

# Improving the Charge Conductance of Elemental Sulfur via Tandem Inverse Vulcanization and Electropolymerization

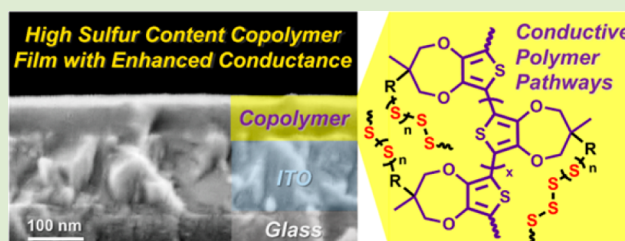
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## S Supporting Information

**ABSTRACT:** The synthesis of polymeric materials using elemental sulfur ( $S_8$ ) as the chemical feedstock has recently been developed using a process termed inverse vulcanization. The preparation of chemically stable sulfur copolymers was previously prepared by the inverse vulcanization of  $S_8$  and 1,3-diisopropenylbenzene (DIB); however, the development of synthetic methods to introduce new chemical functionality into this novel class of polymers remains an important challenge. In this report the introduction of polythiophene segments into poly(sulfur-random-1,3-diisopropenylbenzene) is achieved by the inverse vulcanization of  $S_8$  with a styrenic functional 3,4-propylenedioxythiophene (ProDOT-Sty) and DIB, followed by electropolymerization of ProDOT side chains. This methodology demonstrates for the first time a facile approach to introduce new functionality into sulfur and high sulfur content polymers, while specifically enhancing the charge conductivity of these intrinsically highly resistive materials.



The direct use of elemental sulfur as a feedstock for the preparation of high sulfur content copolymers is an attractive route to a unique class of materials exhibiting intriguing electrochemical and optical properties for lithium–sulfur (Li–S) batteries,<sup>1–5</sup> infrared optics,<sup>6</sup> and nanomaterials.<sup>7–9</sup> We recently developed a polymerization methodology termed *inverse vulcanization* where molten elemental sulfur is employed as both a comonomer and the solvent in a facile route to polymeric materials with a high content of sulfur.<sup>1</sup> Our initial reports on inverse vulcanization have demonstrated that the intrinsic chemical instability of polymeric sulfur,<sup>10</sup> along with its poor processing characteristics,<sup>11</sup> can be circumvented by copolymerization of  $S_8$  with 1,3-diisopropenylbenzene (DIB) yielding poly(sulfur-random-1,3-diisopropenylbenzene) (poly(*S-r*-DIB)) to form chemically stable and processable materials. Synthetic accessibility to these very high sulfur content copolymers enabled the application of these materials in high refractive index IR optics<sup>6</sup> and as active cathode materials in Li–S batteries.<sup>2,3</sup>

Despite the advantages afforded by inverse vulcanization, numerous synthetic challenges remain which preclude optimal performance of sulfur and sulfur-based copolymers in target applications such as Li–S batteries. The extreme resistivity of sulfur (ca.  $10^{15} \Omega\cdot\text{m}$ )<sup>12</sup> is a principal limitation in fully exploiting its exceptional capacity versus lithium in electrochemical devices. The highly resistive nature of  $S_8$  is commonly addressed by blending with conductive carbons or fabrication of nanocomposite materials with conductive inclusions.<sup>13</sup> We aim

to overcome this limitation by expanding the scope of inverse vulcanization to include functional comonomers designed to enhance the electrical properties of the resulting sulfur copolymer. These new materials comprise an intriguing class of electroactive polymers that incorporate both electrochemically active S–S bonds and conductive polythiophene units. Sulfur-based copolymers with both improved electrical and electrochemical properties are also anticipated to also produce improved polymeric cathode materials for Li–S batteries.<sup>14</sup>

