

Synthesis of Tethered Polystyrene-*block*-Poly(methyl methacrylate) Monolayer on a Silicate Substrate by Sequential Carbocationic Polymerization and Atom Transfer Radical Polymerization

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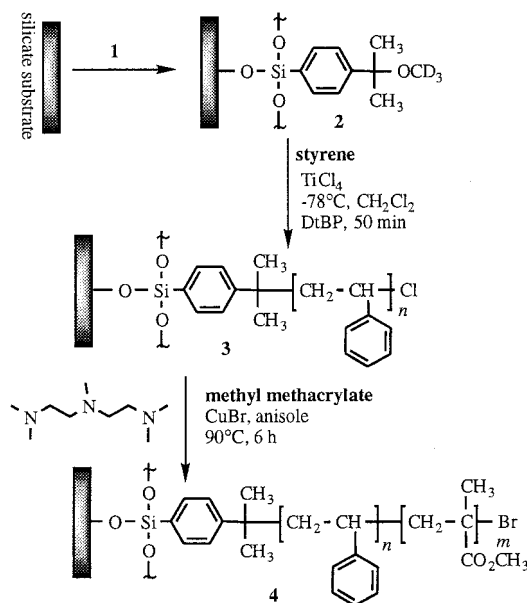
Received December 28, 1998

An assembly of tethered polymer chains in mutual proximity are called “polymer brushes”.^{1–3} The amount of theoretical work^{4–7} on polymer brushes equals or exceeds the amount of experimental information^{8–10} available concerning properties and structure. Even less is known about diblock polymer brushes. Because diblock copolymers have a propensity to self-organize, we are interested in the behavior of diblock copolymers that have one chain end confined by covalent attachment to a surface. In this communication, we describe the synthesis of diblock copolymer brushes which exhibit surface reorganization in response to block-selective solvents.

Fabrication of tethered polymers has involved covalent attachment and polymer physisorption. For polymer absorption, diblock copolymers are used where one block strongly adsorbs to the surface.¹¹ A disadvantage of these systems is thermal and solvolytic instability. Polymers with a covalent bond to the surface can circumvent this shortcoming. Tethering has been accomplished by grafting preformed polymers to tethering sites (“grafting to”)^{12,13} or by polymerizing from surface-immobilized initiators (“grafting from”). Examples of the latter approach include styrene polymerization using surface-immobilized azo compounds,¹⁴ hyperbranched polymer films,¹⁵ methyl methacrylate (MMA) polymerization using a surface-immobilized initiator for atom-transfer radical polymerization (ATRP),¹⁶ and *N*-carboxyanhydride polymerization by amine-functionalized surfaces.¹⁷

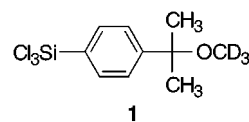
Here we report the formation of polystyrene-*block*-PMMA (PS-*b*-PMMA) films by a sequential carbocationic polymerization of styrene followed by radical polymerization of MMA. To our

Scheme 1



knowledge, the formation of block copolymer brushes by the “grafting from” approach is unprecedented. We have characterized these films by tensiometry, FTIR, XPS, and ellipsometry.

Scheme 1 depicts the synthetic scheme for tethered PS-*b*-PMMA block copolymers. Our approach starts with surface immobilization of trichlorosilane-1, which is an initiator for carbocationic polymerization.^{18,19}



Silane-1 was deposited on silicate substrates (either silicon ATR crystals or silicon semiconductor wafers) using conventional methods. We chose a deuterated silane so that FTIR could be used to estimate initiator efficiency via the intensity of ν_{C-D} .

Treatment of substrate-2 with styrene under carbocationic polymerization conditions²⁰ led to tethered PS. We also monitored styrene polymerization via film thickness using ellipsometry. X-ray photoelectron spectroscopy (XPS) results and water contact angles ($\theta_a = 100 \pm 1^\circ$, $\theta_r = 83 \pm 1^\circ$) were consistent with an overlayer of PS. The PS thickness was controlled by experimental conditions. Decreasing solvent polarity (by diluting CH_2Cl_2 with methylcyclohexane), decreasing $[\text{TiCl}_4]$, or adding dimethylacetamide (a Lewis base) decreased the PS film thickness.²¹ Solvent extraction did not diminish the PS intensity in the FTIR spectrum, which is consistent with a covalently attached polymer.

