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Surface-initiated atom transfer radical polymerization of polyhedral oligomeric silsesquioxane (POSS) methacrylate from flat silicon wafer

Renxu Chen [a], Wei Feng [a], Shiping Zhu [a,*], Gianluigi Botton [a], Beng Ong [b], Yiliang Wu [b]

[a] *Department of Chemical Engineering, McMaster University, 1280 Main Street West, Hamilton, Ont., Canada L8S 4L7*
[b] *Materials Design and Integration Laboratory, Xerox Research Centre of Canada, Mississauga, Ont., Canada L5K 2L1*

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Abstract

A polyhedral oligomeric silsesquioxane (POSS) methacrylate monomer, i.e. 3-(3,5,7,9,11,13,15-heptacyclopentyl-pentacyclo [9.5.1.1.^{3,9}1.^{5,15}1^{7,13}]-octasiloxane-1-yl) propyl methacrylate (POSS-MA), was directly grafted from flat silicon wafers using surface-initiated atom transfer radical polymerization (ATRP). Two methods were used to improve the system livingness and control of polymer molecular weights. By 'adding free initiator' method, a linear relationship between the grafted poly(POSS-MA) layer thickness and monomer conversion was observed. By 'adding deactivator' method, the poly(POSS-MA) thickness increased linearly with reaction time. Poly(POSS-MA) layers up to 40 nm were obtained. The chemical compositions measured by X-ray photoelectron spectroscopy (XPS) agreed well with their theoretical values. Water contact angle measurements revealed that the grafted poly(POSS-MA) was extremely hydrophobic. The surface morphologies of the grafted polymer layers were studied by an atom force microscopy (AFM).

Keywords: Atom transfer radical polymerization (ATRP); Surface modification; Polyhedral Oligomeric Silsesquioxane (POSS)

1. Introduction

Polyhedral oligomeric silsesquioxane (POSS) is a cage-like silsesquioxane with an inner inorganic silicone $(SiO_{1.5})_x$ framework and eight external organic substituents. POSS particles have diameters from 1 to 3 nm and are considered to be the smallest possible particles of silica [1]. POSS particles with various organic substituents have been successfully synthesized [2–6]. These organic substituents can be either total hydrocarbons, or various functional groups. These organic substituents make the particles compatible with organic polymers and biologic systems, which open up a new way to incorporate inorganic silica particles into organic polymer systems.

Recently, POSS monomers that contain polymerizable functional groups have attracted a great attention for their potentials in preparing organic–inorganic hybrid systems. POSS monomers can be either homopolymerized or copolymerized with other monomers to develop a novel class of hybrid polymers. Studies have shown that POSS-containing polymers have excellent material properties, such as extremely high thermal stability, good oxidation resistance, and enhanced mechanical strength [7–10]. A variety of polymerization techniques have been used to prepare different kinds of hybrid polymers. In 1995, Lichtenhan et al. synthesized a methacrylate functionalized POSS monomer (POSS-MA) and (co)polymerized the monomer via conventional free radical polymerization [11]. Mather and Haddad prepared a series of random copolymers of norbornyl functionalized POSS with norborene by ring-opening metathesis polymerization (ROMP) [12]. Phillips et al. used condensation polymerization to prepare POSS-modified polyimide from POSS-containing dianiline [13]. Pyun and Matyjazewski synthesized POSS-MA polymers of low polydisperties (1.14) by atom transfer radical polymerization (ATRP). They also synthesized linear and star block copolymers of POSS-MA through a 'macro-initiator' approach [14,15].

Although there are many reports on the preparation and properties of POSS containing polymers, most investigations were focused on 'free' polymer systems. To the best of our knowledge, no work has been done to study POSS-containing polymer chains, which are covalently bonded to surfaces. In recent years, surface-initiated ATRP is well recognized as a very convenient method to prepare well-defined polymer brushes from surfaces. A variety of (meth)acrylic and styrenic

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* Corresponding author. Tel.: +1 905 525 1940; fax: +1 905 521 1350.
E-mail address: zhuship@mcmaster.ca (S. Zhu).

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monomers have been successfully grafted from various surfaces by surface-initiated ATRP, however, most of these monomers have small side groups. There is no work about grafting of monomers with rigid and bulky side groups, such as POSS monomers. In grafting polymer chains from a confined surface via surface-initiated ATRP, the size and rigidity of monomer side group have great effects on the grafting process. For example, the grafting density of tethered polymer chains, a key parameter for surface-initiated ATRP, decreases with increasing the size of monomer side group. Therefore, we made an effort to graft POSS monomers from various surfaces by surface-initiated ATRP and aimed to understand the effect of POSS side group on the grafting.

