Surface-Tethered Conjugated Polymers Created via the Grafting-From Approach

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ABSTRACT: Polyacrylate brushes with pendent terthiophenes [poly(terthiophene methyl methacrylate) (PTTMM)] were successfully grown from indium tin oxide and gold with surface-initiated atom transfer radical polymerization. The films formed on both substrates were characterized by ellipsometry and Fourier transform infrared spectroscopy. Using cyclic voltammetry, we electrochemically crosslinked the PTTMM brush to form a conjugated polymer network. The conjugation lengths in the film were increased as evidenced by ultraviolet–visible spectroscopy. Additionally, an atomic force microscopy study on the surface-modified solid substrate revealed the formation of a smooth and uniform polymer brush with a low surface roughness, even after electrochemical crosslinking. These uniformly grafted conducting polymer brushes may find use in photovoltaic devices. © 2014 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2015**, *132*, 41363.

INTRODUCTION

Over the past several decades, π-conjugated organic polymer materials have been extensively investigated as active elements in sensors,[1a] optoelectronic[1b] and semiconducting devices,[2] and electroluminescent, photoconducting, electron-transporting, hole-transporting, and ion-dopable materials.[3] One of the most widely used materials is polythiophene, which has attractive properties, such as a high electrical conductivity, electrochromism, and electroluminescence.[4] Polythiophene and related polymers are synthesized by two general methods, direct electropolymerization from electrode surfaces and step-growth methods, such as the chemical coupling of dibromo monomers or chemical oxidation by $FeCl_3$ and other oxidants.

Electropolymerization conveniently deposits electroactive polymers directly onto sensor substrates and permits control over the coating thickness because the polymerization proceeds by the application of a precisely controlled potential. Despite these advantages, poor interfacial adhesion between the conducting polymer and the electrode is a major concern.[5–10] One strategy for improving the adhesion is to form conducting polymers from polymerizable precursors preadsorbed on a metallic substrate (gold, nickel, or platinum) via thiol functional groups.[5–7] An alternative approach is to graft conducting polymers onto metal oxide surfaces, such as indium tin oxide (ITO),[9] where the key step is the chemisorption of a preformed conducting polymer or its precursor. More recently, conjugated polymer network films have been grafted on conducting surfaces by the synthesis of precursor polymers from monomers with pendant electroactive units followed by the elaboration of the pendant unit by electropolymerization or chemical oxidation.[11–17] The resulting polymer films are intrinsic conducting polymer networks having both intermolecular and intramolecular crosslinks between the pendant monomer units.

Surface-initiated atom transfer radical polymerization (ATRP) is an attractive alternative for modifying surfaces because the surface properties can be easily modified through variation of the composition of the polymer brush, grafting density, degree of polymerization,[18] and so on; most importantly, the delamination of the polymer layer from the surface can be eliminated. Recently, Jhaveri and Carter[19] reported the successful grafting of disubstituted polyacetylene brushes grown from modified silicon and quartz surfaces with a transition-metal-catalyzed polymerization technique. Snaith et al.[20] used surface-initiated ATRP to produce tethered poly(triarylamine acrylate) hole-transport materials for use in photovoltaic devices. Compared to devices prepared by solution-casting methods, devices prepared from tethered polymers showed enhanced conductivity; this was attributed to control over the polymer architecture and morphology. Gopalan

et al.[21] showed an easy approach for generating well-defined poly(3-hexylthiophene) (P3HT) brushes on SiO$_2$ surfaces with a click reaction between ethynyl-terminated P3HT and an azide terminated self-assembled monolayer (SAM) on SiO$_2$. Another facile route for preparing conducting polymer brushes on a solid surface is the immobilization of cyclopentadienyl end-capped P3HT with cyclopentadiene–maleimide Diels–Alder ligation.[22] Recently, Malmstrom et al.[23] demonstrated an attractive but simple route for grafting an electrically addressable conductive polymer [poly(3,4-ethylenedioxythiophene)] onto large-area gold-coated electrodes by electropolymerization and used as an ATRP initiating site to grow pH-responsive poly(acrylic acid) brushes therefrom. Advincula et al.[24] grew poly(vinyl carbazole) brushes from an ITO surface by surface-initiated free-radical polymerization, controlling the graft density and brush length. In a second step, they crosslinked the poly(vinyl carbazole) brush electrochemically to obtain a conjugated polymer network. Nowadays, conducting polymer brushes grafted onto solid surface find applications ranging from controlled protein absorption/cell adhesion,[25] enzyme immobilization,[26] and light harvesting[27] to stimuli-responsive surfaces.[28,29] At the same time, nonconductive polymer brushes grown from conducting polymer films are also gaining popularity as electrochemically switchable surfaces.[30–33]

Herein, we wish to report the growth of poly(terthiophene methyl methacrylate) from gold and ITO substrates with ATRP. Moreover, the electropolymerization of the pendant terthiophene groups from the polyacrylate brush was used to form conducting crosslinked polymer network films of oligothiphene and polythiophene. All of the obtained surface-grafted polymers were analyzed by ellipsometry, Fourier transform infrared (FTIR) spectroscopy, ultraviolet–visible (UV–vis) spectroscopy, cyclic voltammetry (CV), and atomic force microscopy (AFM).

EXPERIMENTAL

Materials
Unless otherwise noted, all chemicals were obtained from Aldrich. 11-Mercapto-1-undecanol (97%), 2-bromopropionyl bromide (97%), 3-thiophenemethanol, thiophene-3-carbaldehyde, tetrakis(triphenylphosphine) palladium, thiophene-2-boronic acid, methacryloyl chloride (98%), N,N-dimethylformamide (DMF; 99.8%), dimethoxyethane (98%), NaBH$_4$, Cu(I)Cl (99.9%), Cu(I)Br (99.9%), and hexmethyltriethylenetetraamine (HMTETA; 99%) were used as received. Triethylamine (Et$_3$N) and acetonitrile were distilled from calcium hydride under reduced pressure and under an inert atmosphere. Tetraethylammonium perchlorate (TEAP) was dried in vacuo at 80°C for 12 h and stored in a glovebox. Gold-coated Si wafers [200 nm of Au sputtered on 20 nm of Cr on Si (100) wafers] and ITO-coated glass slides were obtained from Delta Technologies.

