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Simultaneous Coating of Silica Particles by Two Diblock Copolymers

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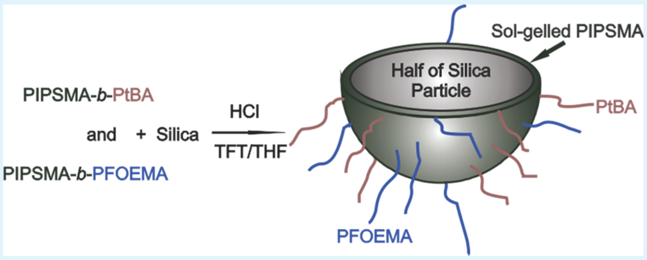
Supporting Information

ABSTRACT: Silica particles have been coated by two diblock copolymers, P1 and P2, through a one-pot reaction, and the resultant particles were characterized. The P1 and P2 used were synthesized by anionic polymerization and denote PIPSMA-*b*-PFOEMA and PIPSMA-*b*-PtBA, respectively. Here PIPSMA, PFOEMA, and PtBA correspond individually to poly[3-(triisopropyloxysilyl)propyl methacrylate], poly(perfluorooctylethyl methacrylate), and poly(*tert*-butyl acrylate). Catalyzed by HCl, the PIPSMA blocks of P1 and P2 co-condensed onto the surface of the same silica particles, exposing the PtBA and PFOEMA blocks. The relative amounts of grafted P1 and P2 could be tuned by changing the P1 to P2 weight ratio and were quantified by thermogravimetric analysis. The vertical segregation of the PFOEMA and PtBA chains could also be adjusted. Casting a dispersion of the coated particles in a solvent selective for either PFOEMA or PtBA onto glass plates or silicon wafers yielded films consisting of bumpy silica particles whose surfaces were enriched by the polymer that was soluble in the casting solvent. Particulate coatings with tunable surface wetting properties were obtained by changing either the proportion of grafted P1 and P2 or the casting solvent for coated silica. When a silica dispersion in perfluoromethylcychohexane (C_7F_{14}) was cast, films of coated silica that had P1 weight fractions of 25, 50, and 75% were all superhydrophobic because the particle surfaces were enriched by PFOEMA, which was selectively soluble in C_7F_{14}.



KEYWORDS: *block copolymer, unimolecular coating, mixed brushes, and stimuli-responsiveness*

1. INTRODUCTION

Particles decorated by two surface polymers may have many applications. For example, particles covered by a fluorinated polymer with a low surface energy are highly oil and water repellant but do not adhere well to each other or to any substrate.[1] This difficulty in achieving durable coatings can be overcome by using particles bearing two types of surface chains. While the fluorinated chains will render water and oil repellency, the other functional chains will promote adhesion via bond formation with either the coating substrate or with a glue that binds to the substrate.[2] Water-dispersible superparamagnetic particles bearing a water-soluble polymer can be bio-conjugated for immunoassay applications.[3,4] If another polymer capable of resisting protein deposition and helping reduce non-specific binding is also grafted onto these particles, the accuracy of the immunoassay may be improved.[5,6]

This paper reports the preparation of silica particles decorated by two types of polymer chains. The particles were obtained from the simultaneous coating of silica particles by two diblock copolymers. It also describes the tunable surface segregation patterns of the grafted polymer chains and the switchable wetting properties of films cast from dispersions of these particles. The two diblock copolymers used were PIPSMA-*b*-PFOEMA (P1) and PIPSMA-*b*-PtBA (P2), where PIPSMA, PFOEMA, and PtBA denote poly[3-(triisopropyloxysilyl)propyl methacrylate], poly(perfluorooctylethyl methacrylate), and poly(*tert*-butyl acrylate), respectively. PFOEMA was chosen because of its low surface energy and its water and oil repellency. PtBA was used because it could be readily hydrolyzed to poly(acrylic acid) (PAA). As will be reported in a forthcoming paper, PAA can readily react with epoxy resin and help anchor these PFOEMA-bearing particles onto surfaces of this glue to yield robust fluorinated particulate coatings. The PIPSMA blocks were targeted because they were sol-gel forming and the silanol groups generated from triisopropyloxy hydrolysis could readily couple with the silanol groups of silica particles to yield siloxane bonds, Si−O−Si.[7] Also, the silanol groups generated via PIPSMA hydrolysis could condense with each other, yielding a crosslinked sol-gelled PIPSMA layer that was covalently attached to silica.[1] Using these two diblock copolymers, silica particles with surface PtBA and PFOEMA chains were obtained via the one-pot co-condensation of the hydrolyzed PIPSMA blocks of the different copolymers.

Diblock copolymers have been used to coat silica particles. In a block-selective solvent and presence of a favorable interaction between the insoluble block and silica (or another substrate), the insoluble block of a diblock copolymer can readily deposit and spread on silica (or another substrate). The soluble block,

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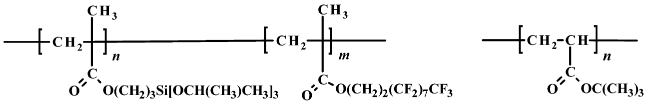

PIPSMA-*b*-PFOEMA PtBA

if crowded enough, stretches into the solvent like bristles of a brush. Because of this, such a unimolecular diblock copolymer layer has been traditionally called a brush layer.[8−11] Although unimolecular coating is readily prepared from this method, the grafting density obtainable from this approach is normally low because of the diffusional barrier created by the polymer chains in an existing brush against the incorporation of further polymer chains.

In this study, a chemical "graft-to" method was used to prepare mixed diblock copolymer unimolecular layers. Although this approach appears straightforward conceptually, we have not found reports on the use of diblock copolymers for this purpose or even the use of diblock copolymers bearing a surface binding block for brush preparation. A related example involved the deposition of a diblock copolymer from a selectively poor solvent for the photo-cross-linkable block of the copolymer. After brush formation on silica particles or glass plates via physical deposition, the deposited block was then photolyzed to yield a crosslinked anchoring layer.[12,13]

Despite lack of diblock copolymer examples, such an approach has been used to chemically graft ABC triblock copolymers.[14−16] For example, Ward and coworkers[14] prepared polystyrene-*block*-poly(4-urethanopropyl triethoxysilylstyrene)-*block*-poly(methyl methacrylate) and grafted the triblock copolymer to silicon surface via sol−gel chemistry of the middle block. This middle block pinning strategy has also been used by Minko and coworkers[15] and Yang and coworkers[16] to coat silica particles for stabilizing Pickering emulsions. Other more remotely related studies dealt with the preparation of core-shell block copolymer micelles[17,18] or particles[5,6] bearing mixed shells. The cores in these cases were not pre-existing but were formed simultaneously with the shell during a one-step self-assembly process.

