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Synthesis, Characterization, and Properties of Tethered Polystyrene-*b*-polyacrylate Brushes on Flat Silicate Substrates

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ABSTRACT: Surface-immobilized polystyrene-*b*-polyacrylate brushes have been synthesized on silicate substrates from chlorine-terminated polystyrene (PS) brushes by atom transfer radical polymerization (ATRP). ATRP of methyl methacrylate (MMA), methyl acrylate (MA), and (*N*,*N*-dimethylamino)ethyl methacrylate (DMAEMA) produced tethered diblock copolymer brushes, which were characterized by ellipsometry, FTIR-ATR, tensiometry, and XPS. “Control” polymerizations supported a radical mechanism for the MMA polymerization. The thickness of the polyacrylate terminal block was controlled by free initiator concentration. All three diblock copolymer brushes underwent self-reorganization and exhibited different surface properties in response to different solvent treatments. For PS-*b*-PMMA and PS-*b*-PMA brushes, treatment with CH_2Cl_2 resulted in localization of PMMA and PMA at the air interface; treatment with cyclohexane localized the PS block at the air interface. PS-*b*-PDMAEMA brushes exhibited a similar behavior using cyclohexane and THF/H_2O (v/v = 1:1).

Introduction

Fabricating polymer brushes on a solid substrate is an effective way to control the surface properties and has been used in many important technologies.[1−3] Methods for the preparation of polymer brushes include physisorption of block copolymers,[4] grafting preformed end-functionalized polymers to the substrate (“grafting to”),[5] and in situ formation of polymer chains from the surface (“grafting from”).[6−27] The “grafting from” technique is performed by an in situ surface initiated polymerization from immobilized initiators in which monomers can easily diffuse through the existing polymer layer. As a result, the grafting density and brush thicknesses are generally higher than other methods. Initiators can be immobilized onto the substrate surfaces by treatment of a substrate with glow discharge or plasma in the presence of a gas.[6−9] However, the types and amount of the initiators are not well defined. Immobilized initiators can also be obtained by chemical methods. Traditionally, it involves a series of chemical steps to fix the initiators on the surface.[10−12] Anchor molecules, usually a coupling agent, are first linked to the surface followed by reaction with initiator precursors. Just like treatment with glow-discharge and plasma, this multistep process may introduce side products complicating the situation that result in a poor understanding of the initiation mechanism. To eliminate these problems, self-assembled monolayer (SAM) techniques have been used to immobilize initiators on the substrate in one step. Rühe and co-workers[13−18] have used this technique; in addition, they incorporated a cleavable functional group in the initiator molecule which allows the degrafting of polymer chains for analysis of molecular weight and molecular weight distribution. This strategy has produced polymer brushes with a high tethering density and has been extended into the fabrication of patterned polymer brushes.

To achieve a better control of molecular weight and molecular weight distribution and to synthesize block copolymer brushes, researchers have used living polymerization methods to make brushes. Living or “controlled” polymerizations that have been used in the synthesis of polymer brushes by a “grafting from” approach include TEMPO-mediated radical,[19] living anionic,[20,21] living carbocationic,[22] atom transfer radical polymerization (ATRP),[19,23,24] and ring-opening metathesis polymerization (ROMP).[25]

Theoretical investigation of polymer brushes has been extended from flexible neutral homopolymer brushes into charged polymer brushes,[28−33] semiflexible polymer brushes,[34] liquid crystalline polymer brushes,[35,36] and block copolymer brushes.[37−43] Many interesting properties have been revealed using self-consistent-field calculations, scaling arguments, or computer simulations. The behavior of tethered diblock copolymer brushes is especially interesting because the microphase separation tendency of diblock copolymers will be affected by the covalent attachment of one end of polymer chain onto a substrate. In addition to the Flory−Huggins interaction parameter (χ), overall molecular weight (N), volume fraction of one block (f), Kuh length (flexibility of the backbone), surface density of chains, fixation of diblock copolymer chain ends onto the solid surface via a covalent bond, environmental conditions (solvent, temperature), and surface free energy of each block in the air are also critical in determining the behavior of tethered diblock copolymers. Theoretical work has suggested that patterned films with various novel structures could form from tethered block copolymer brushes.[38−42]

We initiated a project to synthesize tethered diblock copolymer brushes on flat silicate substrates, investigate their behavior in response to different solvent treatments, and experimentally pursue pattern formation.[44−48] In this paper, we report the synthesis of tethered polystyrene-*b*-polyacrylate copolymer brushes and the response of these diblock copolymer brushes to different solvent treatments. The synthesis of polystyrene (PS) brushes using carbocationic polymerization has been detailed in a previous publication.[46] We have synthesized three terminal polyacrylate blocks where the surface-bound block of PS remained constant. The terminal blocks that have been synthesized include poly(methyl methacrylate) (PMMA), poly(methyl acrylate)

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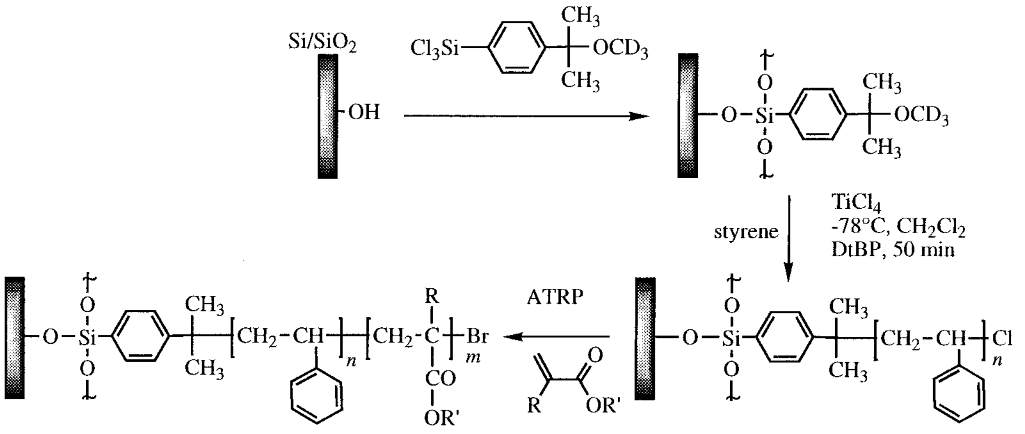
Scheme 1. Synthesis of PS-*b*-polyacrylate Brushes on a Silicate Substrate



