Synthesis of Well-Defined Mixed Poly(methyl methacrylate)/Polystyrene Brushes from an Asymmetric Difunctional Initiator-Terminated Self-Assembled Monolayer

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Received August 31, 2003
Revised Manuscript Received September 28, 2003

The intriguing structures and properties of mixed homopolymer brushes that consist of two or more distinct homopolymer chains randomly or alternatively immobilized on a surface with high grafting densities have attracted considerable interests in both fundamental studies and technology developments over the past decade.[1−19] Theoretical studies have discussed whether symmetric binary mixed homopolymer brushes on a planar substrate phase separate laterally, resulting in a "ripple" state, or vertically, forming a "layered" state under equilibrium melt conditions, and have predicted that the "ripple" state should be the one to appear.[3,4] Phase separation is expected to occur at a molecular weight 2.27 times that for the same polymers in a simple blend at its demixing threshold. The spatial period of the pattern is predicted to be in the order of the polymer chain root-mean-square end-to-end distance and to be independent of the interaction strength between the two polymer chains.[3,4,7] The self-assembly behavior of binary brushes under exposure to solvents is also of great interest.[7−9] Layered structures may appear in asymmetric binary polymer brushes.[8] Moreover, studies by Müller[10] and Minko et al.[11] have revealed two "dimple" phases in solvents at large incompatibilities or asymmetric compositions, where different species form clusters which arrange on a quadratic or hexagonal lattice. By tuning parameters such as tethering densities, chain lengths, types of polymer chains, solvents, temperature, etc., various surface structures and properties could be achieved by mixed homopolymer brushes. Experimental studies began very recently, and both "grafting to" and "grafting from" approaches have been successfully used to fabricate various binary mixed homopolymer brushes on flat substrates.[11−19] The behavior of the resultant binary mixed brushes in response to different solvent treatments has been reported, and the responsive nature of these surface materials has been demonstrated. However, the phase behavior of binary mixed homopolymer brushes under equilibrium melt conditions has not been experimentally investigated. We have initiated an effort to prepare well-defined binary mixed homopolymer brushes with controlled molecular weights, narrow molecular weight distributions, and high, tunable grafting densities and to investigate their self-assembly behavior under various conditions.

In a previous publication,[18] we reported the synthesis of mixed poly(methyl methacrylate) (PMMA)/poly(styrene) (PS) brushes on silicon wafers by combining atom transfer radical polymerization (ATRP) and nitroxide-mediated radical polymerization (NMRP) from mixed initiator-terminated self-assembled monolayers (SAMs) using a two-step process. Mixed SAMs were prepared by coadsorption from toluene solutions containing both ATRP-initiator- and NMRP-initiator-terminated organotrichlorosilanes with predetermined molar ratios. A similar strategy was also reported by Ejaz et al. to synthesize binary brushes from mixed SAMs of two triethoxysilanes.[20] Although the mixed monolayers have been extensively studied for many years and no macroscopic phase separation has been reported,[21−27] it remains unclear how the two different species are distributed in the mixed SAMs and to what extent they are mixed. Preferential adsorption of one species has been reported (e.g., from the solution containing fluorinated and alkyl trichlorosilanes), but spectroscopic data collected by Lagutchev et al. using sum frequency generation spectroscopy indicated that close adsorption occurred and well-mixed SAMs were obtained.[27] To avoid possible preferential adsorption of one species from the solutions of two trichlorosilanes and possible phase separation (in whatever length scale), we designed and synthesized an asymmetric difunctional initiator-terminated SAM (Y-SAM) as illustrated in Scheme 1. The corresponding trichlorosilane is 2-(4-(2′-oxa-13′-trichlorosilyltridecyl)phenyl)-2-(2″,2″,6″,6″-tetramethyl-1-piperidinyloxy)ethyl 2-bromo-2-methylpropionate (Y-silane). Y-SAM ensures the mixing of the ATRP and NMRP initiators at the molecular level and thus the well-mixing of the two different polymers that are subsequently grown from them. Y-silane was prepared by a four-step procedure as outlined in Scheme 2. 4-Vinylbenzyl chloride reacted with free radicals generated from benzoyl peroxide at 80 °C in the presence of 2,2,6,6-tetramethylpiperidinoxy produced **1** in a yield of 10%. The reaction between undecylenyl alcohol and **1** catalyzed by NaH afforded **2**, which was then reacted with 2-bromo-2-methylpropionyl bromide to incorporate the moiety of an ATRP initiator. Y-silane was then obtained by hydrosilylation of the precursor **3**. Detailed synthetic procedures and characterization data can be found in the Supporting Information.

