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Synthesis of binary mixed homopolymer brushes by combining atom transfer radical polymerization and nitroxide-mediated radical polymerization

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Abstract

This communication describes a novel strategy to synthesize binary mixed homopolymer brushes from mixed self-assembled monolayers (SAMs) on silica substrates by combining atom transfer radical polymerization (ATRP) and nitroxide-mediated radical polymerization (NMRP). Mixed SAMs terminated by ATRP and NMRP initiators were prepared by coadsorption of two corresponding organotrichlorosilanes from toluene solutions. Mixed poly(methyl methacrylate) (PMMA)/polystyrene (PS) brushes were synthesized by ATRP of MMA at 80 °C followed by NMRP of styrene at 115 °C. Corresponding 'free' initiators were added into the solutions to control the polymerizations. We have found that the brush thickness increases with molecular weight in a nearly linear fashion. For a series of binary brushes consisting of PMMA of molecular weight of 26,200 and PS of various molecular weights, we have observed a transition in water contact angles with increasing PS molecular weight after CH_2Cl_2 treatment. Moreover, binary mixed polymer brushes with comparable molecular weights for two grafted polymers undergo reorganization in response to environmental changes, exhibiting different wettabilities.

Keywords: Binary mixed homopolymer brushes; Atom transfer radical polymerization; Nitroxide-mediated radical polymerization

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1. Introduction

Binary mixed homopolymer brushes are composed of two distinct polymer chains randomly immobilized on a solid substrate with high grafting densities [1–8]. In addition to the deformed conformations assumed by polymer chains, microphase separation between immiscible polymers and/or between polymer chains and solvents occurs, enriching the phase behavior of these polymer brush systems. Theoretical studies have discussed whether symmetric binary polymer brushes phase separate laterally ('rippled state') or vertically ('layered state') under melt conditions, and have predicted that the 'rippled state' should be the only one observed [2,3]. The spatial period of the pattern is predicted to be of the order of polymer chain root mean square end-to-end distance and independent of the interaction strength between the two polymers [3,8]. It is still unknown whether lateral phase separation results in a 'striped', or a checkerboard, or a random pattern [3]. The behavior of binary polymer brushes under exposure to solvents is also of great interest. Layered structures may appear in asymmetric binary polymer brushes [6]. Moreover, micellar structures may form if a mixed solvent is used and the solvent composition is gradually changed. By tuning parameters including tethering density, chain lengths, Flory–Huggins interaction parameters, solvents, and temperature, various surface structures and properties could be achieved by mixed homopolymer brushes.

Little experimental study has been performed on such polymer brushes due to the difficulties in the preparation of well-defined polymer brush systems. Only in the past few years the synthesis of binary polymer brushes has been reported by conventional radical polymerizations from surface-immobilized azo initiators [9–11]. In this approach, the second polymer was synthesized from residual surface-immobilized azo initiator that was not decomposed in the growth of the first polymer from the surface. This approach lacks good control of molecular weight, molecular weight distribution, and tethering density. We have designed a

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novel strategy to synthesize well-defined binary mixed homopolymer brushes from mixed initiator-terminated self-assembled monolayers (SAMs) by combining two controlled/'living' free radical polymerization techniques, atom transfer radical polymerization (ATRP) and nitroxide-mediated radical polymerization (NMRP) (Scheme 1). Note that homopolymer brushes have been successfully fabricated by either of them [12,13]. These two controlled/'living' radical polymerization techniques have different mechanisms and are carried out at different temperatures [14,15]. By taking advantage of the differences between these two techniques, Tunca et al. have synthesized block copolymers using an asymmetric difunctional initiator in a two-step procedure [16,17]. This communication is the first report of our efforts toward the synthesis, characterization, and applications of well-defined mixed homopolymer brushes.

