Synthesis of Cationic *N*-[3-(Dimethylamino)propyl]methacrylamide Brushes on Silicon Wafer via Surface-Initiated RAFT Polymerization

NERGIZ GURBUZ,[1] SERKAN DEMIRCI,[2] SERKAN YAVUZ,[1] TUNCER CAYKARA[1]

[1]Department of Chemistry, Faculty of Arts and Sciences, Gazi University, 06500 Besevler, Ankara, Turkey

[2]Department of Chemistry, Faculty of Arts and Sciences, Ahi Evran University, 40100 Aşık Paşa, Kırşehir, Turkey

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ABSTRACT: Surface-initiated reversible addition-fragmentation chain transfer (SI-RAFT) polymerization of *N*-[3-(dimethylamino)-propyl]methacrylamide (DMAPMA) on the silicon wafer was conducted in attempt to create controllable cationic polymer films. The RAFT agent-immobilized substrate was prepared by the silanization of hydroxyl groups on silicon wafer with 3-aminopropylthriethoxysilane (APTS) and by the amide reaction of amine groups of APTS with ester groups of 4-cyano-4-((thiobenzoyl) sulfanyl) pentanoic succinimide ester (CPSE); followed by the RAFT polymerization of DMAPMA using a "free" RAFT agent, that is, 4-cyanopentanoic acid dithiobenzoate (CPAD) and an initiator, that is, 4,4′-azobis-4-cyanopentanoic acid (CPA). The formation of homogeneous tethered poly(*N*-[3-(dimethylamino)-propyl]methacrylamide) [poly(DMAPMA)] brushes, whose thickness can be tuned by reaction time varying, is evidenced by using the combination of grazing angle attenuated total reflectance-Fourier transform infrared spectroscopy, X-ray photoelectron spectroscopy, atomic force microscopy, and water contact-angle measurements. The calculation of grafting parameters from the number-average molecular weight, $\overline{M}_n$ (g/mol) and ellipsometric thickness, *h* (nm) values indicated the synthesis of densely grafted poly(DMAPMA) films and allowed us to predict a polymerization time for forming a "brush-like" conformation for the chains. © 2010 Wiley Periodicals, Inc. J Polym Sci Part A: Polym Chem 49: 423–431, 2011

KEYWORDS: reversible addition-fragmentation chain transfer (RAFT); stimuli-sensitive polymers; surfaces

INTRODUCTION Polymer brushes consist of ordered assemblies of polymeric chains that are terminally grafted or adsorbed onto a substrate (polymer, gold, silicon, mica, etc.) surface at one or more anchoring points.[1–3] Anchoring of the polymeric chains in close proximity to each other results in high amounts of steric repulsion and chemical potential difference, which causes the free chain ends to "stretch" away from a collapsed or "mushroom" state on the surface to an extended or "brush-like" configuration. The change from the typical random walk configuration to the stretched shape of polymer brushes provides unique properties that are not observed in similar bulk systems.[1,2]

Generally, polymer brushes are prepared via two basic methods such as "grafting to" and "grafting from."[1,3–10] "Grafting to" involves the reaction of appropriate end-capped functional groups or side pendant groups in the polymers with surfaces. This method is simple, but the grafting density is fairly low because the diffusion of polymer chains to the surface of substrates is hindered sterically.[2,11] This limitation can be circumvented by the "grafting from" method, in which initiating groups are anchored onto the substrate surface followed by *in situ* polymerization. Because the diffusion of a small monomer molecule to activated initiator sites or growing polymer chains which are covalently attached to the surface are easier relatively, higher grafting density can be achieved. Moreover, the polymer brushes prepared by this method are thermally and solvolitically stable and have uniform film thickness.

The most widely used and versatile polymerization technique to prepare polymer brushes by the "grafting from" method are the various surface-initiated controlled living free radical polymerization (SI-CLRP) methods, such as atom transfer radical polymerization,[12–15] nitroxide-mediated polymerization,[16,17] and reversible addition-fragmentation chain transfer (RAFT) polymerization.[18–20] These surface-initiated polymerization techniques have received much attention because of their ability to provide simple and versatile routes for preparing well-defined, narrow polydispersity index (PDI) polymer brushes with both simple and complex architectures on a substrate surface. The main advantages of surface-initiated reversible addition-fragmentation chain transfer (SI-RAFT) polymerization when compared with other SI-CLRP techniques include the ability to polymerize a wide variety of monomers; polymerizations may be conducted over a wide range of temperatures; it allows for the preparation of polymer brushes with functional end groups.[21–24]

Correspondence to: T. Caykara (E-mail: caykara@gazi.edu.tr)
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The basic routes that are used to form polymer brushes utilizing SI-RAFT polymerization include utilization of a surface-bound initiator with free RAFT agent in solution and immobilization of the RAFT agent to a surface with free initiator in solution for subsequent polymerization. The first approach used was surface-immobilized initiators with the addition of free RAFT agent in solution to form polymer brushes via SI-RAFT polymerization.[25–29] The disadvantage of this approach is that for a well-defined SI-RAFT polymerization, all chains should be initiated at the same time via the free RAFT agent. Because of the fact that initiators dissociate and initiate chains over a wide temperature range, use of surface-bound initiators may lead to nonuniform films.[30,31] The most promising means of formation of high grafting density, uniform polymer brushes using SI-RAFT polymerization is via attachment of the RAFT agent, as it is truly a "grafting from" method.[32–34]

Although a number of cationic monomers or their nonionic precursors have been polymerized in solution by RAFT technique,[35–37] to our knowledge, no SI-RAFT polymerization of a (meth)acrylamido monomer bearing an amino group has been previously reported.