Y-SAM was prepared by immersing "Piranha"-treated silicon wafers in 1.0 mM toluene solutions of Y-silane at 45 °C typically for 15 h. (It has been reported that the self-assembly of octadecyltrichlorosilane monolayer on the oxidized Si (100) surface is initiated by a mechanism of homogeneous growth at temperatures $\geq$ 40 °C.[28]) The advancing and receding contact angles of water on Y-SAM after cleaning were 84° and 72°, respectively. Ellipsometry study using a refractive index of 1.45 for Y-SAM showed that the thickness of Y-SAM was 17.6 Å, suggesting a monolayer structure. The samples were then used for the fabrication of mixed PMMA/PS brushes by sequential ATRP of MMA and NMRP of styrene (Scheme 1). We chose ATRP to grow the first polymer and NMRP for the second polymer because the activation of ATRP initiators is a bimolecular process, while the free radicals in NMRP are generated by thermal decomposition which is a unimolecular process.[29,30] A unimolecular activation mechanism is preferred for the synthesis of the second type of polymer chains from the surface because of the steric hindrance presented by the existing polymer chains. Surface-initiated ATRP of MMA was carried out at 75

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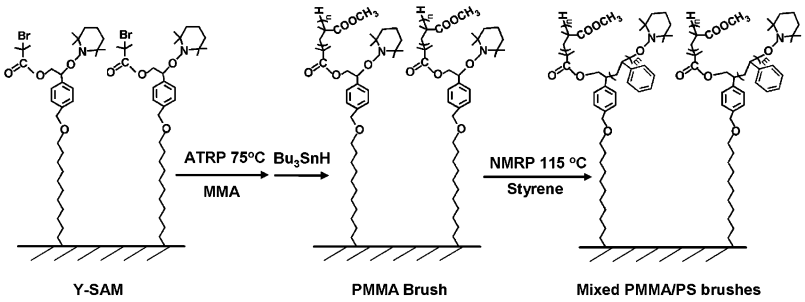
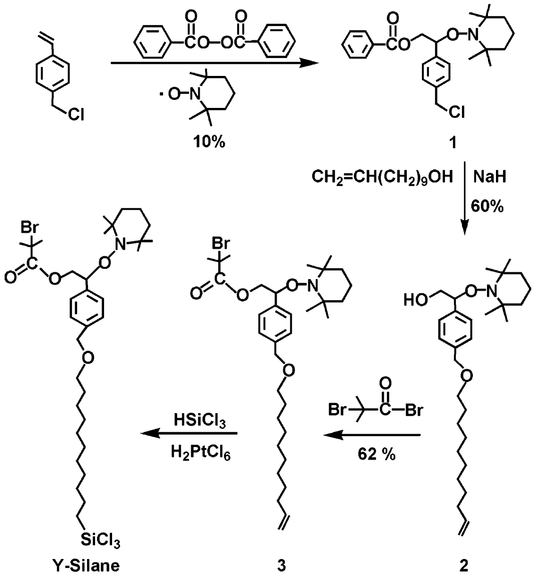
10.1021/ma035285p CCC: $25.00

