Preparation, Characterization, and Tunable Wettability of Poly(ionic liquid) Brushes via Surface-Initiated Atom Transfer Radical Polymerization

Xiaoyan He,[†] Wu Yang,*[,†] and Xiaowei Pei[‡]

College of Chemistry and Chemical Engineering, Northwest Normal University, Lanzhou 730070, P.R. China, and State Key Laboratory of Solid Lubrication, Lanzhou Institute of Chemical Physics, Chinese Academy of Sciences, Lanzhou 730000, P.R. China

Received October 28, 2007; Revised Manuscript Received April 30, 2008

ABSTRACT: The synthesis of well-defined poly (ionic liquid) brushes with tunable wettability using surface initiated atom transfer radical polymerization (ATRP) was reported. Various characterization techniques including ellipsometry, static water contact angle measurements, attenuated total reflection infrared spectroscopy (ATR-FTIR), X-ray photoelectron spectroscopy (XPS), and atomic force microscope (AFM) were used to characterize the films for each surface modification step. Kinetic studies revealed a linear increase in polymer film thickness with reaction time, indicating that chain growth from the surface was a controlled process with a "living" characteristic. Furthermore, the surface of poly (ionic liquid) brushes with tunable wettability, reversible switching between hydrophilicity and hydrophobicity can be easily achieved by exchanging their counteranions.

Introduction

Surface properties of the materials are essential to their interactions with environments.[1] The development of new technologies, such as micro- and nanoelectromechanical systems, photovoltaics, novel sensors, and new biomaterials, demands precise control of surface properties such as adhesion, friction, environmental response, and biocompatibility.[2–5] Recently, wettability control has attracted extensive interests for the development of smart devices, such as self-cleanness,[6] discrete liquid droplet manipulators[7] or tunable optical lenses.[8] Due to the correlation with a surface tension gradient, a more dominant force in micro/nanoscale, wettability control provides a more flexible and efficient way for versatile applications. As we know, wettability depends on surface free energy and surface roughness. So it a key to construct an appropriate surface structure for wettability control. In many cases, tethering of polymer brushes on a solid substrate can serve as an effective method for modifying the surface properties of the substrate.[9] Polymer chains can be covalently grafted to a surface via either the "grafting to" or "grafting from" technique. Because of its high tethering density, the "grafting from" technique is more attractive. In this technique, initiator groups are first immobilized on the surface of the substrate. Subsequent polymerization from the surface-immobilized initiator moieties leads to the formation of tethered polymers on surfaces.

In the past few years, the synthesis of surface tethered polymer brushes by a "grafting from" approach has garnered more and more attention.[10–12] Among various types of polymerization methods, surface-initiated atom transfer radical polymerization (ATRP) has attracted much attention for its controlled/living character, tolerance of functional groups, and mild experimental requirements. A variety of homo- and copolymer brushes have been synthesized with ATRP.[13–22]

Ionic liquids (ILs), are molten salts at ambient temperature with low melting point (<100 °C), low flammability. Recently, room temperature ILs have been widely studied because of their remarkable properties including nonvolatility, chemical and thermal stability and high ionic conductivity.[23–25] The polymeric forms of ionic liquids might constitute a new class of polymer materials with exceptional properties, such as high thermal stability and excellent mechanical and electrochemical properties.[26–29] To date, however, there has been little study on the synthesis of poly(ionic liquids).

Considering the above factors, herein, a poly (ionic liquid) brush modified surface with tunable wettability, reversible switching between hydrophilicity and hydrophobicity is reported. Such modified surfaces are obtained by simply fabricating a poly [1-(4-vinylbenzyl)-3-butyl imidazolium hexafluorophosphate] (PVBIm−PF_6) brushes on a flat silicon substrate via surface-initiated atom transfer radical polymerization (ATRP). The tunable wettability of PVBIm−PF_6 brushes can be achieved by exchanging their counteranions. The obtained switchable surfaces may have wide applications in functional textiles and intelligent microfluidic switching. Figure 1 shows the process for the immobilization of the ATRP initiator on the surface of silicon wafer and growth of PVBIm−PF_6 brushes from silicon wafer via surface-initiated ATRP polymerization.

Experimental Section

Materials. *N*-Butylimidazole (Aldrich, 98%), *N*,*N*,*N*′,*N*′,*N*″-pentamethyldiethylenetriamine (PMDETA, Aldrich 99%), 2-bromoisobutyryl bromide (Aldrich, 98%), ethyl 2-bromoisobutyrate (EBiB) (Aldrich, 98%), 3-aminopropyltriethoxysilane (APS), and butyronitrile were obtained from Kanto Chemical Co. 2,6-Di-*tert*-butyl-4- methylphenol (DBMP) (Aldrich, 98%), ammonium hexafluorophosphate (Aldrich, 98%), and 4-vinylbenzyl chloride (Aldrich, 90%) were used as received. Other reagents were of analytical grades and used as received. All aqueous solutions were prepared with the deionized water. The silicon (111) wafers were purchased from Shanghai Wafer Work Corp., China. They were cleaned using freshly prepared "piranha" solution (70/30 v/v, concentrated H_2SO_4/30% H_2O_2) at 100 °C for at least 2 h and then rinsed with distilled water followed by ethanol and dried under a stream of clean nitrogen ***(Caution!)***. The synthesis of the surface-bound initiator, 2-bromo-2-methyl-*N*-(3-(triethoxysilyl)propyl) propanamide (BTPAm) was carried out according to the ref 30.

* Corresponding author. E-mail: yangw@nwnu.edu.cn, Telephone (fax): +86-931-7971989.

[†] College of Chemistry and Chemical Engineering, Northwest Normal University.

[‡] State Key Laboratory of Solid Lubrication, Lanzhou Institute of Chemical Physics, Chinese Academy of Sciences.

