Mixed Poly(methyl methacrylate)/Poly(ethylene glycol) Brushes: Study of Switching Behavior in Selective Solvent

Libang Feng, Yanping Wang, Shunhua Wang

School of Mechatronic Engineering, Lanzhou Jiaotong University, Lanzhou 730070, China

ABSTRACT: The mixed polymer brushes composed of two incompatible polymers, poly(methyl methacrylate) and poly(ethylene glycol), were successfully synthesized via a sequential grafting to method, which was confirmed by water-contact angle and ellipsometric measurements. The resulted mixed polymer brushes could undergo conformational rearrangements upon exposure to different selective solvents, and then the lateral segregation in non-selective solvent and perpendicular segregation in selective solvent happened. As a result, the mixed polymer brushes exhibited the ripple morphology and dimple morphology in corresponding solvent, respectively, and which led to changes in water-contact angle and surface composition as a function of bulk composition of the mixed polymer brushes. Moreover, the switching properties as the surface composition, wettability and topographical images could occur in a controlled and reversible fashion. © 2009 Wiley Periodicals, Inc. J Appl Polym Sci 112: 2112–2119, 2009

Key words: mixed brushes; poly(methyl methacrylate); poly(ethylene glycol); selective solvent; switching; wettability; morphology

INTRODUCTION

Smart or switchable surfaces are capable of responding to very subtle changes in the surrounding environment such as pH,[1] surface pressure,[2] temperature,[3] light,[4] and solvent quality.[5,6] The responses are caused by the reorganization of the internal or surface structure of the grafted layers. Such surfaces hold great promise in applications of nanoelectromechanical, bioanalytical and microfluidic devices,[7–9] drug delivery and biomimetic materials,[10] chemical gates,[11] and protein adsorption.[12]

Recently, much attention has been paid to binary polymer brushes composed of two immiscible polymer chains since reversible switching of surface properties can be observed for these mixed brushes grafted to a solid substrate.[13–15] Therefore, this kind of polymer brushes is also one of smart materials. The surface composition, and hence, the surface energy, adhesion, friction, and wettability of the mixed brushes can be "tuned" to a desired physical state. This provides a means for the fabrication of "smart surfaces" with new sophisticated properties such as self-cleaning and self-refreshing abilities or superhydrophobic behavior.[16,17]

Generally, the polymer brush can be synthesized by two techniques as grafting-from[18,19] and grafting-to.[20,21] For example, Zhao and coworkers[22,23] synthesized the mixed polymer brushes containing poly (methyl methacrylate) (PMMA) and polystyrene (PS) segments by grafting-from method, and they observed a transition in water-contact angles with increasing PS molecular weight after dichloromethane treatment. Feng and coworkers[24] synthesized PMMA/PS brushes as well and found that both water-contact angle and the oxygen concentration varied depending on whether the substrate was immersed in a nonselective solvent [tetrahydrofuran (THF)] or selective solvent for PS (cyclohexane) or PMMA (isobutanol). Minko and coworkers[25–27] synthesized PS and poly(2-vinyl pyridine) mixed brushes by grafting-to technique, and found that the mixed brushes could be switched between different surface energetic states upon exposure to different selective solvents. In this study, a new mixed polymer brushes containing PMMA and poly(ethylene glycol) (PEG) segments was synthesized by grafting-to method, and the switching behavior of the mixed brushes exposure to different selective solvents was investigated in detail.
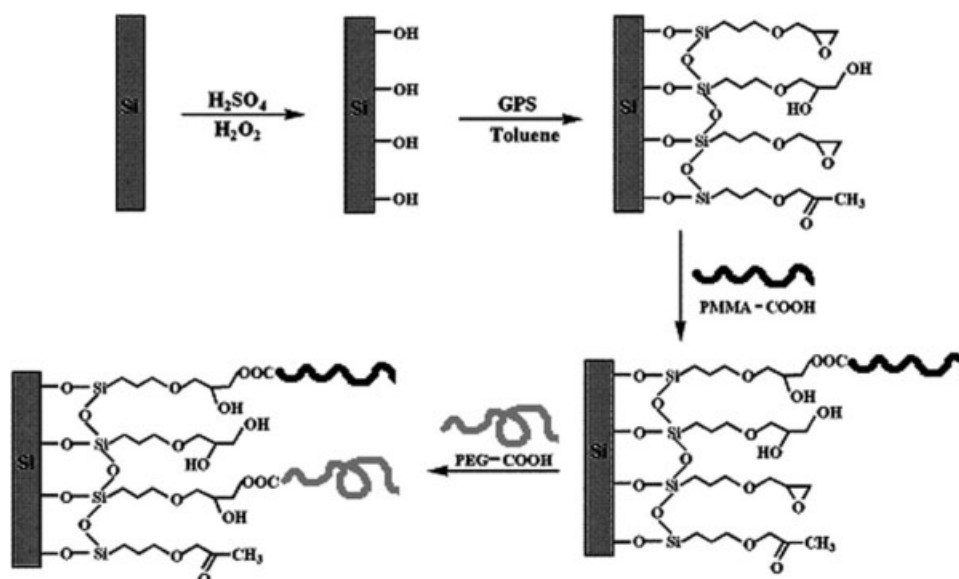
EXPERIMENTAL

