Polymer Chemistry

DOI: 10.1002/anie.201309398

Bandgap Engineering through Controlled Oxidation of Polythiophenes**

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Abstract: *The use of Rozen's reagent ($HOF{\cdot}CH_3CN$) to convert polythiophenes to polymers containing thiophene-1,1-dioxide (TDO) is described. The oxidation of polythiophenes can be controlled with this potent, yet orthogonal reagent under mild conditions. The oxidation of poly(3-alkylthiophenes) proceeds at room temperature in a matter of minutes, introducing up to 60% TDO moieties in the polymer backbone. The resulting polymers have a markedly low-lying lowest unoccupied molecular orbital (LUMO), consequently exhibiting a small bandgap. This approach demonstrates that modulating the backbone electronic structure of well-defined polymers, rather than varying the monomers, is an efficient means of tuning the electronic properties of conjugated polymers.*

The continued success of flexible organic electronic materials brings a demand for high-performance conjugated polymers (CPs).[1] This imposes a challenge to develop viable chemical transformations[2] that can be used to fine-tune optoelectronic properties,[3] thus broadening the scope of applications of CPs in various solution-processed devices.[4] Along this vein, there is a need to expand the arsenal of n-type materials. In particular, n-type CPs that have uniform molecular mass distribution and well-defined end-group functionality are highly desirable.[5] With these goals in mind, we aim to develop mild and metal-free postpolymerization modifications to access polymers made up of monomers that cannot be otherwise polymerized.[6]

n-Type semiconducting polymers and other low-bandgap materials are commonly synthesized by polymerizing monomers that possess the functionality desired in the final product.[7] However, what if these monomers cannot be made or polymerized? Or, maybe they can be polymerized, but only by step-growth methods that yield polydisperse materials. In these cases, an alternative approach is to perform post-polymerization modifications to change the electronic properties of CPs synthesized by controlled polymerization techniques, while maintaining end-group functionality. The selection of aromatic monomers for chain-growth polymerization is limited, thus leaving the option of altering the chemical structure of well-defined CPs as an attractive route to develop viable bandgap-engineering strategies. Developing the chemistry of CPs is challenging,[8] but given that poly(alkylthiophenes),[9] a p-type family of semiconductors, are widely studied materials, the exploitation of thiophene chemistry may help meet the demand for new fundamental transformations in polymer chemistry.

The motivation to use the thiophene moiety as a means to drastically change the electronic properties of CPs has its basis at the molecular level. Barbarella et al. demonstrated that thiophene-1,1-dioxide (TDO) stabilizes the lowest unoccupied molecular orbital (LUMO)[10] of conjugated materials to the extent that they can be used as electron acceptors.[11] This is also seen in TDO-containing polymers synthesized by step-growth polymerization.[12] However, it is a challenge to obtain TDO small molecules (and monomers) by conventional oxygen-transfer chemistry, such as oxidations with *meta*-chloroperoxybenzoic acid (mCPBA).[13] In an elegant approach, Rozen's reagent,[13] a stable form of hypofluorous acid with acetonitrile ($HOF{\cdot}CH_3CN$), has been demonstrated to oxidize oligomers up to quaterthiophene.[14] But the challenge remains—the synthesis of monodisperse, telechelic n-type semiconducting materials is underdeveloped.[1c,5a]

Due to the limited range of reactions that can be conducted on sulfur within thiophene-containing polymers, and the fact that TDO cannot be polymerized by chain-growth methods, we describe a strategy to access telechelic TDO-containing polymers: rather than starting with oxidized monomers, we treated polythiophenes with Rozen's reagent to probe the use of this oxidation as a robust and orthogonal chemical transformation. We demonstrate that the electronic properties of CPs can be tuned by varying the degree of oxidation. As model systems, the oxidations of polyalkylthiophenes (polymers **P1**–**P3**) and poly(9,9-dioctyl-9*H*-fluo-