Synthetic accessibility to functional 3,4-propylenedioxythiophene (ProDOT) monomers<sup>15</sup> provided an attractive route to prepare electroactive comonomers for inverse vulcanization with sulfur. Such ProDOT derivatives have enabled direct “wiring” of conductive polymer pathways through nanocomposite thin films<sup>16</sup> and been shown to be readily processable.<sup>17</sup> Furthermore, the efficacy of polymers bearing pendant electropolymerizable moieties as precursors to materials with conjugated polymer inclusions has been aptly demonstrated with conventional polymer systems by a number of groups,<sup>18,19</sup> notably Sotzing et al.<sup>20–24</sup> and Advincula et al.<sup>25–27</sup>

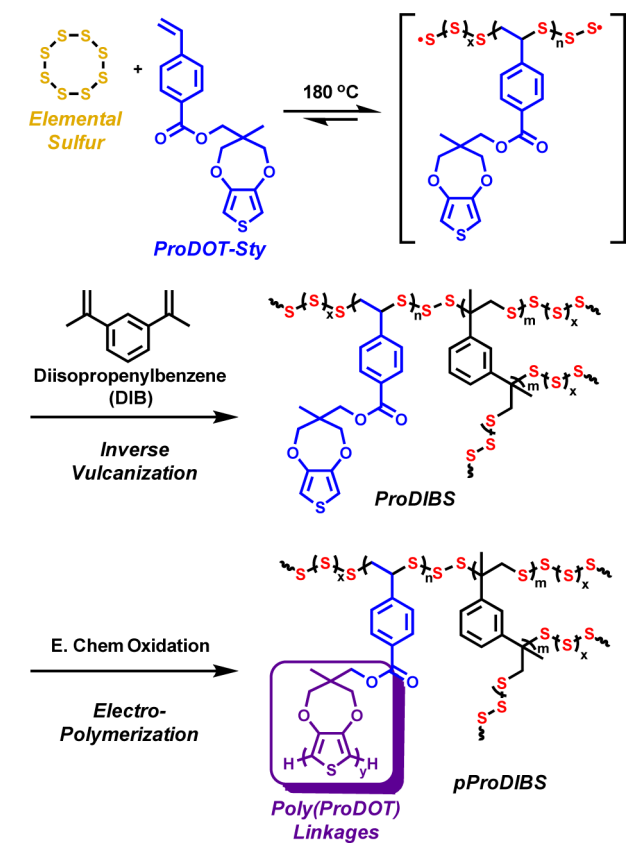
Herein, we report the incorporation of functional styrenic comonomers, specifically with pendant 3,4-alkylenedioxythiophene groups (i.e., ProDOT-Sty, Scheme 1), into high

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**Scheme 1. Synthesis of Sulfur and Thiophene Based Copolymers Using Tandem Inverse Vulcanization and Electropolymerization of S<sub>8</sub> and ProDOT-Sty**



sulfur content copolymers via inverse vulcanization. This key synthetic advance allowed for the installation of electroactive side chain groups that were post-electropolymerized. We previously established the utility of ProDOT-Sty for synthesizing polymeric materials with electroactive polymer components via sequential controlled radical and oxidative polymerization.<sup>28</sup> Furthermore, we found that ProDOT-Sty was miscible with liquid sulfur, enabling direct copolymerization via free radical processes. Using this approach, soluble and chemically stable sulfur copolymer precursors carrying ProDOT side chain groups were solution processed into thin films onto supporting electrode substrates. Post-electropolymerization then enabled preparation of high sulfur content copolymers with conjugated poly(ProDOT) segments. The electrical properties of this novel sulfur copolymer were interrogated with electrochemical impedance spectroscopy (EIS) which revealed a greater than 95% decrease in the charge transfer resistance ( $R_{CT}$ ) upon installation of the conductive polymer pathways.

