Macromolecules **2001,** *34,* 1837−1844

Amphiphilic Polymer Brushes Grown from the Silicon Surface by Atom Transfer Radical Polymerization

Xiangxing Kong, Tadashi Kawai, Jiro Abe, and Tomokazu Iyoda*

Department of Applied Chemistry, Graduate School of Engineering, Tokyo Metropolitan University, 1-1 Minami-Ohsawa, Hachioji, Tokyo, 192-0397 Japan

Received July 5, 2000; Revised Manuscript Received November 28, 2000

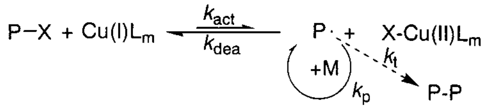
ABSTRACT: Homopolymer and block amphiphilic polymer brushes on silicon wafers have been successfully prepared by combining the self-assembled monolayer of initiator and atom transfer radical polymerization (ATRP). Two methods for self-assembly of initiator monolayer were compared: One was to treat the silicon surface with 6-((2-bromo-2-methyl)propionyloxy)hexyltrichlorosilane solution (solution method), and the other was to treat it with the vapor of 3-aminopropyl)triethoxysilane, followed by amidization with 2-bromoisobutyric acid (vapor method). While the solution method produced particles due to cross-linked products of the chlorosilane on silicon surface, the vapor method gave a uniform surface. The homopolymer brushes of poly(methyl methacrylate) (PMMA) and poly(acrylamide) (PAAM) were prepared by ATRP on the modified silicon wafer by the initiator. The amphiphilic block copolymer brushes consisting of PAAM and PMMA blocks were obtained by using the homopolymer brush as the macroinitiator for the second ATRP polymerization of another monomer. XPS revealed that the first polymer layer of the surface was partly covered with the second polymer layer after block copolymerized with the second monomer. AFM measurement of the amphiphilic block polymer brush imaged different morphology when they were treated with water and toluene. The amphiphilic polymer brush was stretched out from the surface and the individual polymer chains have sufficient free volume to permit the conformational change in different solvents.

Introduction

The synthesis of dense polymer film (or polymer brush) chemically bonded onto the surface of silicon or glass, has gained much attention in recent years.[1−9] In many cases, these films can serve as effective etching barriers for microlithographic application, yield excellent mechanical and chemical protection, alter the chemical and electrical interface characteristics of the underlying substrates, and provide new pathways to functionalize surface for molecular recognition and sensor device. Different from the conventional grafting or casting film, the preparation of polymer brush grafted from the surface includes two-step processes, the self-assembly of initiator and the controlled polymerization. Langmuir−Blodgett film, self-assembled film (e.g., organosulfur on Au, or organosilane on silicon or quartz), and microcontact printing, etc., have been used for the self-assembly of the initiator, and various polymerization reactions, including anionic,[3] cationic,[3] ring-opening,[3] radical,[4−6] and metathesis polymerization,[7] have been developed to prepare the polymer brushes.

Among all the polymerizations for synthesis of polymer brush, living polymerization is the most important one, due to its ease to control the thickness and the composition of the brush. Atom transfer radical polymerization (ATRP) is one of the well-developed controlled living polymerization.[10,11] Unlike cationic or anionic polymerization, ATRP has been used under ambient conditions for homocopolymerization or block-copolymerization of most of the common monomers such as styrene, methyl (meth)acrylate, methyl acrylate, 2-hydroxyethyl (meth)acrylate, 4-vinylpyridine, acrylamide, etc.[10] Reversible atom transfer equilibria between the transition metal complex and the growing radicals may keep the concentration of the radicals low enough to depress the radical coupling termination, thus controlling the radical polymerization precisely (Scheme 1).

Scheme 1



Many researches have focused on the hydrophobic polymer brushes, e.g. PMMA, polystyrene (PSt), etc.[12] Only a few hydrophilic brushes, e.g., PAAM,[13] quarternized poly(4-vinylpyridine),[14] and patterned poly(acrylic acid),[9b] were reported. Amphiphilic block copolymer brush is an interesting material due to its potential application. The synthesis of amphiphilic block brush was reported by hydrolysis of the poly(styrene-*b*-*tert*-butyl acrylate) brush to form amphiphilic poly(styrene-*b*-acrylic acid).[15] The direct synthesis of amphiphilic block copolymer brush on the surface might be interesting by successive ATRP technique without the following hydrolysis procedure if we choose the proper monomers.

In this paper, homopolymer and block polymer brushes were prepared by combining the self-assembly of initiators and the ATRP technique. Two kinds of self-assembly methods of initiator on the substrate were compared here. The first hydrophobic PMMA brush was grafted from the surface initiator monolayer and then was used as the macromonomer initiator to form hydrophilic PAAM block copolymer brush, or vice versa. The resulting polymer brushes were analyzed by FT-IR, XPS, AFM, and contact angle measurements.

Experimental Section

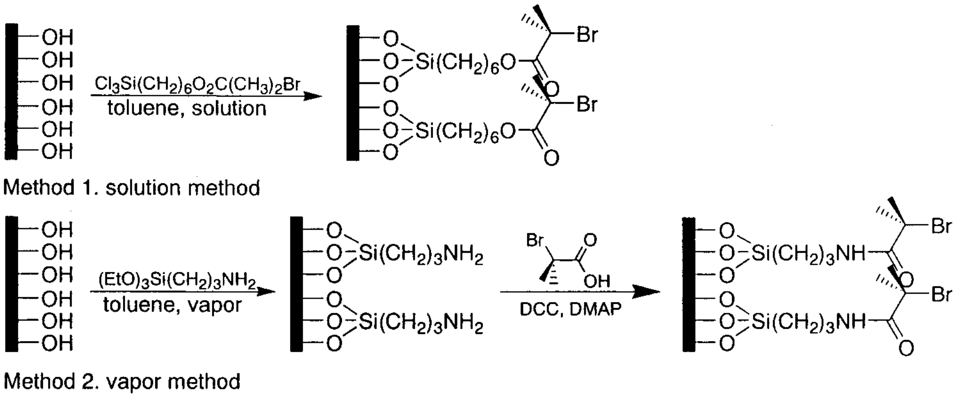
Chemicals. Dicyclohexyldicarbodiimide (DCC), *p*-(dimethylamino)pyridine (DMAP), anisole, ethyl 2-bromoisobutryate

---

* To whom correspondence should be addressed.

