Intrinsically Conducting Polymer Networks of Poly(thiophene) via Solid-State Oxidative Cross-Linking of a Poly(norbornylene) Containing Terthiophene Moieties

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ABSTRACT: Herein we describe the preparation of intrinsically conducting poly(thiophene) via two different routes: solution- and solid-state cross-linking of terthiophene moieties. The solution-state cross-linking of terthiophene moieties was performed using conventional electrochemical polymerization in which insoluble cross-linked polymer was precipitated onto the electrode from electrolyte solution of the monomer by oxidative coupling of terthiophene units in the monomer, 5-norbornene-*endo*-2,3-bis(methylene-3′-[2,2′:5′,2″]-terthiophene acetate). In the alternative route, a precursor polymer, poly(norbornylene), prepared from the ring-opening metathesis polymerization (ROMP) of 5-norbornene-*endo*-2,3-bis(methylene-3′-[2,2′:5′,2″]-terthiophene acetate), was coated on either a conducting or insulating surface, and then the terthiophene units were cross-linked to form intrinsically conductive polymer (ICP) via electrochemical and chemical oxidation, respectively. More highly conjugated ICP was observed by performing oxidative cross-linking of the polymer in the solid state, in contrast to the cross-linked intrinsically conducting polymer prepared via electrochemical polymerization of 5-norbornene-*endo*-2,3-bis(methylene-3′-[2,2′:5′,2″]-terthiophene acetate) from solution. Electrical conductivities for the polymers obtained via solid-state chemical oxidative cross-linking were on the order of 1×10^{-3} S/cm.

Introduction

Intrinsically conducting polymers (ICPs) are of primary interest to many researchers due to their potential impact in numerous viable commercial applications[1] such as organic light-emitting diodes (LED),[2] electrochromic windows,[3] volatile organic gas sensors,[4,5] energy storage batteries,[6] nonlinear optics,[7] protective coatings for corrosion prevention,[8] and charge dissipating films.[9] Many academic studies performed in both university and industrial settings have had a bearing on the commercialization of ICPs, and presently, academic studies are largely being explored for the use of ICPs in molecular-scale (nanoscale) electronics.[10]

Generally, ICPs are prepared via either chemical or electrochemical means. Chemical syntheses include either oxidative coupling of heterocyclic ring systems such as pyrrole, thiophene, indole, aniline, etc., utilizing chemical oxidants such as ferric chloride, iodine, ammonium persulfate, etc.,[11] or metal-mediated coupling polymerizations[12] of halogenated aromatic systems. Electrochemical oxidative polymerization is a facile technique that has been utilized to precisely control the oxidation potential for polymerization and to study the resulting electronic properties of the polymer. Typically, electrochemical polymerization entails oxidative coupling of monomers in a stepwise manner to produce insoluble oligomers that electroprecipitate onto the working electrode surface. Electrochemical polymerizations carried out in this fashion are low yielding with a predominance of the starting monomer residing in the electrolyte solution after polymerization. Oftentimes, because of the rigid character of the resulting polymers, ICPs are infusible and are not soluble in many common organic solvents, thereby leading to major difficulty in their processing.[1,4]

To increase processability, both main chain substituted and transition metal containing ICPs have been prepared.[13−17] By far, the most common method for obtaining organic soluble ICPs has been to introduce alkyl substituents to the monomer, thereby producing polymer with an alkyl-substituted backbone.[1] One of the more recent techniques reported for preparing tractable ICPs has been to append heterocyclic moieties from the backbone of a processable polymer such as a poly(siloxane) or poly(norbornylene).[18,19] Electropolymerization of a solution containing the precursor polymer with heterocyclic appendages resulted in the precipitation of a presumably cross-linked thin film of electroactive polymer on the electrode surface. Of particular concern in the following technique are the effects that the size of the prepolymer have on the nucleation/growth mechanism of ICP production on the working electrode, slower diffusion coefficients with respect to single ring system monomers, and viscosity effects.

Unlike previous reports on the electrolyte solution-soluble polymer precursors to ICP networks, we report the solid-state cross-linking of a precursor poly(norbornylene) containing oxidatively polymerizable terthiophene side groups. Furthermore, within this study we compare the electrochemical polymerizations of the monomer and the electrochemically solid-state induced

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cross-linking of the ICP network precursor poly(norbornylene). We have also demonstrated the use of chemical oxidants used in solution for the cross-linking of the herein described ICP network polymer precursors. This work will lead to further insight into the use of such ICP network polymer precursors for the preparation of nanoscale electronic components.

Experimental Section

Chemicals. 5-Norbornene-2-*endo*,3-*endo*-dimethanol and oxalyl chloride were purchased from Aldrich Chemical Co. and used as received. Methylene chloride (CH_2Cl_2), triethylamine (Et_3N), and acetonitrile (CH_3CN) were distilled over calcium hydride (CaH_2) under nitrogen before use. Dry diethyl ether was purchased from J.T. Baker Inc. and used without further purification. Grubb's alkylidene catalyst was purchased from Strem Chemicals Inc. and used without further purification. Deuterated chloroform ($CDCl_3$) used for NMR characterization was purchased from Aldrich Chemical Co. and used as received. Tetrabutylammonium perchlorate (TBAP) was prepared via addition of 70% perchloric acid solution purchased from Fisher Scientific to an aqueous solution of tetrabutylammonium bromide (TBABr) purchased from ACROS organics. After filtration, TBAP was recrystallized from ethanol. Iron(III) chloride and hydrazine monohydrate were used as received from Strem Chemicals Inc. and ACROS Organics, respectively. (2,2′:5′,2″-Terthiophene)-3-acetic acid, **1**, was prepared in accordance with the literature procedure.[20]

Instrumentation. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker 400 FT-NMR spectrometer. ^{1}H NMR data are reported as follows: Chemical shift (multiplicity: b = broad signal, s = singlet, d = doublet, t = triplet, dd = doublet of doublets, dt = doublet of triplet, and m = multiplet). ^{1}H and ^{13}C chemical shifts are reported in ppm downfield from tetramethylsilane (TMS) reference using the residual protonated solvent resonance as an internal standard. Elemental analysis was performed at Galbraith Laboratories. Number-average molecular weight and polydispersity index (PDI) were obtained using a Waters 150-C plus GPC equipped with UV/vis, refractive index, and evaporative light scattering detectors.

