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Synthesis of Surface Initiated Diblock Copolymer Brushes from Flat Silicon Substrates Utilizing the RAFT Polymerization Technique

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ABSTRACT: The synthesis of a variety of well-defined diblock copolymer brushes, including poly(methyl methacrylate) (PMMA)-*b*-poly(2-(dimethylamino)ethyl methacrylate) (PDMAEMA), PMMA-*b*-poly(styrene) (PSty), and PSty-*b*-poly(methyl acrylate), was achieved via surface immobilized reversible addition−fragmentation chain transfer (RAFT) polymerization. Initially, silicon surfaces were modified with RAFT chain transfer agents (CTAs) by utilizing a modified atom transfer addition reaction involving a silicon wafer modified with (11-(2-bromo-2-methyl)propionyloxy)undecyltrichlorosilane and dithiobenzoyl disulfide. Diblock copolymer brushes were then prepared via sequential surface initiated RAFT polymerization from the immobilized CTA. Various characterization techniques including ellipsometry, contact angle measurements, grazing angle attenuated total reflectance−Fourier transform infrared spectroscopy, and X-ray photoelectron spectroscopy were used to characterize the immobilization of CTAs on the silicon wafer and the subsequent polymer formation. The addition of free CTA was required for the formation of well-defined diblock copolymer brushes, which subsequently resulted in the presence of free polymer chains in solution. The free polymer chains were isolated and used to estimate the molecular weights and polydispersity index of chains attached to the surface.

Introduction

Polymer brush systems consist of ordered assemblies of polymeric chains that are terminally grafted or absorbed onto a surface or interface at one or more tethering points.[1−3] Tethering of the chains in close proximity to each other results in high amounts of steric repulsion and osmotic pressure which causes the free chain ends to "stretch" away from a collapsed state on the surface to an extended or "brushlike" configuration. The change from the typical random walk configuration to the stretched character of polymer brushes provides unique characteristics that are not found in similar bulk systems.[1,2] These properties have led to novel applications in areas such as microelectronics, tailoring of surface properties, nanopatterning, thermoresponsive adhesives, biomedical studies, and controlled gene/drug delivery.[1,3−10]

Polymer brushes have been prepared via two basic routes: physisorption of the polymer to a surface and covalent attachment by chemical reaction at the surface.[1,3−10] Covalently bound polymers overcome many of the inherent issues associated with physically absorbed polymer brush systems, such as low grafting densities and both thermal and solvolytic instabilities. Probably the most widely used technique to covalently attach polymer chains to a surface is the "grafting from" technique. This technique has been widely used to successfully produce polymer brushes that are thermally and solvolitically stable, have uniform film thicknesses, and have high grafting densities. The "grafting from" technique is based on the diffusion of a small monomer molecule to activated initiator sites or growing polymer chains, which are covalently attached to the surface. A wide range of planar, rodlike, and spherical surfaces have been utilized via the "grafting from" approach using a variety of polymerization techniques, including ring-opening metathesis polymerizations, anionic and cationic polymerizations, conventional free radical, and controlled living free radical polymerization (CLRP).[1−19]

Arguably, the most widely used and versatile polymerization method to prepare polymer brushes via the "grafting from" technique are the various CLRP techniques, such as atom transfer radical polymerization (ATRP), nitroxide-mediated polymerization, and reversible addition-fragmentation chain transfer (RAFT) polymerization. These polymerization techniques have received much attention because of their ability to provide simple and versatile routes for synthesizing well-defined, narrow polydispersity index (PDI) polymers with both simple and complex architectures. The key difference between traditional free radical polymerization and CLRP is the presence of a reversible activation and deactivation process that permits controlled growth of a polymer with minimal termination reactions, resulting in polymer chains with "living" end groups. ATRP is arguably the most widely used CLRP technique for preparation of surface initiated polymer brushes; however, RAFT offers potential benefits over ATRP in the polymerization of functional monomers. RAFT is an exceptionally versatile CLRP technique that is based on a reversible degenerative chain transfer mechanism in which thiocarbonylthio compounds act as chain transfer agents (CTAs) providing controlled growth of polymer chains (Scheme 1).[20−23] Probably the most crucial step in performing a successful RAFT polymerization is the selection of an appropriate CTA. The R and Z groups (see Scheme 1) both play vital roles in controlled polymer growth. The R group must be a good free radical leaving group and efficiently reinitiate polymerization and the Z group should stabilize the intermediate radical. A variety of different compounds have been used as RAFT CTAs, including dithioesters, trithiocarbonates, xanthates, and dithiocarbamates. Two widely used RAFT CTAs for the polymerization of a wide variety of monomers are cumyl dithiobenzoate (CDTB) and *S*-1-dodecyl-*S*′-(α,α′-dimethyl-α″-acetic acid) trithiocarbonate (DATC) (Figure 1).[24−26] The main advantages of RAFT polymerization when compared to other CLRP techniques include the ability to polymerize a wide variety of monomers, including styrenics, acrylamides, acrylates, methacrylates, and vinyl esters; poly-

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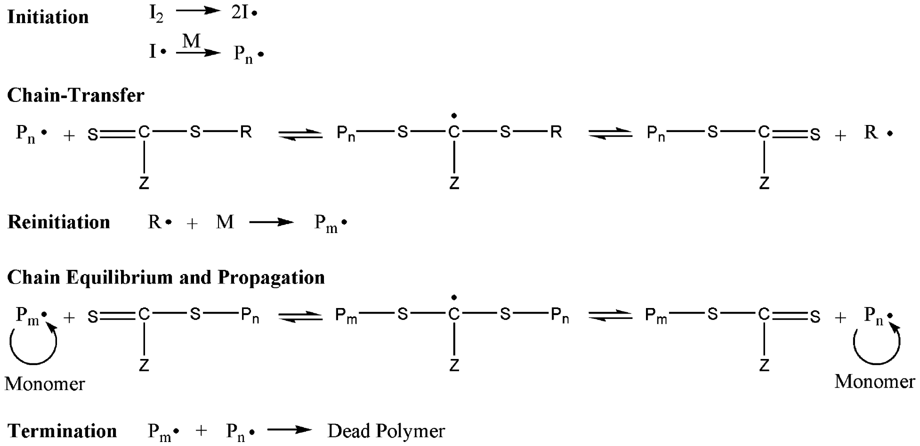
Scheme 1. General Reversible Addition−Fragmentation Chain Transfer Polymerization Mechanism



merizations may be conducted under bulk, solution, emulsion, and miniemulsion conditions; it may be conducted over a wide range of temperatures; it has exceptional functional group tolerance which allows for the preparation of highly functional materials; and it allows for the preparation of materials with complex and advanced architectures.[20−23] Despite these advantages, RAFT has only recently received substantial attention when it comes to the preparation of polymer brushes using the "grafting from" approach.

While the work examining the use of surface initiated RAFT polymerization in the preparation of polymer brushes has, to date, been somewhat limited, those that have investigated this area have taken diverse approaches.[2,6−9,17,18,27−41] The basic routes that have been employed to form surface initiated polymer brushes utilizing RAFT include utilization of a surface bound free radical initiator with free CTA in solution and immobilization of the RAFT agent through the R or Z groups for subsequent polymerization. The first approach taken by several groups utilized surface immobilized free radical initiators with the addition of free CTA in solution to form surface immobilized polymer chains via RAFT polymerization.[8,27−31] The disadvantage of this approach is that for a well-defined RAFT polymerization all chains should be initiated at the same time via the R group of the CTA. Because of the fact that thermal free radical initiators dissociate and initiate chains over a wide temperature range, use of surface immobilized free radical initiators may lead to nonuniform films. Groups such as Stenzel, Perrier, and Neoh have synthesized polymer brushes via RAFT using the Z-group approach.[32−34] Since the RAFT agent is always covalently attached to the surface, this technique resembles a "grafting to" approach, which becomes diffusion-controlled as the molecular weight is increased and is inclined to form films with low grafting densities and poor film uniformity. The most promising means of formation of high density, uniform polymer brushes using RAFT polymerization is via attachment of the CTA through the R group, as it is truly a "grafting from" technique. Several approaches have been taken to form brushes through R-group attachment of the CTA. Grignard reagents have been used to form surface immobilized RAFT CTAs in both solution and on surfaces, such as cellulose, silica nanoparticles, and multiwalled carbon nanotubes.[6,9,35−38] Several groups have immobilized CTAs on surfaces via the R group by using condensation reactions between surface hydroxyl (−OH) and amino (−NH_2) functionalities and 4-cyanopentanoic acid dithiobenzoate.[39−41]

