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Enhancement of the Physical Properties of Poly((2-terthiophenyl)norbornene) through Cross-Linking Pendant Terthiophenes

Brian R. Stepp and SonBinh T. Nguyen*

Department of Chemistry and the Center for Nanofabrication and Molecular Self-Assembly, Northwestern University, 2145 Sheridan Road, Evanston, Illinois 60208-3113

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ABSTRACT: The synthesis of norbornene polymers containing 2-terthiophenyl side chains, poly((2-terthiophenyl)norbornene), by ring-opening metathesis polymerization (ROMP) and the cross-linking of pendant terthiophene units to form conductive polymers is reported. Physical characteristics including conductivity, thermal stability, electrochromic activity, fluorescence, and surface topography are evaluated for the resulting cross-linked ROMP polymers and compared to those of poly(terthiophene). The in-situ conductivity of cross-linked ROMP polymer films doped with PF_6^- was approximately half that of poly(terthiophene) films. However, thermal stability was substantially higher for powders formed from chemically cross-linked ROMP polymers, which retained 60% of their total mass at 800 °C compared to a total decomposition of non-cross-linked ROMP polymers at 500 °C. Electrochemically deposited films of cross-linked ROMP polymers proved to have considerably higher thermal stability and smoother, more uniform surfaces than films of poly(terthiophene). The root-mean-square value of electrochemically cross-linked ROMP polymer films, derived from atomic force microscopy images (AFM), was approximately 6 nm while that of poly(terthiophene) films prepared in the same manner was 118 nm. These cross-linked films display a reversible electrochromic color change when oxidatively doped.

Introduction

Electrically conducting organic polymers have attracted considerable attention due to their potential applications in electronic devices.[1] Organic polymers are attractive for device application in view of their light weight, their processability, and their tailorability. Exciting developments have been made in the application of conducting polymers to organic light-emitting diodes (OLEDS),[2,3] energy-storage devices,[4] photovoltaics,[5] and electrochromic materials for displays and smart windows.[6] Extensive studies have been carried out on conducting polymers obtained by oxidative polymerization of thiophenes,[7] bithiophenes,[8] and terthiophenes.[9] Recently, terthiophene polymers have been used successfully in the making of white[10] and multicolor[11] OLED devices. However, potential problems with the use of these “native” conducting polymers in thin-film applications include the wide range of conjugation lengths and the lack of surface uniformity (i.e., high roughness) which can make the fine-tuning of electrooptic properties and device applications difficult.[12−14] Recent work has shown that addition of alkyl chains to the thiophene subunits[15] or bridging polymers with conducting cross-links[16] allows for the tuning of polymer conductivity, processability, and local morphology.

We recently reported the synthesis of norbornenyl-substituted thiophene and terthiophene monomers and their ability to doubly polymerize.[17] These unique polymers could potentially be used in sensor applications, OLED devices, or electrochromic materials due to their conductivity, excellent thermal properties, and surface characteristics. In this paper we report the synthesis of ROMP polymers of 3′-(*exo*-5-norbornene-2-oxy)methyl-2,2′:5′,2′′-terthiophene (**1**) and explore the effects of chain length on the physical properties of the resulting ROMP polymers under a variety of cross-linking conditions.

Experimental Section

General Considerations. All reactions were carried out under an inert atmosphere using standard Schlenk techniques or in an inert-atmosphere glovebox, unless otherwise noted. All solvents were purified using the Dow-Grubbs solvent purification system,[18] collected under argon into Strauss flasks, and degassed with nitrogen prior to use. Deuterated solvents were purchased from Cambridge Isotope Laboratories and used without further purification. ^1H NMR spectra were recorded on a Varian Mercury 400 FT-NMR spectrometer (^1H 400.178 MHz). GC-MS experiments were recorded on a Hewlett-Packard HP 6980 series instrument equipped with an HP-5 column (initial temperature was set at 50 °C for 2 min with a ramp of 20 °C/min and a final temperature of 280 °C). Gel-permeation chromatography (GPC) was performed on a Waters 2487 liquid chromatograph equipped with Breeze software, Shodex KF-803L and Shodex KF-806L GPC columns in series with a Shodex KF-G guard column, a Waters 2487 dual λ absorbance detector, and a Waters 2410 refractive index detector. THF was used as the eluent at a flow rate of 1.0 mL/min, and the instrument was calibrated with 15 polystyrene standards (Aldrich, 760−1.8×10^6 Da). Thermal gravimetric analysis (TGA) of chemically cross-linked polymers was carried out on a TA Instruments SDT 2960 Simultaneous DTA-TGA. A TA Instruments model 2950 thermogravametric analyzer was used for TGA of cross-linked polymer films on a gold electrode. Cyclic voltammetry was performed on a CHI900 scanning electrochemical microscope. A conventional three-electrode cell was used for all electrochemical experiments (indium−tin oxide (ITO)-coated glass or 50 nm Au/Si (Au on Si substrate) working electrode, Ag/Ag^+Cl^- reference electrode, and Pt wire counter electrode). ITO-coated glass substrates, purchased from Delta Technologies, were cleaned by immers-

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* To whom correspondence should be addressed. E-mail: stn@northwestern.edu.