R, R' = CH_3; PS-*b*-PMMA
R = H, R' = CH_3; PS-*b*-PMA
R= CH_3, R'= $CH_2CH_2N(CH_3)_2$; PS-*b*-PDMAEMA

(PMA), and poly((*N*,*N*-dimethylamino)ethyl methacrylate) (PDMAEMA). We varied the terminal block purposefully to study the influence of miscibility (PMMA vs PMA) and hydrophobicity (PMMA vs PDMAEMA) on the surface behavior and dynamics of a tethered diblock copolymers.

Results

Synthesis of Tethered PS-*b*-polyacrylate Brushes on Flat Silicate Substrates. The synthesis of tethered PS-*b*-polyacrylate brushes on flat silicate substrates via a "grafting from" approach is illustrated in Scheme 1. A carbocationic initiator was immobilized onto the silicate substrates by a self-assembly technique. Then surface-initiated carbocationic polymerization of styrene produced tethered PS brushes followed by ATRP of an acrylate monomer to achieve diblock copolymer brushes. MMA, methyl acrylate (MA), and (*N*,*N*-dimethylamino)ethyl methacrylate (DMAEMA) were used in the synthesis of the second block.

Previous FTIR-ATR study of surface-initiated carbocationic polymerization indicated that the initiator efficiency under typical polymerization conditions was low (≈7%), and a sequential, second carbocationic polymerization involved both PS chain ends and immobilized initiators.[46] To avoid the initiation from the immobilized cumyl methyl ether initiator in the synthesis of the second block, we used ATRP to synthesize the second block. Coca and Matyjaszewski [49] successfully synthesized PS-*b*-PMMA copolymers in solution by carbocationic polymerization and ATRP. The chlorine-terminated PS chain end is an initiator for both carbocationic polymerization and ATRP. One advantage of ATRP is the larger number of available monomers for radical polymerization.

The detailed experimental conditions for ATRP from tethered PS chain ends are described in the Experimental Section. We chose multidentate amines such as *N*,*N*,*N*′,*N*′,*N*″-pentamethylethylenediamine (PMDETA) and 1,1,4,7,10,10-hexamethyltriethylenetetraamine (HMTETA) as ligands[50] instead of bipyridine and alkyl-substituted bipyridines such as 4,4′-di-*n*-heptyl-2,2′-bipyridine. The polymerization was carried out in a Schlenk tube at elevated temperatures. The sample was then removed from the polymerization mixture and cleaned by extraction with CH_2Cl_2 or THF overnight followed by characterization with tensiometry, FTIR-ATR, X-ray photoelectron spectroscopy (XPS), and ellipsometry.

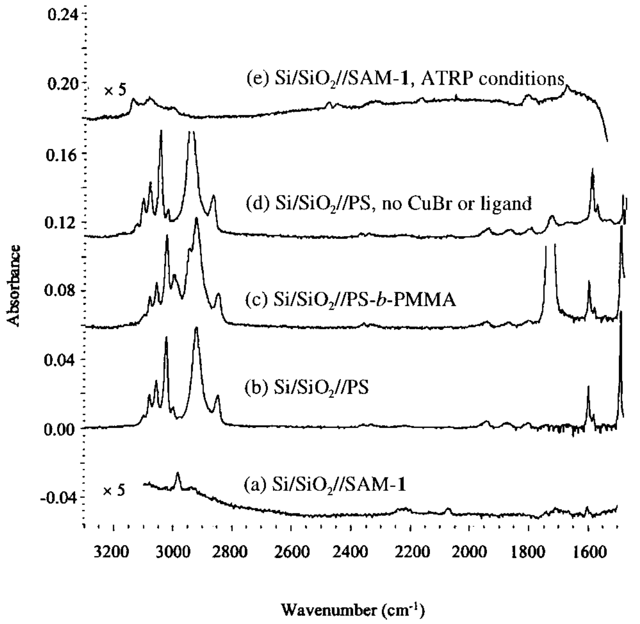


Figure 1. FTIR-ATR spectra of (a) Si/SiO$_2$//SAM-**1**; (b) Si/SiO$_2$//PS (tethered PS brush), film thickness = 26 nm; (c) Si/SiO$_2$//PS-*b*-PMMA (tethered PS-*b*-PMMA brush), film thickness = 35 nm; (d) Si/SiO$_2$//PS after attempted ATRP of MMA in the absence of CuBr and ligand; (e) Si/SiO$_2$//SAM-**1** after treatment with MMA under ATRP conditions.

PS-*b*-PMMA Brushes. The FTIR-ATR spectrum (see Figure 1c) revealed that a strong peak appeared at 1732 cm^{-1}, which was assigned to the carbonyl stretching vibration of the ester group in PMMA. On the basis of ellipsometry, the film thickness in the dry state increased from 26 to 35 nm for a tethered PS brush that was subjected to ATRP with MMA.