Synthesis of 5-Norbornene-*endo*-2,3-bis(methylene-3′-[2,2′:5′,2″]-terthiophene acetate), 2. To a 100 mL three-neck round-bottom flask that had been vacuum-dried and nitrogen-purged was added 0.873 g (2.8 mmol) of (2,2′:5′,2″-terthiophene)-3′-acetic acid, **1**. Dry CH_2Cl_2 (20 mL) was added under nitrogen, followed by the addition of 1.27 g (0.01 mol) of oxalyl chloride. The reaction was continued with stirring for 2 h at room temperature after which the solvent and excess oxalyl chloride were removed under vacuum, and the resulting acid chloride was redissolved in 20 mL of dry diethyl ether. In a separate 100 mL three-neck round-bottom flask which was vacuum-dried and under nitrogen was added 5-norbornene-2-*endo*,3-*endo*-dimethanol (0.208 g, 1.35 mmol), and to this flask was added 20 mL of dry diethyl ether followed by the addition of 0.8 mL of triethylamine. The (2,2′:5′,2″-terthiophene)-3′-acetic acid chloride solution dissolved in 20 mL of dry diethyl ether was added dropwise over a 20 min period. The mixture was then stirred for an additional 10 min and poured into 50 mL of water. The organic layer was separated, and the water layer was washed with diethyl ether (3 × 50 mL). The organic portion was washed with brine, separated, combined, and then dried over magnesium sulfate and filtered, and then the solvent was removed under vacuum. The resulting oil was dissolved in 5 mL of CH_2Cl_2, and column chromatography was performed on silica gel using CH_2Cl_2 as an eluent to yield 0.431 g (46%) of the desired product, **2**, as a light yellow solid powder. ^{1}H NMR ($CDCl_3$): 1.29 (d, ^{1}H), 1.48 (dt, ^{1}H), 2.50 (m, 2H), 2.83 (m, 2H), 3.73 (s, 4H), 3.83 (dd, 2H), 3.90 (dd, 2H), 6.10 (t, 2H), 7.00 (dd, 2H), 7.07 (dd, 2H), 7.11 (s, 2H), 7.16 (dd, 2H), 7.19 (dd, 2H), 7.20 (dd, 2H), 7.32 (dd, 2H). ^{13}C NMR ($CDCl_3$): 34.97, 43.78, 44.21, 63.54, 123.79, 123.97, 124.77, 126.17, 126.41, 126.71, 127.22, 127.87, 127.95, 128.56, 130.59, 132.11, 134.75, 135.85, 136.65, 170.41. FTIR: 3105 and 3068 cm^{-1} (aromatic and vinylic C−H stretching); 2971, 2930, and 2868 cm^{-1} (aliphatic C−H stretching); 1731 cm^{-1} (ester C=O stretch); 1245 cm^{-1} (ester C−C−O stretching). Elemental analysis: Calcd for $C_{37}H_{30}O_4S_6$: C, 60.82; H, 4.11. Found: C, 59.92; H, 4.75.

Synthesis of Poly(2a). A solution of 5-norbornene-*endo*-2,3-bis(methylene-3′-[2,2′:5′,2″]-terthiophene acetate), **2** (194 mg, 0.266 mmol), in dry CH_2Cl_2 (1.5 mL) was injected into a three-necked round bottom flask, previously vacuum-dried and nitrogen purged, under nitrogen containing 11.5 mg of Grubb's alkylidene catalyst (0.014 mmol) and 2 mL of CH_2Cl_2. The mixture was allowed to stir for 30 min followed by irreversible termination via the addition of 0.5 mL of ethyl vinyl ether. The solution was then concentrated under vacuum. The polymer was precipitated twice in pentane (50 mL), filtered and then dried under vacuum to yield 126 mg (65%) of poly(**2a**) as a light tan powder. ^{1}H NMR ($CDCl_3$): 1.18 (b, 1H), 1.78 (b, 1H), 2.17 (b, 2H), 2.46 (b, 2H), 3.51 (b, 4H), 4.04 (b, 4H), 5.18 (b, 2H), 6.89 (b, 2H), 6.95 (b, 2H), 7.05 (b, 4H), 7.10 (b, 4H), 7.24 (b, 2H). ^{13}C NMR ($CDCl_3$): 36.0, 43.8, 44.2, 63.5, 124.0, 124.8, 126.2, 126.4, 126.7, 127.8, 127.9, 130.6, 132.1, 134.8, 135.9, 136.6, 170.4. FTIR: 3104 and 3068 cm^{-1} (aromatic and vinylic C−H stretching); 2950, 2904, and 2965 cm^{-1} (aliphatic C−H stretching); 1731 cm^{-1} (ester C=O stretch); 1240 cm^{-1} (ester C−C−O stretching) GPC analysis: $M_n = 22\,000$ g/mol (PDI = 1.37), as determined using monodisperse polystyrene standards.

