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A new selenium-based RAFT agent for surface-initiated RAFT polymerization of 4-vinylpyridine

Serkan Demirci [a], Selin Kinali-Demirci [b], Tuncer Caykara [b,*]

[a] Department of Chemistry, Faculty of Arts and Sciences, Amasya University, 05100 Amasya, Turkey
[b] Department of Chemistry, Faculty of Science, Gazi University, 06500 Ankara, Turkey

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ABSTRACT

A new selenium-based reversible addition-fragmentation chain transfer (RAFT) agent, 4-cyanopentanoic acid diselenobenzoate (RAFT-Se), was synthesized and utilized in the surface-initiated RAFT polymerization of 4-vinylpyridine (4VP) on silicon substrate. The results indicate that the RAFT-Se can control the surface-initiated RAFT polymerization, as evidenced by the number-average molecular weight that increase linearly with monomer conversion, molecular weights that agreed well with the predicted values, and the relatively low polydispersity indexes. The surface-initiated RAFT polymerization with the RAFT-Se was the same polymerization mechanism as its analog, 4-cyanopentanoic acid dithiobenzoate (RAFT-S). The grafting density of the poly(4-vinylpyridine) brushes prepared in the presence of RAFT-Se ($\sigma_{\text{RAFT-Se}}$) and RAFT-S ($\sigma_{\text{RAFT-S}}$) was estimated to be about 0.51 and 0.66 chains/nm^2, respectively. In addition, the end of polymer chains on silicon substrate contains selenium element which may be useful in biosensor applications.

1. Introduction

Modification of the surface properties of silicon substrates is central to many areas of research, ranging from biomaterials to advanced microelectronics [1,2]. A stable, densely packed polymer chains covalently bonded to the silicon substrate can be used, for example, as recognition layers in biosensors [3], and as passivation layers in microelectromechanical systems [4]. Conventionally, free radical polymerization is used to graft vinyl polymers from solid substrate surface such as gold, glass, silicon etc. accepting the disadvantage that the molecular weight and molecular weight distribution of the grafted chains are not controlled. With the advent of controlled free radical polymerization methods, such as nitroxide-mediated polymerization (NMP) [5–7], atom transfer radical polymerization (ATRP) [8–10], single electron transfer living radical polymerization (SET-LRP) [11,12] and reversible addition-fragmentation chain transfer (RAFT) [12–14] polymerization, it is now possible to synthesize polymers with predetermined molecular weight and low polydispersity for a great variety of vinyl monomers. RAFT is of particular interest as a very wide range of vinyl monomers can be polymerized in a controlled manner under moderate reaction conditions (low temperature and tolerance to oxygen) via this method.

RAFT has also contributed to generate polymer brushes via a grafting to approach [15–20]. Surface-initiated RAFT polymerization from the initiator-containing self-assembled monolayers is attractive, since a high density of initiators can be immobilized on the solid substrate and the initiation mechanism is more well-defined. Covalent attachment of initiator monolayers directly silicon surfaces via Si—C bonds, in the absence of the native oxide layer, has also attracted a great deal of attention, because of the thermal and chemical stability of the resulting Si—C bonds [1,21,22].

On the other hand, RAFT polymerization involves a reversible addition-fragmentation cycle, in which transfer of the dithioester groups between the activated and dormant polymer chains maintains the controlled character of the polymerization process. Because of the analog of selenium (Se) with sulfur (S) in electronic structure, selenium-based RAFT agents have also been explored in RAFT polymerization [23–25]. Recently, Zhu et al. [25] synthesized selenium-based RAFT agents and used them as the RAFT agents for vinyl acetate polymerization. They [24] also reported the RAFT polymerization of styrene using the similar phosphinodiselenoic esters under UV irradiation. Zhang et al. [26] have synthesized a new hyperbranched polyselenide with multicatalytic sites at the branching units which acts as a new glutathione peroxidase mimic. Considering that selenium is an indispensable element in human body, the introduction of selenium into polymer chains have been used as bio-related materials in biological applications [27–30]. However, although selenium is an essential trace element, it can be dangerous for life if the amount

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* Corresponding author. Tel.: +90 3122021124; fax: +90 2122279.
E-mail address: caykara@gazi.edu.tr (T. Caykara).

