High Density Cationic Polymer Brushes from Combined "Click Chemistry" and RAFT-Mediated Polymerization

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ABSTRACT: A simple method for preparing cationic poly[(arvinylbenzyl)trimethylammonium chloride)] [poly(VBTAC)] brushes was used by combined technology of "click chemistry" and reversible addition-fragmentation chain transfer (RAFT) polymerization. Initially, silicon surfaces were modified with RAFT chain transfer agent by using a click reaction involving an azide-modified silicon wafer and alkyne-terminated 4-cyanopentanoic acid dithiobenzoate (CPAD). A series of poly(VBTAC) brushes on silicon surface with different molecular weights, thicknesses, and grafting densities were then synthesized by RAFT-mediated polymerization from the surface immobilized CPAD. The immobilization of CPAD on the silicon wafer and the subsequent polymer formation were characterized by X-ray photoelectron spectroscopy, water contact angle measurements, grazing angle-Fourier transform

INTRODUCTION The surface modification of silicon or gold substrates with polymeric chains to form functional structures has attached extensive interest owing to their potential applications in electronics, optics, catalysts, and biosensors.^{1–5} Among various solid substrates, silicon wafers are substrates of choice to prepare the polymer brushes due to their chemical resistance, mechanical stability, and relatively low costs.^{6,7} So far, silicon substrates coated with well-defined polymeric chains have been achieved by various polymerization techniques. Among them, controlled radical polymerization approaches such as nitroxide-mediated polymerization (NMP),^{8,9} atom transfer radical polymerization (ATRP),¹⁰⁻¹⁴ single-electron transfer living radical polymerization (SET-LRP),¹⁵⁻¹⁷ and reversible addition-fragmentation chain transfer (RAFT) polymerization¹⁸⁻²⁷ have been widely applied to graft polymeric chains onto solid substrates since they can afford well-defined polymers with controlled molecular weight, low polydispersity, and variable functionality. Among the available controlled free radical techniques, RAFT polymerization has arguably the most important commercial significance. RAFT works with a wide range of monomers compared with ATRP and does not need such critical

r consform **KEYWORDS**: click chemistry; morphology; reversible addition fragmentation chain transfer (RAFT) polymerization; surfaces gold experimental conditions as NMP and SET-LRP. However, low strucgrafting density and a difficulty in the fabrication of surface

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grafting density and a difficulty in the fabrication of surface immobilized RAFT chain transfer agent are two major problems, which hinder the use of RAFT-mediated polymerization for synthesis of polymer brushes. The polymer chain density is directly related to important surface properties such as hydrolytic stability and fundamental dimensions such as brush height.^{28,29} By taking advantage of the properties of high density polymer brushes one can create novel surfaces with smart or responsive systems. There is a clear need to increase the grafting density of polymer brushes on silicon surface and simplify the immobilization of RAFT chain transfer agent.

infrared spectroscopy, atomic force microscopy, and ellipsom-

etry analysis. The addition of free CPAD was required for the

formation of well-defined polymer brushes, which subse-

quently resulted in the presence of free polymer chains in so-

lution. The free polymer chains were isolated and used to

estimate the molecular weights and polydispersity index of

chains attached to the surface. In addition, by varying the po-

lymerization time, we were able to obtain poly(VBTAC)

brushes with grafting density up to 0.78 chains/nm² with

homogeneous distributions of apparent needle-like structures.

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With the development of click chemistry, it is possible that immobilization of RAFT chain transfer agent can be simplified, defined, and modularized. Click reactions have showed high yields and exceptional tolerance toward a wide range of functional groups and reaction conditions in the material science.^{30–34} Therefore, the combination of click reaction and RAFT polymerization can be a powerful strategy for preparation of polymer brushes on silicon or gold substrates.

