Covalent Graft Polymerization and Block Copolymerization Initiated by the Chlorinated SiO_2 (SiO_2-Cl) Moieties of Glass and Oriented Single Crystal Silicon Surfaces

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Received November 1, 2004
Revised Manuscript Received January 3, 2005

Introduction. The ability to manipulate and control the physicochemical properties of SiO_2 surfaces (e.g., glass, oxide-covered silicon, and silica surfaces) is of crucial importance in the fabrication of biochips and microarrays,[1−5] catalysis,[6−8] and analytical chemistry.[9−12] Modification of SiO_2 surfaces has traditionally been accomplished via reactions of organoalkoxysilanes, such as alkylchlorosilane, alkylalkoxysilane, and alkylaminosilane, with surface silanols (SiOH) to form the SiO−SiR bonds.[3,4,7−16] However, the resultant Si−O bonds that link the organic layers to the oxide surfaces are thermally labile and susceptible to hydrolytic cleavage.[6,17] Stable monolayers can be covalently attached to SiO_2 surfaces via robust Si−C bonds.[6,17,18] Tethering of polymer brushes on a solid substrate is an alternative and effective method for increasing the spatial density of functional groups on the substrate surface.[19−21]

Atom transfer radical polymerization (ATRP) is a recently developed "living" or "controlled" radical polymerization method.[22−24] It is possible to prepare well-defined polymer brushes on various substrates via surface-initiated ATRP.[19,20,25−27] In the preparation of polymer brushes, polymerization initiators were immobilized on the substrate surfaces, usually through coupling agents and functional intermediates in multistep processes. Although the bond energy (391 kJ/mol) of Si−Cl bond is larger than that (327 kJ/mol) of the C−Cl bond,[28] the Si−Cl surface is quite reactive and readily susceptible to hydrolysis.[28−30] This work shows that the chlorinated SiO_2 (SiO_2-Cl) surfaces are themselves effective macroinitiators for surface-initiated ATRP. Well-defined polymer brushes of methyl methacrylate (MMA) and (2-dimethylamino)ethyl methacrylate (DMAEMA), as well as their block copolymers with glycidyl methacrylate (GMA), have been tethered directly on glass slides and oxide-covered Si(100) substrates. This one-step surface-initiated ATRP using SiO_2-Cl moieties as the initiators for the formation of robust Si−C bonded polymer-SiO_2 hybrids is shown schematically in Scheme 1.

Experimental Section. Standard microscope slides and (100)-oriented single-crystal silicon wafers were sliced into 1.2 cm × 1.2 cm square chips. They were first treated with "piranha" solution (a mixture of 98 wt % concentrated sulfuric acid (70 vol %) and hydrogen peroxide (30 vol %)) for 24 h at room temperature.[4,5] After washing thoroughly with deionized water, the substrates were dried under reduced pressure. They were then immersed in a dry THF solution containing 1 vol % $SOCl_2$ and 0.1 vol % DMF for 4 h at room temperature to give rise to the SiO_2-Cl surfaces.[5] The substrates were then removed from the chlorination solution, washed with THF, and transferred to the ATRP reaction mixture. The SiO_2-*g*-P(MMA) and SiO_2-*g*-P(DMAEMA) hybrids were prepared as follows: 3.0 mL of MMA (or DMAEMA), 27.8 mg (or 17.8 mg) of CuCl, 7.5 mg (or 4.8 mg) of $CuCl_2$, and 117.1 μL (or 75.1 μL) of *N,N,N′,N″,N″*-pentamethyldiethylenetriamine (PMDETA) were introduced into 3 mL of dry DMF in a Pyrex tube containing the SiO_2-Cl substrate to give rise to a [monomer]:[CuCl]:[$CuCl_2$]:[PMDETA] molar ratio of 100:1:0.2:2. The reaction was allowed to proceed at 85 °C for 3 h. After the reaction, the polymer−SiO_2 hybrids were washed and extracted thoroughly with excess acetone (for the SiO_2-*g*-P(MMA) hybrids) and doubly distilled water and ethanol (for the SiO_2-*g*-P(DMAEMA) hybrids). The hybrids were subsequently immersed in a large volume of their respective solvent system for about 48 h to ensure the complete removal of the adhered and physically adsorbed polymers, if any. The solvents were stirred continuously and changed every 8 h. For the preparation of the P(MMA)-*b*-P(GMA) and P(DMAEMA)-*b*-P(GMA) copolymer brushes, the SiO_2-*g*-P(MMA) and SiO_2-*g*-P(DMAEMA) substrates were used instead of the SiO_2-Cl substrates. The reactions were carried out in DMF/water (1/1, v/v) at room temperature for 3 h. The washing/extraction procedures with excess acetone for the diblock copolymer brushes were similar to those described above. The chemical composition of the modified SiO_2 surfaces was determined by XPS. The static water contact angles were measured by the sessile drop method, using 3 μL water droplets, in a telescopic goniometer. The thickness of the polymer brushes was determined by ellipsometry.[26]