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exceeds the tolerable limits. Lee et al. [23] successfully synthesized phosphinodiselenoic esters and used them as RAFT agents in styrene polymerization. Thus, introduction the selenium into polymer chains by controlled way would favor such researches. Although the selenium containing RAFT agents were used in both homogeneous and heterogeneous media, their use for the synthesis of polymer brushes have not been reported to date.

In this study, we describe for the first time the synthesis of a new selenium containing RAFT agent, 4-cyanopentanoic acid diselenobenzoate (RAFT-Se) for comparison to mediate the surface-initiated RAFT polymerization of the pH-responsive monomer 4-vinylpyridine (4VP). The electrostatic changes arising from the protonation/deprotonation of the pyridine groups of poly(4VP) are responsible for tuning the surface charge [31–34] that provides an attractive strategy for immobilization of DNA, enzymes, and polyanionic drugs via electrostatic interactions. According to the mechanism of surface-initiated RAFT polymerization, the chain ends of the polymer brushes are ideally terminated by the dithioester or diselenoester groups. It is expected that the introduction of selenium-contained RAFT agents into the 4VP polymerization would extend the available database of RAFT agents that may be used to successfully perform surface-initiated RAFT polymerization of 4VP and develop a potential bio-related polymer brush with controllable molecular weight and structure.

2. Experimental

2.1. Materials

4-Vinylpyridine (4VP, 95%, Aldrich), 4,4′-azobis(4-cyanovaleric acid) (ACVA, $\geq$98%, Aldrich), benzyl chloride (99%, Aldrich), selenium ($\geq$99.5%, Aldrich), sulfur ($\geq$99.5%, Sigma–Aldrich), potassium ferricyanide(III) (99%, Sigma–Aldrich), pyridine (99.8%, Aldrich), diethyl ether ($\geq$99%, Sigma–Aldrich), dichloromethane (98.5%, Sigma–Aldrich), acetone (99.8%, Sigma–Aldrich) and ethanol (99.8%, Sigma–Aldrich), were purchased commercially. Dimethylformamide (DMF, $\geq$98%, Aldrich) was distilled over $CuSO_4$ before use. Silicon (111) wafers (n-type) obtained from Shin-etsu, Handoutai, and cleaned using "piranha" solution (30/70 30% aqueous hydrogen peroxide solution/sulfuric acid) at 90 °C for 2 h. It should be noted that piranha solution is extremely reactive and as such should be handled with great care. The synthesis and immobilization of initiator, 4,4′-azobis-4-cyanopentanoyl chloride (ACVC), on silicon substrate have been reported previously [35]. Briefly, the cleaned silicon wafers were etched for 1 min in a 2% hydrofluoric acid solution, quickly rinsed in degassed deionized water and dried in a stream of nitrogen. t-Butyloxycarbonyl (t-BOC)-protected allylamine (20 μL) was introduced onto the freshly prepared Si–H surface. After irradiation with a UV light ($\lambda = 254$ nm), the modified surfaces were ultrasonically washed with 25% trifluoroacetic acid (TFA) in dichloromethane followed by a 3 min rinse in 10% NH_4OH to remove the t-BOC protecting group and dried in a stream of nitrogen. Next, pyridine and four pieces of amine-functionalized silicon substrate were added to a 1 M solution of ACVC in anhydrous dichloromethane. After the reaction, the silicon substrates with the surface immobilized azo initiator (Si-Azo) were recovered from the reaction mixture and repeatedly washed with dichloromethane, acetone, ethanol, and dried under a stream of nitrogen.