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In this study, we report the successful preparation of high density, well-defined cationic poly[(*ar*-vinylbenzyl)trimethylammonium chloride)] [poly(VBTAC)] brushes on silicon wafer. Our strategy includes (i) synthesis of alkyne-terminated RAFT chain transfer agent, (ii) preparation of azide-modified silicon wafers, (iii) facile click reaction to immobilize RAFT chain transfer agent, and (iv) RAFT-mediated polymerization from the surface immobilized RAFT chain transfer agent. The formation of cationic poly(VBTAC) brushes was evidenced by using ellipsometry, X-ray photoelectron spectroscopy (XPS), grazing angle-Fourier transform infrared spectroscopy (GA-FTIR), atomic force microscopy (AFM), and contact-angle goniometer. Grafting densities of the immobilized RAFT chain transfer agent and polymer chains on silicon wafer were calculated and compared with the literature values.

EXPERIMENTAL

Materials and Sample Preparation

(*ar*-Vinylbenzyl)trimethylammonium chloride (VBTAC), *N*-(3-(dimethylamino)propyl)-*N'*-ethylcarbodiimide hydrochloride (EDC), 4-(*N*,*N*-dimethylamino)pyridine (DMAP), 4,4'-azobis(4-cyanopentanoic acid) (ACPA), di-*tert*-butyl dicarbonate, dimethyl sulfoxide, dimethylformamide (DMF), tetrahydrofuran, methanol, dichloromethane (DCM), hydrogen peroxide, copper sulfate, magnesium sulfate, and sodium ascorbate were purchased from Aldrich. ACPA was recrystallized from methanol. 3-Bromopropyltrimethoxysilane (BPTS, 97%) was obtained from Fluka. Propargyl alcohol, sodium azide, and hydrofluoric acid were provided by Acros Organics.

Synthesis of Alkyne Terminated RAFT Chain Transfer Agent

4-Cyanopentanoic acid dithiobenzoate (CPAD) was synthesized according to the literature procedure.³⁵ CPAD (1.14 g; 4.095 mmol), EDC (0.785 g; 4.095 mmol), DMAP (0.5 g; 4.095 mmol), and 10 mL of DCM were added to a round bottomed flask and stirred for few minutes under nitrogen atmosphere. Propargyl alcohol of 0.5 mL (8.5 mmol) was added, and the mixture was stirred overnight at room temperature. The product was washed with acidic water, water, and brine several times and dried under reduced pressure. Alkyne-terminated CPAD was obtained without further purification. ¹H-MNR (400 MHz, CDCl₃, δ , ppm): 7.9 (d, 2H, *o*-ArH), 7.6 (t, 1H, *p*-ArH), 7.4 (t, 2H, *m*-ArH), 4.4 (s, 2H, $O-CH_2-$), 3.7 (s, 1H, C=CH), ~2.8-2.4 (m, 4H, $-CH_2CH_2-$), 1.95 (s. 3H, $-CH_3$). IR (ATR, cm⁻¹): 2234 (v, C=N), 2121 (v, C=C), 1726 (vs. C=O), and 1040 (s, C=S).

Synthesis of Azide-Modified Silicon Wafers

The silicon (111) wafers (*n*-type, obtained from Shin-etsu, Handoutai, Japan), $3 \times 1 \text{ cm}^2$, 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 H₂SO₄:H₂O₂ (v/v: 70/30) for another 30 min. The wafers were then rinsed with a large amount of deionized water and 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 silicon wafers were immersed in a solution of BPTS (1%, v/v), in dry toluene, for 4 h at 120 °C. The wafers were then washed with toluene, DCM in an ultrasonic bath, and dried in a vacuum. The bromopropyl-modified silicon wafers were immersed in a saturated solution of sodium azide in DMF for 18 h at 80 °C. Finally, the azide-modified silicon wafers were rinsed with DMF, sonicated in ethanol and water for 3 min, and dried in a stream of nitrogen.

Preparation of RAFT Chain Transfer Agent Immobilized Silicon Wafer

Alkyne-terminated CPAD (3.0 g) were dissolved in 100 mL of DMF and the mixture was stirred for 10 min in an inert atmosphere. The azide-modified silicon wafers were placed into the solution and then, a solution of $CuSO_4$ (0.05 g) in 10 mL of water and another solution of sodium ascorbate (0.12 g) in 10 mL of water were added orderly into the solution. The reaction mixture was reacted at 50 °C for 24 h. The RAFT chain transfer agent immobilized silicon wafers were recovered from the reaction mixture and repeatedly washed with DMF and acetone in an ultrasonic bath, and dried under a stream of nitrogen.

