Synthesis and Characterization of Stimuli-Responsive Semifluorinated Polymer Brushes Prepared by Atom Transfer Radical Polymerization

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ABSTRACT: "Grafting from" surface-initiated atom transfer radical polymerization (ATRP) techniques were used to synthesize semifluorinated diblock copolymer brushes from silica substrates. Synthesis of either a polystyrene or poly(methyl acrylate) homopolymer brush was performed first (inner block) followed by polymerization of a semifluorinated monomer (outer block). The semifluorinated outer block consisted either of poly(pentafluorostyrene), poly(heptadecafluorodecyl acrylate), poly(pentafluoropropyl acrylate), or poly(trifluoroethyl acrylate). Analysis of the homopolymer and diblock copolymer brush layers was conducted using ellipsometry, ATR–FTIR, tensiometry, XPS, and AFM. Solvent-induced diblock rearrangement experiments were performed using a selective solvent for the hydrocarbon polymer block to generate a fluorine-deficient surface. With the exception of the systems containing PHFA, all the diblock systems were shown to exhibit water contact angles typical for the hydrocarbon polymer block after solvent treatment. Poor rearrangement for diblock copolymer brushes containing PHFA was observed when compared to all other semifluorinated diblock copolymer systems. The extent of diblock rearrangement was correlated to the calculated values for the solubility parameters of each block.

Introduction

Recently, the synthesis of polymer brushes has garnered attention, due in part to their unique properties and applications.[1-4] Colloidal stabilization,[5] surface property tailoring, "chemical gates",[3] and microlithographic patterning[6] have been discussed as potential applications for these materials. Polymer brushes can be described as polymer chains tethered to a surface or interface with a sufficiently high grafting density such that the chains are forced to stretch away from the tethering site.[7] The formation of these tethered chains is generally done by two techniques—physisorption or chemical bonding of chains to an interface. Typically in polymer physisorption, a diblock copolymer is used in which one of the blocks strongly adsorbs to the surface while the other block stretches away to form the brush layer.[8] However, the physical nature of the tethering renders the brush thermally and solvolytically unstable as well as yielding poor control of grafting density.

Covalently grafting chains to the surface, by either the "grafting to" or "grafting from" technique, can overcome these shortcomings. In the "grafting to" method, preformed polymer chains containing a suitable end-functionalized group are reacted with a surface to obtain the desired brush.[9] Although the brush layer exhibits thermal and solvolytic stability, it inherently possesses a low grafting density and film thickness on the surface. This observation is due to the inability of large polymer chains to diffuse to the reactive surface sites that are sterically hindered by surrounding bonded chains. To circumvent these disadvantages, a "grafting from" technique is utilized in which the polymer brush layer is generated in situ from a surface immobilized initiator.[10] The immobilized initiator, which is predominantly formed via a self-assembled monolayer (SAM) containing the initiator group,[11] controls the grafting density of the brush by deposition uniformity and initiating efficiency. Brush layer thickness is controlled by monomer diffusion to the propagating chain end rather than macromolecule diffusion to the surface, thus resulting in thicker brush layers of higher density.

By combining SAM formation with "living" free radical polymerization techniques, control of the polymer brush layer thickness and architecture can be obtained. One of the most robust "living" free radical polymerization methods is copper-catalyzed atom transfer radical polymerization (ATRP) system.[12] Uniform chain growth with a minimized amount of chain termination can be achieved, resulting in controlled molecular weight and narrow polydispersity, which in turn leads to controlled brush thickness.[13] Sequential activation of the dormant chain ends in the presence of different monomers allows for the synthesis of diblock copolymer brush layers. Previous studies have shown that diblock copolymer brushes undergo surface rearrangement when exposed to various solvents.[14] With this premise in mind, we attempted to synthesize semifluorinated diblock copolymer brushes in order to utilize the immiscibility of fluorocarbons/hydrocarbons as a rearrangement mechanism and capitalize on the wetting properties of fluoropolymers.[15] As well as exhibiting superb oil and water resistance, fluoropolymer materials are biocompatible, making them suitable for medical applications and drug delivery.[15] In the work reported here, we synthesized and characterized diblock copolymer brushes using semifluorinated acrylate and styrene monomers.

Experimental Section

Materials. Unless otherwise stated, all reagents were purchased from Aldrich Chemical Co. Pentafluorostyrene (PFS, Oakwood Products, 99%), heptadecafluorodecyl acrylate (HFA, 97%), pentafluoropropyl acrylate (PFA, Oakwood Products, 98%), trifluoroethyl acrylate (TFA, Oakwood Products, 99%), styrene (S, 99%), and methyl acrylate (MA, 99%) were passed through a column of activated basic alumina (~150 mesh) prior to use. (11-(2-Bromo-2-methyl)propionyloxy)un-

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decyltrichlorosilane was synthesized as described in the literature.[16] Purification of copper(I) bromide (98%) was done according to literature methods.[17] N,N,N',N',N'-Pentamethyldiethylenetriamine (PMDETA, 99%), ethyl 2-bromoisobutyrate (E2Br-iB, 98%), anhydrous anisole (99%), anhydrous toluene (99.8%), ethyl acetate (99%), trifluorotoluene (99%), fluorobenzene (99%), and copper(II) bromide (98%) were used without further purification. Silicon ATR crystals (25 × 5 × 1 mm) were purchased from Harrick Scientific while the silicon wafers were purchased from Polishing Corporation of America.