In this study, we detail the facile preparation of well-defined cationic poly(*N*-[3-(dimethylamino)propyl]methacrylamide) [poly(DMAPMA)] brushes directly in aqueous media utilizing the dithioester-immobilized silicon surface as RAFT agent. The resulting polymer brushes were analyzed by grazing angle-Fourier transform infrared spectroscopy (GA-FTIR), X-ray photoelectron spectroscopy (XPS), atomic force microscopy (AFM), and water contact-angle measurements.

EXPERIMENTAL

Materials

All chemicals were purchased from Aldrich at the highest available purity and used as received unless otherwise noted. CPA was recrystaliized from methanol. DMAPMA was distilled over calcium hydride immediately prior to polymerization.

Wafers Cleaning and Silane Treatment

The silicon (100) wafers (*n*-type, obtained from Shin-etsu, Handoutai, Japan; 3×1 cm^2) were ultrasonically cleaned for 5 min in succession with acetone, ethanol, and water and then etched with a 5% hydrofluoric acid solution. After being washed with deionized water, the silicon wafers were put into an ultrasonic bath of H_2SO_4:H_2O_2 (v/v: 70/30) for another 30 min. The wafers were then rinsed with a large amount of deionized water. The wafers were exposed in UV/ozone chamber (Irvine, CA: Model 42, Jelight Company) for 15 min prior to modification to remove hydrocarbon and produce a hydrophilic surface. The hydroxylated waters were exposed to a solution of 3-aminopropylthriethoxysilane (APTS; 1%, v/v) in dry toluene for 2 h at 60 °C. Afterward, the wafers were washed with toluene, dichloromethane in an ultrasonic bath, and dried in a vacuum.

Synthesis of RAFT Agent

4-Cyanopentanoic acid dithiobenzoate (CPAD) was synthesized according to the literature procedure[38] utilizing a small amount of acetic acid (0.5%, v/v) in the chromatographic eluent to enhance chromatographic resolution.

^{1}H (300 MHz, δ, ppm, $CDCl_3$): 1.95 (s. 3H, —CH_3), ~2.40–2.80 (m, 4H, —CH_2CH_2—), 7.40 (t, 2H, m-ArH), 7.59 (t, 1H, p-ArH), 7.91 (d, 2H, o-ArH).

Then the compound CPAD (10 mmol) and *N*-hydroxysuccinimide (10 mmol) were dissolved in 20 mL of anhydrous dichloromethane. After dicyclohexylcarbodiimide (10 mmol) was added to the solution, the mixture was stirred at 22 °C in the dark for 16 h. A white byproduct was filtrated out, and the filtrate was concentrated. The concentrated liquid was purified through a gel column with ethyl acetate:hexane (1:3, v/v) as eluent. Then, the CPSE was obtained.

^{1}H NMR (300 MHz, $CDCl_3$, δ, ppm,): 1.94 (s, 3H, —CH_3), ~2.30–2.75 (m, 4H, —CH_2CH_2—C(CN)—(CH_3)—), 2.84 (s, 4H, —OC—CH_2CH_2—CO—), 3.19 (m, 2H, —OC—CH_2CH_2—C(CN)—(CH_3)—), 7.40 (t, 2H, m-ArH), 7.58 (t, 1H, p-ArH), 7.90 (d, 2H, o-ArH).

Immobilization of the RAFT Agent on the Silicon Surface

The APTS-modified silicon wafers were introduced into the solution of CPSE (5.4 mmol) in 20 mL of anhydrous dichloromethane. The reaction mixture was left to react at 22 °C in the dark for 60 h. The silicon wafers were recovered from the reaction mixture and repeatedly washed with dichloromethane and acetone in an ultrasonic bath, and dried under a stream of nitrogen.

SI-RAFT Polymerization Procedure

The SI-RAFT polymerization of DMAPMA (10 mmol) was carried out in buffer (1.6 mL, pH = 5.0, 0.27 mol/L acetic acid, and 0.73 mol/L sodium acetate), initiator CPA (0.01 mmol), and free RAFT agent CPAD (0.08 mmol) at 0 °C in a glass reactor, which was designed to hold six RAFT agent-immobilized silicon wafers oriented normal to the base of the reactor. To ensure smooth stirring and prevent damage to the surfaces of the substrates, we isolated the magnetic stirring bar at the center of device from the slides by a 1-cm-high glass O-ring. The solution was diluted to 10-mL volume with the buffer solution and degassed by purging with nitrogen for 20 min. The polymerization reaction was stirred vigorously at 70 °C, and from time to time, small samples (~2 mL) were removed with a syringe. The molecular weight distribution of the polymer was measured by gel permeation chromatography (GPC). For ellipsometric measurements, samples were also removed from the reactor at different times and washed with the buffer solution and ethanol in an ultrasonic bath. The slides were dried with N_2, and the ellipsometric thicknesses of the dry polymer films were measured at three different spots on each sample and averaged.