RAFT-Mediated Polymerization Procedure

The RAFT-mediated polymerization of VBTAC (29.4 mmol) was carried out in buffer (28 mL, pH = 5.0, 0.27 mol L^{-1} acetic acid, and 0.73 mol L^{-1} sodium acetate), initiator ACPA (0.025 mmol), and free RAFT agent CPAD (0.125 mmol) at 0 °C in a glass reactor, which was designed to hold six RAFT chain transfer 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 1cm-highglass O-ring. The solution was diluted to 30 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 (\sim 2 mL) were removed with a syringe. The molecular weight distribution of the polymer was measured by aqueous size exclusion chromatography (ASEC). For ellipsometric measurements, the 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 N₂, and the ellipsometric thicknesses of the dry polymer films were measured at five different spots on each sample and averaged.

Characterization Techniques

GA-FTIR spectra of the polymer brushes were carried out using a Thermo Nicolet 6700 spectrometer coupled with a Mercury Cadmium Telluride detector and a Smart SAGA grazing angle (80°) attachment. The spectra were taken at a resolution 4 cm⁻¹ after 128 scans accumulation for an acceptable signal/noise ratio. XPS spectra were recorded on a SPECS XPS spectrometer equipped with a Mg K α 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 μ L, 18 M Ω cm⁻¹ resistivity) was used as the wetting liquid. The morphology of the surfaces was recorded on an atomic force microscope (Park Systems XE70 SPM Controller LSF-100 HS). A triangular shaped Si₃N₄ 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⁻¹. The force between the tip and the sample was 0.87 nN. The absolute molecular weights and polydispersities of poly(VBTAC) were determined by ASEC at ambient temperature using Ultrahydrogel columns (120, 250, 500, and 1000 Å; Waters), Wyatt Technology Optilab T-rEX RI detector ($\lambda = 690$ nm), a Wyatt Technology Dawn Heleos II multi-angle laser light scattering detector (λ = 658 nm), and 1 wt % acetic acid/0.1 M $Na_2SO_{4(aq)}$ as the eluent at a flow rate of 1.0 mL min⁻¹. The dn/dc of poly(VBTAC) (0.172 mL g⁻¹) in the above eluent was determined at 25 °C with a Wyatt Technology Optilab T-rEX RI detector ($\lambda = 690$ nm). Ellipsometric measurements were conducted in ambient conditions using an ellipsometry (model DRE, EL X20C) equipped with a He-Ne laser (λ = 632.8 nm) at a constant incident angle of 75° . The average dry thickness of polymer brushes 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)].³⁶

The grafting density (σ , chains/nm²) and anticipated average distance between grafting points, *D* (nm) of the poly(VBTAC) brushes were calculated from the dry polymer thickness, *h* (nm) and the number-average molar weight, \overline{M}_n (g mol⁻¹; the molecular weight of the grafted polymer chains is assumed to be similar to that of the free polymer in solution) values using eqs 1 and 2.^{37,38}

$$\sigma = \frac{h\rho N_{\rm A}}{\overline{M}_{\rm n} \times 10^{21}} \tag{1}$$

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

where ρ (1.05 g cm⁻³) is the density of polymer and N_A (6.02 $\times 10^{23}$ mol⁻¹) is Avogadro's number. The expected poly(VBTAC) chain conformation in good solvent was deduced from the comparison of *D* with the corresponding Flory radius ($R_{\rm F}$ nm) of the unperturbed chains calculated from eq 3³⁸

$$R_{\rm F} = b(\overline{DP}_{\rm n})^{3/5} \tag{3}$$

where \overline{DP}_n is the degree of polymerization and *b*, is the effective segment length (assumed to be 0.3 nm for VBTAC monomer).³⁹

RESULTS AND DISCUSSION

Immobilization of CPADB on Silicon Wafer

The Si—OH surface was functionalized via a simple two-step procedure. First, a self assembled monolayer (SAM) of BPTS



FIGURE 1 GA-FTIR spectra of (a) Si-BPTS, (b) Si-N₃, (c) Si-CPAD, and (d) poly(VBTAC) brush (Polymerization time = 120 min).