Characterization Methods
^{1}H-NMR and ^{13}C-NMR analyses were carried out at room temperature (RT) on a Varian UnityPlus-500 spectrometer at 500 and 300 MHz, respectively, with the chemical shifts reported in parts per million and referenced to signals from residual protons in the solvent. The film thicknesses were measured with a rotating analyzer ellipsometer (model M-44, J. A. Woollam) at an incident angle of 75°. The data were analyzed with WVASE32 software and

thickness and refractive index determinations were performed on at least three spots on each substrate. The refractive index of the films was assumed to be 1.5 and was then fitted with the film thickness. Reflectance FTIR spectroscopy was performed with a Nicolet Magna-IR 560 spectrometer containing a PIKE grazing angle (80°) attachment. UV–vis measurements were taken on an Agilent Technologies 8453 spectrometer. AFM images were obtained in tapping mode with Multimode AFM and NanoScope IV software (Digital Instruments, Santa Barbara, CA) at RT. A tapping-mode probe (NSC15) with a nominal frequency of 300 kHz was used for all of the experiments.

Synthesis of 3-Methylthienyl Methacrylate (MTM)
3-Thiophenemethanol (5.7 g, 50 mmol), dry Et$_3$N (7.3 g, 71 mmol), and CuCl (25 mg) were dissolved in 35 mL of anhydrous diethyl ether. A solution of methacryloyl chloride (5.35 g, 51 mmol) in 35 mL of anhydrous diethyl ether was added slowly at 0°C. The resulting mixture was stirred for 2 h and then filtered through a silica gel column to remove triethylammonium chloride. After solvent evaporation, the residue was stirred overnight in a 1:1 mixture of methylene chloride and 2M NaOH. The organic layer was separated, washed twice with water, and dried over CaCl$_2$. After solvent evaporation, the residue was distilled in vacuo (Vigreux column).

bp (1 mmHg) = 90°C. Yield: 70%. ^{1}H-NMR (400 MHz, CDCl$_3$, δ): 1.9 (s, CH$_3$), 5.1 (s, OCH$_2$), 5.5 (s, vinyl H), 6.1 (s, vinyl H), 7.06 (m, ring H), 7.2 (m, ring H).

Synthesis of [2,2′:5′,2″-Terthiophen]-3′-yl Methyl Methacrylate (TTMM)
Synthesis of 2,5-Dibromoformyl-3-thiophene (1). Under an inert atmosphere, a solution of Br$_2$ (0.56 mL, 20 mmol) in anhydrous CHCl$_3$ was added dropwise to a solution of thiophene-3-carboxaldehyde (0.5 mL, 5.5 mmol) in anhydrous CHCl$_3$ (1.5 mL) kept at 60°C. The reaction mixture was refluxed for 5 h, brought to RT, and then poured into about 10 mL of ice–water. The organic phase was neutralized with a Na$_2$CO$_3$ saturated solution, dried with MgSO$_4$, filtered, and evaporated to dryness. The residue was chromatographed on flash silica gel 60 with 90/10 hexane/ethyl acetate as the eluant to give a yellowish orange solid. Crystallization from the heptanes afforded a pale yellowish needlelike crystal in 40% yield.

^{1}H-NMR (400 MHz, CDCl$_3$, δ): 9.80 (s, 1H, CHO), 7.34 (s, 1H, H4).

Synthesis of 3′-Formyl-2,2′:5′,2″-terthiophene (2). A 50-mL, three-necked flask equipped with a condenser, magnetic stirrer, and N$_2$ inlet was charged with **1** (0.21 g, 0.77 mmol), tetrakis(triphenylphosphine) palladium(0) (0.053 g, 0.046 mmol), and 8 mL of 1,2-dimethoxyethane. After 10 min of stirring at RT, thiophene-2-boronic acid (0.24 g, 1.84 mmol) was added; this was followed by the addition of 5 mL of an aqueous 1M NaHCO$_3$ solution. The reaction mixture was refluxed for 4 h under nitrogen. After it was cooled to RT, the mixture was filtered, and the organic solvent was evaporated under reduced pressure. After the removal of the solvent, 10 mL of water was added to the residue, and the mixture was extracted with diethyl ether (3 × 50 mL). The combined organic phases were

washed with water and then by a brine solution and dried over $MgSO_4$. After filtration and solvent evaporation, the crude product was chromatographed on flash silica gel 60 with 90/10 hexanes/ethyl acetate as the eluant. The removal of the solvent yielded a greenish yellow powdery solid.

Yield = 75%. ^{1}H-NMR (400 MHz, $CDCl_3$, δ): 10.09 (s, 1H, CHO), 7.57 (s, 1H, $H4'$), 7.51 (dd, 1H, $J = 5.1$ Hz, $J = 1.2$ Hz, $H5$), 7.32 (dd, 1H, $J = 3.6$ Hz, $J = 1.2$ Hz, $H3$), 7.30 (dd, 1H, $J = 5.1$ Hz, $J = 1.2$ Hz, $H5''$), 7.23 (dd, 1H, $J = 3.6$ Hz, $J = 1.2$ Hz, $H3''$), 7.17 (dd,1H, $J = 5.1$ Hz, $J = 3.6$ Hz, $H4$), 7.05 (dd, 1H, $J = 5.1$ Hz, $J = 3.6$ Hz, $H4''$).

Synthesis of 3′-Hydroxymethyl-2,2′5′,2′′-terthiophene (3). Compound **3** was synthesized a procedure similar to that reported by Zanardi et al.[34] in 95% yield.