Results and Discussion. The SiO_2-Cl surfaces were prepared according to the method reported in the literature.[5] Clean glass slides and oxide-covered Si(100) substrates were exposed individually to the THF solution containing thionyl chloride (1 vol %) and DMF (0.1 vol %) for 4 h at room temperature to give rise to the $SiO_2-Cl(g)$ surfaces (for the glass slides) and the $SiO_2-Cl(w)$ surfaces (for the oxide-covered silicon wafers), respectively. Figure 1 shows the X-ray photoelectron spectroscopy (XPS) wide scan spectra of the $SiO_2-Cl(g)$ surface (part a) and the $SiO_2-Cl(w)$ surface (part b). A weak Cl 2p signal at the binding energy (BE) of about 200 eV, characteristic of covalently bonded Cl,[31] is discernible on each of the substrates, consistent with the presence of a chlorinated surface monolayer.

MMA and DMAEMA were selected as the model monomers for the preparation of the polymer−SiO_2 hybrids via surface-initiated ATRP. One of the unique characteristics of the polymers synthesized by ATRP is the preservation of active end groups during the polymerization process. To confirm the existence of "living" chain ends, a third functional monomer, GMA, was chosen for the synthesis of diblock copolymer brushes, using the MMA and DMAEMA homopolymer brushes as the macroinitiators (Scheme 1). We used the method of addition of Cu(II) complex ($CuCl_2$) to control the concentration of the deactivating Cu(II) complex[26] during the surface-initiated ATRP process on the SiO_2-Cl