10.1021/ma001152h CCC: $20.00 © 2001 American Chemical Society
Published on Web 02/10/2001

Scheme 2



(EBiB) (all from Wako), 3-aminopropyl)triethoxysilane (from Shin Etsu) 2,2′-bipyridine, were used without further purification. *N*,*N*-Dimethylformamide (DMF) was distilled under vacuum after drying with $CuSO_4$. Toluene was dried over 4 Å molecular sieves before use. CuCl and CuBr (all from Wako) were purified to remove Cu(II) by precipitation from the corresponding concentrated acid by addition of water under nitrogen atmosphere. MMA (from Wako) was distilled under vacuum and stored in a refrigerator. AAM (from Wako) was recrystallized from benzene.

4,4′-Di-*n*-heptyl-2,2′- bipyridine (dhbpy) was synthesized by coupling the 1-bromohexane and 4,4′-dilithiomethyl-2,2′-bipyridine.[12b] The surface initiator 6-((2-bromo-2-methyl)-propionyloxy)hexyltrichlorosilane was prepared by hydrosilylation of 5-hexen-1-yl 2-bromo-2-methylpropionate with trichlorosilane.[9a]

Substrate Treatment. The silicon (111) wafers (3 cm × 1 cm) were ultrasonically cleaned for 5 min in succession with acetone, ethanol, and water and then were etched with a 5% hydrofluoric acid solution. After being washed with distilled water, the silicon wafers were put into an ultrasonic bath of H_2SO_4:H_2O_2 (v/v: 70/30) for another 45 min. The wafers were then rinsed with a large amount of distilled water. The contact angle of water on the glass surfaces was nearly 10°, revealing the high cleanness and uniformity of the surfaces. The silicon wafers were then modified by the following methods 1 and 2 (Scheme 2).

Method 1 (Solution Method). The pretreated hydrophilic silicon wafer was placed into a solution of the 6-((2-bromo-2-methyl)propionyloxy)hexyltrichlorosilane (5 μL) in 10 mL of dried toluene and was allowed to stand in the solution for 18 h without stirring. The wafer was removed from the solution and cleaned by an ultrasonic bath in toluene for 1 min and was rinsed again with toluene, acetone, and ethanol. The modified silicon wafer was used after dried in a stream of nitrogen.

Method 2 (Vapor Method). Aminopropylsilanation of silicon wafer was carried out according to Haller.[16] After being washed with toluene and acetone and dried with a nitrogen stream, the wafers were then immersed into a solution of 0.20 mmol of 2-bromo-2-methylpropionic acid (33.4 mg) and 0.05 mmol of DMAP (6 mg) in 10 mL of dried methylene chloride. The solution was cooled to 0 °C, and then 0.25 mmol of DCC (51.6 mg) was added; the solution was left overnight at room temperature. The wafers were taken out and rinsed with toluene and acetone again and were immediately used for surface polymerization after being dried with a nitrogen stream.

PAAM Films on Silicon Wafer. In a tube, the above-modified wafer was immersed into 10 mL of a DMF solution of 2.00 mol/L acrylamide and 0.025 mol/L of 2,2′-bipyridine. After being bubbled with a nitrogen stream for 5 min, 9.9 mg of CuCl (0.01 mol/L) was added. The tube was sealed under nitrogen and heated with an oil bath at 120 °C for several hours. The film was washed with a large quantity of water, and immersed in large amount of water for 1 day to remove the adsorbed free PAAM.

PMMA Films on Silicon Wafer. A dry tube was charged with 0.1 mmol of CuBr, 0.2 mmol of dhbpy, and the initiator-anchored silicon wafer. After being degassed with nitrogen for 10 min, a solution of MMA (3.8 mL), anisole (6.2 mL), and ethyl 2-bromoisobutyrate (EBiB) (3 μL), was added using syringes. The tube was sealed under nitrogen and immersed in an oil bath at 90 °C. After several hours, the polymerization solution was cooled to room temperature to terminate the polymerization. The polymer solution was diluted with THF. After we filtered out the catalyst with alumina column, the filtrate was used to measure the molecular weight of free polymer by GPC. The silicon wafer was immersed in THF, and washed with THF to remove the adsorbed free PMMA.

PAAM/PMMA and PMMA/PAAM Block Polymer Brushes on Silicon Wafer. After the first layer of PAAM (or PMMA) brush formed, the polymer brush was used as the anchored-initiator for the polymerization of MMA (or AAM) use the same polymerization condition as shown above.

Treatment of Si/PAAM/PMMA and Si/PAAM/PMMA Brushes with Water. The amphiphilic brushes on silicon

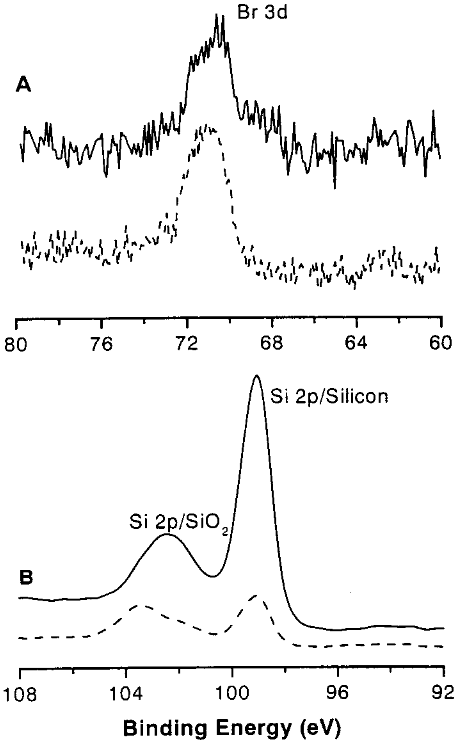


Figure 1. XPS spectra of the self-assembled initiator monolayer modified with solvent method (solid line) and vapor method (dash line): (A) the peak of Br 3d and (B) the peak of Si 2s.