^{1}H-NMR (400 MHz, $CDCl_3$, δ): 7.33 (dd, 1H, $J = 5.1$ Hz, $J = 1.0$ Hz, $H5$), 7.23 (s, 1H, $H4'$), 7.22 (dd, 1H, $J = 5.1$ Hz, $J = 1.0$ Hz, $H5''$), 7.20 (dd, 1H, $J = 3.6$ Hz, $J = 1.0$ Hz, $H3$), 7.17 (dd, 1H, $J = 3.6$ Hz, $J = 1.0$ Hz, $H3''$), 7.07 (dd, 1H, $J = 3.6$ Hz, $J = 5.1$ Hz, $H4$), 7.02 (dd, 1H, $J = 3.6$ Hz, $J = 5.1$ Hz, $H4''$), 4.74 (s, 2H,CH_2), 1.78 [s (br), 1H, OH].

Synthesis of TTMM. Compound **3** (4.5 g), 3.15 mL of dry Et_3N, and CuCl (25 mg) were dissolved in 50 mL of dry diethyl ether. A solution of freshly distilled methacryloyl chloride (1.68 mL) in 50 mL of dry diethyl ether was added slowly at 0°C, and the mixture was stirred for 2 h. The solution was filtered through a silica gel column to remove triethylammonium chloride, and the solvent was evaporated to dryness. The residue was stirred overnight in a 1:1 mixture of methylene chloride and 2M NaOH. The organic layer was separated, washed twice with water, and dried over $CaCl_2$. After solvent evaporation, the residue was recrystallized from diethyl ether to provide TTMM as green crystals.

Yield = 50%. ^{1}H-NMR (400 MHz, $CDCl_3$, δ): 7.37 (dd, 1H, $J = 5.5$ Hz, $J = 1.0$ Hz, $H5$), 7.25 (dd, 1H, $J = 5.5$ Hz, $J = 0.5$ Hz, $H4'$), 7.22 (m, 2H, $H5''$), 7.20 (dd, 1H, $J = 3.5$ Hz, $J = 1.0$ Hz, $H3$), 7.11 (dd, 1H, $J = 4.0$ Hz, $J = 5.0$ Hz, $H3''$), 7.04 (dd, 1H, $J = 4.0$ Hz, $J = 5.5$ Hz, $H4$), 6.18 (s, vinyl H), 5.62 (s, vinyl H), 5.24 (s, OCH_2), 2.0 (s, CH_3). ^{13}C-NMR (100 MHz, $CDCl_3$, δ): 167.41, 136.84, 136.38, 136.15, 134.65, 134.52, 133.32, 128.14, 128.12, 127.0, 126.79, 126.76, 126.29, 125.09, 124.29, 60.49, and 18.61. High-resolution mass spectroscopy (MS): mass-to-charge ratio Calcd. for $C_{17}H_{14}O_2S_3{}^+$: 346.0156. Found: 346.0150.

Synthesis of the Silane Initiator
The trichlorosilane initiator was synthesized by a slight modification of previously published procedures.[18b] 2-Bromoisobutyryl bromide (1.85 mL, 15.0 mmol) was added dropwise to a stirring solution of allyl alcohol (1.02 mL, 15.0 mmol) and Et_3N (2.51 mL 18.0 mmol) in dichloromethane (10 mL) at 0°C under a nitrogen atmosphere. After 1 h of stirring, the solution was warmed to RT and stirred for another 3 h. The formed precipitate was then removed under reduced pressure, and the organic layer was washed with an aqueous saturated NH_4Cl solution followed by water. The organic layer was then dried over anhydrous $MgSO_4$ and the solvent removed *in vacuo*. The product was puri-fied by column chromatography (silica) with 9:1 hexane/ethyl acetate as the eluent. The solvent was then removed under reduced pressure to yield the clear, liquid product prop-2-enyl-2-bromo-2-methyl propionate (1.72 g, 8.31 mmol, 55.4% yield).

^{1}H-NMR (400 MHz, $CDCl_3$, δ): 1.94 (s, 6H), 4.66 (d, 2H), 5.27 (d, 1H), 5.38 (d, 1H), 5.93 (m, 1H).

A solution of hexachloroplatinic acid (21 mg, 51 μmol) in 1:1 v/v ethanol and 1,2-dimethoxyethane (3.75 mL) was added drop-wise to a solution of prop-2-enyl-2-bromo-2-methyl propionate (0.97 g, 4.7 mmol) in trichlorosilane (15 mL, 0.15 mol) under a nitrogen atmosphere. The reaction was stirred (in the dark) for 18 h. Toluene (5.0 mL) was then added, and unreacted trichloro-silane was removed under reduced pressure. Dichloromethane (20 mL) was added and then removed *in vacuo* to remove all of the remaining trichlorosilane. The resulting product, 2-bromo-2-methyl propionic acid 3-trichlorosilanyl propyl ester, was used without further purification.

^{1}H-NMR (400 MHz, $CDCl_3$, δ): 1.50 (m, 2H), 1.93 (m, 8H), 4.20 (m, 2H).

**Preparation of the Initiator Immobilized Flat Substrates**
ITO slides ($\sim$1 cm^2) were first sonicated in acetone (10 min); this was followed by sonication in isopropyl alcohol (10 min). All substrates were cleaned in a UV/O_3 chamber for 1 h. The ITO substrates were then placed in a about a 1 mM solution of the trichlorosilane initiator containing about 10 mM Et_3N in toluene. The substrates were left covered in the solution at RT for 18 h under an N_2 atmosphere. The substrates were then removed and successively washed with toluene, sonicated for 1 min in toluene, washed with acetone, washed with ethanol, and dried under a stream of nitrogen. The surfaces were stored under nitrogen until further use. Like the ITO surfaces, the gold surfaces were also cleaned in a UV/O_3 chamber for 15 min, modified by the thiol-terminated ATRP initiator,[35] and stored under nitrogen for future use.

