Preparation of Silane-Terminated Polystyrene and Polymethylmethacrylate Self-Assembled Films on Silicon Wafer

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ABSTRACT: End silane functionalized polystyrene and polymethylmethacrylate were prepared through radical chain-transfer reaction and characterized with gel-permeation chromatography. The chain-transfer constants of mercaptopropyltrimethoxysilane for the polymerization of styrene and methylmethacrylate were determined to be 8.48 and 0.67, respectively, from the slopes of $1/DP_n$ versus $[S]/[M]$ lines. The ultrathin films of the end silane–terminated polymers were prepared by self-assembly onto hydroxylated silicon wafers. The water contact angle on the resulting ultrathin films and the film thickness were measured. The morphology and chemical features of the films were observed and investigated by means of atomic force microscopy and X-ray photoelectron spectroscopy. Results indicated that the chain-transfer agent played a key role in making it possible for the silane-terminated polystyrene and polymethylmethacrylate to be self-assembled on Si(111), whereas the thickness and surface quality of the ultrathin films were dependent on the molecular weights of the polymers. © 2004 Wiley Periodicals, Inc. J Appl Polym Sci 92: 1695–1701, 2004

Key words: self-assembly; films; radical polymerization; silane-terminated polymer; chain-transfer reaction

INTRODUCTION

Polymer–solid interfaces have seen widespread applications in aerospace, aircraft, automotive, microelectronics, and the food packing industries, to name but a few.[1] The adhesion between the substrate and polymer and the cohesive strength of the polymer bulk are the key issues because they determine the serviceability and reliability of the materials. The most widely studied molecular self-assembly technique can meet the demands by fabricating closely packed interlayers and by covalently bonding of self-assembled molecules onto substrate surfaces.[2] Typical self-assembly systems include silanes on hydroxylated substrates, such as glass slides, silicon wafers, and aluminum, and thiol compounds (such as thiol, thiolate, disulfide, etc.) on transition metals such as Au, Ag, and Cu. Although the self-assembly of small molecules has been the focus of extensive investigations, few experimental studies are available on the assembly of polymers and especially on the comparison of the experimental results to the theoretical exploration.[3] The self-assembled polymer films are frequently currently prepared through layer-by-layer deposition, which, however, can be applied only to polyanions and polycations,[4] and is limited by the weak intermolecular mechanical strength and poor bonding between the polymer films and the substrate.

The mechanical stability of self-assembled polymer film on a substrate can be effectively increased by incorporating sticker groups in the polymer molecular chain to form hydrogen, covalent, and ionic bonds, given the strong interaction between the sticker groups and the substrate solid surface.[5] If these reactive groups distribute randomly along the polymer chains, the absorbed polymer would have lateral conformation.[5–8] In a similar manner, the end-grafted polymer film known as polymer brushes can be prepared from end-group functionalized polymer by the reaction of the end reactive group with the surface functionalities.[9–23] End-group functionalized polymers with controlled molecular weight and well-defined structure can be prepared through the capping reaction of anion polymerization of appropriate reagents carrying the expected functional groups. However, anionic polymerization cannot be applied to those monomers with active groups such as hydroxyl,
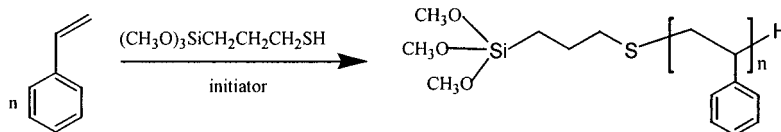
Scheme 1 Preparation of end silane–terminated polystyrene through chain-transfer reaction.