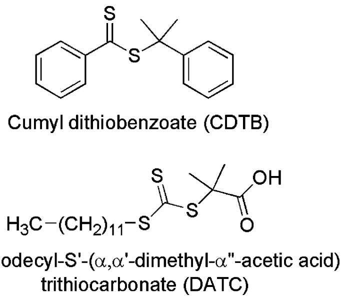


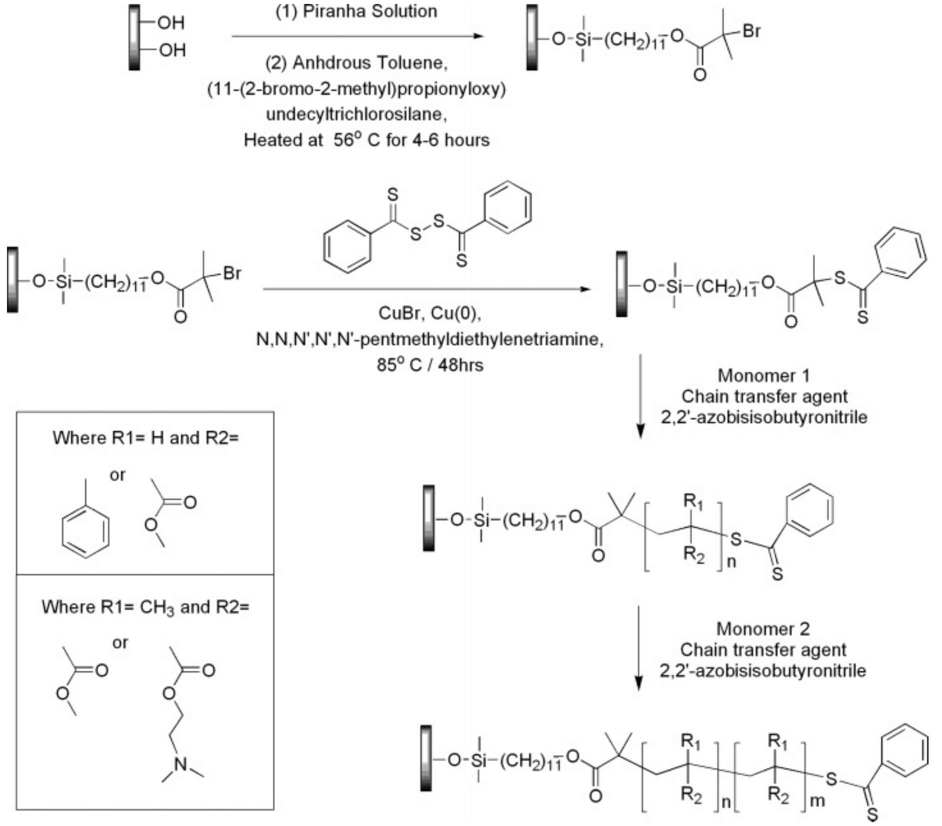
Figure 1. Chemical structure of the "free" chain transfer agents used in this work.

Since ATRP is arguably the most widely used CLRP technique for preparation of surface initiated polymer brushes, a means of converting surface immobilized ATRP end groups to RAFT CTAs would be beneficial. Recent work by Wager et al. provides a simple method of converting ATRP macroinitiators in solution to RAFT mediators.[42] Fukuda and co-workers used a similar technique for the conversion of a surface immobilized ATRP macroinitiator to a terminal RAFT moiety.[43] However, Wager showed the presence of Cu(0) was needed in order to shift the equilibrium to Cu(I) and ensure effective conversion.[42] Herein, we report a novel surface modification technique that utilizes a modified atom transfer addition (ATA) reaction to form surface immobilized RAFT CTA for use as a template for the formation of diblock copolymer brushes. The modified ATA reaction was mediated by addition of excess dithiobenzoyl disulfide and Cu(0) to favor surface conversion to a dithioester moiety. In this work we selected styrene (Sty), methyl acrylate (MA), methyl methacrylate (MMA), and 2-(dimethylamino)ethyl methacrylate (DMAEMA) as model monomers for the synthesis of homopolymer and diblock copolymer brushes from flat silicon substrates. In each case, either CDTB or DATC (Figure 1) was added as sacrificial CTA in order to control the surface polymerization and form polymer in solution. Scheme 2 illustrates the general route taken for the synthesis of diblock copolymer brushes from flat silicon surfaces utilizing surface initiated RAFT polymerization techniques.

Experimental Section

Materials. Copper (∼45 μm, powder, 99%), copper bromide (CuBr) (99%), anhydrous pyridine (99.0%), anhydrous tetrahydrofuran (stabilized with butylated hydroxytoluene, 99.9%), MA (stabilized with 10−20 ppm MEHQ, 99%), MMA (stabilized with quinol, 99%), DMAEMA (stabilized with 0.2% MEHQ, 99%), Sty (stabilized with 10−15 ppm *tert*-butylcatechol, 99%), and benzyl chloride (99%) were purchased from Acros Chemicals. Anhydrous methanol, ethyl ether, potassium ferricyanide, and 30% hydrogen

Scheme 2. General Procedure for Preparation of Atom Transfer Addition Modified Surfaces and Subsequent Diblock Copolymer Brush Formation via Reversible Addition−Fragmentation Chain Transfer Polymerization



peroxide were purchased from Fisher Scientific. Elemental sulfur (reagent grade, particle size ∼100 mesh), sodium methoxide (30 wt % solution in MeOH), *N*,*N*,*N*′,*N*′,*N*′-pentamethyldiethylenetriamine (99%) (PMDETA), ethyl 2-bromoisobutyrate (98%) (E2-BiB), 2,2′-azobis(isobutyronitrile) (98%) (AIBN), α-methylstyrene (99%), anhydrous toluene (99.8%), *ω*-undecylenyl alcohol (98%), and 2-bromoisobutyryl bromide (98%) were purchased from Aldrich. Trichlorosilane (98%) was obtained from Alfa Aesar. All other solvents were used as received from Mallinckrodt. Sty, MA, and MMA were passed through a basic alumina column and stored in the freezer prior to use. DMAEMA was distilled under pressure and stored in the freezer prior to use. CuBr was purified via the literature procedure.[44] AIBN was recrystallized twice from methanol prior to use. Unless otherwise noted, all other chemicals were used as received. Silicon wafers were purchased from Wafer World, Inc., and cut into 2 × 6 cm pieces using a diamond-tipped glass cutter.

Synthesis of (11-(2-Bromo-2-methyl)propionyloxy)undecyltrichlorosilane) (BMP TCS). BMP TCS was synthesized as discussed in the literature.[15] ^{1}H NMR (300 MHz, CDCl$_3$, δ, ppm): 1.28−1.44 (br m, 16H, $SiCl_3(CH_2)_2(C\mathbf{H}_2)_8$), 1.59−1.68 **(**m, 4H, $SiCl_3(C\mathbf{H}_2)_2$), 1.78−1.81 (d, 6H, $O{=}CC(C\mathbf{H}_3)_2Br$), 4.08−4.19 **(**t, 2H, $COOC\mathbf{H}_2$).

Synthesis of Dithiobenzoic Acid. Dithiobenzoic acid was synthesized following literature procedures.[45] Dithiobenzoic acid was not characterized as it degrades readily.