Substrate Cleaning and Initiator Deposition. ATR crystals and silicon wafers were cleaned by treatment with freshly prepared "piranha" solution (70/30, v/v, concentrated H_2SO_4/30% aqueous H_2O_2) at 90 °C for at least 2 h. The samples were then removed and rinsed with copious amounts of deionized water and ethanol followed by drying in an air stream. It should be noted that the "piranha" solution is extremely reactive and should be handled with care. Into a dried round-bottom flask were placed a freshly cleaned silicon wafer and ATR crystal. The flask was sealed using a septum and flushed with high-purity nitrogen for 30 min. Dry toluene (10 mL) and a 25 vol % solution of the trichlorosilane initiator in toluene (0.2 mL) were added to the flask via a syringe, and the flask was heated at 60 °C for 4 h under an atmosphere of nitrogen. The silicon wafer and ATR crystal were then removed and sequentially washed with CH_2Cl_2 and ethanol followed by drying with an air stream.

Typical Procedure for Surface ATRP from a Flat Silicon Substrate. An initiator modified ATR crystal and silicon wafer were placed in a 100 mL Schlenk flask and sealed with a rubber septum. The flask was degassed and back-filled with nitrogen three times and left under a nitrogen atmosphere. CuBr, anisole, and monomer were added to a separate 100 mL Schlenk flask with a magnetic stir bar. The flask was sealed with a rubber septum and degassed by purging with nitrogen for 1 h. PMDETA was added to the mixture via a syringe, and the solution was stirred at 90 °C until it became homogeneous (approximately 15 min). The solution was then transferred to the flask containing the ATR crystal and silicon wafer via a cannula, followed by the addition of free initiator (E2Br-iB) via a syringe. The polymerization was allowed to proceed at 90–100 °C for 24 h (styrene) or 6 h (methyl acrylate), after which the ATR crystal and silicon wafer were removed. To remove untethered polymer chains, the ATR crystal and silicon wafer were placed in a Soxhlet extractor and extracted with THF for 24 h followed by sonication in THF for 30 min and sequential rinsing with CH_2Cl_2 and ethanol. Final concentrations were as follows: $[S]_0 = 3.9$ M, $[PMDETA]_0 = 25$ mM, $[CuBr]_0 = 12$ mM, $[E2Br-iB]_0 = 10$ mM or $[MA]_0 = 3.7$ M, $[PMDETA]_0 = 30$ mM, $[CuBr]_0 = 15$ mM, $[E2Br-iB]_0 = 15$ mM.

Diblock Copolymer Synthesis. Preparation of diblock copolymers was conducted in a manner similar to that for the homopolymer brushes. The order of the blocks in the diblock brush was determined by the order of polymerization from the surface. For example, a Si/SiO2//PS-*b*-PHFA brush was synthesized by first forming a Si/SiO2//PS brush on the surface, followed by the polymerization of HFA from the Si/SiO2//PS brush. For all of the diblock syntheses, except that of Si/SiO2//PS-*b*-PPFS, E2BriB free initiator was used to set up the ATRP equilibrium. In the case of the Si/SiO2//PS-*b*-PPFS brush, CuBr2 deactivator was used. Deactivator was added to the second reaction flask containing the surface samples followed by vacuum evacuation/N2 back-filling to purge the flask of air. Cannula transfer of reaction solution to this flask took place as with the homopolymer brush synthesis. Final concentrations for syntheses from Si/SiO2//PS were as follows: $[PFS]_0 = 1.45$ M, $[PMDETA]_0 = 21$ mM, $[CuBr]_0 = 10$ mM, $[CuBr_2]_0 = 1$ mM at 110 °C for 5 h in *o*-xylene; $[HFA]_0 = 1.6$ M, $[PMDETA]_0 = 20$ mM, $[CuBr]_0 = 10$ mM, $[E2Br-iB]_0 = 5$ mM at 90 °C for 24 h in trifluorotoluene; $[TFA]_0 = 2.6$ M, $[PMDETA]_0 = 30$ mM, $[CuBr]_0 = 15$ mM, $[E2Br-iB]_0 = 15$ mM at 90 °C for 20 h in trifluorotoluene; or $[PFA]_0 = 2.6$ M, $[PMDETA]_0 = 30$ mM, $[CuBr]_0 = 15$ mM, $[E2Br-iB]_0 = 15$ mM at 90 °C for 20 h in trifluorotoluene. Final concentrations for syntheses from Si/SiO2//PMA were as follows: $[PFS]_0 = 1.45$ M, $[PMDETA]_0 = 21$ mM, $[CuBr]_0 = 10$ mM, $[CuBr_2]_0 = 1$ mM at 110 °C for 5 h in *o*-xylene; $[HFA]_0 = 1.6$ M, $[PMDETA]_0 = 20$ mM, $[CuBr]_0 = 10$ mM, $[E2Br-iB]_0 = 5$ mM at 90 °C for 24 h in trifluorotoluene; $[TFA]_0 = 2.6$ M, $[PMDETA]_0 = 30$ mM, $[CuBr]_0 = 15$ mM, $[E2Br-iB]_0 = 15$ mM at 90 °C for 20 h in trifluorotoluene; or $[PFA]_0 = 2.6$ M, $[PMDETA]_0 = 30$ mM, $[CuBr]_0 = 15$ mM, $[E2Br-iB]_0 = 15$ mM at 90 °C for 20 h in trifluorotoluene.

Solvent Treatment of Diblock Surfaces. Surfaces were treated with different solvents in order to test surface rearrangement properties. Samples were exposed to a good solvent for both blocks in order to extend the brushes and have the outer fluoropolymer block reside at the air/polymer interface. After testing the fluorine-rich surface samples, the brushes were then exposed to a solvent that was a poor solvent for the outer fluoropolymer block and a good solvent for the inner hydrocarbon polymer block.

