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Communications to the Editor

Synthesis and Properties of Polydithieno[3,2-*b*:2′,3′-*d*]pyrroles: A Class of Soluble (Chiral) Conjugated Polymers with a Stable Oxidized State

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Regioregular poly(3-alkylthiophene)s (P3ATs) represent a class of soluble, conjugated polymers, which show good conductivities in the doped (oxidized) state.[1] In films or nonsolvents, the polymer strands planarize, causing a red shift, and the coplanar strands aggregate. If chiral side chains are used, the polymer strands pack in a chiral, helical way, and macromolecular chirality is present in the aggregated state.[2]

P3ATs show a very limited stability in their oxidized state. Moreover, it has appeared to be very difficult to dope the material (which is usually performed with I_2 vapor) reproducibly. This greatly limits the possibilities of these materials to be used in electrical applications and to study their properties in the doped state. One possibility to diminish, but not fully exclude, this instability is to create holes in the alkyl phase, in which the counterion can incorporate.[3] Another approach consists of lowering the oxidation potential of the polymers. An excellent example is poly(3,4-ethylenedioxythiophene) (PEDOT), which shows a very high stability in both neutral and oxidized state. Unfortunately, PEDOT is achiral.

Here, we show that poly(N-substituted dithieno[3,2-*b*:2′,3′-*d*]pyrrole)s (PDTPs) are a class of soluble, conjugated polymers with excellent stability in both neutral and oxidized states. They can be considered as fused-ring analogues of P3ATs. Also, a chiral polymer was prepared and its chiral properties were evaluated in both states.

The polymers were prepared by an oxidative coupling in chloroform under an argon atmosphere of N-substituted DTPs[4] using $FeCl_3$ as an oxidant (Scheme 1). This is a promising alternative for electrochemically polymerized PDTPs.[5]

After polymerization, the polymer was precipitated in methanol and washed thoroughly with water to remove inorganic salts and was collected in the oxidized state. The crude material was reduced with hydrazine and extracted first with hexane (to remove the lower-molecular-weight fraction) and then with tetrahydrofuran (THF). Finally, the concentrated THF solution was added dropwise to methanol to obtain the purple polymers in 13−14% yield. GPC analysis in THF toward polystyrene standards revealed $\bar{M}_w$ of 2.3 and 1.9 kg/mol (**2a** and **2b**, respectively) and *D* (polydispersity) of 1.3 and 1.2 (**2a** and **2b**, respectively). These molecular weights are also confirmed by MALDI−TOF experiments, in which $\bar{M}_n$ was determined at 1.7 and 1.3 kg/mol (**2a** and **2b**, respectively). Since a significant amount of insoluble material was formed, we believe that only the lower-molecular-weight fraction was recovered by extraction with THF. This might explain the lower yields and molecular weights. Also, the fact that the use of other oxidants (i.e., $NOBF_4$ and even NBS) results in similar yields and molecular weights supports the hypothesis that this is due to the inherent limited solubility of the polymer and not to the polymerization reaction. Efforts to increase the solubility, and consequently the yields and molecular weights, are ongoing.

The structure of both polymers was confirmed by ^1H and ^{13}C NMR spectroscopy. Taken the symmetric structure of the monomer into account, regioregularity is not an issue in these polymers, provided that no 2,4′-

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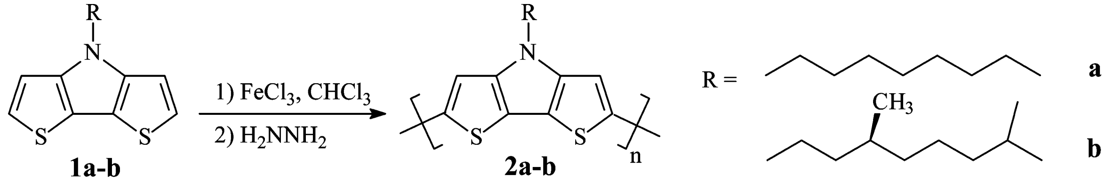
Scheme 1. Synthesis and Structure of the Polymers 2a and 2b



couplings are present. Since only one signal for α-CH_2 is present in both ^1H and ^{13}C NMR spectra, this possibility can be ruled out. However, some small peaks in the aromatic region are present, which can be assigned to end groups.

DSC experiments reveal that both polymers do not show a T_g or a melting peak; instead, they start to degrade around 200 °C.