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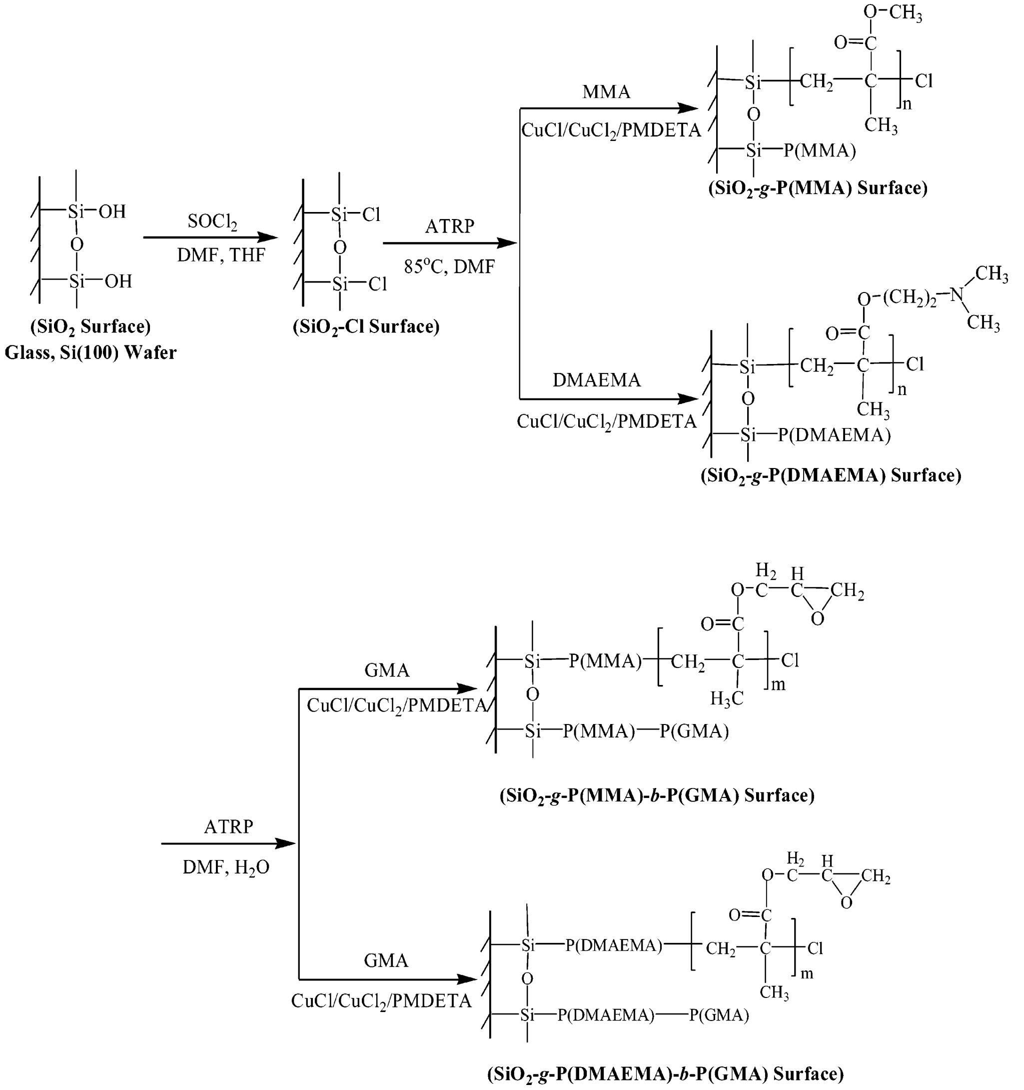
10.1021/ma0477605 CCC: $30.25

Scheme 1. Schematic Diagram Illustrating the Process of Surface-Initiated Atom Transfer Radical Polymerization (ATRP) from the Chlorinated SiO_2 (SiO_2-Cl) Surface (MMA = Methyl Methacrylate, DMAEMA = (2-Dimethylamino)ethyl Methacrylate, GMA = Glycidyl Methacrylate, and PMDETA = *N,N,N′,N″,N″*-Pentamethyldiethylenetriamine)



surface. The ratio of [monomer]:[CuCl (catalyst)]:[$CuCl_2$ (deactivator)]:[PMDETA (ligand)] was controlled at 100:1:0.2:2.

