

pH-Detachable Polymer Brushes Formed Using Titanium–Diol Coordination Chemistry and Living Radical Polymerization (RAFT)

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Received October 8, 2008; Revised Manuscript Received March 5, 2009

ABSTRACT: pH-detachable poly(styrene) brushes formed on indium–tin oxide (ITO) glass substrates using metal complex chemistry and reversible addition–fragmentation chain transfer (RAFT) polymerization was described. These pH-detachable polymeric brushes were generated using both “graft-from” and “graft-to” methodologies. The methodologies involved either the surface self-assembly of catechol-functional RAFT agents (graft-from) or catechol-terminal polymer chains (graft-to) onto the ITO substrate via titanium–diol coordination. The stepwise functionalization of the ITO glass surfaces was characterized successfully using X-ray photoelectron spectroscopy (XPS) and contact angle measurement. Poly(styrene) brushes generated using the “graft-from” method were denser than those generated using the “graft-to” method, as exemplified by atom force microscopy (AFM) and quantified using cyclic voltammetry. Poly(styrene) brushes assembled using both methods could be detached easily by manipulating the pH of the brush environment. Cyclic voltammetry was utilized to calculate precisely the surface coverage of the RAFT functionality and polymeric brush density.

Introduction

The creation of polymer brushes on a variety of surfaces has been seen as desirable for a number of applications in anticorrosion, antifouling, microelectronics, surface tailoring, nanopatterning, and drug delivery.^{1–6} Polymer brushes can be prepared by two basic approaches. First, the postpolymerization conjugation of polymeric chains onto the targeted surface (also called “graft-to” methodology) or, second, the in situ generation of chains directly from the surface (also called “grafted from” methodology). In general, the “grafted from” approach generates polymer brushes with a higher density and homogeneity compared to the “graft-to” method. Polymeric brushes can also be constructed from more complex polymeric architectures, such as diblocks or triblocks, to achieve unique properties.^{7–9} Furthermore, polymer brushes can also be tailored as either homogeneous or heterogeneous.^{10–12} Brushes can be built up on flat substrates^{3,5,13–15} or on 3D constructs such as particles^{12,16–20} or multiwalled carbon nanotubes.^{4,21,22} A variety of polymerization methods have been developed to generate versatile polymeric brushes, including, atom transfer radical polymerization (ATRP),^{14,23–27} nitroxide-mediated radical polymerization (NMRP),²⁸ and reversible addition–fragmentation chain transfer (RAFT) polymerization^{29–31} as the mostly widely utilized living polymerization techniques.^{29,32–34} The RAFT polymerization technique has some advantages over the other living radical polymerization methods, particularly where highly functional monomers are targeted (e.g., carboxylic acids, sugars, or acrylamides).² These functional monomers are frequently used for targeting applications in bio-nanotechnology.^{35–40}

Polymeric brushes can be bound onto the surfaces of substrates using a number of approaches, among which covalent

bonding,⁴¹ click chemistry,⁴² and physisorption⁴³ are frequently adopted. Brushes formed by covalent bonding will have advantageous properties such as high grafting density as well as thermal and solvent stability.¹⁵ However, in some applications it might be desirable to have less tenacious bonding to allow for removal (and possible subsequent reattachment) of the brushes, allowing regeneration of the surface through a convenient recycling regime. Possible applications would include membranes where facile regeneration of the surface might lead to a new approach to antifouling.

Similar to other metal complexation chemistry,^{44–47} Ti complexes have been extensively developed as functional materials^{44,48} and as catalysts for a variety of reactions, such as polymerizations,^{49,50} epoxidations,^{51–53} silylcyanation,^{54,55} and others.^{56–58} Titanium alkoxides have also been used as a powerful tool in the enantioselective epoxidation of allylic alcohols.^{59,51,56} Presently, they are indispensable precursors in the synthesis of almost all natural products.^{60,61} In these applications, titanium alkoxides were used in conjunction with 1,2-diol-terminated derivatives, such as tartaric acid, as catalytic reagents. A noteworthy property of these Ti–diol complexes is that they can be dissociated easily, in weak basic environments, into the diol-terminated precursors and a Ti(OH)₄ precipitate. It occurred to us that this chemistry could be analogous with click chemistry in coupling efficacy and therefore applied to build up polymeric architectures for nanotechnology applications. In this particular case, with the design feature of facile reversibility, so the structures can be assembled and disassembled at will. Messersmith and co-workers have generated polymer brushes on Ti substrate using “graft-from” methodology via ATRP polymerization for cell fouling resistance, where an ATRP initiator with catechol end group was immobilized on Ti substrate.⁶²

In this study we report, for the first time, titanium–diol chemistry as a tool for preparing pH-detachable polymer brushes on an ITO glass substrate. This substrate was selected to allow us to use cyclic voltammetry to analyze the brush density via a simple procedure. A RAFT agent was first modified with a

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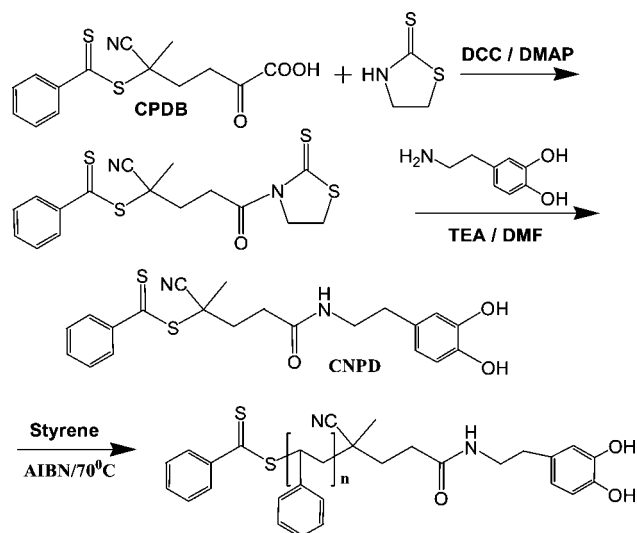
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Scheme 1. Synthesis of 4-Cyano-*N*-[2-(3,4-dihydroxyphenyl)ethyl]penyramide Dithiobenzoate (CNPD) and CNPD Controlled Polymerization of Styrene^a



^a The abbreviations in are given in the Materials part of the Experimental Section.

catechol functional group, followed by self-assembly onto the ITO substrate modified with 1,2-diol surface ligands using titanium–diol coordination chemistry. The direct surface grafting of polystyrene was then performed using the RAFT mechanism to afford polymeric brushes in situ. As a comparison, polymer brushes were also prepared by self-assembly of pregenerated polymeric chains with catechol terminal groups via the same coordination chemistry.