Surface-Initiated Polymerization on the Gold and ITO Substrates
In an N_2-filled drybox, 0.7 mg of CuBr and 5.55 mg of HMTETA were added to a round-bottomed flask containing 1 mL of a degassed solution of TTMM monomer (500 mg) in DMF (DMF/ monomer $\approx$ 1:1 v/v). The mixture was well-stirred and heated in an oil bath to 50°C until a transparent green solution formed. The prepared solution was then transferred into a small vial containing an initiator-modified Au substrate to start the surface-initiated polymerization. After a set reaction time at 50°C, the substrate was removed from the vial, washed with tet-rahydrofuran (THF) and isopropyl alcohol sequentially, and then dried under a flow of N_2. Similar polymerization conditions were applied for growing MTM from the surfaces.

Electrochemistry
All electrochemical modifications were performed with a CHI650a computerized potentiostat (CH Instruments, Inc., Austin, TX).The electrochemical experiments, that is, CV, were carried out in acetonitrile containing TEAP ($\sim$5 $\times$ $10^{-2}M$) as a conducting salt. All experiments were carried out in a glovebox under an inert and dry atmosphere at RT. In a three-electrode
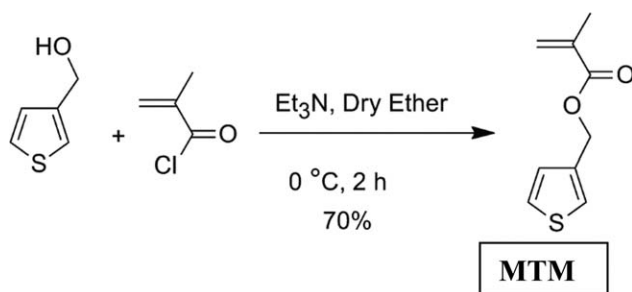
Scheme 1. Synthesis of MTM.

system, the working electrode (gold- or ITO-coated glass substrate) was placed between the reference electrode (Pt wire) and the counter electrode (graphite). All of the potentials were measured in this study with respect to a Pt wire used as a quasi-reference electrode. For this reason, the potentials could not be directly compared. Poly(terthiophene methyl methacrylate) (PTTMM) films (~30 nm) on ITO and gold substrates were placed in a 0.1M TEAP solution in acetonitrile under an inert atmosphere to prevent overoxidation. Then, the substrates were scanned at a 100 mV/s rate from −25 to 1500 mV for up to 20 cycles to crosslink the PTTMM film electrochemically (shown later in Scheme 4).

RESULTS AND DISCUSSION

Monomer Synthesis

As shown in Schemes 1 and 2, the synthesis of MTM and the precursors to TTMM, that is, compounds **1**, **2**, and **3**, were synthesized by modified versions of the procedures of Yagci et al.[36] and Seeber et al.[34] TTMM was obtained in high purity by the reaction of **3** with methacryloyl chloride in dry diethyl ether, similar to the synthesis of monomer MTM. Methacrylate monomers were chosen for their facile polymerization via ATRP, whereas the polymerizable thiophene and terthiophene groups showed good conducting properties in related polymers.[17,37,38]

Synthesis of the Silane Initiators for ITO Substrates

Typically, an 11-carbon long alkyl chain in trichlorosilane initiators is used to ensure a well-defined SAM on ITO. However, we used a short alkyl chain because the longer chain could act as a resistive element and inhibit the polymerization of the pendent thiophene methacrylates. The initiator was synthesized according to the method of Huck et al.[20] The esterification of 2-bromoisobutyryl bromide with allyl alcohol followed by the hydrosilation of the intermediate ester was performed to obtain the desired trichlorosilane initiator. The trichlorosilane functionality was chosen because trifunctional organosilanes are more reactive toward surfaces than their monosubstituted analogues.[39] These SAMs were expected to be stable because of the formation of polysiloxane networks bound to the substrate surface.[40,41] For gold surfaces, we used a well-known 11-carbon-long ATRP initiator[35] because shorter chain initiators failed to form uniform SAMs on the gold surfaces.

### Deposition of the SAMs onto the ITO Surface

The formation of trichlorosilane-based SAMs on the silica surface is well known.[40] However, the generation of a well-defined SAM on an ITO surface was more difficult because of the high

surface roughness of the ITO and the low coverage of hydroxyl groups.[42] Nevertheless, some methods have produced SAMs on ITO. Examples include microcontact printing,[43] a 1-h soak in a 1 mM solution of the chlorosilane at RT,[44] and the refluxing of a solution of trimethoxysilane in toluene over ITO for a period of 7 days.[42] In the latter case, Markovich and Mandler[42] achieved about 90% coverage of the surface sites. Because of the higher reactivity of a trichlorosilane compared to a trimethoxysilane, the reaction was carried out in a manner similar to the method reported by Huck et al.[20] at RT (to prevent polymerization) for 18 h. In addition, Et₃N was added[18b] to drive the reaction to completion. Although this SAM deposition method may not provide complete surface coverage, estimates of the initiator efficiency suggested that about 10% of the surface-bound initiating molecules initiate a polymer brush,[45] and therefore, having less than full surface coverage should not be a significant factor in polymer brush synthesis. Typically, a full ITO wafer was completely derivatized, stored under nitrogen, and fractured into (~1 × 2 cm²) pieces just before use. The surfaces were stable, and the polymerizations carried out with 1-year old initiator monolayers gave similar film thicknesses under similar polymerization conditions.

### Synthesis of the Polymer Brushes from Gold and ITO Surfaces

The syntheses of the poly(thiophene methyl methacrylate) (PMTM) and PTTMM brushes from gold and ITO surfaces are shown in Scheme 3. Films on gold surfaces were characterized with ellipsometry, but for ITO surfaces, tapping-mode AFM was used to measure the PTTMM film thicknesses because the film absorbed light, which made the ellipsometric measurement ambiguous.

