Synthesis of Polymer Brushes on Silicate Substrates via Reversible Addition Fragmentation Chain Transfer Technique

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ABSTRACT: Reversible addition fragmentation chain transfer (RAFT) has been used to synthesize polymer brushes. Styrene, methyl methacrylate, and *N*,*N*-dimethylacrylamide brushes were prepared under RAFT conditions using silicate surfaces that were modified with surface-immobilized azo initiators. Films with controlled thicknesses were produced. RAFT was also used to synthesize PS-*b*-PDMA and PDMA-*b*-PMMA block copolymer brushes that displayed reversible surface properties upon treatment with block-selective solvents.

Introduction

Polymer brushes are long-chain polymer molecules that are covalently attached by one end to a surface at a relatively high coverage, which leads to stretching of the chains away from the interface to avoid overlapping.[1,2] This stretching along the direction normal to the grafting surface is different from the behavior observed in flexible polymer chains adopting random-walk configurations. Recently, many theoretical and experimental studies have been published on the structures and properties of polymer brushes.[3−5]

There are two general ways to synthesize tethered polymer chains: physisorption and covalent attachment. In polymer physisorption, block copolymers, with one block interacting strongly with a surface and the other block having weak interactions with it, adsorb onto a suitable substrate. However, weak interaction between the substrate and the block copolymer can lead to thermal and solvolytic instabilities.[6] This drawback can be overcome by covalently attaching polymer chains to the substrate. Tethering can be accomplished by either “grafting to” or “grafting from” techniques. In the “grafting to“ technique, end-functionalized polymer molecules react with an appropriately treated substrate to form tethered chains. However, as the grafting density increases, it becomes increasingly harder for new chains to diffuse to the surface and react with it. This can lead to low surface graft densities. This limitation can be overcome by utilizing the “grafting from” method. In this technique, a surface-immobilized initiator starts the polymerization and monomer adds to the growing polymer brush.

Progress in polymer synthesis techniques makes it possible to produce polymer brushes with controlled lengths and specific chain architectures. Polymerization methods that have been used to synthesize polymer brushes include cationic,[7−9] anionic,[10,11] ring-opening metathesis,[12] nitroxide-mediated radical,[13] and atom transfer radical polymerization methods.[13−15] Recently, reversible addition fragmentation chain transfer (RAFT), a new method for achieving controlled free radical polymerization, was introduced for solution polymerizations.[16] It involves a reversible addition fragmentation cycle, in which transfer of a dithioester moiety between active and dormant species maintains the controlled character of the polymerization (Scheme 1). The focus of this work is synthesis of polymer brushes utilizing the “grafting from” method and controlling the brush polymerization initiated by surface-immobilized azo-type initiator via the RAFT technique.

Experimental Section

Materials. Methyl methacrylate (MMA, Aldrich), *N*,*N*-dimethylacrylamide (DMA, Aldrich), and styrene (Aldrich) were dried over CaH_2, vacuum distilled to remove stabilizer and stored cold under nitrogen. Toluene, benzene, tetrahydrofuran (THF), *N*,*N*-dimethylformamide (DMF), heptane, and pyridine (all from Aldrich, anhydrous grade) were used as received. Nonporous silica (Aerosil 300, Degussa-Huls) was dried overnight at 100 °C before use. 2-Phenylprop-2-yl dithiobenzoate[16] and azoundecylchlorosilane initiators[4] were synthesized as described in the literature. 2,2′-Azobisisobutyronitrile (AIBN, Aldrich) was recrystallized from acetone. All other reagents were used as received from either Aldrich or Fisher. Silicon ATR crystals ($25 \times 5 \times 1$ mm) were obtained from Harrick Scientific. Silicon wafers were purchased from Semiconductor Processing, Inc., and cut into 25×10 mm pieces using a diamond-tipped glass cutter.