Synthesis of Dithiobenzoyl Disulfide (DTBDS). The synthesis of DTBDS was carried out according to methods in the literature.[45] ^{1}H NMR (60 MHz, CDCl$_3$, δ, ppm): 7.45 (dd, 4H, *m*-aromatic), 7.60 (m, 2H, *p*-aromatic), 8.07 (d, 4H, *o*-aromatic). ^{13}C NMR (300 MHz, CDCl$_3$, δ, ppm): 127.5 (*m*-aromatic), 128.0 (*o*-aromatic), 132.7 (*p*-aromatic), 219.0 (C═S). FTIR (cm^{-1}): 1021 (C═S), 3010 aromatic stretches.

Synthesis of CDTB. CDTB was prepared by a modification of the method of Le, Moad, Rizzardo, and Thang.[21] Dithiobenzoic acid was rinsed with ether and then acidified with concentrated sulfuric acid. The ether layer was then collected and dried over calcium carbonate. Solvent was removed via a rotary evaporator, and the product was used immediately. Dithiobenzoic acid (17 g, 0.11 mol), carbon tetrachloride (70 mL), and α-methylstyrene (18.7 mL, 0.143 mol) were added to a 100 mL round-bottom flask equipped with a stir bar. The reaction was heated to 56 °C and stirred for 4 h. Solvent was removed via a rotary evaporator, and the crude product was purified by column chromatography (basic alumina oxide, *n*-hexane as the eluent). Solvent was removed again, and the product was purified a second time using column chromatography (silica gel, 2:8 chloroform:cyclohexane eluent). Solvent was removed, and the product was purified a third time using column chromatography (silica gel:hexane eluent). Solvent was removed, and the product was dried in an oven at 45 °C overnight (yield = 8.25 g, 35%). ^{1}H NMR (60 MHz, CDCl$_3$, δ, ppm): 2.03 (s, 6H, $(C\mathbf{H}_3)_2$) 0.45 (dd, 4H, *m*-aromatic), 7.60 (m, 2H, *p*-aromatic), 8.07 (d, 4H, *o*-aromatic). ^{13}C NMR (300 MHz, CDCl$_3$, δ, ppm): 27.9 ($SC(CH_3)_2$), 56.1 ($SC(CH_3)_2$), 126.4 (*m*-aromatic), 127.8 (*o*-aromatic), 131.4 (*p*-aromatic), 143.8 (C(C═S)), 145.6 ($C{-}C(CH_3)_2$), 226.7 (C═S). FTIR (cm^{-1}): 1020 (C═S), 2940−3090 aromatic stretches.

Synthesis of DATC. DATC was prepared via Lai et al.'s literature procedure[22] (yield = 6.05 g, 4%). ^{1}H NMR (60 MHz, CDCl$_3$, δ, ppm): 0.89 (t, 3H, $(CH_2)_{11}C\mathbf{H}_3$), 1.25−1.53 (m, 18H, $(C\mathbf{H}_2)_9CH_3$), 1.73 (s, 8H, $SC(C\mathbf{H}_3)_2COOH$ and $C\mathbf{H}_2(CH_2)_9CH_3$), 3.35 (t, 2H, $C\mathbf{H}_2(CH_2)_{10}CH_3$). FTIR (cm^{-1}): 1702 (C═O), 1065 (C═S).

Purification of Silicon Wafers. Silicon wafers were cleaned using a 30:70 v/v solution of 30% hydrogen peroxide and concentrated sulfuric acid. The solution was heated for 2 h at 100 °C. *Caution: piranha solution is extremely caustic.* Wafers were cleaned in deionized water, methanol, and methylene chloride sequentially, characterized, and used immediately for subsequent modification.

Deposition of BMP TCS. Previously cleaned wafers were placed in clean, dry glass tubes containing 25 mL of anhydrous toluene. BMP TCS (0.5 mL of 25 wt % solution) was added directly into the toluene by syringe, and the tubes were sealed. The reaction was heated to 56 °C for 4 h. Wafers were removed and sequentially cleaned with toluene, methanol, and methylene chloride and then dried in a stream of air.

General Procedure for Modified Surface ATA Reaction. Anhydrous toluene (15 mL) and CuBr (0.0750 g, 0.00105 mol) were added to a 150 mL Schlenk flask equipped with a stir bar. Anhydrous toluene (10 mL) and DTBDS (0.4598 g, 1.500 $\times$ 10^{-3} mol) were added to a separate 150 mL Schlenk flask. Both were sealed with rubber septum and then purged in an ice bath with high-purity nitrogen for 30 min and subsequently left under a high-purity nitrogen atmosphere. Into a third 150 mL Schlenk flask, a previously deposited bromosilane initiator wafer and Cu(0) (0.1495 g, 2.354 $\times$ 10^{-3} mol) were added, sealed with a rubber septum, and subjected to three evacuation−nitrogen purge cycles before being left under a nitrogen atmosphere. After 30 min, PMDETA (0.48 mL, 0.0023 mol) was added to the CuBr solution and was allowed to stir for another 10 min to produce a homogeneous solution. The CuBr/PMDETA solution was transferred via cannula into the wafer containing flask, followed by transfer of the disulfide solution by the same method. Finally, E2-BiB (0.15 mL, 0.0010 mol) was added to the combined solutions via syringe and the reaction was allowed to heat at 85 °C for 48 h. After this time, the wafers were removed and cleaned sequentially with toluene, methanol, and methylene chloride and then dried in a stream of air.

Synthesis of PMMA Brush via RAFT Polymerization. CDTB (0.170 g, 6.24 $\times$ 10^{-4} mol), AIBN (0.0205 g, 1.25 $\times$ 10^{-4} mol), anhydrous toluene (26.1 mL), and MMA (23.9 mL, 0.223 mol) were added to a 150 mL Schlenk flask. The solution was degassed for 30 min in an ice bath and left under a high-purity nitrogen atmosphere. To a second 150 mL Schlenk flask was added a wafer with an ATA-modified surface. This flask was sealed with a rubber septum, subjected to three evacuation−nitrogen purge cycles, and left under a nitrogen atmosphere. The monomer mixture was then transferred via cannula to the wafer flask. The reaction flask was heated to 60 °C for 22 h, after which the silicon wafer was removed, and untethered polymer was removed from the wafers via Soxhlet extraction for 24 h at 60 °C in tetrahydrofuran. Free polymer from the polymerization solution was isolated by evaporating residual monomer and solvent under vacuum at 50 °C overnight.

Synthesis of PSty Brush via RAFT Polymerization. DATC (1.6393 g, 4.496 $\times$ 10^{-3} mol), AIBN (0.1570 g, 9.561 $\times$ 10^{-4} mol), and Sty (50.0 mL, 0.434 mol) were added to a 150 mL Schlenk flask. The solution was degassed for 30 min in an ice bath and left under a high-purity nitrogen atmosphere. A wafer with an ATA modified surface was added to a second 150 mL Schlenk flask. This flask was sealed with a rubber septum, subjected to three evacuation−nitrogen purge cycles, and left under a nitrogen atmosphere. The monomer mixture was then transferred via cannula to the wafer flask. The reaction flask was heated to 90 °C for 22.5 h, after which the silicon wafer was removed, and untethered polymer was removed from wafers via Soxhlet extraction for 24 h at 60 °C in tetrahydrofuran. Free polymer from the polymerization solution was isolated by evaporating residual monomer and solvent under vacuum at 50 °C overnight.

Synthesis of PMMA-*b*-PSty Brush via RAFT Polymerization. DATC (1.639 g, 4.496 $\times$ 10^{-3} mol), AIBN (0.1570 g, 9.561 $\times$ 10^{-4} mol), and Sty (50.0 mL, 0.434 mol) were added to a 150 mL Schlenk flask. The solution was degassed for 30 min in an ice bath and left under a high-purity nitrogen atmosphere. A PMMA brush modified wafer was added to a second 150 mL Schlenk flask. This flask was sealed with a rubber septum, subjected to three evacuation−nitrogen purge cycles, and left under a nitrogen atmosphere. The monomer mixture was then transferred via cannula to the wafer flask. The reaction flask was heated to 90 °C for 24 h, after which the silicon wafer was removed, and untethered polymer was removed from wafers via Soxhlet extraction for 24 h at 60 °C in tetrahydrofuran. Free polymer from the polymerization solution was isolated by evaporating residual monomer and solvent under vacuum at 50 °C overnight.