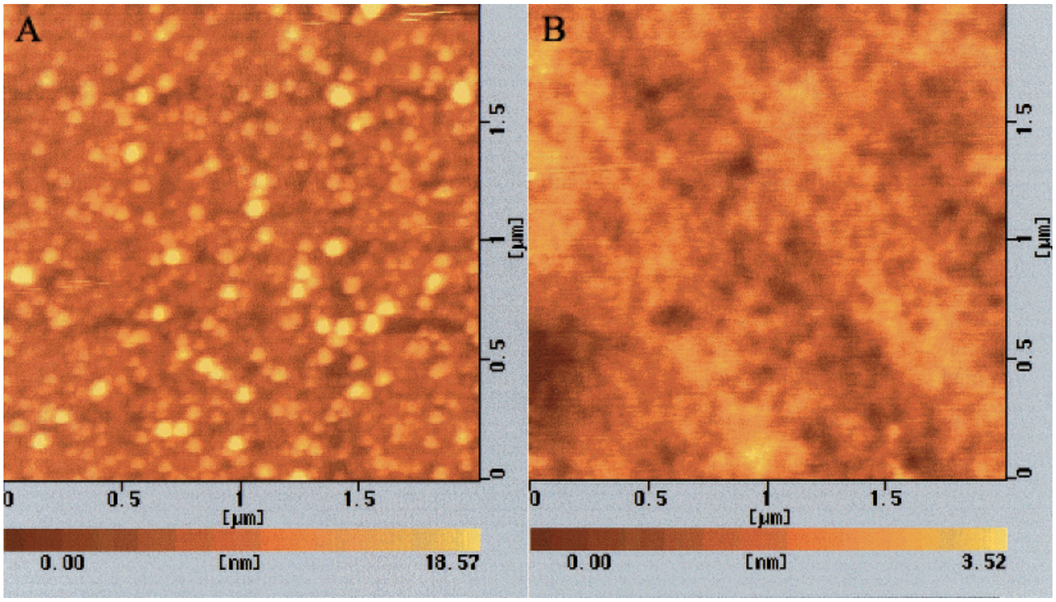


Figure 2. AFM topographic images of the self-assembled initiator monolayer treated by (A) the solution method and (B) the vapor method.

Table 1. Polymerization Data and Contact Angles of Polymer Films[a]

no.	monomer	ligand[b]	solvent	time (h)	M_w[c] ($\times 10^4$)	M_w/M_n[c]	contact angle (θ)[d]
1	MMA	dhbpy	anisole	2	3.73	1.28	66.3
2	MMA	dhbpy	anisole	6	5.08	1.16	–
3	AAM	bpy	DMF	2			12.2
4	MMA/AAM[e]	dhbpy/bpy	anisole/DMF	2/2			52.8
5	AAM/MMA[f]	dpy/dhbpy	DMF/anisole	2/2	1.92	1.07	36.0

[a] Polymerization conditions for MMA: $[M]_0 = 3.6$ M, $[CuBr] = {}^1/_2[dhbpy] = 10$ mM, $[EBiB] = 2$ mM; 90 °C; for AAM, $[M]_0 = 2.0$ M, $[CuCl] = {}^1/_2[bpy] = 0.01$ M, 120 °C. EBiB: ethyl 2-bromoisobutyrate. [b] Key: dhbpy, 4,4′-diheptyl-2,2′-bipyridine; bpy, 2,2′-bipyridine. [c] Polymer formed in the solution, obtained by GPC with standard polystyrene as reference. [d] Contact angle of water at room temperature on the film. [e] PAAM was grafted from the Si/PMMA film (no.1). [f] PMMA was grafted from the Si/PAAM film (no. 3).

wafers were immersed in 10 mL of water for 30−60 min at room temperature. The silicon wafers were removed from the water and dried with a stream of nitrogen followed by investigation with AFM.

Treatment of Si/PAAM/PMMA and Si/PAAM/PMMA Brushes with Toluene. The amphipilic brushes on silicon wafers were immersed in 10 mL of THF for 30−60 min at room temperature. After dried with nitrogen stream, the silicon wafers were immersed into toluene for another 10 min and dried with a nitrogen stream again.

Instruments. Fourier transform infrared (FTIR) spectra of the polymer brushes on silicon wafer were carried out using a Bio-Rad FTS 3000 with an MCT detector cooled with liquid nitrogen in transmission mode. The spectra were taken at a resolution of 2 cm^{-1} after 256-scan accumulation for an acceptable signal/noise ratio. A notch filter was used to remove the spikes caused by the interference of the polished silicon wafer. Contact angle measurements were carried out at room temperature with a contact angle goniometry FCAS-1. Deionized water with a conductivity over 18 MΩ/m was used as the wetting liquid. X-ray photoelectron spectra (XPS) were recorded on a Shimadzu ESCA 3400 spectrometer equipped with a Mg Kα X-ray source. After peak fitting of the C 1s spectra, all the spectra were calibrated in reference to the unfunctionalized aliphatic C 1s component at a binding energy of 285.0 eV.

The morphology of the surface was recorded on an SPA 3700 (Seiko instruments Inc.) scanning force microscope. All the images were recorded under ambient atmosphere. A triangular-shaped Si_3N_4 cantilever with integrated tips (Olympus Co. Ltd.) was used to acquire the images in the contact mode. The normal spring constant of the cantilever was 0.02 N/m. The force between the tip and the sample was 0.087 nN.

Results and Discussion

To prepare the polymer brush from surface, a uniform and densely packed initiator-modified substrate is indispensable. Two methods were adopted to form the initiator monolayer: one was to modify the silicon surface in a toluene solution containing 6-((2-bromo-2-methyl)propionyloxy)hexyltrichlorosilane (solution method), and the other was to treat it with the vapor of 3-aminopropyl)triethoxysilane, followed by amidization with 2-bromoisobutyric acid (vapor method). The contact angles of water on the self-assembled initiator monolayers were 77.1 (solution method) and 69.9° (vapor method), respectively, which were significantly different from the inherent hydrophilic properties of the silicon wafer before the treatment.

After surface modification, XPS was used to confirm the formation of the initiator monolayer. The Br 3d peak was observed around 70 eV in the silicon surface treated by both methods, indicating the formation of the monolayer (Figure 1A).[17] Besides the Br 3d peak, another two peaks of Si 2p were found in both vapor and solution methods at 103.4 and 99.0 eV, which were assigned to the SiO_2 and silicon, respectively.[18] In the case of the solution method, the relative intensity of the peak at 103.4 eV (compared with the peak at 99.0 eV) was higher than that of the vapor method, indicating that SiO_2 gel was formed on the surface in the solution method.

Figure 2 compares the surface morphology of the initiator monolayer by both methods. The surface of the silicon wafer treated by solution method was covered

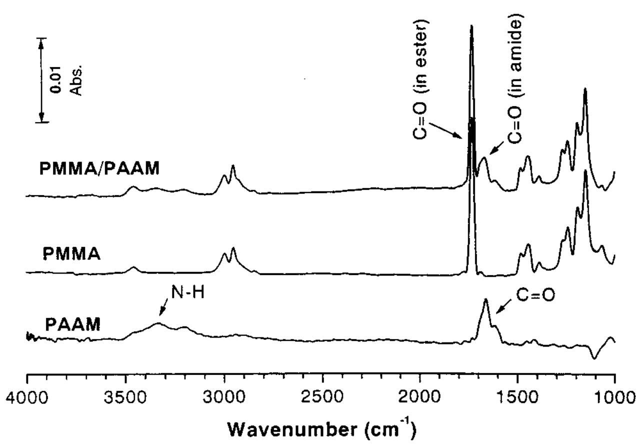


Figure 3. FT-IR spectra of PMMA, PAAM, and their block copolymer PMMA/PAAM brush on the silicon wafer.