carboxyl, and amino groups because of the high activity of anions. This disadvantage could be overcome by using radical polymerization because of the significantly extended monomer compatibility. Therefore it might be feasible to prepare end-group functionalized polymers using radical chain-transfer reaction in free radical polymerization. With this perspective in mind, a widely used silane coupling agent [mercaptopropyltrimethoxysilane (MPS), was chosen as the chain-transfer agent in the radical polymerization of styrene and methyl methacrylate because it possesses a thiol group—a very effective chain-transfer group in radical polymerization[24–26]] and a trimethoxy silyl group that can be used as sticker group in self-assembly.[2] Thus the end silane functionalized polystyrene (PSt) and polymethylmethacrylate (PMMA) were prepared by chain-transfer and reinitiated polymerization (Scheme 1) of styrene (St) and methylmethacrylate (MMA) in the presence of MPS. The resulting silane-terminated PSt and PMMA were characterized by means of thickness and water contact angle measurements, gel-permeation chromatography (GPC), FTIR, and ^{1}H-NMR spectrometry. The assembly behavior of the resulting polymers on hydroxylated silicon wafer substrate was studied and the self-assembled ultrathin films characterized by means of X-ray photoelectron spectroscopy (XPS) and atomic force microscopy (AFM).

EXPERIMENTAL

Materials

MPS is a product from Aldrich (Milwaukee, WI) and was used as received. Styrene and methylmethacrylate were deinhibited by distilling in the presence of sodium hydride. AIBN was recrystallized three times in methanol and dried under vacuum at room temperature. All the solvents were dehydrated before use. Silicon wafers [Si(111)] were used as the substrate.

Polymerization

Monomer was polymerized using AIBN as the initiator in anhydrous toluene at 80°C for 30 min, in the presence of MPS as the chain-transfer agent. The polymerization conditions are listed in Tables I and II. The obtained polymer was precipitated in anhydrous petrol ether (for PMMA) or methanol (for PSt) and the reprecipitation runs were repeated three times to ensure the removal of unreacted monomer, initiator, MPS, and so forth. The purified samples were dried over vacuum at 50°C for 24 h. The conversion rate was estimated to be 10–20%.

Self-assembly

Silicon wafers were first rinsed with acetone ultrasonically and immersed in freshly prepared Piranha solution (3/7 v/v concentrated sulfuric acid and 30% hydroperoxide) for about 0.5 h. Then they were rinsed with ultraclean water and blow-dried with highly purified nitrogen before immersing in the toluene solution of silane-terminated polymer. The concentration of the silane-terminated polymer in toluene was maintained at 1 mg/mL. The bonding reaction was carried out at 70°C for 24 h. The silicon wafers coated with polymer film were extracted with CH_2Cl_2 to remove the unbonded polymer.

Characterization

The weight-averaged molecular weights of the silane-terminated PSt and PMMA were determined from the GPC patterns recorded on an HP-1100 gel-permeation

TABLE I
Preparation and Characterization of Silane-Terminated PSt

Run	M	S	I	$[M]/[S]/[I]$	M_n	M_w	D
1	0.05	0	0.0005	100/0/1	14724	20159	1.369
2	0.05	0.00025	0.0005	100/0.4/1	1760	2845	1.616
3	0.05	0.0005	0.0005	100/1/1	1062	2312	1.469
4	0.05	0.0025	0.0005	100/2/1	520	710	1.26
5	0.05	0.005	0.0005	100/4/1	—	—	—

TABLE II
Preparation and Characterization of Silane-Terminated PMMA[a]

Run	M	S	I	$[M]/[S]/[I]$	M_n	M_w	D
1	0.05	0	0.0005	100/0/1	43668	68127	1.56
2	0.05	0.00025	0.0005	100/0.4/1	20704	29593	1.43
3	0.05	0.0005	0.0005	100/1/1	12722	16284	1.28
4	0.05	0.0025	0.0005	100/2/1	6443	7983	1.23
5	0.05	0.005	0.0005	100/4/1	3521	4164	1.26

[a] M, monomer; S, chain-transfer agent; I, initiator; M_n, number-average molecular weight; M_w, weight-average molecular weight; D, polydispersity index.