was covalently coupled to the Si-OH surface, and the bromine end-groups were then converted into the free azide groups by NaN_3 in DMF, leading to the azide-terminated silicon (Si-N₃) surface. Finally, alkyne-terminated CPAD molecules were chemically anchored to the azide-terminated silicon surface by a click reaction to form a CPAD overlayer. Attachment of CPAD molecules at every modification steps was confirmed with GA-FTIR (Fig. 1), XPS (Fig. 2; Table 1), ellipsometry (Table 2), AFM (Fig. 3), and water contact angle measurements. The formation of the BPTS SAMs on the silicon wafer was confirmed by the presence of the aliphatic $-CH_2$ bands at 2949 cm⁻¹ [Fig. 1(a)]. XPS analysis of the BPTS monolayer [Fig 2(a); Table 1] verifies the presence of C 1s and Br 3d. The C1s region can be curve-fitted to two peaks with binding energies of 285.0 and 285.4 eV, which are assigned to -C-H/C-C and -C-Br groups, respectively. More specific signal was the small bromine peak at 71.5 eV (consisting of Br $3d_{5/2}$ and Br $3d_{3/2}$ peak components at binding energies of about 71.1 and 72.0 eV, respectively), indicated the formation of BPTS monolayer.³⁹ When the bromide groups was converted to azide, analysis of the modified silicon [Fig. 2(b)] revealed a sharp azide band at 2123 cm⁻¹. XPS analysis also confirmed the presence of N 1s [Fig. 2(b)]. The N 1s region can be curve-fitted to two peaks with binding energies of 401.8 and 404.5 eV, which are assigned to $-N=N^+=N$ and $-N=N^+=N$ groups.

In the next modification step, the alkyne-terminated CPAD was attached to the azide-terminated layer by a click reaction. The CPAD immobilization was apparent from the appearance of carbonyl band at 1720 cm⁻¹ in the GA-FTIR spectrum [Fig. 1(c)]. The bands for $C \equiv N$ stretch at 2231 cm⁻¹ and C=S stretch at 1040 cm⁻¹, further confirmed successful covalent coupling of the CPAD on the azide-



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FIGURE 2 N 1s, C 1s, and S 2s core level XPS spectra of (a) Si–BPTS (b) Si–N₃ (c) Si–CPAD, and (d) poly(VBTAC) brush (Polymerization time = 120 min).

terminated layer. The core level XPS spectra of CPAD overlayer consist of N 1s and C 1s peaks curve fitted into the components with binding energies at about 399.8 eV (N–C) and 400.4 eV (N=C) for N 1s and 288.4 eV (C=O), 286.0 eV (C–N), 285.4 eV (C–S), and 285.0 eV (C–C/C–H) for C 1s [Fig. 2(c)]. The immobilization of alkyne-terminated CPAD onto the azide-terminated layer was also confirmed from the appearance of a S 2p peak curve fitted into two components with binding energies at about 162.5 eV (C–S) and 160.9 eV (C=S). The thickness of Si–BPTS, Si–N₃, and Si–CPAD layers were measured by ellipsometry at 0.7 \pm 0.3, 0.9 \pm 0.3, and 2.0 \pm 0.4 nm, respectively, these values are consistent with theoretical values (0.6, 0.8, and 1.8 nm) obtained by *ab initio* calculations. This allows for the following two conclusions. First, molecules within complete monolayers are predominantly oriented along the silicon surface normal and prevent their extended conformation. Second, complete SAMs are tightly packed with a refraction index very close to the known value for bulk packing. The grafting density of RAFT chain transfer agent calculated from molecular weight of the