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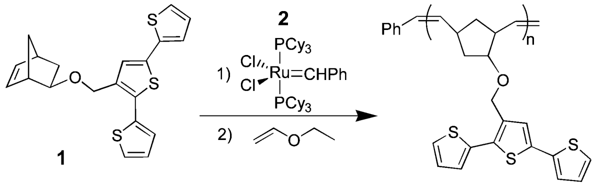
ing in a piranha solution (concentrated H_2SO_4 + 30% H_2O_2 in approximately 3:1 ratio) for 5 min followed by immersion in 1 M HCl(aq) for 5 min and drying under a purified N_2 stream. Silicon substrates were purchased from Montco Silison Technologies, Inc., and coated with Au by chemical vapor deposition (CVD). Interdigitated array (IDA) electrodes (15 μm wide, 4800 μm long, 0.1 μm high, and 15 μm spacing) were purchased from Microsensor Systems Inc. and were used for conductivity studies. A Zeiss Axiovert-100 optical microscope with fluorescence filter kit and a Pixera 600-CL digital image recorder were employed for fluorescence microscopy. A Jasco V-530 UV−vis spectrometer was used to find absorbance maxima for polymer films on ITO glass. Fluorescence spectroscopy was performed using a Jobi Yvon-Spex Fluorolog-3 instrument. Atomic force microscopy (AFM) experiments were carried out on a Digital Instruments scanning probe microscope in tapping mode.

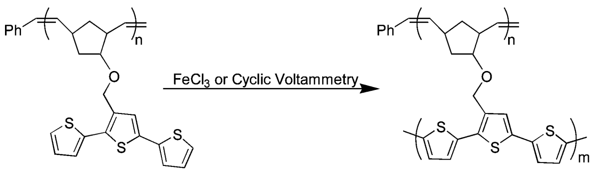
Materials. 3′-(*Exo*-5-norbornene-2-oxy)methyl-2,2′:5′,2″-terthiophene **(1)** was synthesized via literature precedent.[17] All other reagents were purchased from Acros, Strem, or Aldrich Chemical Co. and used without further purification.

Conditions for ROMP of 1. A solution containing an appropriate amount of $Cl_2(PCy_3)_2Ru{=}CHPh$ (**2**) (1.7 mg, 0.0021 mmol; 3.4 mg, 0.0041 mmol; 6.8 mg, 0.0082 mmol; 11.3 mg, 0.0137 mmol; 13.6 mg, 0.0164 mmol; 16.9 mg, 0.0205 mmol; and 22.5 mg, 0.0273 mmol) for the synthesis of 200-, 100-, 50-, 30-, 25-, 20-, and 15-mers, respectively) in CH_2Cl_2 (1 mL) was injected into a stirring solution of **1** (150 mg, 0.41 mmol) in CH_2Cl_2 (5 mL) (eq 1). The mixture was allowed to stir for 20 min and was terminated by the addition of ethyl vinyl ether (1 mL). Volatile components were removed under vacuum; the polymer was precipitated twice from stirring hexane (100 mL) and dried under vacuum to yield a light green powder (**ROMP-poly1**, 140 mg, 93%).



(1)

Oxidative Cross-Linking of ROMP-poly1 and Polymerization of Terthiophene with $FeCl_3$. $FeCl_3$ (199 mg, 1.23 mmol) was placed in a 50 mL Schlenk flask containing a magnetic stirring bar, and CH_2Cl_2 (10 mL) was added to make a brown-black suspension. A solution of **ROMP-poly1** (50 mg, 0.14 mmol of terthienyl units) in CH_2Cl_2 (5 mL) was injected into the flask, and the mixture was refluxed under nitrogen for 24 h (eq 2). The reaction contents were poured into MeOH (50 mL) and filtered to give a brown powder. The crude polymer was further purified via a Soxhlet extraction (reflux MeOH, 24 h) and dried under vacuum (60 mTorr, 12 h) to yield a dark powder (45 mg, 90%). 2,2′:5′,2″-Terthiophene was chemically polymerized in this same manner (eq 3) to give powder poly(terthiophene**)**.



(2)

(3)

Electrochemical Cross-Linking of ROMP-poly1 and Polymerization of Terthiophene. Dark orange films were formed by the electrochemical cross-linking of **ROMP-poly1** (6 mg, 0.014 mmol) on ITO-coated glass in 0.1 M tetrabutylammonium hexafluorophosphate ($TBAPF_6$)/CH_2Cl_2 (5 mL) by repeated scanning between −0.35 and 1.80 V or −0.35 and 1.27 V at a scan rate of 100 mV/s (eq 2). Films that were immediately removed from the CH_2Cl_2/electrolyte solution and placed in the open atmosphere dried too quickly and were prone to cracking. Hence, evaporation of solvent was controlled by allowing the film to dry for 2 min inside the electrochemical cell, just above the liquid surface. 2,2′:5′,2″-Terthiophene was also electrochemically polymerized in this same manner (eq 3) to give films of poly(terthiophene). For TGA studies, films were similarly prepared from **ROMP-poly1** and terthiophene using a Au/Si working electrode.

In-Situ Conductivity of Cross-Linked Films. Cross-linked films of **ROMP-poly1** and poly(terthiophene) were deposited on IDA electrodes using the electrochemical methods described in the previous section. During polymer deposition, both leads of the IDA were connected and used as the working electrode, and 30 layers were deposited for each film. The polymer-coated array was then placed in a monomer-free electrolyte solution and scanned for 3 cycles. Although the continuity of the resulting film over the entire IDA electrode can be visually ascertained using an optical microscope, it can also be verified electrochemically in a fresh electrolyte solution. Cycling the two bands together and then individually between −0.35 and 1.27 V gave identical $I-V$ curves, indicating good communication between the individual leads of the array.[19] In-situ conductivity as a function of doping potential was measured using Wrighton's methods[19−21] as adapted by Reynolds.[22] Static potentials ranging from 0.0 to 1.30 V were used to dope the polymer films. In general, one band of electrodes was held at the desired potential, and the other band was cycled ±0.05 V from the desired potential (0.001 V/s scan rate). After two complete cycles, no hysteresis was observed, indicating that the film is fully doped. The resistance of the film is measured using the $I-V$ data of the third cycle.

