Grafting of polymers from electrodeposited macro-RAFT initiators on conducting surfaces

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A novel route for grafting polymers via electropolymerization of a macro-reversible addition fragmentation chain-transfer (RAFT) agent onto a conducting surface is reported. The electro-deposition of the chain transfer agent (CTA) on the conducting surface was done using cyclic voltammetry (CV). The statistically exposed dithiobenzoate moieties served as a CTA for the polymerization of styrene on a matrix of an electrodeposited conjugated polymer. The polystyrene (PS)-modified substrate was then used as the macro-CTA for the synthesis of the second block of poly-tert-butyl acrylate (PTBA) on the surface. The polymerization from the surface was characterized by surface analytical methods including AFM, XPS, and contact angle measurements.

1. Introduction

The fabrication of nanostructured ultrathin films is of considerable interest for creating functional coatings for optical devices, biomedical implants, sensors, and electronic semiconductors. Methods of producing these ultrathin films range from simple evaporative to directed-assembly techniques including spin-coating, Langmuir–Blodgett films [1], layer-by-layer [2], and droplet evaporation to name a few. However, these polymer films can be easily desorbed or delaminated under the right solvent and temperature conditions. To circumvent this problem, surface-initiated polymerization (SIP) has been used to immobilize polymers at interfaces [3]. In this method, polymer brushes are usually grown from initiators or chain transfer agents (CTAs) covalently tethered on surfaces to create a more robust film of high grafting density. This is typically done by self-assembled monolayers (SAM) on the surface either through initiator thiols, for gold surfaces, or silanes, for hydroxyl-terminated surfaces. For reversible addition fragmentation chain transfer (RAFT) polymerization, the CTA was first immobilized and subsequent polymerization using the “grafting from” approach was demonstrated from different surfaces such as silica-nanocomposites, silica nanoparticles with combination of click-chemistry and RAFT polymerization, silicon wafers, carbon nanotubes, clay, Cds nanoparticles, cellulose and membranes [4]. Although this strategy addresses the issue of film stability on these surfaces, specific initiators and CTAs may have limited application towards electrode interfaces and the electrochemical environment. This is the case especially with thiol derivatives which can be reductively desorbed at specific potentials. Moreover, the issue of macroinitiator functionality in electrochemically active interfaces has not been widely explored. To our knowledge, only one report has demonstrated RAFT grafting from indium–tin oxide (ITO) recently using titanium-diol coordination. In their case, the RAFT agent was self-assembled on the surface by a catechol-functional RAFT agent and not directly electrodeposited as in our case [5].

Herein, we report a novel method of introducing a CTA on conducting and electrode substrates via direct electrografting (Scheme 1). Conveniently, only one type of CTA was needed to graft polymers on both gold and indium tin oxide (ITO) electrode surfaces, i.e. no need for a separate thiol or silane derivative synthesis. The presence of the electro-active moiety, thiophene, in the CTA, enabled its direct surface immobilization through electropolymerization. The growth of the polymer brush from the electro-immobilized CTA was then demonstrated by using the surface initiated RAFT polymerization (SI-RAFT). The RAFT technique should extend the versatility of the system towards a wide range of monomers...
Moreover, by using anodic electropolymerization to introduce the CTA on the surface, a $g$-conjugated or conducting polymer film can be deposited simultaneously, which presents a broad range of potential applications in sensors, electro-optical materials, and semiconductor devices [7]. Thus, the combination of the SI-RAFT polymerization of different functional polymers with conducting or $g$-conjugated polymers may serve as a platform for a novel class of ultra-thin polymer films with multiple stimuli mechanisms ranging from solvent-selective to electrochemical response.

2. Experimental part

2.1. Materials

Reagent chemicals and monomers were purchased from Aldrich and were used without further purification unless otherwise indicated. Tetrahydrofuran (THF) used in the syntheses was distilled from sodium benzophenone. Styrene and tert-butylacrylate (TBA) were passed through a column of activated basic alumina to remove the inhibitor. 2,2-azobis(isobutyronitrile) (AIBN) which was recrystallized twice from ethanol.