chromatograph (Hewlett–Packard, Palo Alto, CA) equipped with Ultrastyragel column (7.8 × 300 mm) and a UV (for PSt) and differential refraction meter (for PMMA) detector, at a flow rate of tetrahydrofuran eluent of 0.8 mL/mL, with reference to that of polystyrene standards. The FTIR spectra of the synthetic polymer films were recorded on a Bio-Rad IR spectrometer (Bio-Rad, Hercules, CA) with 128 scans at a resolution of 4 cm^{-1}. The chemical states of the interesting elements in the self-assembled films of PSt and PMMA on Si(111) were determined on a PHI-5702 multifunctional X-ray photoelectron spectroscope (XPS), at a takeoff angle of 45° and with a resolution of ±0.2 eV, using Mg–K$_\alpha$ irradiation as the excitation source and the binding energy of contaminated carbon as reference (C$_{1s}$ at 284.6 eV). The morphologies of the self-assembled films were observed with a Shimadzu-5500 atomic force microscope (AFM; Shimadzu, Kyoto, Japan), using tapping mode scanning and Si$_3$N$_4$ tip. The static contact angles of water on the self-assembled films of end silane functionalized PSt and PMMA were measured on a CA-A contact angle meter at room temperature and a relative humidity of 50 ± 5%. The thickness of the self-assembled films was measured on a Gaertner L116C ellipsometer (Skokie, IL) with He–Ne laser (λ = 632.8 nm) and at a fixed incidence angle of 70°. The refractive indices were selected as 1.50 and 1.48 for PSt and PMMA, respectively, and used to calculate the film thickness. Five replicate measurements were carried out to determine the contact angles and film thickness and the averaged values of the replicate tests were cited in this article.

RESULTS AND DISCUSSION

Preparation and characterization of silane-terminated polystyrene

The chain-transfer process constitutes two continuous steps: transfer of thiyl hydrogen to the propagating radical chains followed by reinitiated polymerization, whereby a thiyl radical adds to a monomeric double bond.[25] Another characteristic of radical polymerization in the presence of a chain-transfer agent is the strong dependency of molecular weight on the molar

ratio of the chain-transfer agent to the monomer ($[S]/[M]$). Therefore, by using MPS as the chain-transfer agent, not only can we realize the functionalization of the polymer chain at one end by introducing trimethoxylsilyl group (CH$_3$O)$_3$Si– but we can also modify the molecular weight by changing the $[S]/[M]$ ratio.

Figure 1 illustrates the GPC traces of the PSt prepared with different $[S]/[M]$ values and constant initiator concentration. It can be seen that the eluent time increases with increasing $[S]/[M]$, which indicates that the molecular weight of the obtained polymer decreases with increasing $[S]/[M]$. This observation agrees well with the conventional regulation that thiol compounds belong to the group of high-efficiency chain-transfer agents. Therefore in the present work, MPS acts as both a molecular weight modifier and a carrier of the functional silane group. The molecular weight of PSt generated from the radical polymerization of St in the absence of MPS (concentration 0%) was determined to be 20,159, whereas no precipitate was found when the polymer solution was poured into an excessive amount of methanol at a $[S]/[M]$ ratio of 4%. In other words, the polymerization of St was significantly inhibited by the excess amount of MPS, because in this case the radical chain transfer occurred so frequently that it was impossible for the
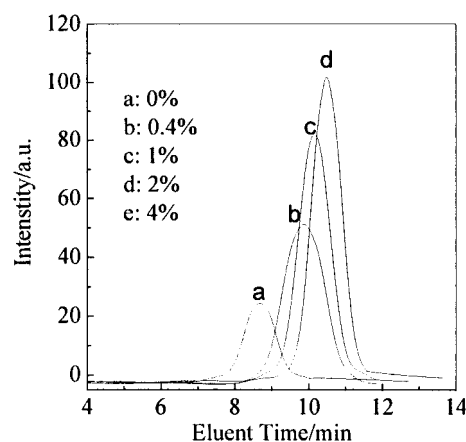

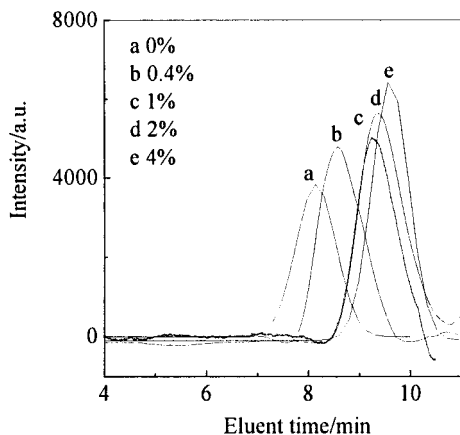**Figure 1** GPC eluent curves of PSt with different $[S]/[M]$ ratios.