Thermal Gravimetric Analysis (TGA). Powder samples of **ROMP-poly1,** chemically cross-linked **ROMP-poly1**, and poly(terthiophene) (4−6 mg) were loaded into the TGA instrument and heated from 40 to 900 °C at a rate of 3 °C/min under an inert atmosphere (N_2). Films of cross-linked **ROMP-poly1** and poly(terthiophene) on a Au/Si electrode were evaluated by the same method using a bare Au/Si electrode as the reference. Percent weight loss of the samples was recorded over the temperature range.

Electrochemical Doping with ClO_4^-. Films of electrochemically cross-linked **ROMP-poly1** and poly(terthiophene) on ITO-coated glass were transferred into a three-electrode cell containing an acetonitrile solution of the supporting electrolyte (0.1 M tetrabutylammonium perchlorate (TBAP)). Using the electrochemical setup described previously, with ITO-coated glass as the working electrode, the polymer films were doped by scanning the potential from either −0.35 to 1.80 V or −0.35 to 1.27 V.

Fluorescence Microscopy. Films of electrochemically cross-linked **ROMP-poly1** and poly(terthiophene) on ITO-coated glass were excited by a mercury lamp, and digital images were recorded. Excitation and emission light were passed through a pair of fluorescence filters before viewing (excitation filter options: 340−380, 460−500, or 533−587 nm; emission filter options: 435−485, 510−560, or 608−682 nm).

Fluorescence Spectroscopy. Films of electrochemically cross-linked **ROMP-poly1** and poly(terthiophene) on ITO-coated glass were excited by a xenon lamp at absorbance maxima, and emission spectra were recorded.

Atomic Force Microscopy. High-resolution surface images were obtained by atomic force microscopy (AFM) and were used to determine the roughness, or root-mean-square (rms), of films electrochemically deposited on ITO electrodes. Tapping-mode AFM scans were taken of the various cross-linked ROMP polymers and poly(terthiophene) at 0.5 Hz with image sizes from 100 to 1 μm.

Results and Discussion

Ring-Opening Metathesis Polymerizations. ROMP reactions were carried out using catalyst **2** at monomer/

Table 1. Polymer Characterization Data for the ROMP of 1

monomer/ catalyst	M_n (g/mol)	PDI	monomer/ catalyst	M_n (g/mol)	PDI
15	8 429	1.28	50	20 153	1.12
20	11 796	1.24	100	31 697	1.10
25	11 915	1.22	200	60 323	1.16
30	13 161	1.18			

Table 2. Root-Mean-Square (rms) Roughness Values of Cross-Linked ROMP-poly1 and Poly(terthiophene) Films on ITO-Coated Glass[a]

	rms roughness (nm)	
polymer	deposited from −0.35 to 1.27 V	deposited from −0.35 to 1.80 V
polyterthiophene	117.9	531.0
X-linked 15-mer	7.2	199.7
X-linked 30-mer	5.1	340.8
X-linked 50-mer	5.8	127.8

[a] Each film is the result of three deposition scans.

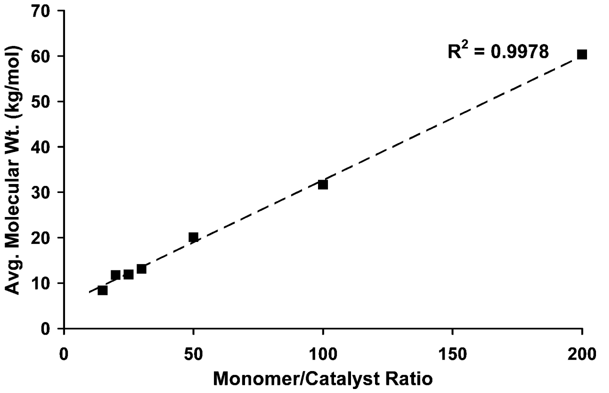


Figure 1. Number-average molecular weight (M_n) for each polymer plotted against the monomer-to-catalyst ratio.

catalyst ratios of 15, 20, 25, 30, 50, 100, and 200. The resulting polymers are reasonably monodispersed (Table 1), and the plot of M_n vs monomer/catalyst ratio is linear (Figure 1) as would be expected for a living polymerization.

Electrochemical and $FeCl_3$-Induced Polymerization Experiments. Terthiophene units are known to undergo oxidative polymerization, either electrochemically[23,24] or in the presence of $FeCl_3$,[25−27] to form poly(terthiophene). Hence, oxidative coupling of pendant terthiophene groups on preexisting polymer chains such as **ROMP-poly1** will result in cross-linked polymers. Dark, insoluble powder samples of cross-linked **ROMP-poly1** and poly(terthiophene) were prepared using $FeCl_3$-induced oxidative polymerization and were analyzed by TGA. Solutions of either **ROMP-poly1** or terthiophene undergo electrochemical oxidation to form orange films on ITO-coated glass. Growth of film layers is evidenced by the increase in peak current as the electrode is cycled (Figure 2a). Using this technique, 1−6-layer films were made from all five **ROMP-poly1** samples and terthiophene. Consistent with slow ion diffusion in and out of the film as it gets thicker, the oxidation potential (E_{ox}) and reduction potential (E_{red}) peaks of the polymer film shift with increasing number of scans. Further, electrochemically cycling a premade film at various scan rates leads to an increase in current and separation of E_{ox} and E_{red} peaks as scan rate increases (Figure 2b). These results exemplify the effects of slow ion diffusion and are similar to those observed by Wrighton and co-workers for a derivatized gold electrode.[28]

