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Nanopatterned Electrochromic Conjugated Poly(terthiophene)s via Thermal Nanoimprint Lithography of Precursor Polymer

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Polyterthiophene nanostructures consisting of periodic nanolines were prepared using the precursor polymer approach in conjunction with nanoimprint lithography. Precursor polynorbornylenes consisting of terthiophene side chains were prepared from their corresponding norbornylene monomers via ring opening metathesis polymerization. A copolymer consisting of terthiophene norbornylene and acetate norbornylene repeat units with a 50:50 composition exhibited a glass transition temperature of 52°C. Nanolines of percursor polynorbornylene were prepared by thermal nanoimprint lithography. The nanoimprinted precursor polymer was then converted to conjugated conductive polymer via chemical and electrochemical oxidation of the terthiophene side units. Nanoimprinted lines of conductive polyterthiophene exhibited high electrochromic contrast at 437 nm.

Keywords: nanoimprint lithography; polythiophene; conductive polymer; electrochromic; precursor route; terthiophene; polynorbornylene

1 Introduction

Rapid nanopatterning of conjugated conductive polymers continues to be a challenge to researchers due to the relative intractability of these polymers compared to conventional polymers. Patterning CPs at the micro regime has involved photochemical lithography (1), micromolding (2), electropolymerization with modified electrode (3), line patterning (4), microcontact printing (5), inkjet printing (6), and electrophoretic patterning from colloidal suspension (7). Inganas, et al. reported that submicron gratings of PEDOT-PSS were observed to have higher coloration eficiencies due to the diffraction (8). Recently, there has been main focus on the patterning of CP at nano-scale to meet the future demands of the electronic devices. Mirkin and coworkers demonstrated the electrostatically driven patterning of conducting polymers via Dip-Pen Nanolithography (DPN) (9). Liu and coworkers have shown the direct-writing of conjugated polymer via electrochemical-DPN where EDOT was electropolymerized at the AFM tip/substrate interface (10). The other variation of DPN technique was also demonstrated by Dravid and coworkers to pattern conductive polymer via

acid-promoted polymerization of pyrrole (11). There have been also reports of electrochemical polymerization of precursor polymer film into conducting nanopattern by applying the positive (12) or negative (13) bias to a conductive AFM tip. We have reported electrostatic spinning as a technique to generate conjugated polymer nanofibers over relatively large substrate (14). Rapid processing of conjugated conductive polymer nanostructures remains a challenge primarily due to the lack of processability of these systems due to the rigidity of the polymer backbone. The precursor polymer approach to conductive polymers is a viable approach in that the precursor polymer processability is equivalent to conventional processable polymers.

Nanoimprint lithography (NIL) is a rapid and inexpensive method to pattern arbitrarily complex features at nanoscale over a large area with sub-10-nm resolution (15). However, the intractability of CP limits their patterning by this technique as the process requires the deformation of polymer under heat and pressure. Makela et al. have shown NIL of conductive polyaniline from the polymethylmethacrylate/polyaniline-camphor sulfonic acid mixture dissolved in m-cresol (16). However, toxicity and low volatility of m-cresol may limit its use. Recently, Tan et al. demonstrated NIL of PEDOT-PSS involving the use of glycerol as a plasticizer (17). Carter and coworkers have demonstrated NIL of polyacrylates with pendant thiophene groups that can be further polymerized using chemical oxidant or Grignard metathesis (GRIM) in the presence of 3-alkyl thiophene to produce patterned

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conducting polymer brushes (18). This procedure generates poly(3-alkyl thiophene) in solution as a side product.