TABLE 1 Atomic	Concentration a	nd Binding Er	nergies Giv	en High Re:	solution XF	S for Si-BP	TS, Si-N ₃ , Si-CF	AD, and Po	oly(VBTAC)	Brushes ^a			
		N 1s				C 1s		S	2p	Si	2p	Br	p
Sample	$-N = \frac{N}{N} = N$	$\underline{N}/\underline{N}H_3^+$	C C	C=0	N C	S C	CC/CH	C N	S=C	Si-O	Si–Si	Br 3d _{3/2}	Br 3d _{5/2}
Si-BPTS													
Energy (eV)	I	I	I	I	I	285.4 ^b	285.0	I	I	103.4	99.3	72.0	71.1
Conc. (%)	I			59.5				I		21.6		18.9	
SiN ₃													
Energy (eV)	404.5	401.8	I	I	286.2	I	285.0	I	I	103.4	99.2	I	I
Conc. (%)	39.8			37.1				I		23.0		I	
Si-CPAD													
Energy (eV)	I	400.4 ^c	399.8	288.4	286.0	285.4	285.0	162.5	160.9	I	101.5	I	I
Conc. (%)	15.4			66.3				5.2		13.1		I	
Poly(VBTAC) 30	min ^d												
Energy (eV)	Ι	402.2	400.1	I	286.2	285.5	285.0	163.0	161.3	I	101.5	I	I
Conc. (%)	7.5			87.3				4.0		1.2		I	
Poly(VBTAC) 60	min ^d												
Energy (eV)	I	402.2	400.0	I	286.1	285.3	285.0	162.8	161.2	I	I	I	I
Conc. (%)	7.9			90.3				1.8		I		I	
Poly(VBTAC) 120	min ^d												
Energy (eV)	I	402.1	400.0	I	286.1	285.4	285.0	162.9	161.1	I	I	I	I
Conc. (%)	9.2			89.9				0.9		I		I	
^a Binding energies	are calibrated to a	liphatic carbon	at 285.0 eV.										

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Binding energies are calibrated to aliphatic carbon Binding energy attributable to the C–Br species. Binding energy attributable to the $\overline{\rm N=N}$ species. Polymerization time.

TABLE 2	Grafting	Parameters	Calculated	for	Poly(VBT	AC)
Brushes						

Polymerization		6	Л	R_	
Time (min)	<i>h</i> (nm)	(chain/nm ²)	(nm)	(nm)	D/2R _F
15	$8.7~\pm~2.0$	0.36	1.87	3.83	0.24
30	16.8 ± 1.5	0.43	1.72	5.14	0.17
60	32.1 ± 1.6	0.54	1.53	6.65	0.12
90	$44.7~\pm~1.5$	0.66	1.39	7.25	0.10
120	60.5 ± 2.1	0.78	1.28	7.84	0.08

CPAD molecule and from the thickness according to eq 1 was 2.06 groups/nm² which is higher than the literature grafting density of RAFT chain transfer agent (0.15–0.68 groups/nm²).^{40,41} The RAFT chain transfer agent group is sterically large; hence, direct immobilization is inefficient. By an initial silanization reaction with BPTS (2.76 group/nm²) followed by nearly a quantitative azide displacement of bromide, we can use click chemistry to introduce a RAFT chain transfer agent

with a much higher grafting density even though click chemistry with chain transfer agent is not 100%.

Surface morphologies of the Si—OH substrate after BPTS, azide and CPAD modifications are shown in Figure 3. The Si—OH surface is rather uniform and smooth, with a root-mean-square (rms) roughness value of about 0.32 nm. The Si-BPTS, Si—N₃, and Si—CPAD surfaces remain molecularly uniform with rms roughness values of about 0.49, 0.59, and 0.91 nm, respectively. Finally, as illustrated by inset images in Figure 3, the variation in static water contact angles for the functionalized silicon surfaces suggests that the hydrophilicity of the silicon surfaces can be readily tuned. The static water contact angle of the Si—OH surface is about 2.4 \pm 0.3°. The water contact angles for the Si-BPTS, Si—N₃, and Si—CPAD surfaces are about 56.4 \pm 0.7, 49.7 \pm 0.5, and 55.4 \pm 0.5°, respectively.

RAFT-Mediated Polymerization of VBTAC on the Silicon Wafer

For a high grafting density of the polymer, it is important to introduce RAFT chain transfer agent on the substrate surface



FIGURE 3 3D (left) and 2D (right) AFM topography images (5 × 5 μ m, *z* scale is 10 nm) in ambient conditions and photographs of 4 μ L water droplets (top) on (a) Si–BPTS, (b) Si–N₃, (c) Si–CPAD, and (d) poly(VBTAC) brush (σ = 0.78 chains/nm²). The cross sections corresponding to the black line shown in the AFM images are given below each image.