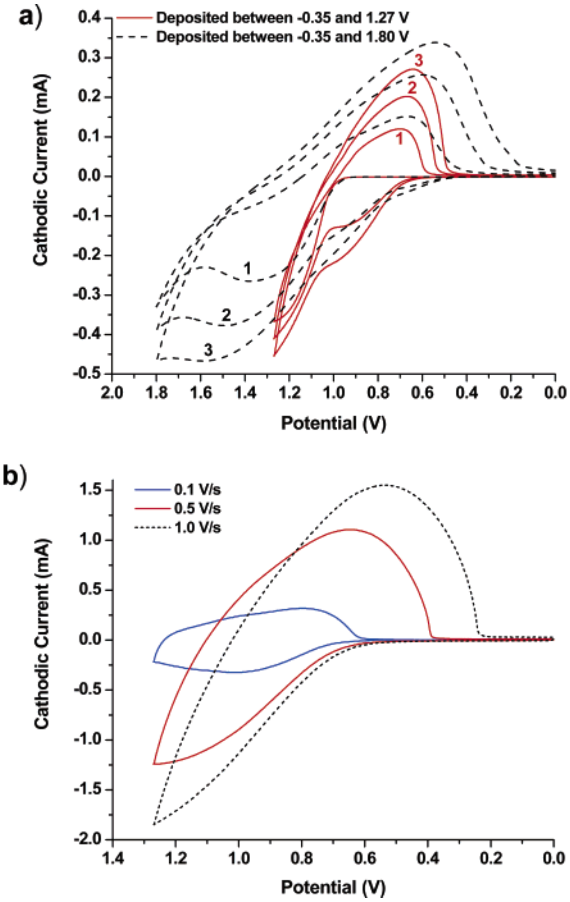


Figure 2. (a) Films of **ROMP-poly1** are electrochemically cross-linked on ITO-coated glass by repeated scanning from −0.35 to 1.27 V (red traces) and −0.35 to 1.80 V (black traces). Peak current increases and peak potential shifts as subsequent layers (1−3) are deposited. (b) A three-layer film of cross-linked **ROMP-poly1** (deposited on ITO-coated glass) is electrochemically cycled at 0.1, 0.5, and 1 V/s in [0.1 M $TBAPF_6/CH_2Cl_2$]. Increasing the rate attenuates ion mobility in and out of the film, thereby increasing peak-to-peak separation.[28]

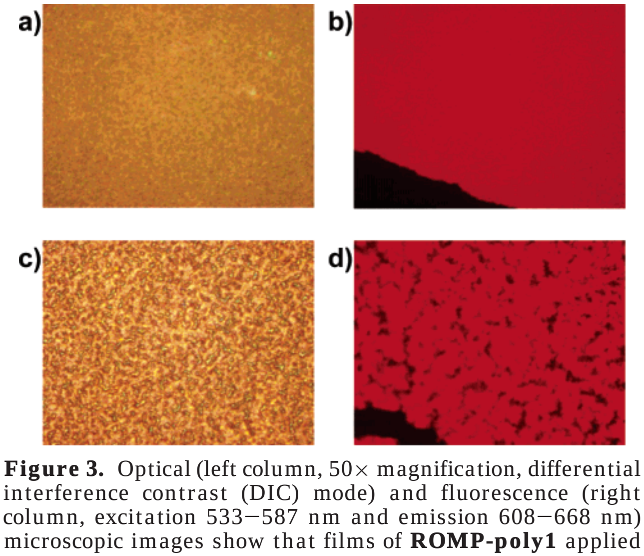


Figure 3. Optical (left column, 50× magnification, differential interference contrast (DIC) mode) and fluorescence (right column, excitation 533−587 nm and emission 608−668 nm) microscopic images show that films of **ROMP-poly1** applied between 0.0 and 1.27 V (a and b) are more uniform than those applied between 0.0 and 1.80 V (c and d).

Visually, the films of cross-linked **ROMP-poly1** were more uniform than films of poly(terthiophene). Films

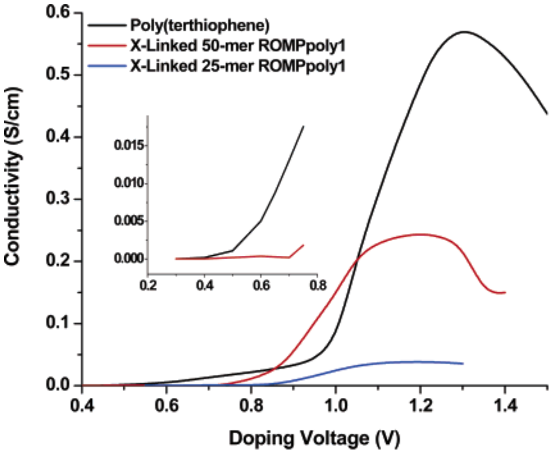


Figure 4. In situ conductivity of poly(terthiophene) and cross-linked **ROMP-poly1** vs doping potential. The inset demonstrates the difference in turn-on voltages for poly(terthiophene) and cross-linked **ROMP-poly1**. The drops in conductivity after 1.25 V are a consequence of over-oxidation.

formed by scanning from −0.35 to 1.80 V were opaque, while those formed by scanning up to a maximum voltage of 1.27 V were translucent and had better optical and thermal properties than those formed at 1.80 V (Figure 3). These observations are consistent with formation of the irreversible overoxidation product described by Kossmehl.[29] Overoxidation results in an insulating film,[30] which was apparent by a gradual reduction in peak current after three cycles from −0.35 to 1.80 V.