Substrate Preparation. ATR crystal and silicon wafers were cleaned by treatment with freshly prepared “piranha” solution (70/30, v/v, concentrated H_2SO_4/30% H_2O_2) at 100 °C for 2 h and were then rinsed with distilled water followed by EtOH and dried with a stream of clean air.

General Preparation of Silane Monolayers on Silicon Wafers, ATR Crystals and Silica Gel. A freshly cleaned ATR crystal, silicon wafer, or 0.1 g of oven-dried silica gel was placed into a solution of 0.05 g of a silane (either a monofunctional and trifunctional chlorosilane) in 10 mL of toluene and 0.25 mL of pyridine. The reaction mixture was allowed to react at room temperature under nitrogen atmosphere overnight. Following deposition, the modified substrates were rinsed with CH_2Cl_2 and EtOH and dried with a stream of clean air.

General RAFT Solution Polymerization. A single-neck round-bottom flask was charged with monomer, benzene or toluene (0.3 mL per 1 mL monomer), DMF (0.03 mL per 1 mL monomer), initiator (0.006 M) and 2-phenylprop-2-yl dithiobenzoate (0.0098 M). The solution was degassed by three consecutive freeze−pump−thaw cycles. Under N_2, 2 mL of this mixture was transferred into each of 8 dried and purged vials. All the vials were placed into a preheated oil bath. At designated time intervals, one vial was removed and the contents were analyzed. Conversions were analyzed by ^1H NMR using DMF as a reference. For GPC characterization, a sample of the reaction mixture was dissolved in DMF and filtered through a 0.2 μm syringe filter.

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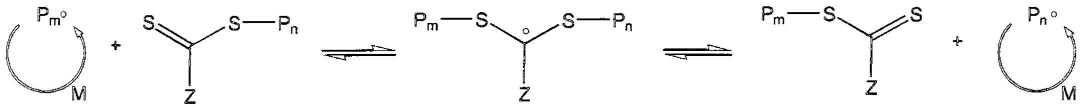
Scheme 1



Surface-Initiated RAFT Polymerizations on Silicon Wafers, ATR Crystals, and Silica Gel. A single-neck round-bottom flask containing functionalized substrate was charged with monomer, benzene or toluene (1 mL per 1 mL of monomer), DMF (0.1 mL per 1 mL of monomer), AIBN, and 2-phenylprop-2-yl dithiobenzoate. The solution was degassed by three consecutive freeze−pump−thaw cycles. The reactions were carried out in a preheated oil bath at 60 °C. At designated time intervals, aliquots were removed to determine percent monomer conversion and molecular weight of the unattached polymer chains. Following polymerization, the modified substrates were extracted with CH_2Cl_2 overnight, washed with EtOH, and dried in the vacuum oven overnight at room temperature. Typical polymerization times for PMMA and PDMA brushes were 12−24 h; typical times for PS brushes were 24−48 h.

Sequential Surface-Initiated Polymerizations on Silicon Wafers and ATR Crystals. A stock solution containing monomer, benzene or toluene (1 mL per 1 mL of monomer), AIBN, and 2-phenylprop-2-yl dithiobenzoate (0.0147 M) was degassed by three consecutive freeze−pump−thaw cycles. A single-neck 15 mL round-bottom flask containing functionalized substrates was degassed and charged with 5 mL of the stock solution. The reactions were carried out in a preheated oil bath at 60 °C for PS and 90 °C for PDMA. At designated time intervals, the substrates were removed, extracted with CH_2Cl_2 overnight, washed with EtOH, and dried with a stream of compressed air. A small piece of the silicon wafer was broken off for further analysis, while the rest was placed into a single-neck 15 mL round-bottom flask. This flask was degassed and charged with a fresh 5 mL of the stock solution and placed in the preheated oil bath. The reaction was repeated several more times.