In this work, we report the polymerization of an *iso*-butyl substituted POSS-MA monomer from self-assembled monolayers (SAM) of ATRP initiators that are covalently immobilized on the flat silicon wafers. The grafted poly-(POSS-MA) films are characterized by ellipsometry, X-ray photoelectron spectroscopy (XPS), contact angle measurement, and atom force microscopy (AFM).

2. Experimental part

2.1. Materials

3-(3,5,7,9,11,13,15-Heptacyclopentyl-pentacyclo[9.5.1.1.^{3,9} 1.^{5,15}1^{7,13}]-octasiloxane-1-yl) propyl methacrylate (POSS-MA) was purchased from Hybrid Plastics Company, Fountain Valley, CA. Trichlorosilane (99%), 2-bromoisobutyryl bromide (98%), 10-undecen-1-ol (98%), 1,1,4,7,10,10-hexamethyltriethylenetetramine (HMTETA) (97%), ethyl 2-bromoisobutyrate (EBIB) (98%), hydrogen hexachloroplatinate (IV) hydrate (H_2PtCl_6, 99.9%), CuCl (99.999%), and $CuBr_2$ (99.999%) were supplied by Aldrich and were used as received. Toluene and tetrahydrofuran (both HPLC grade) were obtained from Caledon Laboratories Ltd. Toluene was distilled twice before use. Double-sided polished silicon wafers (P-doped, (100)-oriented, 10–20 Ω cm resistivity, 0.56-mm thickness) were supplied by University Wafer Company (Boston, MA) and cut into 5×5 mm^2 pieces using a Micro Ace Series 3 dicer (Loadpoint Ltd, England). Deionized water with a resistivity of 18 MΩ cm was prepared from a Millipore Milli-Q filtration system. Ultra-high-purity-grade argon was used in this study.

2.2. Synthesis of initiator

The surface-attachable initiator 11-(2-bromo-2-methyl) propionyloxy undecyl trichlorosilane was synthesized from 10-undecen-1-ol according to the published procedure [16]. ^{1}H NMR ($CDCl_3$, 200 MHz) δ 4.16 (t, 2H, OCH_2, $J=8.8$ Hz), 1.90 (s, 6H, CBr–CH_3), 1.27–1.74 (m, 20H, CH_2CH_2).

2.3. Preparation of initiator-functionalized silicon wafer

Si(100) wafers were washed with the 'piranha' solution (a mixture of 70 vol% concentrated sulphuric acid and 30 vol% hydrogen peroxide) to remove organic residues. The wafers were rinsed with copious amount of deionized water, dried in argon flow. The wafers were then immersed in HF solution to remove the native oxide film and placed into UV–ozone cleaner for 30 min to grow a uniform oxide film. The clean wafers were placed in a crystallizing dish to that a solution of initiator (15 μl) in dry toluene (15 ml) was added. Triethylamine (25 μl) was also added. The dish was covered and left at room temperature for 18 h. The wafers was then rinsed successively with toluene, acetone, methanol and then dried in an argon stream.

2.4. ATRP of POSS-MA from initiator-functionalized silicon wafer

A representative ATRP grafting run with an added amount of free initiator is as follows: initiator-functionalized silicon wafers were placed into glass tubes separately. These tubes, capped with rubber septa, were deoxygenated with argon for 10 mins POSS-MA (1.415 g, 1.50 mmol) and CuCl (9.9 mg, 0.10 mmol) were placed into a 10-ml flask that contained a magnetic stir bar. The flask was fitted with a rubber septum and purged with argon. Toluene (3.00 ml) and HMTETA (55.3 μl) were added to the flask via syringe (both were bubbled for 1 h with argon prior to the use). The mixture was stirred and degassed with argon until a homogeneous brown solution was formed (about 10 mins). The flask was kept at room temperature. EBiB initiator (14.4 μl, 0.10 mmol) was added into the mixture via syringe. The reaction mixture was homogenized by an intense agitation and quickly transferred into the prepared glass tubes that contained initiator-functionalized silicon wafers via a cannula. These tubes were placed into an oil bath of 50 °C. After desired periods of polymerization time, the tubes were sampled and unsealed. The silicon wafers were taken out from solution, rinsed with THF, cleaned ultrasonically for 2 h in THF, rinsed again with THF, and then dried in a nitrogen stream.