Preparation of Poly(2b) by Oxidative Electrochemistry. Before polymerization, a platinum button working electrode (2 mm diameter) was polished using 0.05 μm particle size alumina powder, washed with acetone, and dried. The electrochemical polymerization of 5-norbornene-*endo*-2,3-bis(methylene-3′-[2,2′:5′,2″]-terthiophene acetate), **2** (0.01 M), was carried out in 0.1 M TBAP/ACN by scanning between the potentials of 0.0 and 0.9 V at a scan rate of 0.1 V/s. The polymerization was carried out under a nitrogen blanket.

Preparation of Poly(2c) via Oxidative Electrochemistry. A 1 wt % solution of poly(**2a**) in methylene chloride was prepared. A thin film of poly(**2a**) was cast from this solution by dipping either a platinum button (2 mm diameter), gold button, or platinum wire in the poly(**2a**)/methylene chloride solution followed by air-dry for approximately 5 min. The electrochemical cross-linking of poly(**2a**) was then carried out in 0.1 M TBAP/ACN (10 mL) solution by cycling twice between 0 and 0.85 V at a scan rate of 50 mV/s.

Preparation of Poly(2c) Using Iron(III) Chloride. A 1 wt % solution of poly(**2a**) in methylene chloride was spun-coat at a rate of 1000 rpm onto a glass slide (2.2 cm × 2.2 cm). The resulting film was light yellow with a thickness of 0.5 μm as measured by Alpha-Step 200 profilometry from KLA-Tencor Co. The cross-linking of the poly(**2a**) was performed by dipping the film into an acetonitrile solution containing 0.01 M $FeCl_3$ for 5 min. Immediately after dipping (ca. 2 s), the initially yellow film turned dark blue.

Exposure of Poly(2a) to Iodine. A 1 wt % solution of poly(**2a**) in methylene chloride was spun-coat at a rate of 1000 rpm onto a glass slide (2.2 cm × 2.2 cm). Using an Alpha-Step 200 profilometer from KLA-Tencor Co., the thickness of the film was measured to be 0.5 μm. The film was placed inside a desiccator with iodine, and then the desiccator was placed in an oven at a temperature of 80 °C for 2 h. The color of the film was initially yellow and then turned rust brown.

Electrochemistry. All electrochemical experiments were performed using a CH Instruments 660A potentiostat. A three-electrode cell was used consisting of a working, counter, and reference electrode. The reference electrode was a nonaqueous Ag/Ag^+ reference electrode consisting of a silver wire immersed in a glass capillary body fitted with a Vycor tip and filled with a 10 mM silver nitrate, 0.1 M TBAP/ACN solution. The Ag/Ag^+ reference electrode was calibrated to be 0.455 V vs the normal hydrogen electrode (NHE) using a 10 mM ferrocene standard solution.

Optoelectrochemistry. A Perkin-Elmer Lambda 900 UV−vis−NIR spectrophotometer was used, and the data was reported using UV Winlab software. The polymer, poly(**2a**), was deposited onto an indium-doped tin oxide (ITO)-coated glass working electrode electrochemically from a 10 mM solution of the monomer, **2**, in 0.1 M TBAP/ACN by scanning from 0 to 0.9 V at a scan rate of 0.1 V/s. The UV−vis−NIR spectra were taken upon sequentially oxidizing the polymer film. The ITO-coated glass had a nominal resistance of 100 ohms with a dimension of 7 mm × 50 mm × 0.7 mm and was purchased from Delta Technologies, Ltd.

UV−vis−NIR Study upon Sequential Reduction of Poly(2c) with Hydrazine. A thin film of poly(**2a**) was obtained on a glass slide (2.2 cm × 2.2 cm) by spin-coating at 1000 rpm from a 1 wt % solution of poly(**2a**) in methylene chloride. The resulting 0.5 μm thick film was then oxidized upon dipping into an acetonitrile solution containing 0.01 M $FeCl_3$ for 1 min, after which the initially yellow film turned dark blue. The consistency UV−vis−NIR spectrum was then obtained after washing the film with acetonitrile. Hydrazine reduction was performed by dipping the film into an acetonitrile solution. Subsequently, a drop of 0.005 M hydrazine/acetonitrile solution was added to the acetonitrile containing the film, and the film was allowed to sit in this solution for 1 min before removal and taking the UV−vis−NIR spectrum. This process was then repeated several times, and eventually, the film was dipped into 0.005 M hydrazine/acetonitrile for full reduction.

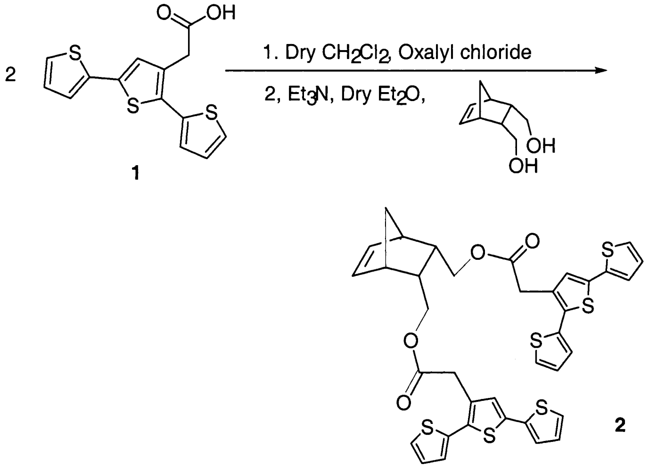
Conductivity Measurements. Conductivity was measured using a four-point collinear array utilizing a Keithley Instruments 224 constant current source to supply 1 μA across the outer leads and measuring the voltage difference between the two inner leads using a Keithley Instruments 2700 multimeter. Resistance was calculated using Ohm's law, and the conductivity was determined in accordance with the equation $\sigma = l/twR$, where σ is the conductivity in units of S/cm, R is the resistance in ohms, l is the distance between the two inner leads in cm, w is the width of the film in cm, and t is the film thickness in cm. It should be noted that the conductivity was performed under normal laboratory conditions with a humidity of ca. 50%.