10.1021/ma702389y CCC: $40.75
Published on Web 06/07/2008

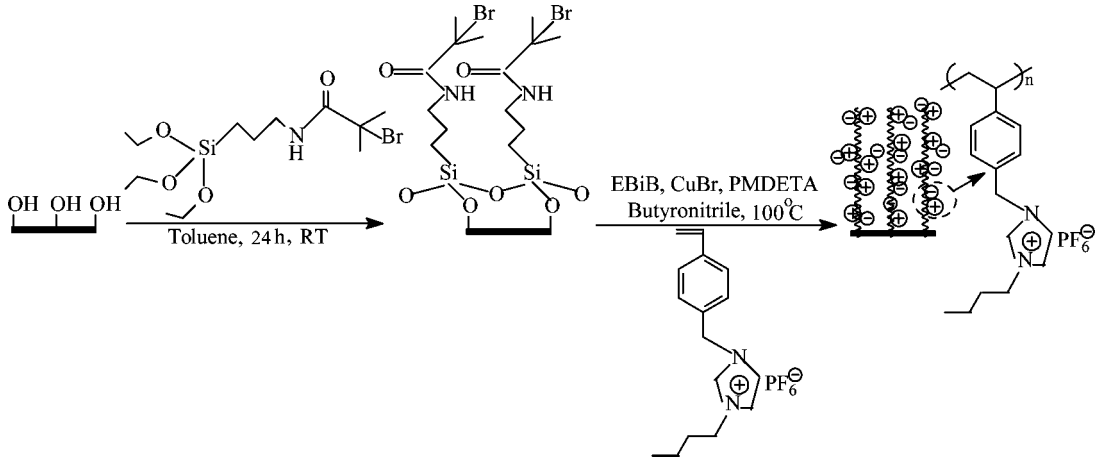

Figure 1. Scheme for the preparation of PVBIm−PF_6 brushes via surface-initiated ATRP polymerization.

Synthesis of the Ionic Liquid Monomer 1-(4-Vinylbenzyl)-3-butylimidazolium Hexafluorophosphate (VBIm−PF_6). *N*-Butylimidazole (6.2 g, 50 mmol), 4-vinylbenzyl chloride (8.4 g, 55 mmol), and the inhibitor DBMP (0.08 g) were put into a dried flask. The reaction mixture was stirred at 42 °C under N_2 for 50 h to yield a very viscous liquid, 1-(4-vinylbenzyl)-3-butylimidazolium chloride. The compound was washed with ethyl ether and dried overnight under vacuum at room temperature to give a transparent, viscous liquid in a yield of 85%. ^{1}H NMR (400 MHz, δ, ppm, D_2O): 0.81 (3H, t, J = 7.2 Hz, −CH_3), 1.22 (2H, m, N−CH_2CH_2−CH_2−CH_3), 1.74 (2H, m, N−CH_2−CH_2−CH_2CH_3), 4.09 (2H, t, J = 7.2 Hz, N−CH_2−$CH_2CH_2CH_3$), 5.17 (2H, s, Ph−CH_2−N−), 5.13 (1H, d, J = 10.8 Hz, CH_2=CH−), 5.76 (1H, d, J = 17.6 Hz, CH_2=CH−), 6.69 (1H, m, CH_2=CH−), 7.27 (2H, d, J = 8.4 Hz, Ph), 7.41 (2H, d, J = 8.4 Hz, Ph), 7.51 (2H, d, J = 1.6 Hz, N−CH=CH−N), 8.77 (1H, s, N−CH−N). ^{13}C NMR (400 MHz, δ, ppm, D_2O): 138.2 (N−CH−N), 135.8 (CH_2=CH−), 135.2 (Ph), 133.3 (Ph), 129.0 (Ph), 127.0 (Ph), 122.8 (N−CH=CH−N−Bu), 122.4 (N−CH=CH−N−Bu), 115.5 (CH_2=CH−), 52.5 (Ph−CH_2−N−), 49.5 (N−CH_2−$CH_2CH_2CH_3$), 31.3 (N−CH_2−CH_2−CH_2CH_3), 18.9 (N−CH_2CH_2−CH_2−CH_3), 12.8 (N−$CH_2CH_2CH_2$−CH_3). MS: (ESI+) m/z 241 $[M - Cl]^+$, (ESI−) m/z 35 $[Cl]^-$. HRMS: (ESI+) m/z calcd for $[C_{16}H_{21}N_2]^+$, 241.1699; found, 241.1697.

The target compound was prepared via anion exchange according to a modification method of Tang et al.[31] Typically, to a solution of 1-(4-vinylbenzyl)-3-butylimidazolium chloride (2.76 g, 10 mmol) and the inhibitor DBMP (0.03 g) in 15 mL of dry acetone, the solution of ammonium hexafluorophosphate (1.80 g, 11 mmol) in 15 mL of dry acetone was added. After the mixture was stirred at 30 °C for 60 h, the solution was filtered, and the filtrate was evaporated under reduced pressure to yield 3.41 g of a white, waxy solid. The crude product was washed with water and ethyl ether and stored in a refrigerator. Silver nitrate testing indicated no chloride present. mp: 87−89 °C. ^{1}H NMR [400 MHz, δ, deuterated dimethyl sulfonyl oxide (DMSO-d_6)]: 0.83 (3H, t, J = 7.2 Hz, −CH_3), 1.23 (2H, m, N−CH_2CH_2−CH_2−CH_3), 1.76 (2H, m, N−CH_2−CH_2−CH_2CH_3), 4.11 (2H, t, J = 7.2 Hz, N−CH_2−$CH_2CH_2CH_3$), 5.35 (2H, s, Ph−CH_2−N−), 5.29 (1H, d, J = 10.8 Hz, CH_2=CH−), 5.82, (1H, d, J = 17.2 Hz, CH_2=CH−), 6.70 (1H, m, CH_2=CH−), 7.36 (2H, d, J = 8 Hz, Ph), 7.48 (2H, d, J = 8.4 Hz, Ph), 7.73 (2H, d, J = 1.2 Hz, N−CH=CH−N), 9.08 (1H, s, N−CH−N). ^{13}C NMR (400 MHz, δ, DMSO-d_6): 137.9 (N−CH−N), 136.1 (CH_2=CH−), 136.0 (Ph), 134.2 (Ph), 128.9 (Ph), 126.9 (Ph), 123.0 (N−CH=CH−N−Bu), 122.8 (N−CH=CH−N−Bu), 115.6 (CH_2=CH−), 52.0 (Ph−CH_2−N−), 48.9 (N−CH_2−$CH_2CH_2CH_3$), 31.4 (N−CH_2−CH_2−CH_2CH_3), 18.9 (N−CH_2CH_2−CH_2−CH_3), 13.3 (N−$CH_2CH_2CH_2$−CH_3). MS: (ESI+) m/z 241 $[M - PF_6]^+$, (ESI+) m/z 145 $[PF_6]^-$. HRMS: (ESI+) m/z calcd for $[C_{16}H_{21}N_2]^+$, 241.1699; found, 241.1700.