Although the graft-to method has not been used to simultaneously graft two diblock copolymers, it has been utilized to graft end-functionalized homopolymers, which contained one reactive end group per chain. The grafting densities achievable using these polymers were again normally low.[19] This shortcoming was recently overcome using a two-step grafting process.[19] In the first step, a poly(glycidyl methacrylate) (PGMA) layer was grafted onto a substrate, such as silica, via a reaction between the substrate surface functional group(s) and some of the epoxy groups of PGMA. The desired polymers were subsequently grafted to this PGMA layer in the second step by reacting the end groups of the polymers with the residual epoxy groups. The PGMA layer helped increase polymer grafting density probably for similar reasons that allowed a poly(acrylic acid) layer deposited onto silicon to help increase the grafting density of triblock copolymer nanotubes bearing terminal amino groups.[20] Firstly, the glycidyl or epoxy groups may be more reactive than the original surface groups, which were normally hydroxyl groups. Secondly, far more epoxy groups were produced than the original surface functional groups consumed. Thirdly, the epoxy groups were distributed in a thin PGMA layer and had more mobility than the original surface functional groups, which were fixed rigidly on the solid 2D surface. This grafting method yielded dense mixed brush layers with switchable surface properties.[21,22]

The most popular method for growing mixed brush layers has been the "graft-from" method.[23] This firstly involved an initiator-grafting step.[24] If the grafted initiator was a traditional free radical initiator, a polymer chain could be produced within 1 s after free radical generation. If the first monomer was allowed to polymerize for a time that was shorter than the decomposition half-life of the grafted initiator, sufficient initiator would remain after the first polymer was produced in situ. The substrate was then removed from the first monomer, rinsed, and immersed into a solution of the second monomer to graft the second polymer.[25] While this approach was simple, it offered little control over the molecular weight and its distribution. An alternative was to first immobilize a Y-shaped bi-initiator onto a substrate. Different monomers were subsequently polymerized via different controlled mechanisms to yield densely grafted mixed brushes,[23,26] whose phase separation in the solid state has been recently observed by TEM.[27] The obvious advantage of this approach was the molecular weight and molecular weight distribution control. A general advantage of the graft-from method was in the high chain grafting densities achievable.[23]

2. EXPERIMENTAL SECTION

Materials and Reagents. Tetrahydrofuran (THF, Caledon, >99%) was dried by refluxing it with sodium and a small amount of benzophenone until a deep purple color developed and was distilled immediately before use. A dioxane solution of HCl (4.0 M) was purchased from Aldrich and was diluted to 1.0 M by addition of THF before use. The monomer 3-(tri-2-propoxysiyl)propyl methacrylate (TPOSPMA) was synthesized following the method described in the literature.[28] *sec*-Butyllithium (1.4 M in cyclohexane) and the monomer *tert*-butyl acrylate (tBA, ≥99%) were purchased from Aldrich. The tBA monomer was purified by vacuum distillation firstly over calcium hydride and then over trioctyl aluminum before use. Diphenyl ethylene (97%, Aldrich) was purified by distillation in the presence of *sec*-butyl lithium. Tetraethoxysilane (TEOS, 99.0%), LiCl (Aldrich, 99.99+%), α,α,α-trifluorotoluene (TFT, Acros, 99+%), perfluoromethylcyclohexane (Aldrich, 90%), ammonia (Caledon, 28−30%) and isopropanol (Fisher, 99.5%) were used as received.

Polymer Synthesis. The polymers were prepared by anionic polymerization in THF at −78 °C. The initiator used was generated by reacting *sec*-butyllithium with excess diphenyl ethylene. Each monomer was polymerized for 2 h. Because the preparation of P1 has been recently reported[1] and the polymerization of tBA has been reported multiple times by our group in the past,[29,30] these polymerization procedures will not be repeated here.

Polymer Characterization. ^{1}H NMR analysis of P2 was performed in $CDCl_3$ on a Bruker Avance 500 MHz spectrometer. P1 and P2 were analyzed by size exclusion chromatography (SEC) at 36 °C using a Waters 515 system equipped with a Waters 2410 differential refractive index detector. This system utilized three columns, including one Waters μ-Styragel 500 Å column and two Waters Styragel HR 5E columns. The mobile phase was chloroform, which was set to a flow rate of 1.00 mL/min. The system was calibrated by monodisperse polystyrene standards.

Silica Particles. The silica particles used were synthesized following the Stöber method.[31,32] Tetraethoxysilane (2.0 g) was dissolved into 21 mL of isopropanol to yield a homogeneous solution before 0.8 mL of an aqueous ammonia solution (28 wt %) was added with vigorous stirring. This mixture was refluxed at 60 °C for 4 h, and the resultant silica particles were settled via centrifugation for 10 min at 3050 *g*. After the supernatant was discarded, the particles were re-dispersed into 10 mL of isopropanol, resettled via centrifugation, and subsequently decanted from the supernatant. This rinsing process was repeated thrice, and the final particles were dried overnight under vacuum before use.

Silica Coating. Silica was coated by P1 and/or P2 in TFT/THF using HCl as the catalyst. TFT was used to ensure the dispersion of the final particles, which bore a PFOEMA corona. Unless otherwise mentioned, the silica particles were always coated using the standard conditions, which involved performing the grafting reaction at 21 °C for 10 h in TFT/THF at a THF volume fraction (f_{THF}) of 9.1%. The molar ratio between IPSMA, HCl, and water was 1/1/2 ($n_{Si}/n_{HCl}/n_{H2O}$). The weight ratio used between polymers consisting of P1 and/or P2 and SiO_2 (m_P/m_S) was 0.08/1.00.

Specifically, P1 and/or P2 were initially dissolved into THF at 5.0 mg/mL. Dry silica particles (5.0 mg) were then mixed with 3.0 mL of TFT in a 20 mL vial and ultrasonicated for 60 s to disperse the particles. To this dispersion were then added 0.080 mL of the 5.0-mg/mL polymer solution mixture in THF, 0.08 mL of the HCl solution (1.0 M in THF) and 3.0 μL of H_2O. The reaction was performed at room temperature for 10 h before it was centrifuged at 3050 *g* for 10 min to settle the particles. After the supernatant was removed, the particles were re-dispersed into 2.0 mL of TFT and centrifuged again to settle the particles and to remove the catalyst, byproducts, and any residual polymer that was not grafted. The particles were then vacuum-dried for 2 h in a 100 °C oven.

Dynamic Light Scattering. For DLS analysis, bare and coated silica particles were separately redispersed into methanol and into TFT at ~0.5 mg/mL. The samples were clarified by filtration through 1.2-μm filters. Dynamic light scattering (DLS) measurements were performed at 20.0 °C using a Brookhaven BI-200 SM instrument equipped with a BI-9000AT digital correlator and a He−Ne laser (632.8 nm). The sample temperature was regulated by circulating water from a thermostated bath, and the scattering angles used were 30, 40, 45, 50, 60, 70, 80, and 90°. The data were analyzed using the Cumulant method[33] to yield the hydrodynamic diameters (d_h) and the polydispersity indices (K_1^2/K_2). The d_h values reported for each sample were the averages from 6 measurements. To calculate d_h, the TFT refractive index and viscosity[34] used were 1.414 and 0.5505 cP, respectively, whereas those for methanol[35] were 1.329 and 0.5513 cP, respectively.