Characterization

GA-FTIR spectra of the polymer brushes on silicon wafer were collected utilizing a Harrick Scientific GA-FTIR attachment coupled with a Thermo Nicolet 6700 spectrometer, collecting 128 sample scans, and utilizing Nicolet's OMNIC software. XPS spectra were recorded on a SPECS ESCA 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 aliphatic C 1s component at a binding energy of 285.0 eV. The water contact-angle measurements were conducted at room temperature using a goniometer (DSA 100, Krüss) equipped with a microliter syringe. Deionized water (5 μL, 18 MΩ cm resistivity) was used as the wetting liquid. The morphology of the surfaces was recorded on an AFM (Park Systems XE70 SPM Controller LSF-100 HS). A triangular-shaped Si_3N_4 cantilever with integrated tips (Olympus) was used to acquire the images in the noncontact mode. The normal spring constant of the cantilever was 0.02 N/m. The force between the tip and the sample was 0.87 nN. Ellipsometry measurements were conducted in ambient conditions using an ellipsometer (model DRE, EL X20C) equipped with a He–Ne laser ($\lambda = 632.8$ nm) at a constant incident angle of 75°. The average dry thickness of poly(DMAPMA) films on silicon wafer was determined by fitting the data with a three-layer model [native silicon (refractive index, $n = 3.86$) + silicon oxide layer ($n = 1.46$) + organic layer ($n = 1.47$)].[39] The molecular weight of the free polymer, relative to poly(ethylene glycol) standards, was determined by Waters Breeze model GPC, using Waters 2000-1000-500 hydrogel columns, Waters Refractive Index detector RI 2412, and 1 wt % acetic acid/0.1 M $Na_2SO_{4(aq)}$ as the eluent at a flow rate of 0.3 mL/min.

Grafting parameters, including grafting density, σ (chain per nm^2), and average distance between grafting sites, D (nm), were calculated from the ellipsometric thickness, h (nm), using eqs 1–3[40]

$$\sigma = \frac{h\rho N_A \times 10^{-21}}{\overline{M}_n} \tag{1}$$

$$D = \left(\frac{4}{\pi\sigma}\right)^{1/2} \tag{2}$$

where ρ (1.27 g/cm^3) is the density of dry poly(DMAPMA) film,[41] N_A is Avogadro's number, and $\overline{M}_n$ the number-average molecular weight of the grafted polymer chains, which is assumed to be similar to that of the free polymer in solution. The expected poly(DMAPMA) chain conformation in ambient conditions was deduced from the comparison of D with the corresponding Flory radius ($R_{F,coll.}$) of the collapsed chains calculated from eq 3[42]

$$R_{F,coll.} = b\overline{DP}_n^{1/3} \tag{3}$$

where $\overline{DP}_n$ is the number-average degree of polymerization and b is the effective segment length (assumed to be 0.3 nm for DMAPMA monomer).

RESULTS AND DISCUSSION

Immobilization of CPAD on Silicon Wafer

Ability of APTS to form dense and ordered monolayers on a silicon substrate extensively described in the literature.[43,44] In this study, the covalent attachment of CPAD on silicon surface was achieved by a two-step method. First, APTS self-assembled monolayer with NH_2 groups exposed outside served as adhesive layers. Then, CPSE molecules were chemically adsorbed on NH_2 groups of APTS to form a CPAD overlayer. Attachment of groups at every modification steps was confirmed with GA-FTIR (Fig. 1), XPS (Fig. 2, Table 1), ellipsometry (Table 2), AFM (Fig. 3), and contact-angle (Fig. 3) measurements. The presence of APTS on the silicon surface was confirmed by the presence of peaks at ~2920 and 2970 cm^{-1}, which are assigned to CH_2 stretching and C—H stretching vibrations, respectively [Fig. 1(A)]. XPS analysis of the APTS monolayer [Fig. 2(A), Table 1] verifies the presence of oxygen (O 1s), carbon (C 1s), and nitrogen (N 1s). There is a small amount of variation in the atomic ratio of C to O (C/O = 0.87) in comparison with the expected theoretical value (C/O = 1.0). This was mainly assigned to sample contamination (by atmospheric gases and organic dusts), as it could also be observed for hydroxylated silicon (presence of C and O). The N 1s peak, shown in Figure 2(A), has two peaks centered at 400.0 and 401.1 eV, also indicating the presence of APTS molecules on the substrate. The peak at 400.0 eV was assigned to the nitrogen in the free —NH_2 groups and that at the higher binding energy was taken to indicate hydrogen-bonded amine or positively charged quaternary nitrogen of the form $-\overset{+}{N}H_3$.[45,46]

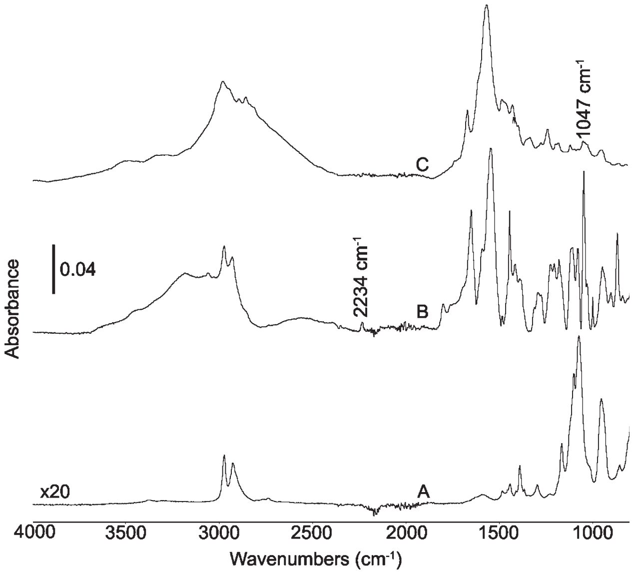


FIGURE 1 GA-FTIR spectra of (A) APTS-modified silicon and (B) RAFT agent-immobilized silicon (C) poly(DMAPMA) brushes synthesized for 10 h.