Preparation of Diblock Copolymer Brushes on Silicon Wafers and ATR Crystals. A single-neck round-bottom flask containing functionalized substrates was charged with monomer, benzene or toluene (1 mL per 1 mL of monomer), AIBN, and 2-phenylprop-2-yl dithiobenzoate. The solution was degassed by three consecutive freeze−pump−thaw cycles. The reactions were carried out in a preheated oil bath at either 60 °C (for PS and PMMA block) or 90 °C (for PDMA block). At designated time intervals, the substrates were removed, extracted with CH_2Cl_2 overnight, washed with EtOH, and dried with a stream of compressed air. After analysis, the substrates were placed into a single-neck 15 mL round-bottom flask, degassed, and charged with the second monomer, benzene or toluene (1 mL per 1 mL of monomer), AIBN, and 2-phenylprop-2-yl dithiobenzoate. The solution was degassed by three consecutive freeze−pump−thaw cycles. The reactions were carried out in a preheated oil bath. After polymerization, the substrates were removed, extracted with CH_2Cl_2 overnight, washed with EtOH, and dried with a stream of compressed air.

Degrafting Polymer Brushes from the Substrate via Acid-Catalyzed Transesterification. The procedure of Rühe and co-workers[4] was modified slightly. A single-neck round-bottom flask containing 0.5 g of polymer-modified silica gel was charged with 100 mL of toluene, 10 mL of MeOH, and 0.05 g of *p*-toluenesulfonic acid. The mixture was heated to reflux overnight. The reaction mixture was then transferred to a centrifuge tube and centrifuged for 15 min. The supernatant solution which contained the cleaved polymer chains was decanted. Toluene was added to the solid, and the mixture was centrifuged for 15 min. This procedure was repeated two more times. The remaining solids were dried in a vacuum oven overnight at room temperature. The combined toluene extractions were added to the decanted reaction mixture and the solvent was removed in vacuo to afford crude degrafted polymer chains. The degrafted chain sample was purified by precipitation into methanol or hexanes.

Characterization. ^1H NMR spectra were recorded on a Varian Gemini-300 spectrometer. Routine molecular weight analysis was performed with a Waters 501 pump, 2 PLgel (Polymer Laboratories) mixed D columns (5 μm) and a Waters 410 differential refractometer. The eluent was DMF and flow rate was 0.7 mL/min. Molecular weights were calibrated by comparison to narrow MWD distribution PMMA standards (200 to 1.0×10^6) and PS standards (680 to 3.0×10^6) (Polymer Laboratories). Data analysis was performed with the E−Z Chrom software package. TGA analysis was run in nitrogen atmosphere using a DuPont model 2000TGA. DSC was used to calculate graft density on silica gel as described in the literature.[4] FTIR-ATR spectra were recorded using a Nicolet System 730 spectrometer with a modified 4XF beam condenser (Harrick Scientific). Spectra were recorded at 2 cm^{-1} resolution, and 500 scans were collected. Contact angles were determined using a Rame Hart NRL-100 contact angle goniometer equipped with an environmental chamber and tilting base mounted on the vibrationless table (Newport Corp.). Advancing and receding values were determined using the tilting stage method at 35° tilt angle. Droplet size values were 10 μL. Ellipsometric measurements were performed on a Gaertner model L116C ellipsometer with He−Ne laser (λ = 633 nm). For the calculation of the layer thickness, refractive index values of $n = 1.455$ (for silicon oxide),[17] $n = 1.45$ (for the initiator layer), $n = 1.4893$ (for PMMA),[18] $n = 1.5894$ (for PS),[18] and $n = 1.513$ (for PDMA)[18] were used, and an average of 10 measurements were recorded. XPS measurements were performed on a Perkin-Elmer instrument using Al Kα radiation at the MATNET Surface Analysis Center at Case Western Reserve University. The incidence angle of X-rays was 45° with respect to surface normal.