For the surface samples where PS was the inner block (Si/SiO2//PS-*b*-PPFS, Si/SiO2//PS-*b*-PHFA, Si/SiO2//PS-*b*-PPFA, or Si/SiO2//PS-*b*-PTFA), cyclohexane was used as the poor solvent for the fluoropolymer block. A different good solvent was used for each of these systems to extend the brushes and expose the outer block to the surface. Fluorobenzene was used for Si/SiO2//PS-*b*-PPFS, and trifluorotoluene was used for the Si/SiO2//PS-*b*-PHFA, Si/SiO2//PS-*b*-PPFA, and Si/SiO2//PS-*b*-PTFA brushes. Solvent exposures were performed at 60 °C for 1 h for each of the diblock copolymer systems.

For the surface samples where PMA was the inner block (Si/SiO2//PMA-*b*-PPFS, Si/SiO2//PMA-*b*-PHFA, Si/SiO2//PMA-*b*-PPFA, and Si/SiO2//PMA-*b*-PTFA), the good solvent used was fluorobenzene for the PPFS-based diblock copolymer brush and trifluorotoluene for the fluoroalkyl acrylate-based diblock copolymer brushes. Acetone was used as the poor solvent for fluoropolymer for the PPFS-based brush while ethyl acetate was used for the poly(fluoroalkyl acrylate)-based brushes. As with the PS-based samples, solvent exposures were at 60 °C for 1 h for each of the diblock copolymer brush systems. For all systems, the surfaces were tested after each solvent exposure via tensiometry, AFM, and XPS.

Characterization Methods. FTIR-ATR spectra were recorded using a Nicolet System 730 spectrometer using a modified 4XF beam condenser (Harrick Scientific). Spectra were recorded at 2 cm^{-1} resolution, and 500 scans were collected. Contact angles were determined using a Rame Hart NRL-100 goniometer equipped with a tilting base mounted on a vibrationless table. Advancing and receding contact angles of a 10 μL drop were determined using the tilting stage method. Ellipsometry measurements were performed on a Gaertner model L116C ellipsometer with a He–Ne laser ($\lambda = 632.8$ nm) and a fixed angle of incidence of 70°. For the thickness layer calculations, refractive indices of $n = 1.455$ (for silicon oxide),[18] $n = 1.508$ (for initiator layer), $n = 1.5894$ (for PS),[18] $n = 1.48$ (for PMA),[18] $n = 1.385$ (for PHFA), $n = 1.407$ (for PTFA),[18] $n = 1.385$ (for PPFA),[18] and $n = 1.473$ (for PPFS)[19] were used. AFM was performed using a multimode scanning probe microscope (Park Scientific Autoprobe CP) in intermittent-contact mode with a silicon tip. The AFM images were obtained at room temperature in air. X-ray photoelectron spectroscopy (XPS) was performed on a Perkin-Elmer instrument using Al Kα radiation at the MATNET Surface Analysis Center at Case Western Reserve University. The takeoff angle was 45°, and the incidence angle of X-rays was 45° with respect to the surface normal, making the X-ray to electron angle 90°. Survey spectra were taken after the sample was treated with different solvents.

Results and Discussion

Synthesis and Characterization of Tethered Semifluorinated Diblock Copolymer Brushes. Scheme 1 illustrates the general ATRP "grafting from" approach used to synthesize the tethered semifluori-
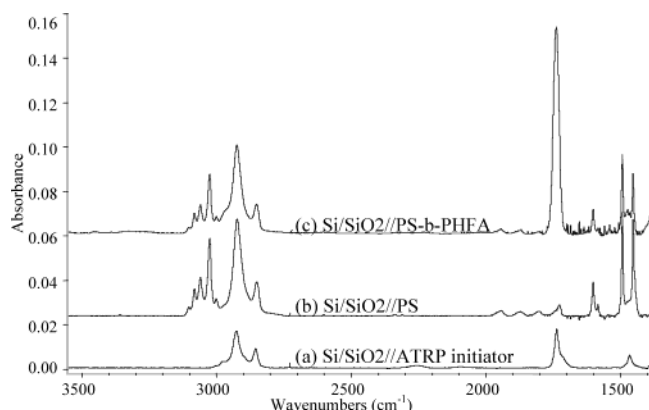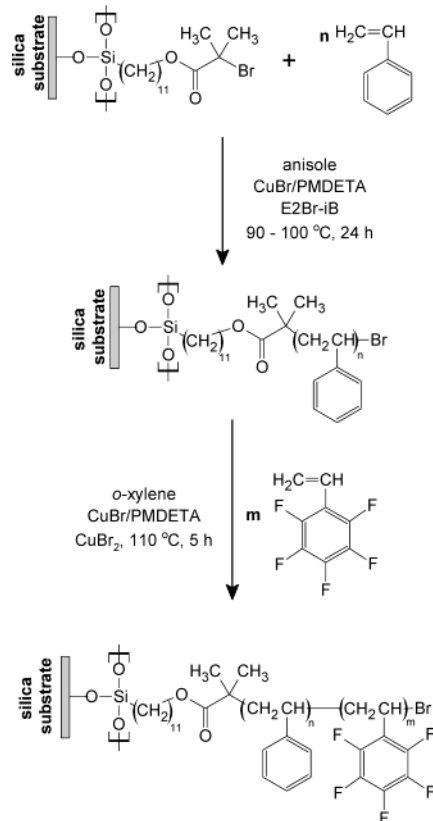
Figure 1. ATR−FTIR of spectra of (a) Si/SiO$_2$//bromoisobutyrate initiator, (b) Si/SiO$_2$//PS (tethered PS brush), and (c) Si/SiO$_2$//PS-*b*-PHFA.