Results

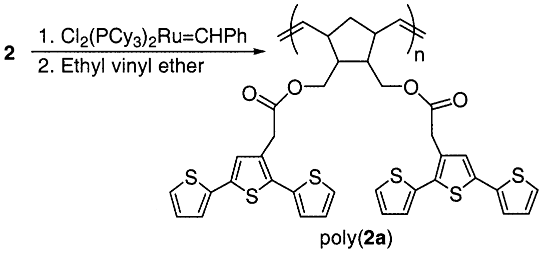
Monomer Synthesis. 5-Norbornene-*endo*-2,3-bis-(methylene-3′-[2,2′:5′,2″]-terthiophene acetate) was prepared in a five-step procedure starting from 3-thiophene acetic acid. The first step involved preparation of the ethyl ester followed by bromination utilizing molecular bromine in order to prepare ethyl 2,5-dibromothiophene-3-acetate. Palladium-catalyzed Stille coupling of ethyl 2,5-dibromothiophene-3-acetate with 2 equiv of 2-(tributylstannyl)thiophene yielded ethyl [2,2′:5′,2″]-terthiophene-3′-acetate. The ester group was then hydrolyzed to yield [2,2′:5′,2″]-terthiophene-3′-acetic acid, **1**. 5-Norbornene-*endo*-2,3-bis(methylene-3′-[2,2′:5′,2″]-terthiophene acetate), **2**, was prepared from **1** in a two-step procedure (Scheme 1). **1** was first converted to the acid chloride utilizing an excess of oxalyl chloride. After reaction, both the solvent and excess oxalyl chloride were removed under vacuum. The acid chloride was then added to a solution of 5-norbornene-2-*endo*,3-*endo*-dimethanol at room temperature in order to obtain the desired product, **2**, in an overall purified 46% yield. The structure of the monomer was confirmed using ^{1}H and ^{13}C nuclear magnetic resonance (NMR) spectroscopy, Fourier transform infrared spectroscopy (FTIR), and elemental analysis.

Ring-Opening Metathesis (ROMP) Polymerization of 2. The monomer, **2**, was polymerized using ROMP in accordance with Scheme 2. The ROMP polymerization was performed using Grubb's alkylidene catalyst in dry CH_2Cl_2 under an inert atmosphere. The complete polymerization of monomer **2** occurred within 30 min, giving a poly(norbornylene) of structure poly(**2a**) in a 65% yield. The GPC characterization indicated a number-average molecular weight of 22 000 g/mol (PDI = 1.37). The structure and purity of poly(**2a**) were verified by ^{1}H NMR, ^{13}C NMR, and FTIR.

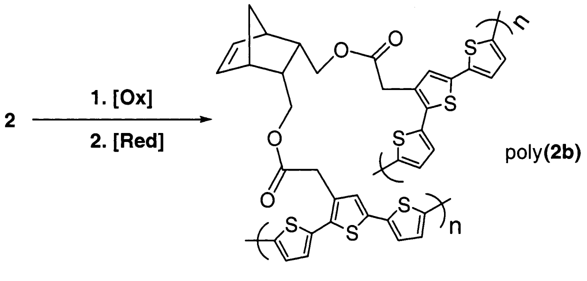
Scheme 1. Preparation of 5-Norbornene-*endo*-2,3-bis(methylene-3′-[2,2′:5′,2″]-terthiophene acetate), 2



Scheme 2. Ring-Opening Metathesis Polymerization (ROMP) of 2



Scheme 3. Electrochemical Polymerization of 2



Electrochemical Polymerization of 5-Norbornene-*endo*-2,3-bis(methylene-3′-[2,2′:5′,2″]-terthiophene acetate), 2. The electrochemical polymerization of the monomer, **2**, was performed in accordance with Scheme 3 utilizing cyclic voltammetry. Electrochemical polymerization of thiophene moieties typically proceeds through the positions α to sulfur on the thiophene ring.[21] Since there are a total of two terthiophene units in the monomer, the resulting polymer is expected to be cross-linked as the structure of poly(**2b**) suggests in Scheme 3.

Figure 1A depicts the cyclovoltammetric oxidative polymerization of **2**. The experiment was initiated at 0 V, a potential at which no electron transfer takes place as indicated by the lack of current. The potential was then scanned in the positive direction at a rate of 100 mV/s. At 0.66 V there is an onset for an oxidative process that can be attributed to the oxidation of the terthiophene moieties of **2**. Upon further scanning, a peak current results at a potential of 0.82 V. It should be noted that between the potentials of 0.66 V and the

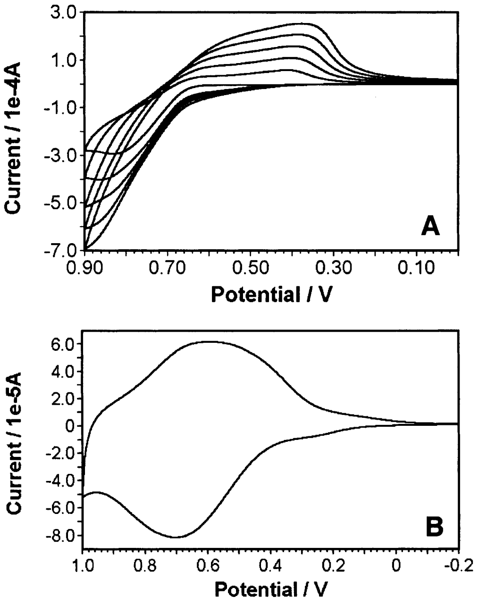


Figure 1. Oxidative electrochemical polymerization of **2** at a scan rate of 100 mV/s (A) and the cyclic voltammetry of the resulting polymer, poly(**2b**) (B), at 100 mV/s in 0.1 M TBAP/ACN electrolyte solution using a Pt button working electrode. Potentials reported vs Ag/Ag$^+$ nonaqueous reference electrode (0.455 V vs NHE).