Materials

Carboxyl-terminated PEG (PEG-COOH) was synthesized by refluxing of PEG monomethyl ether

Scheme 1 Schematic diagram of the synthesis of mixed polymer brushes.

(MPEG, M_n = 5000 g/mol, from Fluka Company and dehydrated before use) with excessive succinyl anhydride in THF. The resulted PEG-COOH was purified by multiple precipitations from THF solution using diethyl ether. Carboxyl-terminated PMMA (PMMA-COOH, M_n = 5300 g/mol, M_w = 8700 g/mol, T_g = 92°C) was synthesized by radical polymerization of MMA using 2, 2′-azobis(isobutyronitrite) as initiator and 3-mercaptopropionic acid as chain transfer agent; 3-Glycidoxypropyl trimethoxysilane (GPS) from Aldrich was used as received. THF, dichloromethane, ethanol, and toluene were dried on molecular sieves before use.

The highly polished Si wafer (namely, pristine Si wafer) was used as a substrate. The wafer was first cleaned in dichloromethane in an ultrasonic bath for 30 min, and then placed in a piranha solution (7 : 3 of concentrated sulfuric acid/30% hydrogen peroxide) at 60°C for 1 h. Finally, rinsed with deionized water for three times, and the resulted sample was denoted as Si-OH.

Preparation of the mixed polymer brushes

The mixed polymer brushes containing PMMA and PEG chains were prepared on Si substrate with carboxyl-terminated PMMA and PEG, respectively, by grafting to method as described in Scheme 1. The typical preparation procedure was carried out in three-step as follows: First, GPS-modified Si surface (Si-GPS) was fabricated from 1 vol % GPS solution in toluene at room temperature under nitrogen stream for 16 h. Second, a thin film of PMMA-COOH was prepared onto the surface of GPS-modified Si wafer by spin-coating 1 wt % PMMA-COOH solution in toluene, and then heated at the temperature of 110 or 120°C for different time. The resulted surface was designated as Si-PMMA. Third, PEG-COOH chains were grafted onto the PMMA grafted Si wafer by covering the PMMA grafted silicon wafer onto PEG-COOH powder at 120°C for 10 h. Additionally, polymer brush containing PEG chains only (Si-PEG) was also prepared via grafting PEG-COOH onto GPS-modified Si wafer. The details on the preparation have been reported in previous literature.[28]

Sample characterization

Ellipsometry

Layer thickness and grafted amounts were evaluated at λ = 640 nm and an incidence angle of 70° using an instrument of Rudolph auto EL-II Null-Eliipsometer (NJ). Measurements were performed for each sample after each step of the grafting, and the measurements of the previous step were used as a reference for the calculation of ellipsometry data. At least five measurements at different locations were carried out for each sample. The surface coverage (Γ, mg/m^2) of the polymer brushes was calculated from the ellipsometry thickness of the layer, h (nm), by the following equation[29]:

$$\Gamma = h\rho \qquad (1)$$

where ρ is density of attached macromolecule. The density of PMMA and PEG was assumed to be 1.18 and 1.09 g/cm^3, respectively, in our calculation.

Contact angle measurements

Water-contact angle was performed by sessile drop technique using OCA15 instrument (Dataphysics Instruments Company, Germany) at ambient conditions (temperature : 20°C, and the relative humidity: 80%). The static contact angle of water was measured at contact time $t = 15$ s after a drop of deionized water (2 μL) application. The reported values were an average of three individual measurements on different regions of the same sample. To estimate the predicted water-contact angle of each polymer brush at the surface, the Cassie equation[30] was used:

$$\cos \theta = f_1 \cos \theta_1 + f_2 \cos \theta_2 \qquad (2)$$

where f_1 and f_2 represent the fractions of each polymer, θ_1, θ_2 are the measured contact angles for the pure polymers, and θ is the contact angle for the mixed brushes.