Herein, we describe a process wherein precursor polymer is nanopatterned using thermal NIL and then later converted to conjugated conductive polymer via conversion using chemical or electrochemical oxidation in the solid-swollen state (19). Advantages of solid state oxidative conversion are: a) the precursor polymer behaves like conventional polymers in that they can exhibit low glass transition temperatures and exhibit high solution viscosities; b) Within the conversion process, the precursor polymer transforms into the conductive polymer not following a nucleation and growth mechanism and thereby allowing for fewer optical defects and, generally, smoother morphology; c) After conversion, the conductive polymers are part of a crosslinked insoluble network; d) The solid state structure of the precursor polymer is maintained in the conversion to conjugated conductive polymer; e) Conversions are near quantitative in that the starting mass of precursor polymer is equivalent to the mass of conjugated polymer produced after solid-state oxidation. Here, we demonstrate the ability to rapidly pattern 200 nm periodic gratings of precursor polymer on *ca.* 58 cm^2 indium doped tin oxide coated glass and the conversion of this precursor polymer in the solid-swollen state to conjugated conductive polymer via both electrochemical and chemical oxidation. The patterned conjugated poly(terthiophene) lines exhibit high contrast at λ_{max} of 437 nm.

2   Experimental

2.1   Materials

Acetonitrile and chloroform were purchased from ACROS. Acetonitrile was dried and distilled over calcium hydride before use. Tetrabutylammonium perchlorate was prepared by reaction of tetrabutylammonium bromide with perchloric acid in water. Tetrabutylammonium perchlorate was filtered and then recrystallized from ethanol and dried before use. NOTE: perchloric acid and organic perchlorates should be handled with caution. The materials safety data sheets for these compounds should be carefully read before use of these reagents.

2.2   Instruments

A full-wafer thermal nanomprintor (Nanonex, NX-1000) was used for the nanoimprinting. Atomic force microscopic images were recorded in tapping mode on an Asylum Research MFP-3d atomic force microscope. A CH Instruments 660A potentiostat was used for all electrochemical experiments. A Perkin-Elmer Lamda 900 UV-Vis-NIR spectrometer was used for UV-Vis-NIR spectra.

3   Results and Discussion

A precursor random copolynorbornylene, **1**, having repeat units with terthiophene and with acetate was prepared by

ring opening metathesis polymerization of 5-norbornene-2-(methylene-3′-[2,2′:5′,2″]-3T acetate) **(NM3T)** and 5-norbornene-2-acetoxymethyl **(NA)** in equimolar feed ratio using Grubbs generation I alkylidene catalyst followed by the irreversible termination using ethyl vinyl ether (Figure 1) (14). The copolymer structure and composition were determined by ^{1}H-NMR, and found to be 1:1 with respect to terthiophene:acetate groups. The number average molecular weight and polydispersity index were found to be 68,000 D and 1.2, respectively, as determined by gel permeation chromatography using monodisperse polystyrene standards. The glass transition temperature (T_g) for polymer 1 is 52°C.