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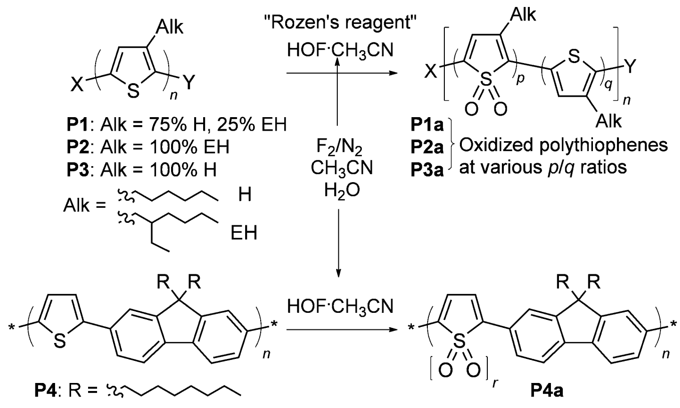
[**] This work was funded by the Center for Re-Defining Photovoltaic Efficiency through Molecule Scale Control, an Energy Frontier Research Center (EFRC) funded by the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences under Award Number de-sc0001085, and in part by NYSTAR. H.L. and A.L.B. acknowledge support by the Office of Naval Research (N000141110636) for UPS measurements, which were carried out as part of the Polymer-Based Materials for Harvesting Solar Energy, an EFRC funded by the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences under Award Number de-sc0001087.

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/anie.201309398.



Scheme 1. Oxidation of thiophene-containing polymers using Rozen's reagent.

rene-*co*-thiophene) **P4** were carried out as shown in Scheme 1.

Taking advantage of Grignard metathesis (GRIM) polymerization, we synthesized polymers **P1**–**P3**, resulting in materials with narrow polydispersity index values (PDIs) in the range of 1.1–1.2 (Scheme 1, details shown in the Supporting Information). We used 2-ethyl-1-hexyl (EH) side chains to improve solubility of **P1** and **P2**.[15] In order to monitor the extent of oxidation, **P1** (6.8 $\mathrm{kg\,mol^{-1}}$, PDI = 1.1) was reacted with various amounts of HOF·CH_3CN (0.25, 0.5, 1, 1.5, 2, and 4 equivalents per thiophene unit). Polymer **P1** contained 4-methoxyphenyl end-groups, where the methoxy protons serve as NMR handles since they are not affected by the oxidation. Upon addition of Rozen's reagent to the polymer in solution, the oxidations were fast, at room temperature, with the solutions changing color from orange to deep purple in a matter of seconds. The reaction mixtures were allowed to stir at room temperature for 45 min to maximize the extent of oxidation. Purification was simple: washing with basic salts, extraction, and trituration (see the Supporting Information for details).

The optical absorption spectra (UV/Vis) showed dramatic changes as the number of equivalents of HOF·CH_3CN was varied (Figure 1 A and Figure S1 in the Supporting Information). The pristine polymer has an optical absorption onset (λ_{onset}) at 540 nm (optical energy gap, $E_g \approx 2.3$ eV). As the number of HOF equivalents per thiophene unit increased, the λ_{onset} red-shifted, indicating a reduced bandgap that saturated at $E_g \approx 1.6$ eV upon addition of 2 or 4 equivalents of HOF. These polymers display optical properties similar to those made by polycondensation of TDO and thiophene monomers.[12c] Infrared spectra of the resultant polymers showed distinctive S=O peaks, indicating oxidation had taken place at the sulfur position (Figure S2 in the Supporting Information).