2.2. Synthesis of RAFT-Se and RAFT-S

RAFT-Se was synthesized by a modification of the previously published protocol [36], except selenium was used in place of sulfur. Sodium methoxide (30% solution in methanol, 0.5 mol), anhydrous methanol (100.0 mL), and elemental selenium (0.5 mol) were added to 500 mL round-bottomed flask equipped with magnetic stir bar. This mixture was stirred for 1 h prior to the dropwise addition of benzyl chloride (0.25 mol), at room temperature under an argon atmosphere. The reaction mixture was heated in an oil bath at 67 °C for 12 h. After this time, the reaction mixture was cooled to 7 °C using an ice bath. The precipitated salt was removed by filtration and the solvent removed in vacuum. To the residue was added deionized water (250.0 mL), and solution was filtered to finally yield a solution of sodium diselenobenzoate.

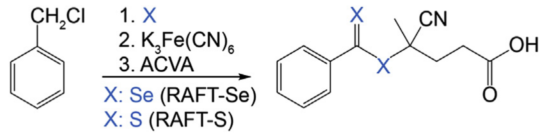
Potassium ferricyanide(III) (0.1 mol) was dissolved in deionized water (500.0 mL). Sodium diselenobenzoate solution (250.0 mL) was transferred to a 1 L conical flask equipped with a magnetic stir bar. Potassium ferricyanide solution was added dropwise to the sodium diselenobenzoate via an addition funnel over a period of 1 h under vigorous stirring. The precipitate was filtered and washed with deionized water. The solid was dried in vacuo at room temperature overnight.

250 mL round-bottomed flask was added distilled ethyl acetate (100.0 mL). To the flask was added dry ACVA (0.1 mol) and di(selenobenzoyl) disulfide (0.05 mol). The reaction solution was heated at reflux for 24 h. The ethyl acetate was removed in vacuum. The target compound was recrystallized from benzene (Scheme 1). RAFT-Se: Yield 32%, ^1H NMR ($CDCl_3$, δ, ppm): 10.1 (br, 1H, OH), 7.8–7.3 (m, 5H, ArH), 2.7–2.3 (m, 4H, $-CH_2CH_2-$), 2.2 (s, 3H, $-CH_3$). FT-IR (ATR-FTIR, υ, cm^{-1}): 3300–3100 (s, br, COO–H), 2242 (v, $C\equiv N$), 1710 (vs, C=O), 853 (s, C=Se). MALDI-TOF: calcd. for $C_{13}H_{13}NO_2Se_2$ 373.1678, found 374.0983 ($+H^+$).

4-cyanopentanoic acid dithiobenzoate (RAFT-S) was synthesized according to a previously published protocol [36] and detailed above except sulfur was used in place of selenium (Scheme 1). RAFT-S: Yield 48%, ^1H NMR ($CDCl_3$, δ, ppm): ^1H NMR ($CDCl_3$, δ, ppm): 10.2 (br, 1H, OH), 7.9–7.4 (m, 5H, ArH), 2.8–2.3 (m, 4H, $-CH_2CH_2-$), 1.9 (s, 3H, $-CH_3$). FT-IR (ATR-FTIR, υ, cm^{-1}): 3300–3100 (s, br, COO–H), 2234 (v, $C\equiv N$), 1706 (vs, C=O), 1040 (s, C=S).

2.3. Surface-initiated RAFT polymerization procedure

Surface-initiated RAFT polymerization of 4VP from Si-ACVC was performed using two kinds of RAFT agent (RAFT-Se and RAFT-S) and free initiator (ACVA). The molar ratio was [4VP]:[RAFT Agent]:[free ACVA] 250:1:0.2. A dry glass reactor, which was designed to hold six azo initiator-immobilized silicon wafers oriented normal to the base of the reactor, was charged with RAFT agent (2.4 mmol), 4VP (64.7 mL, 0.6 mol), DMF (35 mL), and ACVA (0.13 mg, 0.48 mmol). After three freeze-pump thaw cycles, the reaction mixture was immersed in a thermostated oil bath at 70 °C, and from time to time, small samples (~3 mL) were removed with a syringe. After 24 h, reaction was quenched by precipitation in methanol. The polymer was filtered and purified by a Soxhlet extraction with methanol to remove poly(4-vinylpyridine) [poly(4VP)] homopolymer. The molecular weights and molecular weight distributions of the polymers were measured by size exclusion chromatography (SEC). For ellipsometric measurements, the substrates were also removed from the reactor at different times and washed with the buffer solution and ethanol in an ultrasonic bath. The substrates were dried with N_2, and the ellipsometric thicknesses of the dry polymer films were measured at five different spots on each sample



Scheme 1. Synthesis of RAFT-Se and RAFT-S.

and averaged. The conversion of the polymerization was determined gravimetrically.