Synthesis of PMMA-*b*-PDMAEMA Brush via RAFT Polymerization. CDTB (0.0850 g, 3.120 $\times$ 10^{-4} mol), AIBN (0.0103 g, 6.27 $\times$ 10^{-5} mol), anhydrous toluene (13.1 mL), and DMAEMA (11.9 mL, 0.0706 mol) were added to a 150 mL Schlenk flask. The solution was degassed for 30 min in an ice bath and left under a high-purity nitrogen atmosphere. A PMMA brush modified wafer was added to a second 150 mL Schlenk flask. This flask was sealed with a rubber septum, subjected to three evacuation−nitrogen purge cycles, and left under a nitrogen atmosphere. The monomer mixture was then transferred via cannula to the wafer flask. The reaction flask was heated to 60 °C for 44 h, after which the silicon wafer was removed, and untethered polymer was removed from wafers via Soxhlet extraction for 24 h at 60 °C in tetrahydrofuran. Free polymer from the polymerization solution was isolated by evaporating residual monomer and solvent under vacuum at 60 °C overnight.

Synthesis of PSty-*b*-PMA Brush via RAFT Polymerization. CDTB (0.109 g, 4.00 $\times$ 10^{-4} mol), AIBN (0.0200 g, 1.22 $\times$ 10^{-4} mol), and MA (20.3 mL, 0.225 mol) were added to a 150 mL Schlenk flask. The solution was degassed for 30 min in an ice bath and left under a high-purity nitrogen atmosphere. A PSty brush modified wafer was added to a second 150 mL Schlenk flask. This flask was sealed with a rubber septum, subjected to three evacuation−nitrogen purge cycles, and left under a nitrogen atmosphere. The monomer mixture was then transferred via cannula to the wafer flask. The reaction flask was heated to 60 °C for 24 h, after which the silicon wafer was removed, and untethered polymer was removed from wafers via Soxhlet extraction for 24 h at 60 °C in tetrahydrofuran. Free polymer from the polymerization solution was isolated by evaporating residual monomer and solvent under vacuum at 50 °C overnight.

Characterization. Ellipsometric measurements were carried out on a Gaertner ellipsometer, model L116C, with a 632.8 nm helium−neon laser at a 70° angle of incidence. Refractive indices were fixed at 1.455 for all respective surface modifications and brushes. Contact angle measurements were performed utilizing a Rame-Hart goniometer with a 10.0 μL syringe. Static (θ_s), advancing (θ_a), and receding (θ_r) water contact angles were recorded at 0° and 35°. Five measurements were taken across each sample, with their average being used for analysis. Grazing angle attenuated total reflectance (GATR)−Fourier transform infrared (FTIR) spectra were collected utilizing a Harrick Scientific GATR−FTIR attachment coupled with a Thermo-Electron Nicolet 4700 spectrometer, collecting 256 sample scans, and utilizing Nicolet's OMNIC software. All NMR spectra were obtained from a Varian Gemini 300 MHz spectrometer using the MestReC software package. All samples were collected using deuterated chloroform ($CDCl_3$) at 25 °C. Molecular weight analysis was performed utilizing gel permeation chromatography (GPC) coupled with a multiangle laser light scattering (MALLS) detector. The GPC is comprised of a HP1084B liquid chromatograph with two HP Plgel5-lm Mixed-D columns with a linear range of molecular weights from 200 g/mol to 400 000 g/mol connected in series. A Waters R401 differential refractometer (λ = 800 nm, LED lamp) and a miniDAWN MALLS unit (λ = 690 nm, 20 mW laser, three detector angles: 45°, 90°, and 135°, Wyatt Technologies) were used as detectors. HPLC grade THF was used as eluent at a flow rate of 0.7 mL/min. All polymer samples were dissolved in THF (5 mg/mL) and were injected using a 0.45 μL syringe filter. The GPC was standardized using both PSty and PMMA standards. The refractive index increments (d*n*/d*c*) for PSty, PMMA, PMA, and PDMAEMA were 0.126, 0.086, 0.056, and 0.0345 mL/g, respectively.[46] Molecular weight data analysis was performed using Wyatt Technology Astra Software. XPS measurements were performed on a Physical Electron 5800 ultra-high vacuum XPS−Auger spectrometer at Colorado State University. The incidence angle of X-ray was 45° with respect to surface normal. Atomic percentages were adjusted by removing contributions of oxygen from silicon oxide.

Results and Discussion

Recently, CLRP techniques have received a great deal of attention for the synthesis of polymers in solution due to their ability to provide simple and versatile routes for the preparation of well-defined, narrow PDI polymers of both simple and complex architecture.[20,26] In the preparation of polymer brushes via the "grafting from" technique, CLRP techniques have offered many advantages, namely control over the thickness of the brush, uniformity in the surface of the brush, and the ability to produce brushes of complex architecture.[1,2,5] These advantages have made CLRP the technique of choice in the preparation of well-defined polymer brushes and arguably the most common CLRP technique used is ATRP. While ATRP is a very powerful technique for the synthesis of polymer brushes, it has some limitations, particularly in regards to the polymerization of highly functional monomers.[20,26] RAFT polymerization is a much more versatile CLRP technique with regards to the polymerization of functional monomers compared to ATRP. However, while RAFT is becoming a well-established method for the synthesis of controlled, functional polymers in solution, only recently have examples begun to appear in literature utilizing RAFT polymerization for the synthesis of polymer brushes via the "grafting from" technique.[2,6−9,17,18,27−41] As the mechanism of a successful RAFT polymerization requires that all chains are initiated at the same time, preferably by CTA, arguably the best way to prepare polymer brushes via RAFT is by the immobilization of CTAs. A number of research groups have reported various techniques for the immobilization of RAFT CTAs, ranging from modification of functionalized surfaces using Grignard reagents and condensation reactions to the preparation of methoxysilanes containing RAFT CTAs for direct deposition.[2,6−9,17,18,27−41] Herein, we report on a novel method for the immobilization of a RAFT CTA onto a silicate surface for the preparation of well-defined diblock copolymer brushes using RAFT polymerization. To achieve this, a traditional ATRP initiator was first immobilized on the surface and then converted to a RAFT CTA using a modification of an ATA reaction. Following immobilization of the RAFT CTAs, both homopolymer and diblock copolymer brushes were prepared via RAFT polymerization.

Immobilization of RAFT CTAs on Flat Silicate Substrates via ATA. The preparation of a flat silicate substrate containing immobilized RAFT CTAs is illustrated in Scheme 2. Initially, a bromoisobutyrate ATRP initiator, BMP TCS, was deposited on a cleaned silicon wafer by a self-assembly technique. BMP TCS has been widely used for the preparation of polymer brushes via the "grafting from" technique using ATRP.[1,2,15] As such, the preparation and deposition of this initiator have been well studied. Confirmation of the deposition of the BMP TCS was achieved by ellipsometry, goniometry (Table 1), GATR−FTIR, and XPS (Figures 2 and 3). Ellipsometry data for the immobilized BMP TCS showed a slight variability in the thickness, ranging from 2.3 to 5.2 nm. This was attributed to the fact that the "anchoring group" for BMP TCS is a trichlorosilane, which is prone to undergo some degree of surface cross-linking, as has been previously reported.[47] Contact angles for the BMP TCS initiator layers were relatively uniform and compared well with those shown in literature.[15] The GATR−FTIR spectrum of the immobilized BMP TCS (Figure 2a−c) shows peaks at approximately 2850 and 2930 cm^{-1}, which are assigned to the CH$_2$ stretching and the C−H stretching vibrations, respectively, and at ~1740 cm^{-1}, which is assigned to the carbonyl stretching vibration of the ester group. XPS analysis of the immobilized BMP TCS (Figure 3a and Table 2) verifies the presence of bromine (Br 3d), carbon (C 1s), and oxygen (O 1s). There is a small amount of variation in the atomic percentage of bromine for each deposition. This is attributed to the error introduced into these measurements by both the overall variation in the BMP TCS layer, caused by variable cross-linking of the trichlorosilane, and by the calculation used to remove the Si peak from the spectra to give the adjusted atomic percentages. However, while there is variation for the atomic percentage of bromine between different samples, variation across the surface of one sample was negligible.