The extent of oxidation was determined by ^{1}H NMR spectroscopy, which shows that all of the polymers contain a mixture of oxidized and unoxidized units; a maximum of approximately 60 % incorporation of TDO was achieved with 4 equivalents of Rozen's reagent per thiophene monomer. The aromatic peaks located downfield from the chloroform peak (> 7.3 ppm) are characteristic of TDO, and the upfield peaks (< 7.3 ppm) correspond to the unoxidized units (with the exception of the peak at 7.4 ppm, which corresponds to the aromatic end-groups).[12c] These peaks are broader due to the random nature of the polymer oxidation. The methoxy peak at 3.86 ppm served as a point of calibration to calculate the percentage of oxidized thiophene units. As a result, the extent of oxidation can be controlled by the number of HOF·CH_3CN equivalents used in the reactions. It is worth noting that we consider all the polymers to be random copolymers of thiophene and TDO. It is unlikely that any oxidations stopped at the thiophene-1-oxide stage (mono-oxidation) since this is never observed with the HOF·CH_3CN oxidation of oligothiophenes.[14] The thermal decomposition depends on the extent of oxidation. Thermogravimetric analysis (Figure S4 in the Supporting Information) shows that **P1a** containing 60 % TDO is stable below 225 °C, and the least oxidized polymers can

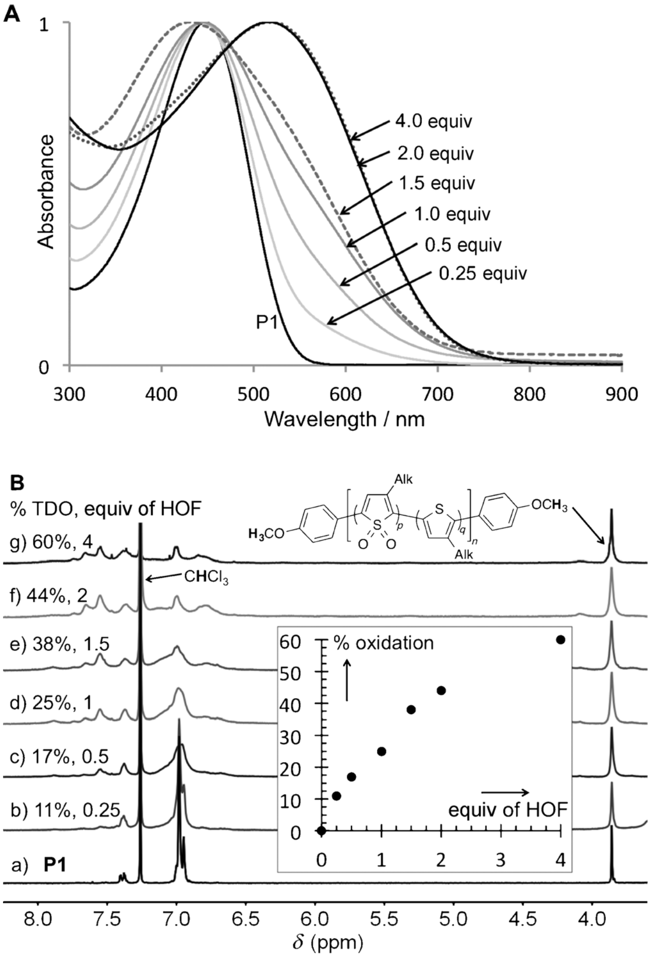


Figure 1. A) Normalized UV/Vis spectra (in chloroform) of **P1** and its oxidized products obtained with increasing equivalents of HOF (0.25 to 4 equiv) per thiophene repeat unit. B) ^{1}H NMR spectra of **P1** and its oxidized products, as the number of equivalents of HOF increased as follows: b) 0.25 equiv, c) 0.5 equiv, d) 1 equiv, e) 1.5 equiv, f) 2 equiv, g) 4 equiv; % TDO indicates the percentage of TDO units in the oxidized polymers. Inset: plot of the number of HOF equivalents vs. percent oxidation (i.e. % TDO units).