In-Situ Conductivity. Films of cross-linked **ROMP-poly1** and poly(terthiophene) were deposited over the surface of IDA electrodes, and the in-situ conductivity of each polymer film was then measured as a function of doping potentials (Figure 4).[19−22] Films derived from cross-linked 50-mer and 25-mer samples of **ROMP-poly1** show appreciable conductivity, albeit lower (about 2.5× for the cross-linked 50-mer **ROMP-poly1**) than that obtained for native poly(terthiophene) prepared in the same manner. This is likely due to a loss of rotational freedom caused by the poly(norbornene) backbone.[16] Conductivity may potentially be enhanced if longer oligothiophene units are used in place of the terthiophene substituent on monomer **1**. For example, penta- or heptathiophene should improve conductivity by increasing the conjugation length of the poly(terthiophene) cross-links. We note that the turn-on voltages for poly(terthiophene) and cross-linked **ROMP-poly1** are quite different. While the former is considerably more conductive, it has a broad turn-on voltage region that spans from 0.4 V to greater than 1.0 V. On the other hand, cross-linked **ROMP-poly1** demonstrates a sharper and more distinct turn-on voltage range of 0.7−0.9 V, presumably due to a narrower distribution of conjugation segments. This well-defined transition between off and on conductive

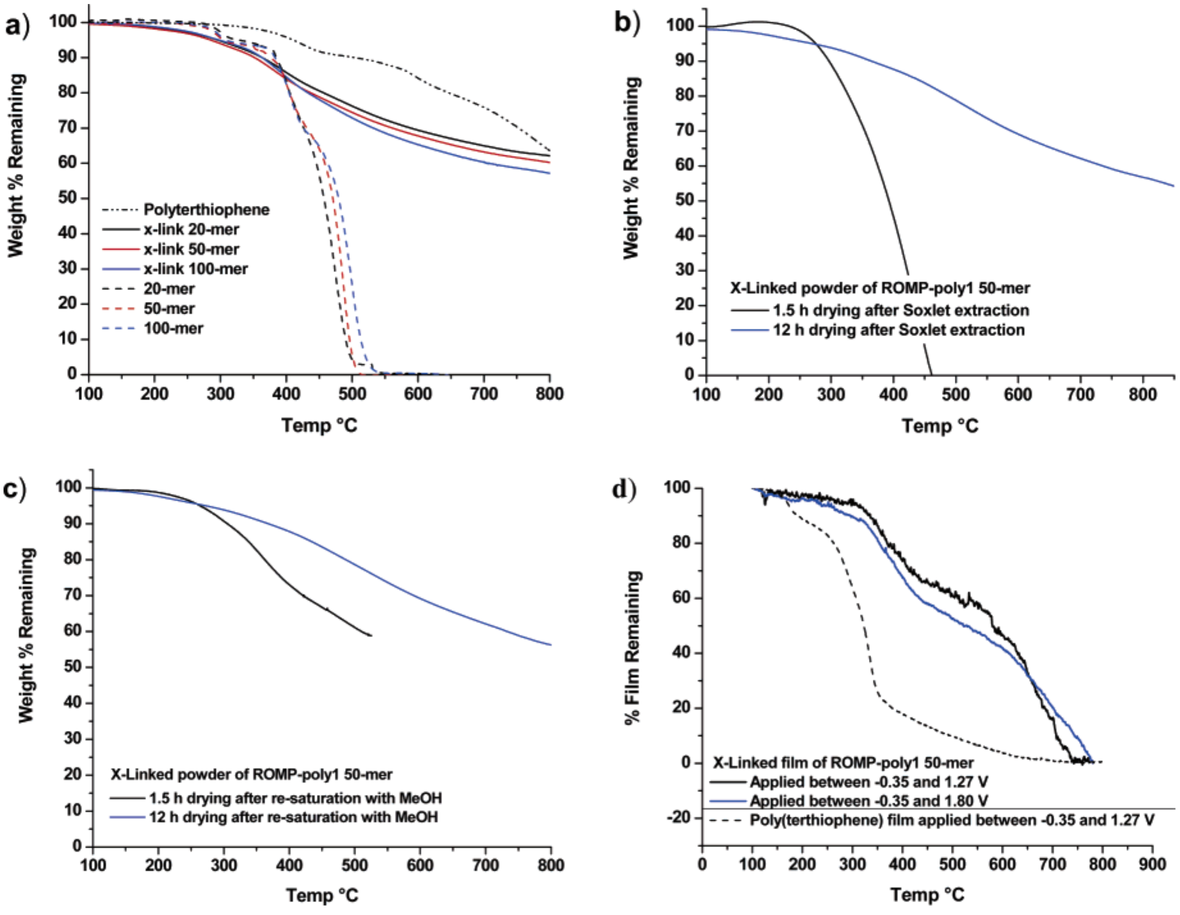


Figure 5. (a) TGA curves for poly(terthiophene), three **ROMP-poly1** samples of different chain lengths (monomer/catalyst ratio of 20, 50, and 100), and the corresponding cross-linked polymers. (b) TGA results illustrating the effect of incomplete drying for a sample of cross-linked 50-mer **ROMP-poly1**. (c) TGA curves illustrating the effect of reexposing a sample of cross-linked 50-mer **ROMP-poly1** to MeOH followed by drying over different periods of time. (d) TGA results for 50-layer films of electrochemically cross-linked 50-mer **ROMP-poly1** and polyterthiophene on Au/Si substrates.

states is a potential advantage for our cross-linked ROMP polymer in switching applications.

Interestingly, attempts to measure the in-situ conductivity of cross-linked 100-mer and 200-mer samples of **ROMP-poly1** were unsuccessful due to our inability to grow continuous films across the two bands of the IDA electrode in several solvents and solvent mixtures. For these polymers, films were observed to only grow directly on the surface of the gold fingers of the IDA and did not spread across the two bands of electrodes, as seen for the lower weight polymers (vide supra). This is probably due to reduced solvation of the longer polymers which results in more intrachain cross-linking and less radial growth.