2.4. Characterization techniques

The nuclear magnetic resonance (NMR) spectra were recorded on a Bruker-Spectrospin Avance DPX 400 Ultra-Shield NMR spectrometer with chemical shifts in ppm (for $CDCl_3$, tetramethylsilane was used an as internal standard). The size exclusion chromatography (SEC) analysis of poly(4VP) was performed with an Waters system consisting of a binary pump, an autosampler, a temperature controlled column oven, and differential refractometer. The analytical separation was performed on Waters Styragel HR4 and HR6 columns (7.8 × 300 mm) at 27 °C with a flow rate of 1 mL/min. Monodisperse polystyrene standards (Shodex) were used to calibrate the molecular weights. The ellipsometric measurements were conducted in ambient conditions using an ellipsometry (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 polymer brushes on silicon substrate was determined by fitting the data with a three-layer model [37]. The grafting density (σ, chains/nm^2), average distance between grafting points, D (nm) and radius of gyration (R_g, nm) of the polymer chains were calculated from the dry polymer thickness, h (nm), the number-average molar weight and $\overline{M}_n$ (g/mol) (The molecular weight of the grafted polymer chains is assumed to be similar to that of the free polymer in solution [38,39]) values using Luzinov equation [40]. The X-ray photoelectron spectra were recorded by using X-ray photoelectron spectrometer (XPS) (Thermo Scientific). XPS was used by means of a flood gun charge neutralizer system equipped with a monochromated Al K-α X-ray source (hυ = 1486.6 eV). Charging neutralizing equipment was used to compensate sample charging, and the binding scale was referenced to the aliphatic component of C1s spectra at 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 atomic force microscope (AFM, Park Systems XE70 SPM Controller LSF-100 HS). A triangular shaped Si_3N_4 cantilever with integrated tips (Olympus Co. Ltd.) was used to acquire the images in the non-contact 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.

3. Results and discussion

It has been reported that in the preparation of polymer brushes, a uniform a dense layer of immobilized initiators is indispensable [35]. In this study, the azo initiator-immobilized on the silicon substrate was used to initiate the growth of the polymer brushes in the presence of chain transfer agent for RAFT polymerization. The azo initiator ACVC was immobilized on the hydrogen-terminated silicon (Si 111) (Si–H) surface by the three-step process. First, UV-induced coupling of *t*-BOC protected allylamine with Si–H surface, and then conversion of the *t*-BOC protected allylamine into the free amine groups by TFA produce the amine-terminated Si–NH_2 surface. Subsequent the amide reaction of the Si–NH_2 with the ACVC initiator yields the Si-Azo surface. The presence of a Cl 2p