2. Experimental

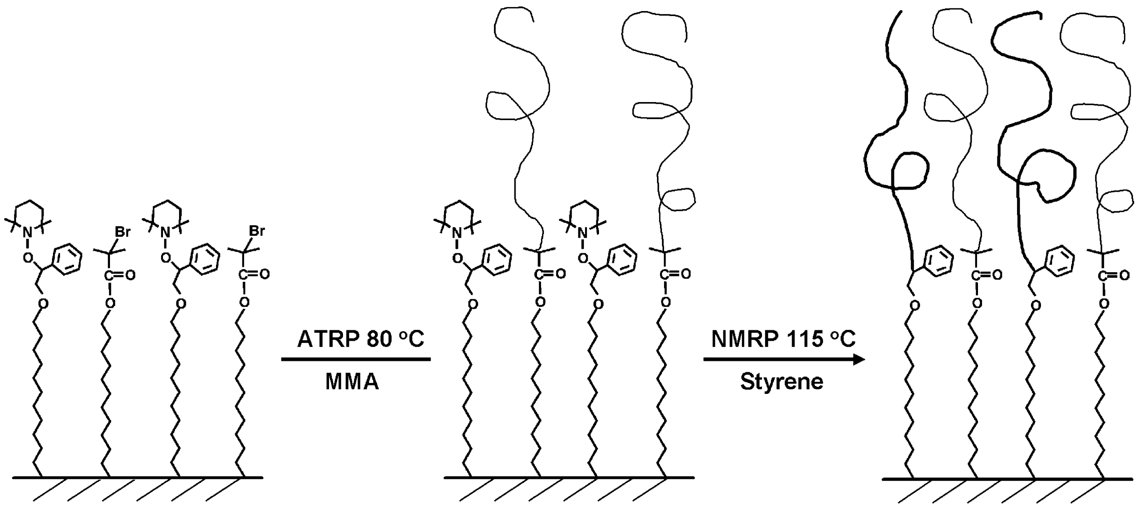
2.1. Materials and measurements

Styrene (99%, Aldrich) and methyl methacrylate (MMA, 99%, Aldrich) were distilled over CaH_2 and stored in a refrigerator before use. CuBr (98%, Aldrich) was purified according to the published procedure [18]. All other chemical reagents were purchased from either Aldrich or Fisher and used without further purification. Nuclear magnetic resonance was performed on a Varian Mercury 300 MHz NMR spectrometer using $CDCl_3$ as the solvent. Gel permeation chromatography (GPC) was carried out using a modular Knauer GPC system with a HPLC K-501 pump, a UV-K2501 detector, a RI-K2301 refractive index detector, and 5 μm PSS–SDV gel, 10^2–10^5 linear Å 60 cm, and 100 Å 60 cm columns. The data were processed using Polymer Standards Service software (PSS WinGPC). Tetrahydrofuran (THF) was used as the carrier solvent at a flow rate of 1.0 mL/min at 23 °C. Standard monodisperse polystyrenes (Polymer Laboratories, USA) were used for calibration. The brush thicknesses were determined with an ellipsometer EL X-02C (DRE-Dr. Riss Ellipsometerbau GmbH, Germany). Contact angle measurements were made with a Rame-Hart goniometer (Model 100–00) using a Gilmont syringe with a 24-gauge flat-tipped needle. Water advancing and receding contact angles were recorded while water was added to and withdrawn from the drop, respectively.

1-(3′-Oxa-1′-phenyl-14′-trichlorosilyltetradecyloxy)-2,2,6,6-tetramethyl-piperidine (silane-**1**) and (11′-trichlorosilylundecyl) 2-bromo-2-methylpropionate (silane-**2**) were synthesized by use of the same or similar procedures reported in literature [12,18,19]. For silane-**1**, ^1H NMR ($CDCl_3$) δ (ppm) 1.09–1.70 (m, 33H), 1.98 (s, 3H, CH_3), 2.54 (complex m, 2H), 3.38 (m, 2H), 3.78 (m, 1H), 3.97 (m), 6.15 (br s, 1H), 7.25–7.38 (m, 3H, aromatic), 7.50 (dd, 2H, aromatic); ^{13}C NMR ($CDCl_3$) δ (ppm) 15.70, 19.55, 21.01, 22.11, 22.21, 24.26, 26.05, 27.55, 28.50, 28.98, 29.05, 29.32, 29.46, 29.50, 31.77, 37.03, 37.25, 70.18, 71.18, 71.38, 72.82, 86.79, 127.86, 128.36, 128.67, 137.26. For silane-**2**, ^1H NMR ($CDCl_3$) δ (ppm) 1.26–1.68 (m, 20H), 1.91 (s, 6H), 4.14 (t, 2H); ^{13}C NMR ($CDCl_3$) δ (ppm) 22.22, 24.27, 25.75, 28.31, 28.98, 29.13, 29.28, 29.41, 29.44, 30.76, 31.79, 56.00, 66.14, 171.74.