Precursor polymer, **1**, is soluble in numerous common organic solvents like chloroform, methylene chloride, tetrahydrofuran, and toluene. A 100 nm thick film of **1** was prepared on 58 cm^2 indium doped tin oxide coated glass slides by spin casting from a 1% w/v solution of **1** in chloroform. A silicon mold consisting of periodic 200 nm gratings having 20 nm width lines separated by 180 nm width gaps was prepared by e-beam lithography, and used for nanoimprint lithography. The trenches of the gratings were 80 nm deep. Thermal nanoimprint lithography was carried out by first heating the precursor polymer coated substrate to 100°C, a value above the glass transition of precursor polymer **1**, followed by pressing the mold into the polymer film with a pressure of 1100 bar to allow the polymer to flow into the mold spacings. The mold was removed after cooling the system to 30°C, a temperature at which precursor polymer 1 transitions to a glassy state. Atomic force microscope images of the pattern obtained (Figure 2a) shows, on average, 180 nm width lines of precursor polymer **1** with an average spacing of 20 nm (Figure 2a). The height of the pattern was determined to be 80 nm, the approximate depth of the trenches in the mold. The thickness of the residual layer varied from 1.5 nm to 1.7 nm across the imprinted region. NIL generally resulted in a residue between isolated
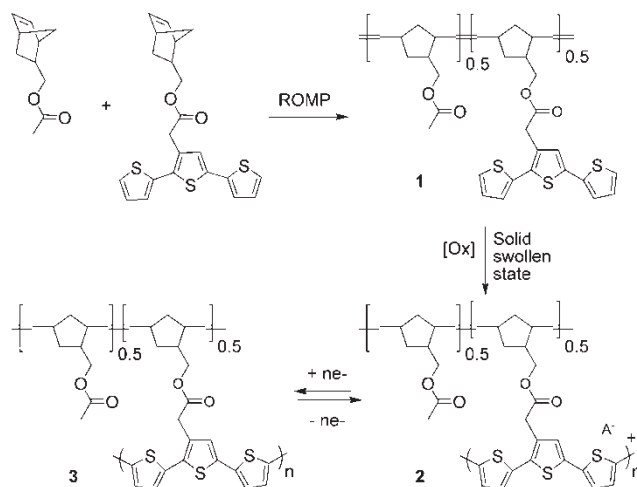
Fig. 1.   Solid-state oxidative conversion of precursor polymer **1** to prepare conductive polymer, **2**, and subsequent reduction/oxidation between **2** and **3**.
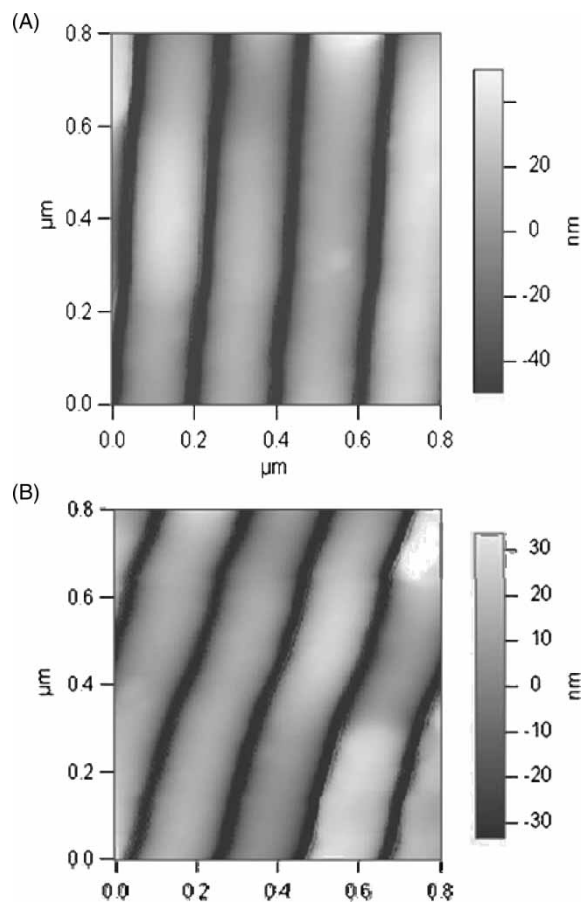
Fig. 2. Atomic force microscope images of precursor polymer **1** nanolines (A), and conjugated poly(terthiophene) **3** nanolines after solid-state oxidative conversion (B).

features, and thickness variation of the residual layer is dependent on the pattern density or layout of the pattern (20). The residual layer can be removed via reactive ion etching (RIE). As is evidenced from the AFM image, some portions of the lines appear to pull from the substrate as a result of removing the mold, a trademark of NIL using a hard mold.