be stable at higher temperatures, up to 310 °C for 11 % TDO (Table S1 in the Supporting Information). Adding more than 4 equivalents of oxidizing agent to either **P1** or **P2** does not result in a greater extent of oxidation, but rather leads to unwanted side reactions and partial disruption of conjugation of the polymer backbone, as observed by NMR and UV/Vis spectroscopy (see the Supporting Information). We postulate that the nucleophilicity of thiophene units adjacent to TDOs decreases as the oxidation proceeds, thus eventually reaching a point at which the remaining thiophenes can not be oxidized. Similar trends were observed with **P2**, where the EH branching yielded a more soluble polymer (Figures S8–S12 in the Supporting Information). In the case where the soluble alkyl chain was hexyl (**P3**), the solubility of the oxidized polymer decreased, and the material precipitated out of solution as the oxidation proceeded. These experiments show that this is a powerful reaction for bandgap engineering of well-defined thiophene-containing polymers. In contrast, when we attempted this reaction with the oxidizing agent mCPBA, at most 15 % incorporation of TDO was achieved after a reaction time of 2 days and a tedious workup procedure (Scheme S4 in the Supporting Information).

We also tested the selectivity of this oxidation reaction. If Rozen's reagent can oxidize thiophenes selectively in the presence of other functional groups, this would open up the possibility of developing telechelic and block copolymers from TDO-containing polymers. The hydroxy group is used extensively as a functional handle.[16] Thus we were intrigued as to whether Rozen's reagent could oxidize polythiophenes without also oxidizing hydroxy groups. In order to demonstrate the orthogonality of the oxidation reaction the telechelic polymer **Br-P1-OH** (12.0 kg mol^{-1}, PDI = 1.1) was oxidized with 2 equivalents of HOF. The ^{1}H NMR spectrum before and after oxidation is shown in Figure 2. It is evident that the methylene protons remain after treatment with Rozen's reagent. The peak is broad because the product is a random copolymer of thiophene and TDO, thus there is variability in the electronic environment adjacent to the functional group. We also confirmed that a primary alcohol can survive in a small-molecule model system (Figure S12 in the Supporting Information). Retaining this functional handle opens up the possibility of further functionalizing this polymer.[17]

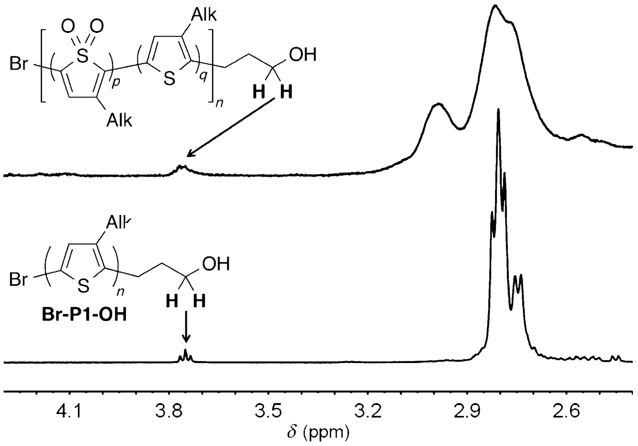


Figure 2. Oxidation of **Br-P1-OH**, and ^{1}H NMR spectra before and after oxidation; the peaks at 3.75 ppm, corresponding to the protons in bold.