PMTM brushes were grown from gold surfaces at 55°C in anhydrous DMF with a CuBr/HMTETA catalyst. This system was previously shown to be compatible with the synthesis of methacrylate monomers via ATRP[46] and was also proven to be
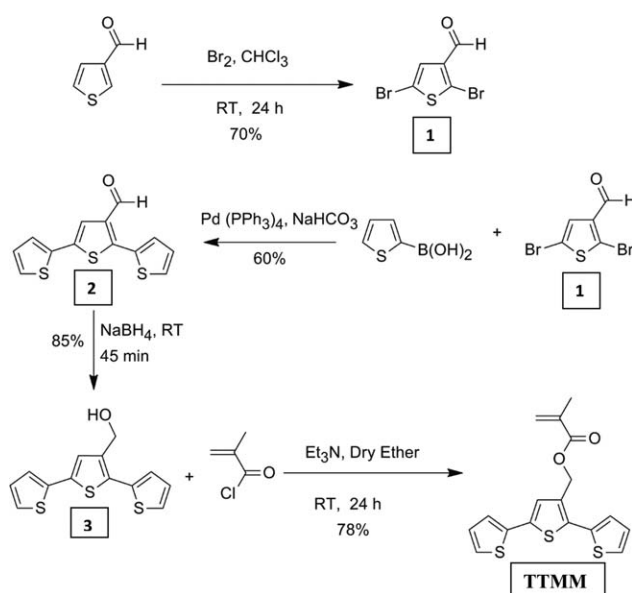

Scheme 2. Synthesis of TTMM.
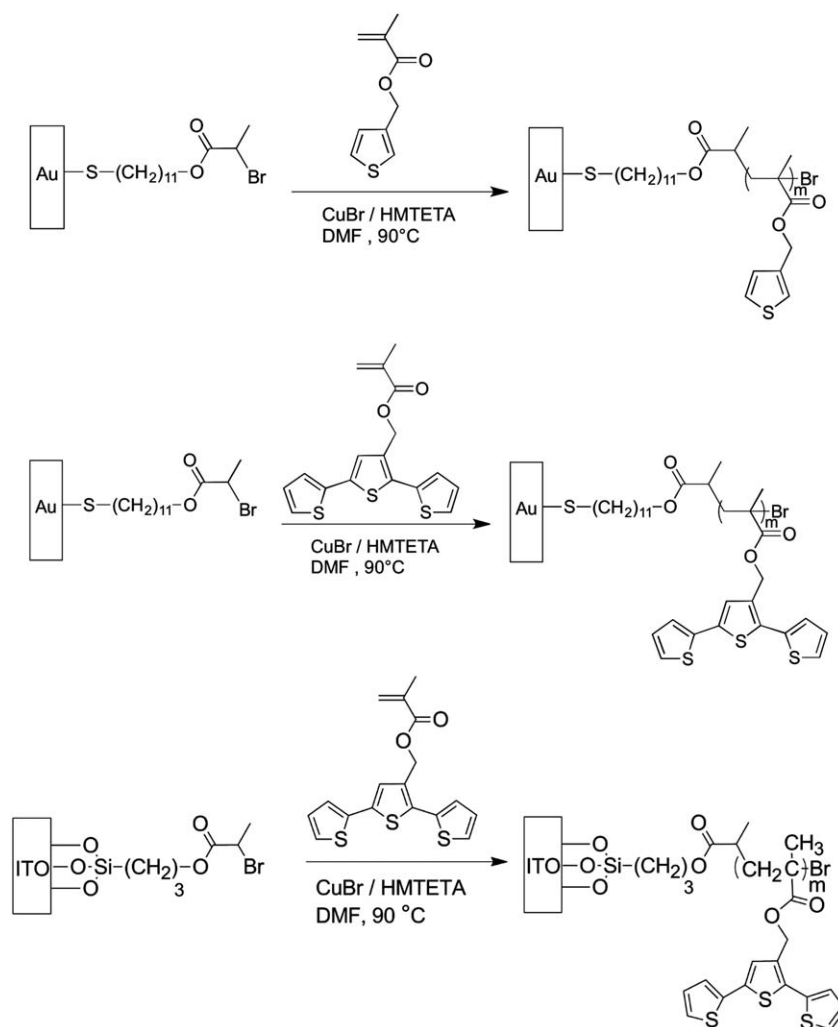
Scheme 3. Surface-initiated polymerization of MTM from a gold surface (top), TTMM from a gold surface (middle), and TTMM from an ITO surface (bottom).

successful for the synthesis of PMTM brushes. The PMTM brush was typically synthesized from a concentrated polymerization solution (1 g/mL), which allowed access to a greater range of film thicknesses. Similar solutions were also used for the synthesis of the PTTMM brushes.

The kinetic plots for the syntheses of both brushes (Figure 1) showed the characteristics of significant termination during ATRP;[47] the polymer chains initially grew rapidly, and as termination consumed the growing chain ends, the plots plateaued. Complete termination occurred more quickly for the PTTMM systems than for PMTM. High radical concentrations resulted in increased probability of radical combination and termination of growing polymer chains. Usually, increasing the reaction temperature provides thicker films, but when the polymerization temperature was increased from 55 to 90°C, the growth rate for PTTMM brushes grown on the ITO surfaces did not increase. It should be mentioned here that high-temperature polymerization on a gold surface is not possible because of the presence of thermally labile Au—S bonds (the Au—S bond was labile above 60°C).[35]

Although no $CuBr_2$ was explicitly added to the polymerizations, Cu(II) was present in the system as a consequence of the oxidation of CuBr in the presence of an initiator.[18c] For the PTTMM brushes, early termination may have been related to the stronger complexing ability of the terthiophene units with Cu(II) of the monothiophenes, as evidenced by a previous report.[48] Thus, Cu(II) generated during the initiation of polymerization was sequestered by the pendent terthiophene of TTMM; this led to a high concentration of radicals and almost no deactivation.