final potential before reversing the potential, 0.90 V, electrochemical oxidative coupling and polymerization of the terthiophene moieties take place. Thus, for a single cyclovoltammetric scan, the polymerization proceeds for a total of ca. 4.8 s. Upon scanning in the reverse direction, it is immediately evident that the oxidation is an irreversible process. Furthermore, as observed from a mirror placed beneath the working electrode, it is evident that there is formation of a blue precipitate on the electrode surface. Upon scanning further in the reduction direction, a cathodic peak current occurs at 0.41 V. This cathodic process is attributed to the reduction of the conductive polymer formed on the electrode surface from the oxidized/conductive state to the neutral state. The occurrence of this reductive process at a diminished potential relative to the terthiophene moiety indicates the presence of a species with a more extended conjugation. The potential is then reversed at 0 V, and a second scan started. Into the second scan, anodic current first becomes prevalent at 0.48 V, well below that for the onset for oxidation of the pendant terthiophene moieties of **2**, and is attributed to the oxidation of the conjugated polymer on the working electrode surface. Again, at ca. 0.66 V, there is an onset for monomer oxidation inducing further polymerization. Additional polymerization is indicated by the increased cathodic current response observed at 0.41 V for the reduction of the conducting polymer. Upon subsequent scans, polymerization proceeds in a facile manner as is evident by the regular intervals for the cathodic peak current (ca. $5e^{-5}$ A/cycle). This indicates that the conductive polymer is of sufficient conductivity to serve as a working electrode; otherwise, if the polymer were insulating or polymerization only proceeded at the platinum surface, there would be retardation in the rate of oxidative polymerization.

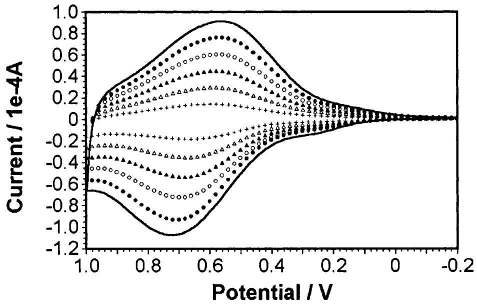
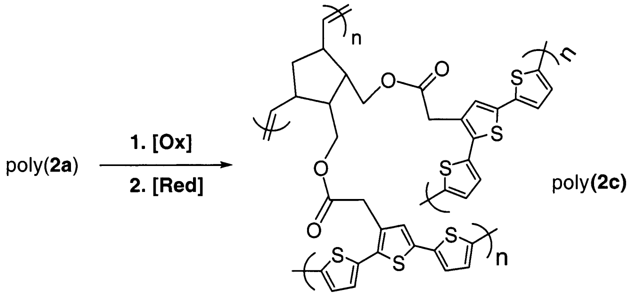


Figure 2. Scan rate dependency study of poly(**2b**) at scan rates of 25, 50, 75, 100, 125, and 150 mV/s in 0.1 M TBAP/ACN electrolyte solution. Potentials reported vs Ag/Ag$^+$ nonaqueous reference electrode (0.455 V vs NHE): (+) 25, (△) 50, (▲) 75, (○) 100, (●) 125, and (—) 150 mV/s.

Scheme 4. Oxidatively Induced Cross-Linking of Poly(2a)



After polymerization of **2**, the electrode coated with a polymer of general structure poly(**2b**) was washed with acetonitrile and placed into a monomer-free solution of 0.1 M TBAP/ACN in order to isolate the electrochemical processes of the polymer. Figure 1B shows the fifth cyclic voltammogram obtained for poly(**2b**) at a scan rate of 100 mV/s. It should be noted that five cyclic voltammograms were required for the stabilization of the current response. It should also be noted that the first cyclic voltammogram was significantly different from the proceeding four in that there was a very large oxidation occurring at a peak potential of 0.95 V (2.7e^{-4} A). Typically for freshly prepared conducting polymers, there is a hysteresis period required in order for the ion movement processes in and out of the polymer upon oxidation and reduction to stabilize. As indicated by Figure 1B, the half-wave redox potential of the polymer is ca. 0.62 V. Figure 2 shows the results for changing the scan rates for the cyclic voltammetry of poly(**2b**). The polymer is adhered to the electrode surface as indicated by the linear increase of peak current with respect to the scan rate.