AFM observation

The surface morphology of the film was observed by an atomic force microscope (AFM, SPA 300HV, Seiko Instruments, Japan) in ultra-light-tapping mode at ambient conditions. A micro-fabrication cantilever with constant of ~ 20 N/m and a scan rate of 2 Hz was used.

Switching procedure

The samples of Si wafers grafted PMMA and PEG chains were exposed for 10 min to solvents with different quality, such as THF, ethanol, and toluene. After each treatment with a particular solvent, the samples were withdrawn from the solution to air-dry at ambient conditions. A cover was placed over the sample during drying to prevent disruption of the sample by air currents. After exposing in each solvent, the samples were allowed to sit for 1 h. Then the contact angle and the surface morphology were measured. The experiment was repeated several times with each sample to verify the reversibility of the switching property. At ambient conditions, the dry PMMA film is in glassy state and the dry PEG presents in crystals, consequently, the film morphology is stable for a certain time and the water-contact angle at the surface could reflect the switching behavior of the mixed polymer brushes.

RESULTS AND DISCUSSION

Modifying of Si wafers

Expoxysilanes are classical compounds that have been used to enhance the stability and integrity of polymer/inorganic interfaces.[31] Thereupon, GPS,
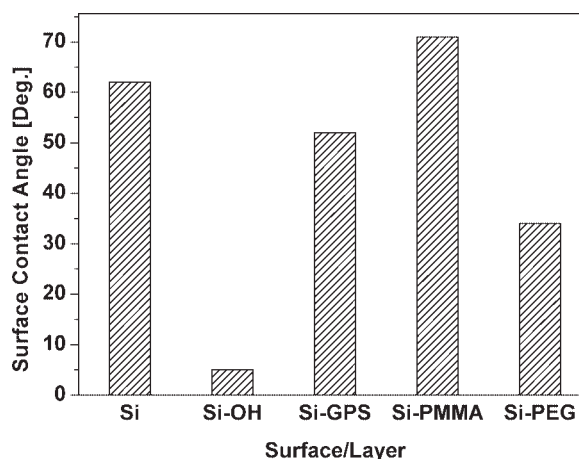

Figure 1 Water-contact angles of different layers on the Si substrate.

one of expoxysilanes, was served as the modify reagent to treat the Si wafer, which had been dealt with a piranha solution. And then the GPS-grafted surfaces were used to graft PMMA and/or PEG chains. The modified surfaces were examined by water-contact angle and ellipsometry measurements.

Contact angle measurements allow estimation of how the surface is screened with the (macro)molecules deposited on the substrate. Therefore, it was used to monitor the availability of each disposal steps, and Figure 1 shows the contact angle values of the pristine Si wafer and Si substrates covered with different molecular layers. We can find that the contact angles at the Si substrates changed remarkably after each disposal step, demonstrating that the surface wettability varied upon different layers. In specific, the water-contact angle of the pristine Si wafer was about 62° ± 1°, whereas the contact angle of Si wafer after treating in a piranha solution, namely, Si-OH, decreased to below 7°. The Si wafer with GPS layers (Si-GPS), had a contact angle of 52° ± 1°, marked higher than that of the Si wafer freshly treated with piranha solution, which indicated that the Si surface was completely covered with the GPS molecules after GPS grating. By contrast, the water-contact angle of PMMA-grafted surface (Si-PMMA) increased to around 71° ± 2°, whereas PEG-grafted surface (Si-PEG) had a contact angle of 34° ± 2°. Results revealed that the PEG-grafted surface had better wettability than PMMA-grafted surface because PEG was more hydrophilic than PMMA. These facts demonstrated that PMMA and PEG chains could be successfully grafted onto the surface of GPS-modified Si wafers, respectively, via the reaction between —COOH and epoxy groups.