Thermal Gravimetric Analyses. Under an inert atmosphere (N_2), TGA scans were performed on samples of various chain lengths of **ROMP-poly1**, cross-linked **ROMP-poly1**, and poly(terthiophene) to test the effects of chain length and cross-linking methods on the thermal stability of these polymers (Figure 5a). The thermal stability of both the parent ROMP polymers and the corresponding cross-linked ROMP polymers showed no appreciable dependence on ROMP backbone chain length. Cross-linked polymers exhibited an increase in thermal stability and displayed temperature profiles that are much better than those of the parent polymers and only slightly worse than that of poly(terthiophene).

For accurate measurements of thermal stability, it is critical to completely dry all polymer samples prior to TGA runs. Incomplete drying can lead to a significant reduction of thermal stability (Figure 5b). This apparent reduced thermal stability can be attributed to "incomplete curing": as the temperature rises, a detrimental reaction between the trapped protic solvent and the polymer can occur. The potential reducing ability of protic solvents has been noted for oxidized polyterthiophene.[31] Exposure of a "cured" sample, which had been previously dried under high vacuum for 12 h, to methanol and running TGA after short (1.5 h) and long (12 h) drying times supported this hypothesis (Figure 5c). After 1.5 h of drying under vacuum, the methanol-exposed sample shows a significant decrease in stability compared to the 12 h dried sample; however, the thermal stability does not decrease to the extent of the initial incompletely dried sample (cf. Figure 5b). On the other hand, the methanol-exposed sample that went through the long drying time shows the same stability as the parent sample.

The thermal stability of electrochemically cross-linked films of **ROMP-poly1** and poly(terthiophene) deposited on Au/Si substrates was also tested by TGA (Figure 5d). Compared to the powder samples of cross-linked polymer, the film samples are not as stable. However, cross-linked films of **ROMP-poly1** possess higher overall stability compared to films of poly(terthiophene) prepared in the same way, which can be a potential advantage in device applications. Thermal stability was moderately improved for films deposited between −0.35 and 1.27 V compared to those deposited between −0.35 and 1.80 V.

Electrochromic Behavior of Cross-Linked ROMP-poly1 and Poly(terthiophene) upon Doping. Similar to observations made using other thiophene-based and terthiophene-modified polymers,[32−34] films of electrochemically cross-linked **ROMP-poly1** and poly(terthiophene) displayed electrochromic properties when oxidatively doped (Figure 6). The color change was identical for both polymer films; however, scans between −0.35 and 1.80 V were irreversible while those between −0.35 and 1.27 V were reversible (Figure 7). For the former, the color change for films become less distinguishable and became noticeably darker after each cycle. This behavior can also be observed in PF_6^--containing electrolytes.

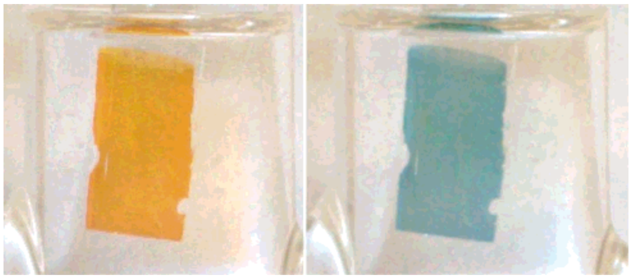


Figure 6. A three-layer film of electrochemically cross-linked 20-mer **ROMP-poly1** changes from orange (left) to dark blue (right) in a perchlorate-containing electrolyte as the cell voltage is increased from −0.35 to 1.27 V. This dopant-induced color change is reversible over 20 or more cycles.

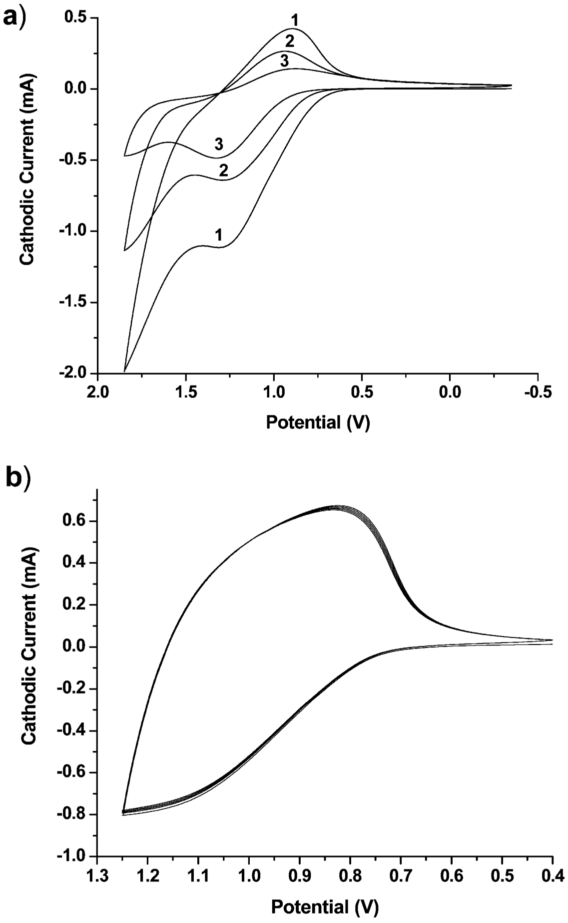


Figure 7. Current−voltage behavior of two three-layer films of electrochemically cross-linked 20-mer **ROMP-poly1**. (a) Because of overoxidation, peak current decreases with each subsequent cycle when one film is scanned between −0.35 and 1.80 V. (b) $I-V$ behavior remains constant over five cycles when another identical film is scanned between −0.35 and 1.27 V.