Immobilization of the ATRP Initiator onto the Silicon Wafer. Previously cleaned wafers were immersed in a 10 mM solution of BTPAm in anhydrous toluene and were heated to 55 °C for 4 h without stirring, and then the solution was left overnight at room temperature. The wafers were removed from the solution and cleaned by an ultrasonic bath in toluene for 1 min and were rinsed again with toluene, acetone, and ethanol and then dried in a stream of nitrogen. The wafers were directly used for surface-initiated ATRP experiments.

Synthesis of Poly[1-(4-vinylbenzyl)-3-butylimidazolium hexafluorophosphate] (PVBIm−PF_6) Brushes via Surface-Initiated ATRP. Into a 50 mL dry Schlenk flask, the initiator-immobilized silicon wafers were placed. The flask was degassed and backfilled with nitrogen three times and left under a nitrogen atmosphere. Then the ionic liquid monomer 1-(4-vinylbenzyl)-3-butyl imidazolium hexafluorophosphate (VBIm−PF_6) (1.928 g, 5.0 mmol), CuBr (0.0072 g, 0.05 mmol), and butyronitrile (4.0 mL) were added to another 25 mL Schlenk flask which was equipped with a stirrer bar and sealed with a rubber septum. This flask was degassed by purging with nitrogen for 1 h. PMDETA (0.0173 g, 0.1 mmol) was added to the mixture via a syringe, and the solution was stirred at 100 °C for about 10 min until it became homogeneous. The solution was syringed to the flask containing the initiator-immobilized silicon wafers, followed by the addition of free initiator EBiB 7.3 μL (0.05 mmol) via a syringe to start the surface-initiated polymerization. After a desired reaction time at 100 °C, the silicon wafers were removed from the flask and rinsed with *N*,*N*-dimethylformamide (DMF). To remove physically absorbed polymer chains, the silicon wafers were placed into a Soxhlet extractor and extracted with DMF for 12 h. The wafers were then dried in a stream of nitrogen. The polymer (PVBIm−PF_6) generated in the solution by the sacrificial initiator were taken from the flask and dried under vacuum at 40 °C to remove the residual solvent (butyronitrile). Then the samples were diluted with DMF containing $CuBr_2$ and kept in a refrigerator for GPC measurements. As a comparison, ATRP of VBIm−PF_6 directly on the bare silicon−OH substrate without immobilization of the initiator was also carried out by a similar procedure. After polymerization, the silicon wafers were rinsed with DMF and Soxhlet extracted with DMF for 12 h and the sample was marked as **SPIL**.

Tuning the Wettability of Poly(ionic liquid) Brushes by Exchanging Their Counteranions. The PVBIm−PF_6 modified silicon wafer was immersed in 30 mL of DMF for a few minutes. Then the wafer was removed and reimmersed in 0.2 M NaCl aqueous solution for 1 h. The wafer was removed from the flask and rinsed with distilled water some times and Soxhlet extracted with distilled water for 12 h. Then it was dried in a stream of nitrogen. The reversibly altered wettability from hydrophilic to hydrophobic can be achieved by immersing the hydrophilic wafer in 0.1 M NH_4PF_6 aqueous solution for 30 min.

Table 1. Ellipsometric Film Thicknesses and Water Contact Angles of Poly(ionic liquid) Brushes[a]

samples	reaction time (h)	film thickness (nm)[b]	static water contact angle (deg)
Si−OH		0.8 ± 0.1	5 ± 3
Si−initiator		1.9 ± 0.2	66 ± 3
Si−PVBIm−PF_6(1)	1	6 ± 0.5	92 ± 3
Si−PVBIm−PF_6(2)	2	9 ± 1.0	93 ± 3
Si−PVBIm−PF_6(3)	6	19 ± 1.5	95 ± 3
Si−PVBIm−PF_6(4)	12	36 ± 2.0	95 ± 3
Si−PVBIm−PF_6(5)	18	53 ± 3.0	95 ± 3
Si−PVBIm−PF_6(6)	24	56 ± 3.0	97 ± 3
Si−PVBIm−Cl[c]		34 ± 2.0	41 ± 3
SPIL(1)	2	1.0 ± 0.1	6 ± 3
SPIL(2)	6	1.0 ± 0.1	6 ± 3

[a] Reaction conditions: [VBIm-PF_6]:[EBiB]:[CuBr]:[PMDETA]=100:1:1:2, [VBIm−PF_6]=5.0 mmol, butyronitrile as the solvent, temperature 100 °C. [b] Thicknesses were determined by ellipsometry and were an average of five samplings. [c] Obtained from Si−PVBIm−PF_6(3).

Measurement. The thickness of polymer layer was measured with a spectroscopic ellipsometer (Gaertner model L116C). The static water contact angles were determined by using a KYOWA CA-A contact angle goniometer. Images of the patterned polymer layers were obtained with an atomic force microscope (AFM) (Seiko Instruments Inc.) in a tapping mode. The X-ray photoelectron spectroscopy (XPS) analysis was carried out on a PHI-5702 multifunctional XPS, using Al Kα radiation as the exciting source. The binding energies of the target elements were determined at a pass energy of 29.35 eV, with a resolution of ± 0.3 eV, using the binding energy of the gold (Au 4f: 84.0 eV) as the reference. Hydrogen and carbon nuclear magnetic resonance (^{1}H NMR and ^{13}C NMR) spectra were measured with an INOVA 400 MHz spectrometer with DMSO-d_6 or D_2O as the solvent. Electrospray ionization (ESI) mass spectra were performed on a Waters ZQ-400 instrument (Manchester, UK). ESI−HRMS spectra were obtained on a Brucker Daltonics APEX II mass spectrometer. Gel permeation chromatography (GPC) was used to measure molecular weights and molecular weight distributions with respect to poly(ethylene glycol) (PEG) standards. GPC experiments were carried out at 70 °C in DMF (with 0.05 M LiBr to suppress interactions with column packing) using a Waters 150CV instrument fitted with a differential refractometer detector. The monomer conversions were measured with ^{1}H NMR by the intensity ratio of the double bond CH_2=CH− (5.3, 5.9 ppm) and the methylene group N−CH_2−CH_2CH_2−CH_3 (4.1 ppm). The attenuated total reflection infrared spectroscopy (ATR−FTIR) was recorded on a Nicolet 870 infrared spectrometer equipped with a smart ATR accessory with 256 scans and a resolution of 4 cm^{-1}.