Initially, the thickness of the native SiO_2 layer was 21–24 Å, and the thickness of GPS layer 14–15 Å measured by ellipsometry, indicating that the GPS

TABLE I
Surface Thickness (h), Coverage (Γ), and Composition of Mixed Polymer Brushes

Sample	S1	S2	S3	S4	S5	S6	S7	S8	S9
h (nm)									
PMMA	0.89	1.16	1.72	2.42	3.00	3.32	3.70	3.76	4.06
PMMA+PEG	4.28	4.28	4.34	4.31	4.21	3.97	4.22	4.19	4.25
Γ (mg/m^2)									
PMMA	1.05	1.37	2.02	2.86	3.54	3.92	4.36	4.43	4.79
PEG	3.70	3.40	2.86	2.05	1.32	0.71	0.58	0.47	0.21
PEG fraction (%)	79.3	72.8	60.5	43.7	28.8	16.3	12.5	10.3	4.5

layer was composed of 1–1.6 coupling GPS molecules as the chain length of single GPS molecule with fully extended conformation was 9.50 Å from computer model.[32] The thickness of the PMMA and PEG layers was about 4.05 and 4.15 nm when single PMMA-COOH or PEG-COOH were completely grafted onto the GPS-modified surface and that the grafting reaction has reached its saturation point, respectively, which further confirmed that PMMA and PEG chains could be successfully grafted onto the Si surface, respectively, by the designed grafting process.

Synthesis of mixed polymer brushes

In our experiment, the mixed polymer brushes containing PMMA and PEG chains were synthesized with three-step procedure. First, we covalently grafted GPS to the surface of Si wafers. Second, we prepared nine different amount of PMMA brush on the GPS-modified Si wafers. In the third step, we grafted PEG on each Si wafer containing previously grafted PMMA. The grafting of PMMA and PEG were examined by water-contact angle and ellipsometry measurements. The mixed polymer brushes with various compositions of PMMA and PEG could be obtained by regulating the grafting time and temperature, and results are summarized in Table I.

Generally, the thicknesses of the resulted mixed brush layers were between 4.34–4.19 nm, which were higher than those of single PMMA-grafted layer (about 4.05 nm) or PEG-grafted layers (about 4.15 nm). The reason that led to this result was that polymer chains in the mixed brushes might stand more erect than those of single PMMA or PEG-grafted layers after the nonselective solvent treatment (such as THF) owing to PMMA and PEG are incompatible polymers under the ambient conditions, and which then resulted in the mixed polymer brushes had thicker layers. On the other hand, the surface coverages of the grafted mixed polymers were between 4.5 and 5.0 mg/m^2, which remained relatively constant on the whole. Moreover, the surface coverages of PEG decreased as those of PMMA layers increased. The successful synthesis of the PMMA/PEG mixed brushes from polymers of similar molecular weights but different chemical compositions have also been confirmed by X-ray photoelectron spectroscopy (XPS) and atomic force microscope (AFM) measurements, which has been reported recently.[28]

Wettability of mixed polymer brushes

Wettability can reflect the chemical composition at the surface of the investigated sample.[25–27] In our experiment, the surface wettability of the resulted mixed brushes was evaluated using the water-contact angle. The samples were exposed to THF, which is a good solvent for both PMMA and PEG. Consequently, both polymer chains could be swollen in the favorable solvent with the structure locked in place as THF evaporated completely. The water-contact angles of the resulted mixed polymer brushes with various compositions varied between $34° \pm 2°$ (for pure PEG-grafted surface) and $71° \pm 2°$ (for pure PMMA-grafted surface) (as shown in Fig. 1 and Table II), indicating both PMMA and PEG

TABLE II
Water-Contact Angle of Mixed Brushes Treated with Different Quality of Solvent

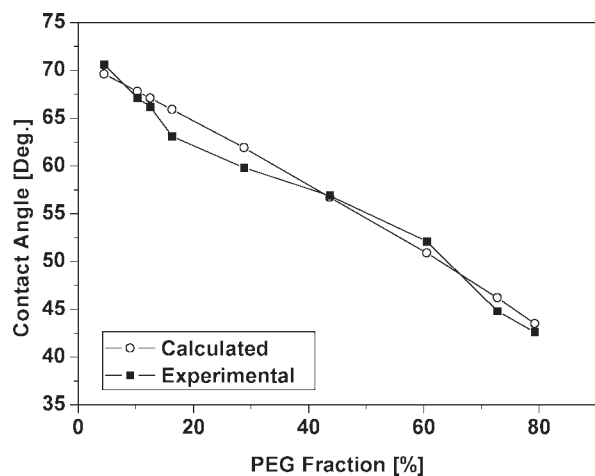| Sample	S1	S2	S3	S4	S5	S6	S7	S8	S9
PEG fraction (%)	79.3	72.8	60.5	43.7	28.8	16.3	12.5	10.3	4.5
Water-contact angle (°)									
After THF	42.6	44.8	52.1	56.9	59.8	63.1	66.2	67.1	70.6
After toluene	49.2	51.4	56.3	59.5	64.2	66.7	69.2	70.6	71.8
After ethanol	39.2	40.7	43.9	47.2	53.0	57.4	59.8	61.4	64.3
Difference between toluene and ethanol	10.0	10.7	12.4	12.3	11.2	9.3	9.4	9.2	7.5

Figure 2 Water-contact angles for mixed polymer brushes after exposed in THF versus the brush composition: (○) values calculated using the Cassie equation; (■) experimentally measured values.

segments appeared at the air interface after THF treatment. Furthermore, the water-contact angle decreased gradually with the increase of the bulk content of grafted PEG in mixed brushes, which indicated that the wetting property of the mixed brushes was a function of the chemical composition and both polymers contributed to the surface energy of the mixed brushes.