2.2. Characterization

NMR spectra were recorded on a General Electric QE-300 spectrometer at 300 MHz for $^1$H. UV–Vis was recorded on an Agilent 8453 spectrometer. GPC was carried out on a Viscotek 270 instrument with a triple detector array (RLS, IV, RI, or UV) equipped with 2 GMHHR-M and 1 GMHHR-L mixed bed ViscoGel columns (eluent: THF; flow rate: 1 mL min$^{-1}$). CV was performed on an Amel 2049 potentiostat and power lab/4SP system with a three-electrode cell. In all the measurements, the counter electrode was a platinum wire, and ITO or gold was used as a working electrode. Atomic force microscopy (AFM) imaging was performed under ambient conditions with a PicoSPM II (PicoPlus, Molecular Imaging) in the intermittent contact mode. Ellipsometric measurements were carried out using the Multiskop, Optrel GBR with a 632.8 nm helium–neon laser at 60° angle of incidence. Refractive indices were fixed at 1.50 for all respective surface modifications except for polystyrene (PS) and poly($t$-butylacrylate) (PTBA), which were 1.55 and 1.46, respectively. The Au-glass electrodes were cleaned with a plasma ion cleaner (Plasmod, March). X-ray photoelectron spectroscopy (XPS) was carried out in a Physical Electronics 5700 instrument with photoelectrons generated by the non-monochromatic Al Kα irradiation (1486.6 eV). Photoelectrons were collected at a take-off angle of 45° using a hemispherical analyzer operated in the fixed retard ratio mode with an energy resolution setting of 11.75 eV. The binding energy scale was calibrated prior to analysis using the Cu 2p3/2 and Ag 3d5/2 lines. Charge neutralization was ensured through co-bombardment of the irradiated area with an electron beam and the use of the non-monochromated Al Kα source. This placed the adventitious C 1s peak at a binding energy of 284.6 eV.

2.3. Synthesis of the electrograftable CTA (Scheme 2)

2.3.1. Synthesis of 4-Cyano-4-((thiobenzoyl)sulfanyl)pentanoic acid (1) [1].

4,4’-Azobis(4-cyanovaleric acid) (4.19 g, 0.0149 mol) and bis(thiobenzoyl)disulfide (3.07 g, 0.01 mol) were dissolved in ethyl acetate (200 mL) in a 500 mL round-bottom flask equipped with a condenser. The mixture was degassed by bubbling through with N$_2$ and heated to reflux for 20 h under N$_2$. The reaction was allowed to cool to room temperature, and the solvent was removed in vacuum. The crude product was purified by column chromatography (silica gel) with ethyl acetate: hexanes 2:3 as the eluent. After the removal of solvent, the red fraction gave 4-cyano-4-((thiobenzoyl)sulfanyl)-pentanoic acid as a red oil. The product solidified upon sitting at $-20^\circ$C. $^1$H NMR (CDCl$_3$) δ (ppm): 1.93 (s, 3H, $\text{CH}_3$); 2.38–2.80 (m, 4H, $\text{CH}_2\text{CH}_2$); 7.42 (m, 2H, $m$-$\text{ArH}$); 7.56 (t, 1H, $J$ = 8 Hz, $p$-$\text{ArH}$); 7.91 (d, 2H, $J$ = 7.3 Hz, $o$-$\text{ArH}$). $^{13}$C NMR (CDCl$_3$) δ (ppm): 24.1, 29.5, 32.9, 45.6, 118.4, 126.7, 128.6, 133.1, 144.4, 177.3, 222.1.