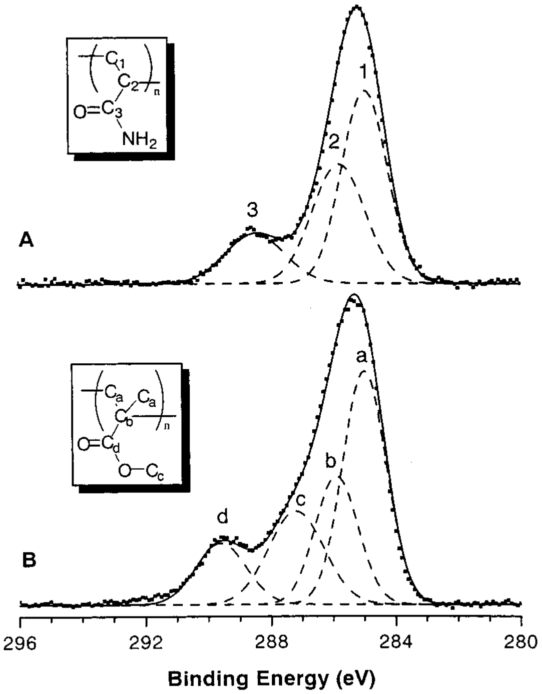


Figure 4. C 1s XPS spectra of (A) PAAM and (B) PMMA homopolymer brushes on silicon wafer. Key: peak fitting, solid line; experimental curve, dotted line; different carbon, dashed line.

with particles with a size in the range of 50–100 nm, which might be the cross-linked products of chlorosilane. In contrast, the vapor method provided a uniform surface; therefore, it was used to form the uniform polymer brush.

To obtain an amphiphilic polymer brush, a hydrophobic polymer and a hydrophilic polymer should be accumulated successively by controlled living polymerization. ATRP has been successfully used in the polymerization of MMA in solution to yield narrow polydispersity homopolymers.[12a] The PMMA brush was first prepared by Tsujii et al.,[5a] and the PAAM brush was reported by Wirth et al.[13] On the basis of their techniques, we choose MMA and AAM as two monomers for the amphiphilic block copolymer brush.

Because of the difficulty to obtain the molecular weight of the polymer brush, we use the "free" polymer formed by free initiator in solution to monitor the surface-grafted polymerization process. The free initiator plays not only as an indicator of the polymerization but also as a controller for the ATRP on the surface. Without the free add-in initiator in the solution, the polymer film formed is heterogeneous under the light. In this case, only the surface-bound initiator was used for ATRP; the polymerization would proceed by a redox initiation because of the too low concentration of deactivated species (Cu(II)) formed at the beginning of the polymerization.

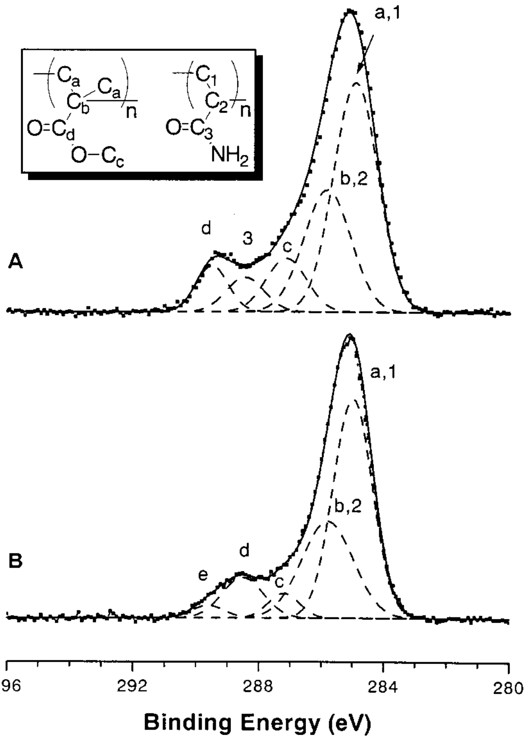


Figure 5. C 1s XPS of (A) PMMA/PAAM and (B) PAAM/PMMA block polymer brushes on silicon wafer. Key: peak fitting, solid line; experimental curve, dotted line; different carbon, dashed line.

Table 1 summarized the results of the surface polymerization. PMMA and PAAM homopolymer brushes were first formed onto the silicon wafer, respectively. The polydispersity of the "free" PMMA polymer remained lower than 1.3 (Table 1, nos. 1 and 2).

When DMF was used as the solvent for polymerization of AAM in the presence of "free" initiator, some white precipitate appeared in the maroon polymerization solution, indicating the formation of the PAAM polymer in the DMF solution. After the formation of homo-grafting polymerization of PMMA and PAAM brushes, we carried out the block polymerization from the first polymer brush, whose end group, C–Cl bond, should be the macroinitiator for the second polymerization (Table 1, nos. 4 and 5).

Figure 3 shows the IR spectra of polymer brushes on the silicon wafer. In the spectra of PAAM brush, a broad peak was observed in the region of 3200–3500 cm^{-1} (N–H stretching vibration in amide), and two peaks appeared at 1665 and 1615 cm^{-1} (carbonyl in amide due to the formation of hydrogen bond with amide group).[19] In the case of the block polymer brush of Si/PMMA/PAAM, the absorption peaks of C–H and C=O in the PAAM layer were superimposed on the spectrum of PMMA brush.

XPS was used to characterize the surface of the polymer brushes. Both the Si/PAAM and the Si/PMMA/