Results and Discussion

Initiator Monolayer Characterization. To graft polymer chains from the surface, a uniform and dense initiator layer on the silicon substrate is important. The immobilization of ATRP initiator on a flat silicate substrate is illustrated in Figure 1. In this paper, a bromoisobutyrate ATRP initiator, BTPAm, was synthesized and deposited on a cleaned silicon wafer by a self-assembly technique. Confirmation of the deposition of the BTPAm was achieved by ellipsometry, goniometry (Table 1), ATR-FTIR (Figure 2), XPS (Figure 3), and AFM (Figure 4). The initiator self-assembled monolayer was formed on the silicon wafer surface with a thickness of 1.9 ± 0.2 nm measured by ellipsometry. Immobilization of the ATRP initiator BTPAm on a flat silicon substrate resulted in an increase in the static water contact angle from 5 to 66°, and the static water contact angle of the BTPAm initiator layers were relatively uniform. The contact angle and ellipsometry data are listed in Table 1.

The presence of the initiator monolayer was also confirmed by ATR-FTIR (Figure 2a). In the spectra of bromosilane initiator modified substrate, the peaks between 970 and 1195 cm^{-1} were attributed to Si−O stretching vibration. The broad peak around 1585−1620 cm^{-1} was assigned to amide (N−H bending) and amide (C=O stretching). Figure 3 shows the typical XPS survey spectrum and high-resolution elemental scan of Br_{3d}, C_{1s}, and N_{1s}, which were recorded from the bromosilane initiator BTPAm modified silicon surface. The C_{1s} core-level spectrum of the Si−initiator surface included three peak components having BEs at about 284.7, 286.4, and 288.2 eV, attributable to the C−H/C−C, C−Br/C−NCO, and *O*=C−N species, respectively. The N_{1s} peak at the BEs of about 399.9 eV was attributed to the *O*=C−N species. By calculating the peak area of each element, it was found that the [N]:[Br] ratio for the bromosilane initiator BTPAm modified silicon surface was about 1.1:1 which was in fairly good agreement with corresponding theoretical value. The presence of the Br_{3d} and N_{1s} peaks at the BEs of about 71.4 eV, 399.9 eV and the appearance of the *O*=C−N peak component in the C_{1s} core-level spectrum indicated that the initiator species for the subsequent ATRP reaction has been successfully immobilized on the silicon surface. From the AFM morphological image of the ATRP initiator monolayer (Figure 4), it could be seen that the initiating monolayer was very homogeneous and smooth. The film arrayed densely and the thickness of the film was about 2 nm. The AFM results were in good accordance with ellipsometry measurements.

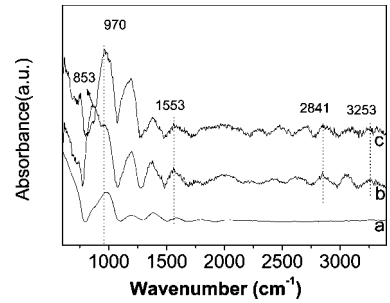

Figure 2. ATR-FTIR spectra: (a) bromosilane initiator modified silicon; (b) PVBIm−PF_6 brush modified silicon; (c) PVBIm−Cl brush modified silicon surface.

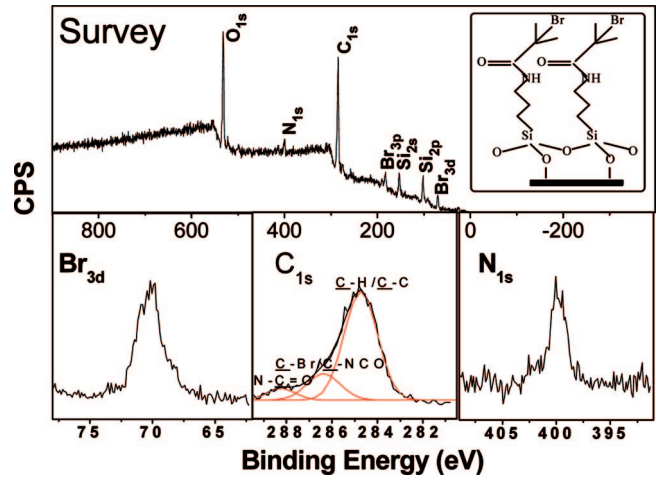

Figure 3. XPS survey spectrum and high-resolution elemental scan of Br_{3d}, C_{1s}, and N_{1s} of the bromosilane initiator modified silicon surface.

Preparation and Characterization of PVBIm−PF_6 Brushes via a Surface-Initiated ATRP Reaction. ATRP can be used as an effective tool in synthesizing dense and homogeneous polymer layers or brushes from initiator immobilized substrate surface. ATRP of ionic liquid monomer VBIm−PF_6 from the bromosilane initiator modified substrate was accomplished in the presence of EBiB as a sacrificial free initiator.

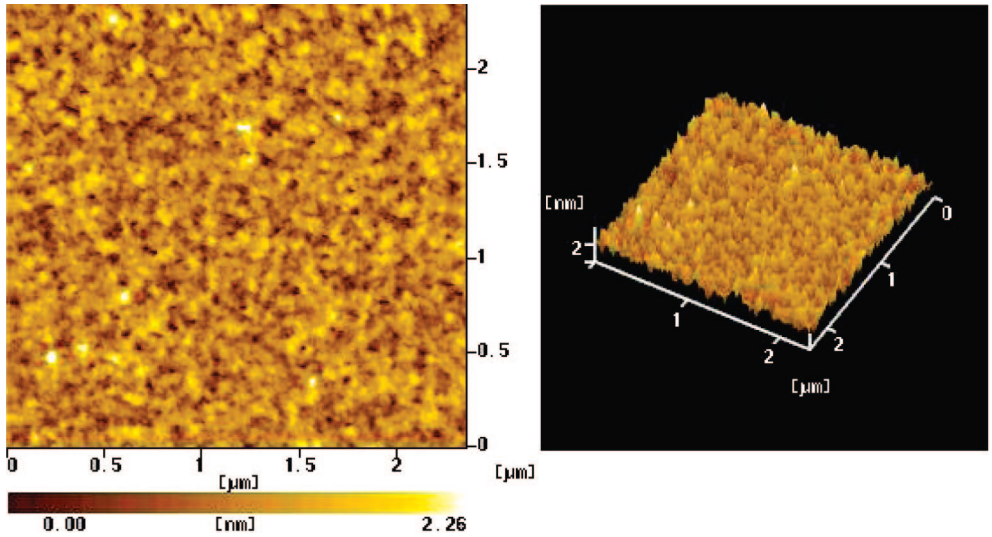

Figure 4. AFM topography and 3D image of the initiator layer modified silicon surface.