In the next modification step, the CPSE is attached to the APTS layer. CPAD immobilization was apparent from the appearance of amide I band at 1650 cm^{-1} (C=O stretching vibration) and amide II band at 1550 cm^{-1} (N—H bending and C—N stretching vibrations) in the GA-FTIR spectrum [Fig. 1(B)]. The peaks for C≡N stretch at 2234 cm^{-1} and C=S stretch at 1047 cm^{-1}, further confirmed successful covalent coupling of the CPAD on the APTS layer. The core level XPS spectra of CPAD overlayer consist of O 1s, N 1s, and C 1s peaks curve fitted into the components with binding energies at about 532.3 eV (C=O) for O 1s, 400.8 eV (N—C, N≡C) for N 1s, and 287.1 eV (C=O), 286.2 eV (C—N), 285.6 eV (C—S), and 285.0 eV (C—C/C—H) for C 1s. The immobilization of CPAD onto APTS layer was also confirmed from the appearance of a S 2p peak curve fitted into two

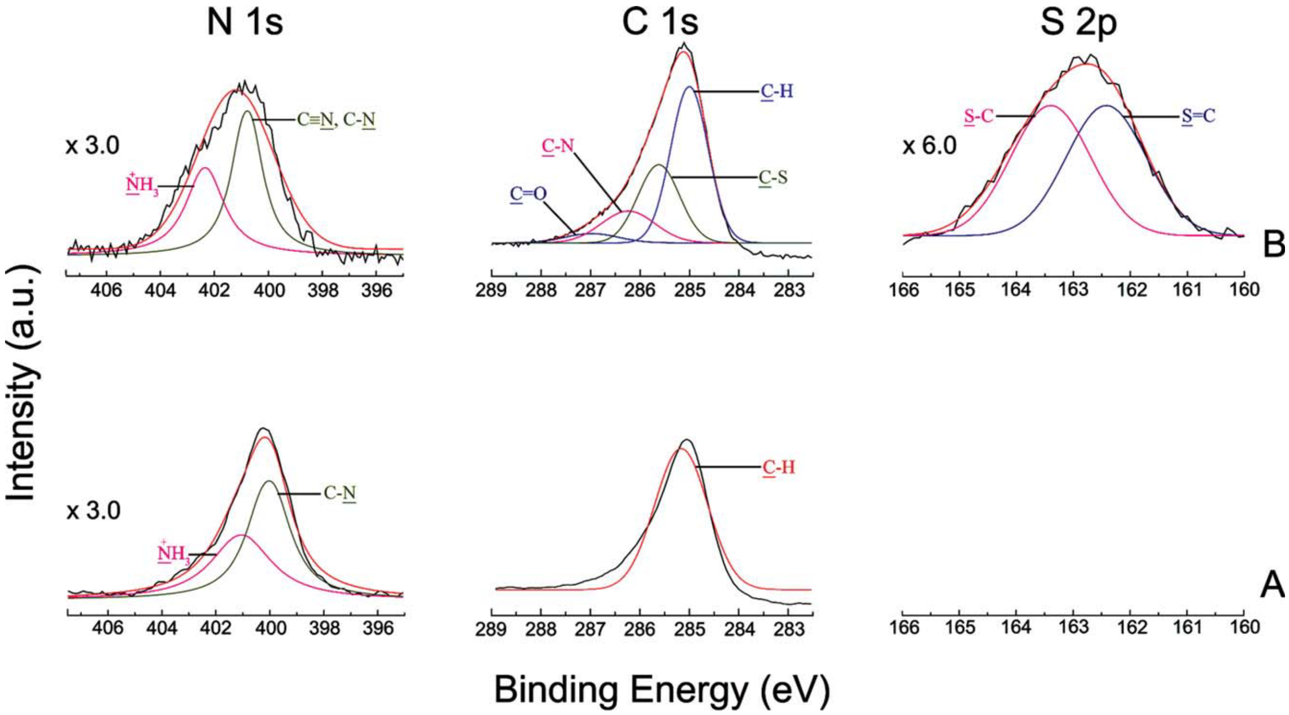


FIGURE 2 N 1s, C 1s, and S 2s core level XPS spectra recorded for (A) APTS-modified silicon and (B) RAFT agent-immobilized silicon. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

components with binding energies at about 163.4 eV (C—S) and 162.4 eV (C=S). The thicknesses of APTS and CPAD layers were measured by ellipsometry at 0.6 ± 0.2 nm and 1.5 ± 0.4 nm, respectively, these values are consistent with literature data.[43,44,47] Surface morphologies and cross sections of silicon substrate after APTS and CPAD immobilizations are shown in Figure 3. Analysis of APTS monolayer indicated a root-mean-square (RMS) roughness of 0.3 nm, whereas a significant RMS increase (RMS ∼ 1.4 nm) could be measured after immobilization with CPAD. Finally, as illustrated by inset images in Figure 3, the immobilization of reactive CPAD induced a drastic change in surface wettability characterized

TABLE 1 Atomic Concentrations and Binding Energies Given High-Resolution XPS for APTS-Modified Silicon, CPAD Immobilized Silicon, and Poly(DMAPMA) Brushes[a] Synthesized for Three Different Times

	O 1s	N 1s			C 1s			S 2p		
Samples	C=$\underline{O}$	C—$\underline{N}^+$	C—$\underline{N}$	$\underline{C}$=O	$\underline{C}$—N	$\underline{C}$—S	$\underline{C}$—C	C—$\underline{S}$	C=$\underline{S}$	Si 2p
APTS layer										
Energy (eV)	–	401.1	400.0	–	–	–	285.0	–	–	108.0
Conc. (%)	38.7	14.6			33.5			–		13.2
CPAD layer										
Energy (eV)	532.3	402.4	400.8	287.1	286.2	285.6	285.0	163.4	162.4	108.0
Conc. (%)	17.4	9.1			59.4			8.3		5.8
Polymer, 2 h										
Energy (eV)	532.4	402.3	400.8	287.2	286.1	285.5	285.0	163.4	162.7	108.0
Conc. (%)	9.3	17.4			72.6			0.5		0.2
Polymer, 6 h										
Energy (eV)	532.2	402.3	400.8	287.2	286.1	285.4	285.0	163.4	162.6	–
Conc. (%)	9.1	17.6			72.9			04.		–
Polymer, 10 h										
Energy (eV)	532.2	402.2	400.9	287.0	286.2	285.7	285.0	163.4	162.7	–
Conc. (%)	8.8	17.7			73.3			0.2		–

[a] Binding energies are calibrated to aliphatic carbon at 285 eV.