Experimental Section

Materials. Dopamine·HCl (Aldrich, 98%), triethylamine (TEA) (99%, Aldrich), Ti(OPr)₄ (Aldrich, 99.999%), 3-aminopropyltriethoxysilane (APTES) (Aldrich, 97%), tartaric acid (Aldrich, 99%), 2,2'-azobis(isobutyronitrile) (AIBN) (Sigma-Aldrich, 98%), styrene (Aldrich), carbon tetrachloride (Aldrich, 99%), dimethylformamide (DMF) (Ajax Finechem, >99.8%), dichloromethane (Univar >99.5%), tetrahydrofuran (THF) (Unichrom, >99.7%), hexane (Univar, >95%), anhydrous sodium sulfate (Unilab, >99%), diethyl ether (Univar, >99%), ethyl acetate (Univar, >99.5%), Na₂CO₃ (Univar, >95%), 1-ethyl-3-(3-dimethylaminopropyl)carbodiimide hydrochloride (EDC) (Sigma, 98%), 1,3-dicyclohexylcarbodiimide (DCC) (Aldrich, 99%), 2-mercapto-2-thiazoline (Aldrich, 98%), 4-(dim-

ethylamino)pyridine (DMAP) (Aldrich, 99%). ITO glass was purchased from SPI Supplies, West Chester, PA. 4-Cyanopentanoic acid dithiobenzoate (CPDB) was synthesized following reported methods.⁶³

Synthesis of 4-Cyano-*N*-[2-(3,4-dihydroxyphenyl)ethyl]penyramide Dithiobenzoate (CNPD). The synthesis of 2-mercaptothiazoline ester (2) of CPDB (1) was performed following the reported method.⁶⁴ TEA (0.175 g, 1.74 mmol) was added slowly to a solution of dopamine·HCl (0.323 g, 1.70 mmol) in DMF (4 mL). The resulting mixture was stirred for 10 min, followed by the addition of 2-mercaptothiazoline ester (0.660 g, 1.74 mmol). After stirring the reaction for 24 h, phosphate buffer (20 mL, pH 4.0) was added to obtain a pink precipitate. The precipitate was then filtered to afford a pink solid product (0.683 g, 95%). ³⁰⁰MHz ¹H NMR (CDCl₃) δ (ppm): 7.87–8.00 (d, 1H, CH=C), 7.53–7.58 (t, 1H, CH=CH), 7.36–7.42 (t, 2H, CH=CH), 6.79–6.81 (d, 1H, C-CH=CH), 6.71–6.72 (s, 1H, C-CH=C), 6.56–6.58 (d, 1H, CH-CH=C-OH), 5.93 (s, NH), 3.45–3.47 (t, 2H, CH₂-CO), 2.66–2.68 (t, CH₂-NH), 2.54–2.61 (m, CH₂-C, 1H), 2.46–2.48 (m, 2H, CH₂-C=C), 2.34–2.41 (m, CH₂-C, 1H), 1.88 (s, 3H, CH₃). ⁷⁵MHz ¹³C NMR (CDCl₃) δ (ppm): 20.96 (CH₃), 23.94 (H₂C-CO), 31.80 (H₂C-CO), 33.94 (CH₂-C), 45.91 (tertiary C), 51.09 (NH=CH₂), 115.52 (CH=C-OH), 115.74 (CH=C-OH), 118.66 (CN), 120.72 (CH=CH), 126.60 (CH=CH), 128.51 (C=CH), 130.69 (C=CH), 133.06 (C=CH), 142.86 (C=C-C=S), 144.08 (C-OH), 144.25 (C-OH), 171.40 (C=O), 222.51 (C=S).

Polymerization of Styrene Controlled by CNPD in Solution. A solution of styrene (2.36 g, 2.17 × 10⁻² mol), CNPD (0.030 g, 7.25 × 10⁻⁵ mol), and AIBN (3.00 × 10⁻³ g, 1.83 × 10⁻⁵ mol) was prepared in dioxane (4 mL), yielding a homogeneous solution. The resulting solution was then divided into five aliquots and deoxygenated with nitrogen for 30 min, followed by incubation in a preheated water bath at 70 °C. These five samples were removed from the water bath at successive intervals (9, 20, 28, 43, and 60 h polymerization) and quenched by exposure to air. The monomer conversion of each sample was determined by ¹H NMR in CDCl₃. The polymers were purified by repeatedly precipitation of the reaction mixture in hexane and then dried under vacuum.

Step-by-Step Modification of ITO Substrate with RAFT Agent. A number of ITO glass pieces (1 cm × 1 cm) were cut and cleaned in soap water and ethanol for 30 min, respectively, under sonication, followed by the drying under nitrogen stream and then incubated in 3-aminopropyltriethoxysilane (APTES) solution (0.1 M) in ethanol for 20 min. The APTES-modified substrates were washed with copious volumes of ethanol and dried under a nitrogen stream, followed by the incubation in an aqueous solution of tartaric acid (0.05 M) and EDC (0.1 M) for 5 h. After washing with water and drying under a stream of nitrogen, the tartaric acid-modified ITO substrates were incubated in Ti(OPr)₄ solution (10 mM) of CH₂Cl₂ for 10 min, then washed with excess CH₂Cl₂, and dried under nitrogen stream, followed by the incubation in CNPD solution

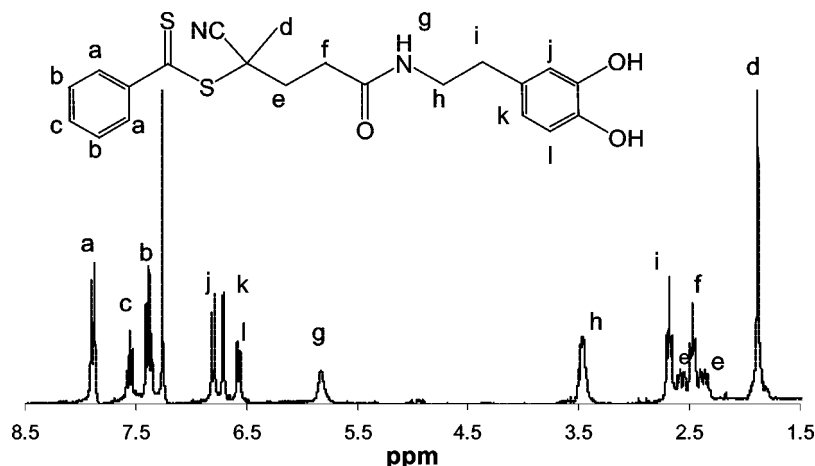


Figure 1. ¹H NMR spectrum of 4-cyano-*N*-[2-(3,4-dihydroxyphenyl)ethyl]penyramide dithiobenzoate (CNPD) in CDCl₃.