However, the PTTMM film thicknesses were intentionally kept low to ensure their crosslinking by electrochemical methods. In thicker films, electrochemical-based crosslinking may be hindered by the low permeation rates of anions or monomer through the PTTMM matrix. The PMTM and PTTMM brushes grown from gold surfaces were characterized by FTIR spectroscopy (Figure 2). The spectra for PMTM and PTTMM showed the expected bands for the carbonyl peak around 1733 cm^{-1}. For the PMTM and PTTMM brushes, the bands at 786 and 833 cm^{-1} were characterized as C—H out-of-plane bending and deformation vibrations, respectively. Other bands appeared at
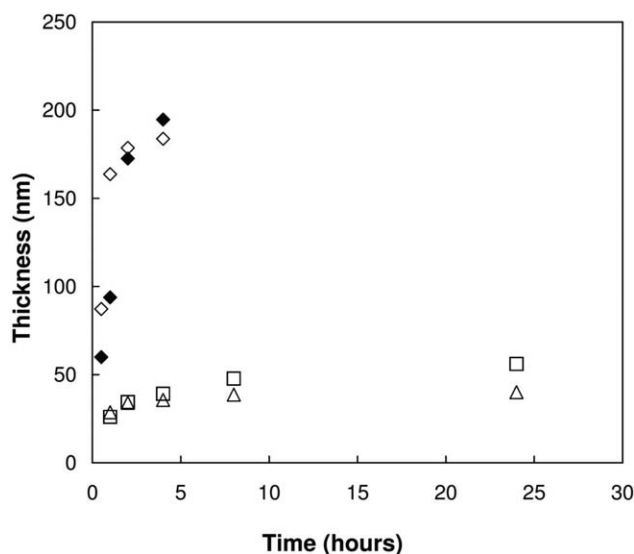
Figure 1. Evolution of the ellipsometric brush thickness with time for the polymerization of PMTM and PTTMM from gold and ITO surfaces: (◆) PMTM brush grown on a gold surface, (◇) PMTM brush grown on an ITO surface, (□) PTTMM brush grown on a gold surface, and (△) PTTMM brush grown on an ITO surface.

3100, 2900, and 2860 cm^{-1} and were attributed to the sp^2 C—H stretching and deformation vibrations of —CH$_2$ group (from the acrylate part) asymmetric and symmetric stretching, respectively. In addition, the two bands for the PTTMM brush at 1384 and 1450 cm^{-1} were assigned to the methylene deformation and ring-stretching vibrations of C=C, respectively. The bands at 1160 and 1135 cm^{-1} were generated by C—H wagging vibrations and an in-plane C—H deformation. The peak at 950 cm^{-1} corresponded to C—S bonds in the polymer chains.
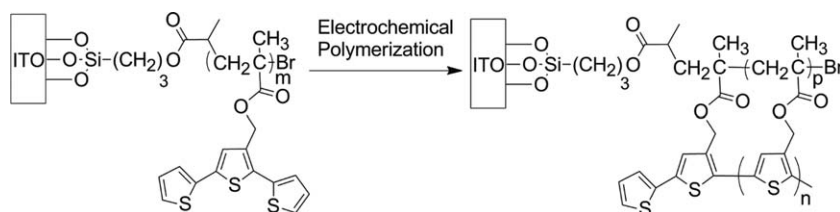
Electrochemical Crosslinking
Around 30 nm thick PTTMM films on ITO and gold substrates were crosslinked electrochemically (Scheme 4) by CV scanning at a 100 mV/s rate from −25 to 1500 mV for up to 20 cycles (Figure 3) under a nitrogen atmosphere.

The direct electrochemical polymerization of the PMTM brush was not achievable under our conditions but was consistent with previous reports of the low reactivity of thiophenes substituted with esters in the 3 position.[38] PTTMM's higher reactivity originated from the extended π structure of the terthienyl moiety,[38] which lowered the oxidation potential of the PTTMM brush relative to PMTM. In addition, the terthienyl unit was less sterically challenged with respect to coupling in the 2- and 5″-positions compared to the 2 and 5 positions of a single thienyl unit.
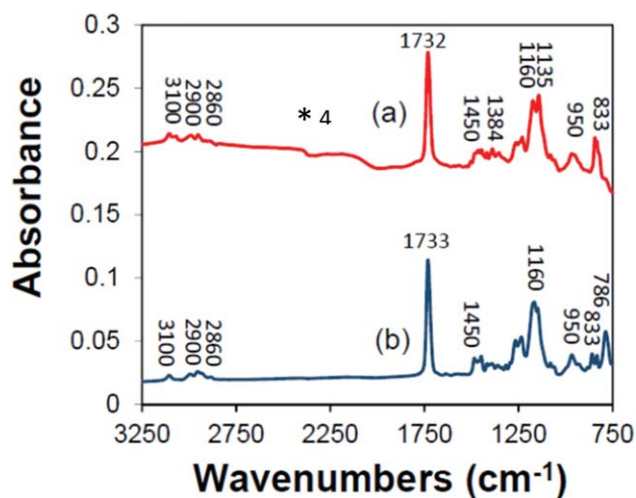

Figure 2. Representative example of the normalized reflectance FTIR spectroscopy of gold surfaces grafted with (a) a 50-nm PTTMM brush and (b) a 100-nm PMTM brush (normalization of spectra based on a carbonyl peak at 1733 cm^{-1}). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