The presence of grafted MMA polymer (P(MMA)) and DMAEMA polymer (P(DMAEMA)) on the SiO_2−Cl surfaces was confirmed by XPS analysis and ellipsometry measurement. The corresponding glass slide surfaces after graft modification are referred to as the SiO_2-*g*-P(MMA)(g) and SiO_2-*g*-P(DMAEMA)(g) surfaces, while the corresponding silicon wafer surfaces as the SiO_2-*g*-P(MMA)(w) and SiO_2-*g*-P(DMAEMA)(w) surfaces. The C 1s core-level spectra (Figure 1c,d) of the SiO_2-*g*-P(MMA)(g,w) surfaces can be curve-fitted with three peak components with BE's at about 284.6, 286.2, and 288.4 eV, attributable to the *C*−H, *C*−O, and O=*C*−O species, respectively,[31] in an approximate area ratio of 3:1:1, consistent with the chemical structure of P(MMA). The wide scan spectra of the SiO_2-*g*-P(DMAEMA)(g,w) surfaces (Figure 1e,f) reveal the presence of C 1s, N 1s, and O 1s signals. The high-resolution N 1s spectra of both surfaces consisted predominately of a single peak component at the BE of about 399 eV, attributable to the neutral amine species[31] of P(DMAEMA). These results are consistent with successful graft polymerization of MMA and DMAEMA on the SiO_2 surfaces. The thicknesses of the grafted P(MMA) (for the SiO_2-*g*-P(MMA)(g,w) surfaces) and P(DMAEMA) (for the SiO_2-*g*-P(DMAEMA) (g,w) surfaces) brushes, obtained after 3 h of ATRP in dried DMF at 85 °C, are about 8, 7, 12, and 10 nm, respectively. Their corresponding surface graft densities were estimated to be about 44, 39, 46, and 38 equivalent monomer units/nm^2 (Table 1).

The static water contact angles of the glass and pristine (oxide-covered) Si(100) surfaces were about 20°. It is difficult to obtain a reliable static water contact angle for the SiO_2−Cl surface because of its susceptibility to hydrolysis.[28−30] In the presence of grafted P(MMA) and P(DMAEMA) brushes, the SiO_2 surfaces became more hydrophobic, and their contact angles were about 70° and 58°, respectively (Table 1).

The thickness of the grafted P(MMA) and P(DMAEMA) brushes on the SiO_2−Cl surfaces increases approximately linearly with polymerization time, as shown in Figure 2. This result suggests that the chain growth from the SiO_2−Cl surface is consistent with a “controlled” or “living” process. Control experiments on the pristine glass slide and oxide-covered Si(100) surfaces revealed no increase in organic layer thickness