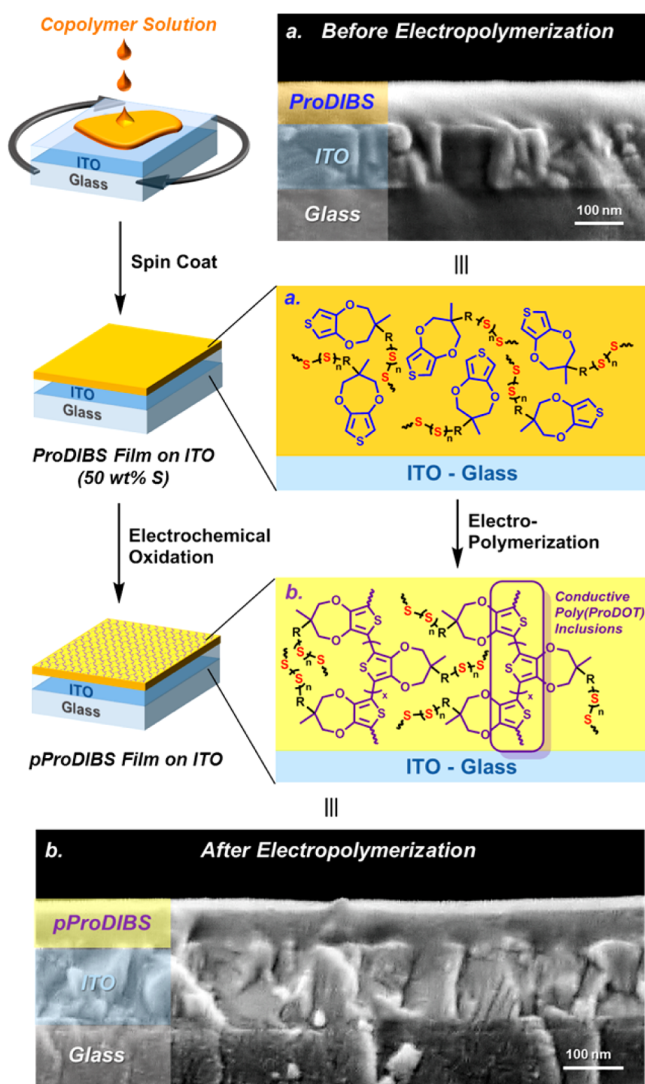
To prepare a sulfur-rich copolymer with electropolymerizable side chains, the inverse vulcanization of S<sub>8</sub> and ProDOT-Sty was conducted in liquid sulfur. The polymerization was thermally initiated using homolytic ring-opening polymerization (ROP) of S<sub>8</sub> to form copolymers of ProDOT-Sty and sulfur which were successively reacted with DIB to yield poly(ProDOT-Sty-random-DIB-random-sulfur) (ProDIBS). ProDIBS was then solution processed into thin films on indium tin oxide (ITO) and subjected to electropolymerization conditions to form interconnected poly(ProDOT) segments in the sulfur copolymer matrix (Scheme 1).

ProDOT-Sty was chosen as the multifunctional monomer to enable postelectropolymerization due to its chemical compatibility with sulfur. In this case, the styrenic moiety readily copolymerized with S<sub>8</sub> using free radical processes while also imparting miscibility in liquid sulfur. The use of ProDOT-Sty was also attractive due to its straightforward synthesis from commercially available starting materials where, briefly, transesterification of 3,4-dimethoxythiophene with tris-(hydroxymethyl)ethane followed by a Stieglich esterification with 4-vinylbenzoic acid yielded the styrenic functional thiophene in large quantities and good yield.<sup>28</sup>

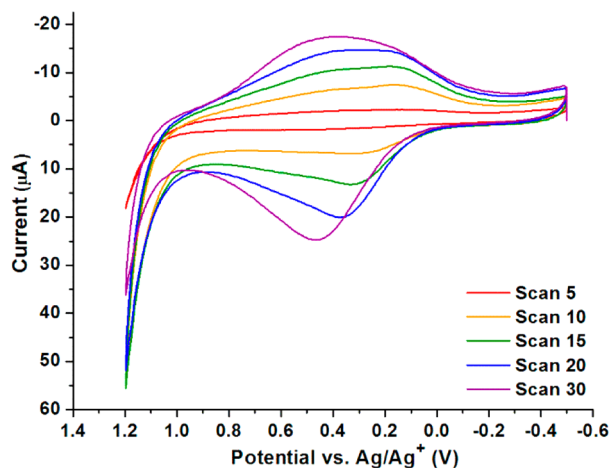
Successful incorporation of ProDOT-Sty into a chemically stable high sulfur content copolymer necessitated a two-step terpolymerization sequence. Initially ProDOT-Sty was reacted with liquid sulfur diradicals to afford linear copolymeric species. However, linear copolymers of sulfur and vinylic comonomers have also been found to suffer a similar propensity for depolymerization at RT as in the case of polymeric sulfur. Hence, a modest amount of DIB was added after the initial poly(ProDOT-Sty-*r*-sulfur) copolymerization, which afforded chemically stable, glassy copolymers. The effective suppression of depolymerization afforded by DIB also introduced branching and presumably intramolecular “loops” formed by termination of sulfur radicals.<sup>1</sup>