TABLE 2 Grafting Parameters Calculated for APTS-Modified Silicon, CPAD Immobilized Silicon, and Poly(DMAPMA) Brushes[a] Synthesized for Three Different Times

Samples	h (nm)	σ (chains per nm^2)	D (nm)	$R_{F,coll.}$ (nm)	$D/2R_{F,coll.}$
APTS layer	0.6 ± 0.2	3.96	0.57	–	–
CPAD layer	1.5 ± 0.4	2.46	0.72	–	–
Poly(DMAPMA), 2 h	6.0 ± 1.0	0.55	1.52	1.07	0.71
Poly(DMAPMA), 6 h	10.0 ± 1.2	0.62	1.43	1.24	0.58
Poly(DMAPMA), 10 h	19.3 ± 2.0	0.77	1.29	1.44	0.45

[a] h is the dry poly(DMAPMA) film thickness measured by ellipsometry, σ is the grafting density calculated from eq 1, D is the average distance between grafted chains deduced from eq 2, and $R_{F,coll.}$ is the Flory radius of a collapsed chain calculated from eq 3.

by a large decrease of static water contact-angle from 68.4 ± 0.4° (APTS monolayer) to 58.9 ± 0.2° (CPAD overlayer).

Formation of Cationic Poly(DMAPMA) Brushes on Silicon Substrates via SI-RAFT

As mentioned in the Introduction, the SI-RAFT process has been described for the preparation of polymer brushes on silicon substrates modified with RAFT agents. This method provided higher grafting densities compared with coupling reactions performed via "grafting to" method in solution, as excluded volume interactions, which restrict surface accessibility for polymer chains, are screened out in the SI-RAFT polymerization. An illustration of immobilization of RAFT agent onto silicon substrate modified with APTS and

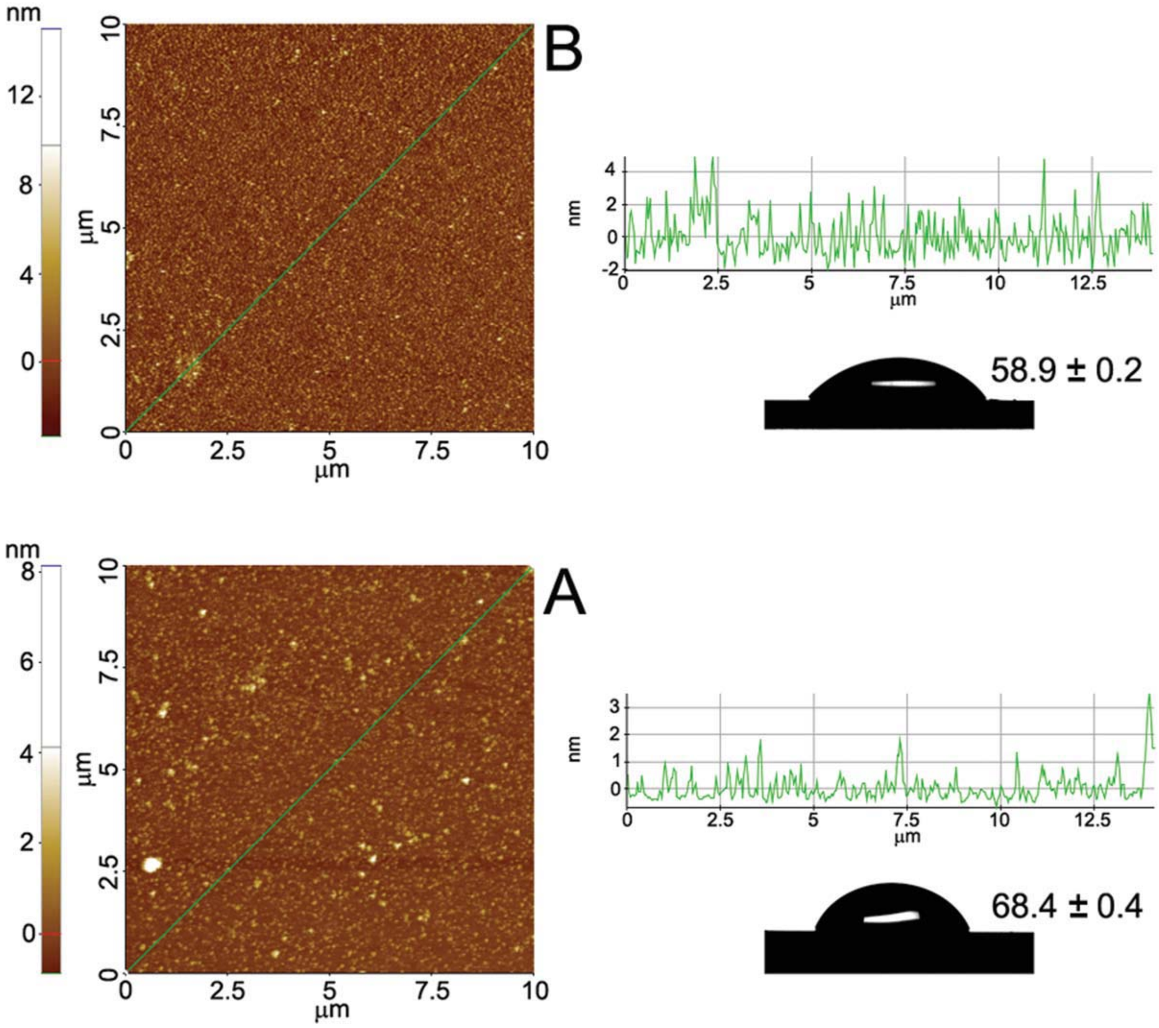
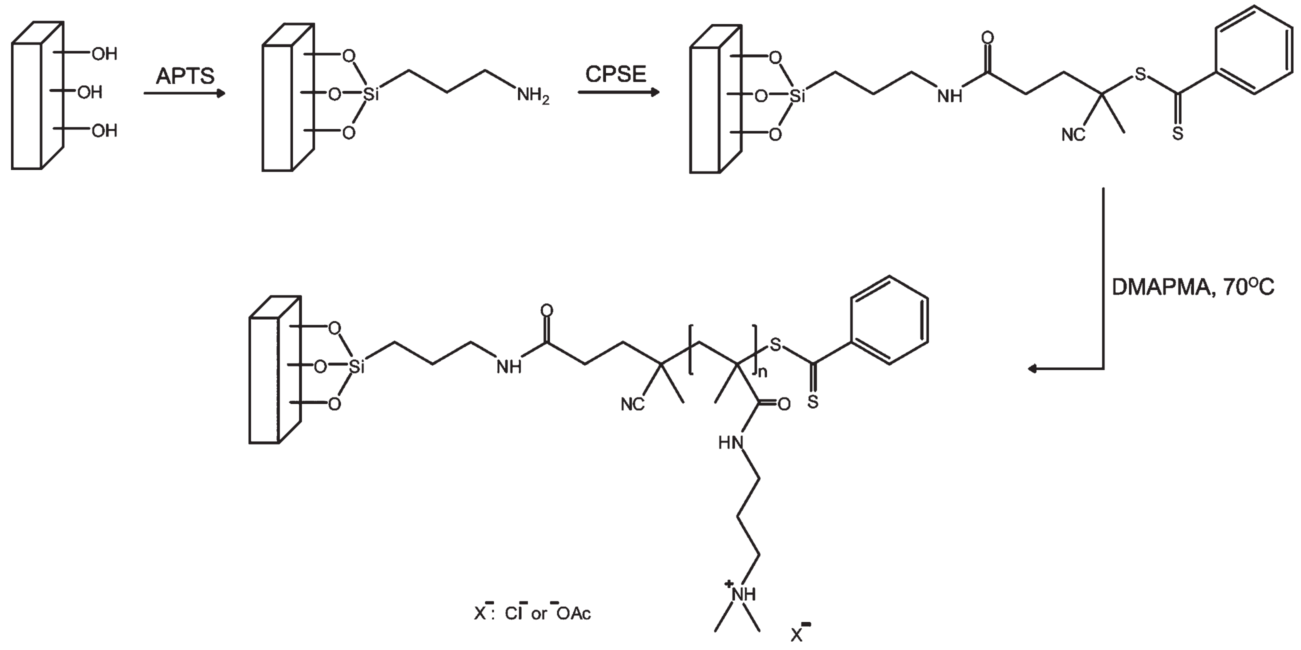