Figure 2 GPC eluent curves of PMMA with different $[S]/[M]$ ratios.

Figure 3 $1/DP_n$ versus $[S]/[M]$.

chain to grow. Similar GPC curves for the polymerization of MMA under the same conditions are recorded in Figure 2, with the exception that the eluent time is shortened. The preparation and characterization of the silane-terminated PSt and PMMA are listed in Tables I and Table II, respectively. The silane functionalized PSt was also characterized by means of NMR and FTIR, as a reference. The chemical shifts at 3.04 and 7.02/7.26 ppm determined with NMR are attributed to the methoxyl hydrogen and acryl hydrogen, respectively, indicating the incorporation of trimethoxylsilyl groups in the polymer molecular chain. The apparent absorbance band at 1101 cm^{-1} for the two polymers determined with FTIR is identified as Si—O, which further confirms the successful silane termination of the polymers.

The polymerization degree can be expressed as

$$1/DP_n = k_t[R]/k_p[M] + C_s[S]/[M] + C_m + C_i + C_p$$

(1)

$$= k_t[R]/k_p[M] + C_s[S]/[M]$$

(2)

where k_t and k_p refer to the termination and propagation constants; C_s, C_m, C_i, and C_p are the chain-transfer constants of the chain-transfer agent, monomer, initiator, and polymer, respectively; and $[R]$, $[M]$, and $[S]$ refer to the concentration of radical, monomer, and chain-transfer agent. Because the chain-transfer constants of the initiator, monomer, solvent, and polymer
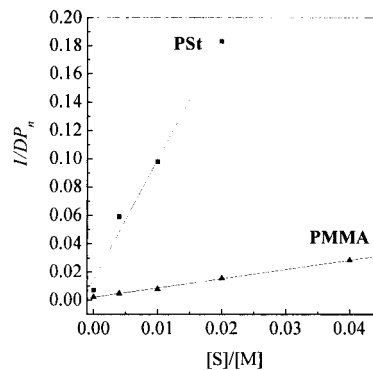
are so small and usually at a magnitude level of 10^{-4}, they can be neglected compared with those of thiol compounds.[26] Accordingly, the kinetic equation can be rewritten as in eq. (2), where $1/DP_n$ linearly corresponds to $[S]/[M]$ and the slope of the $1/DP_n$ versus $[S]/[M]$ line is just the chain-transfer constant C_s. Figure 3 shows the variation of $1/DP_n$ with $[S]/[M]$ for the polymerization of St and MMA. The C_s determined from the slope of the straight lines in Figure 3 is 8.48 and 0.67, respectively. St shows a much higher C_s than that of MMA, indicating that MPS is more effective as a chain-transfer agent for St than for MMA. The above observations conform to what was previously reported that the chain-transfer constants of mercaptobutane as the chain-transfer agent were 21 and 0.6, respectively, for the polymerization of St and MMA.[26]

Self-assembly

The self-assembly of the target silane-terminated polymers on a single crystal silicon wafer [Si(111)] is illustrated schematically in Scheme 2 using PSt as an example. The silicon wafers treated with Piranha solution were completely hydrophilic, with a water contact angle below 5°. Previous reports showed that the treated Si surface had a hydroxyl group density of 4–5 OH/nm^2 and might absorb a thin water layer of 2–5 molecules thick.[2] In the self-assembling process, the trimethoxysilyl radicals might be hydrolyzed in the presence of minor absorbed water and led to the formation of trihydroxysilyl-terminated polymer that could be condensed with the surface hydroxyl groups
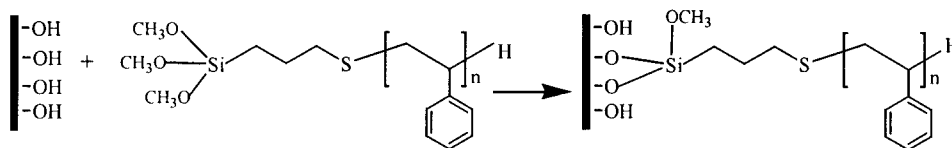
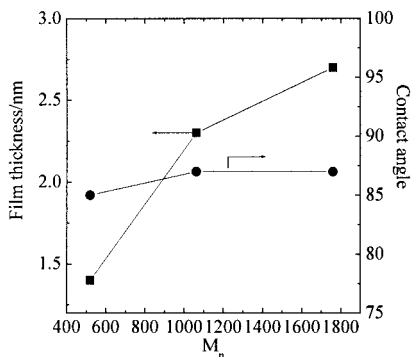**Scheme 2** Self-assembly of trimethoxysilane-terminated polystyrene on hydroxylated silicon wafer.