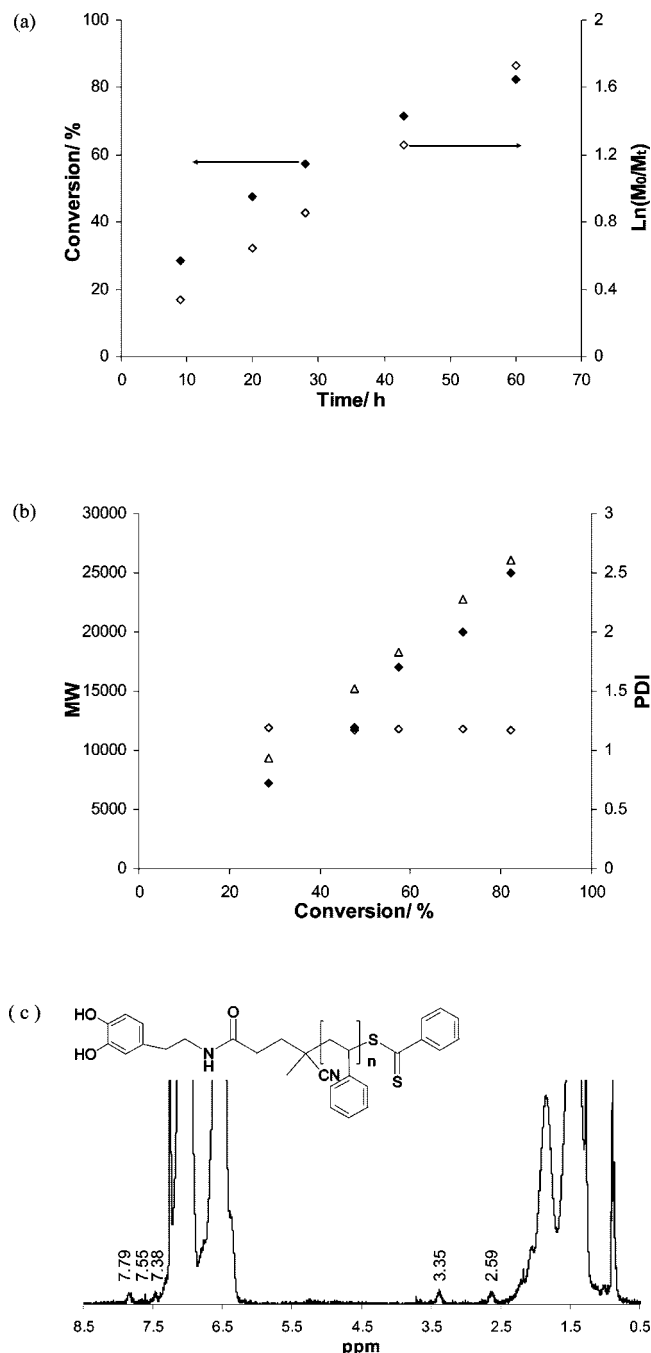


Figure 2. (a) Kinetics of polymerization of styrene controlled by catechol-terminated RAFT agent, CNPD. (b) Evolution of M_n (molecular weight by number), M_{theo} (theoretical molecular weight), and polydispersity (PDI) against the monomer conversion (filled diamond represents the MW calculated from GPC, empty triangle represents the theoretical value calculated using the equation $M_{\text{theo}} = (\text{mole ratio of St to CNPD}) \times \text{conversion} \times \text{MW}^{\text{CNPD}} + \text{MW}^{\text{CNPD}}$, and empty diamond represents PDI. (c) ^1H NMR of purified PS (M_w , 10 000; PDI, 1.14) in CDCl_3 .

(10 mM) of CH_2Cl_2 for 1 h and then washed thoroughly with copious CH_2Cl_2 prior to the in situ surface polymerization procedure. The ITO substrates were put aside after each step modification for control analysis when necessary.

In Situ Grafting of Polystyrene (PSt) Brushes (Graft-From). Two pieces of CNPD-modified ITO glass ($1 \text{ cm} \times 1 \text{ cm}$) were placed in two vials with the modified surface facing up, followed by the addition of one-half of a polymerization mixture [styrene (2.36 g, 0.0217 mol), CNPD (0.032 g, 7.73×10^{-5} mol), and AIBN (3.80×10^{-3} g, 2.32×10^{-5} mol) in 4 mL of dioxane]

to each vial. These two vials were then sealed and deoxygenated with argon for 30 min, followed by incubation in a preheated water bath at 70°C . These four polymerizations were then stopped at 28 and 43 h, respectively, by removing the glass slides from the polymerization mixture and exposure to air. The glass slides were then washed with copious amounts of CH_2Cl_2 and dried under nitrogen prior to cyclic voltammetry, AFM, XPS, contact angle, and cleavage analysis.

Preparation of Polymer Brushes by Postpolymerization Self-Assembly (Graft-To). A piece of ITO substrate ($1 \text{ cm} \times 1 \text{ cm}$) modified with APTES, tartaric acid, and $\text{Ti}(\text{OPr})_4$ as described above was incubated in a solution of polystyrene (PSt) (prepared from the solution polymerization as described above, M_n 10 000 from ^1H NMR, PDI 1.14) in CH_2Cl_2 (10 mM). After 3 h the slide was washed with copious amounts of CH_2Cl_2 and then dried with nitrogen, prior to characterization.