Control Polymerization Experiments. To determine that the polymerization of MMA resulted from a radical polymerization mechanism and not from a thermal or some other polymerization, a control polymerization was carried out. An ATR prism to which PS brushes were tethered was immersed in a mixture of anisole and MMA; the mixture was degassed by bubbling with argon for 30 min and heated at 90 °C for 6

h. No CuBr and ligand were added into the polymerization system. The FTIR-ATR spectrum (Figure 1d) showed that ATRP in the absence of catalyst did not produce tethered PMMA. The sample was cleaned by rinsing with CH_2Cl_2 and placed in a Schlenk tube containing CuBr followed by addition of anisole and MMA. The mixture was degassed by bubbling with argon for 30 min followed by addition of the ligand, PMDETA. The polymerization was run at 90 °C for 6 h. After extraction with CH_2Cl_2, the FTIR-ATR spectrum displayed a strong carbonyl peak at 1732 cm^{-1}.

This control experiment is consistent with our view that MMA was polymerized from chlorine termini by a radical polymerization mechanism. To further confirm that the polymerization of MMA started from chlorine-terminated PS chain ends and not from a surface-immobilized cumyl methyl ether initiator, a second control experiment was carried out. An ATR prism to which PS chains are tethered and another ATR prism coated with the cumyl methyl ether initiator were placed in the same Schlenk tube and subjected to identical ATRP conditions. No PMMA appeared on the initiator monolayer-coated ATR prism (Figure 1e).

From these two control experiments, we conclude that the polymerization of MMA occurred at PS chain ends. However, we do not know what percent of PS chains started the block copolymerization. We also do not have information about the molecular weight of the tethered diblock copolymers.

Control of PMMA Thickness. The thickness of the PMMA layer can be controlled by the concentration of free ATRP initiator in solution. The radical concentration on the surface is extremely low compared with solution ATRP. If 0.1% total radicals were terminated by adventitious radical scavengers in solution ATRP, very good results can be achieved. But for our surface case, if the same amount of radicals was terminated, it would result in a PMMA layer with a very low thickness. We speculated that the adventitious radical scavengers would be consumed by radicals generated from free initiator in the solution. Using this method, PMMA blocks with 3−25 nm thicknesses could be reproducibly produced. Figure 2 shows the IR spectra of four tethered diblock copolymer brushes obtained under the same reaction conditions except for the free initiator concentration. The polymerization conditions and PS thickness are summarized in Table 1. The free initiator was 1-phenyl-1-chloroethane (PHECl), which has a similar structure to the chlorine-terminated PS chain ends. The FTIR-ATR spectra clearly indicate that the intensity of carbonyl peak increased with decreasing free initiator concentration in accord with our expectations. In polymerization runs 3 and 4, the same [PHECl] resulted in similar PMMA thicknesses.

On the basis of the mechanism of ATRP, the PMMA chain ends should be bromine-terminated. A second ATRP of MMA was carried out on a PS-*b*-PMMA brush (no. 1 in Table 1) under the following conditions: 90 °C, 6 h, $[MMA]_0 = 4.67$ mM, $[CuBr]_0 = [ligand]_0 = 18.82$ mM, $[PHECl]_0 = 1.66$ mM. The PMMA layer thickness increased 5 nm in accord with our expectation that the chain ends remain active for ATRP.

Extension of Diblock Synthesis to PMA and PDMAEMA. Using the same strategy, PS-*b*-PMA brushes tethered on flat silicate substrates were successfully synthesized. ATRP was carried out on a 24 nm PS brush at 110 °C for 24 h with methyl 2-bromopropionate as the free initiator. After polymerization, the sample was extracted with THF or CH_2Cl_2 for 24 h. The FTIR-ATR spectrum displayed a strong carbonyl absorption peak at 1733 cm^{-1} (Figure 3c); ellipsometry indicated that the film thickness increased 9 nm.

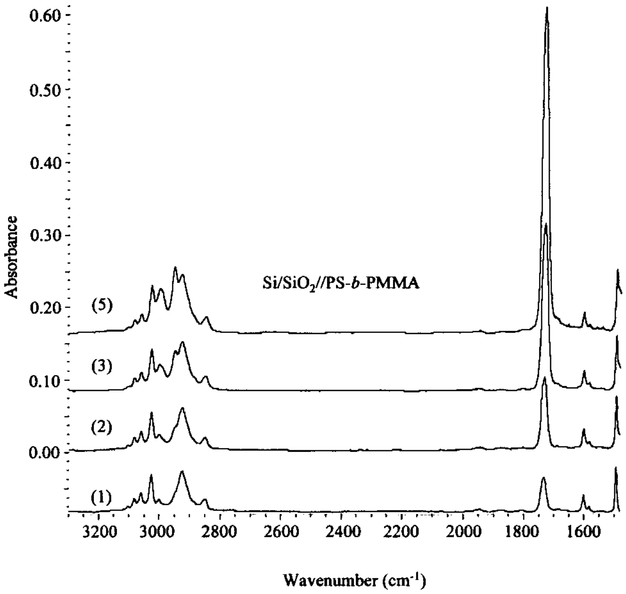


Figure 2. FTIR-ATR spectra of a series of Si/SiO_2//PS-*b*-PMMA brushes obtained under identical ATRP conditions except for different free initiator concentrations; description of PS brushes and the concentration of free initiator are summarized in Table 1.

Table 1. Effect of 1-Phenyl-1-chloroethane (PHECl) on the Thickness of the PMMA Layer in PS-*b*-PMMA Brushes[a]

no.	PS thickness (nm)	PHECl concn (mM)	PMMA thickness (nm)
1	30.0	18.88	1.0
2	27.5	4.96	3.2
3	25.3	1.66	12.2
4	23.0	1.66	12.4
5	28.0	0.76	23.6

[a] Polymerizations were carried out at 90 °C for 6 h, $[MMA]_0 = 4.67$ M, $[CuBr]_0 = 18.82$ mM, $[ligand]_0 = 19.09$ mM. The standard deviation of thickness values is <1 nm.