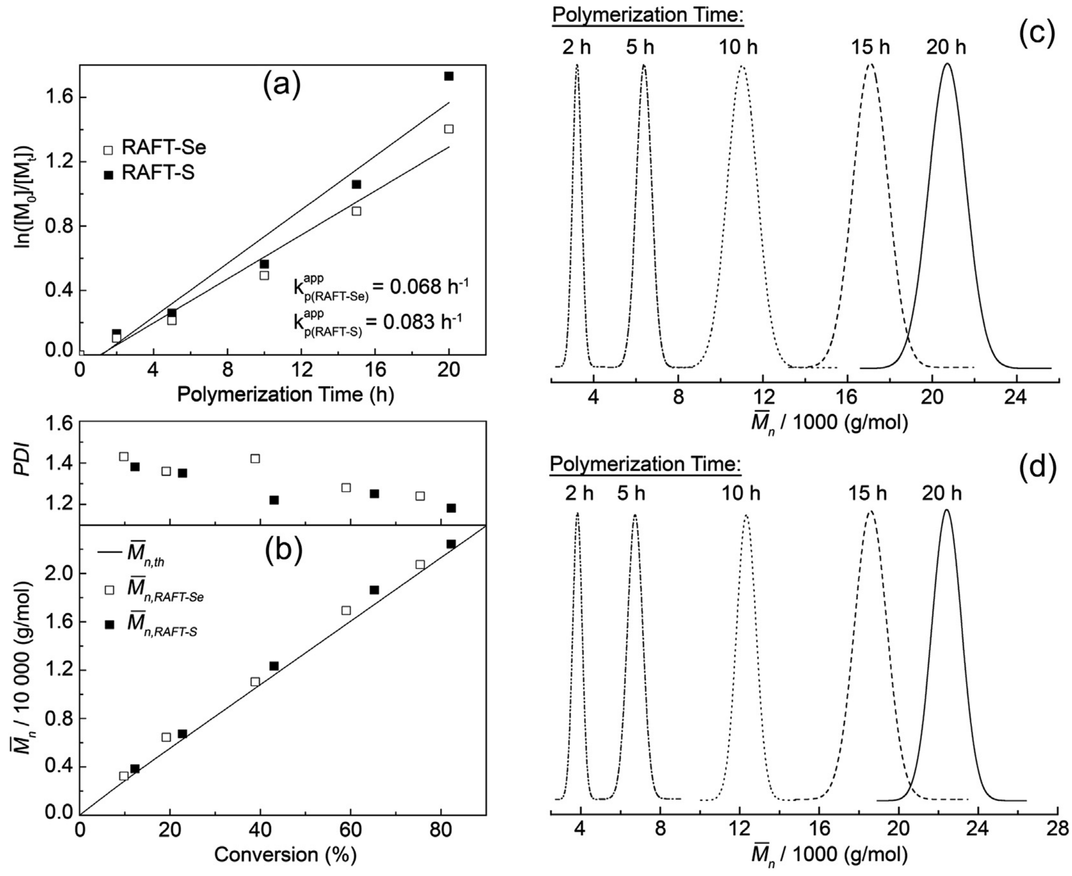


Fig. 1. Results of surface-initiated RAFT polymerization of 4VP in DMF at 70 °C, [4VP]:[RAFT-Se or RAFT-S]:[free ACVA] = 250:1:0.2 polymerization kinetics (a), molecular weights and polydispersity indices of poly(4VP) with increasing monomer conversion (b), SEC chromatograms of the free poly(4VP) synthesized in the presence of RAFT-Se (c) and RAFT-S (d) at different monomer conversions.

peak at approximately 200 eV for the Si-Azo surface indicates that the azo initiator has been successfully immobilized on the silicon surface (Fig. 1). After immobilization of ACVC, the thickness of the monolayer on the Si-Azo surface was about 2.1 ± 0.6 nm.

In this study, two kinds of RAFT agent, RAFT-Se and RAFT-S with same R and Z groups (Scheme 1), were synthesized and used as chain transfer agents in surface-initiated RAFT polymerization of 4VP, respectively. Surface-initiated RAFT polymerization of 4VP was carried out in the presence of a free initiator ACVA, a RAFT agent (RAFT-Se or RAFT-S) and the initiator-immobilized substrate to produce free poly(4VP) and the corresponding polymer brushes on the substrates simultaneously (Scheme 2). The kinetics and living features of the polymerization explored and compared. The polymerization kinetics was given in Fig. 2a. A linear increase in the semilogarithmic kinetic plots was observed for all the cases, and there was an induction period of about 2 h (*vide infra*). The main reason of the induction period maybe partly due to the lower decomposition rate of intermediate radical [41] or the impurity of chain transfer agent [42]. The apparent propagation rate constants (k_p^{app}) in the presence of RAFT-Se and RAFT-S were 0.068 and 0.083 h^{-1}, respectively. Excellent control of the molecular weights, which increased linearly with conversions, and low polydispersity values around 1.43 were achieved for two agents (Fig. 2b). The SEC traces of the free polymers shown in Fig. 2c–d are unimodal and clear shift of the traces to smaller elution time (higher molecular weight) with the polymerization time. These results indicated that both of the RAFT-Se and RAFT-S are effective RAFT agents in controlling the polymerization of 4VP.