Preparation of Sol−Gelled P1 and P2 Sample. Sol−gelled P1 or P2 samples were prepared by sol-gelling P1 or P2 under similar conditions to those used to coat the silica particles, except the silica particles were not present in this case. After a sample was allowed to react for 10 h, it was centrifuged at 17 000 *g* for 10 min to settle the product. The solid product was re-dispersed into 2.0 mL of TFT and subsequently centrifuged. The rinsing process was repeated once again before the product was vacuum-dried to yield a white powder.

Thermogravimetric Analyses. Thermogravimetric analyses (TGAs) were performed using a TA Q500 Instrument using air as the heating atmosphere. A typical measurement involved heating a sample from room temperature to 700 °C at a rate of 5 °C/min.

Transmission Electron Microscopy. TFT solutions of silica particles were aero-sprayed onto carbon-coated copper grids and then dried under vacuum at room temperature for 2 h before transmission electron microscopy (TEM) observation. The images were obtained using a Hitachi-7000 instrument that was operated at 75 kV.

Atomic Force Microscopy. Bare silica particles and particles coated by pure P2 were re-dispersed into methanol, and silica particles coated by a mixture of P1 and P2 were re-dispersed into either TFT ($C_7H_5F_3$), perfluoromethylcyclohexane (C_7F_{14}), or methanol at ~1 mg/mL. The specimen solutions were aero-sprayed onto silicon wafers before analysis by tapping-mode atomic force microscopy (AFM) using a Veeco multimode instrument equipped with a Nanoscope IIIa controller. The Nanosensors NCHRSPL AFM tips used had a tip radius of ~5 nm.

Superamphiphobic Films. Polymer-coated silica particles were re-dispersed into TFT at a concentration of 2.0 mg/mL. Microscope slide coverslips were coated by casting and evaporating several droplets of the silica solution onto the slips.

Contact Angle Measurements. All contact angles were measured at room temperature (~21 °C). The static contact angles were measured using 5 μL droplets on a KRUSS K12 tensiometer that was interfaced with image-capturing ImageJ software. The advancing and receding angles were determined by probing expanding and contracting liquid droplets, respectively. For each sample, the contact angles were measured at 5-10 different positions, and the reported values were the averages of these measurements. The precision of these measurements was better than ±2°. The liquids that were used for contact angle measurements included Milli-Q water and diiodomethane (>99%, Sigma-Aldrich).

X-ray Photoelectron Spectroscopy. Silica particles coated using P1 and P2 at a P1 weight fraction f_1 of 50% were re-dispersed into $C_7H_5F_3$. Droplets of this dispersion were then dispensed onto a silicon wafer to yield a particulate film. X-ray photoelectron spectroscopy (XPS) analysis of this film was performed using a Thermo Instruments Microlab 310F surface analysis system (Hastings, U.K.) under ultrahigh vacuum conditions. The Mg Kα X-ray source (1486.6 eV) was operated at a 15 kV anode potential with a 20 mA emission current. Scans were acquired in the Fixed Analyzer Transmission mode with a pass energy of 20 eV and a surface/detector take-off angle of 75°. All spectra were calibrated to the C 1s line at 285.0 eV, and minor charging effects were observed that produced a binding energy increase between 1.0 and 2.0 eV. The background of the spectra were subtracted by using a Shirley fitting algorithm and a Powell peak-fitting algorithm.[36]

3. RESULTS AND DISCUSSION

Diblock Copolymers. The diblock copolymers used in this study were prepared by anionic polymerization. Since the repeat unit numbers were low for the copolymers and large amounts of initiator were used, the initiator utilization efficiencies should be high. Therefore, the synthesized copolymers should possess the targeted repeat unit numbers and an absolute technique such as light scattering was not used to determine the molecular weights of the copolymers. Rather, only ^{1}H NMR was used to confirm the repeat unit ratios between the two blocks of a diblock copolymer and SEC was used to determine the polydispersity indices (M_w/M_n) of the copolymers in terms of polystyrene standards. Using these techniques, P1 was previously determined to have an M_w/M_n value of 1.16 and a repeat unit number ratio of 1.0/1.0.

Chloroform was used as the mobile phase to elute P2 and Figure 1 shows the obtained SEC trace. A quantitative analysis indicated that the polydispersity index based on polystyrene standards was low, at 1.05. ^{1}H NMR spectrum was obtained for P2 in $CDCl_3$ and is shown in Figure 2 together with the peak assignments. Peak integral analysis indicated that the repeat unit ratio between the PIPSMA and PtBA blocks was 1.0/7.0, in agreement with the targeted repeat units of 10 and 70, respectively, for the two blocks.

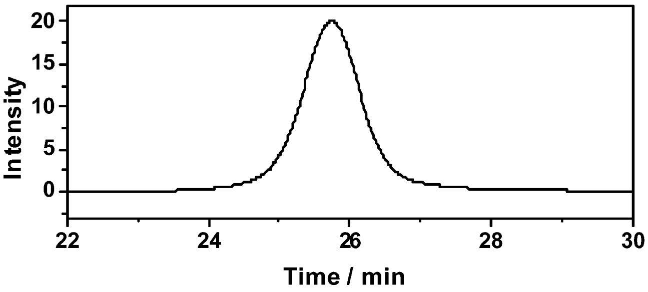

Figure 1. SEC trace for PIPSMA-*b*-PtBA.

Based on the targeted repeat unit numbers of 10 and 10 for P1, a number-average molecular weight of 8.6×10^3 g/mol was

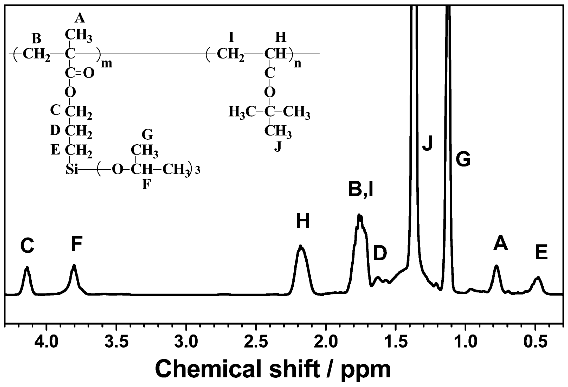

Figure 2. ^{1}H NMR spectrum and peak assignments for PIPSMA-*b*-PtBA.

calculated for P1. For P2, possessing 10 PIPSMA units and 70 tBA units, the molecular weight should be 1.23×10^4 g/mol.

Silica Particles. The silica particles used were prepared through the sol-gel chemistry of tetraethoxysilane using a modified Stöber procedure.[31,32] This process involved the ammonia-catalyzed hydrolysis of the ethoxy groups of tetraethoxysilane in isopropanol to yield silanol groups and the subsequent condensation of the resultant silanol groups into siloxane bonds. According to Bogush et al.,[37] the silica particles prepared under these conditions should have a pore volume fraction of 11−15% and a bulk density of 1.82 g/cm^3, which should be used to relate the weight and volume of the silica particles.