(18) The synthesis of silane-1 involved a four-step sequence. Addition of CH_3MgBr to 4-bromoacetophenone produced the corresponding alcohol, which was treated with iodomethane- d_3 in the presence of KOH. The Grignard reagent was formed by reaction with Mg^0 and was then reacted with SiCl_4 to produce the desired silane-1. The final product was isolated as a 1:1 complex with THF.

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(20) An ATR prism or silicon wafer was placed into a 50 mL Schlenk tube. Anhydrous CH_2Cl_2 , di-*tert*-butylpyridine (DtBP), and styrene were added via syringe. After the solution was cooled to -78°C , TiCl_4 was added. Final concentrations were as follows: $[\text{TiCl}_4]_0 = 0.0236\text{ M}$, $[\text{DtBP}]_0 = 0.012\text{ M}$, and $[\text{styrene}]_0 = 0.75\text{ M}$. After 50 min, methanol was added and the silicate sample was extracted with anisole for 24 h.

(21) Details of these experimental variables will be published in a full-length paper.

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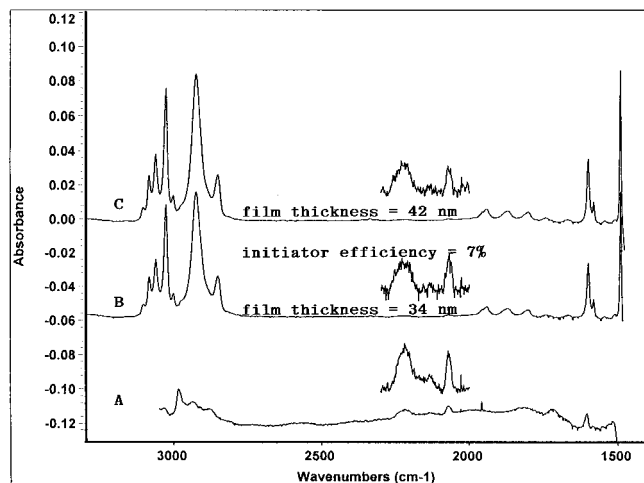


Figure 1. Reflectance FTIR spectra of (a) substrate-2 (absorption intensity is magnified 5 \times), (b) first carbocationic polymerization of styrene, and (c) second, sequential carbocationic polymerization of styrene. The film thickness was determined by ellipsometry. Initiator efficiency was determined by the decrease in intensity for ν_{C-D} at 2075 cm^{-1} .

Figure 1 shows the FTIR spectra of substrate-2 and the PS films formed after carbocationic polymerization. Spectra b and c in Figure 1 represent tethered PS chains formed by sequential styrene polymerizations. Initiator efficiency was determined by monitoring the decrease in intensity for ν_{C-D} at 2075 cm^{-1} . While we assume that styrene polymerization in the second step occurs from chloro-terminated chain ends,²² the spectra in Figure 1 demonstrate that polymerization also involves unreacted initiator sites. Additional polymerization in the second treatment with styrene is supported by an increase in IR intensities and increasing film thickness.

To create a tethered diblock polymer film that did not also involve initiation from immobilized silane-1, we used radical polymerization for the second block. Coca and Matyjaszewski²³ prepared block copolymers of styrene and MMA in solution using carbocationic and ATRP.²⁴ We have applied this synthetic strategy to prepare surface-immobilized diblock copolymer chains. A PS film was immersed in a solution of MMA and polymerized using typical ATRP conditions.²⁵ Evidence for PMMA is based on the appearance of $\nu_{C=O}$ at 1732 cm^{-1} (Figure 2). Based on ellipsometry, the film thickness increases by 9 nm. We observed water contact angles ($\theta_a = 75 \pm 1^\circ$, $\theta_r = 60 \pm 1^\circ$) that correspond to a PMMA surface.²⁶ Attempted MMA polymerization in the absence of ATRP catalyst and ligand does not lead to polymerization; therefore, the grafted PMMA does not arise from a thermal, spontaneous polymerization. Also, we subjected substrate-2 to ATRP conditions and observed no PMMA in the FTIR, which confirms that the cumyl ether is not an effective initiator for MMA polymerization. Therefore, we conclude that MMA polymerization occurred at PS chain ends. The PMMA thickness was affected by time, temperature, and added free initiator.