2.3.2. Synthesis of 2-(thiophen-3-yl)ethyl 4-cyano-4-(phenylcarbonothioylthio) pentanoate, CTA (2)

In a 100 mL round-bottom flask equipped with a stir bar and an addition funnel, a solution of 4-cyano dithiobenzoate pentanoic acid (0.675 g, 2.42 mmol) and 2-(thiophen-3-yl)ethanol (0.36 g, 2.90 mmol), and 4-((dimethylamino)pyridine (DMAP) (30 mg,
0.245 mmol) in 30 mL of dry CH₂Cl₂ was cooled to 0 °C under N₂, N, N′-Dicyclohexylcarbodiimide (DCC) (0.598 g, 2.89 mmol) was dissolved in 5 mL of CH₂Cl₂ and added dropwise to the reaction flask under stirring. After completion of DCC, the reaction was stirred for 5 min at 0 °C and then allowed to warm to room temperature overnight. Then, the solid was removed by filtration, and the filtrate was washed with diluted aqueous sodium bicarbonate (20 mL) and water (2 × 20 mL) and finally dried over anhydrous MgSO₄. The solution was filtered and the solvent removed to yield the crude product mixture as red oil, which was further purified by column chromatography on silica gel using 2:1 hexane/ethyl acetate as eluent. The final product was obtained as viscous red oil (0.342 g, 36.3% yield).¹H NMR (CDCl₃): 2.34–2.73 (m, 4H, CH₂CH₂); 2.98, (t, 2H, CH₂, J = 8 Hz) 4.32 (t, 2H, -OCH₂, J = 7.6 Hz); 6.97 (d, 1H, J = 4 Hz, thiophene); 7.03 (s, 1H, thiophene); 7.28 (d, 1H, thiophene); 7.40 (t, 2H, J = 8.6 Hz, m-CH₂); 7.57 (J, 1H, p-CH₂, J = 8 Hz); 7.91 (d, o-CH₂, 2H, J = 9 Hz).¹³C NMR (CDCl₃): 24.0, 29.4, 29.8, 33.3, 45.6, 64.8, 118.4, 121.6, 125.7, 126.4, 126.6, 133.0, 137.6, 144.5, 171.4, 222.2. Elemental analysis calculated for C₁₉H₁₉NO₂S₃: C, 58.5; H, 4.9; N, 125.7, 126.4, 126.6, 133.0, 137.6, 144.5, 171.4, 222.2. Elemental analysis calculated for C₁₉H₁₉NO₂S₃: C, 58.5; H, 4.9; N, 3.6; O, 8.2; S, 24.6. Found: C, 58.2; H, 4.9; N, 3.7; S, 24.2.

2.4. Electrodeposition of CTA on conducting surfaces

The electrodeposition of the CTA RAFT agent was done using the cyclic voltammetry (CV) technique. In a three-electrode cell, 0.1 M tetrabutylammonium hexafluorophosphate (TBAP) as supporting electrolyte, 0.25 mM of the CTA RAFT agent and 0.75 mM of 9H-carbazole or 1:3 M ratio in CH₂Cl₂ were mixed and stirred sweep-wise until the CTA RAFT agent electrode was platinum. The electrodeposition of the CTA RAFT agent was done using the cyclic voltammetry (CV) technique. In a three-electrode cell, 0.1 M tetrabutylammonium hexafluorophosphate (TBAP) as supporting electrolyte, 0.25 mM of the CTA RAFT agent and 0.75 mM of 9H-carbazole or 1:3 M ratio in CH₂Cl₂ were mixed and stirred sweeping the voltage at a scan rate of 50 mV/s during the electropolymerization on ITO.

2.5. Surface-initiated RAFT polymerization

In a typical run, 5.0 mL of styrene (4.53 g, 43.49 mmol), 47.94 mg (86.98 µmol) of the CTA, 1.42 mg (8.69 µmol) of AIBN initiator and 3.0 mL of THF were added to a 50 mL Schlenk flask and three freeze-pump cycles were carried out to remove any dissolved gas. After that, the contents were stirred gently and purged with nitrogen for one hour. To a second Schlenk tube back-filled with nitrogen the ITO or gold modified polystyrene surfaces and the free polymer were added and then analyzed by gel permeation chromatography (GPC). For the copolymer synthesis, the procedure used was the same as that for polystyrene synthesis, but the monomer used was TBA with the ITO or gold modified polystyrene surfaces and the free polymer was used to estimate the molecular weight and the monomer conversion.