Scheme 1. Synthesis of Si/SiO$_2$//PS-*b*-PPFS Brush on a Silicon Substrate

nated diblock copolymer brushes. Here, the synthesis of a Si/SiO$_2$//PS-*b*-PPFS diblock copolymer brush is shown. Similar synthesis procedures were used to generate the other PS-based and PMA-based semifluorinated diblocks. The initial procedure for the tethered diblock synthesis comprises the solution deposition of a bromoisobutyrate ATRP initiator onto a suitable substrate by self-assembly techniques. In this research, (11-(2-bromo-2-methyl)propionyloxy)undecyltrichlorosilane was synthesized according to literature techniques[16] and utilized as the initiator. Figure 1a depicts the ATR−FTIR spectrum of the immobilized initiator with three predominant peaks. The peaks at 2924 and 2858 cm^{-1} are assigned to the C−H stretching and CH$_2$ stretching vibrations, respectively, while the peak at 1739 cm^{-1} is assigned to the carbonyl stretching vibration of the ester group.

Table 1. Physical Properties of PS-Based Diblock Copolymer Brushes

brush structure[a]	water contact angle[b] (deg)		thickness[c] (nm)
	θ_a	θ_r	
Si/SiO$_2$//PS	96	85	16
Si/SiO$_2$//PS-*b*-PPFS	120	99	5
Si/SiO$_2$//PS	97	85	10
Si/SiO$_2$//PS-*b*-PHFA	127	98	6
Si/SiO$_2$//PS	94	78	13
Si/SiO$_2$//PS-*b*-PPFA	112	92	5
Si/SiO$_2$//PS	96	81	17
Si/SiO$_2$//PS-*b*-PTFA	103	80	6

[a] PS = polystyrene, PPFS = poly(pentafluorostyrene), PHFA = poly(heptadecafluorodecyl acrylate), PPFA = poly(pentafluoropropyl acrylate), and PTFA = poly(trifluoroethyl acrylate). [b] The standard deviation of contact angles was <2°. [c] Thickness determined by ellipsometry and representative of the outer layer.

Table 2. Physical Properties of PMA-Based Diblock Copolymer Brushes

brush structure[a]	water contact angle[b] (deg)		thickness[c] (nm)
	θ_a	θ_r	
Si/SiO$_2$//PMA	74	66	11
Si/SiO$_2$//PMA-*b*-PPFS	118	99	5
Si/SiO$_2$//PMA	80	67	15
Si/SiO$_2$//PMA-*b*-PHFA	126	100	5
Si/SiO$_2$//PMA	81	68	11
Si/SiO$_2$//PMA-*b*-PPFA	115	94	5
Si/SiO$_2$//PMA	74	63	15
Si/SiO$_2$//PMA-*b*-PTFA	102	84	4

[a] PMA = poly(methyl acrylate), PPFS = poly(pentafluorostyrene), PHFA = poly(heptadecafluorodecyl acrylate), PPFA = poly(pentafluoropropyl acrylate), and PTFA = poly(trifluoroethyl acrylate). [b] The standard deviation of contact angles was <2°. [c] Thickness determined by ellipsometry and representative of the outer layer.

The specific ATRP experimental conditions to synthesize the homopolymer and diblock copolymer brushes from the immobilized initiator are given in the Experimental Section. CuBr/PMDETA was used as the catalyst/ligand system for all of the ATRP reactions due to the increased catalyst complex solubility of multidentate amine ligands when employing copper metal as the ATRP catalyst.[20] Previous reports have shown that the low concentration of initiator on flat surfaces results in an insufficient concentration of deactivator to provide adequate control during the ATRP reaction.[21] To address this problem, the addition of free initiator (ethyl 2-bromoisobutyrate, E2BriB)[22] or deactivator (CuBr$_2$)[22] to the reaction solution is necessary to yield a controlled polymerization. With the exception of the PFS polymerizations, E2BriB was added to all of the reaction solutions. Because of the low solubility of PPFS in *o*-xylene,[23] CuBr$_2$ deactivator was added to the PFS polymerization reactions so as to inhibit the formation of free polymer in solution. After each polymerization reaction, the surface samples were extracted in THF for 24 h followed by sonication in THF for 30 min to remove any untethered polymer from the samples.

The surface properties for the PS-based and PMA-based diblock copolymers are given in Tables 1 and 2, respectively. For each entry, the values for the advancing and receding water contact angles as well as the thickness measurements are representative of the outer polymer brush layer only. As can be seen from these tables, the advancing contact angle (θ_a) for the PS and PMA homopolymer brushes were similar to the char-

Table 3. Solvent Treatment of PS-Based Diblock Brushes

| | Si/SiO$_2$//PS-*b*-PPFS[c] | | Si/SiO$_2$//PS-*b*-PHFA[c] | | Si/SiO$_2$//PS-*b*-PPFA[c] | | Si/SiO$_2$//PS-*b*-PTFA[c] | |
solvent[a]	θ_a	θ_r	θ_a	θ_r	θ_a	θ_r	θ_a	θ_r
1st fluorobenzene/ trifluorotoluene[b]	121	90	127	98	112	92	101	82
1st cyclohexane	101	85	110	92	97	78	95	81
2nd fluorobenzene/ trifluorotoluene[b]	119	88	125	97	113	92	101	84
2nd cyclohexane	102	87	111	92	96	77	97	79

[a] Sample immersed in solvent at 60 °C for 1 h. [b] PS-*b*-PPFS brush was treated with fluorobenzene, and all other brushes were treated with trifluorotoluene. [c] The standard deviation of contact angles was <2°.