The silica particles thus prepared were re-dispersed into methanol and aero-sprayed using a home-built device[38] onto a silicon wafer and analyzed by AFM. Aero-spraying was used to atomize the spraying solution and to accelerate the solvent evaporation. This technique helped reduce the chances of block copolymer micellar morphological changes during specimen preparation but it was also used here as a routine technique without an intended special function. Images a and b in Figure 3 show AFM topography and phase images of samples of the silica particles. Aside from occasional surface craters and bumps, which were more apparent in the phase image, the spheres were rather smooth. These defects should not be surprising because the silica particles were formed from the fusion of the primary silica nanoclusters during sol-gel synthesis. TEM images of the silica particles were also obtained. From these images, an average diameter of 415 ± 15 nm was determined for the particles. Here 15 nm denoted the spread in the diameters of different particles rather than the error in measuring the diameters.

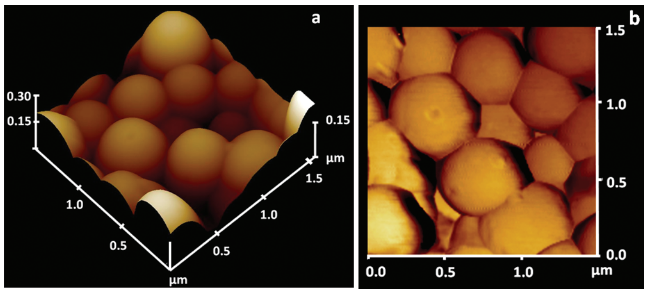

Figure 3. (a) AFM height and (b) phase images of bare silica particles.

The silica particles that were re-dispersed into methanol were analyzed at a regulated temperature of 20.0 °C by DLS to yield their hydrodynamic diameters d_h at different scattering angles θ. Plotted in Figure 4 is the variation of the measured d_h with $\sin^2(\theta/2)$. Evidently, the d_h value increased as θ decreased. Extrapolating θ to zero yielded a d_{h0} value of 488.3 ± 0.8 nm, where 0.8 nm was the extrapolation error for the determined average d_{h0} value.

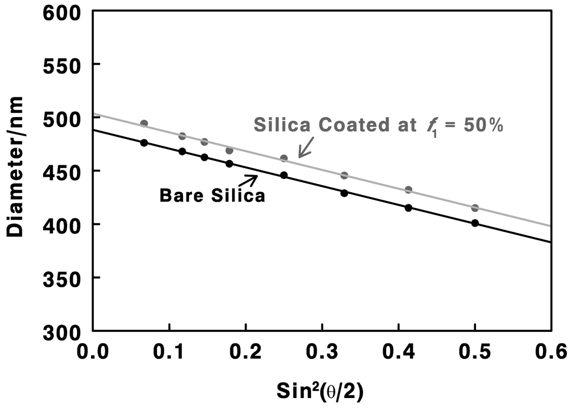

Figure 4. Variation in the DLS d_h values of uncoated silica particles and of silica particles coated at f_1 = 50% as a function $\sin^2(\theta/2)$. The solvents used for the uncoated and coated samples were methanol and trifluorotoluene, respectively.

The d_h increase with decreasing θ was not surprising. Larger particles scatter preferentially at small θ values. At larger θ values where only the smaller particles contribute significantly to the detected intensity, the scattering-intensity-average size should be smaller. This scattering-intensity-average size increased as θ decreased or when the larger particles contributed increasingly towards the scattered intensity.[33,39]

The d_{h0} value was larger than the TEM diameter mainly for two reasons. Firstly, d_{h0} was the scattering-intensity-average or z-average diameter of the particles and the TEM diameter was the number-average value. For a disperse sample, the former term should be larger than the latter. Secondly, the TEM diameter was that of the dry particles, while the d_{h0} value included a contribution from a layer of solvent molecules adsorbed onto the silica particles.

Silica Coating. The sol-gel reaction of the PIPSMA blocks of P1 and P2 were catalyzed by HCl and performed at room temperature for 10 h. The weight ratio used between a polymer or a polymer mixture and silica was always 0.080/1.00. The coated silica particles were settled via centrifugation and thus freed from the un-grafted polymer, catalyst, and other soluble impurities, which remained in the supernatant. Furthermore, the purified coated silica particles were heated in a 100 °C vacuum oven for 2 h to complete the silanol condensation reaction.

Because FT-IR evidence supporting the condensation between the silica surface silanol groups and the silanol groups of sol-gelling PIPSMA has been presented previously,[1] it will not be shown here. Anecdotal evidence supporting the successful silica coating by the block copolymers was the altered dispersion properties of the coated particles. While bare particles were dispersible in methanol but not in trifluorotoluene (TFT), particles coated by a mixture of P1 and P2 were readily dispersed in TFT because of the solubility of both PFOEMA and PtBA in TFT. Although the particles coated at low P1 weight ratios, e.g., at f_1 = 0%, were dispersible in methanol, a good solvent for PtBA, particles coated at sufficiently high f_1 values, e.g., at f_1 = 50%, did not disperse well in methanol because of the insolubility of PFOEMA in this solvent.

An increase in the determined d_{h0} value provided direct evidence of particle coating. Particles coated at f_1 = 50% were studied by DLS. Since these particles did not disperse well into methanol, the solvent used for bare silica analysis, the coated silica particles were analyzed in TFT. Fortunately, the refractive index and viscosity data were accurately known at 20.0 °C for these two solvents.[34,35] Thus, the comparable DLS studies were performed at this temperature.

Figure 4 also shows the variation in the DLS d_h of the coated silica particles with $\sin^2(\theta/2)$. The d_h-vs.-$\sin^2(\theta/2)$ line paralleled that of the uncoated particles, suggesting that the coating procedure did not lead to particle degradation or aggregation and also the coating conformed to the shape of the original silica particles. Extrapolating to zero scattering angle yielded a d_{h0} value of 503.6 ± 1.4 nm. This represented a 15.3 ± 2.4 nm increase relative to that of the uncoated silica. The thickness of the conforming coating should be 7.7 ± 1.2 nm.

Although the above comparative study yielded a reasonable d_{h0} increase, we remind readers of the assumptions made to extract the d_{h0} values. Strictly speaking, d_h is a function of both particle concentration c and $\sin^2(\theta/2)$. The c dependence was not examined in this comparative study because we assumed that the contributions to d_{h0} from the c term cancelled each other for the two types of particles examined. One should further realize that the particle concentrations used were low at 0.5 mg/mL and the contribution of the c term to d_{h0} should be small in each case.

Quantification of Grafted Polymer Amounts. The grafted polymer amount in a coated silica sample could be determined via TGA. TGA curves were obtained by heating samples in air from room temperature to 700 °C at 5 °C/min. The residual weight of each sample at each temperature was then normalized to that measured at 150 °C. The weight at 150 °C was taken as the intrinsic weight of a sample because sorbed moisture would have evaporated and sample degradation would not have begun by this temperature. Plotted in Figure 5a are the normalized TGA curves for uncoated silica particles, silica particles that were coated at f_1 = 50%, as well as P1 and P2 that were sol−gelled under conditions similar to those used to coat the silica particles.