Oxidative Cross-Linking of Poly(2a). Poly(**2a**) consists of a poly(norbornylene) backbone with pendant terthiophene moieties. Films of poly(**2a**) can be easily cast since this polymer is soluble in a number of different solvents such as methylene chloride, toluene, chloroform, and tetrahydrofuran. The pendant terthiophene ring systems allow for oxidative coupling by either electrochemical or chemical means in order to cross-link the polymer to produce conjugated poly(thiophene) chains after electrochemical or chemical reduction as depicted in Scheme 4. Figure 3A shows the oxidative solid-state electrochemical cross-linking of poly(**2a**) which had been previously coated on the working electrode in 0.1 M TBAP/ACN solution. It should be noted that, for the electrochemically induced cross-linking experiments, the electrolyte solution contains no monomer. The only electrochemically polymerizable monomers present are those attached to poly(**2a**) which are confined to the surface of the electrode. This was confirmed by soaking a poly(**2a**) coated platinum

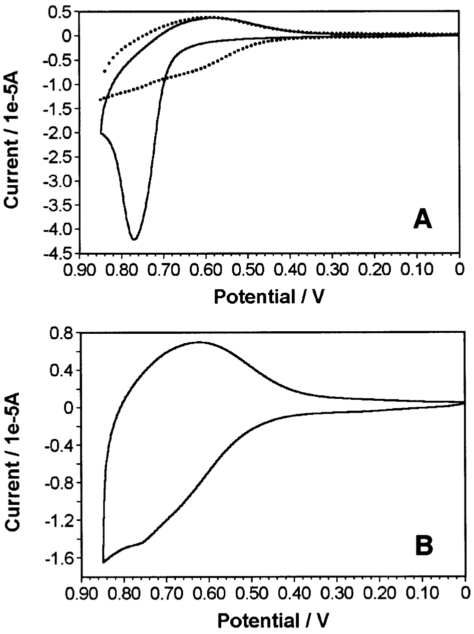


Figure 3. Oxidative electrochemical cross-linking of poly(**2a**) with an approximate film thickness of 0.5 μm at a scan rate of 50 mV/s (A) and the cyclic voltammetry of the cross-linked polymer, poly(**2c**) (B), at 50 mV/s in 0.1 M TBAP/ACN electrolyte solution using a Pt button working electrode. Potentials reported vs Ag/Ag^+ nonaqueous reference electrode (0.455 V vs NHE).

electrode for 10 min in a solution of acetonitrile. Optical spectroscopy on the acetonitrile soak solution showed no presence of terthiophene moieties as indicated by the lack of any absorbance peak at 350 nm.

The cross-linking experiment was initiated at a potential of 0.0 V and scanned in the anodic direction at a scan rate of 50 mV/s. As shown in Figure 3A, at a potential of 0.65 V there is an onset for an irreversible oxidative process that results in a peak at a potential of 0.77 V. Upon reversal to scanning in the cathodic direction, a reduction peak is observed at a lower potential of ca. 0.59 V, which can be attributed to the reduction of intrinsically conductive polythiophene moieties. Upon a second excursion in the anodic direction, there is an onset for oxidation that occurs at approximately 0.42 V, which can be attributed to the oxidation of conjugated polythiophene cross-link units within poly(**2c**). Further scanning in the anodic direction shows a significant reduction in the anodic current response at 0.77 V, which is the oxidation potential of the terthiophene moieties. Scanning in the reverse direction produces a cathodic process with a current response equivalent to that of the first scan, indicating that oxidative coupling was completed after the first oxidative cycle. It was evident from observing the color of the polymer on the platinum button during the electrochemistry shown in Figure 3A that coupling had taken place since the initially yellow film of poly(**2a**) turned dark blue upon excursion above 0.65 V.

Figure 3B shows the cyclic voltammetry of the polymer obtained after the cyclic voltammetry shown in Figure 3A. Hence, this is the third cyclic voltammogram of the series. It should be noted that the oxidation of the polymer is broad with some fine peak detail observed at 0.76 V. The reduction for this process occurs at ca. 0.61 V. Figure 4 shows the current response of poly(**2c**) as a function of the scan rate at 50, 75, 100, 125, and 150 mV/s.

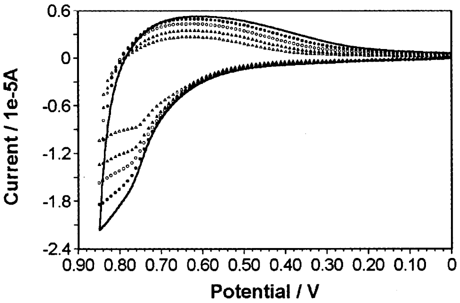


Figure 4. Scan rate dependency study of poly(**2c**) at scan rates of 50, 75, 100, 125, and 150 mV/s in 0.1 M TBAP/ACN electrolyte solution. Potentials reported vs Ag/Ag^+ nonaqueous reference electrode (0.455 V vs NHE): (△) 50, (▲) 75, (○) 100, (●) 125, and (—) 150 mV/s.

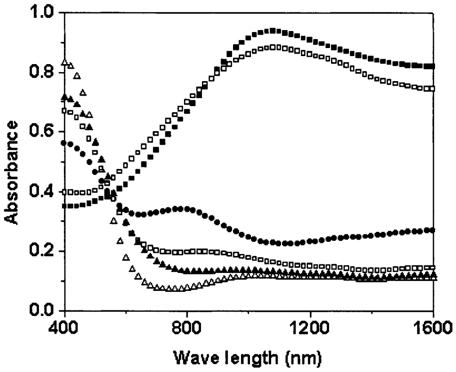


Figure 5. Optoelectrochemistry of poly(**2b**) in 0.1 M TBAP/ACN: (■) 1.0, (□) 0.8, (●) 0.6, (○) 0.4, (▲) 0.2, and (△) 0 V vs Ag/Ag^+.

Chemical oxidative cross-linking of poly(**2a**) was carried out using iron(III) chloride and attempted using iodine as the chemical oxidant. For a 0.5 μm thick film of poly(**2a**) on glass, the oxidative coupling in iron(III) chloride−acetonitrile solution was completed in the initial few seconds of the reaction as indicated by the color change of the polymer film from yellow to blue. The film was washed with acetonitrile and dried, and then the conductivity of the film was measured via a four-point probe to be 1×10^{-3} S/cm. Oxidative coupling of a cast film of poly(**2a**) on a glass slide was also attempted using gaseous iodine. The color change that occurred was not as significant as that observed for the exposure of poly(**2a**) to iron(III) chloride in acetonitrile since after exposure to iodine the film had only turned from yellow to a rust brown. The poly(**2a**) film after iodine exposure did exbihit a conductivity of 1×10^{-3} S/cm under the same conditions as that measured for poly(**2a**) exposed to the iron(III) chloride; however, unlike the iron(III) chloride prepared poly(**2c**), after subjecting the iodine exposed poly(**2a**) to dynamic vacuum for 24 h the sample was too resistive to obtain a conductivity value.