Table 4. Solvent Treatment of PMA-Based Diblock Brushes

| | Si/SiO$_2$//PMA-*b*-PPFS[b] | | Si/SiO$_2$//PMA-*b*-PHFA[b] | | Si/SiO$_2$//PMA-*b*-PPFA[b] | | Si/SiO$_2$//PMA-*b*-PTFA[b] | |
solvent[a]	θ_a	θ_r	θ_a	θ_r	θ_a	θ_r	θ_a	θ_r
1st fluorobenzene/ trifluorotoluene[c]	115	88	126	100	111	94	102	83
1st acetone/ ethyl acetate[d]	79	67	110	90	81	65	74	62
2nd fluorobenzene/ trifluorotoluene[c]	118	92	125	100	112	95	101	85
2nd acetone/ ethyl acetate[d]	82	68	109	91	80	66	79	69

[a] Sample immersed in solvent at 60 °C for 1 h. [b] The standard deviation of contact angles was <2°. [c] PS-*b*-PPFS brush was treated with fluorobenzene, and all other brushes were treated with trifluorotoluene. [d] PS-*b*-PPFS brush was treated with acetone, and all other brushes were treated with ethyl acetate.
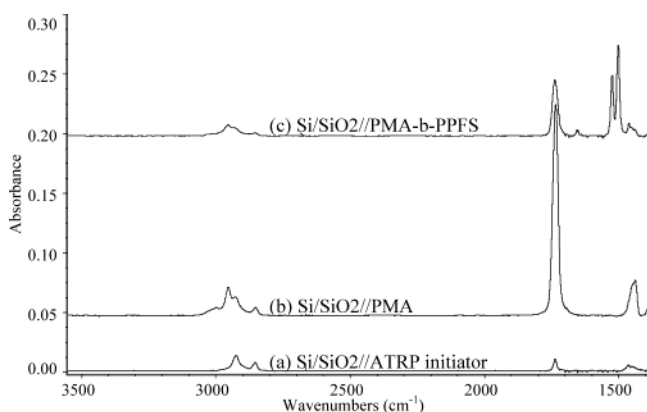

Figure 2. ATR−FTIR spectra of (a) Si/SiO$_2$//bromoisobutyrate initiator, (b) Si/SiO$_2$//PMA (tethered PMA brush), and (c) Si/SiO$_2$//PMA-*b*-PPFS.

acteristic values given in the literature.[24] ATR−FTIR analysis of the PS homopolymer brushes revealed peaks at 3022, 3060, and 3080 cm^{-1}, which were all attributed to the aromatic C−H stretching vibrations (Figure 1b). In addition to these peaks, the aromatic C=C stretching vibrations can also be seen at 1490 and 1447 cm^{-1}. PMA homopolymer brushes exhibited broad aliphatic C−H and CH$_2$ stretching peaks at 2950, 2932, and 2850 cm^{-1} and a sharp, large carbonyl peak at 1730 cm^{-1} (Figure 2b).

From these PS and PMA homopolymer brushes, semifluorinated monomers were polymerized via ATRP to yield semifluorinated diblock copolymer brushes. These monomers were fluorinated styrene (PFS) and acrylate (HFA, PFA, and TFA) derivatives. The water contact angles and outer layer thickness for these respective semifluorinated polymer layers are given in Tables 1 and 2. The advancing contact angle (θ_a) for the fluorinated acrylate layers increases from approximately 102° to 126° as the number of fluorine groups on the alkyl side chain increases, three fluorine groups in TFA to 17 fluorine groups for HFA. The advancing contact angle for PPFS is slightly lower than that of PHFA, 119°

and 126°, respectively. The contact angles for the fluoropolymer brushes were consistent with those for spun-cast homopolymer films tested in this lab. The fluoroalkyl acrylate polymers exhibited ATR−FTIR peaks at 1750 cm^{-1} indicative of a carbonyl group (Figure 1c). The spectra for PPFS depicted peaks at 1520 cm^{-1} that were attributed to the aromatic C=C bonds for the fluorinated benzyl group, which can be seen in Figure 2c.

Solvent Treatment of Diblock Surfaces. Previous studies have investigated the influence of solvent treatment on the surface properties of hydrocarbon diblock copolymer brush systems.[25] These studies showed that treating the diblock copolymers with a solvent that was a good solvent for the inner block and a poor solvent for the outer block resulted in surface rearrangement and pinned micelle formation.[25] Similar solvent treatment experiments were performed on these semifluorinated diblock copolymer systems to determine whether a similar effect could be observed. The diblock brush layers were sequentially exposed to two different solvents to examine the switching response of the layers. A good solvent for both of the brush layers was used to extend the polymer brush, thereby enriching the surface layer in the fluorinated outer block (PPFS, PHFA, PPFA, or PTFA). The second solvent was a poor fluoropolymer solvent but good hydrocarbon polymer solvent. Exposure to this solvent should potentially induce a rearrangement of the diblock copolymer brush to increase the favorable hydrocarbon polymer−solvent interactions and reduce the unfavorable fluoropolymer−solvent interactions. After each solvent treatment, the water contact angle of the polymer brush layer was taken and the process was repeated. Contact angle measurements for these solvent treatments are summarized in Tables 3 and 4.