FIGURE 3 Topography of AFM images in ambient conditions, surface cross-sectional analysis, and static contact angle for (A) APTS-modified silicon (RMS = 0.3 nm) and (B) RAFT agent-immobilized silicon (RMS = 1.4 nm).



SCHEME 1 The immobilization of RAFT agent onto silicon surface and the RAFT-mediated synthesis of poly(DMAPMA) brushes.

subsequent RAFT polymerization to form cationic poly(DMAPMA) brushes is shown in Scheme 1. In this study, SI-RAFT polymerization of DMAPMA from the RAFT agent-immobilized silicon surface was accomplished in the presence of CPAD as a free RAFT agent. It has been reported that the addition of sacrificial or free RAFT agent is required to render the system heterogeneous and slow down the reaction activity.[48] Moreover, introduction of free RAFT agent allows for formation of free polymer in solution, the properties of which have been shown to correlate with the polymer attached to the surface. As insufficient amount of polymer can be degrafted from silicon surfaces for characterization, free polymer can be analyzed to provide an approximation of the molecular weight properties of the immobilized chains. Because of possible entanglement of the free polymer with immobilized chains, all samples were extracted in buffer solutions for 24 h to remove any untethered polymer chains from the surface. Therefore, it is assumed that the molecular weights of the free and grafted polymer chains are similar in our study. The time evolution of the number-average molecular weight, $\overline{M}_n$, and PDI was obtained for free polymer chains by GPC analysis. Typical GPC traces of poly(DMAPMA) chains with the increase of polymerization time are shown in Figure 4. We can clearly observe that the elution peaks shift to higher molecular weight with the increase of polymerization time. After 10 h, the monomer conversion is ~87%; GPC analysis of the poly(DMAPMA) chains reveals a number-average molecular weight, $\overline{M}_n$, of 19,200 g/mol and a PDI of 1.10. The GPC elution peak of poly(DMAPMA) exhibits a discernible tailing at the lower molecular weight side, probably because of premature chain termination during polymerization.