For a representative ATRP grafting run with an added excess amount of deactivator, $CuBr_2$ of 10 mol% with respect to CuCl was added at the beginning of polymerization, instead of free initiator EBiB. All the other procedures were the same as those in the 'adding free initiator' case.

3. Measurements and techniques

3.1. Ellipsometry

The polymer layer thicknesses on silicon wafers were determined by an Exacta 2000 ellipsometer (Waterloo Digital Electronics, Waterloo, ON, Canada) equipped with a He–Ne laser (632.8 nm) at a 70° incident angle. The optical constants (refractive index, extinction coefficient) of Si ($n=3.865$, $k=0.020$) and SiO_2 ($n=1.465$, $k=0$) were used to determine the SiO_2 layer thickness of the freshly cleaned silicon surfaces. The values of $n=1.5000$ and $k=0$ were used to calculate the thickness of the initiator-covered silicon wafers and $n=1.4000$

and $k=0$ for the polymer-covered substrates. The data were collected at three spots on each wafer sample.

3.2. X-ray photoelectron spectroscopy (XPS)

The surface compositions of silicon wafers were determined using a Leybold Max 200 XPS with an aluminum anode non-monochromatic source. Survey scans (0–1000 eV) were performed to identify constitutive elements. These scans were measured with a takeoff angle of 90°. Immediately prior to the measurement, the samples were rinsed with 1,1,2-trichlorotrifluoroethane to remove contaminants.

3.3. Nuclear magnetic resonance (NMR)

The monomer conversion in ATRP grafting in the added free initiator case was measured using a Bruker AC-P200 NMR spectrometer (200 MHz) in *d*-chloroform: $x=1-(I_{\delta=6.14(\mathrm{C}H2=\mathrm{CCH3})}+I_{\delta=5.57(\mathrm{C}H2=\mathrm{CCH3})})/(I_{\delta=0.74\sim 1.22(\mathrm{CH}CH3\text{-}iso\mathrm{butyl})}/42)$.

3.4. Water contact angle measurement

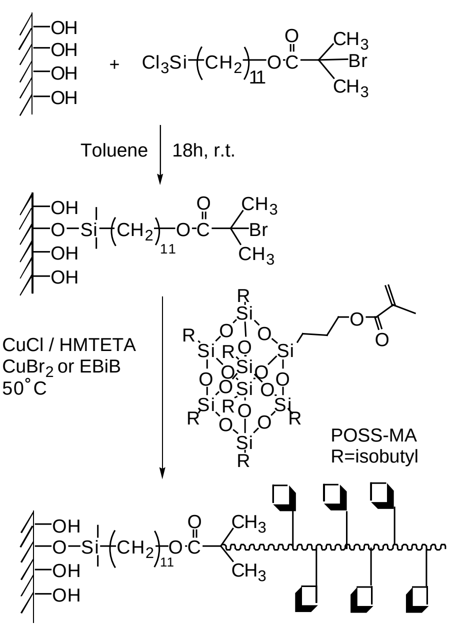
Water contact angles were measured using a Ramé-Hart NRL goniometer (Mountain Lakes, NJ). Silicon wafers were rinsed in methanol and dried in a nitrogen stream immediately prior to the measurement. Advancing and receding contact angles were measured using the sessile drop method.

3.5. Atom force microscopy (AFM)

AFM images were obtained using a NanoScope IIIa Multimode atomic force microscope (Digital Instruments, Inc.). The images were recorded with standard tips in tapping mode at a scan rate of 1.0 Hz. The root-mean-square (RMS) surface roughness was calculated from the roughness profiles.

4. Results and discussion

Scheme 1 shows the procedure for preparing the poly(POSS-MA) films by surface-initiated ATRP. First, ATRP initiators were immobilized on silicon wafers by the reaction of the initiator's trichlorosilane moieties with the surface hydroxy groups. The average thickness of the resulting initiator monolayer was 2.5 nm, as measured by ellipsometry at three different points on the surface. Fig. 1(a) shows the XPS survey spectrum of the initiator-functionalized silicon wafers with a take-off angle at 90°. The successful immobilization of the bromoester initiators on the surface was verified by the appearance of the peaks of C_{1s} (285 eV), O_{1s} (533 eV), Br_{3d} (71 eV). The advancing and receding water contact angles of the wafers were $78.0\pm1.5°$ and $67.5\pm1.8°$, respectively. These contact angles were much higher than the value of $<10°$ for the hydrophilic silicon wafer.