The relationship between the thickness (h, nm) of the poly(4VP) brushes and $\overline{M}_n$ of the corresponding free polymers formed in the presence of RAFT-Se and RAFT-S is shown in Fig. 3. A direct proportion relationship was observed between the $\overline{M}_n$ of the free polymer (we assumed that the free polymer and the brush with the same $\overline{M}_n$ are formed in the same reaction batch [38,39]) and brush thickness ($h = \sigma \overline{M}_n / \rho N_A \times 10^{-21}$ where σ (chains/nm^2) is the grafting density, ρ (1.15 g/cm^3) is the density of polymer and N_A (6.02×10^{23} mol^{-1}) is Avogadro's number [40]). From the slope of the linear line (Fig. 3), the grafting density of the polymer brushes prepared in the presence of RAFT-Se ($\sigma_{\text{RAFT-Se}}$) and RAFT-S ($\sigma_{\text{RAFT-S}}$) was estimated to be 0.51 and 0.66 chains/nm^2, respectively. In this estimation, average distance between grafting points, $D_{\text{RAFT-Se}}$ and $D_{\text{RAFT-S}}$ ($D = (4/\pi\sigma)^{1/2}$) [40], was found to be 1.58 and 1.38 nm, respectively. The radius of gyration (R_g, nm) of poly(4VP) was estimated using the equation: $R_g = b(\overline{DP}_n/6)^{1/2}$ where $\overline{DP}_n$ is the degree of polymerization and b, is the segment length (assumed to be 0.797 nm for poly(4VP) chains) [43]. An indication of having polymeric brushes prepared in the presence of RAFT-Se and RAFT-S can be when the interchain distances are less than the radius of gyration of the corresponding free polymer chains [44]. We have achieved high grafting density for poly(4VP) prepared in the presence of both RAFT-Se and RAFT-S, and the interchain grafting

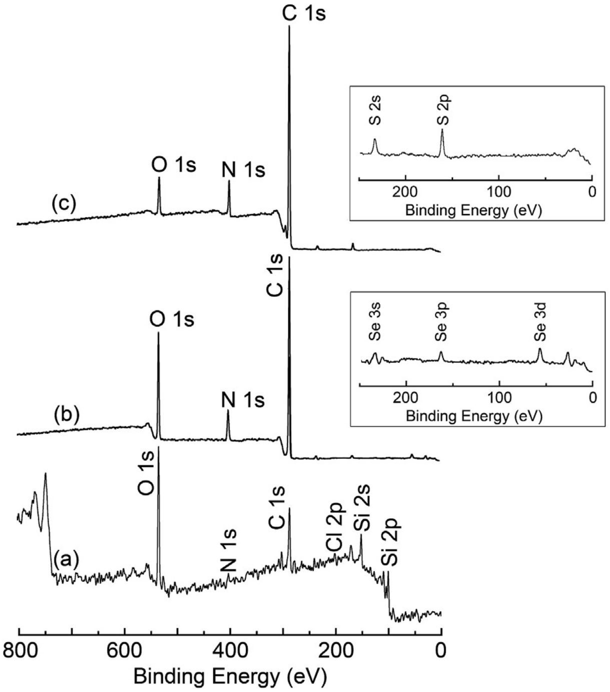
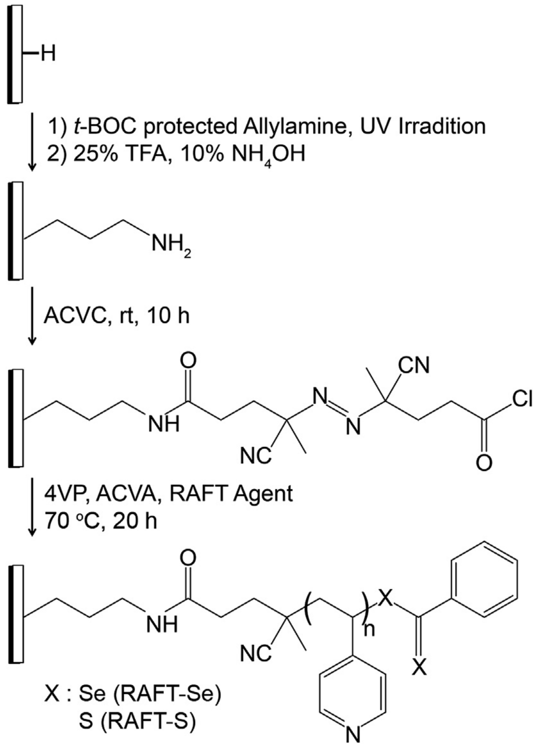