When the silicon surface was grafted with a poly(DMAPMA) layer, the static water contact-angle of the surface had decreased substantially to about 49.2 ± 0.2°, consistent with the hydrophilic nature of poly(DMAPMA). Ellipsometry indicated an increase in thickness from 6.0 ± 1.0 to 19.3 ± 2.0 nm with polymerization time. For these surfaces, grafting parameters, including grafting density, σ (chain per nm^2) and average distance between grafting sites, D (nm), were calculated from dry ellipsometric thicknesses using eqs 1 and 2 given in the Experimental Section. The calculations were conducted by assuming bulk behavior for the polymer films, which is a reasonable estimation considering both the grafting homogeneity and the collapsed state of dry poly(DMAPMA) chains in air. Indicative values of grafting parameters, as well as Flory radius $R_{F,coll.}$ of a collapsed chain calculated from eq 3 are reported in Table 2. Depending on

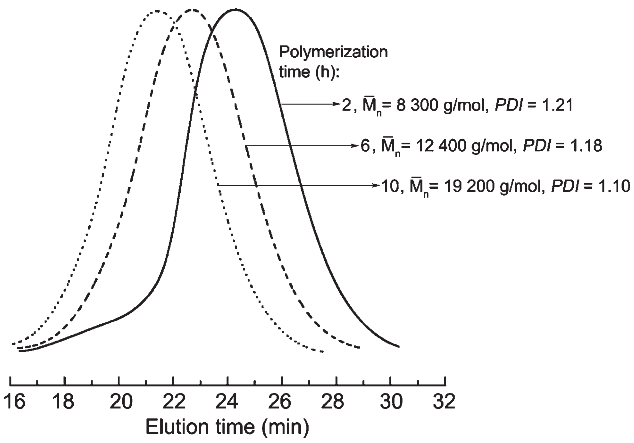


FIGURE 4 Evolution of GPC traces with polymerization time during the SI-RAFT of DMAPMA from RAFT agent-immobilized silicon surface.

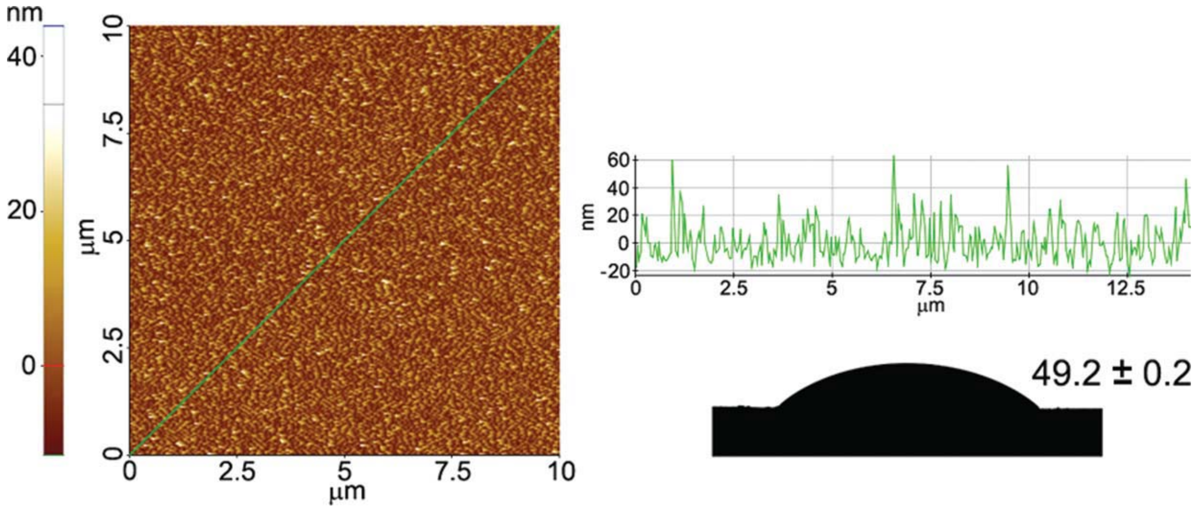


FIGURE 5 10 × 10 μm^2 AFM images in ambient conditions, topology (left), cross-sectional analysis, and static contact angle for poly(DMAPMA) brushes synthesized for 10 h (RMS = 1.7 nm). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

polymerization time, results indicated a grafting density between 0.55 and 0.77 chain per nm^2, which is relatively high. As the grafting density of RAFT agents at the silicon surface was 2.46 chain per nm^2, the RAFT agent efficiently for the SI-RAFT polymerization of DMAPMA can be estimated to be ~31% (87% monomer conversion). Thus, theoretical degree of polymerization ($\overline{DP}_n$) of poly(DMAPMA) chains can be estimated to be ~107 on the basis of monomer conversion (87%) and the calculated RAFT agent efficiency (31%). This generally agrees with the actual $\overline{DP}_n$ of grafted poly(DMAPMA) (~110) obtained from GPC analysis. Most interestingly, comparison of average distances between grafting sites (D) with twice the value of Flory radius, representing the dimension of collapsed chain in ambient conditions, gave in all cases a ratio inferior to 1. As it is generally admitted for grafted polymers, $D/2R_{\mathrm{F,coll.}} < 1$ indicates a stretched, brush-like conformation of the poly(DMAPMA) chains. These findings were consistent with the values reported by Luzinov et al.[40] They calculated a $D/2R_{\mathrm{F,coll.}}$ ratio varying from 0.71 to 0.45 and concluded to formation of densely packed poly(styrene) layers in a brush regime.

Poly(DMAPMA) film morphology was studied by conducting AFM measurements in ambient conditions (Fig. 5). The comparison with Figure 1(B) evidenced significant topography change and surface roughness resulting from polymer formation. Indeed, poly(DMAPMA) chains synthesized for 10 h appear as needle-like structures homogeneously distributed over the entire substrate area. Similar morphologies were observed for the polymer brushes synthesized for 2 and 6 h, however, with random distributions of apparent needle-like structures. The RMS roughness did not exceed 1.7 nm, which is far less than the size of the free polymer chain, indicating extremely homogeneous and uniform surfaces.