As expected, bare silica was thermally stable and experienced little weight loss and had a weight residue of 98.4% when heated from 150 to 600 °C. Over the same temperature range, the sol−gelled P1 and P2 copolymers were mostly decomposed and had residual weights of 4.2 and 4.1%, respectively. Although we do not know the exact reason for these different residual values for P1 and P2 and readers are referred to literature for possible explanations,[40] we see silicone oxide formation from the sol-gelled PIPSMA blocks of P1 and P2 as a possible source for the detected residues. The particles coated at f_1 = 50% had by 600 °C a cumulative weight loss of 7.7% or a residual weight of 92.3%, which was expectantly between those of silica and the sol-gelled polymers. Aside from residue readings, the curves revealed different weight loss patterns for the sol-gelled P1 and P2 copolymers, and these patterns were more clearly seen in the differential TGA curves shown for silica particles coated by P1, by P2, and by P1 and P2 at f_1 = 50%. Although P1-coated silica particles lost weight continuously between 200 and 400 °C, P2-coated silica particles exhibited three major weight loss regions centered near 243, 391, and 530 °C.

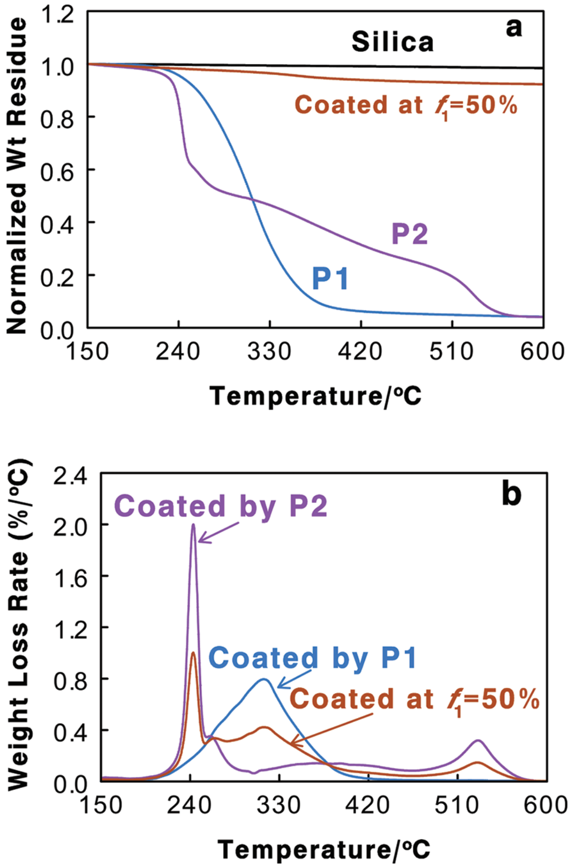

Figure 5. (a) Comparison of TGA curves of silica particles (black), sol−gelled P1 (blue), sol−gelled P2 (violet), silica particles coated by P1 and P2 at f_1 = 50% (brown). (b) Comparison of the differential TGA curves of silica particles coated by P1(blue), P2 (violet), and a mixture of P1 and P2 at f_1 = 50% (brown).

Figure 5 revealed that the sol−gelled P1 and P2 had weight loss patterns identical to those of P1 and P2 that were grafted onto silica. We further assumed that the silica component of a coated silica particle displayed similar thermal behavior as that of an uncoated silica particle. These allowed us to relate, at each temperature, the weight residue of a coated silica sample to those of uncoated silica samples as well as sol−gelled P1 and P2 copolymers. If the residues at a given temperature for sol-gelled P1, sol−gelled P2, silica, and coated silica are R_1, R_2, R_S, and R_{PS}, individually, and the grafted P1 and P2 weight fractions in a coated silica sample are respectively x and y, the following equation applies

$$R_1x + R_2y + (1 - x - y)R_s = R_{ps} \qquad (1)$$

Because there were two unknowns in eq 1, the R_1, R_2, R_S, and R_{PS} values had to be obtained at a minimum of two temperatures to solve for x and y. The weight residues at 300 and 400 °C were used for each coated silica sample to quantify the amounts of grafted P1 and P2. The two temperatures were chosen because the decomposition of P2 and P1 was mainly responsible for the weight loss of a coated silica sample at the lower and higher temperatures, respectively, and the use of the residual values at these temperatures would allow more accurate quantification of the amounts of grafted P2 and P1.

Following this method, the x and y values were calculated for samples coated at different f_1 values and plotted in Figure 6. As f_1 increased, x increased and y decreased linearly, in agreement with the theoretical prediction.

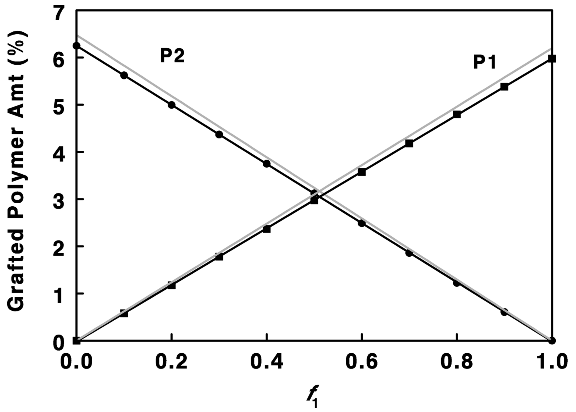

Figure 6. Variation in the determined grafted P1 and P2 weight factions (● and ■) in coated silica samples as a function of P1 feed weight ratio f_1. Although the dark lines were the best fits to the experimental data, the gray lines depicted how the amounts of grafted P1 and P2 would change with f_1 if they were quantitatively grafted.

If all of the isopropyloxy groups of PIPSMA were hydrolyzed and the resultant silanol groups were fully condensed to form siloxane (Si−O−Si) bonds, the effective chemical formula for a sol-gelled IPSMA unit was $C_7H_{11}SiO_{3.5}$, where the oxygen number was not an integer because each of the 3 siloxane oxygen atoms were shared by two Si atoms. Using this effective formula, 0.080 g of P1 was calculated to yield 0.066 g of grafted polymer. Under the standard silica coating conditions, the P1 to silica weight ratio used was 0.080/1.00. Assuming quantitative polymer grafting, the polymer weight fraction in the P1-coated silica should be 0.066/(0.066+1.00) or 6.2%. Assuming quantitative grafting, the P2 weight fraction in a P2-coated silica sample could be calculated analogously and should be 6.5%. When the particles were coated by a mixture of P1 and P2 at a P1 weight fraction of f_1, the grafted P1 weight fraction in the coated silica, as derived in the Supporting Information (SI), should follow

$$x \approx 0.062 f_1 \tag{2}$$

and amount of grafted P2 should follow:

$$y \approx 0.065(1 - f_1) \tag{3}$$

Also plotted in Figure 6 were the straight lines drawn following eqs 2 and 3. The calculated and experimentally determined x and y amounts agreed well with each other. This suggested that the polymers were essentially quantitatively grafted.