Figure 4 Film thickness and contact angle of PSt film versus number-averaged molecular weight.
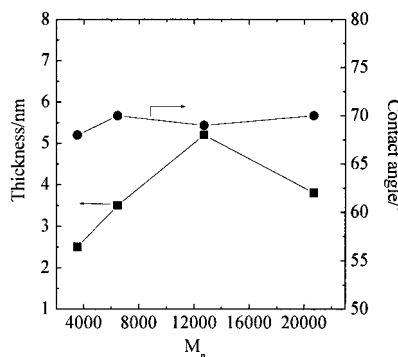

Figure 6 Film thickness and contact angle of PMMA film versus number-average molecular weight.

or condensed intermolecularly. Figure 4 shows the variation of the PSt film thickness versus the molecular weight. The thickness and water contact angle of the film roughly rise with increasing molecular weight of the silane functionalized PSt. For example, the film of PSt with a molecular weight of 520 is 1.5 nm thick and has a relatively smaller water contact angle, indicating that it might be incomplete. This is also confirmed by the magnified AFM image [Fig. 5(a)] of the film where inhomogeneous defects including pinholes and aggregations are visible. Contrary to the above, the self-assembled films of PSt with molecular weights of 1027 and 1702 are as thick as 2.4 and 2.7 nm, respectively, and show increased water contact angles similar to that of PSt film reported elsewhere.[27] The AFM image [Fig. 5(b)] of the self-assembled silane-terminated PSt film with a thickness of 2.4 nm shows that the film is characterized by homogeneous distribution of fine grains and has a root mean roughness as low as 0.5 nm.

Figure 6 shows the variation of contact angle and thickness of the silane-terminated PMMA film with the molecular weight. A similar phenomenon was observed as in the case for the PSt film, except that the

film of PMMA with a molecular weight of 20,704 is slightly thinner than the PSt counterpart. The films of the PMMA with molecular weights of 12,722, 6443, and 3521 are as thick as 5.2, 3.5, and 2.5 nm, respectively. The AFM images of the corresponding PMMA films [thickness of 5.2 and 2.5 nm; Fig. 7(a), (b), respectively] are smooth and constitute fine grains. Moreover, it is difficult to prepare the silane-terminated PSt and PMMA films of larger thickness, which could be related to the stereochemical structure of the polymers. In other words, the difficulty of obtaining thicker silane-terminated PSt and PMMA films is attributed to the relatively large molecular weights and low end-group concentrations in the polymers.