As evident in Figure 1, the oxidized polymers show a narrow bandgap, which is attributed to LUMO stabilization of these systems. Thus, we measured the ultraviolet photoelectron spectra (UPS) in thin films of **P1**, **P1a** (44 % TDO), and **P2a** (55 % TDO) on indium tin oxide (ITO) to investigate their energy levels. For clear comparison, the spectra of the secondary electron cutoff (SEC) region were normalized and the Shirley-type background was removed from the measured HOMO region (Figure S19 in the Supporting Information). In the SEC region, the SEC onset of ITO, **P1**, **P1a**, and **P2a** is seen at 16.68, 17.11, 16.67, and 16.75 eV, which implies that the work function (Ψ) is 4.54, 4.11, 4.55, and 4.47 eV, respectively. The difference of the SEC onset between ITO and each polymer corresponds to the magnitude of its interface dipole (Δ).[23] We observe that the HOMO level of **P1** is closer to the Fermi level than the oxidized polymers (at 0.65 eV), while both **P1a** and **P2a** have the same HOMO level at 1.24 eV below the Fermi level (E_F). As a result, the ionization energy (IE) of **P1**, **P1a**, and **P2a** is evaluated as 4.76, 5.79, and 5.71 eV, respectively. The LUMO level was obtained from the onset of absorption of the thin-film UV/Vis spectra, which corresponds to the optical bandgap of 1.94, 1.76, and 1.67 eV of of **P1**, **P1a**, and **P2a**, respectively. The resulting energy levels are summarized in Figure 3. The pristine polythiophene **P1** exhibits conventional p-type electronic characteristics with a low hole injection barrier (Φ_h, 0.65 eV) and a high electron injection barrier (Φ_e, 1.29 eV) for thin films on ITO with its low IE (4.76 eV). The measured IE and optical bandgap of **P1** are in good agreement with those of P3HT, which is a well-known polythiophene polymer.[24] However, the electronic characteristics of **P1a** and **P2a** are significantly different, with low Φ_e value (0.52 eV for **P1a** and 0.43 eV for **P2a**) and high Φ_h (1.24 eV for both **P1a** and **P2a**) for thin films on ITO with their high IE (5.79 eV for **P1a** and 5.71 eV for **P2a**). Collectively, these data clearly show that the oxidation of polythiophenes leads to a low-lying LUMO, effectively lowering the bandgap.

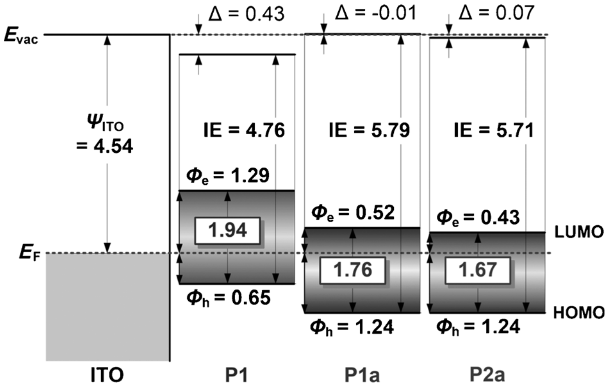


Figure 3. Frontier energy levels obtained from UPS spectra of **P1**, **P1a**, and **P2a**, shown with respect to the work function of ITO.

Figure 3 shows that the electron affinity is enhanced by the oxidation and that the polymer becomes electron-accepting in nature (ca. 4.03 eV, relative to vacuum).[12c,18] One way to probe the electron-accepting properties of this system is to perform a fluorescence-quenching experiment.[1d] The fluorescence of P3HT (electron donor) was monitored as **P1a** (60 % TDO) was added to the sample (Figure 4). We note that the oxidized polymer is weakly fluorescent relative to the pristine polythiophenes (Figure S5 in the Supporting Information). Oxidized **P1a** clearly quenches the fluorescence of P3HT. As the concentration of oxidized **P1a** added to the P3HT increases, the fluorescence drastically decreases. We attribute this to the TDO-containing polymer accepting the excited electron from the P3HT, thus quenching its fluorescence. Additionally, a Stern–Volmer plot yields a K_{SV} value of 11.5 mL mg^{-1} demonstrating the electron acceptor behavior of the TDO-containing polymer (Figure S6 in the Supporting Information). This result implies that these oxidized, well-defined telechelic materials may act as n-type materials.

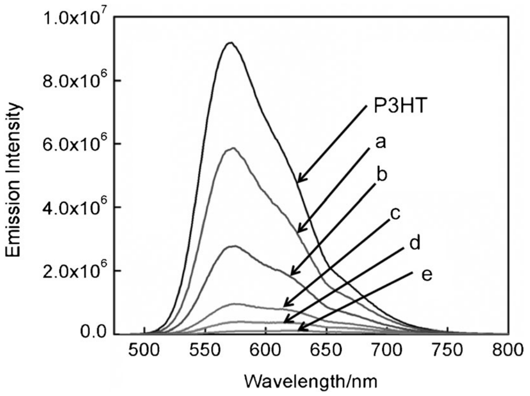


Figure 4. Emission spectra of P3HT and P3HT mixed with various equivalents (X_{eq}) of **P1a** (containing 60 % of TDO); samples were excited at 447 nm in chloroform at a concentration of 10^{-6} M (PL = photoluminescence). X_{eq}: a) 0.5; b) 1; c) 2; d) 3; e) 4.