The Cassie equation[30] provides a basis for comparing experimental results to those predicted values because contact angle is a function of the fraction of each polymer presents on the top layer of the mixed brushes. Experimentally measured values of 71° (θ_1, for PMMA brush) and 34° (θ_2, for PEG brush) were used in our estimations. Using the Cassie equation and values of the brush composition taken from the grafting data (Table I), a plot of the expected contact angle as a function of composition can be calculated, and this along with the experimental data is shown in Figure 2. Results indicated that the contact angles of the experimental values were quite reasonable as compared with those of the calculated ones, which further demonstrated that the mixed polymer brushes were successfully synthesized and the wettability of the mixed brush surfaces was proportional to the chemical composition.

Study of switching behavior

Switching behavior of the mixed brushes was studied by exposing the samples to a selective solvent (toluene or ethanol), and then samples were dried as that described in the experimental part. The brush structure, frozen into a glassy or crystallization state, was investigated using water-contact angle measurements.

The solubility value parameters (δ) of solvents as toluene, THF, and ethanol from literature[33] are 8.9,

9.9, and 12.7 in units of $(cal/cm^3)^{1/2}$, respectively, whereas the values of the solubility parameters are 9.5 and 10.8 in units of $(cal/cm^3)^{1/2}$ for PMMA and PEG, respectively,[33] exhibiting there is much difference in solubility parameters between PMMA and PEG. Therefore, PMMA and PEG are incompatible polymers under the ambient conditions. Accordingly, we can find that toluene is a slightly PMMA-selective solvent whereas ethanol is a slightly PEG-selective solvent. At this point it can be supposed that exposing the mixed brushes to a selective solvent for PMMA or PEG (i.e., toluene for PMMA and ethanol for PEG), the distribution (composition) of the polymer chains at the surfaces would change as compared to that of in nonselective solvent, THF. Consequently, the water-contact angle would change and reflect this phenomenon.

Figure 3 and Table II display results of contact angle measurements after exposed in solvents with different quality. It could be found that water-contact angles of the mixed brushes were higher after treated with toluene than those of treated with THF, suggesting that the surfaces became more hydrophobic after toluene treatment. By contrast, water-contact angles decreased after ethanol treatment as compared to THF treatment, demonstrating that the surfaces were more hydrophilic upon ethanol treatment. Accordingly, we could deduce that for the same mixed polymer brushes, more content of PMMA chains presented at the surface upon toluene treatment. Likewise, more content of PEG segments presented at the surface after exposure upon ethanol. Therefore, the mixed brushes had the wettability switching behavior when they were treated with different quality of solvents. And this switching behavior resulted from the conformational reconstructions
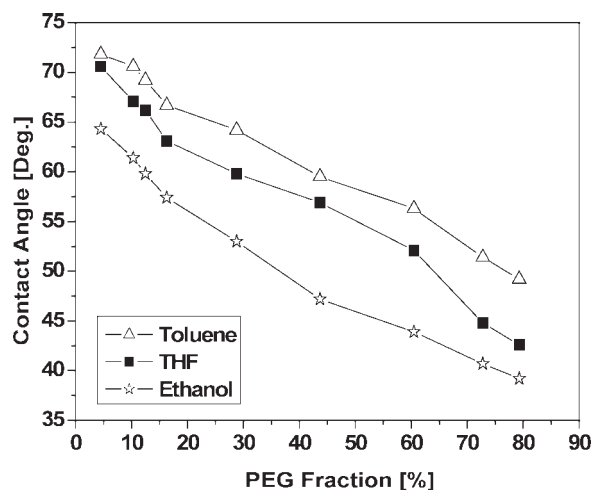