The self-assembled PSt and PMMA films were also justified by FTIR. Figure 8 gives the FTIR spectra of the self-assembled PSt film and the spin-cast PSt film as a control in a selected region between 2700 and 3200 cm^{-1}. The self-assembled PSt film shows an FTIR spectrum that is greatly coincident with that of the spin-cast PSt film. The absorbed bands at 2927 and 2852 cm^{-1} are assigned to the symmetric and asymmetric stretching vibration of C—H along the main chains of PSt, whereas those at 3001, 3026, 3058, and
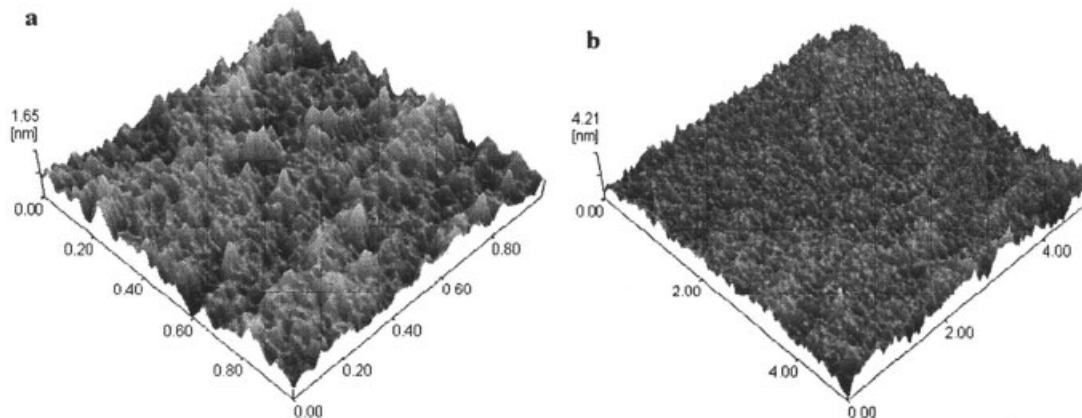

Figure 5 AFM morphology of (a) 1.5-nm and (b) 2.4-nm self-assembled PSt films.
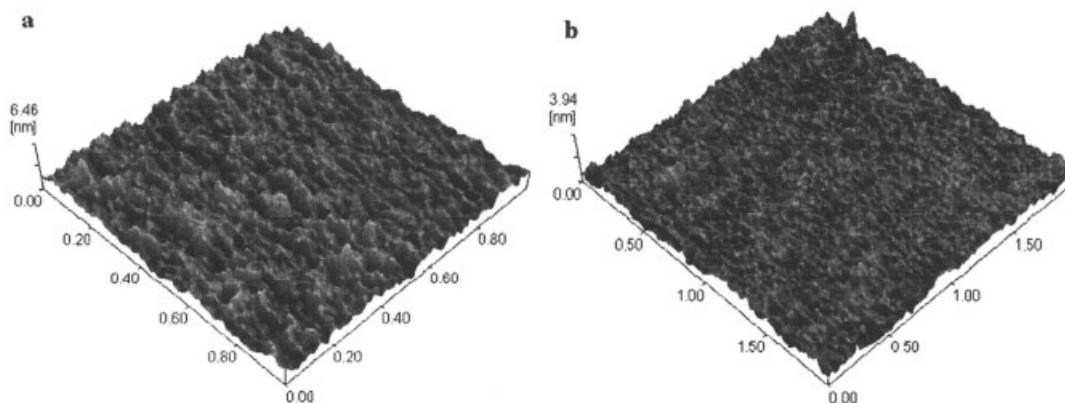
Figure 7 AFM morphology of self-assembled PMMA films of (a) 5.2 nm and (b) 2.4 nm.

3083 cm^{-1} are assigned to the stretching vibration of the aryl C—H. It should be noted that the polymer sample prepared in the absence of the chain-transfer agent cannot be grafted onto the silicon wafer and thus no FTIR absorbing band of C—H is visible in this case. The FTIR spectrum of PMMA film (2.5 nm thick; Fig. 9) gives the stretching vibration of carbonyl group at 1734 cm^{-1} and an apparent absorbance band within 2800–3000 cm^{-1}, which also confirms that the chain-transfer agent plays a key role in making it possible for the corresponding silane-terminated PMMA or PSt to be self-assembled on Si(111).

Figure 10 gives the XPS spectra of C_{1s} and Si_{2p} for bare silicon and PSt film (2.4 nm thick) and PMMA film (2.5 nm thick) on the silicon wafer. The C_{1s} signal of bare silicon is assigned to the unavoidable contaminated carbon. The self-assembled PMMA films of different thickness show C_{1s} signals of increased intensity, with the C_{1s} peaks corresponding to neutral, ether, and carbonyl carbons assigned at 285.0, 286.5, and 289.0 eV[7a], respectively. The Si_{2p} peaks at 103.0 and 98.6 eV are assigned to Si—O and Si—Si, respectively. The intensity of Si—Si for the bare silicon wafer

is larger than that of Si—O, indicating the existence of a very thin oxide layer on the Si wafer surface. After the self-assembly of PSt on the Si wafer, not only does the intensity of Si_{2p} decrease but also that of Si_{2p} assigned to Si—O exceeds that of Si_{2p} assigned to Si—Si. This further proves that the PSt layer has been successfully grafted onto the silicon wafer.