Results

Surface-Initiated RAFT Polymerizations. Scheme 2 shows the general process of surface-initiated RAFT polymerizations using 2-phenylprop-2-yl dithiobenzoate as the chain transfer agent and a substrate-immobilized azo initiator. Homopolymer brushes of PMMA, PDMA, and PS were synthesized on silicon wafers (Table 1). For the surface-initiated RAFT polymerizations, we found that adding free initiator (AIBN concentrations ranging from 0.00368 to 0.0147 M) was advantageous. The thickness of the polymer brushes was proportional to the amount of “free” initiator in the system. The polydispersity of the “free” polymer increased with increasing amount of “free” initiator. For CTA (chain transfer agent)/AIBN ratios 1/0.5 (for PS and PDMA) and 1/0.25 (for PMMA), reasonably thick films were prepared and the polydispersity of the “free” polymer was relatively narrow. Thermogravimetric analysis (TGA) was utilized to assess the amount of polymer brush on silica gel; up to 40% (w/w) polymer was grafted to the silica gel.

Sequential Surface-Initiated RAFT Polymerizations. To test the controlled behavior of the surface-initiated polymerizations, incremental monomer addition experiments were performed. The substrates were removed from the reaction mixture every several h, analyzed and placed into a fresh reaction mixture to resume brush growth. The ATR−FTIR spectra in Figures 1 and 2 illustrate the stepwise growth of the

Scheme 2

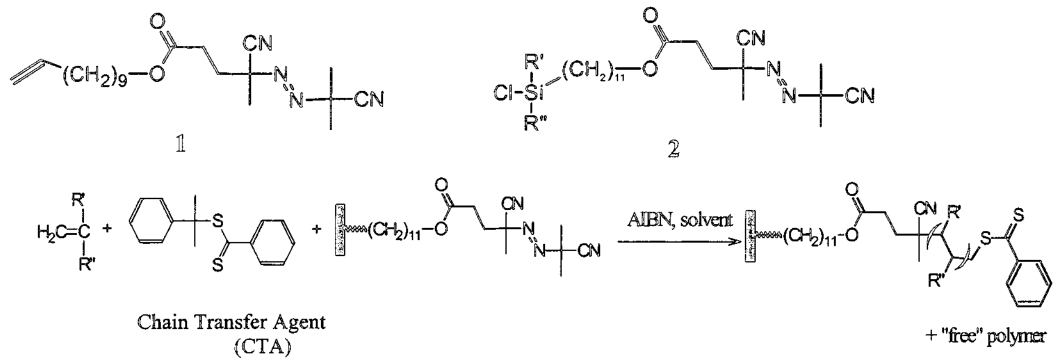


Table 1. Homopolymer Brushes Synthesized via RAFT on Silicon Wafers (CTA = Chain Transfer Agent)

brush	solvent/T^a (°C)	CTA/AIBN ratio	$M_{n(calcd)}$ (g/mol)^b	$M_{n(expt)}$ "free" polymer (g/mol)	PDI of "free" polymer	% convn^c	film thickness^d (nm)
PMMA	benzene/60	1/0.5	18 200	25 400^e	1.72	86	28
PMMA	benzene/60	1/0.25	30 700	21 300^e	1.10	97	16
PDMA	toluene/90	1/0.5	21 800	23 000^e	1.42	100	11
PS	benzene/60	1/0.058	29 200	800^f	1.25		7
PS	benzene/60	1/0.58	3900	3600^f	1.55	20	
PS	benzene/60	1/0.5	30 900	36 800^f	1.40	51	11

[a] Reactions times were 12–24 h for PDMA and PMMA; times were 24–48 h for PS. [b] $M_{n(calcd)}$ = % monomer conversion × (monomer (g)/initiator (mol)). [c] % monomer conversion was determined by gravimetry. [d] Film thicknesses were determined by ellipsometry with ±3 nm instrument error. [e] MW analysis was done by GPC with comparison to PMMA standards. [f] MW analysis was done by GPC with comparison to PS standards.