2.2. Formation of initiator-terminated SAMs on silicon wafers

Silicon wafers were cleaned by freshly prepared 'Piranha' solution (70/30, v/v, concentrated H_2SO_4/30%H_2O_2) at 60 °C for 30 min, and were then rinsed with deionized water and dried with a stream of clean air (Caution: 'Piranha' solution reacts violently with many organic materials and should be handled with great care). For formation of mixed



Scheme 1. Synthesis of binary mixed homopolymer brushes by combining ATRP and NMRP.

initiator-terminated SAMs, predetermined amounts of silane-**1**, -**2**, and toluene were added into a scintillation vial followed by immersion of freshly treated silicon wafers. The total concentration of two trichlorosilanes in toluene was 2 mM. Pure SAMs of silane-**1** (SAM-**1**) and -**2** (SAM-**2**) were also prepared. The typical deposition time was 20 h. After rinsed sequentially with CH_2Cl_2, acetone, methanol, deionized water, and chloroform, the samples were gently brushed with CH_2Cl_2-soaked cotton-tipped applicators and were rinsed again with CH_2Cl_2 followed by drying with a stream of air. In this report, mixed SAMs prepared from a solution containing silane-**1** and -**2** with a molar ratio of 45.6:54.4 (mixed SAM-**3**) were used.

2.3. Synthesis of PMMA brushes from functionalized silicon wafers by ATRP

To a reaction flask containing CuBr were added anisole, MMA, *N*,*N*,*N*′,*N*′,*N*″-pentamethyldiethylenetriamine (PMDETA), and ethyl 2-bromoisobutyrate (2-EBiB) followed by placing a piece of functionalized silicon wafer. Typical concentrations are as follows: $[\mathrm{MMA}]_0 = 5.00$ M, $[\text{2-EBiB}]_0 = [\mathrm{CuBr}]_0 = [\mathrm{PMEDTA}]_0 = 10.0$ mM. The reaction mixture was degassed by freeze-pump-backfilling with nitrogen for three times. The flask was then immersed in an oil bath with a preset temperature of 80 °C for various lengths of time. Precipitation of the reaction mixture in methanol gave PMMA formed from ‘free’ initiators, which was then analyzed by GPC. The silicon wafer was then removed and extensively washed with methylene chloride or extracted with THF.

2.4. Synthesis of polymer brushes by NMRP

To a reaction flask containing functionalized silicon wafers were added styrene and 1-phenyl-1-(2′,2′,6′,6′-tetramethyl-1′-piperidinyloxy)-2-benzoyloxyethane (PTEMPO). Typical concentrations are as follows: $[\mathrm{styrene}]_0 = 8.66$ M (bulk) and $[\mathrm{PTEMPO}]_0 = 17.2$ mM. The mixture was degassed by freeze-pump-backfilling with nitrogen for three times followed by immersion in an oil bath with a preset temperature of 115 °C for various amounts of time. The mixture was then dissolved with methylene chloride (if necessary) and precipitated in methanol. The polymer was collected, dried, and analyzed with GPC. The silicon wafer was removed and exhaustively washed with methylene chloride.

3. Results and discussion

We synthesized a nitroxide-terminated organotrichlorosilane, silane-**1**, and an ATRP initiator-terminated organotrichlorosilane, silane-**2**, according to the methods described in literature [12,18,19]. Mixed SAMs of silane-**1** and -**2** were prepared by coadsorption from toluene solutions of these two organotrichlorosilanes with predetermined molar ratios onto freshly ‘Piranha’ solution treated silicon wafers. Pure SAM-**1** and -**2** on silicon wafers were also prepared. The advancing contact angles (θ_a) of water on SAM-**1** and SAM-**2** were 89° and 85°, respectively. For mixed SAM-**3**, the water θ_a was 86.5°. Although we do not know the ratio of two initiators and how they are distributed in the mixed monolayer, studies by other investigators indicate that the ratios of two components in the mixed SAMs of organotrichlorosilanes are well correlated to the solution concentrations and also suggest a well-mixing for the two components if two organotrichlorosilanes have similar molecular sizes and reactivities and there are no specific interactions among terminal functional groups [20–25].