A well-defined oxidation peak starting at about 1.1 V/Pt (first scan; Figure 3) was observed for the PTTMM brush by CV. Because it is well known that films of grafted poly(alkyl acrylate), for example, poly(ethyl acrylate), do not react upon anodic polarization, this peak could only be attributed to the oxidation of the aromatic thiophene rings. The reduction peak of the accordingly formed PTTMM two-component films was observed at about 0.63 V/Pt during the reverse scan. These observations confirmed that the thienyl rings attached to the conducting substrate (ITO/gold) as a result of the surface-initiated polymerization via ATRP of the parent acrylates (TTMM) remained available for electrochemical polymerization and formed polymers with an extended π-electron conjugation. The voltammetric scans were repeated times (20th scan; Figure 3) or less if the polymerization peak was no longer observable. On the last scan (20th scan), the oxidation peak appeared at a lower anodic potential ($E \approx 0.75$ V/Pt) and corresponded to an extended conjugated system compared to the monomeric terthiophenes.[12,17,49–51] The dedoping peak remained visible. These redox potentials were higher than the values reported for terthiophene reduction under similar conditions,[52] but they were comparable to the data reported by Advincula et al.[24] for copolymers of carbazole and terthiophene containing methacrylate ($E_c = 0.6$ V/Ag/Ag$^+$ and $E_a = 1.08$ V/Ag/Ag$^+$), where E_c and E_a are mean potentials at cathode and anode respectively. The reduced mobility of a thiophene attached to the polymethacrylate chains might explain the formation of polythiophenes with shorter conjugation
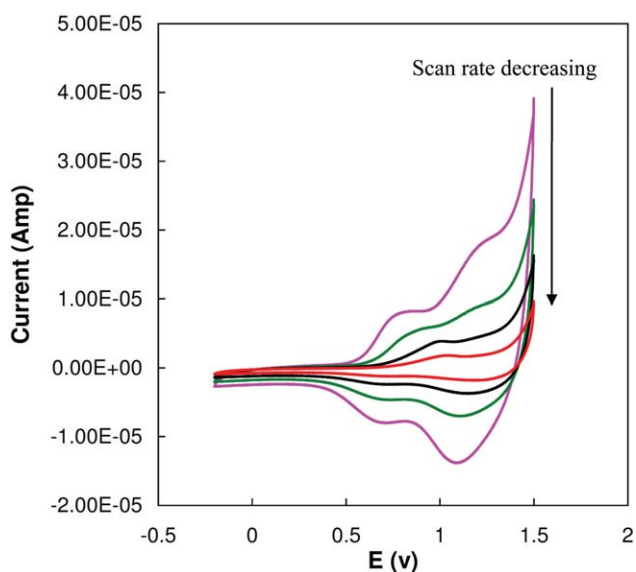

Scheme 4. Electrochemical crosslinking of a PTTMM brush on the ITO surfaces.
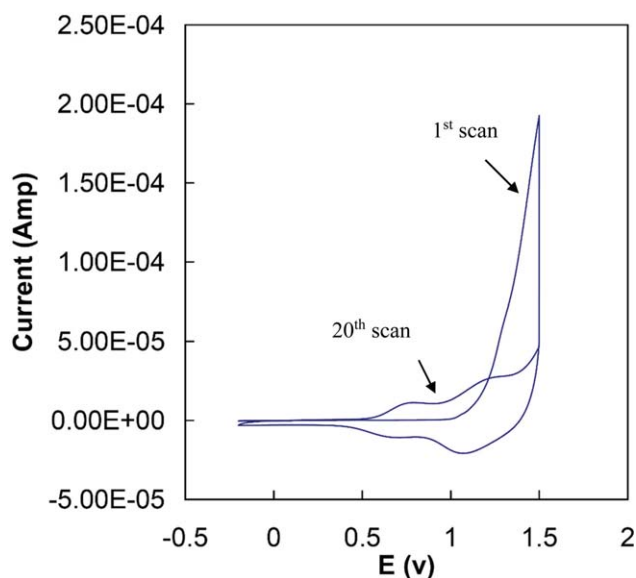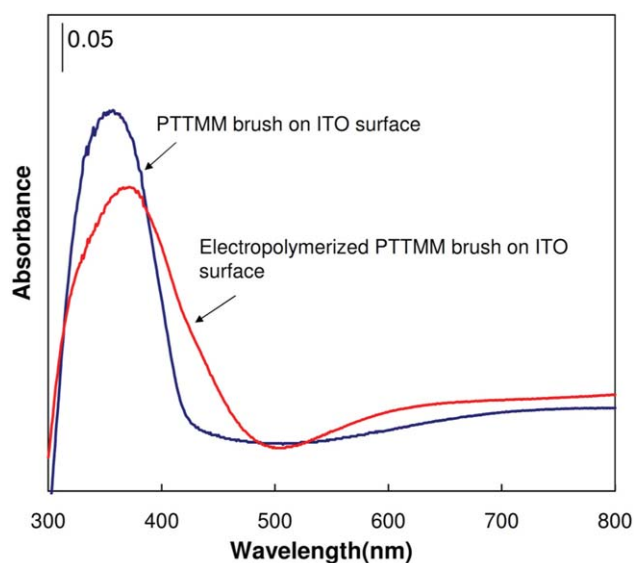
Figure 3. CV (20 cycles) of an approximately 30-nm PTTMM brush coated on an ITO surface from −25 to 1500 mV at 100 mV/s. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

lengths. Scan-rate-dependence studies (Figure 4) of the cross-linked PTTMM brush at scan rates of 20–80 mV/s in a 0.1M TEAP/CH$_3$CN electrolyte solution (potentials are reported relative to Pt as a quasi-reference electrode) revealed linear behavior (Figure S1) similar to the data shown by Sotzing et al.[17] for electropolymerized poly(terthiophene) films. This indicated a surface-confined reaction as the sole phenomenon.

Examination of the films by UV–vis spectroscopy before and after the electropolymerization showed a small spectral difference arising from the formation of conjugated oligothiophene species (Figure 5). The maximum wavelength for the PTTMM brush
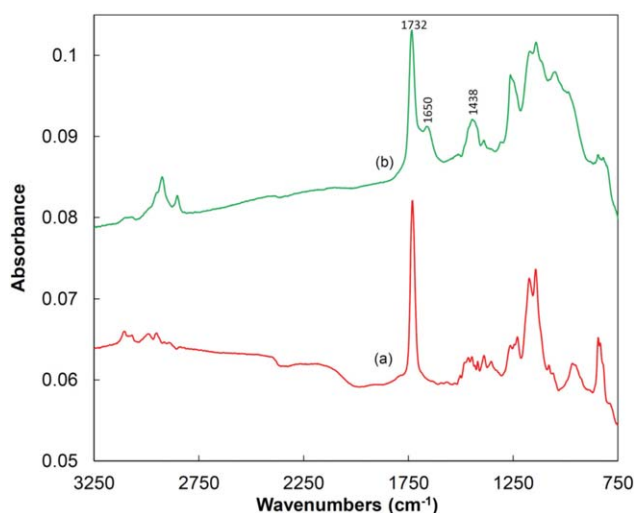