Scheme 1. Surface-initiated ATRP of POSS-MA.

4.1. ATRP grafting of POSS-MA with added free initiator

For surface-initiated ATRP, the limited number of initiator moieties on the surface cannot generate enough deactivator species required for ATRP system. In order to achieve good control of surface-initiated ATRP, additional free initiator or deactivator is added at the beginning of polymerization to assure an adequate deactivator concentration. In this work, we tried both approaches. In the added free initiator case, we run

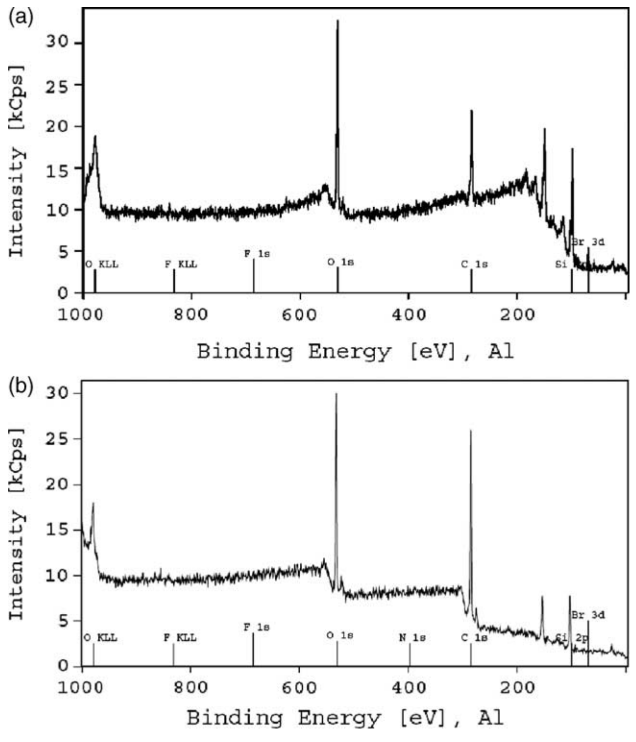


Fig. 1. XPS survey scans at a takeoff angle of 90°: (a) self-assembled initiator layer on silicon wafer; (b) a 33.0-nm-thick poly(POSS-MA) layer.

the polymerization targeting for two degrees of polymerization (DP), one was 15 POSS-MA units and the other was 30. The POSS-MA concentration and [EBiB]/[CuCl]/[HMTETA] molar ratio remained unchanged while the concentration of EBiB was varied to achieve different DPs.

Fig. 2(a) shows the development of poly(POSS-MA) thickness as a function of reaction time. The thickness increased as the polymerization proceeded. For the same period of reaction time, higher [POSS-MA]/[EBiB] ratios (i.e. lower [EBiB]) gave thicker layers. That was because lower [EBiB] generated fewer Cu(II) species in the solution, which resulted in higher reaction rates. Fig. 2(b) shows the grafted poly(POSS-MA) thickness on surface versus monomer conversion in solution. The linear thickness-conversion relationships were observed, suggesting that the polymerization was well controlled with the added free initiator. However, in the 'added free initiator' case, most monomer molecules were consumed by the free initiator in solution, which limited the amount of polymers grafted from the surfaces. Only 5 nm of poly(POSS-MA) layer was achieved at 80% monomer conversion for DP = 30 in Fig. 2(b).

We used the equation $\Gamma = d\rho/M_n$ to estimate the grafting density of poly(POSS-MA), [17] where d is the polymer layer thickness, ρ is the bulk density of poly(POSS-MA) (assumed 1.000 g/cm^3), and M_n is the number average molecular weight of grafted polymer. In general, it is challenging to characterize polymer chains grafted on surfaces, and molecular weights of 'free' polymers in solution are often used for approximation. In the case of poly(POSS-MA) that contains such bulky POSS side groups, an appropriate GPC calibration is also lacking. The hydrodynamic volume of poly(POSS-MA) could be very different from that of polystyrene standard of the same molecular weight [14]. We therefore used the theoretical M_n's in estimating the grafting densities. The estimated grafting densities were 0.18 chains/nm^2 for DP = 15 and 0.15 chains/nm^2 for DP = 30. These low densities are attributed to the large size of the POSS side groups, which imposed significant steric hindrance on the grafting process.