The grafting efficiency of PS is equivalent to the initiator efficiency of **2**. However, we do not know the initiation efficiency

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(25) An ATR prism or silicon wafer was placed into a 50 mL Schlenk tube followed by addition of anisole, MMA, and CuBr. The mixture was degassed by an argon purge and the ligand (*N,N,N,N,N*-pentamethyldiethylenetriamine) was added via syringe. The final concentrations were as follows: [MMA]₀ = 3.6 M, [ligand]₀ = 0.0147 M, and [CuBr]₀ = 0.0145 M.

(26) The water contact angles for a PMMA film prepared by spin coating onto a silicon wafer are $\theta_a = 75 \pm 1^\circ$, $\theta_r = 60 \pm 1^\circ$.

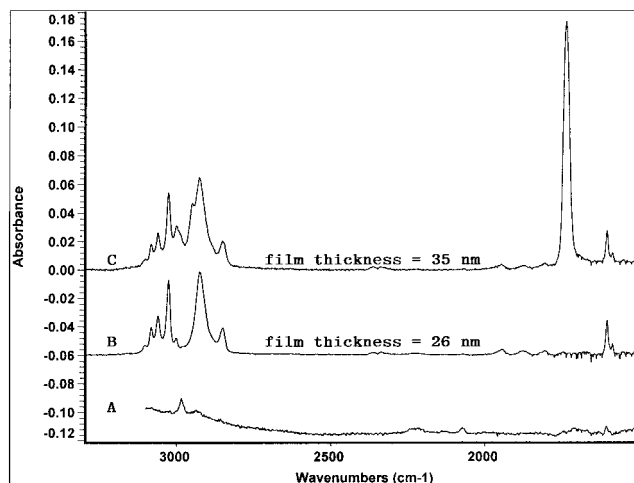


Figure 2. Reflectance FTIR spectra of (a) substrate-2 (absorption intensity is magnified 5 \times), (b) subsequent carbocationic polymerization of styrene; and (c) ATRP of MMA. The film thickness was determined by ellipsometry.

Table 1. Water Contact Angles (deg)

sample description ^{a,b}	θ_a	θ_r
surface-immobilized 1 on Si/SiO ₂ (2)	67	52
PS grafted film (3)	100	83
PS- <i>b</i> -PMMA grafted film (4)	75	60
diblock after methylcyclohexane immersion ^c	98	78
diblock after CH ₂ Cl ₂ immersion ^d	75	59
second methylcyclohexane immersion ^c	97	78
second CH ₂ Cl ₂ immersion ^d	75	60

^a This sample corresponds to Figure 2: PS film thickness = 26 nm, PMMA thickness = 9 nm. ^b Standard deviation for contact angles $\leq 2^\circ$. ^c 30 min immersion in methylcyclohexane at elevated temperature. ^d 30 min immersion in CH₂Cl₂ at room temperature.

of MMA to tethered PS chains. Also, we do not have information about the molecular weight of the tethered diblock copolymers. We are currently preparing diblock copolymers on silica gel and will study the molecular weight of chains after cleavage from the support.

The tethered diblock copolymer undergoes reversible changes in water contact angles as the film is treated with different solvents (see Table 1). Initially, the film exhibits a contact angle characteristic of PMMA; following treatment with methylcyclohexane (a better solvent for PS than for PMMA), the contact angle increases to a characteristic value for PS. Subsequent treatment of the same sample with CH₂Cl₂ (a good solvent for PMMA and PS) reverses this change. Consistent with the low PS grafting efficiency, the tethered chains must be spaced sufficiently far apart to permit large changes in conformational states such that PS segments can localize at the surface in response to treatment with methylcyclohexane.

We have synthesized a tethered block copolymer and have reported large changes in surface composition that are induced by solvent treatment. We feel that these films are good examples of responsive films that possess adaptable adhesion or wettability. We are currently investigating different chemical compositions for the tethered diblocks. In addition, we are studying the surface reorganization phenomena using different surface analytical tools.

Acknowledgment. This work was financially supported by the Army Research Office (DAAH04-96-1-0018).

JA984428Y