well-defined random copolymers from simple monomer mixtures is one of the advantages of "living" free radical procedures when compared to other living polymerization procedures such as anionic and cationic processes.[18] This feature can be exploited in the design of random copolymer brushes, which have the unique opportunity of accurately controlling the surface properties by varying the molar ratio of individual monomers.[19] To demonstrate this point, random copolymer brushes of styrene and 2-hydroxyethyl methacrylate (HEMA) were prepared on silicon wafers. Infrared analysis showed absorbances for both the HEMA and styrenic monomer units, and the variation in relative absorptions corresponded well with the feed ratios, confirming the structure of the brush copolymers. Interestingly, the advancing water contact angle showed essentially no variation with increasing amounts of HEMA; however, the receding contact angle revealed a significant decrease in water contact angle with increasing amounts of HEMA in the random copolymer brush. These results demonstrate not only that surface properties, such as hydrophilicity, etc., can be readily con-

Scheme 5



trolled and manipulated by this random copolymer brush approach but also that the surface may undergo a significant reorganization on exposure to different environments. In the dry state, on exposure to air the surface is hydrophobic, irrespective of the HEMA content, and implies that a significant amount of styrene units are located at the surface. However, on exposure to an aqueous environment, the surface becomes progressively more hydrophilic, indicating that a reorganization of the random copolymer chains occurs and a significant number of HEMA residues have migrated to the surface in response to the presence of water.

An alternative method to nitroxide mediated "living" free radical procedures is the recently introduced atom transfer radical polymerization (ATRP) which has attracted considerable attention[8] and, in a number of aspects, is complementary to alkoxyamine-based systems. For these reasons it was decided to extend the concept of preparing well-defined polymer brushes by "living" free radical procedures to ATRP-based systems. The surface active initiating systems were prepared by initial reaction of hex-5-enol with 2-bromo-2-methylpropionyl bromide in the presence of triethylamine to give the alkene terminated ester, **9**. Hydrosilylation of **9** with trichlorosilane afforded the trichlorosilyl derivative **10**, which could then be attached to a variety of silanol surfaces using the same chemistry as described above (Scheme 4). Polymerization of methyl methacrylate from functionalized silicon wafers was then accomplished by the use of ethyl 2-bromo-2-methylproprionate **11**, as a "added" or controlling initiator in the presence of bis(triphenylphosphine)nickel(II) bromide.[20] In this case, the thickness of the poly(methyl methacrylate) brush could also be controlled in a systematic way by varying the ratio of **11** and MMA in the polymerization mixture (Figure 5). A linear relationship was also observed between brush thickness and conversion which

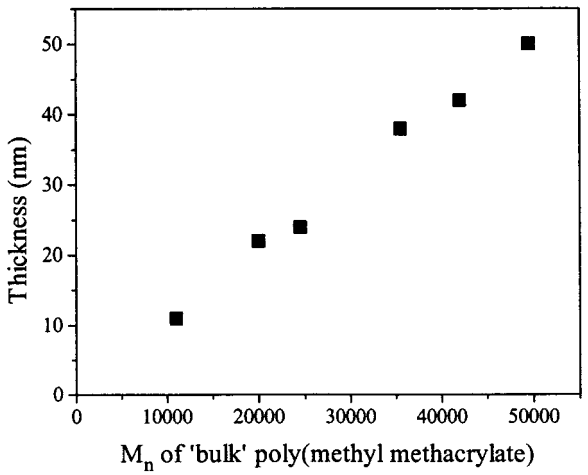


Figure 5. Variation in thickness of poly(methyl methacrylate) brush with molecular weight, M_n, of "bulk" PMMA.

suggests that the growth of polymer brushes from surface bound initiators by ATRP procedures is again a controlled or "living" process. Analysis of the polymer brush by XPS, contact angle measurements, and infrared spectroscopy were all fully consistent with the formation of a poly(methyl methacrylate) brush .

In conclusion, we have demonstrated that initiator functionalized surfaces, suitable for both alkoxyamine and atom transfer living free radical procedures, can be readily prepared, are stable to prolonged storage, and can be used for the controlled synthesis of polymeric brushes. The use of "living" free radical chemistry permits the accurate control of molecular weight or thickness of the brush while maintaining low polydispersities. The compatibility of the process with a variety of functional monomers also leads to novel random copolymer brushes, which can be used to accurately control surface properties. Sequential polymerization of different monomers or monomer mixtures has also been demonstrated, leading to unique block copolymer brushes which may find application as novel drug delivery systems, sensor devices, etc. While the current work has a number of advantages over traditional systems, disadvantages or challenges do exist; these include a high polymerization temperature which may not be compatible with certain substrates, such as polymer films. Large amounts of free polymers are also produced under the bulk polymerization conditions which restricts the use of expensive or scarce monomers. Future work will detail efforts to overcome these challenges.

Acknowledgment. The authors gratefully acknowledge the financial support of the NSF Center for Polymeric Interfaces and Macromolecular Assemblies (DMR-9808677), the NSF Materials Research Science and Engineering Center at the University of Massachusetts, the U.S. Department of Energy, Office of Basic Energy Sciences, under Contract DE-FG03-88ER45375**,** and the IBM Corp.

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MA981290V