The essentially quantitative grafting of P1 and P2 should not be surprising because the polymer to silica weight ratio used in this study was optimal, as established before for P1 grafting.[1] Our previous TGA study indicated that P1 was quantitatively grafted only over a narrow range of P1 to silica weight ratios. At high P1 to silica weight feed ratios, for example, only the amount of P1 required to form a saturated grafted unimolecular diblock copolymer layer was grafted and the residual P1 would be left in the coating solution yielding presumably nanoclusters, whose existence was recently confirmed by a dynamic light scattering study.[41]

Co-Grafting of P1 and P2 onto the Same Silica Particles. DLS and TGA results so far have confirmed the grafting of P1 and P2 onto silica particles but provided no clue on the distribution of the grafted chains. Because of the likely incompatibility between PtBA and PFOEMA, the different diblock copolymers might preferentially graft onto different particles. When they were grafted onto the same particles, they could attach onto the opposite sides of a particle to yield Janus particles,[42,43] form patches enriched by one polymer to yield patched particles,[6,17] or they could graft randomly.

Figure 7 shows AFM topography and phase images of silica particles coated at f_1 = 50% and cast onto a silicon wafer from TFT ($C_7H_5F_3$), a good solvent for both PtBA and PFOEMA. While the particles appeared smooth in the topography image, the phase image clearly revealed the presence of circular or elongated brighter patches dispersed in a darker phase. The smallest dimension of these dark patches was approximately 10 nm. This suggested the binary composition of the surfaces and thus the co-grafting of P1 and P2 chains onto the same particles.

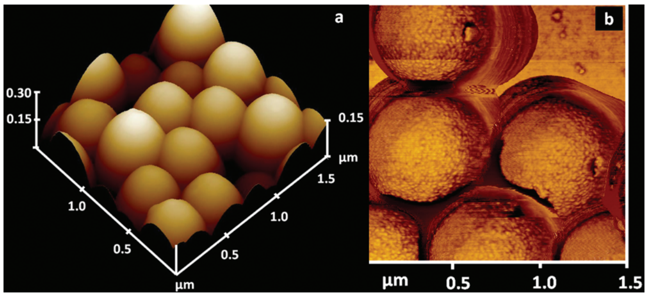

Figure 7. (a) AFM topography and (b) phase images of silica particles coated at f_1 = 50% and sprayed from $C_7H_5F_3$.

Figure 7b could be taken as evidence for the patched grafting of P1 and P2. This was possible because the PFOEMA and PtBA blocks were probably incompatible and would tend to segregate. This segregation had to compete with the grafting reaction, which was probably controlled by kinetics and would predominantly yield a randomly-grafted layer. Patched P1 and P2 grafting occurred because of the simultaneous interplay of the thermodynamic and kinetic factors.

A further literature study, however, revealed that a similar phase image could result even if P1 and P2 chains were randomly distributed. According to Marko and Witten[44] or Zhulina and Balazs,[45] two types of highly incompatible surface chains could be uniformly grafted and thus be uniformly distributed on the grafting substrate. Further away from the substrate, the chains could still laterally segregate into patches with dimensions comparable to the unperturbed root-mean-square end-to-end distance (R_n) of the grafted chains. This picture has been confirmed by Muller using a self-consistent field theory analysis.[46] According to Muller,[46] the lateral segregation pattern of the top part of the grafted chains could change from a rippled phase to a tetragonally-packed dimpled phase, and then to a hexagonally-packed dimpled phase as the incompatibility between the grafted chains increased. Thus, the circular and elongated patches observed in Figure 7b could also be due to a surface dimpled or rippled phase despite the uniform grafting of the P1 and P2 chains.

The theories mentioned above were developed for grafted coiled chains. The PFOEMA block is rod-like due to the steric hindrance rendered by the perfluoroctylethyl (FOE) pendant groups.[47] Furthermore, our system was further complicated by the fact that the FOE units readily formed a liquid crystalline phase at room temperature[48] and the molecular weights of our polymers were low. Thus, the classical theories should be applied with caution to our system. Despite this, the qualitative pictures might be valid here because the PtBA chains were coiled and could bypass a segregated PFOEMA patch and emerge from a PtBA-rich region.

The co-deposition of the two types of polymer chains onto the same silica particles was further supported by comparing the AFM images of silica particles coated at different f_1 and cast from different solvents. Figure 8 compares AFM topography images of silica particles that were coated by pure P2 and coated by a mixture of P1 and P2 at f_1 = 25 and 50% and were cast from either CH_3OH or perfluoromethylcyclohexane (C_7F_{14}). Here CH_3OH and C_7F_{14} were selective towards PtBA and PFOEMA, respectively. While the particles coated by pure P2 were round and smooth and were analogous to those that were coated by pure P1 and studied previously,[1] the particles that were coated by P1 and P2 mixtures were rugged after being cast from these selective solvents. The particles coated by a singular brush were smooth, because the polymer chains collapsed uniformly on the silica surface after solvent evaporation. The particles coated by a mixture of P1 and P2 appeared rugged because the particles were co-grafted by the two different polymers and these two polymers collapsed to different degrees when the particles were last cast from a selective solvent.

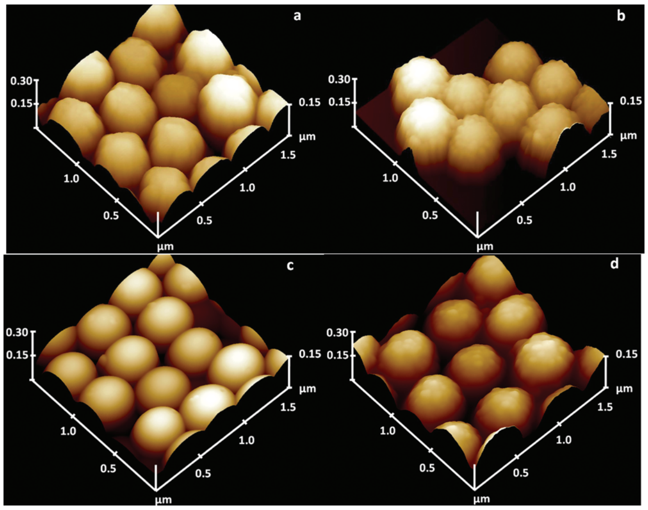

Figure 8. AFM height images of silica particles that were coated at (a) f_1 = 25%, (b) f_1 = 50%, and (c) f_1 = 0% and cast from methanol. Also shown is (d) an AFM image of a silica sample coated at f_1 = 50% and cast from C_7F_{14}.

In conclusion, our AFM study suggests that P1 and P2 co-condensed on the same silica particles. Also, they were grafted either in a patched or uniform fashion.