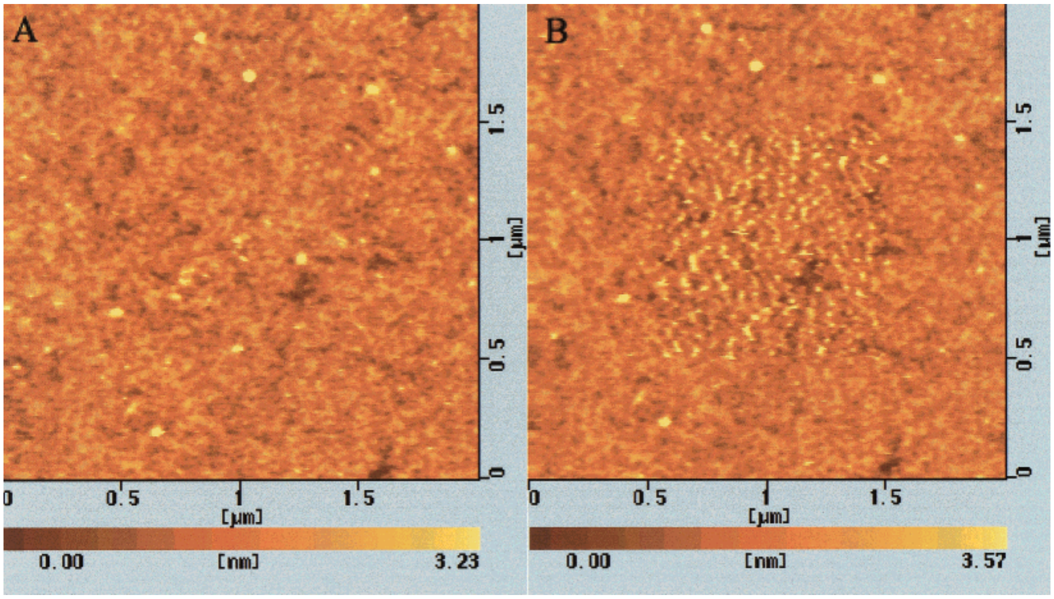


Figure 6. AFM images of PAAM homopolymer brushes on the silicon wafer: (A) before scratching by AFM tip; (B) after scratching by AFM tip (scratching area: center 1 × 1 μm).

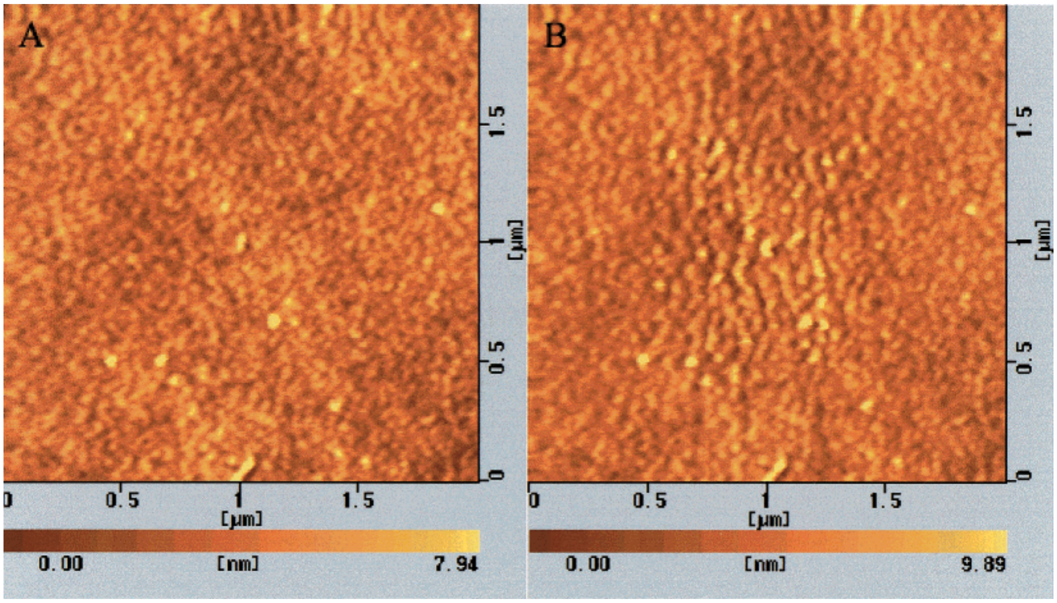


Figure 7. AFM images of PMMA homopolymer brushes on the silicon wafer: (A) before scratching by AFM tip; (B) after scratching by AFM tip (scratching area: center 1 μm × 1 μm).

Table 2. Surface Compositions of Block Polymer Brushes

sample	PAAM (mol %)	PMMA (mol %)
Si/PMMA/PAAM	47	53
Si/PAAM/PMMA	80	20

Table 3. Contact Angle of Water on a Different Kind of Silicon Wafer after Modification at Room Temperature

sample[a]	SiOBr	SiNBr	PAAM	PMMA	PAAM/ PMMA	PMMA/ PAAM
θ_{adv}	77.1	69.9	12.2	66.3	36.0	52.8
θ_{rec}				60.6	8.1	37.5

[a] θ_{adv}: advancing contact angle. θ_{rec}: receding contact angle.

PAAM block polymer brushes showed the N 1s peak, indicating the formation of PAAM brush on the substrate. In the XPS spectra of homopolymers and block polymers, all the C 1s peaks appeared around 285 eV with a broad shoulder at the higher binding energy. According to the reference,[20] careful peak fitting on the C 1s peaks resolves four peaks representing different carbons in PMMA: (1) aliphatic hydrocarbon (*C*−C/*C*−H, at a binding energy of 285.0 eV), (2) an ester-induced β-shifted carbon (*C*−COO at 285.9 eV), (3) the methyl side ester (*C*−O at 287.2 eV), and (4) the carboxyl carbon (*C*=O at 289.6 eV) (Figure 4A). Similarly, the PAAM showed three kinds of carbon: (1) aliphatic hydrocarbon (*C*−C at 285 eV), (2) an amide induced β-shifted carbon (*C*−$CONH_2$ at 285.8 eV), and (3) the amide carbon (*C*ONH_2 at 288.4 eV) (Figure 4B). On the basis of the above results, the C 1s peaks of the block polymers were fitted. Figure 5 shows the peak-fitting curves of the C 1s peaks of block polymer brushes. The area ratio of C 1s peak of carbonyl between PMMA (ester at 289.6 eV) and PAAM (amide at 288.4 eV) in the Si/PMMA/PAAM brush was found to be 9:8, indicating that the surface should contain two kinds of block, PMMA and PAAM. In the case of the Si/PAAM/PMMA brush, the area ratio of C 1s peak of carbonyl between PMMA and PAAM was