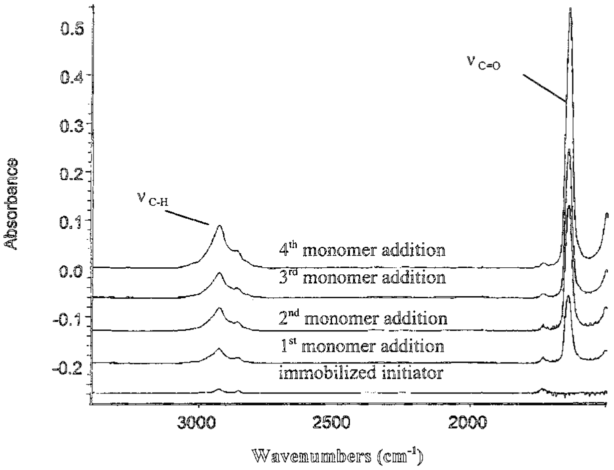


Figure 1. ATR–FTIR spectra for PDMA brush formation using sequential monomer additions.

immobilized PDMA and PS brushes. With each sequential monomer step, a gradual increase was observed for absorptions at 2930 (C–H) and 1645 (C=O) cm^{-1} for PDMA and absorptions at 2930 (sp^3 C–H) and 3050 (sp^2 C–H) for PS. A liner increase of the PDMA and PS brush thicknesses with number of sequential monomer addition as measured by ellipsometry is illustrated in Figures 3 and 4. A control experiment was performed with no RAFT chain transfer agent; no growth of the brush was observed after the first monomer addition.

XPS Study of Reactive Chain Ends. If surface-initiated RAFT occurs by the proposed mechanism (Scheme 1), then the chain ends of the polymer brushes should be terminated by dithioester groups. X-ray photoelectron spectroscopy (XPS) was used to determine the presence of the dithioester chain ends and the change in the intensity of the sulfur peak as a function of sequential monomer additions. A control surface for XPS analysis was synthesized by reacting 2-phenylprop-2-yl dithiobenzoate with immobilized initiator in the absence of monomer to create a dithioester surface. It was determined that the concentration of sulfur on the surface stayed fairly constant over several monomer additions, although values for all brush samples were lower than those for the control surface (Table 2).

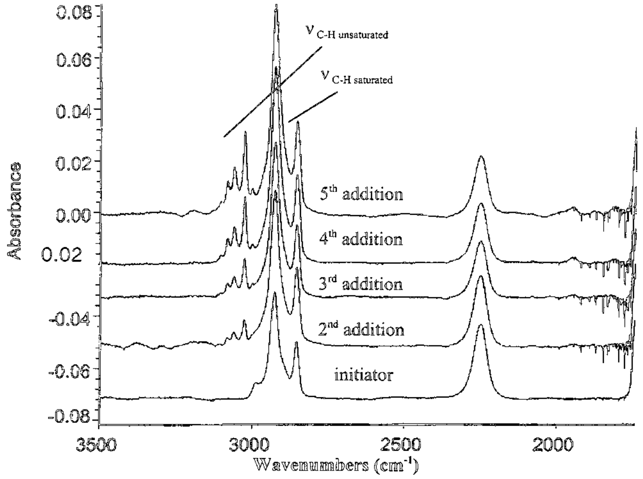


Figure 2. ATR–FTIR spectra for PS brush formation using sequential monomer additions.

Synthesis of Diblock Copolymer Brushes via RAFT. PS-*b*-PDMA and PDMA-*b*-PMMA diblock copolymer brushes were synthesized. ATR–FTIR results are shown in Figures 5 and 6. A 10 nm thickness increase was observed in each case upon addition of the second monomer. This increase correlates with that expected for a polymer brush grown from a well-defined initiator layer under the same reaction conditions.