To further characterize cationic poly(DMAPMA) brushes, samples were then analyzed using GA-FTIR and XPS. GA-FTIR spectra for poly(DMAPMA) brushes synthesized for three different times are represented in Figure 6. In all cases, the presence of poly(DMAPMA) is confirmed by the prominent amide I and II bands recorded at 1650 cm^{-1} (C=O stretching vibration) and 1550 cm^{-1} (N—H bending and C—N stretching vibrations), respectively. Deformation bands because of trimethylamine groups appeared in the 1350–1500 cm^{-1} region. As GA-FTIR is a quantitative method in the case of thin polymeric films, the intensities of amide bands also reflect poly(DMAPMA) film thickness. This was verified using an external calibration curve, which gave film thicknesses in fairly good agreement with those measured by ellipsometry. Also, in

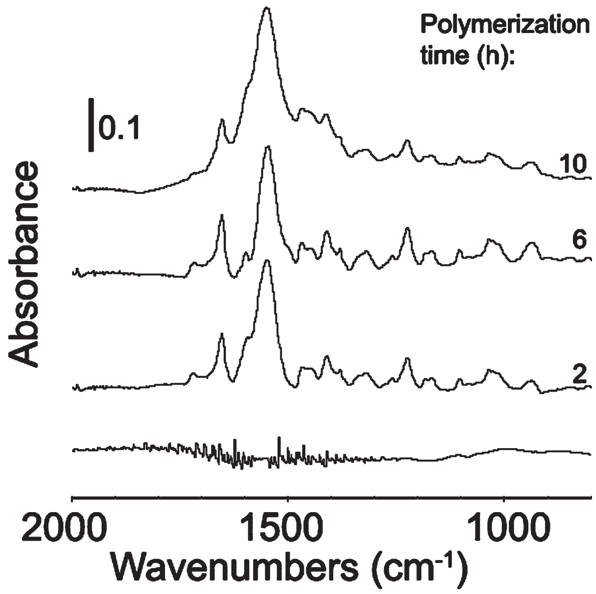


FIGURE 6 GA-FTIR spectra of poly(DMAPMA) brushes synthesized for three different times, and RAFT agent-immobilized silicon surface appears as a baseline.

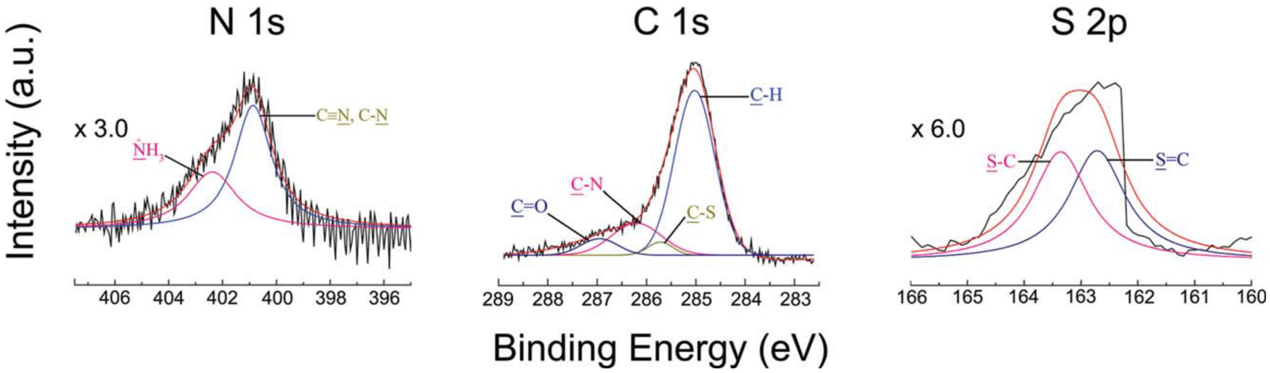


FIGURE 7 N 1s, C 1s, and S 2s core level XPS spectra recorded for poly(DMAPMA) brushes synthesized for 10 h. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Figure 6, GA-FTIR spectra recorded for poly(DMAPMA) brushes showed significant broadening of trimethylamine and amide bands with polymerization time. We believe that the peak broadening for poly(DMAPMA) reflects important interactions of the chemical environment of poly(DMAPMA) amide groups because of the formation of hydrogen bonding.

Elementary composition and values of binding energies given by XPS are summarized in Table 1. Detailed C 1s, O 1s, and N 1s core level spectra recorded for poly(DMAPMA) brushes are also displayed in Figure 7. They show the typical fingerprint of amide groups of the poly(DMAPMA) backbone with binding energies recorded at 287.2 eV (N—C=O), 286.2 eV (C—N) for C 1s, 532.2 eV (O=C) for O 1s, and 400.9 eV (C—N) for N 1s. As indicated in Table 1, similar results were obtained for the poly(DMAPMA) brushes synthesized for three different times. In all cases, atomic compositions were found to be in very good agreement with theoretical value expected for the pure poly(DMAPMA) layer (75.0% C, 16.6% N, and 8.4% O). In addition, the continuous decrease of S 2p signal confirms that the film thickness increases with polymerization time.

CONCLUSIONS

In conclusion, for the first time to our knowledge, SI-RAFT technique has been utilized in the presence of dithiobenzoate-anchored silicon wafer in aqueous media to prepare cationic polymer brushes composed of methacrylamido units bearing tertiary amine groups. The addition of sacrificial RAFT agent results in the formation of free polymer in solution, which was characterized and confirmed the formation of well-defined polymers. The possibility to tune the surface properties (e.g., film thickness, grafting density, wettability, and surface morphology) by varying reaction time is also demonstrated. Unlike other grafting process, SI-RAFT technique in the presence of a surface-immobilized RAFT agent in aqueous media can be advantageously applied to the production of cationic brushes. Studies of the stimuli responsive behavior of cationic poly(DMAPMA) brushes are currently under investigation in our laboratory and will be the subject of an upcoming report.

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