FIGURE 4 Dependence of the poly(VBTAC) film thickness on the polymerization time.

with a high grafting density. But not all of the RAFT chain transfer agent sites on the substrate surface may participate in the growth of polymer chains because the growing chains sterically block access of the adjacent chain transfer agent on the substrate surface. In this case, it is important to have an efficient surface immobilized chain transfer agent to grow a polymer chain. Hence, we attached the reactive CPAD chain transfer agent in order to achieve better efficiency. This chain transfer agent has been reported to have a higher chain transfer efficiency and control over the RAFT polymerization because the carbon attached to the labile sulfur atom bears a radical stabilizing phenyl group.⁴²

The RAFT-mediated polymerization of the cationic VBTAC monomer in aqueous media has already been reported.⁴³ In this study, the RAFT-mediated process was described for the preparation of polymer brushes on the silicon substrate modified with RAFT agent.

GA-FTIR spectrum of poly(VBTAC) brushes synthesized for 120 min are represented in Figure 1(d). The formation of



FIGURE 5 Relationship of In $([M]_o/[M]_t$ with time of RAFTmediated polymerization of VBTAC.



FIGURE 6 ASEC traces of poly(VBTAC) synthesized at different times.

poly(VBTAC) brushes is confirmed the prominent C—H bands recorded at 2800–3000 cm⁻¹ region. Elementary composition and values of binding energies given by XPS are summarized in Table 1. The core level XPS spectra of poly (VBTAC) consist of N 1s and C 1s peaks curve fitted into the components with binding energies at about 402.1 eV (C—N⁺) and 400.0 eV (C—N) for N 1s and 286.1 eV (C—N), 285.4 eV (C—S) and 285.0 eV (C—C/C—H) for C 1s [Fig. 2(d)]. As indicated in Table 1, similar results were obtained for the poly(VBTAC) brushes synthesized for different times. In all cases, atomic compositions were found to be in good agreement with theoretical value expected for the pure poly(VBTAC) layer (90% C and 10% N). In addition, the continuous decrease of S 2p signal confirms that the film thickness increases with reaction time.

The thickness of the polymer brushes grown on the silicon surface as a function of polymerization time is shown in Figure 4. As shown in this figure, the thickness of the poly(-VBTAC) film increased almost linearly with the polymerization time. This result indicates that the process of RAFTmediated polymerization of VBTAC is controlled.

Additional evidence on the controlled polymerization is provided by the "free" poly(VBTAC) formed in the solution. Figure 5 shows the linear relationship between $\ln([M_0]/[M])$ and time, where $[M_0]$ is the initial monomer concentration and [M] is the monomer concentration. This result indicates that the concentration of the growing species remains constant and a first order kinetic is obtained.

The main difference between surface and bulk polymerizations is the probability of chain transfer between the dormant and the activating chains. In surface RAFT polymerization, the probability of chain transfer between two chains (two chains on the surface, or one chain on the surface and another chain in solution) is lower than that between two chains in solution. In this study, RAFT-mediated polymerization of the cationic VBTAC monomer in aqueous media was



FIGURE 7 Evolution of molecular weights (\blacksquare) and polydispersities, PDI (\Box) with monomer conversion.

performed in the presence of free RAFT chain transfer agent in order to better control the polymerization. Additional RAFT agent in solution seems to aid the efficiency of grafting process. Moreover, introduction of free RAFT agent allows for formation of free polymer in solution. Barsbay et al.44 reported that the number-average molecular weight, \overline{M}_{n} , value of polystyrene detached from the cellulose surface by acidic hydrolysis is very close to the value of the corresponding free polystyrene. This finding is of high significance as detaching of the grafted polymer from the silicon surface is often impossible (the detachment procedure for silicon substrates might cause hydrolysis of pendant groups) or very time-consuming. Therefore, we also assumed that the free and the grafted polymers have the same molecular weight and narrow polydispersity, thus proving for the first time the control of grafting process mediated via RAFT polymerization. The free poly(VBTAC) chains were analyzed by ASEC. Typical ASEC traces of free polymers with the increase of polymerization time are shown in Figure 6. We can clearly observe that the elution peaks shift to higher molecular weight with increasing reaction time. After 120 min, the monomer conversion is almost 93%; ASEC analysis of the free polymers reveals a number-average molecular weight, \overline{M}_{n} , of 49,000 g mol⁻¹ and a polydispersity, PDI, of 1.19.