Table 1. Thickness and Contact Angle Data for Diblock Copolymer Brushes

surface structure	Δ thickness (nm)[a]	contact angle data[b] $\theta_{\text{advancing}}$	θ_{receding}
bromosilane initiator	5.2	89	75
atom transfer addition modified surface	−1.4	81	67
poly(methyl methacrylate) (PMMA)	15.2	72	59
PMMA-*b*-poly(styrene) (PSty)	9.8	90	73
bromosilane initiator	3.0	88	74
atom transfer addition modified surface	−0.6	84	70
poly(methyl methacrylate) (PMMA)	15.3	67	55
PMMA-*b*-poly(2-(dimethylamino)ethyl methacrylate)	7.2	60	42
bromosilane initiator	2.3	84	72
atom transfer addition modified surface	0.4	81	70
PSty	7.0	93	79
PSty-*b*-poly(methyl acrylate)	8.7	65	58

[a] Thicknesses were determined by ellipsometry and are an average of five samplings across the sample. Error of thicknesses measured was within ±1 nm. [b] Static, advancing, and receding contact angles were taken at 0° and 35°, respectively, using goniometry and are an average of five samplings across the sample. The standard deviation of contact angles was less than 2°.

Once the bromosilane ATRP initiator was deposited and characterized, a modified ATA reaction was carried out under oxygen-free conditions using CuBr, Cu(0), PMDETA, and DTBDS, to convert the bromine end group of BMP TCS to a dithiobenzoate RAFT CTA (Scheme 2). The conversion of a tertiary bromoisobutyrate initiator to a dithioester modified CTA surface provided an immobilized tertiary R group, which has the ability to efficiently initiate polymerization. The use of this reaction for the modification of ATRP macroinitiators prepared in solution to RAFT macro-CTAs was recently reported by Wagner and co-workers.[42] In this work they were successfully able to modify the bromine end group of PMMA and PDMAEMA prepared by ATRP in solution to a dithiobenzoate end group. Critical to the success of this reaction is the presence of Cu(0), which is required in order to ensure the equilibrium between Cu(I) and Cu(II) lies in favor of the activating species, Cu(I). It should be mentioned at this stage that a similar process was reported by Tsujii and co-workers for the modification of a PSty polymer brush prepared by ATRP to a surface immobilized RAFT macro-CTA.[43] However, in this case Cu(0) was not used in the modified ATA reaction, resulting in uncontrolled re-extension of the PS brush when the RAFT polymerization was attempted. There was also no attempt to form diblock copolymer brushes or form homopolymer and diblock copolymer brushes completely by RAFT polymerization in this report.

Conversion of the immobilized BMP TCS to the RAFT CTA was performed with a 4.5-fold excess of Cu(0) to Cu(I) and a large excess of DTBDS. The excess of DTBDS is used to maximize the probability that the radical generated by activation of the immobilized ATRP initiator will undergo reaction with the DTBDS, thus forming the immobilized RAFT CTA (Scheme 2). Ellipsometry data showed changes in thicknesses after reaction with the DTBDS ranging between −1.4 and 0.4 nm. Negligible changes in thickness were expected in this reaction as the large bromine atom is being replaced with a dithiobenzoate structure. The negative changes in thickness observed are

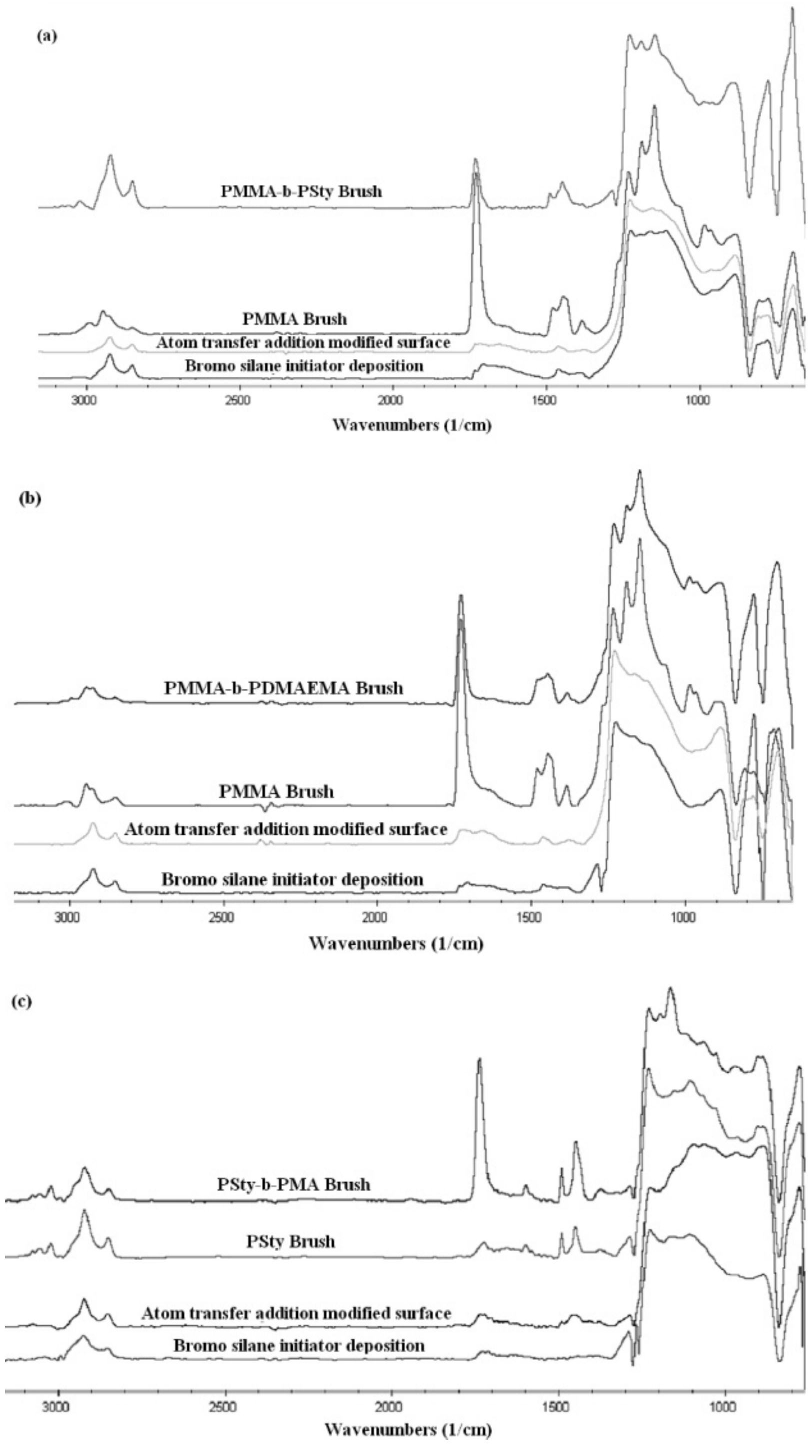


Figure 2. Attenuated total reflectance−Fourier transform infrared spectra for the formation of (a) poly(methyl methacrylate) (PMMA)-*b*-poly(styrene) (PSty), (b) PMMA-*b*-poly(2-(dimethylamino)ethyl methacrylate) (PDMAEMA), and (c) PSty-*b*-poly(methyl acrylate) (PMA) diblock copolymer brush.