The complex CuBr/PMDETA was used as a catalytic system, and butyronitrile was used as the solvent (Figure 1). After the polymerization, every sample was carefully extracted for at least 12 h in a Soxhlet apparatus to remove any physically absorbed polymer chains.

Ellipsometry, contact angle analysis, ATR-FTIR, XPS, and AFM were respectively employed to monitore the formation of the PVBIm−PF_6 brushes. The results of ellipsometry indicated that the thicknesses of the PVBIm−PF_6 films formed on the silicon wafer surface are about 9−56 nm (based on various polymerization time). The variation in PVBIm−PF_6 film thickness was within ±3.0 nm. The static water contact angles of the PVBIm−PF_6 brush surfaces are about 95° (Table 1).

Ellipsometry measurements indicated that no increase in thickness on all the **SPIL** surfaces, which were the polymerization results without immobilization of the initiator, were discernible. The static water contact angles of the **SPIL** surfaces were about 6° similar to the static water contact angles of the Si−OH surface. And no peaks for F_{1s}, P_{2p}, and N_{1s} corresponding to the PVBIm−PF_6 layer were found in the XPS survey spectrum. In the absence of CuBr as a catalyst, similar results were observed on initiator-bound silicon wafers. These results confirmed that the increase in thickness of the PVBIm−PF_6 films was the result of graft polymerization from the initiator immobilized silicon surface. ATR−FTIR spectrum of PVBIm−PF_6 brush modified silicon surface is shown in Figure 2b. After surface initiating polymerization, the characteristic peak at 853 cm^{-1} was assigned to the P−F stretching vibration, the peaks between 2800−3300 and 1553 cm^{-1} were the characteristic adsorption bands of the poly[1-(4-vinylbenzyl)-3-butylimidazolium] cation.

Figure 5 shows the typical XPS survey spectrum and high-resolution elemental scan of F_{1s}, P_{2p}, and N_{1s} of the PVBIm−PF_6 brush modified silicon surface. The peaks for F_{1s} (687.1 eV), P_{2p} (136.2 eV), and N_{1s} (401.7 eV) were clearly seen in the survey spectrum. The N_{1s} peak at the BE of 401.7 eV was assigned to the positively charged nitrogen (N^+) of the poly [1-(4-vinylbenzyl)-3-butylimidazolium] cation. The [N]:[F]:[P] ratio for the PVBIm-PF_6 brush modified silicon surface was about 1.9:6.1:1 which was in fairly good agreement with the theoretical result.

The AFM images also helped to reveal the formation of the PVBIm−PF_6 brushes on the silicon substrate. The surface of the bromosilane initiator modified silicon had a rather uniform and smooth surface. After surface initiating polymerization for 24 h, the surface roughness of the PVBIm−PF_6 brush modified

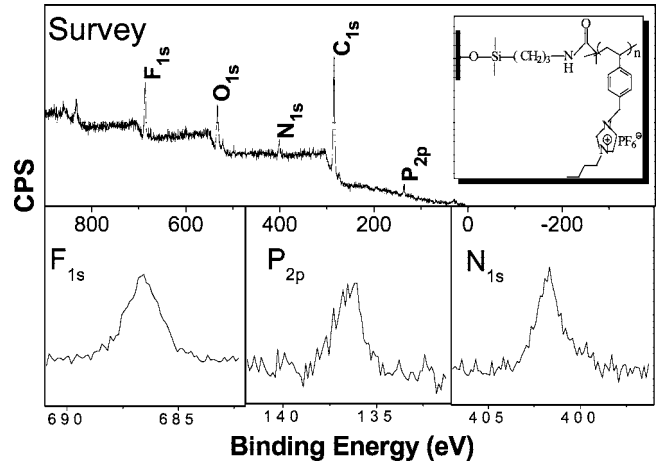

Figure 5. XPS survey spectrum and high-resolution elemental scan of F_{1s}, P_{2p}, and N_{1s} of the PVBIm−PF_6 brush modified silicon surface.

silicon substrate obviously increased (Figure 6). The profile in the AFM image indicated that the PVBIm−PF_6 layer having a thickness of approximately 58 nm, consistent, considering experimental error, with the ellipsometric data. Figure 6 also indicates that the grafted PVBIm−PF_6 chains collapsed and existed as a distinctive overlayer on the surface of silicon substrate. This phenomenon probably resulted from the nanoscaled phase aggregation of the grafted polymer after the surface has been dried. All these observations corroborated the formation of PVBIm−PF_6 brushes on the surface of bromosilane initiator modified silicon substrate.

Controlled surface initiated ATRP requires a minimum amount of a deactivator throughout the polymerization reaction, which can be achieved either by the addition of a deactivator or by the addition of a sacrificial free initiator to the polymerization solution. In this study, we use the sacrificial free initiator approach because the addition of a deactivator can slow down the reaction and can render the system heterogeneous (especially at high temperatures), which in turn complicates the polymerization mechanism and further decreases the rate of polymerization. A further advantage is that the addition of a sacrificial initiator leads to the production of free polymer, which can be used as a measure of the molecular weight characteristics of the obtained chains. Because of the difficulty to obtain the molecular weight of the polymer brush, we use the homopolymer formed by free initiator in solution to monitor the surface-