<sup>1</sup>H NMR spectroscopy of the ProDIBS terpolymer confirmed the successful copolymerization of elemental sulfur, ProDOT-Sty, and DIB (comonomer feed ratios of 50:40:10 wt %, respectively) with complete conversion of the vinylic groups and retention of the electropolymerizable ProDOT functionality in the inverse vulcanization step (see Supporting Information). Size exclusion chromatography (SEC) in tetrahydrofuran (THF) indicated that terpolymers possessed low molar mass and relatively high polydispersity ( $M_{napparent} = 2000$  g/mol;  $M_w/M_n = 1.75$ ) consistent with earlier results for branched poly(S-*r*-DIB) copolymers.<sup>1</sup>

Thin ProDIBS films on ITO electrodes were fabricated by solution processing for performing electrochemical experiments. Films were spun cast from a copolymer solution in CHCl<sub>3</sub>/toluene onto freshly cleaned ITO-coated glass affording homogeneous films with thickness of 88 nm as determined by scanning electron microscopy (SEM) imaging of a film cross-section (Figure 1a). To enable oxidative polymerization of the ProDOT side chains a three-electrode electrochemical cell was employed with the ProDIBS-coated ITO as the working electrode and a platinum mesh counter electrode referenced to Ag/AgNO<sub>3</sub> (all potentials reported herein are referenced to Ag/Ag<sup>+</sup>). The effective area of the ProDIBS film on ITO (1 cm<sup>2</sup>) was immersed in supporting electrolyte (100 mM TBAFP/acetonitrile), and electrochemical polymerization of pendant ProDOT moieties was carried out with potentiodynamic scanning between -0.5 and 1.2 V (Figure 2). An irreversible oxidation was observed upon scanning positive of 1.0 V corresponding to ProDOT oxidation and subsequent electropolymerization. Following the electropolymerization, the appearance of a redox couple at  $E_{1/2} \approx 0.3$  V was observed and shown to increase in peak current upon successive scans (Figure 2). This behavior is characteristic of oxidative doping and reductive de-doping of a conjugated polymer with the increasing peak current indicative of conjugated polymer growth.<sup>29</sup> After installing conductive polymer pathways in the ProDIBS film cross-sectional SEM confirmed the integrity of the film was retained during electrochemical treatment which