Optical Spectroscopy of Poly(2b) and Poly(2c). Figure 5 shows the spectroelectrochemistry of poly(**2b**) obtained through the electrochemical polymerization of **2** onto an indium-doped tin oxide (ITO)-coated glass slide. The experiment starts at a potential of 0.0 V, a potential at which poly(**2b**) is in the reduced form. Essentially, there is no absorbance in this spectrum until ca. 600 nm (2.06 eV), which corresponds to the onset for the π-to-π* transition better known within the field of intrinsically conducting polymers as the band gap (E_g). Upon stepping the potential to 0.2 V, oxidation

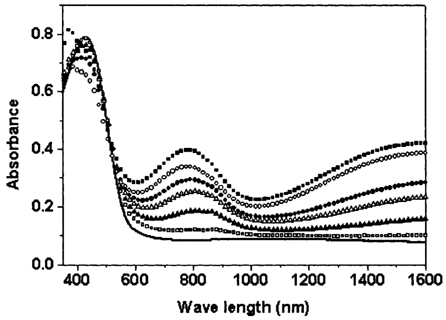


Figure 6. UV−vis−NIR spectra of poly(**2c**): (■) fully oxidized in iron(III) chloride/ACN; (○) 1, (●) 2, (△) 3, (▲) 4, and (□) 5 drops of 0.005 M ACN/hydrazine solution; and (—) fully reduced after dipping the film into acetonitrile containing 0.005 M hydrazine.

of the polymer becomes apparent as indicated by the decrease in absorbance at 400 nm and an increase in the absorbance at lower energies. Upon sequentially oxidizing poly(**2b**), the absorbance for the π to π^* continues to decrease while the absorbance at a lower energy continues to increase. At 1.0 V, a peak at ca. 1100 nm becomes apparent. This peak is commonly attributed to a π-to-bipolaron transition for intrinsically conducting polymers.

Figure 6 shows the UV−vis−NIR spectroscopy for poly(**2c**) as prepared on a glass slide via oxidative polymerization using iron(III) chloride as a function of sequentially reducing with hydrazine. The spectrum for poly(**2c**) as prepared after full reduction with hydrazine exhibits a band gap of ca. 2.15 eV (580 nm) with a peak at an energy of 2.86 eV (440 nm). The first spectrum obtained in the series of the polymer originally in the oxidized form exhibits two peaks at 765 nm (1.62 eV) and 1560 nm (0.79 eV) which can be attributed to the transitions from the valence band to the first and second bipolaron bands. Upon dropwise addition of reducing agent, the polymer is sequentially reduced upon which there is a reduction in the absorbance for the valence-to-bipolaron transitions and an increase in absorbance for the valence-to-conduction band transition.

Discussion

Several researchers have reported the oxidative cross-linking of polymeric systems containing pendant heterocyclic moieties. In these previous reports, the polymer is originally dissolved in solvent, then cross-linked either by chemical reagents[11a] or electrochemically cross-linked, and precipitated onto the electrode surface.[18,22] The choice of polymer backbone is dependent on its inertness to electrochemical side reactions. Therefore, backbones such as poly(ethylene),[23,24] poly(acrylate)s,[25] and polysiloxanes[18,19] have been utilized for supporting electrochemically polymerizable pendant heterocycles. Herein, we have electrochemically and chemically induced cross-linking of poly(norbornylenes) in the solid state via oxidative coupling of pendant terthiophene units.

We have specifically chosen the polynorbornylene backbone due to its ease of preparation via ring-opening polymerization (ROMP). Since this polymerization has been reported to show living characteristics,[26] molecular weight control is greatly facilitated. Furthermore, the hydrocarbon backbone is inert to electrochemical side reactions during oxidative coupling of pendant terthiophene units.[27]

There are several evidences that the polymer has been cross-linked in the solid state to produce intrinsically conductive polymer. Poly(**2a**) is soluble in chloroform; however, after electrochemical or chemical oxidation using iron(III) chloride, the polymer, poly(**2c**), is insoluble. Furthermore, in the electrochemistry shown in Figure 3, it is evident that the oxidative process in the first scan is irreversible and that, upon the second scan, there is an oxidative process that is initiated at a substantially lower potential indicative of a more highly conjugated structure. In addition to this, the current intensity of the peak in the first scan attributed to the oxidation of the terthiophene is substantially diminished in the second scan, indicating that a majority of the terthiophene units within the polymeric matrix were consumed in the initial oxidative process. Terthiophene consumption was also confirmed using UV−vis spectroscopy. The terthiophene unit of poly(**2a**) absorbs at 350 nm, upon oxidative chemical cross-linking of poly(**2a**) utilizing iron(III) chloride, the absorbance peak at 350 nm disappeared, and there is an appearance of a new lower energy absorption at 440 nm.

