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An Electrically Conducting Polyester That Has Isolated Quatrathiophene Units in the Main Chain

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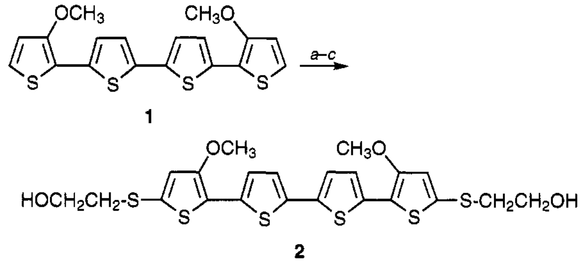
We report a new polymer that has oligothiophene cation radical units in the main chain of a polyester. It is a rare example of an electrically conducting polymer that has alternating conjugated and nonconjugated segments in the main chain. We constructed this polymer to help bridge the intellectual gap between conducting polymers and conducting small molecule crystals. Conducting materials formed from small molecules, e.g., TTF salts, are usually understood in terms of partially oxidized π-stack structures.[1] Conducting polymers like oxidized polythiophene are understood in terms of polarons and bipolarons, i.e., structures confined to the partially oxidized chains.[1,2] Our recent work has utilized oligothiophenes to explore the possibility that π-dimers or π-stacks might also be involved in the conductivity of polymers such as polythiophene. It has been shown that these oxidized oligomers form π-dimers[3] and π-stacks[4] in solution and in the solid state and that the solids are electrically conductive.[4]

The present study follows this research line by producing a conducting polymer that cannot conduct via polarons/bipolarons because it has insulating nonconjugated segments along the main chain. It can, however, conduct via π-stacks formed from the oxidized oligothiophene units that are also part of the main chain. Thus, we have a material that has structural features of both small-molecule conductors and conducting polymers.

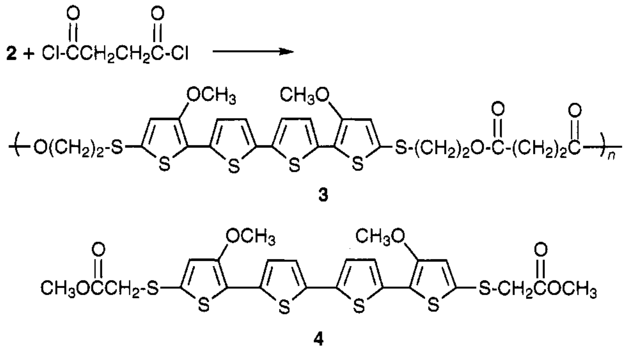
Previous studies of conducting materials composed from polymers with mixed conjugated/nonconjugated main chains include polymers composed of terthiophenes connected with –CHR– groups[5] and "partially eliminated poly(phenylenevinylene)", with statistically scattered unconjugated segments of more or less statistical length,[6] which were prepared, but not oxidized, and poorly understood examples like oxidized polyisoprene.[7] Several reports of conducting oligothiophene–oligosilane copolymers have appeared,[8] but in these the oligosilane units were intended to conjugate with the thiophene sections. Thus, the oxidized polymer reported here appears to be the first authentic example with defined alternating conjugated and aliphatic main chain units that conducts electricity.

Scheme 1



[a] Add 2 equiv of n-BuLi at −78 °C in dry THF, warm to 0 °C for 10 min, cool to −78 °C, add 2 equiv of powder S, warm to 23 °C for 1 h, cool to −78 °C, add 3 equiv of $BrCH_2CH_2OH$, warm to room temperature for 10 h.

Scheme 2



To ensure the stability of the cation radical units, we chose a quatrathiophene substituted with two methoxy groups[4,9] and terminated with electron donor sulfur substituents. We have shown that cation radicals of this type are stable even in water and that they aggregate into π-stacks in water.[4b] The monomer **2** was prepared in one pot, as shown in Scheme 1, starting from the recently reported quatrathiophene **1**.[8] **2** was fully characterized: ^{1}H NMR ($CDCl_3$) (ppm) 7.06 (4H, s, br), 6.95 (2H, s), 3.95 (6H, s), 3.79 (4H, t, J = 7 Hz), 3.00 (4H, t, J = 7 Hz), 2.0 (0.8H, s, br). FAB-HRMS: $C_{22}H_{22}O_4S_6$ 541.9858 (obsd), 541.9842 (calcd). UV–vis: $\lambda_{\max}$ = 430 nm in $CHCl_3$.