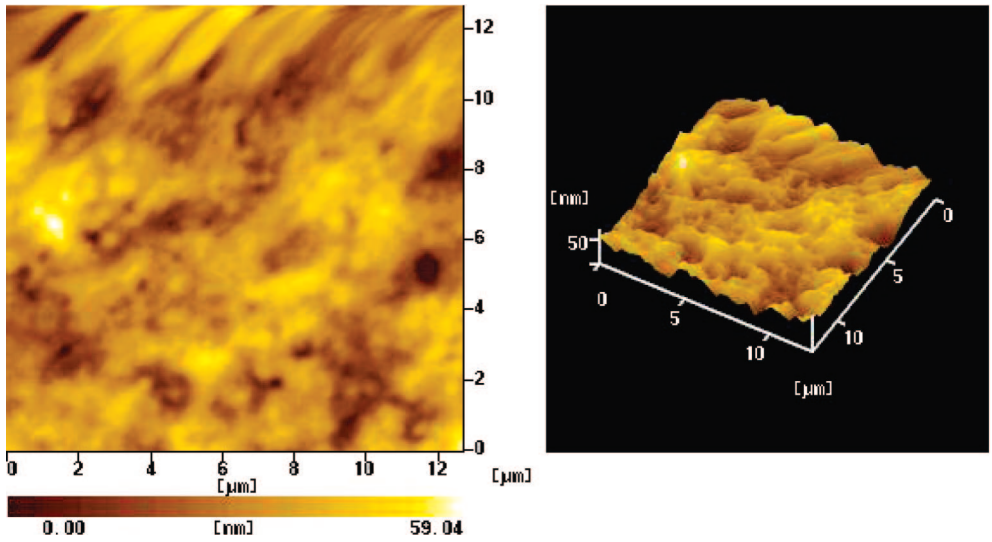

Figure 6. AFM topography and 3D image of the PVBIm-PF_6 brush modified silicon surface.

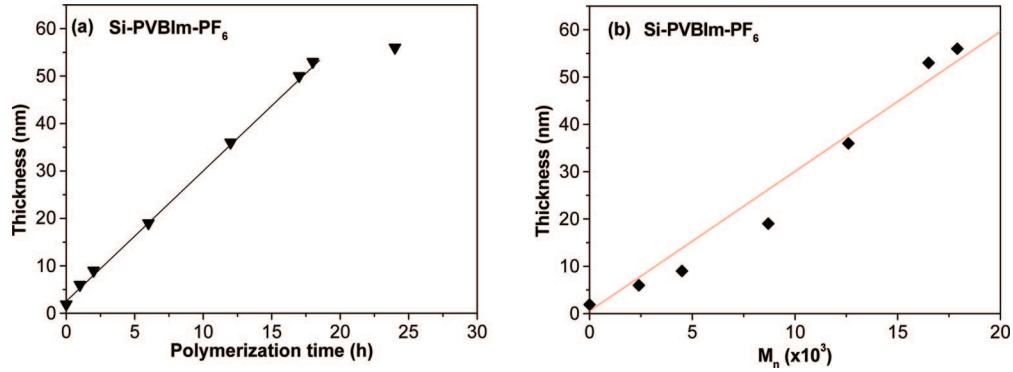

Figure 7. Dependence of the thickness of the PVBIm−PF_6 layer, grown from the initiator immobilized silicon wafer surface via ATRP, on (a) polymerization time and (b) molecular weight (M_n) of the "free" PVBIm−PF_6 formed in the solution.

grafted polymerization process. This treatment was reasonable considering the fact that free and surface-attached polymer molecules had the same molecular weight and molecular weight distribution.[32–35] Furthermore, because ATRP is a "living" polymerization process, the thickness of the polymer brushes should increase linearly with the polymerization time and the molecular weight of the graft polymer.

Figure 7a shows a plot of the thickness of PVBIm−PF_6 film on the silicon surface with the polymerization time. As shown in Figure 7a, the thickness of the grafted PVBIm−PF_6 layer increased linearly with polymerization time till 18 h and then the increase rate reduced and showed a plateau. For example, when the polymerization time was 24 h, the thickness of the film was 56 nm. This was probably due to diffusion limitations of monomer to surface. Figure 7b shows the plot of the thickness of PVBIm−PF_6 film on the silicon surface with the molecular weight (M_n) of the "free" polymer formed in the solution. An approximately linear relationship between them is observed. These results indicated that the process of surface initiated ATRP of VBIm−PF_6 is controlled.

Additional evidence on the controlled polymerization is also obtained from the "free" PVBIm-PF_6 formed by the "free" initiator. Figure 8a shows the linear relationship between $\ln([M_0]/[M])$ and time, where $[M_0]$ is the initial monomer concentration and [M] is monomer concentration. Figure 8b shows the dependence of M_n and polydispersity index (M_w/M_n) of the "free" PVBIm−PF_6 with the conversion of the VBIm−PF_6 monomer. The M_n of the "free" PVBIm−PF_6 increased linearly with monomer conversion increasing, and the polydispersity index was less than 1.3.

General Procedure for the Counteranion Exchange and Reversible Wettability of Poly(ionic liquids) Brushes. Some research groups have demonstrated that the wettability of charged organic films can be tuned by choosing the proper counterions.[36–38] The synthesized PVBIm−PF_6 brushes (36 nm in thickness) contain PF_6^- anions as counteranions and they show a rather hydrophobic behavior, as determined by using contact-angle goniometry (ca. 95°). Exchange of the counteranions simply requires immersion of the PVBIm−PF_6 brushes modified silicon wafers in DMF solution first, and the PVBIm−PF_6 brushes will become slightly swollen. Then the wafer immediately was immersed in 0.2 M NaCl aqueous solution for 1 h. The PF_6^- exchange with Cl^- promotes a drastic change in the wetting properties of the substrate from approximately 95 to 41° (Table 1). Of great interest is the reversibly altered wettability from hydrophilic to hydrophobic, which can be achieved by immersing the hydrophilic silicon wafers in 0.1 M NH_4PF_6 aqueous solution for 30 min. We did not check the threshold concentration needed for the exchange of counteranion. Generally, for transition of hydrophobic to hydrophilic, high salt concentration was required; whereas the switch from hydrophilic to hydrophobic required low concentration of salt. This is apparent due to the different association constants between anions and imidazole cations in ionic liquids.[39]

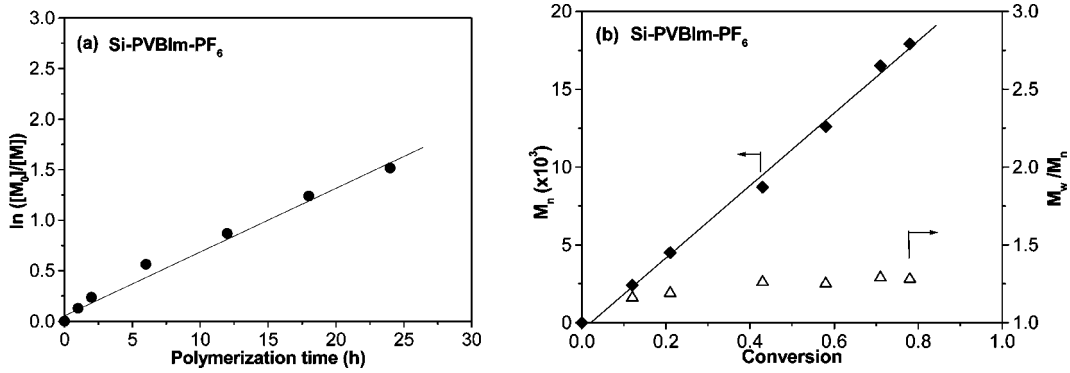

Figure 8. Relationships (a) between ln ([M_0]/[M]) and polymerization time and (b) between M_n of the "free" PVBIm−PF_6 formed in the solution and monomer conversion.