3. Results and discussion

As shown in Scheme 1, the fabrication of the polymer brush starts with the electro-deposition of the CTA copolymerized with carbazole on the conducting surface using cyclic voltammetry (CV). Copolymerization with the carbazole is a direct demonstration of the potential for electropolymerizability with other conducting polymers as previously reported by our group [8]. The statistically exposed dithiobenzoate moieties on the surface then serves as the CTA for polymerization of styrene as the first block. The polystyrene (PS)-modified substrate was then used as the macro-CTA, for the synthesis of the second block of poly-tert-butyl acrylate (PTBA) on the surface. Again, the copolymerization (di-block) demonstrates the feasibility for SIP living polymerization methods in this system [4]. The surfaces were then characterized by atomic force microscopy (AFM), X-ray photoelectron spectroscopy (XPS), ellipsometry, water contact angle, and UV–Vis spectroscopy.

During the electropolymerization process, it can be observed that copolymerization of the thiophene radical is easier than that of carbazole. The oxidation onset of the thiophene bearing CTA with carbazole lowered the onset of oxidation (0.6 V) (Fig. 1a) compared to that of the CTA alone (1.0 V) (Fig. 1b). This is preferred to prevent possible decomposition of the polymer film at higher oxidation potentials [8]. This technique is an advantage because it avoids the use of a thiophene dimer or trimer, to lower the overall oxidation potential of electropolymerization of polythiophenes, which requires multiple steps of synthesis [9]. It can be seen from Fig. 1 that these films have high cyclic stability with the oxidation and reduction waves consistent with a thiophene and carbazole co-electropolymerization. The electropolymerized film on the ITO was characterized further using the UV–Vis spectroscopy, confirming the presence of a π-conjugated polymer at the interface (Fig. 2). The peaks observed at 400 and 760 nm corresponded to the absorption of polaronic conjugated polymer at the interface (Fig. 2). The peaks observed at 400 and 760 nm corresponded to the absorption of polaronic and bipolaron species of the combined polycarbazoles and polythiophenes species [8,10]. The immobilization of the copolymer film was further verified by XPS. The XPS scan of the electropolymerized film (Fig. 3a) reveals the presence of the expected C, O, N, and S signals derived from the statistical distribution of carbazole and CTA functional group [10]. The high resolution scan of the S 2p...
peak confirmed the assignment of thiophene and the dithiobenzoate moieties of the CTA.

The CTA-modified ITO surface was then subjected to SI-RAFT polymerization of styrene and then TBA as a second block. Free CTA was added in the monomer solution to ensure controlled polymerization kinetics and for molecular weight estimation of the polymer brushes (Table 1). Narrow PDI values were obtained (<1.2), signifying a well-controlled polymerization. XPS results of the PS brush and the diblock copolymer of PS-b-PTBA likewise confirmed the successful growth of the polymer brushes. Comparison of the XPS wide scans of the C 1s and O 1s peaks of the PS and the PS-b-PTBA (Fig. 3b and c) corroborated with the expected theoretical distribution of the peaks where greater C 1s peak intensity is observed for the PS brush and an increase in O 1s intensity relative to the C 1s peak was seen after incorporation of the PTBA block. The AFM topographies of the films showed transition in morphological features from the electropolymerized macroinitiator layer (granular) (rms roughness = 0.35 nm) to the formation of the homopolymer (globular) (rms roughness = 0.92 nm) and diblock brushes (ridged features) (rms roughness = 3.87 nm) (Fig. 4). The thickness was determined using ellipsometry and also increased additively from the electro-immobilized carbazole-CTA film (5.3 nm); PS brushes (17.8 nm); diblock copolymer of the PS-b-PTBA (30.7 nm).