This oxidation chemistry was also tested on other thiophene-containing copolymers. Poly(thiophene-*co*-fluorene) (**P4**) was chosen as a good candidate for oxidation, since derivatives containing TDO have been previously synthesized, thus allowing us to draw direct comparisons.[19] Polyfluorenes have found applications in light-emitting diodes due to their excellent optoelectronic properties.[20] Furthermore, there have been efforts to both improve the efficiency of OLEDs and tune the color of the polymers by synthesizing fluorene-based copolymers.[21] Examples of poly(fluorene-*co*-thiophene-1,1-dioxide) have been synthesized by Giovanella, Morgado, and their co-workers by a condensation polymerization reaction using the oxidized thiophene monomer.[19,22] Here, we evaluated the post-polymerization modification (Scheme 1). Figure 5 shows the UV/Vis spectra of the pristine **P4** and the oxidized products (**P4a**) obtained using 4 and 6 equivalents of Rozen's reagent per thiophene monomer. There is a clear red-shift of the λ_{onset} from about 490 nm to 550 nm, and the spectrum of **P4a** closely resembles the absorption spectrum of the polymers synthesized by the polycondensation reaction.[19] Furthermore, the IR spectra show the introduction of distinctive S=O peaks after the oxidation reaction (Figure S14 in the Supporting Information). The extent of monomer oxidation, as deduced from the ^{1}H NMR spectrum, shows a maximum of 30 % oxidized units resulting from the reaction of **P4** and at least 6 equivalents of HOF (Figure S15 in the Supporting Information).

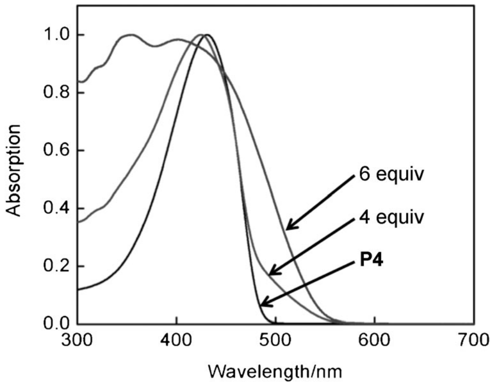


Figure 5. Normalized UV/Vis spectra of **P4** and its oxidized products obtained with increasing equivalents of HOF in chloroform: 4 and 6 equivalents.

In conclusion, we have shown that Rozen's reagent—HOF·CH_3CN—can be used to oxidize thiophene-containing polymers that are synthesized by chain-growth or step-growth polymerizations. This is the first demonstration of this reaction in a postpolymerization strategy. Although poly(3-alkylthiophenes) can only be oxidized up to 60 %, we have shown the many advantages of this route. Starting materials can be prepared by polymerizing commercially available monomers using robust reactions to yield polymers of narrow polydispersity and controlled end-group functionality. The oxidation reaction then takes place in less than an hour at ambient conditions involving facile purification strategies to yield polymers with considerably red-shifted absorption. The oxidation reaction does not require any metal catalysts, which are generally found as contaminants in CPs. These polymers may act as n-type materials given our photoluminescence-quenching results. The reaction has a broad scope, as it can also be applied to copolymers to alter their optoelectronic properties. Lastly, the orthogonality of Rozen's reagent in the presence of hydroxy groups allows further chemistry to take place on these materials, and in particular open up the possibility of preparing block copolymers. We are currently investigating the properties of these materials in various device architectures, in addition to further chemical transformations on the telechelic polymers.

Received: October 28, 2013

Keywords: donor–acceptor systems · n-type materials · polythiophene · Rozen's reagent

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