Cleavage of the Polymer Brushes from the ITO Surface. The cleavage test was carried out by incubating the ITO slides modified with polymer brushes in phosphate buffer (pH 9.0) for 20 min with mild shaking. The slides were then washed with copious amounts of water and CH_2Cl_2 and then dried using a stream of nitrogen successively, prior to AFM analysis.

Analyses. Gel permeation chromatography (GPC) analysis of PSt generated from the solution polymerization was performed in *N,N*-dimethylacetamide (DMAc) (0.03% w/v LiBr, 0.05% BHT stabilizer) at 50°C (flow rate: 0.85 mL min^{-1}) using a Shimadzu modular system comprising a DGU-12A solvent degasser, an LC-10AT pump, a CTO-10A column oven, and an RID-10A refractive index detector. The system was equipped with a Polymer Laboratories 5.0 mm bead-size guard column ($50 \times 7.8 \text{ mm}^2$) followed by four $300 \times 7.8 \text{ mm}^2$ linear PL columns (10^5 , 10^4 , 10^3 , and 500 g mol^{-1}). Calibration was performed with low-polydispersity polystyrene standards ranging from 500 to 10^6 g mol^{-1} .

^1H NMR spectra of RAFT agents and RAFT-polymers were obtained using a Bruker AC300F (300 MHz) spectrometer or a Bruker DPX300 (300 MHz) spectrometer.

Atomic force microscopy (AFM) images were obtained by a Molecular Imaging Picoscan II instrument in tapping mode. Analysis of the AFM images was performed using the WSxM software (version 3, Nanotec Electronica S.L., Spain).

Cyclic voltammetry (CV) was performed using a BAS 100B electrochemical analyzer (Bioanalytical System Inc., Lafayette, Inc.) potentiostat interfaced with a Bootstrap Dimension Penta 12 computer system. The electrochemical cell consisted of a three-electrode system using a polymer-modified ITO glass as the working electrode, platinum foil as the auxiliary electrode, and $\text{Ag}/\text{AgCl}/3.0 \text{ M NaCl}$ electrode (from BAS) as the reference electrode. The electrolyte for the measurement of all the samples was phosphate buffer (pH 7.0).

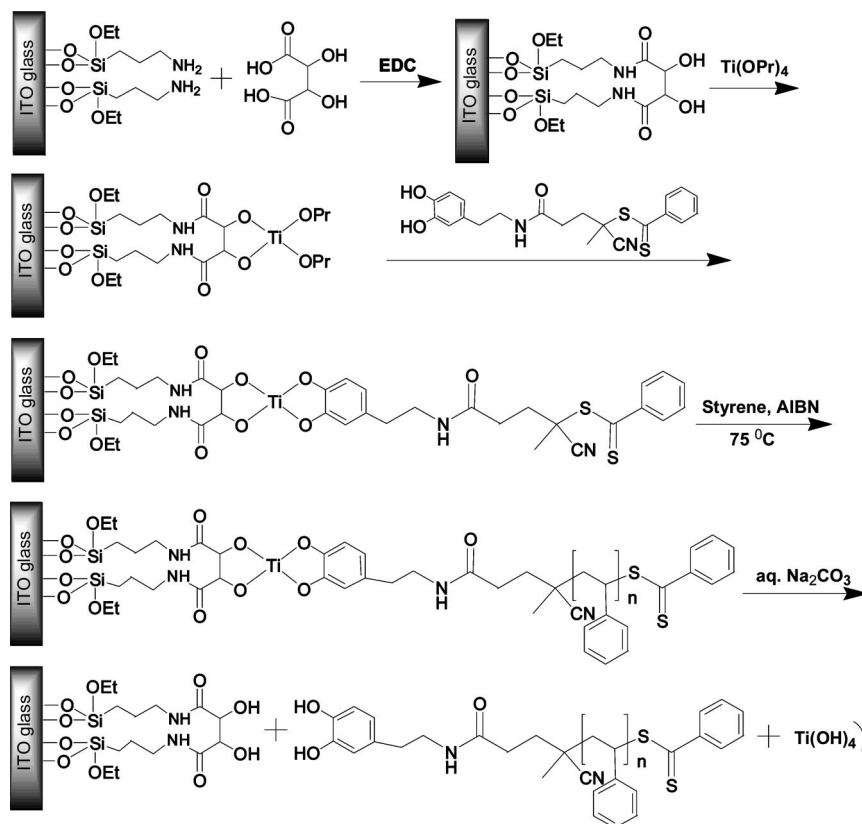
XPS spectra were obtained using an Escalab 220-IXL spectrometer with a monochromated Al $K\alpha$ source (1486.6 eV), hemispherical analyzer, and multichannel detector. The spectra were accumulated at a takeoff angle of 90° with a 0.79 mm^2 spot size at a pressure of less than 10^{-8} mbar.

Contact angles of the ITO substrates resulted from stepwise modification were measured using a KSV Cam 200 contact angle meter. A drop of water ($\sim 10 \mu\text{L}$) was placed on the modified ITO substrate, and the contact angle was determined at 25°C .

Results and Discussion

Synthesis of Catechol-Terminal RAFT Agent (CNPD) and the Subsequent Polymerization in Solution. The procedure for the synthesis of catechol-functional RAFT agent, CNPD, is shown in Scheme 1. The carboxylic-functional RAFT agent, CPDB, was reacted with 2-mercaptothiazoline to yield a mercaptothiazoline ester, followed by the reaction with dopamine in the presence of TEA. Mercaptothiazoline ester is a facile leaving group when attacked by the amine moiety to achieve amide coupling. If CPDB is converted into a more stable ester, e.g., succinimide ester, the amine group of the dopamine would

Scheme 2. Stepwise Modification of ITO Glass Surfaces To Create Reversible Polymer Brushes via Ti–Diol Coordination



first attack the dithioester core, leading to the aminolysis of RAFT agent. Therefore, conversion of the RAFT into a more active ester is necessary in order to achieve amide coupling without destroying the dithioester active center of RAFT.^{64,65} Neutralization of the dopamine·HCl before reaction with CPDB is also necessary, as direct use of dopamine·HCl in the reaction will greatly reduce the coupling efficiency due to the low pH. The amino group is more nucleophilic in basic conditions, enhancing the formation of an amide bond. However, a strong basic medium (pH > 9) will destroy the dithioester structure of RAFT agent. Therefore, a relatively neutral environment is optimal for the coupling reaction. When the RAFT thiazoline ester reacted with the neutralized dopamine·HCl in the presence of 10% DMAP (relative to CPDB) the CNPD with a high reaction yield (95%) was achieved. The ¹H NMR spectrum of CNPD is shown in Figure 1.