within error of the instrument used for these measurements and thus really only indicate an insignificant change in thickness. Goniometry showed a decrease in the advancing contact angle, ranging from 3° to 8°, after conversion to the RAFT CTA. The GATR−FTIR spectrum of the sample after reaction with the DTBDS (Figure 2a−c) indicates few discernible differences to that of the immobilized BMP TCS spectrum. We attribute this to the relatively weak intensity of aromatic C−H and C−C stretches, especially when only one aromatic ring is present per immobilized molecule, and to the fact that the C═S stretching vibration appears in the fingerprint region which is subject to large variation in the GATR−FTIR of silicon wafers. Since the C═S and aromatic stretches were indiscernible in the IR spectra, wide-scan XPS was employed to determine the efficiency of the modified ATA conversion reaction. XPS spectra (Figure 3b) show an obvious atomic percentage decrease of bromine (Br 3d) with a respective appearance of sulfur (S 2s). The proposed modified ATA conversion reaction gives a theoretical ratio of two sulfur atoms for every one bromine atom present on the immobilized BMP TCS (Scheme 2). This was seen in the XPS data with the immobilized BMP TCS having an atomic percentage of bromine (Br 3d) of 1.4%, and following the ATA conversion, the bromine atomic percentage decreases to <0.1%, with a respective increase of sulfur (S 2s) to 2.7%, comparing

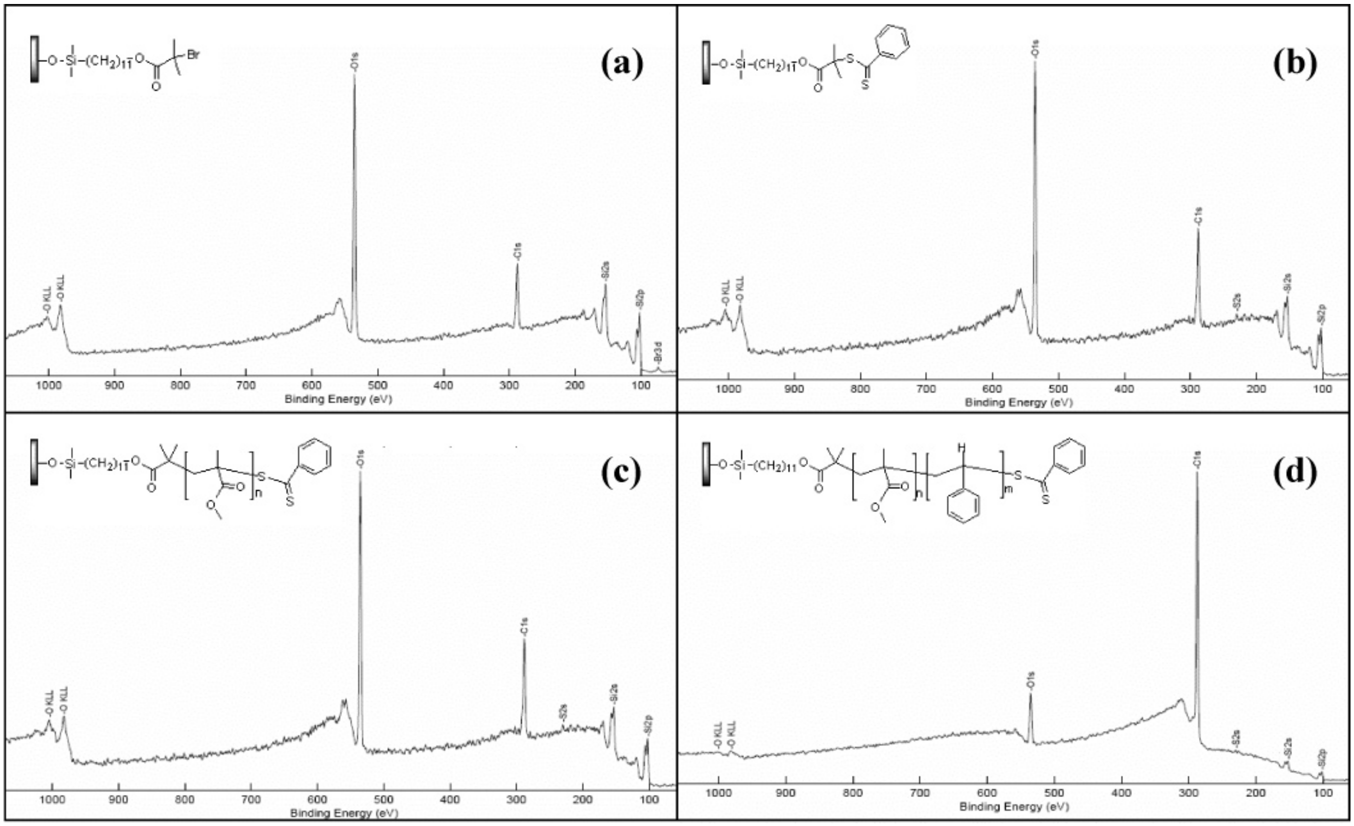


Figure 3. Wide-scan X-ray photoelectron spectra of (a) bromosilane initiator deposition, (b) chain transfer agent modified silicon wafer, (c) poly(methyl methacrylate) (PMMA) homopolymer brush, and (d) PMMA-*b*-poly(styrene) diblock copolymer brush.

Table 2. Adjusted[a] Atomic Percentage of Polymer Modified Silicon Surfaces from Wide-Scan X-ray Photoelectron Spectroscopy

surface structure	C 1s	O 1s	Br 3d	S 2s	N 1s
bromosilane initiator	76.3	21.1	2.6		
atom transfer addition modified surface	78.8	18.4	<0.1	2.1	
poly(methyl methacrylate) (PMMA)	71.6	27.5		0.9	
PMMA-*b*-poly(styrene) (PSty)	95.6	4.1		0.5	
bromosilane initiator	64.0	34.5	1.4		
atom transfer addition modified surface	77.4	25.9	<0.1	2.7	
poly(methyl methacrylate) (PMMA)	73.1	26.2		0.7	
PMMA-*b*-poly(2-(dimethylamino)ethyl methacrylate)	69.8	26.7		0.5	2.0
bromosilane initiator	69.9	29.3	0.8		
atom transfer addition modified surface	91.1	7.6	<0.1	1.3	
PSty	94.0	16.0		0.4	
PSty-*b*-poly(methyl acrylate)	77.7	22.3		0.2	

[a] Atomic percentages were adjusted by removing the expected percentage of oxygen and silicon brought about by the native silicon dioxide layer of silicate wafers.

directly with the theoretical 2:1 sulfur to bromine ratio (Table 2). While this theoretical ratio was not seen in every case, in each case the atomic percentage of bromine (Br 3d) decreased to <0.1% after reaction with DTBDS, indicating the removal of the Br end groups from the immobilized ATRP initiator (Table 2).

To determine the importance of Cu(0) to this reaction, the modified ATA reaction was performed without the addition of Cu(0). When Cu(0) was not used, ellipsometry, goniometry, and GATR−FTIR spectroscopy demonstrated no discernible change from the immobilized BMP TCS. There were no measurable changes in thickness by ellipsometry, which stayed constant at 2.3 nm. Goniometry showed a slight decrease in the advancing and receding contact angles, less than 5°, after attempted conversion to the RAFT CTA. The GATR−FTIR spectrum of the sample after the modified ATA reaction without the addition of Cu(0) indicated no discernible differences to that of the immobilized BMP TCS spectrum. Furthermore, wide-scan XPS did not show a noticeable decrease of bromine, 2.7% to 2.4%, or appearance of sulfur, 0% to 0.1%. This demonstrates that the addition of Cu(0) is vital to ensure the equilibrium between the activating species, Cu(I), and the deactivating species, Cu(II), lies in favor of Cu(I). As is seen in all ATRP reactions, if too much Cu(II) is generated during the reaction, the equilibrium is pushed to the dormant side, thus suppressing formation of the radicals which are required to react with the DTBDS.