Many attempts have been made to synthesize block copolymers containing PDMAEMA in solution; well-defined PMMA-*b*-PDMAEMA and PMA-*b*-PDMAEMA copolymers with low polydispersities have been prepared by ATRP.[54] PS-*b*-PDMAEMA has also been synthesized by ATRP, but the polymerization was not well controlled due to the relatively slow initiation from PS macroinitiator in comparison with the propagation rate of PDMAEMA. The reported polydispersity was 1.83. We attempted the synthesis of tethered PS-*b*-PDMAEMA by ATRP from PS brushes. The polymerization was allowed to proceed at 115 °C for 9 h followed by THF extraction. The FTIR-ATR spectrum is shown in Figure 3d. Characteristic peaks of PDMAEMA such as the carbonyl peak located at 1729 cm^{-1} and two symmetric stretching vibration absorptions of the methyl group in the $N(CH_3)_2$ moiety located at 2820 and 2769 cm^{-1} were observed. Ellipsometry measurements indicated that the film thickness increased from 24 to 26.5 nm.

Tensiometry of Diblock Copolymer Brushes. We used water contact angles to probe the chemical nature

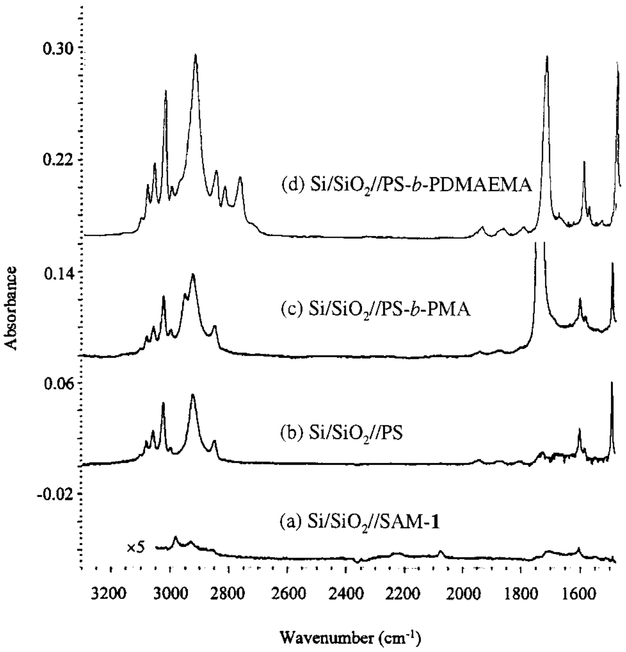


Figure 3. FTIR-ATR spectra of (a) Si/SiO$_2$//SAM-**1**; (b) Si/SiO$_2$//PS (tethered PS brush), film thickness = 24 nm; (c) Si/SiO$_2$//PS-*b*-PMA (tethered PS-*b*-PMA brush), film thickness = 33 nm; (d) Si/SiO$_2$//PS *b*-PDMAEMA (tethered PS-*b*- PDMAEMA brush), film thickness = 26.5 nm.

Table 2. Water Contact Angles[a] (deg) of PS-*b*-polyacrylate Brushes

sample description	θ_a	θ_r
PS-*b*-PMMA after CH_2Cl_2 treatment[b,c]	74	59
PS-*b*-PMMA after cyclohexane treatment[b,d]	99	78
PS-*b*-PMMA after second CH_2Cl_2 treatment[b,c]	74	59
PS-*b*-PMMA after second cyclohexane treatment[b,d]	99	78
PS-*b*-PMA after CH_2Cl_2 treatment[c,e]	68	55
PS-*b*-PMA after cyclohexane treatment[d,e]	98	74
PS-*b*-PMA after second CH_2Cl_2 treatment[c,e]	69	55
PS-*b*-PDMAEMA after THF/H_2O treatment[f,g]	63	44
PS-*b*-PDMAEMA after cyclohexane treatment[f,h]	98	77
PS-*b*-PDMAEMA after second THF/H_2O treatment[f,g]	64	45

[a] The standard deviation of contact angles <2°. [b] PS layer thickness = 28 nm, PMMA layer thickness = 10.8 nm. [c] Immersion in CH_2Cl_2 at room temperature for 30−45 min. [d] Immersion in cyclohexane at 35 °C for 30 min. [e] PS thickness = 24 nm, PMA thickness = 9 nm. [f] PS thickness = 27 nm, PDMAEMA thickness = 3 nm. [g] Immersion in THF/H_2O (1:1, v/v) at 35 °C for 60 min. [h] Immersion in cyclohexane at 35 °C for 60 min.

of the outermost layer in our diblock copolymer brushes. The contact angles (Table 2) of the PS-*b*-PMMA brush ($\theta_a = 74°$) and the PS-*b*-PMA brush ($\theta_a = 68°$) after each brush was treated with CH_2Cl_2 (which is a good solvent for both blocks) indicate that the polyacrylate blocks are localized at the air interface because the contact angles are representative of spun-cast films of the corresponding homopolymers. When the PS-*b*-PDMAEMA brush was treated with H_2O/THF (1:1, v/v), advancing and receding contact angles of 63° and 44° were observed (Table 2). Since PDMAEMA is a water-soluble polymer, the contact angles should be closer to 0°. The possible reason for this difference is that the initiation efficiency in the polymerization of DMAEMA is lower; therefore, the topmost layer is composed of both PS and PDMAEMA chains. Another possibility may be due to the higher surface free energy of PDMAEMA relative to PS. When the sample was removed from the solvent, the PDMAEMA blocks may have aggregated and migrated into the bulk phase to avoid contact with air; the PS chains would remain localized at the air interface due to their lower surface energy.

We also used contact angles to study the influence of block-selective solvents on the copolymer brushes. In our earlier publication, we observed large changes in the contact angles of PS-*b*-PMMA brushes when the samples were treated with cyclohexane or CH_2Cl_2.[44] In this study, we wanted to test the generality of these observations. Table 2 summarizes the results for the three diblock copolymer systems reported here.