Homopolymerization of styrene was first carried out in solution using CNPD for two reasons: (1) to confirm that CNPD can control the polymerization according to the known traits of living radical polymerization, based on the concern that the catechol terminal group of CNPD might inhibit the polymerization, and (2) to prepare a catechol terminal polymer for the postpolymerization self-assembly onto the ITO surface via Ti–diol coordination. As shown in Figure 2a, monomer conversion increased with polymerization time, reaching 82.3% in 60 h. The relationship of number-average molecular weight (M_n) and the polydispersity index (PDI) of the purified polymers relative to the monomer conversion is shown in Figure 2b. The M_n was found to increase linearly, concomitant with conversion. The polydispersity indices (PDI values) were smaller than 1.20 for all the polymers. The theoretical MWs of the polymers were also calculated and found to be in accord with the experimental values (Figure 2b), indicating that the polymerization of styrene was well mediated via the RAFT mechanism. The purified polymers were subjected to ¹H NMR to ensure the integrity of

the terminal catechol group from CNPD, after polymerization. As shown in Figure 2c, the three peaks at 7.79, 7.55, and 7.38 ppm corresponding to the phenyl group on the RAFT residue were clearly observed in the ¹H NMR spectrum, confirming the integrity of the dithioester groups.

Stepwise Modification of ITO Glass Surfaces with RAFT Agent and the Subsequent in Situ Surface Grafting of Polystyrene. As shown in Scheme 2, the cleaned ITO glass surface were first modified with APTES to place amine groups on the ITO surface,^{66,67} followed by the attachment of tartaric acid via amide coupling in the presence of EDC according to well-developed methods.^{66,68} The modified substrate then displayed 1,2-diol surface groups through which the dopamine-modified RAFT with catechol termini could be attached via Ti–diol coordination. It is noteworthy that the coupling of the RAFT molecule onto tartaric-modified surfaces should be performed stepwise, since the simultaneous introduction of the RAFT molecules with the Ti(OPr)₄ precursor would induce the formation of RAFT dimers by a self-coupling mechanism. The same methodology should also be followed for postpolymerization self-assembly of catechol-terminal polymers. In addition, the in situ polymerization of styrene on RAFT-modified ITO surfaces should be performed in a less basic medium (less than pH 9.0) in order to avoid cleavage of the RAFT functionality.

Analyses of the ITO Glass Surfaces, during the Stepwise Modification Process, Using XPS Spectroscopy. The stepwise modification of the ITO substrates was monitored using XPS spectroscopy. XPS spectra of the bare ITO substrate indicated the existence of In, Sn, C, O, and Si (Figure 3a). After modification with APTES and tartaric acid, the XPS spectra confirmed the presence of C, N, O, Si, Sn, and In, but not Ti or S (Figure 3b). The high-resolution region scan for N element was also conducted, but it cannot be used to monitor the surface