Scheme 1. Synthesis of Mixed PMMA/PS Brushes from Y-SAM



Scheme 2. Synthesis of Y-Silane



°C using CuBr and *N*,*N*,*N*′,*N*′,*N*″-pentamethyldiethylenetriamine (PMDETA) as catalytic system in the presence of a "free" initiator, ethyl 2-bromoisobutyrate, for various lengths of time. It has been reported that adding a predetermined amount of a "free" initiator into the reaction mixture helps achieve controlled surface-initiated polymerizations.[18,31] In the previous work,[18] we showed that the NMRP initiator was not activated at 80 °C. Moreover, no noticeable changes were observed in the thickness and contact angles of a 17.8 nm PMMA brush that was synthesized from the SAM of (11′-trichlorosilylundecyl) 2-bromo-2-methylpropionate (silane-**4**, an ATRP initiator) after the exposure to the NMRP conditions. A 33.3 nm thick PS film was obtained from the SAM of 1-(3′-oxa-2′-phenyl-14′-trichlorosilyltetradecyloxy)-2,2,6,6-tetramethylpiperidine (silane-**5**, a NMRP initiator) in the same pot under the same NMRP conditions. However, when exposing a SAM of silane-**4** and a mixed SAM that was prepared from a toluene solution containing silane-**4** and -**5** with a molar ratio of 54.4:45.6 to the NMRP conditions, we observed a ~2.0 nm film thickness increase and a water advancing contact angle of 91°, a characteristic value for PS film, on the SAM of silane-**4**, while a 19.1 nm brush was found from the mixed SAM. Presumably, the C−Br bond in the ATRP initiator was weak and acted as a chain transfer agent in NMRP. To eliminate the possible chain transfers to bromine-terminated PMMA chain ends and the unreacted ATRP initiator in Y-SAM in the synthesis of PS by NMRP, tri-*n*-butyltin hydride (n-Bu_3SnH) was added into the reaction mixtures to in situ remove bromine atoms after ATRP.[32] Control experiments demonstrated that exposing a SAM of silane-**4** and a 10.2 nm PMMA brush grown from Y-SAM to the typical dehalogenation conditions for 10 and 30 min, respectively,[33] completely removed bromine atoms as subsequent attempted ATRPs resulted in no changes in the film thicknesses and water contact angles. We also confirmed that the NMRP initiator in Y-SAM was stable under the typical dehalogenation conditions. After dehalogenation, the silicon wafers with grafted PMMA chains were extensively washed with a series of solvents followed by drying with a stream of air. The polymers formed in the solutions ("free" polymers) were collected and analyzed by gel permeation chromatography (GPC) against PS standards. The brush thicknesses were determined by ellipsometer using the refractive index of PMMA, 1.49. It was observed that the brush thickness increased with the molecular weight of "free" PMMA in a linear fashion (Figure 1), suggesting that

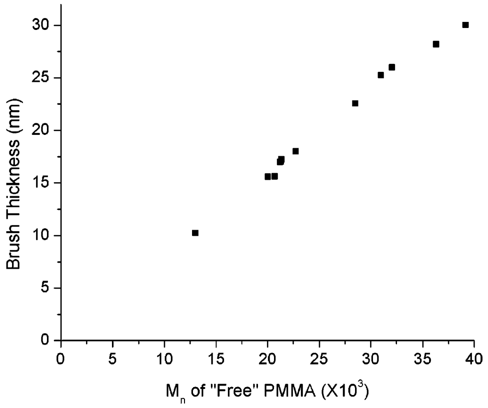


Figure 1. Relationship between the brush thickness and the molecular weight of "free" PMMA formed in the solutions.

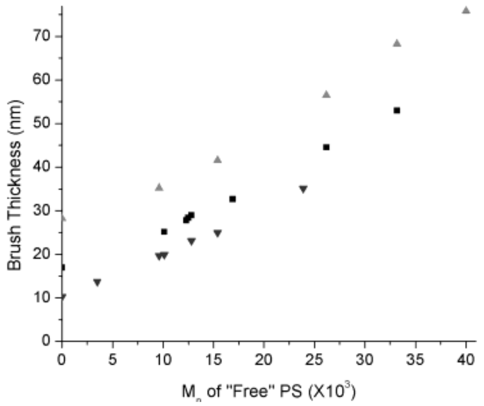


Figure 2. Relationship between the brush thickness and the molecular weight of "free" PS formed in the solutions: (▼) mixed PMMA/PS brushes synthesized from a 10.3 nm thick PMMA brush; (■) mixed brushes synthesized from a 17.0 nm thick PMMA brush; (▲) mixed PMMA/PS brushes synthesized from a 28.2 nm thick PMMA brush.