Optical Properties of Cross-Linked ROMP-poly1. The use of fluorescence microscopy facilitated the macroscopic observation of fluorescence from electrochemically cross-linked 20-mer **ROMP-poly1** and poly-

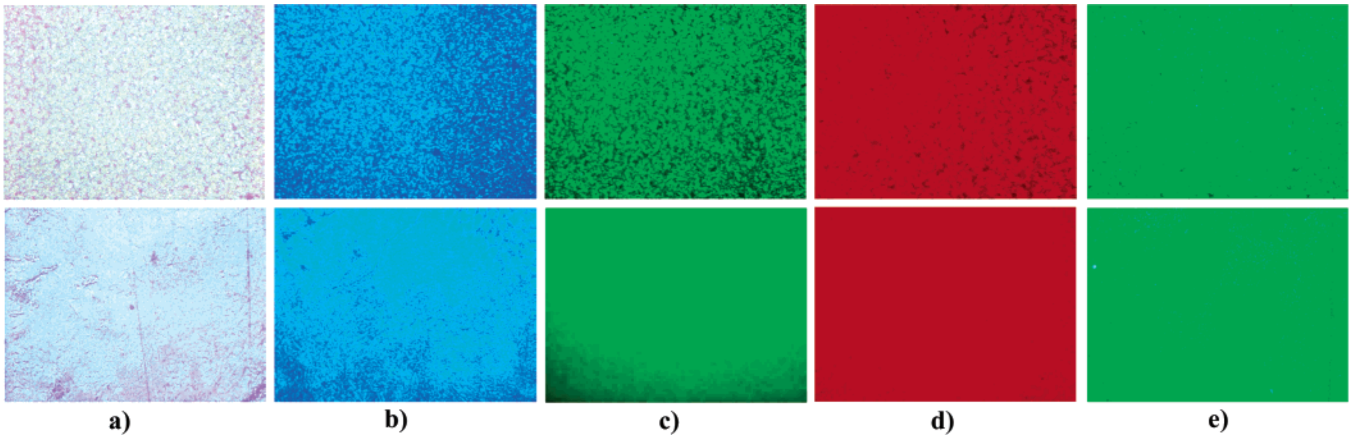


Figure 8. Digital images of three-layer films of poly(terthiophene) (top row) and **ROMP-poly1** (bottom row) were taken from fluorescence microscopy experiments. (a) ex 340−380, em no filter; (b) ex 340−380, em 435−485; (c) ex 460−500, em 510−560; (d) ex 533−587, em 608−668; (e) ex 340−380, em 510−560.

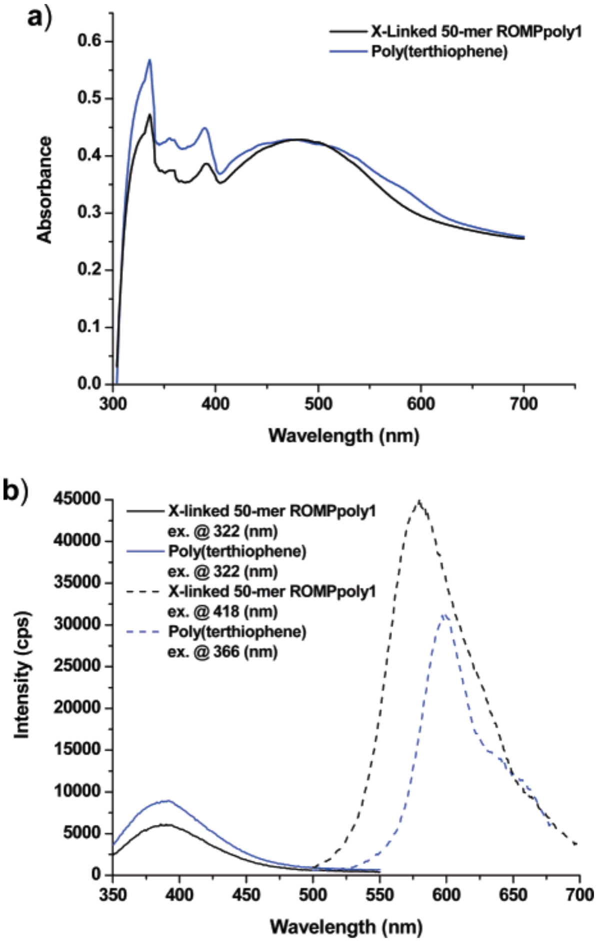


Figure 9. UV−vis (a) and emission (b) spectra for ITO-deposited three-layer films of poly(terthiophene) and **ROMP-poly1** were very similar. Fluorescence spectra were taken using excitation wavelengths of 322, 366, and 418 nm.

(terthiophene) films on ITO-coated glass. Films were excited by filtered light at various wavelengths, causing an emission, which was also filtered before viewing (Figure 8). During fluorescence spectroscopy experiments, films were irradiated at predetermined absorbance maxima (obtained from UV−vis measurements) and their emission spectra collected (Figure 9). In general, both macroscopic fluorescence and emission from **ROMP-poly1** films were chain-length-independent and are very similar to those of poly(terthiophene). However, **ROMP-poly1** films were consistently of a better quality with fewer defects.

Surface Studies Using Tapping-Mode AFM. AFM topographic images demonstrate the smoother texture of cross-linked **ROMP-poly1** films applied between −0.35 and 1.27 V compared to those deposited between −0.35 and 1.80 V and those of poly(terthiophene) (Figure 10). The latter are remarkably similar to those of the SEM images of poly(thiophene) taken by del Valle and co-workers.[35] Phase images of AFM scans suggest that cross-linked **ROMP-poly1** films are amorphous solids with no obvious phase segregation. On the basis of root-mean-square (rms) roughness calculations, all films of cross-linked ROMP-polymers (15-mer, 30-mer, and 50-mer) deposited at lower potentials (−0.35 to 1.27 V) were much smoother (<10 nm rms) than those applied at higher potentials (−0.35 to 1.80 V) or films of poly(terthiophene) (>100 nm rms). The better planarity of the cross-linked **ROMP-poly1** films is likely due to a 2-dimensional layer-by-layer initiation and growth mechanism as described by Alberty and co-workers for films of poly(thiophene-3-acetic acid),[36] while the less ordered poly(terthiophene) films are consistent with the three-dimensional growth mechanism described by del Valle.[35,37]