Precursor polymer **1**, although soluble in many common organic solvents, is not soluble in polar solvents such as acetonitrile but only swollen. Ellipsometry measurements indicate that the polymer swells approximatley 9% in the z, or thickness, direction. Swelling of the precursor polymer, we believe, is important for the solid-state oxidative conversion in that the electrolyte has the ability to penetrate into the precursor polymer film thereby providing a source of anions for positive charges that would form during the conversion process. Furthermore, the solvent serves the role of plasticizing the polymer allowing for polymer chain movement and the ability of terthiophene radical cations formed via oxidation to collide with one another providing a means for coupling to take place to form conjugated conductive polymer. Terthiophene containing precursor polymer nanolines of **1** were converted in the solid-state to conjugated

conducting polymer **2** nanolines by solid-state oxidative conversion in accordance with Figure 1. As indicated by the atomic force microscope images, no significant change in the pattern dimension was observed after solid-state oxidative conversion (Figure 2).

Electrochemical polymerization was performed using a three electrode cell using indium doped tin oxide coated glass with nanopatterned **1** as the working electrode, a blank indium doped tin oxide coated glass as the counter electrode, and a Ag/Ag$^+$ non-aqueous reference electrode immersed into 0.1 M tetrabutylammonium perchlorate/ acetonitrile as the electrolyte solution. Figure 3 shows a cyclic voltammogram for the electropolymerization of **1** carried out in the its solid swollen state. During the first scan in anodic direction, a broad oxidation process is observed with an onset at 0.64 V and a peak at 0.81 V corresponding to the oxidation of terthiophene to its respective radical cation. Once the radical cation is formed it reacts to form conjugated conductive polyterthiophene crosslinks which is evident by the color change of the nanopatterned coating from colorless to blue. The blue color is characteristic of a polythiophene. Upon scanning in the cathodic direction, the reduction of conductive poly(terthiophene), 2, to its neutral state, **3**, ensues as is evident by the change in color form blue to orange with orange being characteristic for a neutral conjugated polythiophene. During the second scan, a broad oxidation process is observed with an onset of 0.4 V corresponding to the oxidation of neutral poly(terthiophene), **3**, to its conductive form, **2**. Then, of particular note is that there is a significant decrease in current response at 0.81 V, the peak oxidation for terthiophene. Since the precursor polymer is confined to the electrode surface, there is a finite amount of terthiophene that can be converted to polyterthiophene. The loss of current indicates that nearly all terthiophenes in the polymer have been converted to polyterthiophene. This result is further substantiated by the later
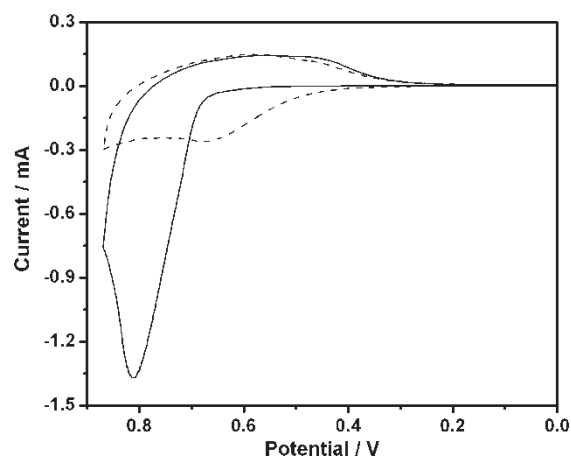
Fig. 3. Solid-state oxidative conversion of **1** in 0.1 M tetrabutylammonium perchlorate/acetonitrile solution at a scan rate of 50 mV/s. Potentials reported vs. Ag/Ag$^+$ non-aqueous reference electrode (0.445 V vs. NHE).

described Vis-NIR studies. Upon scanning in the cathodic direction on the second scan, the current for reduction of the conductive polymer 2 is equivalent to the current for reduction in the first scan. This result would imply that no more polyterthiophene was prepared and that the chemistry was complete after the first anodic scan. The results obtained here for cyclic voltammatric oxidation are approximately the same as those reported earlier for homopolymer precursors containing terthiophenes (19).