Tethered PS-*b*-PMA brushes exhibited similar properties to tethered PS-*b*-PMMA brushes. Treatment with cyclohexane increased the advancing and receding contact angles to 98° and 74°(characteristic values for PS). Subsequent treatment with CH_2Cl_2 changed the contact angles back to their original values; these changes were reversible for many cycles of alternating solvent treatment. Tethered PS-*b*-PDMAEMA brushes also undergo self-reorganization in response to environmental changes. A mixed solvent of THF and water was chosen to treat the PS-*b*-PDMAEMA brushes. For a 30 nm PS-*b*-PDMAEMA brush with a 27 nm thick PS layer, the film exhibited an advancing contact angle of 63° and a receding contact angle of 44° after treatment in THF/H_2O (v/v = 1:1) for 60 min at elevated temperature. Treatment with cyclohexane at 35 °C for 60 min increased the contact angles to 98° and 77°. These changes were also reversible.

The time scale of the contact angle changes is dependent on the relative thicknesses of PS layer and polyacrylate layers. For a sample with 29 nm PS and 3 nm PMMA, reorganization of polymer chains occurred quickly upon immersion in cyclohexane at 35 °C. The polymer brushes exhibited the characteristic contact angles of PS after treatment with cyclohexane in less than 20 min. For a sample with 28 nm PS and 22 nm PMMA, 40 min immersion in cyclohexane at 35 °C resulted in an advancing contact angle of 93° and a receding contact angle of 74°. Longer immersion times (several hours) are needed for this sample to achieve an advancing contact angle of 99°. For a sample with 11 nm PS and 18 nm PMMA, the highest advancing and receding contact angles which can be achieved after immersion in cyclohexane at 35 °C for 3.5 h are 85° and 69°.

X-ray Photoelectron Spectroscopy of Diblock Copolymer Brushes. XPS was used to augment tensiometric data on the composition of diblock copolymer brushes at the air interface. In a previous publication, XPS data for the PS-*b*-PMMA brush were reported.[45] After CH_2Cl_2 treatment of the PS-*b*-PMMA brush, 23.5% oxygen was observed; treatment with cyclohexane produced a sample that displayed only 7.8% oxygen. This large decrease in oxygen is consistent with the migration of PMMA blocks away from the air interface.

The surface compositions of a tethered PS-*b*-PMA brush with 24 nm PS and 6 nm PMA after treatment with CH_2Cl_2 and cyclohexane were obtained from XPS (Figure 4). The oxygen peak O_{1s} decreased significantly after treatment with cyclohexane. Calculations indicated that the PS content in the XPS probing region increased from 38.1% to 88.0% after immersion of this sample in cyclohexane at 35 °C for 60 min. These results are consistent with the contact angle observations and are qualitatively similar to the PS-*b*-PMMA system.

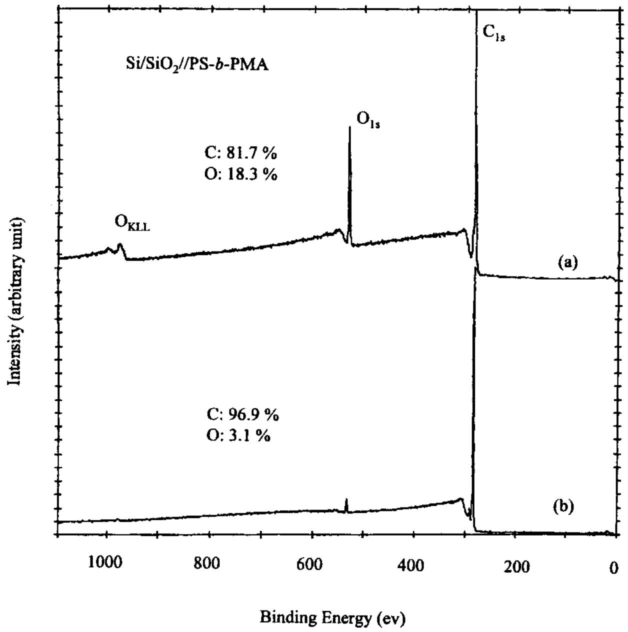


Figure 4. XPS spectra of a tethered Si/SiO$_2$//PS-*b*-PMA brush with 24 nm PS and 6 nm PMA: (a) after treatment with CH$_2$Cl$_2$ at room temperature for 30 min; (b) after treatment with cyclohexane at 35 °C for 60 min.

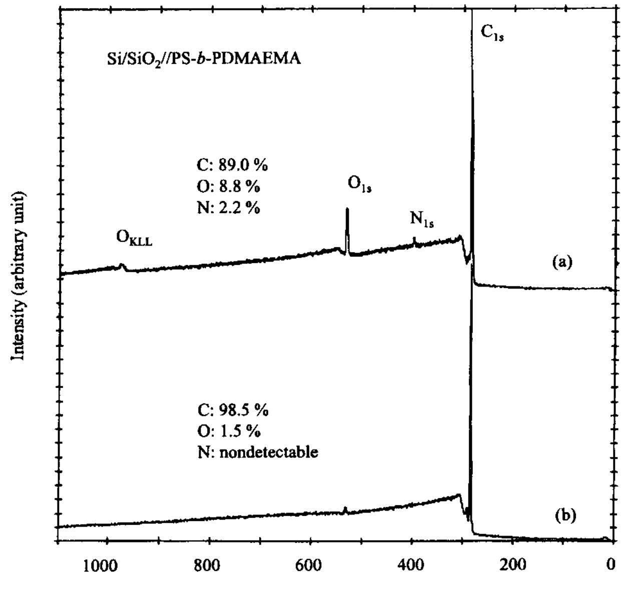


Figure 5. XPS spectra of a tethered Si/SiO$_2$//PS-*b*-PDMAEMA brush with 24 nm PS and 2.5 nm PDMAEMA: (a) after treatment with THF/H$_2$O (1:1, v/v) at room temperature overnight; (b) after treatment with cyclohexane at 35 °C for 2 h.