Fig. 2. Survey scan XPS spectra of Si-Azo (a), poly(4VP) brushes synthesized in the presence of RAFT-Se (b) and RAFT-S (c), respectively.



Scheme 2. Schematic diagram illustrating the process of the surface-initiated RAFT polymerization of 4VP from the Si-Azo surface.

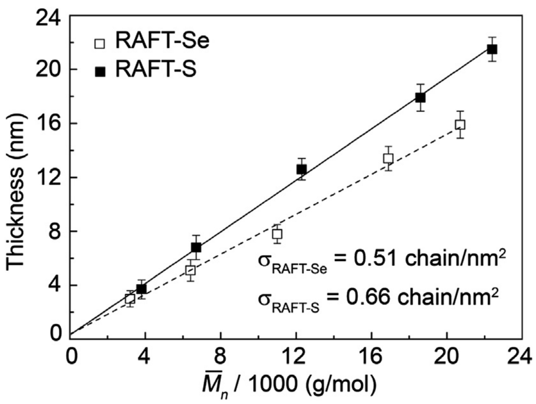


Fig. 3. Evolution of the thickness (h, nm) of the poly(4VP) brushes synthesized in the presence of RAFT-Se and RAFT-S as a function of the number-average molecular weight ($\overline{M}_n$).

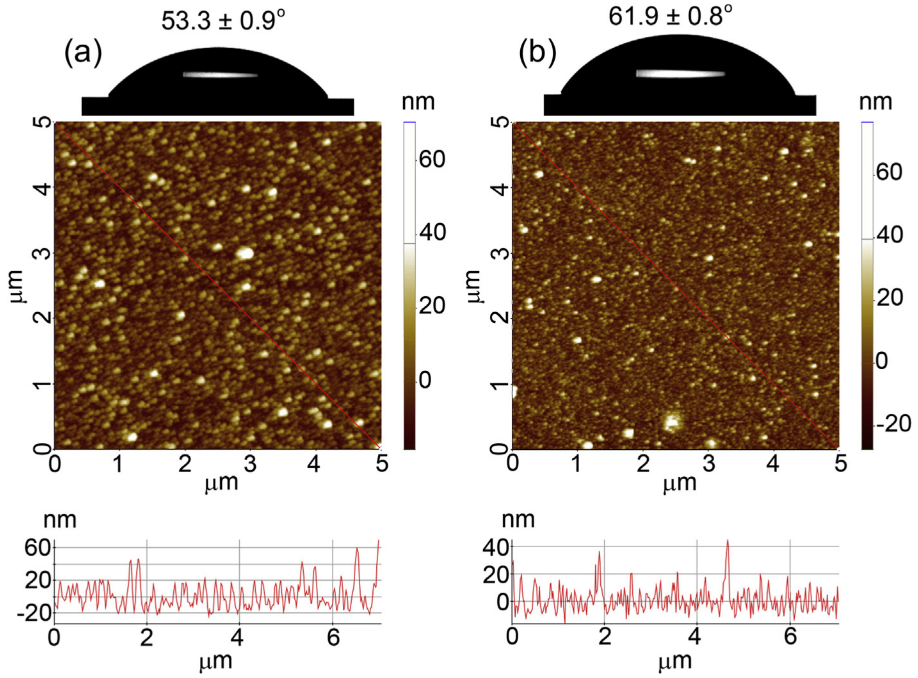


Fig. 4. 2D AFM images (5 × 5 μm^2) and photographs in ambient conditions of 4 μL water droplets (top) on the poly(4VP) brushes synthesized in the presence of RAFT-Se (a) and RAFT-S (b). The cross sections corresponding to the red line shown in the AFM images are given below each image. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

distances are less than the radius of gyration of these free poly(4VP) chains in solution, indicating that the chains are indeed in a stretched brush-like conformations. The formation of poly(4VP) brushes was also confirmed by XPS measurements, as shown in Fig. 2b–c. Two peaks at 400.1, and 285.0 eV were observed, corresponding to nitrogen and carbon, respectively. The atomic ratios of N/C in the poly(4VP) brushes prepared in the presence of RAFT-Se and RAFT-S were estimated to be 0.20/0.80 and 0.17/0.83, respectively, which were relatively close to the theoretical values calculated from atomic composition of poly(4VP) (0.14 N and 0.86 C). Apart from these peaks, there appears three signals at about 229.0, 162.0 and 54.5 eV assignable to Se 3s, Se 3p and Se 3d, respectively, in the survey scan spectrum of the poly(4VP) brushes prepared in the presence of RAFT-Se (Fig. 4a). However, in the survey scan spectrum of the brushes prepared in the presence of RAFT-S, two signals at about 163.5 and 226.2 eV assignable to S 2p and S 2s, respectively, were observed (Fig. 2c). Meanwhile, the disappearance of photoelectron lines of Si indicates that the poly(4VP) films on the surface of the silicon