Figure 5. UV–vis absorption spectra of a 30-nm PTTMM brush grown on an ITO surface (blue line) and an electrochemically crosslinked PTTMM brush on an ITO surface (red line). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

before crosslinking was about 360 nm (characteristic vibronic pattern of terthiophene),[17] and this shifted to about 370 nm after electropolymerization. This pattern was comparable to the sexithiophene-based structure investigated previously.[52,53a] Here, surface-attached but loosely packed oligothiophene tilted from the surface normal showed an absorption peak for sexithiophene similar to that found by previous observation.[54] Additionally, Garnier et al.[55] also reported that the electrochemical polymerization of terthienyl resulted in sexithiophene as the major product after their coupling into a correspondingly less reactive hexamer. In fact, it was observed that the intrinsic reactivity of oligomeric radicals decreased rapidly as their conjugation length increased.

Figure 4. Scan rate dependence study of the PTTMM brushes coated on an ITO surface at scan rates of 20–80 mV/s in a 0.1M TEAP/CH$_3$CN electrolyte solution. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Figure 6. Representative examples of the reflectance FTIR spectroscopy of gold surfaces coated with (a) a 50-nm PTTMM brush and (b) an electrochemically crosslinked PTTMM brush. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
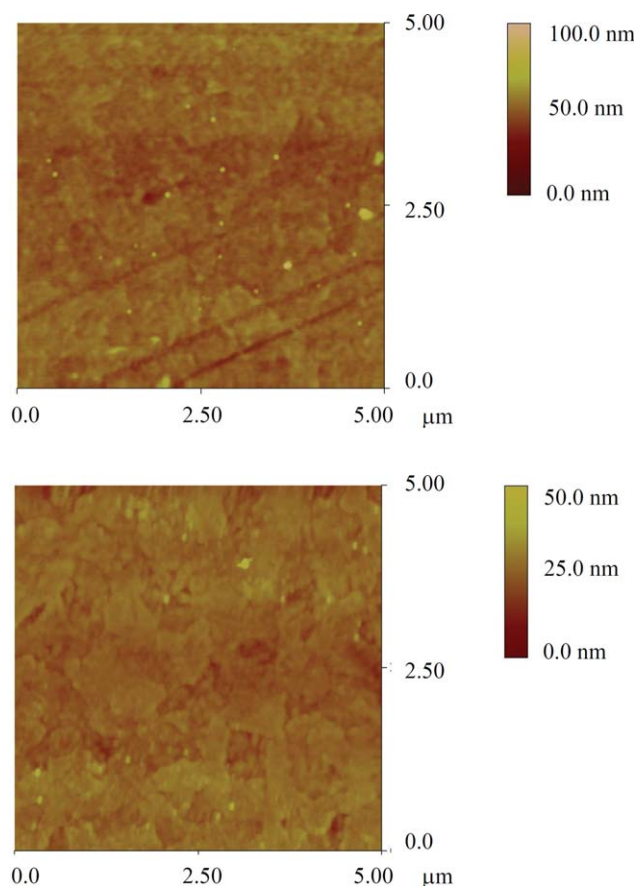
Figure 7. Topographical AFM images of the ITO surface coated with a 30-nm PTTMM brush (upper image) and an electropolymerized PTTMM brush (bottom image) taken with tapping-mode imaging. The upper image is a 5×5 μm^2 survey scan with a high surface coverage and a root mean square roughness of 3.8 nm, as calculated with Nanoscope IV software. The bottom image is a 5×5 μm^2 scan with an root mean square value of 2.9 nm. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Furthermore, with the lower energy threshold of the absorption spectra of the crosslinked polymer brush, the energy band gap was calculated to be 3.3 eV; this correlated well to the reported value of 3.23 eV for sexithiophene.[53,54] IR spectroscopy also supported terthiophene coupling. The spectrum of PTTMM [Figures 2(a) and 6(a)] showed characteristic bands at 3100, 1450, and 833 cm^{-1} due to C—H stretching, wagging, and C—H out-of-plane deformation modes from the thiophene rings, respectively. After crosslinking, these bands decreased dramatically, whereas bands at 1438 and 1650 cm^{-1} appeared because of the C=C stretching vibrations of the thiophene rings, which usually increase with increasing conjugation length[53] [Figure 6(b)]. The persistence of the carbonyl stretching mode at 1732 cm^{-1} in both spectra confirmed that the polymer backbone was apparently unchanged. These results were consistent with a network of conducting polythiophene chains of short conjugation length, perhaps dimers, grown from pristine PTTMM.

The morphology of the pregrafted PTTMM films may have changed upon the oxidation of the terthiophene units. To understand this, the films were investigated with tapping-mode

AFM before and after oxidation. The surface showed an irregular morphology (Figure 7) compared to the smooth films before oxidation. We suspected that anodic oxidation rigidified the polythiophene segments and the polyacrylate chains, and this resulted in a more heterogeneous surface dominated by grains of various sizes, although the surface roughness did not change significantly after oxidation. However, the measurement of film thickness after oxidation was not successful by the available techniques (AFM and ellipsometry) because of surface heterogeneity.

CONCLUSIONS

PTTMM and PMTM brushes were successfully grown from ITO and gold electrodes with surface-initiated ATRP. The resulting films were homogeneous with smooth domains and features, as confirmed by ellipsometry and AFM studies. The PTTMM brushes were electrochemically oxidized by CV to form a crosslinked polymer network with short segments of conjugated polyterthiophene segments (assessed by UV–vis spectroscopy). Unfortunately, the PMTM brush did not get oxidized under similar conditions. Uniformly grafted conducting polymer brushes may be useful in photovoltaic devices.

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