The XPS spectra of a 26.5 nm PS-*b*-PDMAEMA brush with 24 nm PS after treatment with THF/H$_2$O (v/v = 1:1) and cyclohexane are shown in Figure 5. After treatment with cyclohexane, the oxygen content decreased from 8.8% to 1.5% in the XPS probing depth; the nitrogen content decreased from 2.2% to nondetectable in the XPS spectrum.

Discussion

Synthesis of Terminal Polyacrylate Blocks. Our synthetic approach to diblock copolymer brushes starts with the carbocationic polymerization of styrene followed by the ATRP of an acrylate monomer. Like solution ATRP, we have observed that surface-initiated ATRP from PS brushes is general for the three monomers studied here. Evidence for successful acrylate polymerization is based on FT-ATR, XPS, ellipsometry, and water contact angles. In all cases, ellispometric film thicknesses increased. XPS spectra indicated the presence of polyacrylate at the air interface. Likewise, FT-ATR spectra contained characteristic absorptions for the polyacrylate block. The PMMA polymerization was studied in the greatest detail. The PMMA thickness (3−25 nm) can be reproducibly controlled by the concentration of free initiator in solution. Control experiments were consistent with a free-radical polymerization mechanism. Furthermore, it was demonstrated that the cumyl ether initiators used for carbocationic polymerization were inactive under ATRP conditions.

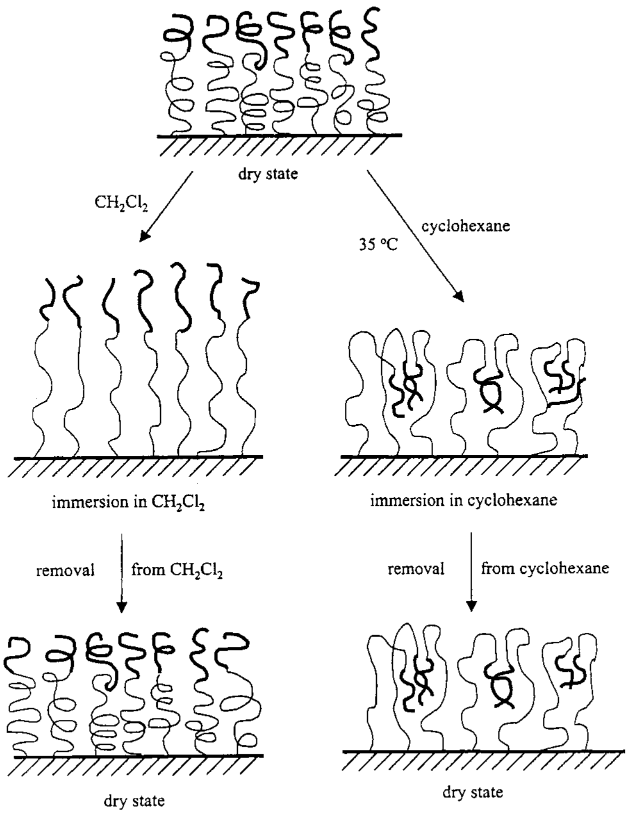
Dynamic Properties of Tethered Diblock Copolymer Brushes. In bulk, diblock copolymers have a tendency to undergo microphase separation. A variety of phase morphologies ranging from spherical, hexagonal, lamellae to gyroid have been discovered and extensively studied.[51,52] In tethered diblock copolymer brushes, the mobility of polymer chains is highly restricted because one end of the polymer chain is covalently connected to the solid surface. The chemically distinct nature of each block and fixation of one end of polymer chains to the surface underlies the unique behavior of polymer brushes. The different interactions of each block with solvents can force the tethered polymer chains to reorganize themselves to minimize the free energy, resulting in interfaces between copolymer brushes and air that exhibit different properties. This preferential interaction of one block with solvents has led to the theoretical prediction of nanopattern formation from tethered diblock copolymer brushes.[38,40]

Experimentally, we have found that tethered diblock copolymer brushes exhibit interesting properties.[44,47] The water contact angles of the films changed dramatically upon treatment with different solvents. XPS results are consistent with contact angle observations. Under appropriate conditions, a nanopattern can form from the tethered diblock copolymer brushes.[45] In the following section, the responses of tethered PS-*b*-PMMA, PS-*b*-PMA, and PS-*b*-PDMAEMA to different solvent treatments will be discussed in terms of contact angle observations and XPS data.

Responses of Tethered PS-*b*-polyacrylate Brushes to Different Solvent Treatments. In earlier publications, we reported the influence of solvent on the surface properties of a PS-*b*-PMMA brush.[44]

Contact angles are very sensitive to the topmost surface composition changes (sensing depth is 0.5−1 nm); many factors such as surface roughness and chemical heterogeneity can have significant effects on the contact angle values. The changes in water contact angles are consistent with XPS spectra where an increasing contact angle (which we have interpreted in terms of PS localization at the air interface) is accompanied by a decrease in the O$_{1s}$ peak in the XPS spectrum. Contact angles changes are dependent on the relative thicknesses of PS and PMMA layers. We have observed that ability of PS segments to localize at the air interface (as deduced by water contact angles) is dependent on the PMMA block thickness. Larger PMMA thicknesses are accompanied by smaller changes in

Scheme 2. Proposed Responses of Tethered PS-*b*-PMMA Brushes to Different Solvent Treatments



water contact angles after the PS-*b*-PMMA brushes are immersed in cyclohexane (cyclohexane is a Θ solvent for PS at 35 °C).