Grafting of Unimolecular Layer. We have previously reported on silica coating by P1 alone and drawn conclusions about unimolecular layer formation from P1 under our coating conditions based on the following considerations:[1] Firstly, the amount of grafted polymer as determined by TGA increased initially with the feed weight ratio (m_p/m_s) between P1 and silica and then approached an asymptote at high m_p/m_s values. This was a trend that would be anticipated for unimolecular layer adsorption.[49,50] Secondly, the thickness of a saturated layer that was grafted at a sufficiently high m_p/m_s value was slightly smaller than the contour length of the fully stretched PFOEMA block. Thirdly, our XPS analysis confirmed that the grafted layer was covered by the PFOEMA block. This suggested that the polymer was grafted via the PIPSMA block and possessed the anticipated layered structure.

A mixture of P1 and P2 replaced P1 and was used to coat the silica particles in this work. Since the polymer to silica weight ratio was optimal for unimolecular layer formation and also the sol-gel chemistry should be the same, a similar unimolecular layer grafting behavior was anticipated: i.e. the PIPSMA blocks of P1 and P2 should anchor onto the silica particles and a mixture of PtBA and PFOEMA should top the sol-gelled PIPSMA blocks.

XPS was used to probe the surface composition of the coated silica samples. Silica particles were coated at f_1 = 50%, dried, and then re-dispersed into $C_7H_5F_3$. This dispersion was cast onto a silicon wafer to yield a silica particulate film for XPS analysis. Figure 9 shows the XPS spectrum of this silica particulate film. The characteristic 2S and 2P peaks of silicon normally observed at 166 and 116 eV were not present.[1] Rather, the fluorine peaks dominated the spectra. Because the sol−gelled PISPMA blocks contained silicon, the spectrum suggested that the PFOEMA block topped the sol−gelled PIPSMA blocks.

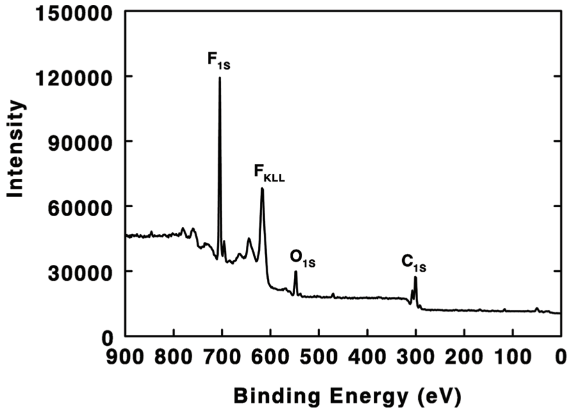

Figure 9. XPS spectrum of silica coated at f_1 = 50% and cast from $C_7F_3H_5$.

The same conclusion could not be made from the XPS spectrum about the location of the PtBA block because PtBA lacked characteristic XPS peaks. However, the PtBA block must have co-existed with the PFOEMA block in the corona because its presence on the surface was essential for explaining the AFM images discussed above.

Although the XPS data above did support a unimolecular layer coating model, stronger support was rendered by the solvated coating thickness of 7.7 ± 1.2 nm obtained from DLS analysis of the silica particles that were coated at f_1 = 50%. At 70 repeat units and possessing a characteristic ratio of 6.25,[51] the PtBA block had a fully stretched chain length of 17.6 nm and an unperturbed root-mean-square end-to-end distance of 4.6 nm. The solvated layer thickness of 7.7 ± 1.2 nm was between 4.6 and 17.6 nm, and was thus a reasonable unimolecular layer thickness.

The thickness of a layer coated at f_1 = 50% after drying could also be calculated based on the assumptions that the silica particles were perfect spheres, the coating was perfectly smooth, and that the polymers were quantitatively grafted. As shown in the Supporting Information, this layer should be 6.0 nm thick, a value that is also reasonable for a unimolecular layer.

Aside from being a unimolecular layer, the chains in this layer should be crowded. Also shown in the Supporting Information are the calculations for the chain grafting densities for coatings prepared at f_1 = 0, 50, and 100% and those for the chain densities at which the grafted chains began to overlap. Because the former densities were much larger than the latter, the grafted PtBA chains should be stretched.

Wetting Properties of Films of Coated Silica. Mixed brushes have attracted attention because of their stimuli-responsive properties.[22,23,26,52] The polymer chains in these layers change their organization and thus modulate their surface properties in response to changes in the external medium, pH, temperature, or ionic strength. The PtBA and PFOEMA blocks in the corona of our particles should also be stimuli-responsive. This has been partially proven so far by AFM, which has revealed that the segregation patterns of PtBA and PFOEMA changed depending on the solvent from which the silica particles were cast. If sufficient silica particles were cast, they fused into particulate films. Thus, another way to verify the responsiveness of the surface structure to the casting solvent has been to monitor the water and oil (CH_2I_2) contact angle changes among these cast silica films.

Figure 10 compares photographs of a water droplet and CH_2I_2 droplets on films of silica coated at f_1 = 75%. The water contact angle on a silica particle film cast from methanol was 166 ± 2°. The CH_2I_2 contacts angles were 130 ± 2, 127 ± 2, and 146 ± 2° on silica particulate films cast from CH_3OH, $C_7F_3H_5$, and C_7F_{14}, respectively. Thus, the contact angles of CH_2I_2 droplets changed depending on the casting solvent that was used for a given silica sample.

Water was further noted to be very unstable on surfaces of particles coated at f_1 = 75% and could readily roll off the surface. To obtain a stable droplet for photography, the droplet had to be dispensed with care and the substrate had to be very level. This behavior and the >150 ° contact angle for water suggested that this surface was superhydrophobic. Also, the contact angle difference between different samples was real and was not an artifact derived from the sample preparation protocol. Despite the crude nature of the particulate film preparation protocol, the contact angle changes were within ±2° for a given sample from different films.

Results of a more comprehensive study are shown in Figure 11, where water and CH_2I_2 contact angle values were plotted as a function of the casting solvent and f_1 at which the silica particles were coated. The general trends were: a) water or oil repellency improved as f_1 increased, (b) films cast from C_7F_{14} were superhydrophobic at all tested f_1 values and possessed the best water or oil repellency, and (c) films cast from methanol possessed better water and oil repellency than those cast from $C_7H_5F_3$ at f_1 = 75% and this trend was reversed at f_1 = 25%.

The improvement in oil and water repellency with increasing f_1 values should not be surprising. A first criterion for enhanced oil and water repellency or amphiphobicity is the low surface tension of the coating. The surface tensions of PtBA[53] and PFOEMA[47] are 31.2 and ~7 mN/m, respectively. Increasing the presence of PFOEMA in a surface should enhance its amphiphobicity.