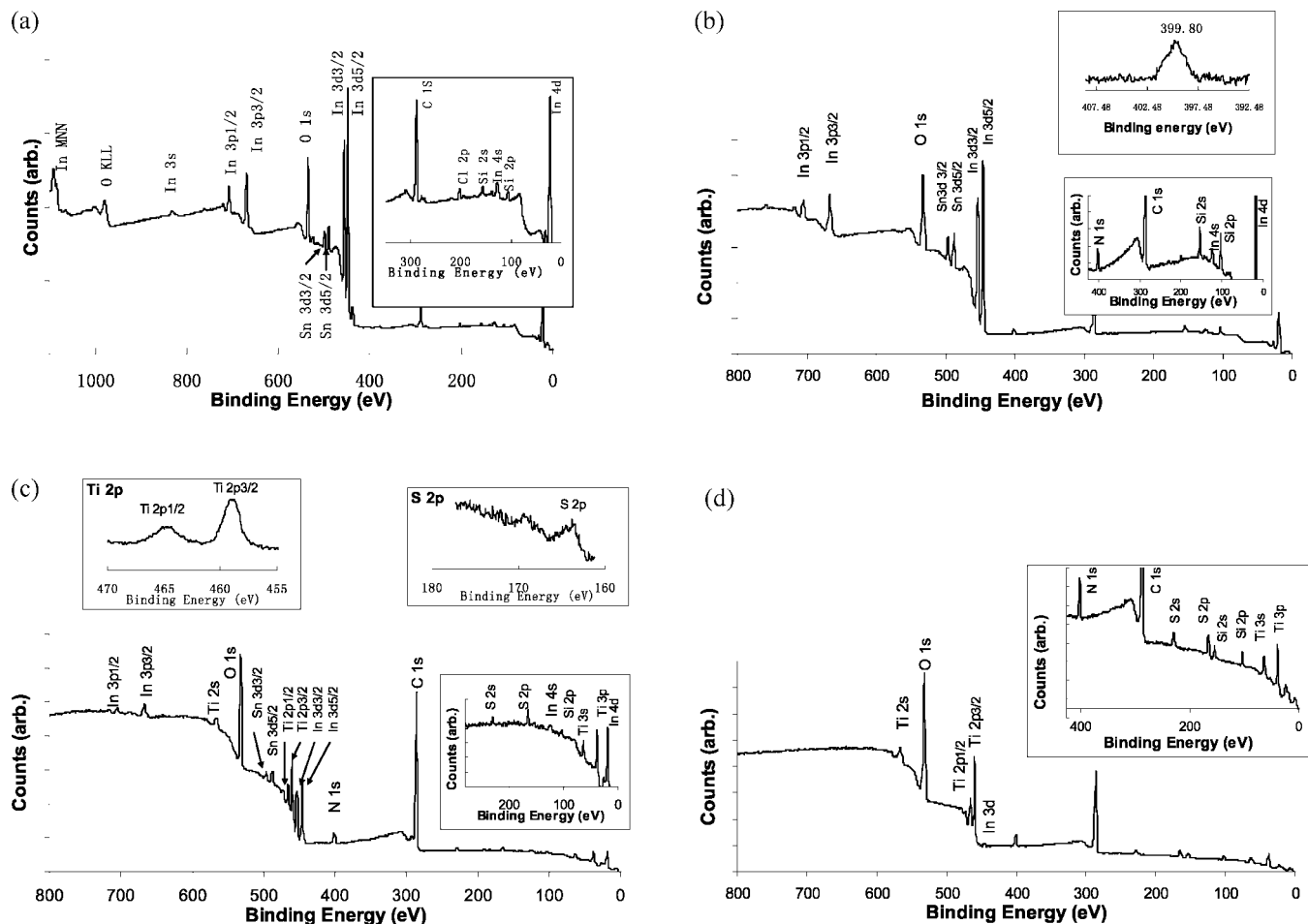


Figure 3. XPS spectra of step-by-step modified ITO surfaces with (a) unmodified bare ITO substrate, (b) 3-aminopropyltriethoxysilane (APTES) and tartaric acid, (c) APTES, tartaric acid, and RAFT agent, CNPD, and (d) APTES, tartaric acid, CNPD, and subsequent in situ polymerization of styrene. All the peaks in the spectra were referenced to the response of C 1s at 285 eV.

Table 1. Contact Angles (θ) of ITO Surface after Stepwise Modifications

modified ITO substrate contact angles (θ) ^a	1	2	3	4	5	6	7
	58 ± 4	76 ± 3	31 ± 2	57 ± 3	83 ± 2	84 ± 3	88 ± 3

^a The contact angles were measured in triplicate, and the average values are reported. S1 represents cleaned ITO substrate, S2 is APTES-modified S1, S3 is S2 modified with tartaric acid, S4 is S3 modified with Ti(OPr)₄, S5 is S4 modified with catechol-terminated RAFT via Ti coordination, S6 is S5 after in situ polymerization of styrene, and S7 is from S4 after surface attachment with catechol-terminal polystyrene.

attachment of tartaric acid through amide coupling, because the primary and secondary amine have only tiny difference in response (399.83 eV in primary amine and 399.81 eV in amide) (upper inset of Figure 3b). However, contact angle analysis can provide more evidence of the successful attachment of tartaric acid, as shown in Table 1. The tartaric acid-modified ITO surface was further modified with Ti(OPr)₄ and subsequently with catechol-functional RAFT agent, CNPD; the spectra clearly showed the presence of Ti and S in addition to C, N, O, Si, Sn, and In (Figure 3c). The high-resolution region scan for Ti and S supplied more elemental information (insets of Figure 3c). The high-resolution scan for S evidenced the existence of S in the RAFT agent as well as the trace oxidized S (response at 169 eV), probably formed due to the oxidation. After in situ polymerization of styrene, the ITO surface was again analyzed by XPS spectroscopy (Figure 3d). The signals corresponding to C, N, O, Si, Sn, Ti, and S could be discerned, despite weaker intensities. The signal corresponding to In was hardly recognizable attributable to the attenuation effect of the brush overlayer. It should be noted that XPS analysis is generally restricted to elements no more than 10 nm below the surface. In a later experiment, where the polymer brushes were cleaved from the surface, XPS was also applied. In this case we confirmed the

disappearance of the Ti signal, consistent with the proposed mechanism for brush removal (the spectrum is similar to Figure 3b; therefore it is not shown).

Analysis of Polymeric Brushes Generated from Both “Graft-To” and “Graft-From” Methodologies Using Atomic Force Microscopy (AFM). The PS brushes were first prepared by postpolymerization and self-assembly of the catechol-terminal PSt on ITO surfaces, tailored with 1,2-diol surface groups, through Ti coordination. When this “graft-to” method was used, the AFM confirms brush formation but some pinholes are observed (as pointed by the arrows in Figure 4a), and the visual evidence suggests a less-dense grafted structure and the polymer brushes are comprised of chains collapsed on the surface of the ITO glass (Figure 4a). In contrast, when the polymer brushes were prepared by in situ polymerization as illustrated in Scheme 2, we observe via AFM (Figures 4b) a brushlike conformation on the ITO surface, with the polymer brushes grown in close proximity to each other, resulting in a high amount of steric repulsion causing the free chain ends to “stretch” away from a collapsed state on the surface.² It should be noted that the exact size of polymeric brushes could not be measured accurately using AFM analyses due to tip convolution effects. When the