Table 1. Contact Angles of Water on a Series of Mixed Brushes Consisting of PMMA and PS of Various Molecular Weights[a]

no.	thickness (nm)	PS M_n	PS M_w	$\theta_a{}^b$ (deg)	$\theta_r{}^b$ (deg)	$\theta_a{}^c$ (deg)	$\theta_r{}^c$ (deg)	$\theta_a{}^d$ (deg)	$\theta_r{}^d$ (deg)	$\theta_a{}^e$ (deg)	$\theta_r{}^e$ (deg)
(a) PMMA: M_n of 13 000 and M_w of 15 100 (Thickness = 10.3 nm)											
1	10.3	0	0	73.5	62	75	64	73	62	75	64
2	13.7	3 500	4 900	73	63	75	64	74	61	74.5	64.5
3	19.7	9 600	12 800	80	66	91	74	80	63	90	71
4	19.9	10 100	13 500	82	71	91	74	80	64	90	75
5	23.1	12 800	16 100	84.5	75	91	79.5	84	71	91	79
6	25.0	15 400	19 300	91	82	91	78	90	78	91	80
7	35.1	23 900	29 500	91	84	91	74	91	82	91	82
(b) PMMA: M_n of 21 200 and M_w of 25 000 (Thickness = 17.0 nm)											
1	17.0	0	0	73	62	75	64	74	63	75	63
2	25.2	10 100	13 500	73.5	62	81	62	73	58	81	62
3	27.8	12 300	16 000	74	63	84	65	73	61	83	63.5
4	28.4	12 500	15 900	73	64	84.5	71	74	61	83.5	69
5	29.0	12 800	16 100	74	63	84.5	70	74	62	85	74
6	32.7	15 400	19 300	84	75	91	82	82	72	90.5	80
7	44.5	23 900	29 500	91	83.5	91	81	91	82	91	81
8	52.9	33 200	41 000	91	84	91	79	90	83	91	83
(c) PMMA: M_n of 36 300 and M_w of 43 400 (Thickness = 28.2 nm)											
1	28.2	0	0	73	62	75	64	74	62	75	63
2	35.2	9 600	12 800	73	60	74.5	63	73	62	75	60
3	41.5	15 400	19 300	73	62	75	61	74	57	75	61
4	56.5	26 200	32 700	80	68.5	91.5	81	80	69	91.5	81
5	68.2	33 200	41 000	87	81	91.5	83	86	75	91	81
6	76.5	40 000	50 600	91	84	91	82	91	82	91.5	81

[a] We assume the grafted polymers have the same molecular weights and polydispersities as "free" polymers. [b] The samples were immersed in $CHCl_3$ for 5 min and then moved out and dried immediately with a stream of air. Water advancing (θ_a) and receding (θ_r) contact angles were recorded. [c] The samples were annealed in a vacuum at 120 °C for 16 h and cooled to room temperature followed by the contact angle measurements. [d] The samples were treated for the second time with $CHCl_3$ for 5 min at room temperature and then dried with a stream of air. [e] The samples were annealed for the second time in a vacuum at 120 °C for 16 h. The standard deviations of contact angle measurements were <2°.

the polymerizations were well-controlled and the grafting density was almost constant. From the molecular weight of the polymer chain (M_n) and the brush thickness (d), the average cross-sectional area per chain, A, can be determined by $A = M_n/(d\rho N_A)$, where ρ is the density (1.2 for PMMA) and N_A is Avogadro's number. We assume that the grafted polymer chains are well correlated with the "free" polymers and have the same molecular weights and polydispersities.[31] Calculation using the point of (22 700 amu, 18.0 nm) in Figure 1 showed that the grafting density was ~1.8 nm^2 per PMMA chain, indicating that the polymer chains were highly stretched away from the surface.

To synthesize binary mixed brushes, the silicon wafers with grafted PMMA brushes were cut into smaller pieces and exposed to the NMRP conditions at 115 °C in the presence of a "free" initiator, 1-phenyl-1-(2′,2′,6′,6′-tetramethyl-1′-piperidinyloxy)-2-benzoyloxyethane, for various amounts of time. After polymerizations, the samples were exhaustively washed with CH_2Cl_2 and $CHCl_3$ to completely remove untethered polymer chains. The brush thickness increased with the molecular weight of "free" PS in a nearly linear fashion in all three sets of samples shown in Figure 2. Considering that these samples are composed of PMMA and PS with various molecular weights, it is difficult to determine the thicknesses by ellipsometry as it is unclear at this stage at what molecular weights PMMA and PS chains in the mixed brushes will phase separate and what kind of structures will form if phase separation occurs. To estimate the film thickness, we used a refractive index of 1.49 for all mixed PMMA/PS brushes, and this might be the reason that the data points of high molecular weights deviated to some degree from the linear increase (the refractive index of PS is 1.59). Calculations using the data points of (9600 amu, 19.7 nm), (10 100 amu, 25.2 nm), and (9600 amu, 35.2 nm) in Figure 2 showed that the typical grafting densities were ~1.6, ~1.9, and ~2.2 nm^2/PS chain for mixed brushes synthesized from 10.3, 17.0, and 28.2 nm thick PMMA brushes, respectively. Steric hindrance should be responsible for the lower grafting density of PS chains synthesized from thicker PMMA brushes. Considering both PS and PMMA chains, the average grafting density was ~1.0 nm^2/chain.