The behavior of diblock copolymer brushes upon treatment with different solvent systems was observed in these films via tensiometry. The advancing water contact angles of a PS-*b*-PDMA (where the PS block is adjacent to the silicate surface) brush increased from 42 to 65° upon treatment with methylcyclohexane at 35

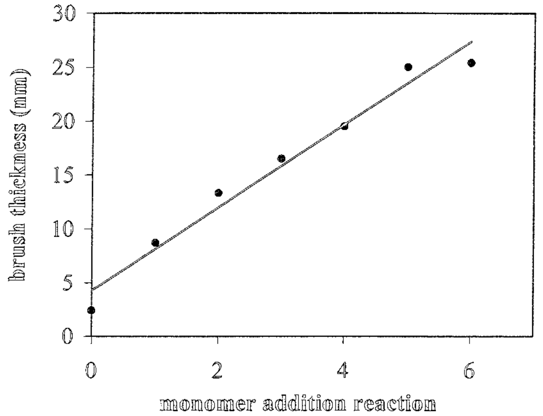


Figure 3. PDMA film thickness change with sequential monomer additions; thicknesses determined by ellipsometry.

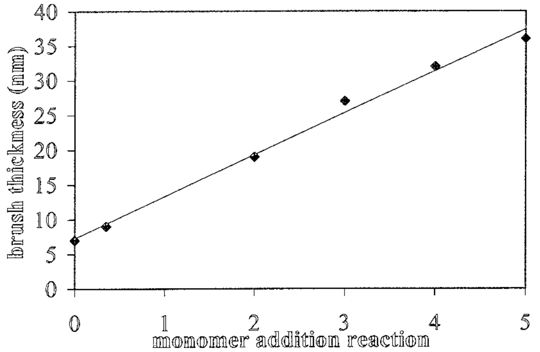


Figure 4. PS film thickness change with sequential monomer additions; thicknesses determined by ellipsometry.

Table 2. XPS Results: Sulfur Concentration for PS Homopolymer

monomer addition	total reacn time (h)	% S concn
1	5	0.12
2	10	0.19
3	15	0.14
4	20	0.13
5	25	0.14
6	30	0.07
control[a]	5	0.35

[a] Control prepared by treating surface-immobilized azo initiator with chain transfer agent in the absence of monomer.

°C for 1 h. Treatment of the same sample with THF/H_2O (1/1, v/v) at 35 °C for 1 h reversed the contact angle to the original value. The advancing water contact angle of the PS homopolymer brush prior to diblock formation was 78°. Normally, a PS overlayer exhibits an advancing contact angle of 100°. We attribute the lower contact angle for the PS brush made by RAFT to the dithioester terminal group. A control sample of dithioester groups was prepared for XPS by reacting the surface-immobilized azo-initiator with RAFT chain transfer agent in the absence of monomer; this sample displayed an advancing contact angle of 77°.

In the case of the PDMA-*b*-PMMA brush, the advancing water contact angle decreased from 66° to 58° after the sample was treated with THF/H_2O (1/1, v/v) at 35 °C for 1 h. Subsequent treatment with CH_2Cl_2 returned the contact angle to the original value. These contact angle changes were reproducible for several cycles of solvent treatment. The advancing contact angle of the PDMA homopolymer brush prior to diblock formation was 33°.

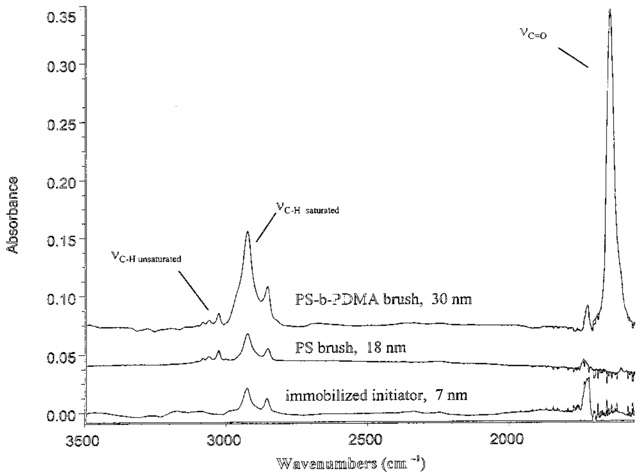


Figure 5. ATR−FTIR spectra of PS-*b*-PDMA brush, film thicknesses were determined by ellipsometry.