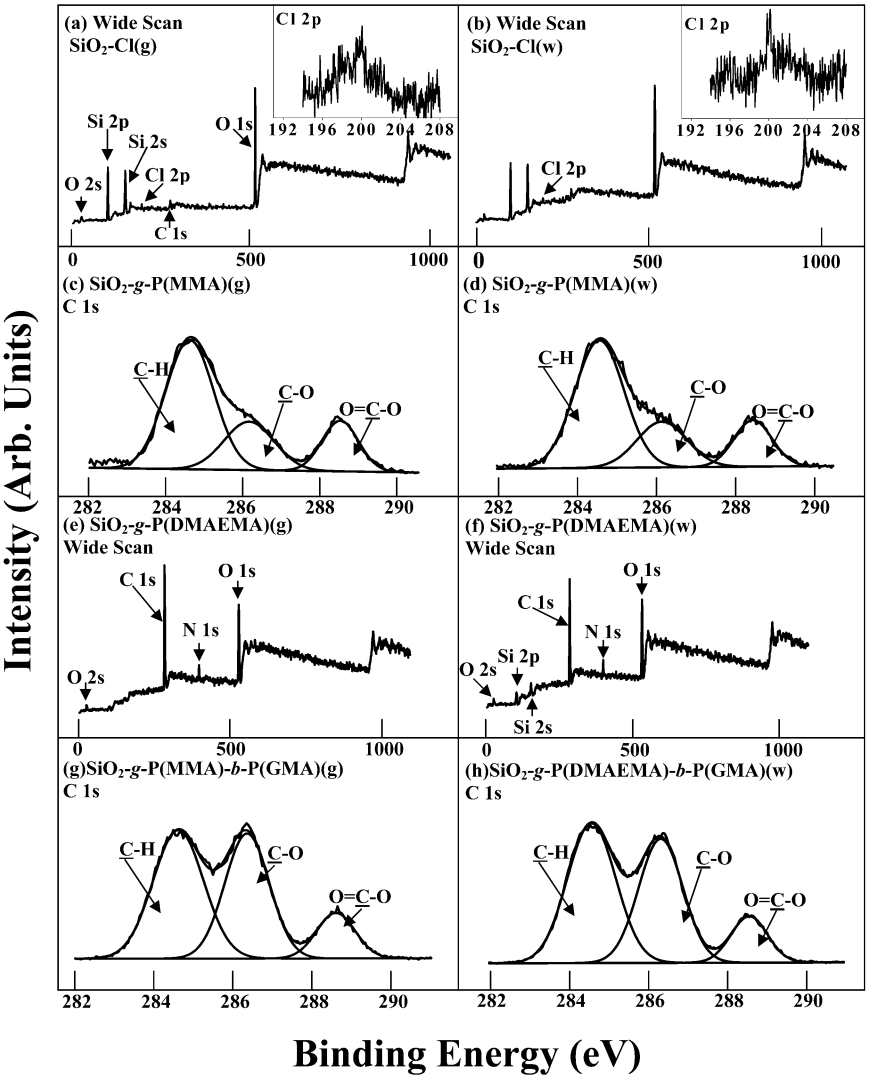


Figure 1. XPS wide scan spectra of the (a) SiO_2-Cl(g) and (b) SiO_2-Cl(w) surfaces, C 1s core-level spectra of the (c) SiO_2-*g*-P(MMA)(g) and (d) SiO_2-*g*-P(MMA)(w) surfaces, wide scan spectra of the (e) SiO_2-*g*-P(DMAEMA)(g) and (f) SiO_2-*g*-P(DMAEMA)(w) surfaces, and C 1s core-level spectra of the (g) SiO_2-*g*-P(MMA)-*b*-P(GMA)(w) and (h) SiO_2-*g*-P(DMAEMA)-*b*-P(GMA)(w) surfaces. (The reaction conditions for all the samples are given in Table 1.)

Table 1. Layer Thickness, Static Water Contact Angle, and Surface Polymer Density of the Polymer−SiO_2 Hybrids Prepared via Surface-Initiated Atom Transfer Radical Polymerization (ATRP) from the Chlorinated SiO_2 (SiO_2-Cl) Surfaces of Glass (g) or Si(100) Wafer (w)

sample	layer thickness (nm)	static contact angle (±3°)[c]	surface density[d] (monomer units/nm^2)
SiO_2-*g*-P(MMA)(g)[a]	8	71	44
SiO_2-*g*-P(MMA)(w)[a]	7	70	39
SiO_2-*g*-P(DMAEMA)(g)[a]	12	58	46
SiO_2-*g*-P(DMAEMA)(w)[a]	10	59	38
SiO_2-*g*-P(MMA)-*b*-P(GMA)(g)[b]	8 + 14	67	44 + 57
SiO_2-*g*-P(DMAEMA)-*b*-P(GMA)(w)[c]	10 + 11	68	38 + 45

[a] Reaction conditions: [monomer]:[CuCl]:[$CuCl_2$]:[PMDETA] = 100:1:0.2:2 in DMF at 85 °C for 3 h. MMA = methyl methacrylate, DMAEMA = 2-(dimethylamino)ethyl methacrylate, and PMDETA = *N,N,N′,N″,N″*-pentamethyldiethylenetriamine. [b] Surface-initiated ATRP of GMA from the SiO_2-*g*-P(MMA)(g) surface (P(MMA) thickness = 8 nm) or the SiO_2-*g*-P(DMAEMA)(w) surface (P(DMAEMA) thickness = 10 nm). Reaction conditions: [GMA]:[CuCl]: [$CuCl_2$]:[PMDETA] = 100:1:0.2:2 in DMF/water (1/1, v/v) at room temperature for 3 h. GMA = glycidyl methacrylate. [c] Static water contact angles for the oxide-covered Si(100) and glass surfaces are about 20°. It is difficult to obtain a reliable static water contact angle for the SiO_2-Cl surface because the Si−Cl bond is susceptible to hydrolysis. [d] Surface density = surface polymer coverage (film thickness × bulk density of the grafted polymer)/molecular weight of the monomer.

when the two non-chlorinated substrates were subjected to the “surface-initiated ATRP” of the two monomers under similar reaction conditions.