UV–vis spectra of both polymers in neutral and oxidized state were recorded in THF solution as well as in thin spin-coated films. Therefore, a solution of **2a,b** in chloroform (4 mg/mL) was spin-coated on glass slides at 2000 rpm. After drying, high-quality films were obtained. In the neutral state, λ_{max} of **2a**, which corresponds to the $\pi-\pi^*$ transition, was 512 nm in solution and 525 nm in film; λ_{max} of **2b** was 512 nm in solution and 521 nm in film. The band gaps are 2.1 eV. Compared to their P3ATs counterparts, the λ_{max} are significantly red-shifted in solution and also slightly in film.[1b,6] Although some influence of the electron-donating nitrogen on λ_{max} cannot be excluded, we expect that the red shift be mainly due to a better molecular overlap, indicating a more planar and rigid structure in *both* solution as film. This is in contrast with P3ATs, in which the polymer is completely molecularly dissolved in good solvents, giving rise to a far less planar structure and, consequently, a much lower λ_{max}. In PDTPs, however, the two thiophene units are locked with respect to each other. This restricts rotation and gives rise to a very rigid and planar structure. In solid state, this effect is much less pronounced, since in PDTPs as well as in regioregular P3ATs, the polymer consists of coplanar strands and high conjugation lengths are observed in both materials.

Second, we have oxidized the polymers in solution as well as in films with I_2. Therefore, an I_2 solution was added to the polymer solution; the films, on the other hand, were oxidized by exposure to I_2 vapor for 5 s. Upon doping, the $\pi-\pi^*$ transition shifts to higher energy, and an additional band, corresponding to transitions from lower-lying molecular orbitals to the depopulated HOMO, appears (Figures 1a and 2a).[7] In solution, λ_{max} of oxidized **2a** and **2b** were 733 and 712 nm, respectively; λ_{max} of oxidized films of **2a,b** were 759 and 769 nm, respectively. The band gaps are 1.4 eV. This dramatic change in λ_{max} is also reflected in its color: upon oxidation, the color changes from deep purple to slightly greenish. The films and solutions of both polymers were stable for at least several weeks in neutral as well as oxidized state, as indicated by their UV–vis spectra. This is in contrast with P3ATs, which cannot be oxidized in solution with I_2 and show a very limited stability (few minutes to hours) in the oxidized state in films. This can be correlated to the oxidation potentials of the materials.[1a] Indeed, poly(3-octylthiophene) shows two pseudo-reversible oxidations at E_{pa} = 0.80 and 1.07 V.[1a] In **2b**, on the other hand, these potentials are shifted to 0.50 and 0.81 V (measured with CV in CH_3CN at 50 mV/s vs Ag^+/Ag; a typical voltagram is included as Supporting Information).

We also investigated whether the doping of the polymers was reproducible and reversible. Therefore, I_2, dissolved in THF (3.0×10^{-4} M), was added to a solution of **2b** in THF. Upon oxidation, the peak at 512 nm gradually disappears and a new peak at 712 nm appears. When the polymer was fully oxidized, the system was back reduced by adding careful amounts of hydrazine (6.0×10^{-3} M, THF). As can be seen from Figure 1, the oxidation/reduction could easily be controlled and proved to be reversible, without any visible decomposition. No isosbestic point was observed during oxidation/reduction, indicating that the oxidation is not a single-step process. The same tendency is observed for the reduction. It is worthwhile to note that the difference in absorbencies for the starting solution (upper curve, Figure 1b) and the fully back-reduced

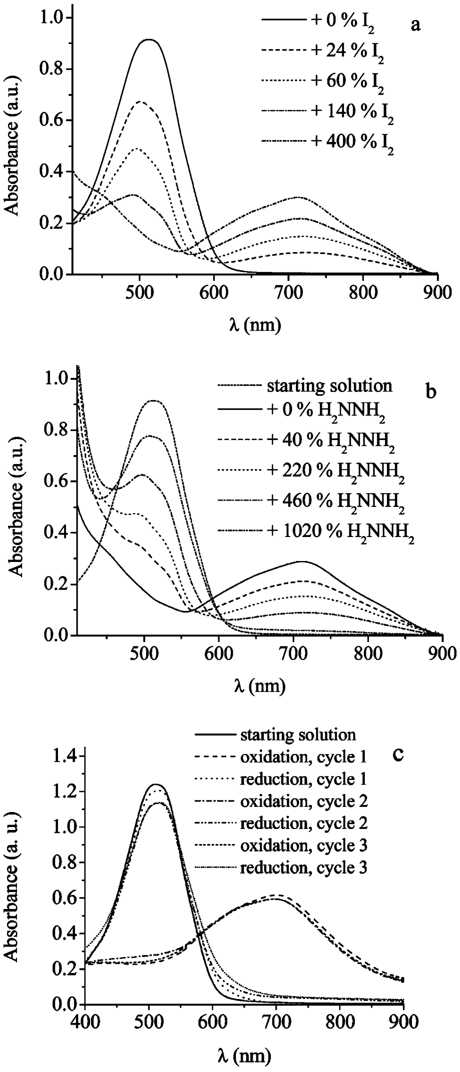


Figure 1. Stepwise oxidation (a) and back-reduction (b) of **2b** in THF (15 mg/L). The added amounts of I_2/hydrazine are mole percentages, calculated toward the repeating units. Chemical switching (c) of **2b** in THF (20.1 mL/L) by oxidation ($NOBF_4$) and reduction (hydrazine).