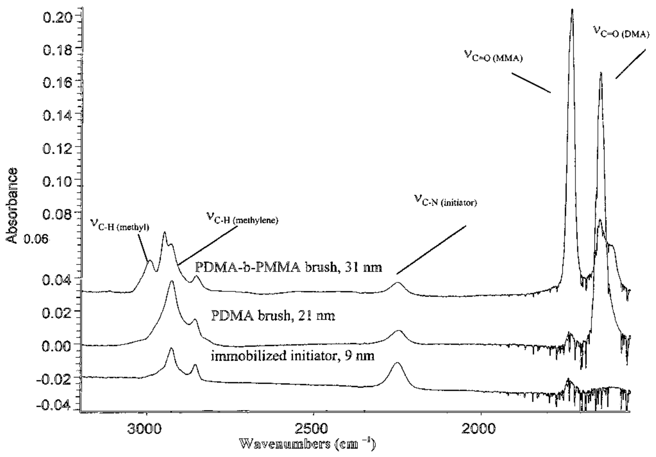


Figure 6. ATR−FTIR spectra of PDMA-*b*-PMMA brush, film thicknesses were determined by ellipsometry.

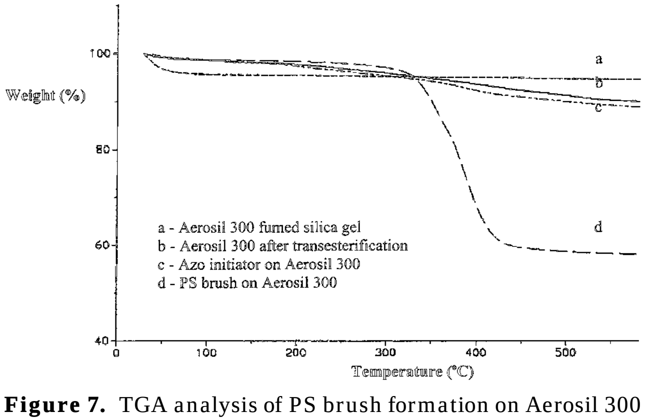


Figure 7. TGA analysis of PS brush formation on Aerosil 300 silica gel: (a) Aerosil 300 fumed silical gel; (b) Aerosil 300 after transesterification; (c) azo initiator on Aerosil 300; (d) PS brush on Aerosil 300.

Cleavage of Polymer Brushes from the Substrate. For degrafting procedures, nonporous silica gel particles were used instead of silicon wafers to increase the surface area for brush growth and, therefore, the amount of polymer that can be recovered after cleavage. Following the literature technique,[4] acid-catalyzed transesterification with methanol was used to cleave PS and PMMA brushes from the surface. Figure 7 shows the TGA results for PS modified silica gel. A 5.4% mass increase was observed after initiator immobilization; an additional 31.0% mass increase was observed after PS brush polymerization. On the basis of TGA analysis, we determined that all polymer was removed after transesterification. GPC analysis of the degrafted PS revealed $M_n = 11\,400$ g/mol and PDI = 1.14. These values are comparable to the "free" PS in this reaction where $M_n = 10\,600$ and PDI = 1.11. Degrafted PMMA was also analyzed by GPC with $M_n = 19\,200$ g/mol and PDI = 1.29. Again the result is comparable to "free" PMMA where $M_n = 15\,900$ and PDI = 1.22. These experiments suggest that analysis of "free" polymer in brush syntheses can provide information about the molecular weight characteristics of the tethered polymers.

Discussion

The behavior of RAFT in solution has been investigated by us and others[16] and demonstrates characteristics of a living polymerization including the following: (a) relatively narrow polydispersity of products, (b) linear molecular weight increase with monomer conversion, (c) linear first-order kinetic plot, and (d) the ability to predict the molecular weight from the ratio of monomer consumed to chain transfer agent.

