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# Synthesis of Polystyrene-*block*-poly(methyl methacrylate) Brushes by Reverse Atom Transfer Radical Polymerization

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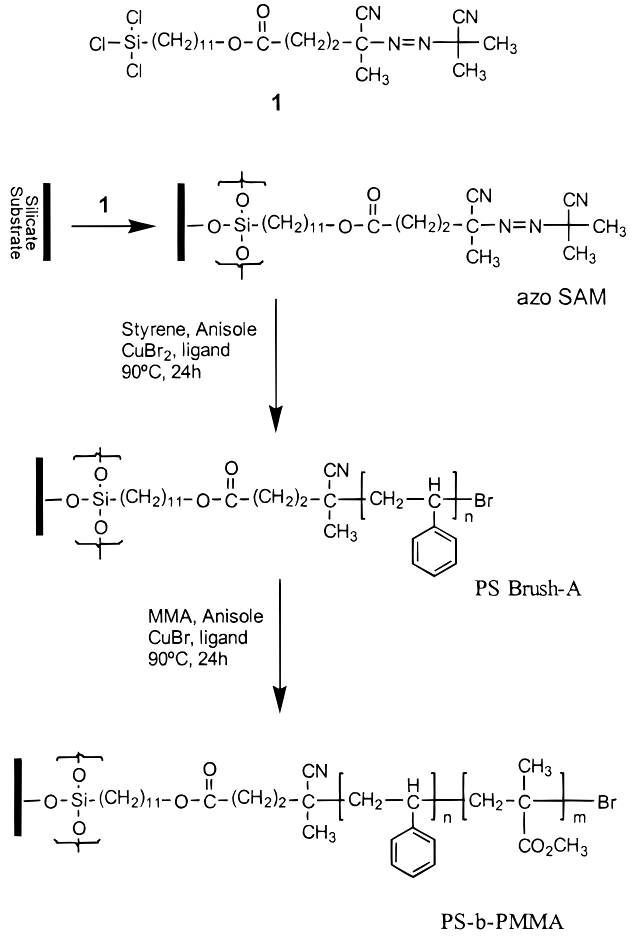
The synthesis of surface tethered diblock copolymer brushes by a “grafting from” approach has recently been reported by our laboratory.[1] These brushes exhibited a reversible change in water contact angle upon exposure to different solvents, presumably due to the ability of the polymers to self-organize. We are interested in further investigating the properties of these materials. In earlier work, we prepared diblock brushes by a sequential process that first involved carbocationic polymerization followed by atom transfer radical polymerization (ATRP). While this method provided the structures and architecture control we desired, we are interested in an experimentally simpler design that might also broaden the scope of possible diblock compositions.

It has been demonstrated that ATRP is an effective route to diblock copolymers.[2−4] The ATRP process produces an end-functional polymer that is used as a macroinitiator for a second monomer, resulting in a block copolymer. Polymer brushes have been synthesized by controlled free radical techniques. Most of the reported methods involve the deposition of a chlorofunctional silane onto a silicate substrate followed by conventional ATRP of the monomer.[5−7] Homopolymer brushes have been produced by this method. Hedrick et al. have reported the synthesis of tethered diblock copolymer brushes from a surface-immobilized nitroxide molecule.[7] Like ATRP, reverse (or alternative) atom transfer radical polymerization, RATRP, has been shown to produce similarly end-functional polymers suitable for continued polymerization.[8−10] RATRP involves initiation by conventional radical initiators in the presence of appropriate transition-metal complexes.

In this communication we report the formation of tethered diblock copolymer brushes by sequential “living”/controlled radical polymerization techniques using RATRP. Our method involves the formation of a terminal bromine functional polymer brush from an immobilized azo initiator under controlled radical conditions. A second block is then polymerized from that brush under ATRP conditions. These diblock copolymer brushes were characterized by ATR-FTIR, ellipsometry, and tensiometry.