Tethered PS-*b*-PMA brushes on flat silicate substrates exhibit similar properties to tethered PS-*b*-PMMA brushes (Table 2). After treatment with CH_2Cl_2, the advancing and receding contact angles are 68° and 55°. Treatment with cyclohexane increased the contact angles to 98° and 74°. These changes are reversible, and the XPS spectra support this surface localization of different block segments. Tethered PS-*b*-PDMAEMA brushes also undergo reorganization in response to environmental changes (Table 2). Treatment with cyclohexane at 35 °C for 60 min increased the contact angles to 98° and 77°. Subsequent treatment with in THF/H_2O (v/v = 1:1) for 60 min at elevated temperatures changed the contact angles back to their original value.

Reorganization Mechanism of Tethered Diblock Copolymer Brushes. For tethered PS-*b*-PMMA and PS-*b*-PMA, CH_2Cl_2 is a good solvent for PS, PMMA, and PMA. When the sample is immersed in this solvent, the polymer chains are forced to stretch away from the interface to avoid contact with neighboring polymer chains. Removing the PS-*b*-PMMA brushes from CH_2Cl_2 condenses the polymer brushes and localizes PMMA blocks at the air interface. The T_g's of PS and PMMA in the bulk state are both around 100 °C, and there is little difference in surface free energies of PS and PMMA. Therefore, The PMMA blocks remain at the air interface, which is supported by contact angle measurements and XPS results. Scheme 2 illustrates this process.

If the sample was immersed in the cyclohexane, we speculate that PMMA chains migrate from the solvent interface and form aggregates with neighboring PMMA blocks to avoid contact with solvent. Although PS blocks have a low mobility because of the covalent bond to the silicon wafer surface and to the PMMA block, they are miscible with cyclohexane and migrate to the solvent interface to form a shield around the PMMA aggregates. On the basis of earlier work that indicated a low ($\approx$7%) initiator efficiency, we believe that the PS chains are sparsely distributed on the surface (average occupied area $\approx$3 nm^2).[46] This low grafting density should facilitate PS segment mobility during the reorganization process. If the PMMA layer is thick compared with the PS layer, it would be difficult for PS chains to localize at the solvent interface and for PMMA to form aggregates that are shielded by PS chains. The thinner the PMMA layer, the easier it is for PS chains to move to the solvent interface. Similar to PS-*b*-PMMA brushes, when PS-*b*-PMA brushes are treated with cyclohexane, a reorganization takes place that localizes the PS segments at the air interface. Our impetus for comparing PMMA and PMA terminal blocks was to probe the effect of the Flory–Huggins parameter on the dynamics of diblock reorganization. The tensiometry and XPS results are similar for both systems in terms of the reversible localization of PS segments at the air interface. In a companion study to this report, we have observed significant differences in the nanomorphology of PS-*b*-PMMA vs PS-*b*-PMA, as deduced by atomic force microscopy.[48]

For PS-*b*-PDMAEMA brushes, the mixed solvent of THF and water (1:1, v/v) is a good solvent for PDMAEMA but a poor solvent for PS chains. Therefore, PDMAEMA blocks have an extended conformation in this solvent, while PS chains remained collapsed. Removing the sample from the mixed solvent results in low advancing contact angles. We speculate that treatment with cyclohexane forces PDMAEMA blocks to aggregate with each other to minimize contact with solvent. The PS chains become swollen and form a shell around PDMAEMA. Consequently, the film exhibits the characteristic contact angles of PS. In all of three systems, the tethered diblock copolymer brushes reorganize themselves to achieve the lowest system free energy in response to the different solvent treatments.

Summary

We have synthesized tethered PS-*b*-PMMA, PS-*b*-PMA, and PS-*b*-PDMAEMA brushes on flat silicate substrates by sequential carbocationic polymerization and ATRP. Upon treatment with different solvents, these tethered diblock copolymer brushes exhibit reversible changes in surface properties, which are revealed by water contact angles and XPS analysis. The unique features of these polymer brushes make them an excellent candidates for smart material design, smart surface fabrication, and chemical sensor design.

Experimental Section

Materials. ATR crystals (25 × 5 × 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. MA, MMA, and DMAEMA (Aldrich) were distilled from calcium hydride and stored in a refrigerator. CuBr was purified according to the literature.[55] All other reagents were purchased either from Aldrich or Fisher and used as received.

Characterization Methods. FTIR-ATR spectra were recorded using a Nicolet System 730 spectrometer using a modified 4XF beam condenser (Harrick Scientific). Spectra were recorded at 2 cm^{-1} resolution, and 500 or 1000 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 a vibrationless table (Newport Corp.). Advancing and receding values were determined using the tilting stage method. Drop volumes were 10 μL. Ellipsometric measurements were performed on a Gaertner model L116C ellipsometer with He−Ne laser (λ = 632.8 nm) and a fixed angle of incidence of 70°. For the calculation of the layer thickness, a refractive index of n = 1.500 for the polymer was used. X-ray photoelectron spectroscopy (XPS) was 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. Survey spectra were taken after the sample was treated with different solvents.

Synthesis of Tethered PS-*b*-PMMA Brushes on Flat Silicate Substrates. The typical procedure for surface ATRP of MMA in the absence of free initiator is as follows. An ATR prism or silicon wafer to which polystyrene brushes were tethered was placed into a 50 mL Schlenk tube containing purified CuBr powder followed by addition of anisole and MMA. The mixture was degassed by purging with argon for at least 30 min, and the ligand (*N*,*N*,*N*′,*N*′,*N*″-pentamethyldiethylenetriamine or 1,1,4,7,10,10-hexamethyltriethylenetetraamine) was added via syringe. The final concentrations were as follows: $[\mathrm{MMA}]_0 = 3.6$ M, $[\mathrm{ligand}]_0 = 0.0147$ M, and $[\mathrm{CuBr}]_0 = 0.0145$ M. Care must be taken to avoid contact between stirring bar and the ATR prism or silicon wafer. The polymerization was allowed to proceed at 90 °C for 6 h. The sample was then removed from the polymerization tube and rinsed with CH_2Cl_2. To remove untethered polymer, the sample was placed in a Soxhlet extractor and extracted with CH_2Cl_2 or THF overnight.