It should be noted that the electrochemical result (Figure 3a) obtained for the cross-linking of poly(**2a**) is analogous to the results previously reported for the electrochemically induced coupling of heterocyclics tethered to an electrode surface.[18] The UV−vis/NIR spectra of the reduced polymer after electrochemical and chemical oxidation as shown in Figures 5 and 6 indicate that there is substantial conjugation. In fact, the band gap of poly(**2c**) prepared from chemical oxidation with iron(III) chloride is identical to that reported for polythiophene, ca. 2.2 eV.[28] Furthermore, optoelectrochemical (Figure 5) and sequential reduction utilizing hydrazine (Figure 6) show behavior indicative of doping and undoping of an intrinsically conducting polymer. Finally, poly(**2a**) after being subjected to chemical oxidative cross-linking utilizing iron(III) chloride exhibits a conductivity of 1×10^{-3} S/cm.

There are clear differences between the electrochemically induced coupling of the terthiophenes of **2** from solution and of the terthiophenes within a film of poly(**2a**). The first difference between the two systems is that there is an abundant supply of terthiophene moieties within the bulk solution for the polymerization of **2**, whereas there is only a limited supply of these moieties in a thin film of poly(**2a**). Therefore, upon repeated cycling of **2**, as shown in Figure 1, the current response for the polymer redox process continues to increase as a function of scan cycle, whereas after the first scan of poly(**2a**) in Figure 3, it is evident that the terthiophenes have been consumed as indicated by the loss of current at 0.77 V. Secondly, from a theoretical perspective, diffusion of the terthiophene containing monomers in solution should be quite different from that of terthiophenes tethered to a polymer in the solid state. The peak current for **2** is attributed to the depletion of terthiophene at the electrode surface and signifies a point at which the oxidation is limited by diffusion of **2** from the bulk solution. The peak current process for poly(**2a**) is slightly more complicated and could depend on the path by which conjugated and conductive polymer segments are formed within the poly(norbornylene) matrix in addition to the diffusion of the terthiophene units caused by segmental motion of the initial linear polymer. As oxidative coupling of terthiophenes takes place, cross-linking ensues which would lead to progressively restricted segmental motion of polymer chains, thereby progressively hindering the migration of oxidized terthiophene units and further oxidative coupling. Nonetheless, as stated earlier, consumption of terthiophene was complete as observed by UV spectroscopy.

The terthiophenes in a film of poly(**2a**) are easier to oxidize and have a more well-defined oxidation peak than those of **2** in solution. For **2**, the peak for terthiophene oxidation occurs at 0.82 V with an onset value of 0.66 V, giving a half-breadth value of the oxidation wave to be 0.16 V. For poly(**2a**), the peak for oxidation occurs at a slightly lower potential of 0.77 V with an onset value of 0.65 V for an overall approximate half-breadth of the oxidation peak being 0.12 V. Both the lower potential for the oxidation peak current and the lower half-breadth value for the oxidation process of poly(**2a**) can be attributed to the terthiophenes being adsorbed to the electrode surface and, throughout the process of oxidation to form conducting polymer cross-links, being adsorbed to a newly generated electrode surface.

In accordance with the UV−vis−NIR, oxidative cross-linking of poly(**2a**) utilizing iron(III) chloride and using electrochemical oxidation is more effective than the electrochemically induced oxidative polymerization of **2** from solution. The reduced form of poly(**2b**) prepared via electrochemical oxidation of **2** and subsequent reduction of the generated intrinsically conducting polymer exhibits a λ_{max} at 400 nm whereas the λ_{max} for poly(**2c**) prepared via iron(III) chloride and via electrochemical oxidation exhibits a λ_{max} at a longer wavelength of ca. 440 nm. It should be noted that after exposing poly(**2b**) to ferric chloride, followed by reduction with hydrazine, the λ_{max} shifted from 400 to 460 nm, indicating that more cross-linking had occurred. Nonetheless, this wavelength is longer than that for the cross-linking induced within a thin film of poly(**2a**). Thus, it can be concluded that intrinsically conductive polythiophene prepared via iron(III) chloride or electrochemical oxidation of poly(**2a**) has a longer conjugation length than intrinsically conductive polythiophene prepared from the solution polymerization of **2**.

We have attempted the coupling of poly(**2a**) utilizing a gas-phase chemical oxidant, iodine vapor, and in water utilizing ammonium persulfate. We have come to the conclusion that the attempts at iodine-induced oxidative coupling simply led to the formation of a charge-transfer complex between iodine and unsaturated units of poly(**2a**). This is indicated by both the color of the resulting film after exposure to gaseous iodine and the loss of conductivity of the iodine exposed poly(**2a**) after subjecting the film to dynamic vacuum. These results are in accordance with the results reported previously by several researchers for the attempt at the iodine-induced coupling of heterocycles pendant from a polyphosphazene backbone[11a] and the results reported for iodine-doped poly(phenylenevinylene)[29] and poly(phenylacetylene).[30] Dipping of a glass substrate coated with poly(**2a**) into a beaker containing a 0.2 M solution of ammonium persulfate in water did not induce a color change or conductivity enhancements in the polymer. Chemical oxidative coupling was only induced from acetonitrile. We conclude from these results that poly(**2a**) when dipped into acetonitrile swells, thereby enhancing the segmental motion of the polymer chains allowing for collisions and hence reactions between oxidized terthiophene moieties.

Conclusion

We have demonstrated that solid-state cross-linking of terthiophene units pendant to a polynorbornylene can be induced oxidatively either via electrochemistry or chemical oxidants. The chemical and electrochemical oxidative cross-linking method of a thin film of polymer containing pendant terthiophenes, poly(**2a**), affords a polymer of higher conjugation length than that of terthiophene monomer, **2**, from solution. One of the distinguishing features of this research is that the electrochemically induced oxidative coupling of poly(**2a**) has the potential to display more control over chemical oxidative coupling since cross-links would start and then propagate from the working electrode surface, whereas chemical oxidation would occur simultaneously throughout the thickness of the film.

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