For the PS-based diblock copolymer brushes, cyclohexane at 60 °C was used as the poor fluoropolymer solvent to drive the fluoropolymer block away from the brush−air interface. The good solvent used to extend the brush was either fluorobenzene or trifluorotoluene

**Table 5. Calculated δ Based on Group Contribution Values Compared to Experimental Values[a]**

monomer	calcd δ $(J/cm^3)^{1/2}$	exptl δ $(J/cm^3)^{1/2}$
methyl acrylate	19.86	19.9–21.3
methyl methacrylate	19.02	18.6–26.2
styrene	19.06	17.4–19.0
heptadecafluorodecyl acrylate	14.15	unknown
pentafluoropropyl acrylate	16.46	unknown
trifluorethyl acrylate	17.46	unknown
pentafluorostyrene	unknown	16.77[b]

[a] All values obtained from published work by van Krevelen.[29]
[b] Value obtained from work by Su.[30]

depending on whether PPFS or a fluoroalkyl acrylate was the fluoropolymer block, respectively. For these semifluorinated diblock copolymer brush systems, PHFA showed incomplete rearrangement because the cyclohexane treatment resulted in an advancing contact angle of 110°, which is higher than expected for a PS layer. The other poly(fluoroalkyl acrylate)s and PPFS diblock copolymer brushes exhibited more extensive rearrangement with the advancing water contact angle (θ_a) decreasing to 99° ± 2° after cyclohexane treatment. All of the semifluorinated diblock copolymer brush samples exhibited reversible surface rearrangement when treated with a good solvent for both blocks.

This same trend was observed when the hydrocarbon polymer inner block was changed from PS to PMA. As with the PS-based diblock brushes, the good solvent used to extend these PMA-based diblock brush samples were trifluorotoluene and fluorobenzene for poly(fluoroalkyl acrylate)s and PPFS, respectively. However, ethyl acetate and acetone were used as the poor fluoropolymer solvents depending on the nature of the outer fluoropolymer block, poly(fluoroalkyl acrylate) or PPFS, respectively. As with the PS-based polymer brushes, PMA-*b*-PHFA showed incomplete rearrangement due to the high water contact angle after treatment with ethyl acetate, $\theta_a = 110°$. The other diblock brushes were able to exhibit complete solvent rearrangement, as indicated by a decrease in contact angle to a value similar to that of the PMA inner block, $\theta_a = 78°$. As would be expected, the tethered semifluorinated diblocks consisting of PMA as the inner block exhibited a greater contact angle difference upon solvent rearrangement than the corresponding PS-based tethered diblocks.

The rearrangement for a diblock copolymer brush has been attributed to several factors.[26] Some of these factors include the lengths of each block, the ratio of one block length to the other, and the Flory–Huggins interaction parameter (χ) for the diblock system. The value of the interaction parameter (χ) can be estimated from the solubility parameters (δ) of the individual diblocks. The larger the difference in solubility parameters, the greater the interaction parameter for the system will be and the lower the chance for complete rearrangement.[27,28] Therefore, comparison of the solubility parameters of the individual blocks can be useful in predicting the ease of rearrangement. Table 5 presents experimental and calculated values of solubility parameters for the polymers of interest here. The calculated solubility parameters were done using a group contribution method as outlined by van Krevelen.[29] The difference between the solubility parameters for PHFA and those for PS or PMA is roughly 5 $(J/cm^3)^{1/2}$, while the difference between the solubility parameters of the other fluoroalkyl acrylates and PPFS

(a)

(b)
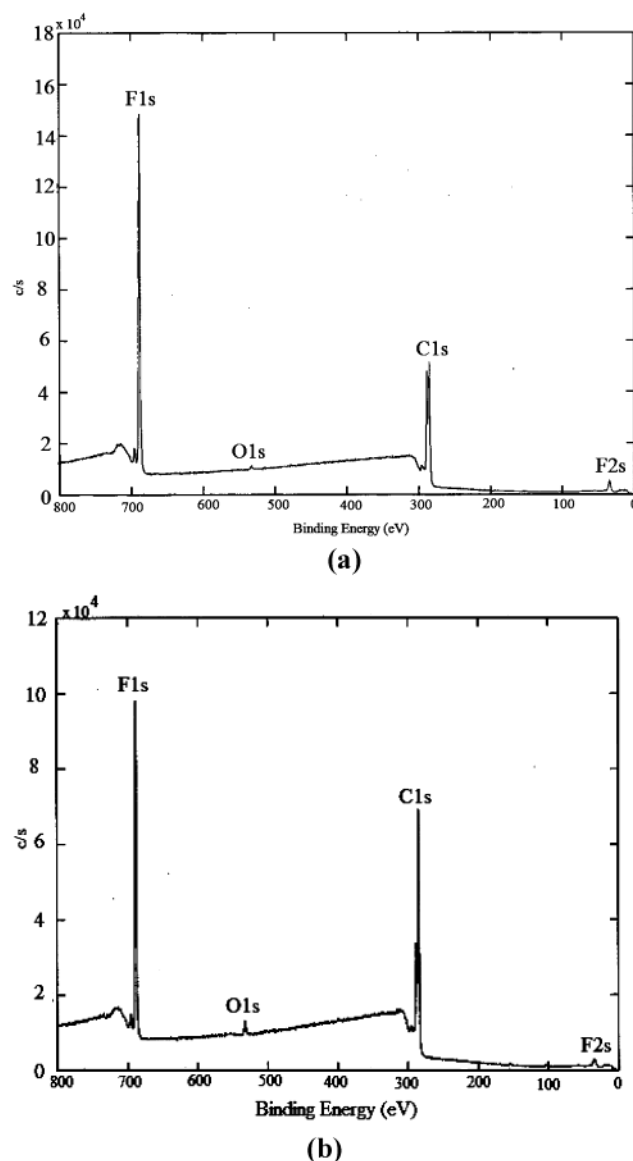
Figure 3. XPS spectra of Si/SiO₂//PS-*b*-PPFS brush (a) after fluorobenzene treatment and (b) after cyclohexane treatment (45° takeoff angle).