To confirm the existence of “living” chain ends, P(MMA)-*b*-P(GMA) and P(DMAEMA)-*b*-P(GMA)) diblock copolymer brushes were prepared from the corresponding SiO_2-*g*-P(MMA) and SiO_2-*g*-P(DMAEMA) surfaces, using the grafted P(MMA) (or P(DMAEMA)) brushes as the macroinitiators. After an ATRP time of 3 h in DMF/water (1/1, v/v) at room temperature, the C 1s core-level line shapes of the SiO_2-*g*-P(MMA)-*b*-P(GMA)(g) (Figure 1g) and SiO_2-*g*-P(DMAEMA)-*b*-P(GMA)(w) (Figure 1h) surfaces can be curve-fitted with three peak components at the BE’s of about 284.6, 286.2, and 288.5 eV, attributable to the *C*−H, *C*−O, and O−*C*=O species, respectively.[31] The three peak components have an

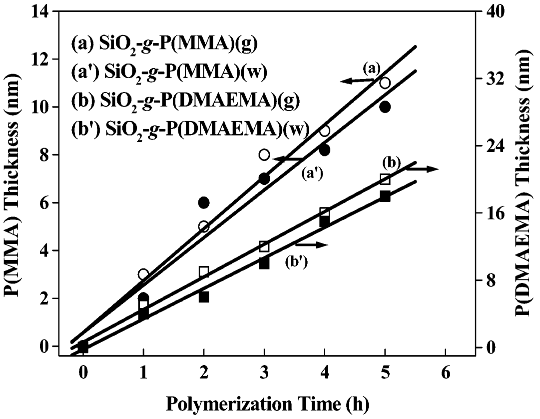


Figure 2. Dependence of the grafted polymer film thickness on the surface-initiated ATRP time for the (a) SiO$_2$-*g*-P(MMA)(g), (a′) SiO$_2$-*g*-P(MMA)(w), (b) SiO$_2$-*g*-P(DMAEMA)(g), and (b′) SiO$_2$-*g*-P(DMAEMA)(w) surfaces. Reaction conditions: [monomer]:[CuCl]:[CuCl$_2$]:[PMDETA] = 100:1:0.2:2 in dry DMF at 85 °C on chlorinated SiO$_2$ (SiO$_2$−Cl) surfaces of glass (g) or Si(100) wafer (w).

approximate area ratio of 3:3:1, consistent with the chemical structure of P(GMA). The thicknesses of the P(GMA) blocks on the glass slide and oxide-covered silicon(100) surfaces are about 14 and 11 nm, respectively, which are larger than the sampling depth of the XPS technique (~7 nm in an organic matrix[32]). The corresponding water contact angles of the two block copolymer surfaces are about 67° and 68° (Table 1), which are comparable to that of the P(GMA) homopolyer.[33] These results confirm that the dormant sites at the grafted P(MMA) and P(DMAEMA) chain ends on the SiO$_2$ surfaces have allowed reactivation during the subsequent block copolymerization process, resulting in the formation of the diblock copolymer brushes.

In summary, chlorinated SiO$_2$ surfaces of glass and Si(100) wafer are effective macroinitiators for surface-initiated ATRP. Well-defined polymer−glass and polymer−Si(100) hybrids, consisting of covalently tethered polymer brushes on SiO$_2$ surfaces of the substrates through robust Si−C bonds, were prepared directly via surface-initiated ATRP from the SiO$_2$−Cl surfaces. In addition to glass substrates and oxide-covered silicon wafers, the present technique should be readily applicable to a wide range of SiO$_2$ surfaces, such as silica surfaces.

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MA0477605