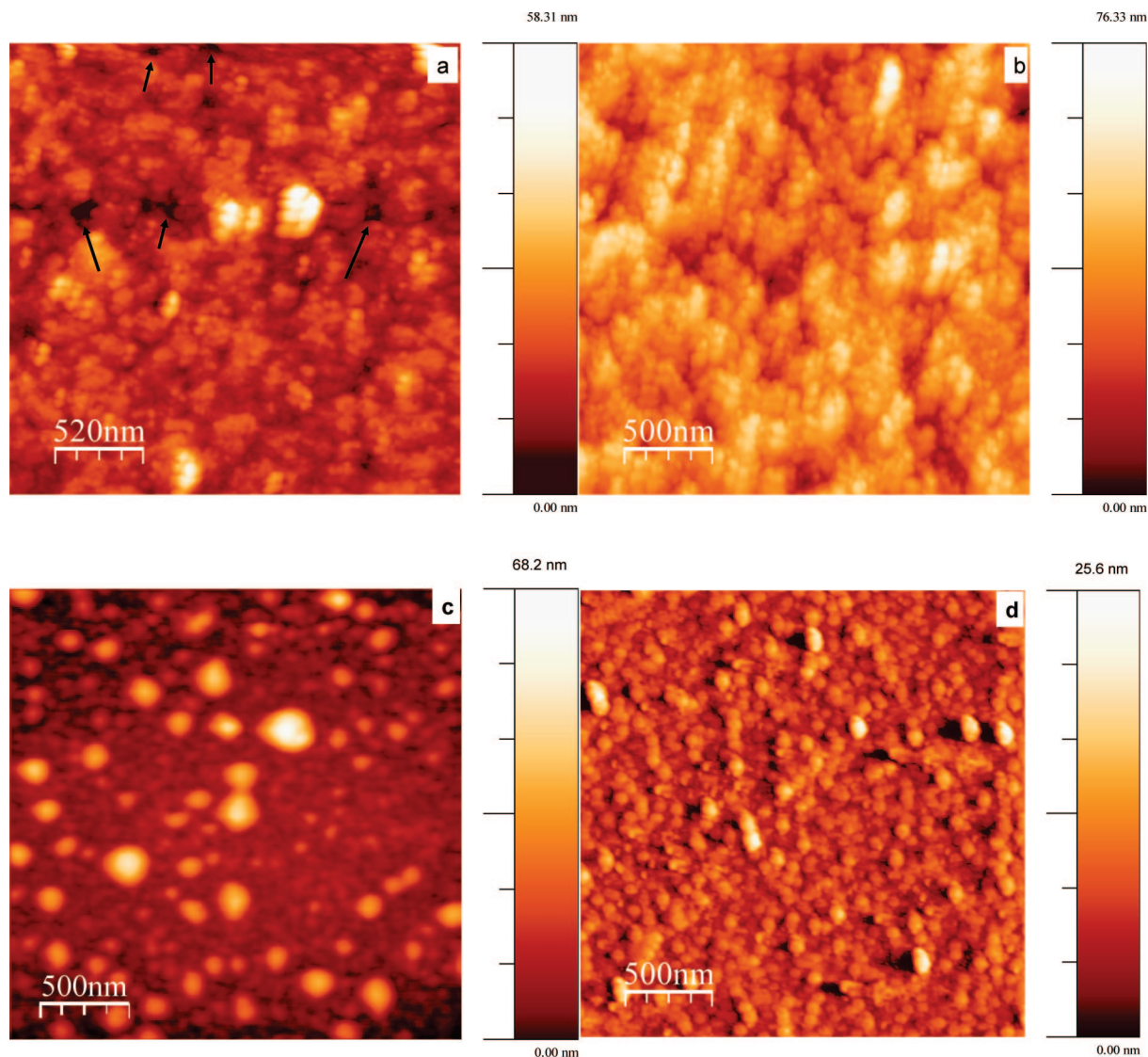
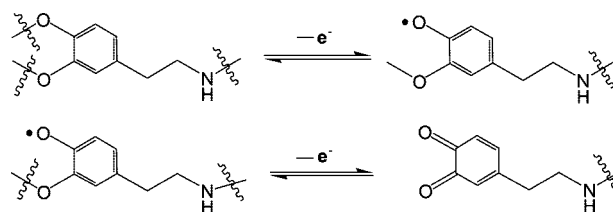


Figure 4. (a) AFM images of ITO surfaces modified with PS brushes by self-assembly of catechol-terminated polystyrene (PSt) (graft-to) (M_n , 10 000; PDI, 1.14) via Ti coordination, (b) PSt brushes generated from the in situ polymerization of styrene for 43 h on CNPD-modified ITO substrate (graft-from), (c) ITO surface created from "graft-from" methodology after brush cleavage, and (d) ITO surface after modification with APTES and tartaric acid only. All AFM images are topography images with the image size $2.5 \times 2.5 \mu\text{m}$. The height profiles were all obtained from topography images that have been leveled by first-order plane subtraction. No other data manipulation was done on the images.

polymeric brush-modified ITO substrate was subject to incubation in phosphate buffer (pH 9.0), the polymer brushes were completely removed from the surface in a short time period. No brushes were observed on the surface as confirmed by AFM analysis (Figure 4c) and XPS measurements (as discussed in the previous section). As a control, the ITO substrate modified with APTES and tartaric acid alone was also analyzed by AFM (Figure 4d). It was observed that the roughness of the ITO substrate after cleavage was significantly increased compared to the substrate before brush attachment, probably due to the damage during the cleavage process.

Characterization of Surface Bounded RAFT Agent and Polymeric Brushes Using Electrochemistry. The electrochemistry of dopamine has been extensively studied on metal and carbon electrodes.^{69–73} It was found that the redox reaction of dopamine proceeds via a sequence of a two-electron step mechanism. Therefore, the redox reaction of the catechol moiety in CNPD will follow the mechanism as illustrated in Scheme 3.⁷⁴ The ITO substrate is a degenerate n-type semiconductor with highly populated positively and negatively charged sites providing numerous applications for surface tailoring and in

Scheme 3. Proposed Mechanism of the Redox Reaction of Catechol Moiety in RAFT Agent, CNPD, and CNPD Controlled Polymer



electrochemical sensors.^{75–78} Dopamine is oxidized easily on ITO surfaces; however, the redox behavior was found to be very irreversible on ITO surface in contrast to other surfaces, indicating that the reduction of a catechol group from quinone is suppressed at the ITO electrode.⁷⁹

When the ITO surface was modified with APTES and tartaric acid alone, no redox peaks were observed in its cyclic voltammogram (CV) (Figure 5a). However, when the CNPD was attached through catechol moiety by Ti coordination, a strong oxidation peak at 328 mV was observed, confirming the