A 58 cm^2 indium doped tin oxide coated glass substrate patterned with **1** was used to study the spectral properties before and after solid state oxidative conversion. Polymer **1** shows a λ_{max} at 355 nm corresponding to the π-to-π^* transition of terthiophene. This value is the same as that obtained for a neat film of **1** and is a strong indication that terthiophene has not been altered during the thermal nanoimprint process. UV-Vis-NIR of patterned polymer **2** obtained after electrochemical oxidation was taken in 0.01 M antimony (V) chloride solution in acetonitrile, and results are shown in Figure 4. The λ_{max} for the π-to bipolaron transition was observed at 1074 nm (1.15 eV) indicating the formation of conductive poly(terthiophene). After washing with acetonitrile, polymer **2** was reduced to neutral poly(terthiophene), **3**, by dipping the substrate with nanopatterned polymer into 0.01 M hydrazine/acetonitrile solution. The nanopattern of **3** has a λ_{max} at 437 nm. 437 is higher than that for terthiophene, 355 nm, indicating that after solid-state oxidation, there is more conjugation for the repeating thiophene structures. The conjugated poly(terthiophene) showed an onset for the π-to-π^*, also referred to as the energy gap (E_g) at 2.21 eV (560 nm). Eg values of 2.1 to 2.2 eV are values typically obtained for poly(terthiophenes). The UV-Vis-NIR results corroborate the results obtained from cyclic voltammetry in that there is no apparent peak for the π-to-π^* transition of terthiophene after solid-state oxidative conversion.

Chemical solid state oxidative conversion was also performed. Nanolines of **1** confined to an indium doped tin oxide coated glass were submerged into 0.01 M ferric chloride in acetonitrile in order to prepare nanopatterns of **2**. The crosslinked poly(terthiophene) that resulted from the chemical oxidation showed near identical electrochemical and optical data to the poly(terthiophene) obtained using electrochemical oxidation.

4 Conclusions

In summary, we have demonstrated that precursor polynorbornylenes consisting of terthiophenes can be thermally nanoimprinted and oxidized, in the solid state, to generate a nanopattern of conjugated conductive polyterthiophene. The precursor method offers tremendous versatility in control of thermal properties in that variation in comonomer composition of the bulky terthiophene side group will have an affect on the glass transition of the polymer. Thus, the copolymer can be thermally tuned for the nanoimprint process. Further, we have no reason to believe that thermal nanoimprint lithography is restricted to terthiophene functionalized copolynorbornylenes. We anticipate that numerous chemically different polymer precursors can be used and that a host of different heterocycles could be used as the monomers for conductive polymer formation. Here, we have shown that nanoimprint lithography is a technique by which any number of conjugated polymer nanostructures can be formed dependent upon the mold used for the nanoimprinting process. not via NIL followed by SOC of the patterned insulating polymer in the solid-swollen state into the patterned conjugated poly(terthiophene). Nanoimprint lithography in conjunction with the precursor poymer approach could be utilized to prepare conjugated polymer nanostructures that could find application as transistors, interconnects, bulk heterojunction for photovoltaics and as optical gratings.

5 Acknowledgements

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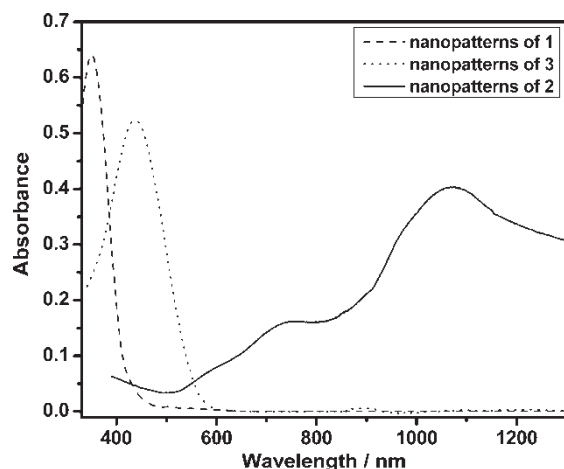

Fig. 4. UV-Vis-NIR of nanolines of polymers **1**, **2**, and **3**.

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