To apply this process to the synthesis of polymer brushes, azo-initiator was immobilized on a silicate surface and used to initiate the growth of polymer chains in the presence of the RAFT CTA. Early attempts to synthesize polymer brushes initiated by surface-immobilized initiator were ineffective. This was attributed to a very low concentration of initiating sites with respect to monomer concentration, which can be terminated by the small levels of impurities present in the reaction mixture. Addition of small amounts of untethered initiator (AIBN) to the system facilitated the growth of brushes by acting as a scavenger for such impurities.

The use of living polymerization techniques for polymer brush synthesis is desirable so that chain lengths can be controlled and complicated brush structures can be prepared. RAFT is a promising technique because of the greater number of monomers that can be successfully polymerized in a controlled manner compared to other living polymerization techniques. To determine whether RAFT is a viable technique for the controlled polymerization of polymer brushes, we conducted sequential monomer additions and block copolymerizations. Ellipsometry, FTIR, and XPS results all confirmed the stepwise growth of the polymer brushes without significant loss of the active dithioester chain ends. Control experiments in the absence of RAFT chain transfer agent confirmed that these results are associated with the RAFT process. The stepwise growth of polymer brushes also shows that this is a "grafting from" process. Some "grafting to" reactions may occur by bimolecular coupling of the active "free" polymer chains in solution and active radicals on the surface. However, this would lead to the termination of the brush macromolecules, and no continuous brush growth would be observed. The continuous stepwise increase observed in brush film thicknesses (see Figures 3 and 4) proves that there are no significant termination reactions occurring during the brush polymerization.

To further understand the growth characteristics of the surface-initiated RAFT polymers, we cleaved PS and PMMA homopolymer chains from high surface area silica and compared the molecular weight characteristics of the cleaved chains to "free" polymer. For both the PMMA and PS systems, both M_n and PDI were comparable for "free" polymer vs cleaved polymer. This result suggests that characteristics of the surface-initiated polymerization can be judged by analysis of the "free" polymer.

We used RAFT to synthesize diblock copolymer brushes. The formation of block copolymer brushes was confirmed by ellipsometry and FTIR. When a control experiment was performed, in which the first block was prepared in the absence of the CTA under the typical reaction conditions, no formation of the second block was observed. This further proves that the dithioester chain ends of the first block are actively involved in the formation of the second block of brushes prepared by RAFT. The reversible rearrangement behavior of the diblocks upon treatment with various solvents has been observed previously.[7,20] It is important to note that upon treatment of the samples with a good solvent for the bottom block, the contact angle values did change in the correct direction, but they never reached the contact angle values of the corresponding homopolymer brush. Also, the contact angles of the PDMA and PMMA terminal blocks prior to solvent reorganization were higher and lower, respectively, compared to the corresponding homopolymer brush systems. We feel that this can be attributed to inefficient diblock copolymer brush formation. That is, the PS-*b*-PDMA system is contaminated with PS homopolymer brushes that did not initiate a block of PDMA; likewise, the PDMA-*b*-PMMA system is mixed with PDMA homopolymer brushes. Thus, the starting contact angles for the two diblock systems represent an average of the upper block and homopolymer brush from the lower layer. We are currently studying these systems in more detail by cleavage of the diblock copolymer brushes from a silica surface followed by analysis with mass spectrometry. So far, these experiments have not produced any definitive conclusions on the relative amounts of homopolymer and block copolymer.

Conclusions

We have demonstrated that RAFT polymerization can be used in preparation of polymer brushes using a surface-immobilized azo-initiator. The use of this process allows the control of the polymer molecular weight and the film thickness while maintaining fairly narrow polydispersities for "free" polymer. Sequential polymerization of different monomers leads to block copolymer brushes, which exhibit rearrangement behavior upon treatment with specific solvents.

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