Figure 7 shows the relationship between molecular weight of the "free" poly(VBTAC) and the conversion of the VBTAC monomer. The number average molecular weight of the "free" poly(-VBTAC) increased linearly with monomer conversion. The poly-dispersities of the polymers were relatively low (1.04–1.19) and the experimental ($\overline{M}_{n,ASEC}$ as determined by ASEC) molecular weights were close to the theoretical ($\overline{M}_{n,theo} = conversion \times [monomer]_0 \times MW_{monomer} / [CTA]_0 + MW_{CTA})$ values. These results also indicate that the RAFT-mediated polymerization of the VBTAC proceeded in a controlled manner.

The grafting density of the poly(VBTAC) chains was calculated from molecular weight of the free polymer (\overline{M}_{n}) and the dry film thickness (h) according to eq 1 and varied between 0.36 and 0.78 chain/nm², which means that poly(VBTAC) chains have grown from 18 to 38% (2.06 CPAD/nm²) of the CPAD fixed on the silicon surface (Table 2). Although the grafting density increases with polymerization time, the increase is nonlinear, which raises the possibility that the chain initiation efficiency is dependent on the fractional coverage of RAFT agents in the BPTS monolayer. It appears that the initiation efficiency decreases with increasing grafting density. At high chain density, crowding within the polymer layer will affect the local concentration of reactants and therefore the relative reaction rates of initiation, propagation, and termination. This is likely to exert the highest effective on reactions between grafted chains, such termination between grafted radicals and degenerative chain transfer between a grafted chain and grafted radical.

To determine whether the grafted polymers are in brush regime, we calculated the distance between grafting sites (*D*) relative to the Flory radius ($R_{\rm F}$), using eqs 2 and 3. It is generally accepted that when $D < 2R_{\rm F}$ end-tethered polymer chains reside in the brush regime, and when $D > 2R_{\rm F}$ the chains are isolated and noninteracting, adopting coiled structures (often referred to as the "mushroom regime").³⁸ As shown in Table 2, base on the $D/2R_{\rm F}$ calculated for poly (VBTAC) chains, the chains are sufficiently crowded such that they will form brushes when solvated.

When the Si—OH surface was grafted with poly(VBTAC) layer, the static water contact angle of the surface decreased substantially to about 38.6 \pm 0.9°, consistent with the hydrophilic nature of poly(VBTAC). poly(VBTAC) film morphology was studied by conducting AFM measurements in ambient conditions [Fig. 3(d)]. Poly(VBTAC) chains synthesized for 120 min appear as needle-like structures heterogeneously distributed over entire substrate area. Similar morphologies were observed for the polymeric brushes synthesized at different times, however, with homogeneous distributions of apparent needle-like structures. Analysis of poly(VBTAC) brushes synthesized for 30 min indicated a rms roughness of 12.1 nm, whereas a slight decrease of 10.6 and 7.9 nm for the brushes synthesized for 60 and 120 min, respectively, indicating homogeneous and uniform surfaces.

CONCLUSIONS

A combinatorial approach based on click chemistry and RAFT-mediated polymerization was used to synthesize welldefined cationic polymeric chains grafted onto silicon wafer. The silicon surfaces were first modified with RAFT chain transfer agent by using "click chemistry" involving an azidemodified silicon wafer and alkyne-terminated CPAD. The click reaction produced a grafting density of 2.06 RAFT agent/nm², a value much higher than previously reported for RAFT agent immobilization. Then the poly(VBTAC) brushes were synthesized by RAFT-mediated polymerization. We exploited the combined use of click chemistry and RAFTmediated polymerization to make polymer brushes with high JOURNAL OF POLYMER SCIENCE Chemistry

grafting density, which opens the route to elaboration of a new family of polymer brushes with potential applications in responsive or smart systems.

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