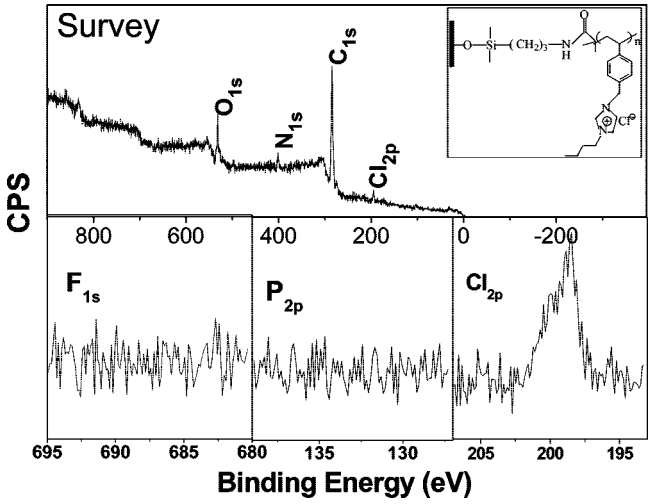

Figure 9. XPS survey spectrum and high-resolution elemental scan of F_{1s}, P_{2p}, and Cl_{2p} of the PVBIm−Cl brush modified silicon surface.

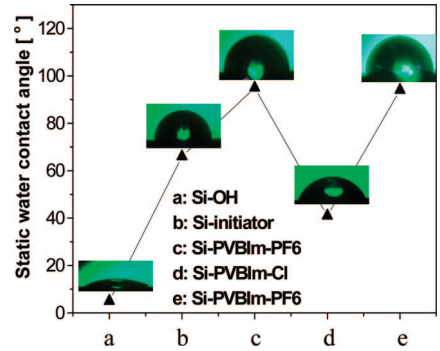

Figure 10. Changes in static water contact angles corresponding to various surfaces of silicon substrates. The insets show five photographs of the shapes of water droplets on different surfaces.

The reversible wettability behavior of the PVBIm−PF_6 brushes was confirmed by contact angle analysis, ATR−FTIR (Figure 2), and XPS (Figure 9). The static water contact angles of the PVBIm−PF_6 brush surfaces are about 95°, but after exchange of the counteranions, the hydrophobic surface turn to hydrophilic surface and the contact angles changed from 95 to 41°. After reversibly alteration of wettability from hydrophilic to hydrophobic, the contact angles come back to 93°. ATR−FTIR spectrum of PVBIm−Cl brush modified silicon surface is shown in Figure 2c. Compared with PVBIm−PF_6 brushes (Figure 2b), after exchange of the counteranions, the obvious change comes from the disappearance of the characteristic peak at 853 cm^{-1} assigned to the P−F stretching vibration.

Figure 9 shows the typical XPS survey spectrum and high-resolution elemental scan of F_{1s}, P_{2p}, and Cl_{2p} of the PVBIm−Cl brushes modified silicon surface. The peaks for F_{1s} (687.1 eV), P_{2p}, (136.2 eV), corresponding to the PF_6^- disappeared in the survey spectrum. The appearance of the Cl_{2p} component at the BE of ~198.5 eV indicated that the PF_6^- has been exchanged with Cl^-. In our previous experiment, after anion exchanging, the PVBIm−Cl brush modified silicon wafer was rinsed with distilled water some times. Through XPS analysis, it was found that the [N]:[Cl] ratio for the PVBIm−Cl brush modified silicon surface was about 1.3:1, which was obviously lower than corresponding theoretical value. This probably due to some "free" Cl^- absorbed onto the surface of silicon in the process of anion exchange. Therefore, after anion exchanging, the PVBIm-Cl brush modified silicon wafer should be Soxhlet extracting with distilled water. XPS results indicate that after Soxhlet extracting, the [N]:[Cl] ratios was about 1.9:1, which was in agreement with the theoretical result.

Once a net hydrophobic substrate is obtained, the wettability can be easily reversed and tuned by simply exchanging the counteranions. Replacing the PF_6^- with hydrophilic Cl^- clearly leads to a change in the contact angle from 95 to 41°. Figure 10 shows the changes in static water contact angles corresponding to various surfaces of silicon substrates. As shown in Figure 10, the plot depicts the reversible behavior of PVBIm-PF_6 brushes over repeated cycles of alternating treatment by PF_6^- and Cl^- exchange. More importantly, if the same counteranion is sequentially replaced via consecutive counteranion exchanges, the surface with tunable wettability, reversible switching between hydrophilicity and hydrophobicity can be easily obtained.

Conclusions

Well-defined poly(ionic liquid) brushes with tunable wettability were successfully produced on the surface of silicon wafer by surface initiated ATRP polymerization. The formation of the poly (ionic liquid) brushes was confirmed by ellipsometry, ATR-FTIR, XPS, and contact angle measurement. The composition of the poly (ionic liquid) brushes was investigated by XPS. AFM analysis of the poly (ionic liquid) brushes indicated that the surface roughness of the PVBIm−PF_6 brush modified silicon substrate obviously increased and the profile in the AFM image corroborated the formation of PVBIm−PF_6 brushes on the surface of bromosilane initiator modified silicon substrate. The tunable wettability of poly (ionic liquid) brushes can be achieved by exchanging their counteranions. Moreover, if the same two counteranions are sequentially replaced, the surface with tunable wettability, reversible switching between hydrophilicity and hydrophobicity can be easily obtained.

Acknowledgment. The authors are grateful to Key Laboratory of Eco-environment Related Polymer Materials of MOE, China, National Natural Science Foundation of China, and Science and Technology Department of Gansu Province for their financial support.