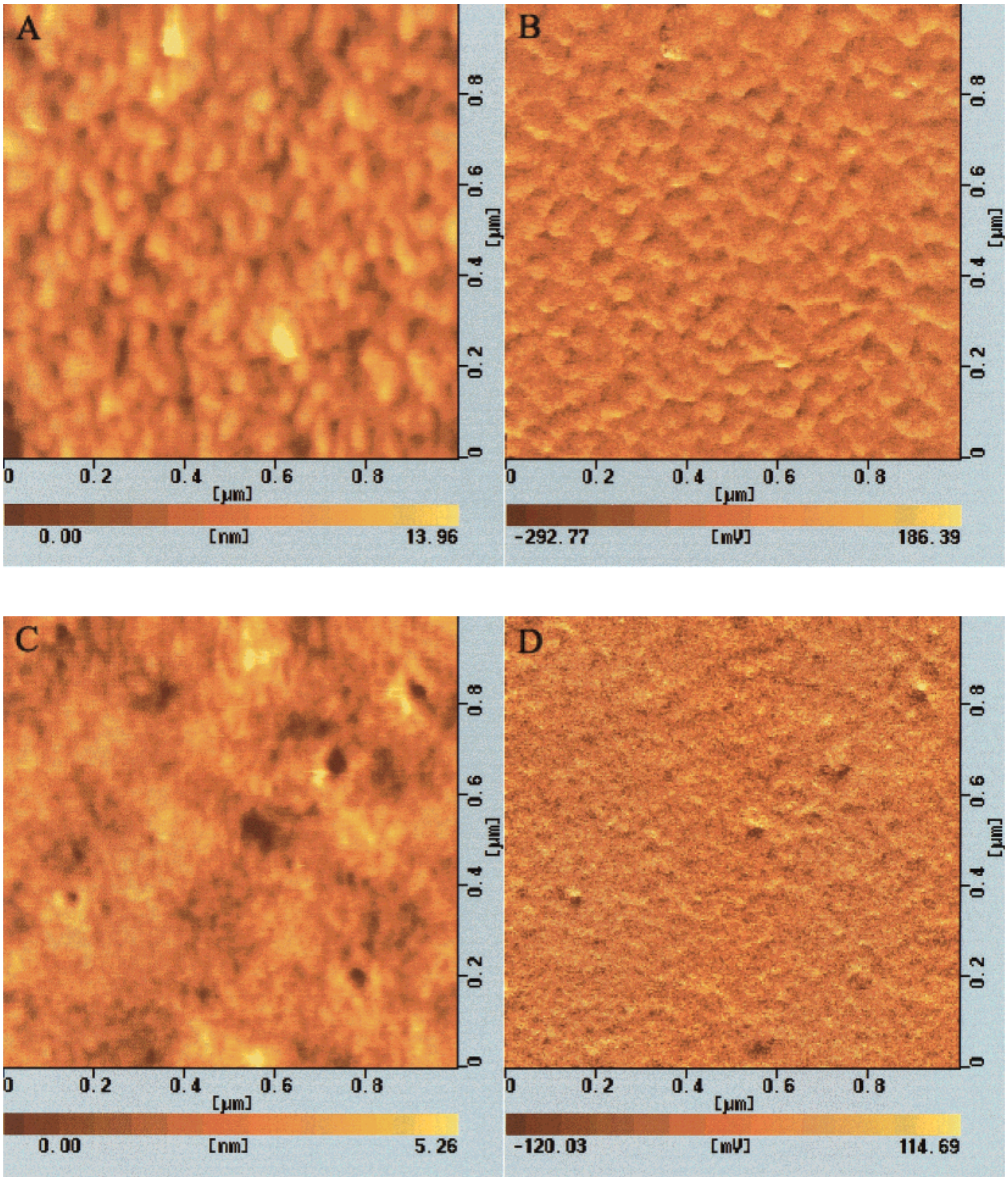
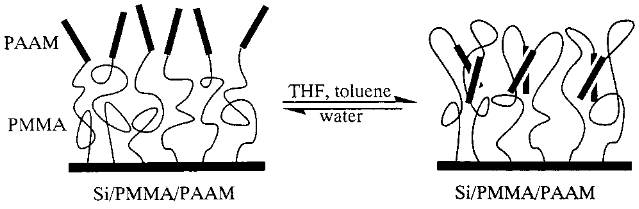


Figure 8. AFM images of PMMA/PAAM polymer brush on the silicon wafer. Topographic (A) and friction mode (B) images of the same region after immersing in water, and topographic (C) and friction mode (D) images of the same region after immersing in toluene.

Scheme 3



found to be 1:4. Therefore, in both cases, the surface was not completely covered with the second layer of polymer. Table 2 shows the surface compositions of the amphiphilic Si/PMMA/PAAM and the Si/PAAM/PMMA copolymer brushes.

Table 3 shows the results of the contact angle measurement of the surface of the polymer brushes. The advancing and receding contact angles of water on the PMMA brush were 66.3 and 60.6°, respectively. The advancing contact angle of the hydrophilic PAAM brush is 12.2°. After MMA was block copolymerized onto the PAAM brush, the contact angle increased to 36.0°, which was, however, smaller than that of the PMMA homopolymer brush. The receding angle was also less than that of the PAAM brush. In the case of the Si/PMMA/PAAM brush, the hydrophilicity of the surface increased but was not the same as that of the PAAM homopolymer brush.

Zhao and co-workers[6] reported that the tethered diblock copolymer film of PSt-*b*-PMMA on silicate substrate underwent reversible changes in contact angles as the film was treated with different solvents. After the PSt-*b*-PMMA film was treated with methylcyclohexane (a better solvent for PS than PMMA), the contact angle increased to a characteristic value for PSt; subsequent treatment of the same sample with CH_2Cl_2 (a good solvent for PMMA and PSt) reversed this change. They contribute that the tethered chains have sufficiently free volume to permit large changes in