Formation of Homopolymer Brushes. To determine the efficiency of the RAFT CTA surface toward surface initiated polymerizations, PMMA and PSty homopolymer brushes were synthesized. In each case, free initiator, AIBN, and free RAFT CTA, either CDTB or DATC, were added to the polymerization system to ensure a controlled polymerization. The addition of the free RAFT CTA has been shown to be required to suppress termination reactions in solution and also due to the fact that such a small amount of RAFT CTA is immobilized on the surface.[18] The addition of free RAFT CTA will also be important in attempting to minimize the amount of radical−radical coupling on the surface. It has been previously shown that due to the fact that locally there is a very high concentration of RAFT CTA when immobilized on a surface, radical migration across the surface, as a result of degenerative chain transfer with other CTAs in close proximity, may result in radical−radical coupling between surface bound chains.[43] This effectively decreases the number of growing chains on the surface resulting in a nonuniform surface and the inability to form block copolymer brushes. The presence of free RAFT CTA in solution will increase the probability that a radical on the surface will react with a free CTA rather than a surface immobilized CTA, thus reducing the likelihood of radical−radical coupling on the surface.

PMMA homopolymer brushes were formed using a 5:1 molar ratio of free RAFT CTA (CDTB) to initiator, in anhydrous toluene at 60 °C for 22 h. The samples were extracted in THF at 60 °C for 24 h to ensure the removal of any untethered polymer from the surface before characterization. The formation of a PMMA homopolymer brush was confirmed by ellipsometry (Table 1), goniometry (Table 1), GATR−FTIR spectroscopy (Figure 2a,b), and XPS (Figure 3). Ellipsometry indicated an increase in thickness of 15.2 and 15.3 nm for two different PMMA brushes prepared under identical conditions. The homopolymer brushes demonstrated advancing contact angles of 67° and 72°, which are comparable to literature data for PMMA brush formation.[1,2] The GATR−FTIR spectra for the PMMA brush demonstrated characteristic peaks at approximately 1720 cm^{-1}, associated with the carbonyl stretch, and at approximately 2920 and 2850 cm^{-1}, which are attributed to the asymmetric CH_2 stretching and the symmetric CH_2 stretching, respectively (Figure 2a,b). XPS analysis of the PMMA brush indicated the presence of carbon, oxygen, and a small atomic percentage of sulfur (Table 2). The adjusted values for the atomic percentage of carbon and oxygen are very close to the theoretical values for PMMA.

PSty homopolymer brushes were formed using a 4.5:1 molar ratio of free RAFT CTA (DATC) to initiator, in the bulk at 90 °C for 22.5 h. The samples were extracted in THF at 60 °C for 24 h to ensure the removal of any untethered polymer from the surface before characterization. Once again the PSty brush was characterized using ellipsometry, goniometry, and GATR−FTIR spectroscopy. Ellipsometry indicated an increased thickness of 17.7 nm, and goniometry demonstrated an advancing contact angle of 93°, which compares well with literature data for the formation of a PSty homopolymer brush (Table 1).[1,2,4] The GATR−FTIR spectra for the PSty homopolymer brush (Figure 2c) also confirmed the presence of PSty due to the expected appearance of aromatic C−H stretching around 3100 cm^{-1} and C═C aromatic doublets at 1420−1480 cm^{-1}.

Sequential Addition for Preparation of Diblock Copolymer Brushes. One of the primary advantages in using CLRP techniques to prepare polymer brushes via the "grafting from" technique is the ability to produce block copolymer brushes by sequential activation of the dormant chain. The preparation of a block copolymer brush is also an excellent way to determine whether the previous sample has retained the "living" characteristics of a well-defined CLRP. Thus, to test the controlled/"living" nature of the surface bound homopolymer brushes prepared via surface immobilized RAFT polymerization, each was used for subsequent formation of diblock copolymer brushes. The procedure to form diblock brushes was similar to that of the homopolymer brushes, with the exception that a preformed homopolymer brush was used instead of an ATA modified wafer. Using homopolymer brushes of either PMMA or PSty, PMMA-*b*-PSty, PMMA-*b*-PDMAEMA, and PSty-*b*-PMA diblock copolymer brushes were formed. The diblock copolymer brushes were characterized using GATR−FTIR spectroscopy, ellipsometry, and contact angle data, along with XPS. For the formation of the PMMA-*b*-PSty brush, the GATR−FTIR spectra (Figure 2a) indicate an increase in intensity of C−H stretches around 3050 cm^{-1}, the appearance of the C═C doublet at 1420−1480 cm^{-1}, and a decreased intensity of the carbonyl stretch representative of the PMMA block, all of which confirm the presence of PSty. Ellipsometry indicated an increase in thickness of 9.8 nm from the original thickness of the PMMA homopolymer brush, and goniometry demonstrated an increase in the advancing contact angle from 72° to 90°, verifying the formation of the PSty outer block (Table 1). Wide-scan XPS spectra (Figure 3d and Table 2) illustrates a decrease in the oxygen atomic percentage, from 27.5% to 4.1%, with a respective increase in the carbon (C 1s) atomic percentage, from 71.6% to 95.6%, after the formation of the PSty outer block. The changes in the atomic percentages in the XPS spectra are explained by the fact that XPS, at a fixed takeoff angle of 45°, is a depth profiling technique. Since the diblock copolymer brush now has PSty at the surface of the brush, the majority of the XPS spectra corresponds to that of PSty.

Formation of a second diblock copolymer brush, PMMA-*b*-PDMAEMA, was again confirmed using the standard characterization techniques. Ellipsometry indicated a thickness increase of 7.2 nm from that of the original PMMA homopolymer brush and goniometry demonstrated a decrease in advancing contact angle from 67° to 60° (Table 1). The decrease in advancing contact angle is expected due to the more hydrophilic nature of PDMAEMA. While the GATR−FTIR spectrum (Figure 2b) shows a shift in the ratio of the CH_2 stretches at ∼2920 cm^{-1}, which is attributed to the addition of the PDMAEMA block, the characteristic peaks for the $-N(CH_3)_2$, which generally appear at ∼2830 cm^{-1}, seem to be overlapping with peaks from the PMMA. To further confirm the presence of the PDMAEMA block, the wide-scan XPS spectra of the PMMA-*b*-PDMAEMA diblock copolymer brush contained ∼2.0 atomic % of nitrogen which is due to the $-N(CH_3)_2$ group of the PDMAEMA.

The final diblock copolymer brush produced was PSty-*b*-PMA. Ellipsometry indicated an increase in thickness of 8.7 nm from the original PSty homopolymer brush, and goniometry demonstrated that the advancing contact angle decreased from 93° to 65° due to the addition of the more hydrophilic PMA (Table 1). The GATR−FTIR spectra confirmed the formation of the PSty-*b*-PMA diblock copolymer brush (Figure 2c) due to the appearance of a carbonyl stretch at 1720 cm^{-1} and an increase in the CH_2 stretch at ∼2920 cm^{-1}. Further analysis of the PSty-*b*-PMA block by wide-scan XPS indicated the presence of carbon, oxygen, and a small atomic percentage of sulfur (Table 2). The adjusted values for the atomic percentage of carbon and oxygen are comparable to the theoretical values for PMA.