and those of these hydrocarbon polymers is roughly 2 $(J/cm^3)^{1/2}$ or less. These comparisons are based on estimates and are not experimentally derived values. However, the calculated values for PMA and PS correlate well with the experimental values. From the solubility parameter calculations and the solvent treatment contact angle results, a correlation between the differences in solubility parameters and the degree of surface rearrangement does exist for these materials. It also shows that the block pair with the larges difference in solubility parameter values (PS-*b*-PHFA and PMA-*b*-PHFA) switches least.

XPS and AFM Analysis of Tethered Diblocks. To further investigate the composition of the tethered diblock copolymer brushes at the air interface after solvent treatment, both XPS and atomic force microscopy (AFM) were used. The sampling depth of the XPS experiments is approximately 5–10 nm, depending on the core level binding energy and the takeoff angle.[25] Figure 3 depicts the XPS spectra for the Si/SiO₂//PS-*b*-PPFS diblock copolymer brush after treatment with fluorobenzene (Figure 3a) and cyclohexane (Figure 3b).
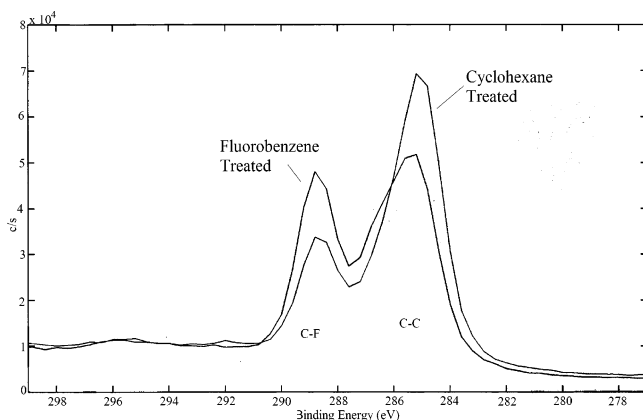
Figure 4. Enhancement of the carbon signals in the XPS spectra of Si/SiO$_2$//PS-*b*-PPFS treated with both fluorobenzene and cyclohexane (45° takeoff angle).

The molar contents of carbon and fluorine after treatment with fluorobenzene were 67% and 33%, respectively. After treatment with cyclohexane, the fluorine content decreased to 24% while the carbon content increased to 76%. In each case a small amount of oxygen could be detected. Calculations indicate that the PS content in the XPS probing region increased from 15% to 37% after treatment with cyclohexane. Figure 4 demonstrates the change in the ratio of carbon−carbon to carbon−fluorine components in the C 1s signal after solvent treatment, again indicating that the degree of PS present in the probed region increases after cyclohexane treatment. While these results indicate that surface rearrangement is occurring to some degree, they are not consistent with previously reported results on the solvent treatment of Si/SiO$_2$//PS-*b*-PMA and Si/SiO$_2$//PS-*b*-PMMA diblock copolymer brushes,[25] nor with our observed contact angle measurements. Similar results were seen with the other diblock copolymer brushes that were tested.

Zhao and co-workers[25] demonstrated that, upon selective solvent treatment of a Si/SiO$_2$//PS-*b*-PMA diblock copolymer brush, the PS content in the region probed by XPS increased from 38% to 88%.[25] This was accompanied by a change in advancing contact angle of 68° to 98°. These results were explained by the reorganization of the diblock copolymer brush to localize PS at the air interface upon treatment with a solvent that was a good solvent for PS but a nonsolvent for PMA. The contact angle results in Table 3 indicate that, upon treatment of the Si/SiO$_2$//PS-*b*-PPFS diblock copolymer brush with cyclohexane, the advancing contact angle decreases from 121° to 101°, suggesting almost complete rearrangement of PS to the air interface. However, the XPS results show that the PS content in the probing region has only increased to 37%. As the depth probed by XPS is approximately 5−10 nm and contact angle measurements are sensitive to compositional changes at a depth of approximately 0.5−1 nm, these results suggest that while rearrangement of the topmost surface is almost complete (contact angle measurements), rearrangement in the XPS probing region is not complete when compared to previous results.

To further investigate the surface rearrangement of semifluorinated diblock copolymer brushes, AFM was used to determine the surface nanomorphology before and after solvent treatment. Figure 5 shows intermittent-contact mode AFM images of the Si/SiO$_2$//PS-*b*-PPFS diblock copolymer brush after treatment with
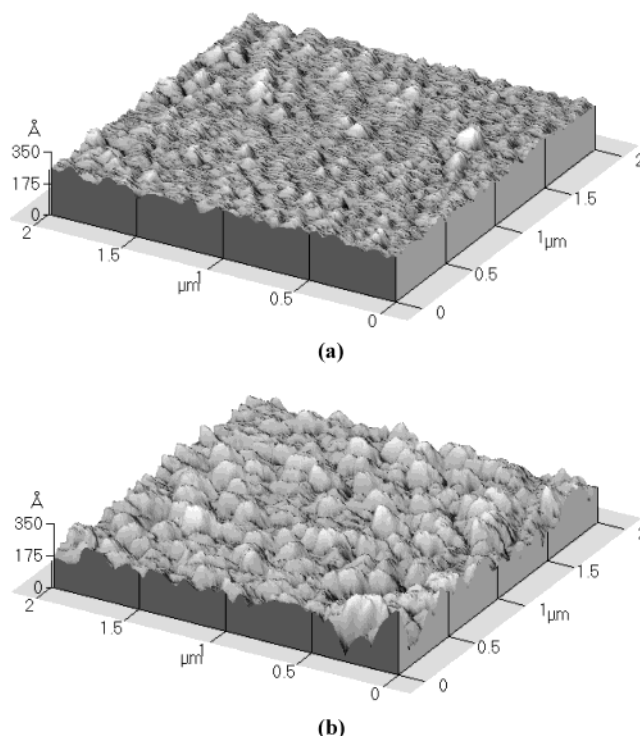