Scheme 1 shows the synthetic method for a tethered polystyrene-*b*-poly(methyl methacrylate) (PS-*b*-PMMA) diblock copolymer brush. The azo-functional trichlorosilane initiator **1** was synthesized according to the method of Prucker and Rühe.[11] This silane was deposited from toluene in the presence of pyridine onto silicate substrates.

**Scheme 1**



Polystyrene brushes were prepared by heating the azo SAMs in the presence of styrene monomer.[12] Experiments were carried out both with (brush A) and without (brush B) the addition of $CuBr_2$ and ligand. The ATR-FTIR spectra in Figure 1 illustrate the effect of $CuBr_2$ on the formation of the polystyrene brushes. The addition of $CuBr_2$ results in lower IR absorption intensity and smaller film thicknesses, as measured by ellipsometry (Table 1). These results indicate that the rate of polymerization is slowed by the presence of the cupric bromide. This is consistent with the role of the $CuBr_2$ as a deactivator;[13] the growing radical abstracts a halogen from $CuBr_2$ to form the reduced CuBr and a dormant chain end.

Polymerization conditions (24 h at 95 °C) were chosen to maximize decomposition of the surface bound initiator. We assumed that the half-life of the initiator would be similar to the solution half-lives of AIBN and 4,4′-azobis(4-cyanovaleric acid). These reaction conditions should prevent the possibility of azo-initiated homopolymerization of MMA in subsequent synthetic steps.

Tethered diblock copolymer brushes were formed by treatment of the polystyrene brushes with methyl methacrylate under ATRP conditions.[14] The ATR-FTIR spectra in Figure 2 show the appearance of $\nu_{C=O}$ at 1737 $cm^{-1}$ for brush A but not for brush B, indicating the formation of diblock copolymer brushes for the brush formed under RATRP conditions. Ellipsometry mea-

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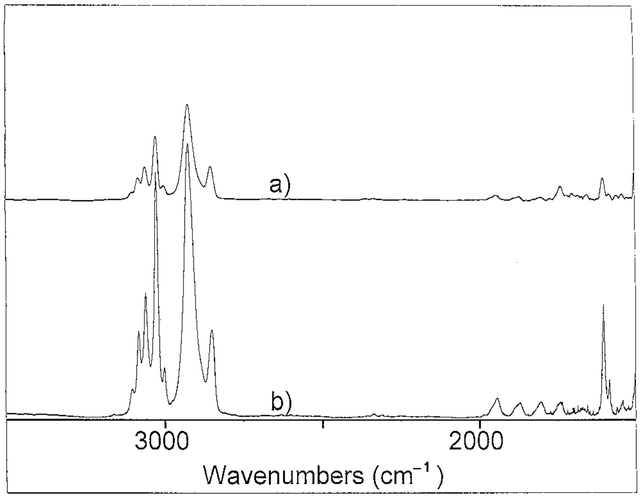

**Figure 1.** ATR-FTIR spectra of PS brushes synthesized by surface-immobilized azo compound: (a) RATRP conditions, (b) non-RATRP conditions.

**Table 1. Thickness Measurements (nm)**[a]

| layer | brush A | brush B |
|---|---|---|
| azo SAM | 2 | 2 |
| PS block | 25 | 70 |
| PMMA block | 6.5 | |

[a] Determined by ellipsometry, standard deviation = 0.6 nm.

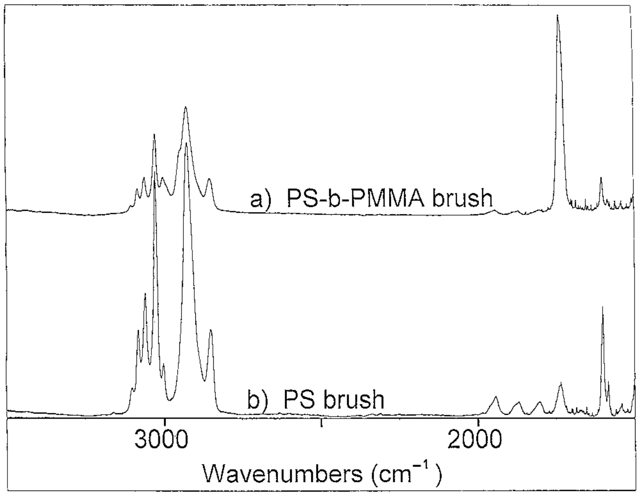

**Figure 2.** ATR-FTIR spectra of brushes after exposure to MMA under ATRP conditions: (a) PS brush made in the presence of $CuBr_2$, (b) PS brush made without $CuBr_2$.