In the following experiments, we used mixed SAM-**3** to synthesize binary mixed PMMA/polystyrene (PS) brushes. Surface-initiated ATRPs of MMA were carried out in anisole at 80 °C using CuBr and PMDETA as catalytic system [26] in the presence of a free initiator, 2-EBiB, for various lengths of time. It has been reported that adding predetermined amounts of a ‘free’ initiator into the reaction mixture is necessary to achieve controlled surface-initiated polymerizations [12,27]. The samples were then extensively washed with CH_2Cl_2 or extracted with THF to remove any noncovalently bound polymer chains completely. Surface analysis by ellipsometry and contact angle measurements demonstrated the formation of PMMA layers on silicon wafers. The value of water θ_a decreased from 86.5° to 74°, which is the characteristic value for PMMA films. A control experiment using SAM-**1** under the same ATRP conditions revealed no changes in SAM-**1** thickness and water contact angles, confirming that PMMA chains were grown from immobilized ATRP initiators. Polymers produced in the solutions (‘free’ polymers) were collected and analyzed by GPC against PS standards. We assume that the grafted polymer chains are correlated with ‘free’ polymers and have the same molecular weights and polydispersities. Fig. 1 shows the relationship between the brush thickness and the number average molecular weight (M_n) of ‘free’ polymers. The polydispersities of all ‘free’ polymers produced in the solutions were found to be ~1.20 except the one with M_n of 4500 (polydispersity = 1.37). A nearly linear increase in brush thickness with molecular weight suggests a good control of polymerizations and an almost constant grafting density. From the molecular weight of the polymer chains (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 number. Calculation using the point of (20,300 amu, 14.3 nm) shows that the grafting density is ~2 nm^2 per PMMA chain, suggesting that the polymer chains are highly stretched from the surface. This finding is comparable to the results reported in literature for homopolymer brushes growing from pure initiator-terminated SAMs [12], i.e. the presence of the second immobilized initiator did not significantly lower the grafting density.

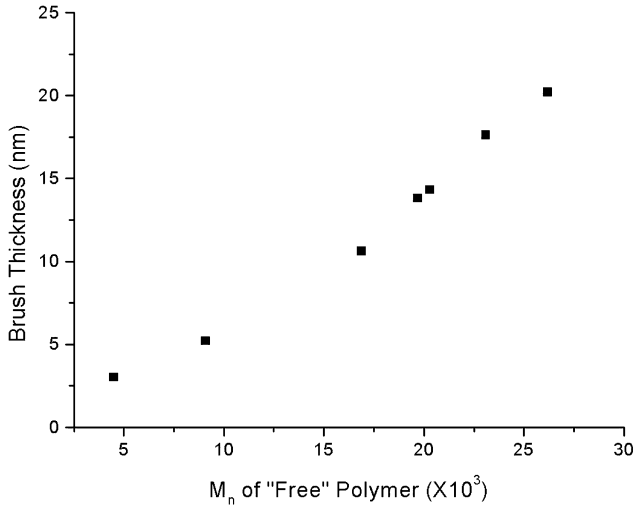


Fig. 1. The relationship between the brush thickness and molecular weight of ‘free’ PMMA produced in solutions.

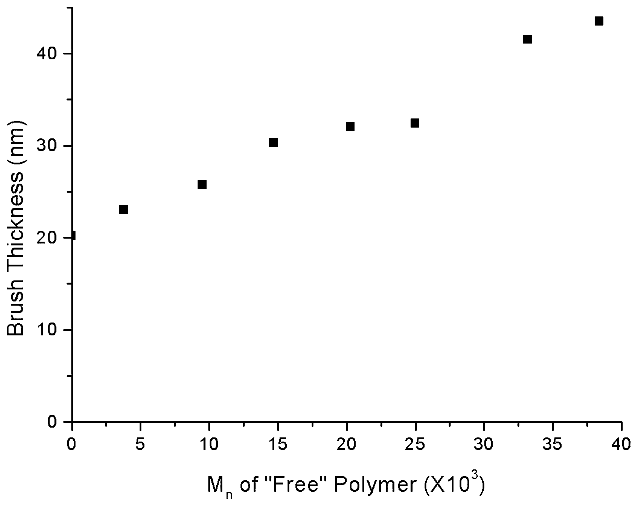


Fig. 2. The relationship between the brush thickness and molecular weight of ‘free’ PS formed in solutions.