Figure 3 Switching behavior of mixed polymer brushes upon exposure to different solvents with the brush composition.
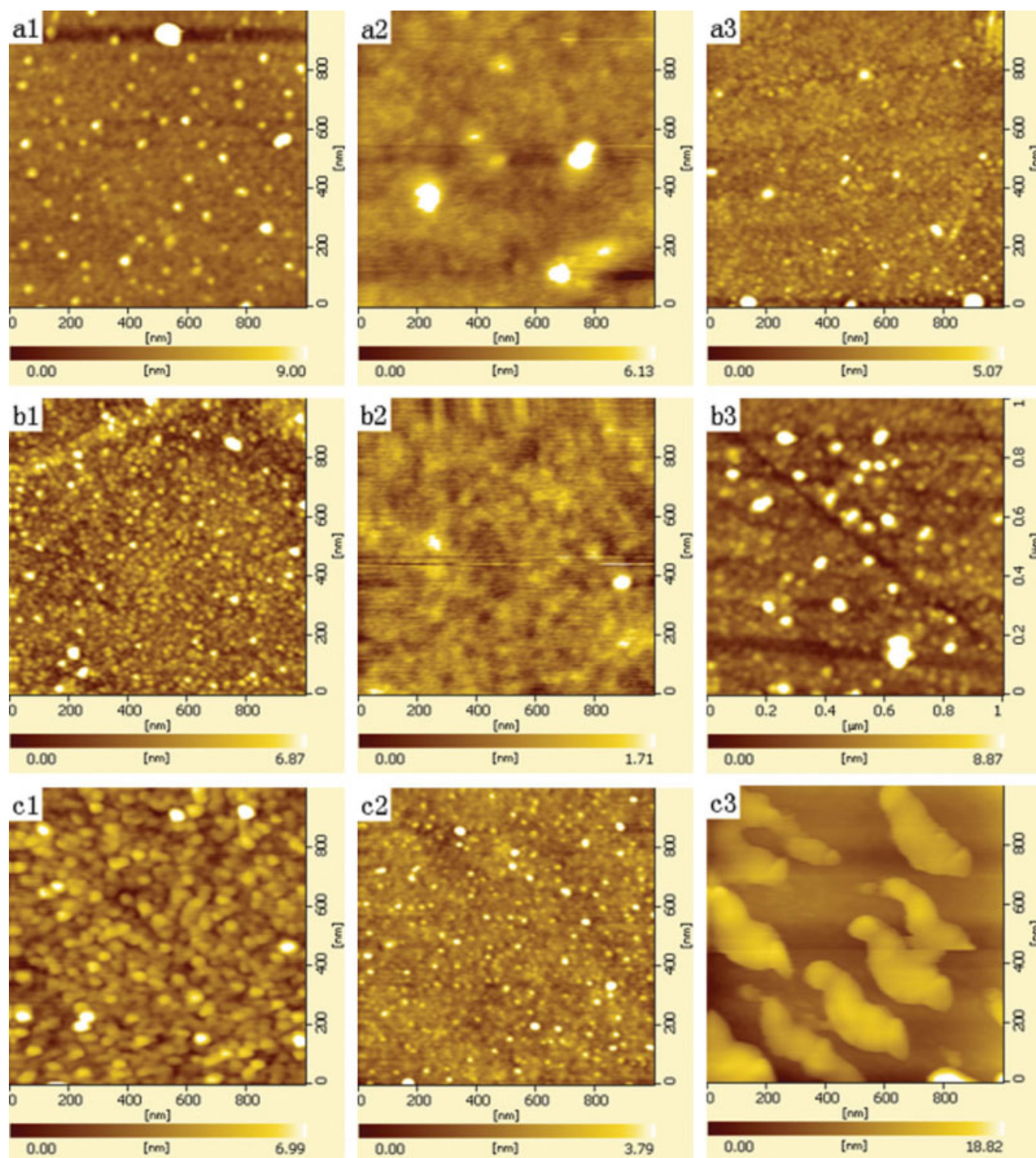
Figure 4 AFM topographical images of mixed polymer brushes upon exposure to different solvents versus PEG content: THF: (a1, a2, a3) 10.3%, Toluene (b1, b2, b3) 43.7%, and Ethanol (c1, c2, c3) 79.3%. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

and then, the distribution of PMMA and PEG segments just appeared at the air interface. Meanwhile, Table II also revealed that differences in water-contact angles between toluene and ethanol treated surfaces were between 7.5° and 12.5°, indicating that the overall degree of switching remained relatively constant.

Moreover, all changes of the surface wettabilities observed experimentally were reversible, namely, if the Si wafer with mixed PMMA/PEG brushes was exposed upon THF again after it was treated in the first solvent (such as toluene or ethanol), the brushes would adjust to the state that of originally presented

as THF treatment, and showed original wetting behavior, and vice versa.