surements indicate an increase of 6.5 nm (Table 1) for brush A with no appreciable change in brush B. The water contact angles for brush A decreased after the MMA polymerization, whereas those of brush B remained unchanged. These facts lead us to conclude that grafting from the functional ends of the tethered polystyrene chains formed diblock copolymer brushes.

The diblock copolymer brushes produced were tested to determine whether they exhibit the previously found reversible contact angle changes upon exposure to segment specific solvents.[1] Each specimen was immersed in methylcyclohexane for 1 h and then dried, and water contact angles were measured on a tilting stage goniometer. The same specimen was then immersed in dichloromethane for 1 h and dried, and contact angles were measured. This process was repeated twice. Depending on the solvent, the diblock brush (brush A) undergoes a surface reorganization that localizes PS (methylcyclohexane) or PMMA ($CH_2Cl_2$) at the interface (Table 2). In contrast, the contact angle of brush B remains unchanged regardless of the solvent treatment. This observation is consistent with a homopolymer structure for brush B. These results are similar to those found for other tethered diblock copolymer brushes produced in our laboratory.

**Table 2. Water Contact Angles (deg)**[a]

| | brush A | | brush B | |
|---|---|---|---|---|
| sample | $\theta_a$ | $\theta_r$ | $\theta_a$ | $\theta_r$ |
| azo SAM | 68 | 57 | 68 | 57 |
| PS film | 92 | 73 | 92 | 70 |
| PS−PMMA film | 74 | 55 | 92 | 69 |
| first $C_7H_{13}$ immersion | 91 | 69 | 92 | 69 |
| first $CH_2Cl_2$ immersion | 73 | 55 | 89 | 70 |
| second $C_7H_{13}$ immersion | 92 | 69 | 92 | 70 |
| second $CH_2Cl_2$ immersion | 77 | 56 | 92 | 68 |

[a] Standard deviation for contact angles <2°.

RATRP is an experimentally simpler route to surface tethered diblock copolymer brushes than the previously reported method and opens the possibility of preparing a wider variety of diblock compositions. These brushes exhibit reversible water contact angles similar to those made by a carbocationic/ATRP strategy. We plan to continue investigating the properties of these tethered copolymers and also those of other diblock compositions. Work is also progressing on the synthesis of a deuterated initiator so that an estimation of initiator efficiency may be made.

## References and Notes

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(12) Silicon substrates were placed into a 100 mL Schlenk flask fitted with a condenser, and 29 mL of a styrene solution in anhydrous anisole was added, $[\text{styrene}]_0 = 3.9$ M. A solution in anisole, of 1 mM $CuBr_2$ and 1.5 mM *N*,*N*,*N*′,*N*′,*N*″-pentamethyldiethylenetriamine, was added at a ratio of 0.011 $\mu L/mm^2$ of substrate surface area. The flask was purged with argon for 15 min and then heated at 90−100 °C for 24 h. After polymerization the substrates were rinsed with $CH_2Cl_2$ and then extracted with THF for 24 h.
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(14) Silicon substrates containing tethered PS brushes were placed into a 100 mL Schlenk flask fitted with a condenser. MMA, CuBr, ligand (*N*,*N*,*N*′,*N*′,*N*″-pentamethyldiethylenetriamine), and 20 mL of anisole were added, and the flask was purged with argon for 15 min. Concentrations were $[\text{MMA}]_0 = 4.0$ M, $[\text{CuBr}]_0 = 0.011$ M, and $[\text{ligand}]_0 = 0.022$ M. The flask was then heated at 90−100 °C for 24 h. After polymerization the substrates were rinsed with $CH_2Cl_2$ and then extracted with THF for 24 h.

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