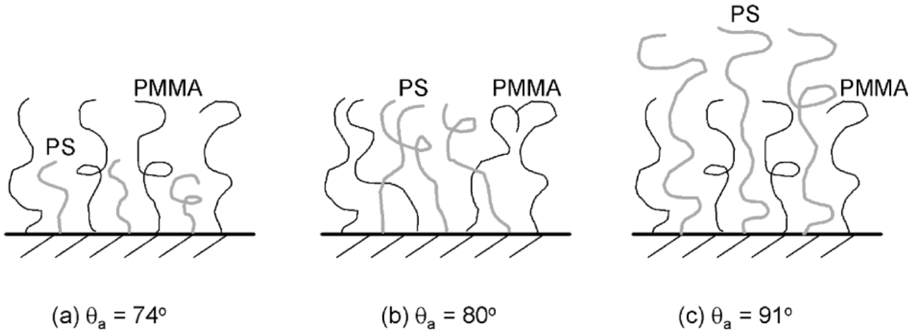
To synthesize binary mixed PMMA/PS brushes with various PS molecular weights, a piece of silicon wafer with 20.2 nm PMMA ($M_n = 26,200$) brushes grown from mixed SAM-**3** was cut into smaller pieces. These pieces were then exposed to NMRP conditions at 115 °C for various amounts of time. Predetermined amounts of a free initiator, PTEMPO, were added into the reaction mixtures to control surface-initiated polymerizations. After polymerizations, the silicon wafers were exhaustively washed with methylene chloride to completely remove any physically absorbed polymers. As shown in Fig. 2, the film thickness increases with molecular weight of ‘free’ PS produced in the solutions in an almost linear format if the point of M_n of 25,000 is excluded. The polydispersities of all ‘free’ polymers were ~1.30. A control experiment exposing 17.8 nm PMMA brushes grown from SAM-**2** to the same NMRP conditions revealed little change in film thickness and water advancing contact angle. Calculation shows that the grafting density is ~2.7 nm^2 per PS chain, which is slightly lower than that of PMMA chains. Considering both PMMA and PS chains, the average grafting density is ~1.2 nm^2 per polymer chain, indicating that the grafted polymer chains are very highly stretched from the interface. The values of water θ_a on these binary mixed polymer brushes changed systematically with PS molecular weight (Table 1). For the mixed brushes with PS molecular weight $< 15,000$ (samples 1, 2, and 3 in Table 1), the advancing contact angles of water were ~74° after treatment with CH_2Cl_2, a good solvent for both PS and PMMA. A layered structure formed with PMMA chains sitting at the top (Scheme 2(a)). When the molecular weights of PS are comparable to those of PMMA chains (samples 4 and 5 in Table 1), the values of water θ_a were ~80°, in between those for PMMA (74°) and PS (91°), indicating both PS and PMMA segments appeared at the air interface after treatment with CH_2Cl_2 (Scheme 2(b)). When the molecular weights of PS are much higher than PMMA (samples 6 and 7 in Table 1), the advancing contact angles of water were ~91° after treatment with CH_2Cl_2, suggesting that the air-brush interface be occupied by PS chains (Scheme 2(c)). The transition observed here demonstrates

Table 1
Contact angles of water on a series of binary polymer brushes consisting of PMMA with M_n of 26,200 and PS of various molecular weights

Sample no.	M_n (PS)	After CH_2Cl_2 (°)[a]		After Cyclohexane (°)[a]		After CH_2Cl_2 (°)[a]	
		θ_a[b]	θ_r[b]	θ_a	θ_r	θ_a	θ_r
1	3800	73	60	73	61	74	61
2	9500	74	63	83	64	74	63
3	14,700	74	61	90	70	73	63
4	20,300	80	70	91	82	81	71
5	25,000	80	66.5	91	80	79.5	64.5
6	33,200	90	81	90	84	90	79
7	38,400	91	83	91	82	91	83

[a] The samples were sequentially treated with CH_2Cl_2 at room temperature for 10 min, cyclohexane at elevated temperature for 30 min, and CH_2Cl_2 at room temperature for 10 min again. The water contact angles were measured after each solvent treatment.

[b] θ_a and θ_r are advancing and receding contact angles of water, respectively.



Scheme 2. Schematic illustration of binary mixed polymer brushes consisting of PMMA with M_n of 26,200 and PS with various M_n after treatment with CH_2Cl_2.

that we have successfully synthesized binary mixed PMMA/PS brushes. Moreover, treatments of the binary brushes of comparable molecular weights for both PMMA and PS chains (samples 3, 4, and 5 in Table 1) with cyclohexane (a better solvent for PS than for PMMA) at an elevated temperature increased the advancing contact angle of water to 91°, implying that PS chains were localized at the air interface. Immersion in CH_2Cl_2 reversed the brushes to their original states.

4. Conclusions

We have successfully synthesized binary mixed PMMA/PS brushes on silica surfaces by combining ATRP and NMRP techniques. The brush thickness increases with molecular weight in a nearly linear fashion. For a series of binary polymer brushes consisting of PMMA with molecular weight of 26,200 and PS of molecular weights ranging from 3800 to 38,400, we have observed a clear transition in water contact angles with increasing PS molecular weights after treatments with CH_2Cl_2. Moreover, binary mixed brushes with comparable molecular weights undergo reorganization in response to different solvent treatments, exhibiting reversible changes in water contact angles. By tuning the relative ratio of the two initiators in mixed SAMs and/or incorporating an inert trichlorosilane, we can tune the whole and relative grafting densities of two distinct polymer chains. The approach reported here enables us to prepare well-defined binary mixed homopolymer brushes and to more precisely test theoretical predictions.

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