CONCLUSIONS

In summary, one of the widely used silane coupling agents, mercaptopropyltrimethoxysilane, was used as the chain-transfer agent in the radical polymerization of styrene and methylmethacrylate. The chain-transfer constants of MPS in the radical polymerization of styrene and methylmethacrylate were determined to be 8.48 and 0.67, respectively, from the slope of $1/DP_n$ versus $[S]/[M]$ lines. The resulting end silane functionalized PSt and PMMA were self-assembled onto silicon wafers to form an ultrathin polymer film. Results indicated that the chain-transfer agent played a key role in making it possible for the silane functionalized PSt and PMMA to self-assemble on the Si(111) and the film thickness was closely related to the molecular weights of the PSt and PMMA. It was easy and
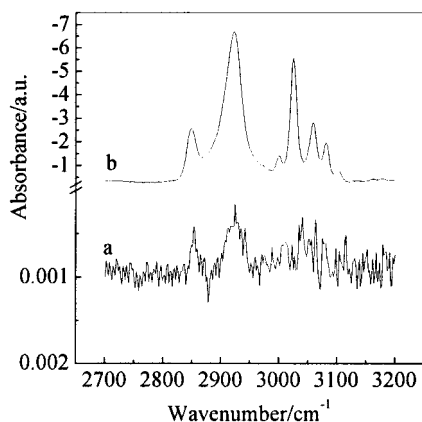

Figure 8 FTIR spectra in C—H absorbance region of (a) self-assembled PSt film and (b) spin-cast PSt film on KBr.
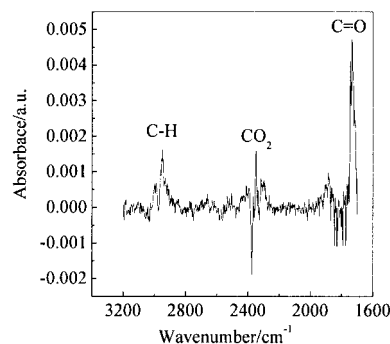

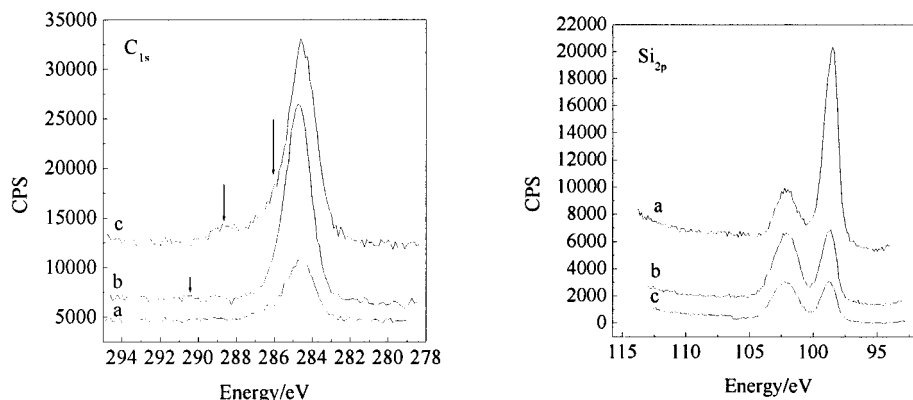**Figure 9** FTIR spectra of self-assembled PMMA film between 3200 and 1700 cm^{-1}.

Figure 10 XPS signals of C_{1s} and Si_{2p} for (a) bare silicon, (b) 2.4-nm PSt film, and (c) 2.5-nm PMMA film.

convenient to achieve the self-assembly of PSt and PMMA using the method in the present work, which could be versatile and extended to other monomers, especially to the functional monomers for the construction of functionalized nanothin film. The resultant surface-active monomers were expected to find potential application in lubricating nano/microelectromechanical systems and in fabricating biocompatible surfaces.

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