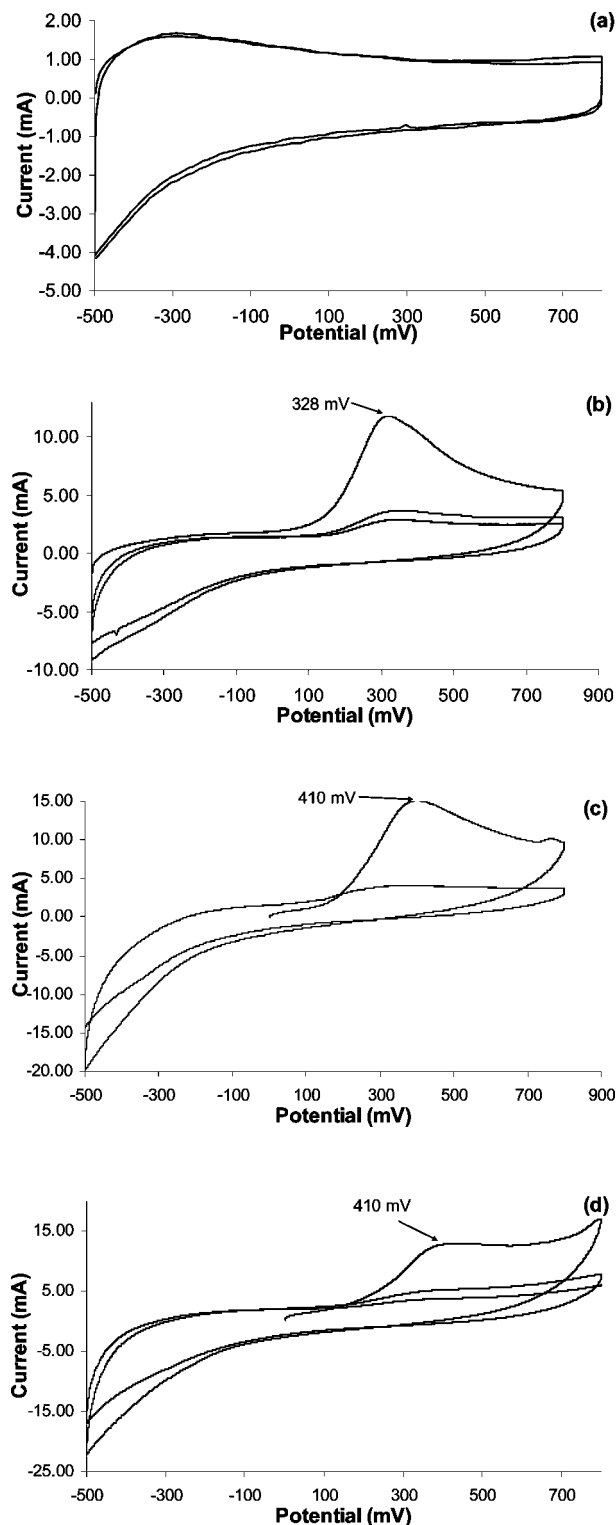


Figure 5. Cyclic voltammograms of ITO substrates from step-by-step modifications (scan rate, 100 mV/s in phosphate buffer (pH 7.0)): (a) modified with APTES and tartaric acid, (b) modified with APTES and tartaric acid and CNPD via Ti coordination, (c) substrate (b) after in situ polymerization of styrene for 28 h (graft-from), and (d) substrate modified with catechol-terminated PS_t through self-assembly (graft-to).

successful attachment of RAFT groups to the ITO substrate (Figure 5b). After the subsequent surface grafting of styrene, the CV of the resulting ITO substrate exhibited a similar oxidation peak to that before surface polymerization. The oxidation peak moved to 410 mV after attachment of polymer brushes, indicating that the oxidation became more difficult once

the redox-active catechol moiety was insulated by the surface generated polymer chains. It is true that the redox active moiety is directly bound to the substrate. However, a fact about the electron transfer in the electrolyte system is that the electron transfer is always accompanied by ion transfer. The insulation of the redox active center (in this case the active center is catechol group) by the polymer brushes will block the access of the electrolyte to the redox site for charge compensation, thus needing more energy (high potential) to perform the oxidation⁸⁰ (Figure 5c). CV was also recorded with the PS brush formed by the “grafting-to” approach. As shown in Figure 5d, a strong oxidation peak at 410 mV was also observed. The cyclic voltammetry analyses have provided evidence that both “graft-from” and “graft-to” methodologies can be used to generate polymeric brushes via Ti–diol coordination.

Cyclic voltammetry has proved to be a convenient tool to calculate the coverage of surface-attached redox species.^{80,81} Katz and co-workers have successfully utilized cyclic voltammetry to quantify the polymer brushes.⁸² The surface coverage of the redox species can be calculated by integrating the area of the oxidation or the reduction peaks, divided by the number of electron transfer events involved in the redox reaction. The coverage of CNPD attached on the ITO surface was found to be 2.9×10^{-10} mol cm⁻² by integrating the area of the first oxidation peak. After in situ polymerization the coverage was measured to be 2.7×10^{-10} mol cm⁻², almost the same as that before polymerization, demonstrating the robustness of the surface construct through Ti complex after in situ polymerization. However, the coverage of the polymer chains obtained from the postpolymerization self-assembly (grafting-to) was calculated to be only 1.2×10^{-10} mol cm⁻², approximately half that from the in situ polymerization. This result is consistent with that observed by the AFM analyses (Figure 4), that is, the brush generated from “graft-to” methodology is less dense than that from the “graft-from” one.

Investigation of the Surface Property of ITO Substrates after Stepwise Modification Using Contact Angle Analysis.

Water contact angles were also utilized to analyze the ITO substrates after stepwise modification. As shown in Table 1, the APTES-modified surface exhibits a significant increase in hydrophobicity when compared to the bare ITO surface. However, when the APTES-modified substrate was further modified with tartaric acid through amide chemistry, the surface became very hydrophilic ($\theta = 31^\circ$), consistent with the presence of hydroxyl groups, confirming the successful attachment of tartaric acid. The further modification of the ITO surface with RAFT agent, CNPD, resulted in an increase of hydrophobicity ($\theta = 83^\circ$), similar to the result of polymer brushes obtained by in situ polymerization of styrene and those by the “grafting-to” approach. The brush surface generated from in situ polymerization had a slightly increased hydrophobicity over that obtained from the “grafting-to” approach.

Conclusions

We have successfully demonstrated a new modular building approach to polymer architectures and nanomaterials. In this first example, we have created pH-detachable polymer brushes on ITO substrates via Ti complex chemistry. Using Ti–diol coordination, polymer brushes could be generated via both “graft-from” and “graft-to” methodologies. The “graft-to” methodology could be used to self-assemble polymer chains with 1,2-diol terminal groups via Ti complexation. The polymeric brushes created using the “graft-from” protocol were much denser and more homogeneous than those generated by post-polymerization self-assembly. The redox properties of terminal catechol groups furnished a convenient means to allow us to calculate the surface coverage of surface-bound RAFT agent

and polymer chain density using cyclic voltammetry. This new synthetic approach allowed us to reversibly remove the brushes from the surface under weakly basic conditions. This Ti–diol chemistry is quite general and can be adapted to other methods of living (and nonliving) polymerization, including NMP and ATRP. In future papers, we will describe the use of this synthetic approach to build up complex polymer architectures in solution and for the surface fictionalization of nanoparticles.

Acknowledgment. T.P.D. thanks the Australian Research Council for Federation Fellowship Award. J.Q.L. acknowledges the UNSW Vice Chancellor's Postdoctoral Research Fellowship. We thank Dr. Volga Bulmus for valuable discussions. The comments of the referees are gratefully acknowledged as they have contributed to a significantly improved manuscript.

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MA802256G