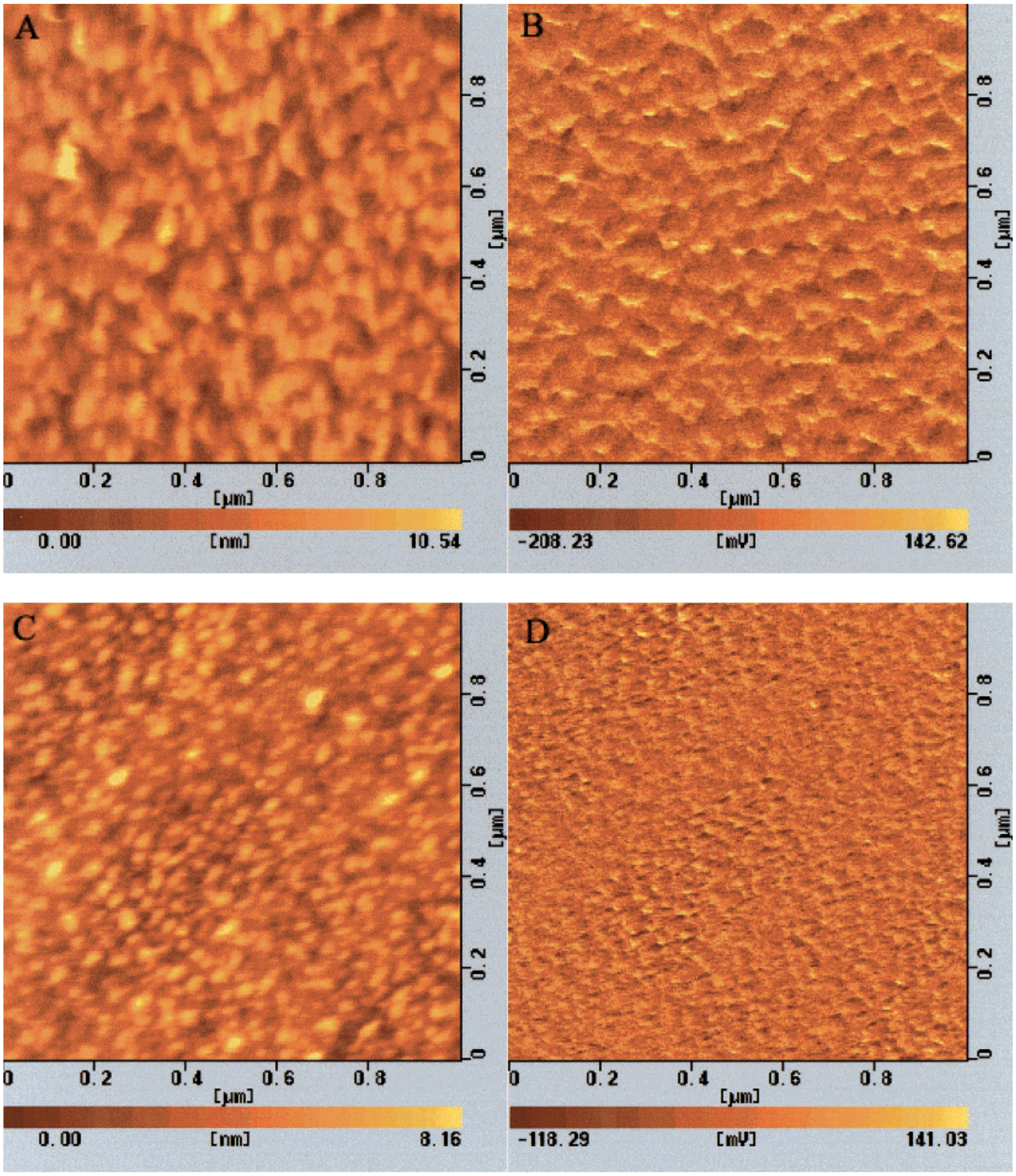


Figure 9. AFM images of PAAM/PMMA polymer brush on the silicon wafer. Topographic (A) and friction mode (B) images of the same region after immersing in water, and topographic (C) and friction mode (D) images of the same region after immersing in toluene.

conformational states when they were treated with the solvents. For the amphiphilic block polymer brush, we tried to treat the surface with several organic solvents and water. Different from Zhao's report, the contact angles of the amphiphilic surface did not change so much. This might be caused by the quick reorganization of the polymer brush when water was dropped on during the measurement of contact angle of water.

SPM was used to check the surface morphology and composition of the polymer brush onto the silicon wafer. Both the PAAM and PMMA homopolymer brushes showed as smooth as the naked silicon wafer. After an image of the PAAM brush was observed (Figure 6A), a 1 μm × 1 μm square area in the center of the image was scratched with the SPM tip at a high frequency and press force on the surface. After this treatment, the scratched region (Figure 6B) showed significant difference in the morphology, while this scratch was not demonstrated in naked silicon wafer. We speculate that the polymer chain was damaged under the scratching of the tip. Because of the wrap between the polymer chains, the broken polymer chains stayed on the polymer brush, showing a rubbed texture of the surface. Similarly, we observed the PMMA brush formed on the surface (Figure 7).

A number of groups have used the SPM to study patterned SAMs and heterogeneous films on surfaces.[21,22] Differences in friction observed by scanning force microscopy have been attributed to different chemical compositions of the surfaces. We use the topographic and friction images measured simultaneously to observe the surface of the block polymer brush. Figure 8A showed a domain texture of the Si/PMMA/PAAM brush after immersing in the water. The average diameter of domain size is in the range of 50–100 nm, and the roughness of the film is 2.1 nm. The friction image obtained at the same time show similar image. After immersing the polymer brush in toluene for half an hour, a smooth surface with a roughness of 0.80 nm was observed (Figure 8C). The friction force micrograph also showed a smooth image. Comparing with the images of the Si/PMMA/PAAM brush treated in two different solvents, we can conclude that the polymer brush should be reorganized by the affinity of the polymer to the solvent. After treatment with water, the hydrophilic PAAM blocks appeared on the surface of the brush and aggregated to form domain texture. After the polymer brush was treated with toluene, the PMMA block was easily swollen in toluene, formed the PMMA layer on the top of the surface after drying. We speculate that the strong segregation between the PMMA block and the PAAM block results in phase separation after treated with different solvents (Scheme 3).

In the case of the Si/PAAM/PMMA brush, similarly the domain texture with a roughness of 1.69 nm was observed after water treatment. After immersion in toluene for half an hour, the surface roughness of polymer brush was found to be 1.77 nm. From the surface coverage of XPS, we know that the surface of the Si/PAAM/PMMA brush has a low coverage of PMMA (20%) on the surface. After treatment of the surface with toluene, the surface not only is covered with PMMA but also is mixed with the hydrophilic PAAM. Therefore, the Si/PAAM/PMMA brush did not show a texture similar to that of the Si/PMMA/PAAM brush after treatment with toluene.

Conclusions

In this paper, homopolymers and block amphiphilic polymer brushes were prepared by combining the self-assembly of initiator and the controlled living polymerization. The formation of the PMMA and the PAAM polymer brushes was confirmed by FT-IR spectra, XPS spectra, and contact angle measurement. The composition of the amphiphilic block polymer brushes was investigated by XPS. The PAAM block in the Si/PMMA/PAAM brush covers 47% of the surface, and the PMMA block in the Si/PAAM/PMMA brush does 20%. AFM analysis of the amphiphilic brushes indicated that different morphologies were formed after treatment with water and toluene, respectively. We speculated that the polymer brush was stretched out from the surface and each polymer chain is flexible enough to permit the conformational change in different solvents. When the amphiphilic brushes were treated with water, the PAAM block would aggregate on the surface. Instead, when the amphiphilic brushes were treated with toluene, the PMMA block might appear on the top surface. We do believe that this study opens up a new avenue to fabricate tailor-made surface by block polymer brush based on self-assembly and controlled living polymerization.