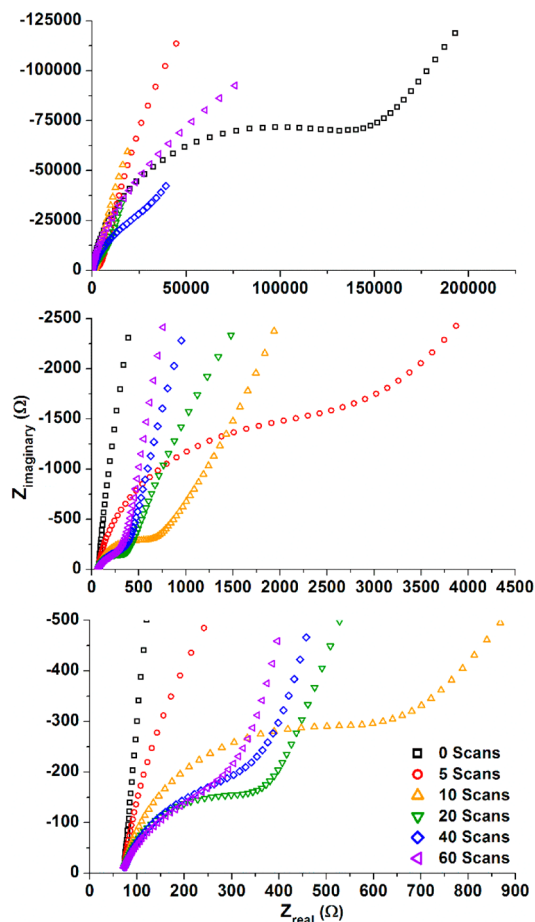
**Figure 1.** Schematic of solution processing and electrochemical oxidation of ProDIBS films with representative cross-sectional SEM images (a) before and (b) after electropolymerization to install conjugated poly(ProDOT) inclusions. Film thickness of the electropolymerized film from SEM was 84 nm.



**Figure 2.** Cyclic voltammogram of potentiodynamic oxidative polymerization scans 5, 10, 15, 20, and 30 of ProDIBS thin film on ITO.

was accompanied by a slight reduction in film thickness (84 nm,  $\sim 4.5\%$ ) consistent with cross-linking of a polymer film.

To interrogate the effect of introducing conjugated polymer moieties on the electrical properties of ProDIBS thin films, electrochemical impedance spectroscopy (EIS) was conducted at varying stages of the electropolymerization (Figure 3).



**Figure 3.** Nyquist plots of impedance spectra of (p)ProDIBS at increasing number of potentiodynamic oxidative polymerization scans with expansions of lower impedance regions (top to bottom). Frequency ranged from 150 kHz to 0.1 Hz.

Impedance spectra of (p)ProDIBS films on ITO were measured between 150 kHz and 0.1 Hz after increasing numbers of oxidative polymerization scans in the three-electrode cell described previously. As conjugated polymers are most conductive in a non-neutral oxidation state, measurements were taken at 0.8 V. Evaluation of EIS data plotted in the complex plane (Figure 3) and interpreted with a modified Randles circuit (Supporting Information, Figure S5) revealed an apparent charge transfer resistance (graphically conveyed as the diameter of the semicircular feature) of 148 k $\Omega$  for pristine ProDIBS. Subsequent to installation of poly(ProDOT) pathways, the impedance response of pProDIBS showed a decrease in  $R_{CT}$  to 2.6 k $\Omega$  after five polymerization scans. Results indicated an even further decrease in  $R_{CT}$  to a minimum of 0.4 k $\Omega$  after 20 or more polymerization scans which is within an order of magnitude of the  $R_{CT}$  reported for poly(dibenzyl-ProDOT) thin films on ITO (96  $\Omega$ )<sup>30</sup> and corresponds to an over 95% decrease in charge transfer resistance in comparison to the pristine ProDIBS. This

observed decrease in  $R_{CT}$  of pProDIBS fundamentally indicates an increase in charge conductance ( $G$ ) as it is simply the inverse of resistance ( $G = R^{-1}$ ). These dramatic effects in the electrochemical charge conductance of pProDIBS films clearly confirmed the presence of conjugated polythiophene segments in the otherwise highly electrically resistive sulfur copolymer matrix.

In conclusion, we report the first example of preparing functional sulfur polymeric materials utilizing the inverse vulcanization methodology, where styrenic ProDOT and polythiophene moieties are incorporated into sulfur-based copolymers. To our knowledge this system is the first report of improving the conductivity of sulfur, or a very high sulfur content polymeric material, using a copolymerization approach. This system points to a new direction in polymer chemistry for the preparation of functional sulfur copolymers and for sulfur materials with enhanced conductivity with potential applications to improve Li–S batteries.

## ■ ASSOCIATED CONTENT

### 📄 Supporting Information

Experimental details for the preparation and characterization of sulfur copolymers. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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### Notes

The authors declare no competing financial interest.

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