The switching behavior of the mixed brushes was also investigated with AFM technique. Figure 4 shows how surface morphologies of the mixed polymer brushes changed with the content of PEG upon THF (nonselective solvent), and toluene and ethanol (selective solvent) treatment. We can found that some isolated domains of PEG crystals with an average diameter of 30–40 nm formed on the surfaces upon treated with the nonselective solvent of THF [Fig. 4(a1)] when PEG amount in the mixed brushes was low, e.g., 10.3%. More PEG crystals were observed on the surfaces with PEG amount increased [Fig. 4(b1)] until PEG crystals began to coalesce [Fig. 4(c1)]. By contrast, the topographical images changed when the same sample was treated with the selective solvent (ethanol or toluene). It could be observed that the surfaces grew much smoother upon exposure to toluene as compared with the surface treated with THF for the sample with the same composition [Figs. 4(a2, b2, and c2)], indicating more PMMA chains migrated to the surfaces. On the other hand, more large PEG crystals came forth on the surfaces upon exposure to ethanol as compared with the surface treated with THF [Figs. 4(a3, b3, and c3)]. These showed that the surface composition of the polymer brushes could reorganize upon exposure to solvents with different quality, which endowed the mixed polymer brushes with the switching behavior.

The switching behavior of the mixed brushes from polymers of comparable molecular weight could be illustrated by two possible types of morphology as shown in Scheme 2 [cross section, the black chains denoting one of the polymers (PMMA or PEG) while the gray chains the other]. Generally, the mixed brushes could exhibit lateral or perpendicular (sandwich-like) segregation upon exposure to different quality of solvents. Lateral structure formation [Scheme 2(a)] was dominant in nonselective solvent, such as THF for PMMA/PEG mixed brushes, and resulted in the ripple morphology, i.e., the two components segregated into elongated domains or stripes. If the solvent was bad for one component (e.g., ethanol for PMMA and toluene for PEG), then most of this polymer would form clusters embedded in a matrix of the other polymer [dimple morphology, Scheme 2(b)]. The matrix component was enriched at the brushes' top, while the component that formed the dimples prevailed at the bottom of the brushes, and this self-assembly determined the surface energetic state and functionality. So the surface morphology was controlled by exposing the mixed brushes to different environments, for instance, solvents with different quality. Thereby,
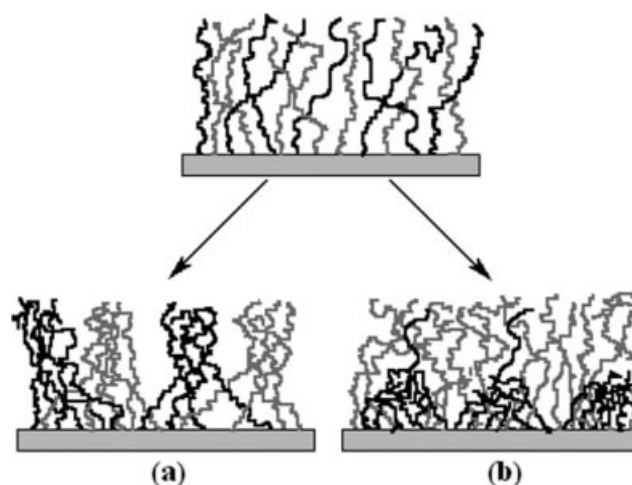
Scheme 2　Schematic illustration of the switching behavior for the mixed polymer brushes: (a) treated in a nonselective solvent; (b) treated in a selective solvent.

the mixed polymer brushes showed marked switching behavior.

CONCLUSIONS

The mixed polymer brushes containing PMMA and PEG segments were successfully synthesized on the GPS-modified Si surface via the sequential grafting of a carboxyl-terminated PMMA on the first step and then a carboxyl-terminated PEG on the second step. The thicknesses of the resulted polymer brushes were between 4.34 and 3.97 nm whereas the water-contact angles were between 71° and 34° in the nonselective solvent, such as THF. The surface morphology of the mixed polymer brushes could undergo reorganization in response to treatment with different quality of solvents. As a result, the mixed polymer brushes presented the ripple morphology in nonselective solvent (for instance, in THF) and the dimple morphology in selective solvent (for example, in toluene and ethanol). Thereupon, the surfaces of the mixed brushes became more hydrophobic after toluene treatment than treated with THF. By contrast, the surfaces were more hydrophilic treated with ethanol than THF treatment. Furthermore, the changes in water-contact angles and surface morphologies were reversible, which endowed the mixed polymer brushes with the outstanding switching behavior.