References and Notes

(1) Xu, C.; Wu, T.; Drain, C. M.; Batteas, J. D.; Fasolka, M. J.; Beers, K. L. *Macromolecules* **2006**, *39*, 3359–3364.
(2) Buriak, J. M. *Chem. Rev* **2002**, *102*, 1271–1308.
(3) Husemann, M.; Morrison, M.; Benoit, D.; Frommer, J.; Mate, C. M.; Hinsberg, W. D.; Hedrick, J. L.; Hawker, C. J. *J. Am. Chem. Soc.* **2000**, *122*, 1844–1845.
(4) Shah, R. R.; Mecerreyes, D.; Husemann, M.; Rees, I.; Abbott, N. L.; Hawker, C. J.; Hedrick, J. L. *Macromolecules* **2000**, *33*, 597–605.
(5) Kong, X.; Kawai, T.; Abe, J.; Iyoda, T. *Macromolecules* **2001**, *34*, 1837–1844.
(6) Cheng, Y. T.; Rodak, D. E.; Wong, C. A.; Hayden, C. A. *Nanotechnology* **2006**, *1*, 1359–1362.
(7) Paik, P.; Pamula, V. K.; Pollack, M. G.; Fair, R. B. *Lab Chip* **2003**, *3*, 28–33.
(8) Kuiper, S.; Hendriks, B. H. W. *Appl. Phys. Lett.* **2004**, *85*, 1128–1130.
(9) Milner, S. T. *Science* **1991**, *251*, 905–914.
(10) Prucker, O.; Rühe, J. *Macromolecules* **1998**, *31*, 592–601.
(11) Maynor, B. W.; Filocamo, S. F.; Grinstaff, M. W.; Liu, J. *J. Am. Chem. Soc.* **2002**, *124*, 522–523.
(12) Wang, Y.; Pei, X.; He, X.; Lei, Z. *Eur. Polym. J.* **2005**, *41*, 737–741.
(13) Yang, Y.; Wu, D.; Li, C.; Liu, L.; Cheng, X.; Zhao, H. *Polymer* **2006**, *47*, 7374–7381.
(14) Wang, X.; Tu, H.; Braun, P. V.; Bohn, P. W. *Langmuir* **2006**, *22*, 817–823.
(15) Hu, D.; Cheng, Z.; Zhu, J.; Zhu, X. *Polymer* **2005**, *46*, 7563–7571.
(16) Zhao, B.; He, T. *Macromolecules* **2003**, *36*, 8599–8602.
(17) Wu, T.; Efimenko, K.; Genzer, J. *J. Am. Chem. Soc.* **2002**, *124*, 9394–9395.
(18) Tomlinson, M. R.; Genzer, J. *Macromolecules* **2003**, *36*, 3449–3451.
(19) Xu, C.; Wu, T.; Drain, C. M.; Batteas, J. D.; Beers, K. L. *Macromolecules* **2005**, *38*, 6–8.
(20) Xu, C.; Wu, T.; Batteas, J. D.; Drain, C. M.; Beers, K. L.; Fasolka, M. J. *Appl. Surf. Sci.* **2006**, *252*, 2529–2534.
(21) Tsujii, Y.; Ejaz, M.; Yamamoto, S.; Fukuda, T.; Shigeto, K.; Mibu, K.; Shiujo, T. *Polymer* **2002**, *43*, 3837–3841.
(22) Zhang, M.; Liu, L.; Wu, C.; Fu, G.; Zhao, H.; He, B. *Polymer* **2007**, *48*, 1989–1997.
(23) Wilkes, J. S.; Zaworotko, M. J. *J. Chem. Soc. Chem. Commun.* **1992**, 965–967.
(24) Wasserscheid, P.; Keim, W. *Angew. Chem., Int. Ed.* **2000**, *39*, 3772–3789.
(25) Huddleston, J. G.; Visser, A. E.; Reichert, W. M.; Willauer, H. D.; Broker, G. A.; Rogers, R. D. *Green Chem.* **2001**, *3*, 156–164.
(26) Ding, S.; Tang, H.; Radosz, M.; Shen, Y. *J. Polym. Sci. Pol. Chem.* **2004**, *42*, 5794–5801.
(27) Masahiro, Y.; Ohno, H. *Electrochim. Acta* **2001**, *46*, 1723–1728.
(28) Washiro, S.; Yoshizawa, M.; Nakajima, H.; Ohno, H. *Polymer* **2004**, *45*, 1577–1582.
(29) Azzaroni, O.; Moya, S.; Farhan, T.; Brown, A. A.; Huck, W. T. S. *Macromolecules* **2005**, *38*, 10192–10199.
(30) Sun, Y.; Ding, X.; Zheng, Z.; Cheng, X.; Hu, X.; Peng, Y. *Eur. Polym. J.* **2007**, *43*, 762–772.
(31) Tang, H.; Tang, J.; Ding, S.; Radosz, M.; Shen, Y. *J. Polym. Sci., Polym. Chem.* **2005**, *43*, 1432–1443.
(32) Werne, V.; Patten, T. E. *J. Am. Chem. Soc.* **2001**, *123*, 7497–7505.
(33) Ohno, K.; Koh, K.; Tsujii, Y.; Fukuda, T. *Macromolecules* **2002**, *35*, 8989–8993.
(34) Yu, W. H.; Kang, E. T.; Neoh, K. G. *J. Phys. Chem. B* **2003**, *107*, 10198–10205.
(35) Matyjaszewski, K.; Miller, P. J.; Shukla, N.; Immaraporn, B.; Gelman, A.; Luokala, B. B.; Siclovan, T. M.; Kickelbick, G.; Vallant, T.; Hoffmann, H.; Pakula, T. *Macromolecules* **1999**, *32*, 8716–8724.
(36) Shen, Y.; Zhang, Y.; Zhang, Q.; Niu, L.; You, T.; Ivaska, A. *Chem. Commun.* **2005**, 4193–4195.
(37) Lee, B. S.; Chi, Y. S.; Lee, J. K.; Choi, I. S.; Song, C. E.; Namgoong, S. K.; Lee, S. *J. Am. Chem. Soc.* **2004**, *126*, 480–481.
(38) Chi, Y. S.; Lee, J. K.; Lee, S.; Choi, I. S. *Langmuir* **2004**, *20*, 3024–3027.
(39) Yu, B.; Zhou, F.; Liu, G.; Liang, Y.; Huck, W. T. S.; Liu, W. *Chem. Commun.* **2006**, 2356–2358.

MA702389Y