These mixed PMMA/PS brushes exhibited a transition in water advancing contact angles with increasing the molecular weight of PS after treatment with $CHCl_3$, a good solvent for both PS and PMMA (Table 1). When the molecular weight of PS was lower than that of PMMA, the brush exhibited a water advancing contact angle (θ_a) of ~74°, a characteristic value for PMMA. When the molecular weights of the two polymer chains were comparable, the value of θ_a was found to be between 74° and 91°. When the chain length of PS was longer than that of PMMA, the film exhibited a θ_a of 91°, implying that the PS chains occupied the air−brush interface after treatment with $CHCl_3$.

To study the behavior under equilibrium melt conditions, these mixed PMMA/PS brushes were annealed in a vacuum at 120 °C, above the T_g's of both PS and PMMA for 16 h to achieve equilibrium states. After cooling to room temperature, water advancing and receding contact angles were recorded, and the data are summarized in Table 1. When the PS chains were very short relative to the PMMA chains (e.g., $M_n = 3500$ and $M_n = 9600$ in Table 1, parts a and c, respectively), the surface exhibited a value of θ_a of 75°, which was the same as that on a pure PMMA brush. With the increase of PS molecular weight, the contact angle underwent a transition from 75° to 91°. However, the transitions after thermal annealing occurred at lower molecular weights than those after treatment with $CHCl_3$. For the samples synthesized from the 10.3 nm thick PMMA brush (Table 1a), a value of 91° for θ_a was first found at PS M_n of 15 400 after treatment with $CHCl_3$ but 9600 after annealing. For the mixed brushes prepared from the 17.0 nm thick PMMA brush (Table 1b), a value of 91° for θ_a was first noted at PS M_n of 23 900 after $CHCl_3$ treatment but 15 400 after thermal annealing. For the samples synthesized from a PMMA brush with a thickness of 28.2 nm, the value of 91° for θ_a was first observed at PS M_n of 40 000 after treatment with $CHCl_3$ but 26 200 after thermal treatment. Similar values of water θ_a were obtained after the treatment with $CHCl_3$ and annealing in a vacuum at 120 °C again. These results suggest more complex phase behavior than has been predicted by theoretical studies. PS has a lower surface free energy than PMMA,[34] which might favor the appearance of PS chains at the air−brush interface. Further investigation is underway.

In summary, we successfully synthesized well-defined mixed PMMA/PS brushes from an asymmetric difunctional initiator-terminated SAM by combining ATRP and NMRP via a two-step process. To eliminate the possibilities of chain transfers to the bromine-terminated PMMA chain ends and unreacted ATRP initiator in Y-SAM in the second polymerization, in situ dehalogenation was carried out by adding n-Bu_3SnH into the reaction mixtures. It was observed that the brush thickness increased with the molecular weight of "free" polymers collected from the solutions in nearly linear fashions. We found that the transitions of water θ_a on three sets of mixed PMMA/PS brushes with increasing the molecular weight of PS occurred at lower molecular weights after thermal annealing in a vacuum at 120 °C for 16 h than those after treatments with $CHCl_3$.

Acknowledgment. The authors thank the University of Tennessee at Knoxville (start-up funds) and the American Chemical Society Petroleum Research Funds (PRF 40084-G7) for supporting this research.

Supporting Information Available: Synthesis of Y-silane, formation of Y-SAM on silicon wafers, dehalogenation of an ATRP-initiator-terminated SAM, synthesis of PMMA brushes from Y-SAM and in situ dehalogenation, attempted ATRP from the dehalogenated ATRP-initiator-terminated SAM and PMMA brush, synthesis of polystyrene from the surface by NMRP, and exposure of **1** to the typical dehalogenation conditions. This material is available free of charge via the Internet at http://pubs.acs.org.

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MA035285P