References

1. Marandi, G. B.; Esfandiari, K.; Biranvand, F.; Babapour, M.; Sadeh, S.; Mahdavinia, G. R. J Appl Polym Sci 2008, 109, 1083.
2. Lee, M.; Kim, J. W.; Peleshanko, S.; Larson, K.; Yoo, Y. S.; Vaknin, D.; Markutsya, S.; Tsukruk, V. V. J Am Chem Soc 2002, 124, 9121.

3. Tian, P.; Wu, Q. L.; Lian, K. J Appl Polym Sci 2008, 108, 2226.
4. Sidorenko, A.; Houphouet-Boigny, C.; Villavicencio, O.; McGrath, D. V.; Tsukruk, V. V. Thin Solid Films 2002, 410, 147.
5. Raviv, U.; Tadmor, R.; Klein, J. J Phys Chem B 2001, 105, 8125.
6. Tsukruk, V. V. Adv Mater 2001, 13, 95.
7. Srivastava, Y.; Marquez, M.; Thorsen, T. J Appl Polym Sci 2007, 106, 3171.
8. Nath, N.; Chilkoti, A. Adv Mater 2002, 14, 1243.
9. Rohr, T.; Ogletree, D. F.; Svec, F.; Frechet, J. M. Adv Funct Mater 2003, 13, 264.
10. Galaev, I. Y.; Mattiasson, B. Trends Biotechnol 1999, 17, 335.
11. Ito, Y.; Ochiai, Y.; Park, Y. S.; Imanishi, Y. J Am Chem Soc 1997, 119, 1619.
12. Ornatska, M.; Jones, S. E.; Naik, R. R.; Tsukruk, V. V. J Am Chem Soc 2003, 125, 12722.
13. Ruths, M.; Johannsmann, D.; Rühe, J.; Knoll, W. Macromolecules 2000, 33, 3860.
14. Huck, W. T. S.; Stroock, A. D.; Whitesides, G. M. Angew Chem Int Ed 2000, 39, 1058.
15. Zhao, B.; Brittain, W. J Prog Polym Sci 2000, 25, 677.
16. Blossey, R. Nat Mater 2003, 2, 301.
17. Chang, K. C.; Chen, Y. K.; Chen, H. J Appl Polym Sci 2008, 107, 1530.
18. Zhou, F.; Jiang, L.; Liu, W. M.; Xue, Q. J Macromol Rapid Commun 2004, 25, 1979.
19. Zhang, J.; Cui, C. Q.; Lim, T. B.; Kang, E. Macromol Chem Phys 2000, 201, 1653.
20. Zdyrko, B.; Klep, V.; Luzinov, I. Langmuir 2003, 19, 10179.
21. Ha, J. U.; Kim, M.; Lee, J.; Choe, S.; Cheong, I. W.; Shim, S. E. J Polym Sci Part A: Polym Chem 2006, 44, 6394.
22. Zhao, B. Polymer 2003, 44, 4079.
23. Zhao, B.; He, T. Macromolecules 2003, 36, 8599.
24. Feng, J. X.; Haasch, R. T.; Dyer, D. J Macromolecules 2004, 37, 9525.
25. Minko, S.; Müller, M.; Motornov, M.; Nitschke, M.; Grundke, K.; Stamm, M. J Am Chem Soc 2003, 125, 3896.
26. Draper, J.; Luzinov, I.; Minko, S. Langmuir 2004, 20, 4064.
27. Minko, S.; Patil, S.; Simon, F.; Eichhorn, K. J.; Motornov, M. Langmuir 2002, 18, 289.
28. Feng, L. B.; Gu, G. X.; Chen, M.; Wu, L. M. Macromol Mater Eng 2007, 292, 754.
29. Henn, G.; Bucknall, D. G.; Vanhoorne, P.; Jerome, R. Macromolecules 1996, 29, 4305.
30. Cassie, A. B.; Baxter, S. Trans Faraday Soc 1944, 40, 546.
31. Lan, L.; Gnappi, G.; Montenero, A. J Mater Sci 1993, 28, 2119.
32. Luzinov, I.; Julthongpiput, D.; Tsukruk, V. V. Langmuir 2000, 16, 504.
33. Brandrup, J.; Immergut, E. A.; Grulke, E. A. Polymer Handbook, 4th ed.; Wiley-Interscience: New York, 1999.