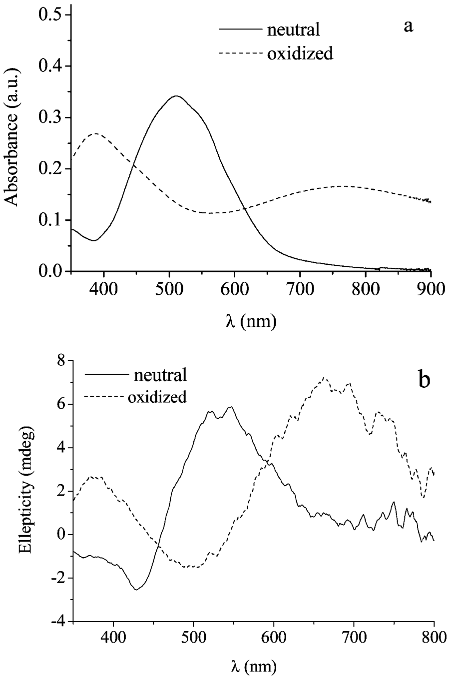


Figure 2. UV−vis (a) and CD (b) spectra of spin-coated films of **2b** in the neutral and oxidized states.

spectrum (second upper curve, Figure 1b) is due to dilution from addition of the I_2 and hydrazine solutions. This cycle of oxidation and back-reduction could be repeated several times without any visual decomposition (Figure 1c). To avoid interference with I_3^- and I_5^- counterions, the oxidation was performed by addition of $NOBF_4$ in this case.

The oxidation process can also be visualized by NMR spectroscopy. Taken the limited solubility of the polymers into account, only ^{1}H NMR spectroscopy was performed. The spectra were taken in CD_2Cl_2. Upon addition of a CD_2Cl_2 solution of I_2, the signal from the aromatic ^{1}H at 7.23 ppm gradually disappears and a new, broader peak at 9.55 ppm arises. No intermediate signal was observed.

We also investigated the (chir)optical properties of a thin film of **2b**. As can been seen in Figure 2a, the neutral polymer film shows some vibronic bands, although this phenomenon is less pronounced than in P3ATs. In the oxidized state, only a broad band, without any vibronic fine structure, is observed. Finally, we examined circular dichroism of the spin-coated films of **2b**. The CD spectra of the polymers showed a great dependence on heat (and time) treatment. The spectra presented in Figure 2b are the spectra of the unannealed films. The spectrum of the oxidized film was taken immediately after oxidation. The neutral film shows a positive bisignate Cotton effect located in the $\pi-\pi^*$ transition band, indicating that the coplanar strands adopt an ordered, chiral conformation.[2] The CD spectrum of the film in the oxidized state is a superposition of two signals: one positive bisignate Cotton effect near 400 nm, located in the $\pi-\pi^*$ transition band, and one positive bisignate Cotton effect in the new band. Since the shape of the CD spectrum does not change, the supramolecular organization in the film essentially remains the same.

It is worthwhile to note that it was also tried to investigate the chiral properties in chloroform solution without and with addition of a nonsolvent, in casu methanol (to form aggregates in solution). In both cases, no optical rotation or CD was observed. This can be ascribed to the fact that no supramolecular packing was present: in the former case, since the polymer is molecularly dissolved in good solvents; in the latter case, since the polymer solution was too dilute to induce any aggregation (as no red shift was observed when methanol was added).

Finally, the conductivity of oxidized polymer films was measured with a four-point probe technique. Therefore, the films were exposed to I_2 vapor for 5 s, which induced complete oxidation, as monitored by UV−vis (band near 525 nm completely disappeared). The conductivity mounted 6 S/cm and was stable for at least 1 week, which is again in contrast with P3ATs and which opens possibilities for future electronic applications.

In conclusion, we have synthesized a new class of conjugated polymers which can be considered as derivatives of P3ATs. The polymers show a unique combination for conjugated polymers of solubility, chirality, and a high stability in both neutral and oxidized states. It was shown by UV−vis and ^{1}H NMR spectroscopy that the oxidation and reduction can be reversibly controlled and that the oxidized state is stable in both film and solution. Finally, we have studied the chiroptical properties of the chiral polymer in neutral and oxidized states.

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Supporting Information Available: Detailed synthetic procedures for the synthesis of polymers **2a,b** and CV of **2b**. This material is available free of charge via the Internet at http://pubs.acs.org.

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