To demonstrate that the surface immobilized PSty chains behave the same as free PSty chain, an attempt was made to produce a diblock copolymer brush using MMA to extend from the PSty homopolymer brush. As expected, this was unsuccessful due to the inherent stability of the tertiary radicals; fragmentation of the intermediate formed during RAFT favors the MMA tertiary radical over that of the secondary Sty radical. Therefore, even if a growing PMMA chain reacts with the CTA end group of the immobilized PSty chains, it will most likely fragment to give the dormant PSty and the original PMMA

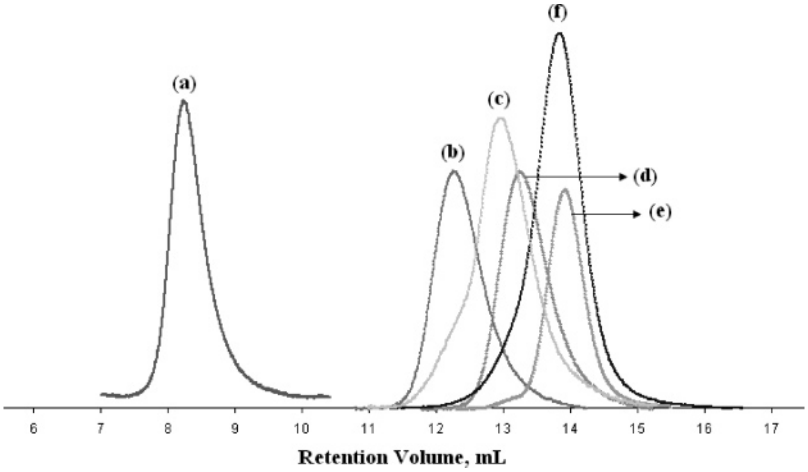


Figure 4. Gel permeation chromatography traces for the solution polymers mediated by addition of sacrificial chain transfer agent: (a) poly(2-(dimethylamino)ethyl methacrylate) (PDMAEMA) with cumyl dithiobenzoate (CDTB) and 2,2′-azobis(isobutyronitrile) (AIBN) in toluene at 60 °C for 24 h; (b) poly(methyl methacrylate) (PMMA) with CDTB and AIBN in toluene at 60 °C for 24 h (PMMA-*b*-poly(styrene) (PSty)); (c) poly(methyl acrylate) in bulk with CDTB and AIBN at 60 °C for 24 h; (d) PMMA with CDTB and AIBN in toluene at 60 °C for 24 h (PMMA-*b*-PDMAEMA); (e) PSty in bulk with *S*-1-dodecyl-*S*′-(α,α′-dimethyl-α″-acetic acid) trithiocarbonate (DATC) at 100 °C for 24 h (PMMA-*b*-PSty); (f) PSty in bulk with DATC and AIBN at 100 °C for 23 h (PSty-*b*-PMA).

radical. Thus, switchover between the PSty homopolymer brush and MMA was unsuccessful, as it is in solution RAFT and ATRP.[15,20] However, by using MA instead of MMA, fragmentation either way is not favored as both the MA radical and the Sty radical are secondary in nature. Therefore, successful formation of a diblock copolymer brush with MA from the PSty homopolymer brush occurred.

To demonstrate the importance of the addition of free RAFT CTA in obtaining a controlled polymerization and, hence, a well-defined polymer brush, preparation of homopolymer brushes was attempted without the addition of free RAFT CTA. The procedure used in preparing the homopolymer brushes and the concentration of reactants used were exactly the same, except no free RAFT CTA was added and due to the viscosity of the reaction medium the polymerizations were stopped after 4.5 h. For both the PSty and PMMA homopolymer brushes prepared without free RAFT CTA the thicknesses were very high, ranging from 90 to 130 nm, and there was a large amount of variation across the surface of the wafer, suggesting growth from the surface was not controlled. To show that the homopolymer brushes prepared without free RAFT CTA did not have the "living" characteristic of a well-defined RAFT polymerization, subsequent diblock formation was attempted. For both the PSty and PMMA homopolymer brushes, the thicknesses did not increase, and there were no changes in either the advancing contact angles or the GATR−FTIR spectra.

Characterization of Sacrificial Polymer Chains. In the case of brushes synthesized from high surface area materials, such as silicon nanoparticles, the surface area is high enough that polymer can be degrafted for direct molecular weight determination. However, in the case of flat silica wafers the concentration of polymer on the surface is extremely small, which makes degrafting and characterization of the polymer extremely difficult. Literature has shown that the addition of sacrificial initiator/CTA to the polymerization system when preparing polymer brushes from silicon wafers not only helps in controlling the polymerization but also results in the formation of "free" or ungrafted polymer in solution.[1,15,18] This free polymer can be easily isolated and characterized using standard techniques, and many researchers have shown that the properties of the free polymer tends to mimic the properties of the polymer on the surface.[15,43] As such, since free RAFT CTA was added to the polymerization in each of the above cases, the polymer formed in solution was isolated and characterized using GPC. In each case the GPC traces for the free polymer (Figure 4) were monomodal and had narrow molecular weight distributions, which are characteristics of well-defined polymers prepared via RAFT polymerization. Theoretical and experimental molecular weights and PDIs for the free polymers isolated in the previous polymerizations are shown in Table 3. For all polymers synthesized, theoretical and experimental weights correlated well, and the PDIs are all below 1.18, indicating that in each case the polymerization was controlled. For the PMMA and PSty systems the molecular weight of the polymer in solution appears to relate well to the thickness of the polymer attached to the silicon wafer. For example, in the case of the PMMA homopolymer brushes, the molecular weight of the polymers in solution were 21 910 and 20 460 g/mol, which corresponded to polymer brush thicknesses of 15.3 and 15.2 nm, respectively. In the case of the PSty, the molecular weights of the polymer formed in solution were 10 680 and 10 760 g/mol, which correspond to a homopolymer brush thickness of 7.0 nm and an outer block thickness of 9.8 nm of PS from PMMA, respectively. It is difficult to make comparison for the PMA and PDMAEMA systems as there is only one of each of these samples. However, the PDMAEMA appears to be less controlled off the surface in comparison to in solution due to the fact that the solution molecular weight of 36 785 g/mol only corresponds

Table 3. Molecular Weight Properties of Solution Polymerizations Determined by Gel Permeation Chromatography

polymer	theor M_n (g/mol)	expt M_n (g/mol)	PDI
PDMAEMA[a]	37 100	36 785	1.17
PMMA[b]	21 810	21 910	1.07
PMA[c]	22 990	29 730	1.18
PMMA[d]	20 590	20 460	1.06
PSty[e]	10 015	10 680	1.06
PSty[f]	8200	10 760	1.10

[a] Poly(2-(dimethylamino)ethyl methacrylate) (PDMAEMA) with cumyl dithiobenzoate (CDTB) and 2,2′-azobis(isobutyronitrile) (AIBN) in toluene at 60 °C for 24 h. [b] Poly(methyl methacrylate) (PMMA) with CDTB and AIBN in toluene at 60 °C for 24 h (PMMA-*b*-poly(styrene) (PSty)). [c] Poly(methyl acrylate) (PMA) in bulk with CDTB and AIBN at 60 °C for 24 h. [d] PMMA with CDTB and AIBN in toluene at 60 °C for 24 h (PMMA-*b*-PDMAEMA). [e] PSty in bulk with *S*-1-dodecyl-*S*′-(α,α′-dimethyl-α″-acetic acid) trithiocarbonate (DATC) at 100 °C for 24 h (PMMA-*b*-PSty). [f] PSty in bulk with DATC and AIBN at 100 °C for 23 h (PSty-*b*-PMA).

to a brush thickness of 7.2 nm. Surface termination may also be another reason for the discrepancy in these values. It should be noted that in the preparation of the diblock copolymer brushes, polymerization to produce the second block only results in the formation of a homopolymer in solution, not a diblock. The reason for this is that a standard RAFT CTA was used in solution not a macro-CTA of the first block. Current work is focused on immobilizing RAFT CTA to high surface area nanoparticles, via the modified ATA reaction, for subsequent formation of brushes for direct comparison of surface and solution molecular weight characteristics.

Conclusions

We have demonstrated a novel method of preparation of a RAFT CTA modified surface which was subsequently used to prepare a series of homopolymer and diblock copolymer brushes. Formation of the RAFT CTA surface involved immobilization of a traditional ATRP surface initiator followed by conversion using a modified ATA reaction. The addition of Cu(0) to the modified ATA reaction was critical in effectively converting the bromo end groups of the ATRP initiator to surface immobilized RAFT CTAs. Using RAFT CTA modified silicon wafers, homopolymer brushes of PMMA and PSty and diblock copolymer brushes of PMMA-*b*-PSty, PMMA-*b*-PDMAEMA, and PSty-*b*-PMA were produced. In each case, addition of free CTA was necessary to control molecular weight growth from the surface and maintain "living" chains. The addition of sacrificial CTA results in the formation of free polymer in solution, which was characterized and confirmed the formation of well-defined polymers. In most cases, film thicknesses correlated well with experimental molecular weights of free polymer chains.

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