The typical procedure for surface ATRP in the presence of free initiator is similar to the procedure described above except that the free initiator, 1-chloro-1-phenylethane (PHECl), was added via syringe after the mixture was degassed with argon for 30 min. The final concentrations were as follows: $[\mathrm{MMA}]_0 = 4.67$ M, $[\mathrm{ligand}]_0 = 19.09$ mM, $[\mathrm{CuBr}]_0 = 18.82$ M, and $[\mathrm{PHECl}]_0 = 1.66$ mM.

Control Polymerization 1. An ATR prism to which PS brushes (23 nm thickness in dry state) were tethered, and a stirring bar were placed in a Schlenk tube followed by addition of 4 mL of anhydrous anisole and 2.4 mL of MMA. The mixture was degassed by bubbling with argon for 30 min. The Schlenk tube was then placed in a 90 °C oil bath. This attempted ATRP in the absence of copper bromide and ligand proceeded for 3 h and was followed by removing the sample from the Schlenk tube and extracting it with CH_2Cl_2 overnight. The sample was subjected to FTIR study.

The same ATR prism that was used in the above-attempted ATRP and a stirring bar were placed in a Schlenk tube containing 27 mg of CuBr, 5 mL of anisole, and 3 mL of MMA. The mixture was then degassed by bubbling with argon for 30 min followed by addition of 40 μL of *N*,*N*,*N*′,*N*′,*N*″-pentamethyldiethylenetriamine via a syringe. The polymerization was allowed to proceed for 4 h at 90 °C. The sample was then taken out of the polymerization tube, extracted with THF overnight, and subjected to FTIR-ATR study.

Control Polymerization 2. An ATR prism coated with cumyl methyl ether initiator monolayer and an ATR prism with a 7.5 nm tethered PS brush and a stirring bar were placed into a Schlenk tube which contained 27 mg of CuBr followed by addition of 15 mL of anisole and 1 mL of MMA. The mixture was then degassed with argon for 30 min. The polymerization was allowed to proceed for 3 h followed by taking samples out of the tube, extracting with CH_2Cl_2, and FTIR-ATR analysis.

Synthesis of Tethered PS-*b*-PMA Brushes on Flat Silicate Substrates. The typical procedure of surface ATRP of MA in the presence of free initiator is as follows. An ATR prism or silicon wafer to which PS bushes were tethered was placed into a 50 mL Schlenk tube containing 6.8 mg of CuBr. 3.5 mL of anisole (or *o*-dichlorobenzene) and 3.5 mL of MA were added by syringe. The mixture was degassed by an argon purge for 30 min. The ligand, *N*,*N*,*N*,*N*,*N*-pentamethyldiethylenetriamine or 1,1,4,7,10,10-hexamethyltriethylenetetraamine, and free initiator, methyl 2-bromopropionate, were added via syringe. Care must be taken to avoid the contact between stirring bar and ATR prism. The final concentrations were as follows: $[\mathrm{MA}]_0 = 5.55$ M, $[\mathrm{ligand}]_0 = 6.80$ mM, $[\mathrm{CuBr}]_0 = 6.77$ M, and $[\text{methyl 2-bromopropionate}]_0 = 1.03$ mM. The polymerization proceeded at 110 °C for 24 h. The sample was then extracted with THF or CH_2Cl_2 for 24 h to remove the untethered polymer.

Synthesis of PS-*b*-PDMAEMA Brushes on Flat Silicate Substrates. The typical procedure of surface ATRP of DMAEMA in the presence of free initiator is as follows. An ATR prism or silicon wafer to which PS bushes were tethered was placed into a 50 mL Schlenk tube containing 1.2 mg of CuBr, 3.5 mL of anisole (or *o*-dichlorobenzene), and 3.5 mL of DMAEMA were added by syringe. The mixture was degassed by an argon purge for 30 min. The ligand, *N*,*N*,*N*′,*N*′,*N*″-pentamethyldiethylenetriamine or 1,1,4,7,10,10-hexamethyltriethylenetetraamine, and free initiator, PHECl, were added via syringe. Care must be taken to avoid the contact between stirring bar and ATR prism. The final concentrations were as follows: $[\mathrm{DMAEMA}]_0 = 2.97$ M, $[\mathrm{ligand}]_0 = 1.30$ mM, and $[\mathrm{CuBr}]_0 = 1.20$ M, $[\mathrm{PHECl}]_0 = 0.76$ mM. The polymerization proceeded at 115 °C for 9 h. The sample was then extracted with THF or CH_2Cl_2 for 24 h to remove the untethered polymer.

Treatment of Tethered PS-*b*-PMMA and PS-*b*-PMA Brushes with CH_2Cl_2. The PS-*b*-PMMA or PS-*b*-PMA brushes were immersed in 20 mL of CH_2Cl_2 or chloroform for 30 or 45 min. The samples were removed from the solvent and dried with a stream of clean air followed by characterization with tensiometry, XPS, and AFM.

Treatment of Tethered PS-*b*-PDMAEMA Brushes with a Mixed Solvent of THF and Distilled H_2O. The PS-*b*-PDMAEMA brushes with 24 nm PS and 2.5 nm PDMAEMA were immersed in 20 mL of mixed solvent of THF and water (1:1, v/v) at elevated temperature for 1 h. The sample was then removed quickly from the mixed solvent and dried with a stream of clean air. Tensiometry and XPS were used to characterize the surface.

Treatment of Tethered Diblock Copolymer Brushes with Cyclohexane. The PS-*b*-PMMA or PS-*b*-PMA or PS-*b*-PDMAEMA brushes were immersed in cyclohexane and heated to 35 °C for 30−60 min. The sample was then removed quickly from the solvent and dried with a stream of clean air. Tensiometry, XPS, and AFM were used to characterize the brushes.

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