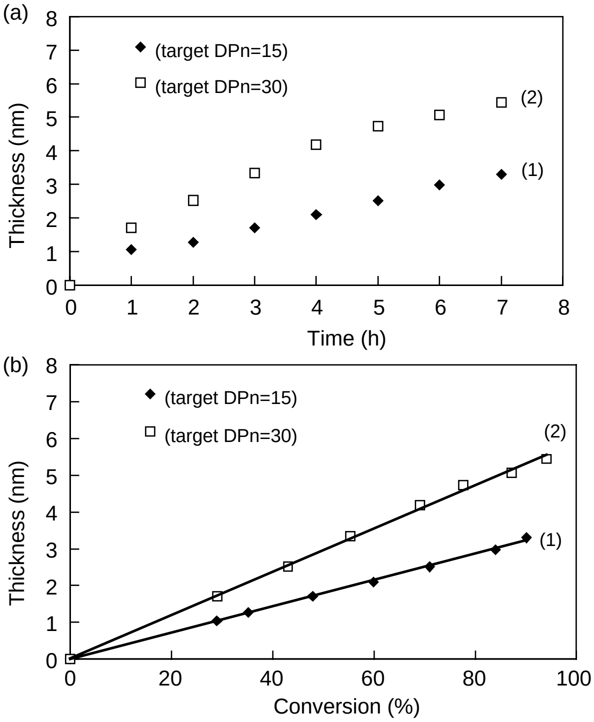


Fig. 2. Poly(POSS-MA) thickness versus (a) polymerization time and (b) monomer conversion with added free initiator. (1) [POSS-MA]/[CuCl]/[EBIB]/[HMTETA] = 15:1:1:2, (2) [POSS-MA]/[CuCl]/[EBIB]/[HMTETA] = 30:1:1:2. [POSS-MA] = 0.50 M. Solvent:toluene.

4.2. ATRP grafting of POSS-MA with added deactivator

The 'adding free initiator' approach did not produce thick poly(POSS-MA) layers. To overcome this drawback, the 'adding deactivator' approach was attempted. Fig. 3 shows the development of polymer layer thickness versus reaction time at different monomer concentrations. The thicknesses of grafted poly(POSS-MA) layers increased linearly with the reaction time, demonstrating good control over the grafting process with the added deactivator. In many surface-initiated ATRP cases, the growth rates of polymer thickness decrease with time because of radical termination. There appeared to be little termination in the grafting of POSS-MA. The reason for this might be that the bulkiness of POSS groups that prevent radicals approaching each other. For a given period of reaction time, the poly(POSS-MA) thickness increased with monomer concentration. With [POSS-MA] = 1.0 M, a poly-(POSS-MA) layer of more than 40 nm was achieved in 7 h. This result demonstrated the effectiveness of the 'adding deactivator' approach in preparing thick poly(POSS-MA) layers.

XPS was employed to elucidate the surface chemical compositions of the grafted poly(POSS-MA) films. Fig. 1(b) shows the survey spectrum of silicon wafer with 33 nm poly(POSS-MA) layer. The successful grafting of poly(POSS-MA) was confirmed by the high intensity of Si_{2p} at BE (binding energy) of 102 eV. The ratio of various elemental species was Si/C/O = 15.6:62.3:22.1, which was very close to the chemical composition of POSS-MA monomer (Si/C/O = 14.0:61.4:24.6). There was also a small peak of Br_{3d} in the

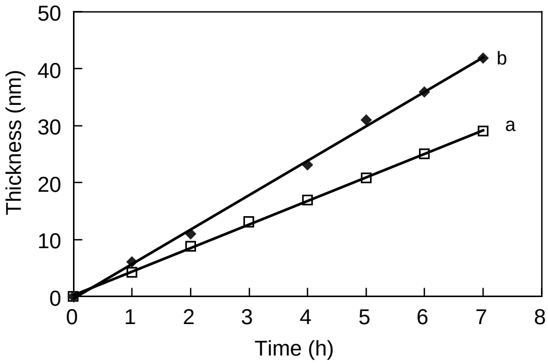


Fig. 3. Poly(POSS-MA) thickness versus polymerization time for different monomer concentrations with added excess deactivator. (a) [POSS-MA] = 0.50 M and (b) [POSS-MA] = 1.0 M. [POSS-MA]/[CuCl]/[CuBr$_2$]/[HMTETA] = 50:1:0.1:2.2. Solvent:toluene.