To investigate the versatility on another electrode, the whole process was also conducted on a gold surface. The thickness and contact angle of the films on each step were monitored to examine the deposition of the films introduced on the surface. Table 2 summarizes the thicknesses and contact angles of the films on the surface after each step. The increasing thickness of the film after each surface modification step proved the stepwise incorporation of the materials deposited beginning with electrodeposition up to the formation of the diblock copolymer. The static water contact angle of the electro-grafted CTA changed from 75° to 97° after the

![Fig. 2. UV–Vis spectrum of the co-electropolymerized CTA (2) and carbazole on ITO surface (0.25 mM CTA 1 and 0.75 mM of carbazole monomer in CH₂Cl₂).](image)

![Fig. 3. (a) XPS wide scan of the co-electropolymerized CTA (S2) and carbazole. (Inset) Narrow scan of the S 2p peak from the electropolymerized film, and XPS narrow scan of the (b) C 1s and (c) O 1s of the PS and PS-b-PTBA brushes.](image)

![Fig. 4. AFM topographies of the (a) electro-copolymerized CBz-TP-CTA, (b) PSTy homopolymer after first RAFT polymerization, and (c) PSTy-b-PTBA diblock copolymer brush after the second RAFT polymerization on ITO substrate. (Inset) The 3-D representation of each topography. A scale bar is equivalent to 1 μm.](image)

**Table 1**

<table>
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<tr>
<th>Polymer</th>
<th>[M]:[CTA]:[I]</th>
<th>(M_n,\text{theory}^{a} \times 10^3)</th>
<th>(M_n,\text{GPC})</th>
<th>%Conv^{b}</th>
<th>PDI</th>
</tr>
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<tr>
<td>PS</td>
<td>500:1:0.1</td>
<td>9410</td>
<td>9.50 × 10³</td>
<td>14.0</td>
<td>1.05</td>
</tr>
<tr>
<td>PTBA</td>
<td>500:1:0.1</td>
<td>12503</td>
<td>1.27 × 10³</td>
<td>15.3</td>
<td>1.09</td>
</tr>
</tbody>
</table>

\(^{a}\) \(M_n,\text{theory} = [M]/[CTA] \times \text{Conv} \times M_W \text{CTA} + M_W \text{PS}

\(^{b}\) Conversion determined by RI response for styrene and NMR for TBA.
growth of the more hydrophobic PS brush and then to 63° after the PTBA block, which is more hydrophilic. The films formed showed stability on the surface as proven by its adhesion even after overnight Soxhlet extractions. This stability originates from the insolvability of the highly cross-linked network of the macroinitiator on the surface as demonstrated in our previous report on electrodeposited macroprecursors [11].

4. Conclusion

In conclusion, we have demonstrated a novel route for the preparation of polymer brushes by combining the techniques of macro-CTA electrodeposition with SI-RAFT polymerization. The CTA with the electro-active thiophene moiety is an initial design, which can be further modified using other types of electroactive groups such as aniline, pyrrole, furan, etc. The versatility to different electrode surfaces was successfully demonstrated on two types of conducting substrates with carbazole copolymerization being utilized to lower the oxidation potential. The subsequent growth of the polymer brushes from the electro-deposited CTA proved that the CTA was electrochemically stable during the electropolymerization stage. Furthermore, the incorporation of the second block of PTBA demonstrated the “living nature” of the macro-CTA PS block. Further development of this method should open a wide range of applications on other metal and metal oxide electrode surfaces. Future work includes incorporation of other electro-optically active conducting polymers and the simultaneous investigation of stimuli-responsive polymer brushes via other SIP mechanisms including ATRP, Metathesis, NMP and others.

Acknowledgements

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.reactfunctpolym.2011.05.013.

References

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Table 2

<table>
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<tr>
<th>Surface</th>
<th>Thickness (nm)</th>
<th>Contact angle (degrees)</th>
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<tr>
<td>CBz-Tp-CTA</td>
<td>2.2 ± 0.2</td>
<td>75 ± 1.03</td>
</tr>
<tr>
<td>PS brush</td>
<td>11.3 ± 1.0</td>
<td>97 ± 0.56</td>
</tr>
<tr>
<td>PS-b-PTBA brush</td>
<td>26.1 ± 1.3</td>
<td>63 ± 0.97</td>
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