Figure 5. AFM images of Si/SiO$_2$//PS-*b*-PPFS brush (a) after fluorobenzene treatment and (b) after cyclohexane treatment.

fluorobenzene (Figure 5a) and cyclohexane (Figure 5b). Treatment of the diblock copolymer brush with fluorobenzene resulted in a relatively smooth surface, with a surface roughness of 1.4 nm, where roughness is defined as the root-mean-square of height deviations taken from the mean data plane. It should be noted that this roughness is significantly larger than the roughness reported for the Si/SiO$_2$//PS-*b*-PMMA brush (0.7 nm) treated with CH$_2$Cl$_2$, which is the equivalent to the fluorobenzene "good solvent" in the semifluorinated system. We speculate that the increased roughness is due to the partial aggregation of the fluorinated blocks, which has been reported for nontethered semifluorinated diblock copolymers.[31] After treatment with cyclohexane, the surface roughness increased to 3.4 nm, as indicated by the "rougher" surface in Figure 5b; however, no discernible regular nanomorphology was observed. Increases in surface roughness were seen with the other semifluorinated diblock copolymer brushes when treated with a solvent selective for the hydrocarbon block.

It has been previously reported that treatment of Si/SiO$_2$//PS-*b*-PMA and Si/SiO$_2$//PS-*b*-PMMA diblock copolymer brushes results in the formation of a regular nanopattern due to the proposed formation of pinned micelles.[26] Theoretical calculations have demonstrated that the formation of pinned micelles is dependent upon the value of χ, the grafting density of the polymer chains, and the lengths of the blocks comprising the tethered block copolymer.[27,28] In the case where the χ value is small, the tethered block copolymer will rearrange to form regular nanopatterns after treatment with block selective solvents. The values in Table 5 indicate that in the case of a diblock copolymer comprised of PS and PMMA the χ value would be small, and as such, the Si/SiO$_2$//PS-*b*-PMMA diblock copolymer brush forms a well-defined nanopattern.[26] In the case of the Si/SiO$_2$//PS-*b*-PMA diblock copolymer brush, the χ value between

PS and PMA is higher, and as such, the nanopattern formed is less defined. In the case where there is a large χ, the tethered diblock cannot form a pinned micelle, and the sample will not form a regular nanopattern.[28] As the χ value between PS and PPFS is relatively large, the fact that no discernible regular nanomorphology was observed in the AFM after cyclohexane treatment (Figure 5b) may be rationalized by these theoretical predictions. However, the increase in the observed roughness, combined with the contact angle and XPS observations, indicates that some type of rearrangement is taking place after treatment with cyclohexane. Aside from the χ value, other factors that may be contributing to the observed nanomorphology of this system include the tendency for fluorinated segments to aggregate and the natural affinity for fluorinated segments to migrate to the air interface.[31] On the basis of the present results, the mechanism of solvent induced rearrangement of semifluorinated block copolymer brushes is complex, and it may be a combination of effects that is responsible for rearrangement being localized to the outermost air interface of the block copolymer brush. Further work is being conducted to investigate the rearrangement of semifluorinated diblock copolymer brushes.

Conclusions

Surface-initiated polymerization using ATRP techniques was used to synthesize a series of semifluorinated diblock copolymer brushes. These brushes were composed of a PS or a PMA hydrocarbon inner block and either a poly(pentafluorostyrene) (PPFS) or a poly(fluoroalkyl acrylate) (PHFA, PPFA, or PTFA) outer block. The synthesized diblock copolymer brushes were characterized using ATR−FTIR, tensiometry, and ellipsometry. The diblock copolymer brushes were treated with a good and poor fluoropolymer solvent to induce rearrangement of the chains at the surface. Tensiometry data indicate the polymer brush layers reversibly rearrange to form either a hydrocarbon polymer enriched or a fluoropolymer enriched air−polymer interface depending upon the nature of the solvent. The tethered diblocks consisting of a PMA inner block resulted in a greater contact angle difference upon rearrangement than their PS-based counterparts. This is to be expected due to the lower contact angle of PMA surfaces compared to that of PS surfaces. The highly fluorinated PHFA diblock copolymer systems exhibited incomplete surface rearrangement which we attributed to a large χ value between PHFA and PS or PMA. XPS experiments indicated substantial fractions of fluorinated segments were still present in the upper 5−10 nm of the polymer brush surface after treatment with a poor fluoropolymer solvent. This suggests the rearrangement is localized to the near-surface region, since tensiometry probes the outermost surface. Finally, AFM results were consistent with the contention that this rearrangement typically perturbs the surface morphology, leading to an increase in roughness. The images suggest the materials do not undergo the traditional rearrangement

mechanism to form pinned micelles on the surface, and the intrinsic fluorine properties play some role in their rearrangement.

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