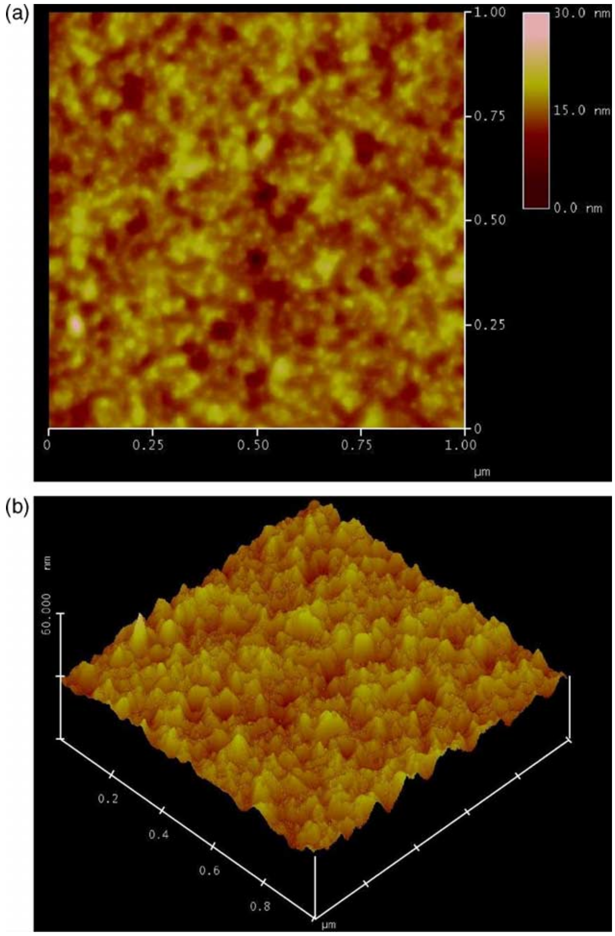


Fig. 4. AFM image of silicon wafer covered with 26.7 nm of poly(POSS-MA) (height scale 30 nm).

spectrum. This observation supported that the growth of poly(POSS-MA) from surface proceeded in a living manner. The water contact angles of the surface samples were also assessed. The advancing water contact angles were about 102.7±1.3°, demonstrating the hydrophobic nature of poly(POSS-MA). The receding water contact angles were about 92.5±2.3°. The contact angle hysteresis was comparable to that of the initiator monolayers, which were much smoother than the poly(POSS-MA) layers. A possible explanation is that the contact angle hysteresis is also affected by the chemical heterogeneity of the surface. For the initiator monolayers, both hydrophobic methyl and hydrophilic carboxylate groups are near the surface. When the surface was wetted with water, the hydrophobic groups pinned the motion of contact line as the liquid advanced and thus increased the contact angles. When water receded, the hydrophilic groups held back the draining motion of contact line and thus decreased the contact angle. In contrast, for poly(POSS-MA) layers, there were only hydrophobic isobutyl-POSS groups at the surface because of the large size of POSS. As a result, the surface had no holding effect on the receding of water drop.

The surface morphologies of poly(POSS-MA)-grafted silicon wafers were studied by an AFM. Fig. 4 shows the AFM image of a silicon wafer with 26.7 nm poly(POSS-MA) layer. The surface roughness was somewhat high (~1.61 nm). However, compared to the large size of POSS (average diameter of 1–3 nm), this roughness was still acceptable.

5. Conclusions

In summary, poly(POSS-MA) was successfully grafted from flat silicon wafer surfaces by surface-initiated ATRP. Two approaches were attempted and both gave good control over the ATRP grafting process. With the 'adding free initiator' approach, poly(POSS-MA) thickness increased linearly with monomer conversion. With the 'adding deactivator' approach, poly(POSS-MA) thickness increased linearly with reaction time. Poly(POSS-MA) layers of more than 40 nm thick were achieved. The surface chemical compositions studied by XPS agreed with their theoretical values. Water contact angle and AFM studies revealed that the grafted poly(POSS-MA) surfaces were smooth. The work provided a simple and effective approach to prepare well-defined POSS-containing polymer films from flat surfaces.

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