Conclusions

ROMP polymerization of **1** at monomer/catalyst ratios of 15, 20, 25, 30, 50, 100, and 200 proceeded well and resulted in near monodispersed polymers (PDI < 1.30). Oxidative polymerization of **ROMP-poly1** by either $FeCl_3$ or electrochemistry yielded dark powders or orange films of cross-linked **ROMP-poly1**, respectively. Electrochemically cross-linked films of **ROMP-poly1** deposited between −0.35 and 1.27 V are transparent and of better quality than those deposited between −0.35 and 1.80 V. Films of cross-linked **ROMP-poly1** are smoother and more uniform than corresponding poly(terthiophene) films, as evidenced by optical and atomic force microscopy. In-situ conductivity measurements demonstrated dopant-induced conductivity and improved on/off characteristics for cross-linked **ROMP-poly1** films (as compared to poly(terthiophene) films). TGA experiments under an inert atmosphere (N_2) showed that bulk samples of the cross-linked ROMP-polymers are considerably more heat-resistant than the non-cross-linked ROMP-polymers and that increasing the chain length of polymer backbone beyond 20 mono-

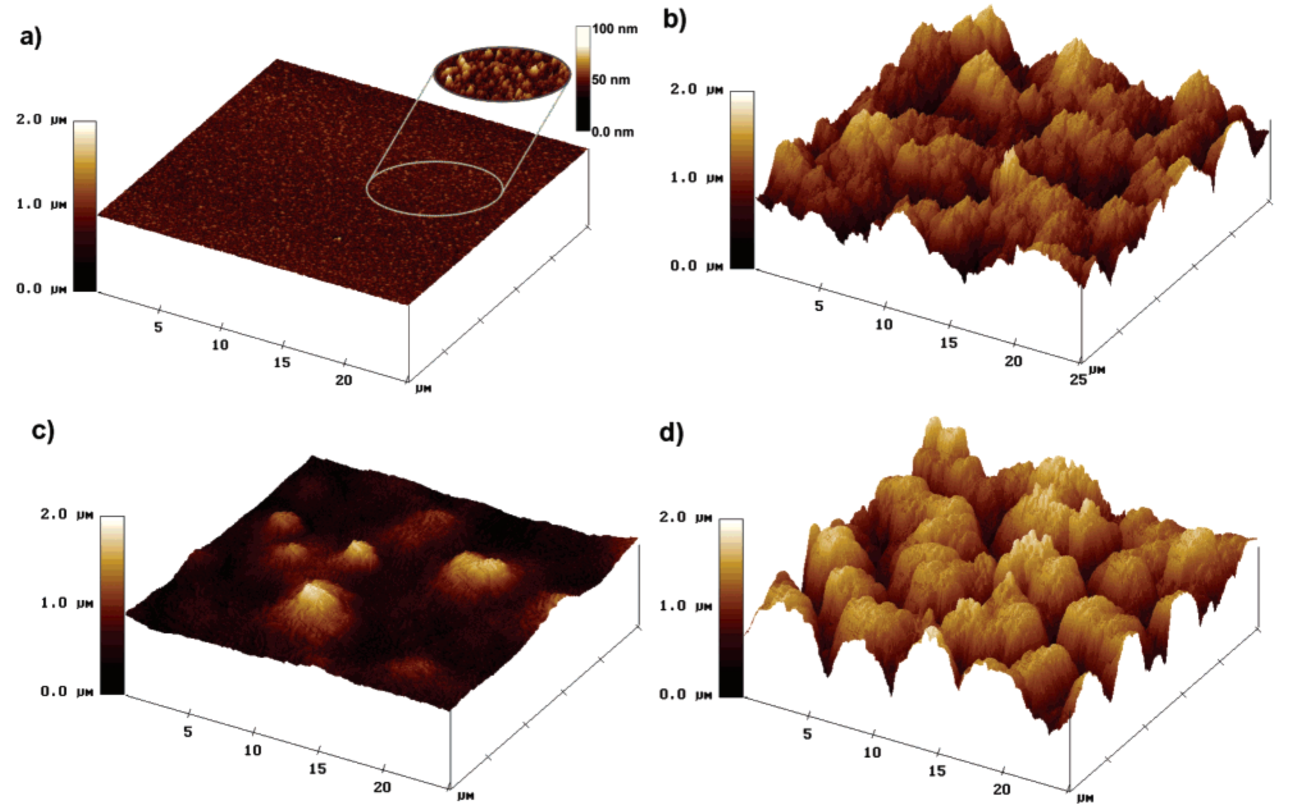


Figure 10. AFM images of (a) cross-linked 30-mer **ROMP-poly1** film deposited between −0.35 and 1.27 V (inset with reduced *z* range to show detail), (b) cross-linked 30-mer **ROMP-poly1** film deposited between −0.35 and 1.80 V, (c) poly(terthiophene) film deposited between −0.35 and 1.27 V, and (d) poly(terthiophene) film deposited between −0.35 and 1.80 V. Each film is the result of three deposition scans.

mer units has little effect on the stability of the cross-linked polymer. Of note is the high stability of electrochemically deposited films of cross-linked **ROMP-poly1** compared to poly(terthiophene) films prepared in the same manner. Doping the cross-linked films with ClO_4^- revealed an interesting electrochromic color change from orange to blue, which was reversible provided that the voltage was not cycled above 1.27 V. The better switching characteristics, along with improved film uniformity and thermal stability of the materials obtained by cross-linking pendant terthiophene groups on a poly((2-terthiophenyl)norbornene) backbone, make these materials a viable area of research for polymeric devices.

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