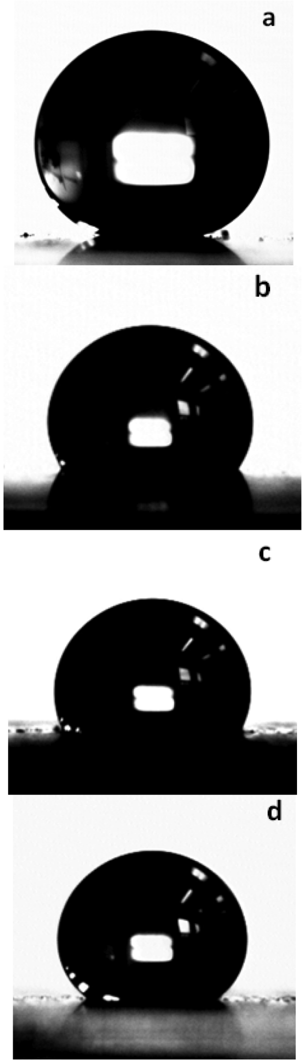

Figure 10. Photographs of (a) water and (b−d) diiodomethane droplets on films of silica particles coated at f_1 = 75%. The casting solvents for the particulate films were (a, b) CH_3OH, (c) $C_7F_3H_5$, and (d) C_7F_{14}, respectively.

Films cast from C_7F_{14} should have the best amphiphobicity because C_7F_{14} was a selective solvent for PFOEMA. Casting from such a solvent should help enrich the surface with PFOEMA.

When cast from methanol, a selective solvent for PtBA, the silica surfaces should be enriched with PtBA. From surface tension considerations alone, films of these silica particles should have the lowest H_2O and CH_2I_2 contact angles. While this was true on films of silica coated at f_1 = 25%, the H_2O and CH_2I_2 contact angles were larger on films of silica particles that were coated at f_1 = 75% and cast from methanol than on those cast from $C_7H_5F_3$, a mutual solvent for PtBA and PFOEMA. A comparison of the AFM images in Figures 7 and 8 suggested that the particles cast from methanol bore nanometer-sized bumps while those cast from $C_7H_5F_3$ did not. Thus, the former particles had higher surface roughness. It is well know that surface roughness also helps increase droplet contact angles if the droplet contact angle on a flat substrate is already >90°.[54−56] Thus, the surface roughness of the silica coated at

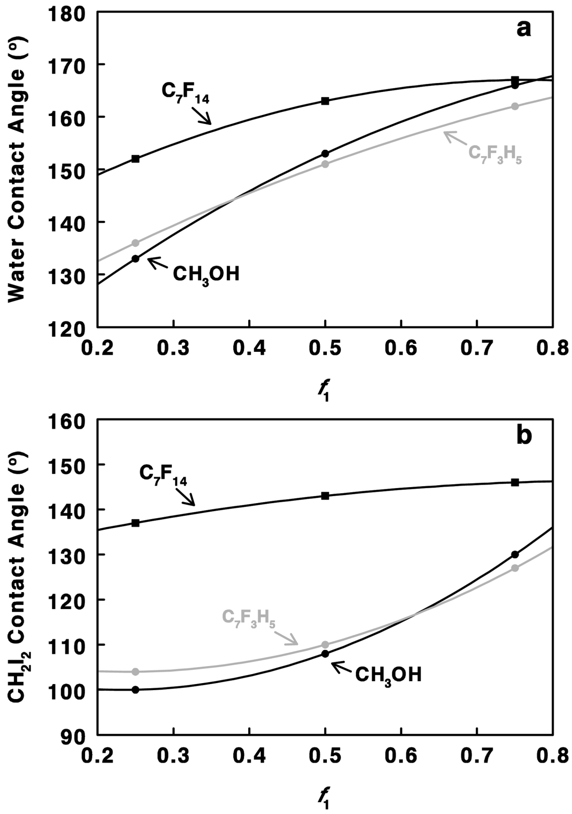

Figure 11. Plot of variation in the (a) H_2O and (b) CH_2I_2 droplet contact angles on silica particulate films with various particle coating f_1 values and spraying solvents.

f_1 = 75% probably played a more important role than the surface composition in boosting the liquid contact angles.

Significant contact angle changes, from 133 to 152° for H_2O and from 100 to 137° for CH_2I_2, were observed on films of silica coated at f_1 = 25% by changing the casting solvent from CH_3OH to C_7F_{14}. However, these changes were, by no means, dramatic when compared with some of those reported in the literature.[57,58] Two factors probably contributed to this. Firstly, both PtBA and PFOEMA were hydrophobic and a switch from superhydrophobicity to superhydrophilicity would be unlikely if these two polymers were used. Secondly, neither the PFOEMA nor the PtBA block used was long enough for one block to fully cover the other block when the particles were cast from a block-selective solvent for PFOEMA or PtBA. This was also deduced from a comparison of the XPS spectra shown in Figure S1 in the Supporting Information for particulate films of silica coated at f_1 = 50% but cast from different solvents including $C_7F_3H_5$, C_7F_{14}, and CH_3OH. The spectra all looked very similar regardless of the casting solvent, suggesting the thinness of the topping PFOEM or PtBA layer relative to the pathlength of the X-ray-generated electrons. Despite this non-dramatic effect, solvent-switchable surfaces have definitely been achieved from silica particles that were simultaneously coated by two diblock copolymers.

4. CONCLUSIONS

PFOEMA-*b*-PIPSMA (P1) and PIPSMA-*b*-PtBA (P2) with low polydispersity indices were synthesized by anionic polymerization. Catalyzed by HCl, P1 and P2 were co-grafted in one-pot reaction onto silica particle surfaces. A simple and effective method based on TGA has been developed for determining the amounts of grafted P1 and P2 copolymers. The copolymers were shown to graft essentially quantitatively under the applied coating conditions. The relative quantities of grafted P1 and P2 copolymers could be tuned by changing the P1 and P2 weight ratios. An AFM study suggested that P1 and P2 copolymers were co-grafted onto the same silica particles in either a patched or uniform fashion. XPS analysis indicated that the PFOEMA block topped the sol-gelled PIPSMA block, suggesting polymer grafting by the PIPSMA block. When studied by DLS, the silica particles coated at f_1 = 50% exhibited a hydrodynamic diameter increase of 15.3 ± 2.4 nm or a solvated coating thickness of 7.6 ± 1.2 nm. The reasonable grafted layer thickness and the desired layered structure of the grafted layer suggested that P1 and P2 were grafted as a unimolecular layer. More interestingly, this mixed unimolecular layer bearing PFOEMA and PtBA coronal chains was stimuli-responsive. The wetting properties of films of the cast particles changed with the casting solvent. Casting from C_7F_{14}, a selective solvent for PFOEMA, enriched the surfaces with PFOEMA and thus increased the oil and water repellency of the silica particulate films. Also, the oil and water repellency improved as f_1 increased under otherwise identical conditions. When they were cast from C_7F_{14}, films of silica coated at f_1 = 25, 50, and 75% were all superhydrophobic.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Derivation for eqs 2 and 3, the calculation of the thickness of dried grafted polymer layers, the calculation of the grafted polymer chain densities, demonstration of the crowdedness of the grafted chains, and the XPS spectra of coated silica particles cast from different solvents (PDF). This material is available free of charge via the Internet at http://pubs.acs.org

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Notes

The authors declare no competing financial interest.

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