Acknowledgment. Dr. Lei Jiang, Beijing Institute of Chemistry, P. R. China, was grateful acknowledged for his valuable discussion. This work was partially supported by Grant-in-Aid for Scientific Research (A) (No. 11305061), and Scientific Research on Priority Area (B) of "Development of Molecular Conductors and Magnets by Spin-Control" (No.730/11224207) and of "Electrochemistry of Ordered Interfaces" (No. 282/09237256) from the Ministry of Education, Science, Sports, and Culture, Japan. The authors acknowledge the financial support of Tokyo Ohka Foundation. X.K. thanks the Japanese Society for Promotion Science for a postdoctoral fellowship and acknowledges financial support from the Japanese Ministry of Culture and Education.

References and Notes

(1) (a) Chang, Y.-C.; Frank, C. W. *Langmuir* **1996**, *12*, 5824. (b) Chang, Y.-C.; Frank, C. W. *Langmuir* **1998**, *14*, 326.

(2) (a) Jaworek, T.; Neher, D.; Wegner, G.; Wieringa, R. H.; Schouten, A. J. *Science* **1998**, *279*, 57. (b) Ingall, M. D. K.; Houeyman, C. H.; Mercure, J. V.; Bianconi, P. A.; Kunz, R. R. *J. Am. Chem. Soc.* **1999**, *121*, 3607.

(3) (a) Jordan, R.; Ulman, A.; Kang, J. F.; Rafailovich, M. H.; Sokolov, J. *J. Am. Chem. Soc.* **1999**, *121*, 1016. (b) Jordan, R.; Ulman, A. *J. Am. Chem. Soc.* **1998**, *120*, 243.

(4) (a) Prucker, O.; Rühe, J. *Macromolecules* **1998**, *31*, 602. (b) Prucker, O.; Rühe, J. *Macromolecules* **1998**, *31*, 592. (c) Prucker, O.; Rühe, J. *Langmuir* **1998**, *14*, 6893. (d) Prucker, O.; Naumann, C. A.; Rühe, J.; Knoll, W.; Frank, C. W. *J. Am. Chem. Soc.* **1999**, *121*, 8766.

(5) (a) Ejaz, M.; Yamamoto, S.; Ohno, K.; Tsujii, Y.; Fukuda, T. *Macromolecules* **1998**, *31*, 5834. (b) Ejaz, M.; Ohno, K.; Tsujii, Y.; Fukuda, T. *Macromolecules* **2000**, *33*, 2870.

(6) (a) Zhao, B.; Brittain, W. J. *J. Am. Chem. Soc.* **1999**, *121*, 3557. (b) Zhao, B.; Brittain, W. J.; Zhou, W.; Cheng, S. Z. D. *Macromolecules* **2000**; *33*, 8821.

(7) Weck, M.; Jackiw, J. J.; Rossi, R. R.; Weiss, P. S.; Grubbs, R. H. *J. Am. Chem. Soc.* **1999**, *121*, 4088.

(8) Seshadri, K.; Atre, S. V.; Tan, T. T.; Lee, M.-T.; Allara, D. L. *J. Am. Chem. Soc.* **1997**, *119*, 4698. (b) Tao, T.-T.; Pandian, K.; Lee, W.-S. *Langmuir* **1998**, *14*, 6158.

(9) (a) Husseman, M.; Malmström, E. E.; McNamara, M.; Mate, M.; Mecerreyes, D.; Benoit, D. G.; Hedrick, J. L.; Mansky, P.; Huang, E.; Russell, T. P.; Hawker, C. J. *Macromolecules* **1999**, *32*, 1424. (b) 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. (c) Shah, R. R.; Mecerreyes, D.; Husemann, M.; Rees, I.; Abbott, N. L.; Hawker, C. J.; Hedrick, J. L. *Macromolecules* **2000**, *33*, 597. (d) Husemann, M.; Mecerreyes, D.; Hawker, C. J.; Hedrick, J. L.; Shah, R.; Abbott, N. L. *Angew. Chem., Int. Ed. Engl.* **1999**, *38*, 647.

(10) (a) For review papar, see: Patten, T. E.; Matyjaszewski, K. *Adv. Mater.* **1998**, *10*, 901. (b) Xia, J.; Zhang, X.; Matyjaszewski, K. *Macromolecules* **1999**, *32*, 3531.

(11) (a) Uegaki, H.; Kotani, Y.; Kamigaito, M.; Sawamoto, M. *Macromolecules* **1997**, *30*, 2249. (b) *Ibid.* **1998**, *31*, 6756. (c) Nishikawa, T.; Kamigaito, M.; Sawamoto, M. *Ibid.* **1999**, *32*, 2204.

(12) (a) Grimaud, T.; Matyjaszewski, K. *Macromolecules* **1997**, *30*, 2216. (b) Matyjaszewski, K.; Patten, T. E.; Wang, J. *J. Am. Chem. Soc.* **1997**, *119*, 674.

(13) (a) Huang, X.; Doeski, L. J.; Wirth, M. J. *Anal. Chem.* **1998**, *70*, 4023. (b) Huang, X.; Wirth, M. J. *Macromolecules* **1999**, *32*, 1694.

(14) Biesalski, M.; Rühe, J. *Macromolecules* **1999**, *32*, 2309.

(15) 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.

(16) Haller, I. *J. Am. Chem. Soc.* **1978**, *100*, 8050.

(17) The XPS spectra of Br 3d peak could be theoretically used to follow the polymerization procedure. Unfortunately, we observed that the peak of Br 3d decayed very quickly under measurement due to the loss of the bromine under a prolonged X-ray irradiation. A similar phenomenon has been reported in: Rieke, P. C.; Baer, D. R.; Fryxell, G. E.; Engelhard, M. H.; Porter, M. S. *J. Vac. Sci. Technol. A* **1993**, *11*, 2292.

(18) Sieval, A. B.; Demirel, A. L.; Nissink, J. W. M.; Linford, M. R.; van der Mass, J. H.; de Jeu, W. H.; Zuilhof, H.; Sudhölter, E. J. R. *Langmuir* **1998**, *14*, 1759.

(19) Silverstein, R. M.; Webster, F. X. *Spectrometric Identification of Organic Compounds*, 6th ed.; John Wiley & Sons: New York, 1997.

(20) Watts, J. F.; Leadley, S. R.; Castle, J. E.; Blomfield, C. J. *Langmuir* **2000**, *16*, 2292.

(21) Overney, R. M.; Meyer, E.; Frommer, J.; Brodbeck, D.; Lüthi, R.; Howald, L.; Güntherodt, H.-J.; Fujihara, M.; Takano, H.; Gotoh, Y. *Nature* **1992**, *359*, 133.

(22) van der Vergte, E. W.; Hadziioannou, G. *Langmuir* **1997**, *13*, 4357.

MA001152H