substrate is thicker than the XPS probing depth (~10 nm) [45,46]. In the topographic AFM images of the poly(4VP) brushes prepared in the presence of RAFT-Se and RAFT-S using the non-contact mode, the root-mean-square (rms) values of the surface roughness were found to be 4.18 and 3.23 nm in 5 × 5 μm^2 scanning areas, respectively (Fig. 4). No significant roughness differences were observed between the surfaces of the brushes prepared for both cases, suggesting the formation of homogeneous graft layers and hence homogeneity in grafting densities. The water contact angles of the poly(4VP) brushes prepared in the presence of RAFT-Se and RAFT-S were found to be 53.3 ± 0.9 ad 61.9 ± 0.8°, respectively, meaning that the surfaces are hydrophilic.

4. Conclusions

A new selenium-based RAFT agent (RAFT-Se) was synthesized accompany with its sulfur analog (RAFT-S). 4VP was graft polymerized on the silicon surface via the surface-initiated RAFT polymerization technique, using RAFT-Se or RAFT-S as the chain transfer agent and surface immobilized azo species as the initiator. Kinetic studies revealed a linear increase in the thickness of the surface-graft polymerized film with reaction time, indicating that the chain growth from the surface was a controlled process with a “living” character. The grafting density of the poly(4VP) brushes prepared in the presence of RAFT-Se ($\sigma_{\text{RAFT-Se}}$) and RAFT-S ($\sigma_{\text{RAFT-S}}$) was estimated to be about 0.51 and 0.66 chains/nm^2, respectively. AFM images revealed that surface-initiated polymerization via the RAFT process had preceded uniformly on silicon surfaces. To the best of our knowledge, this maybe the first example of using a selenium-based RAFT agent in the surface-initiated RAFT polymerization of 4VP. Hence, the present study has illustrated that new surface functionalities and molecular architecture arising well-defined graft chains with selenium-based end group can be incorporated onto the silicon substrates via surface-initiated RAFT polymerization.

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