The polymer **3** was prepared in 87% yield by condensation of **2** with succinyl chloride in THF/pyridine under argon (Scheme 2). After reaction at room temperature and then 50 °C, the reaction was quenched in methanol

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and the precipitated yellow polymer was filtered, washed, and dried. It had very good solubility in common organic solvents, such as CH_2Cl_2 and $CHCl_3$. ^1H-NMR ($CDCl_3$) (ppm) 6.8−7.1 (6H, m), 4.29 (4H, t, br), 3.93 (6H, s, br), 3.0 (4H, t, br), 2.63 (4H, s, br). IR (cm^{-1}) 3439, 3060, 2932, 1728, 1550, 1450, 1367, 1204, 1150, 1090, 995, 791. UV−vis: λ_{max} = 430 nm in $CHCl_3$. The intrinsic viscosity $[\eta]$ of the polymer in $CHCl_3$ was 0.27 dL g^{-1} at 25 ± 0.01 °C, using a Ubbelohde-type viscometer. GPC (1 wt % of polymer **3** solution in THF passed through 0.45 μm filter before injection; temperature 30 °C; flow rate 1 mL/min) showed a band with the peak corresponding to MW = 13 000 using polystyrene as a reference.

A 0.5 mM (in quatrathiophene units) solution of polymer **3** in CH_2Cl_2 was oxidized with 1.5 equiv of iodine. The color changed immediately. The optical spectra showed peaks at 280 and 370 nm from I_3^-; and at 562, 892, and near 2000 nm from the oxidized quatrathiophene units. The NIR optical conduction band is expected if cation radicals are formed and aggregate into π-stacks.[4] Also expected for such a stack structure was the shift of the $\pi-\pi^*$ bands compared to those bands from unaggregated cation radicals.[3] Since $\mathbf{2}^+$ was not soluble in CH_2Cl_2, $\mathbf{4}^+$ was used as a model cation radical with the same chromophore as the oxidized polymer. $\mathbf{4}^+$ produced electrochemically in CH_2Cl_2 and Et_4NBF_4 is unaggregated as expected and has $\pi-\pi^*$ bands at 702 and 1250 nm. In the more polar CH_3CN, π-dimers $(\mathbf{4}^+)_2$ can be observed in equilibrium with the unaggregated $\mathbf{4}^+$.[3] The π-dimers have $\pi-\pi^*$ bands at 588 and 930 nm. Thus, as expected[3,4,10] and theoretically predicted,[11] π-aggregation shifts the $\pi-\pi^*$ bands to shorter wavelength. The stack structure was further confirmed by performing partial oxidations to give mixed valence stacks with NIR λ_{max} at even longer wavelengths.[12]

The preparation of soluble π-stacked cation radicals in a nonpolar solvent such as CH_2Cl_2 is to our knowledge unprecedented. The formation of such aggregates usually requires water as solvent to disperse the charges built up on the stack.[4,10,13] Here it seems that the propensity of polymers to aggregate enhances the formation of stacks, but further study is in order to explicate the observation.

Films of the neutral polymer were cast onto glass slides from CH_2Cl_2 solution. Four copper wires were attached using carbon paste, and the films were exposed to iodine vapor. The ohmic conductivity increased with time (Figure 1) reaching 0.3 S cm^{-1}. There was no evidence for polarization when the polarity was switched, and there was no depletion over several hours indicating electronic and not ionic conductivity. The film could be redissolved to give the expected solution spectrum and then reduced to provide a solution with the UV−vis and NMR spectra of the starting polymer, indicating no degradation. Films of poorer quality could be formed by casting from CH_2Cl_2 solutions of **3** which had been oxidized with 1.5 equiv of I_2. The conductivity (σ = 0.8 S cm^{-1}) was measured by pressing a pellet of this material. NIR/IR spectra of oxidized polymer were taken as KBr disks or as a film cast on a silicon wafer and then oxidized. They showed the expected broad absorbance throughout the region 1500−3000 nm due to the conduction band and vibrational bands from the ester functionality, especially the carbonyl at 1728 cm^{-1}.

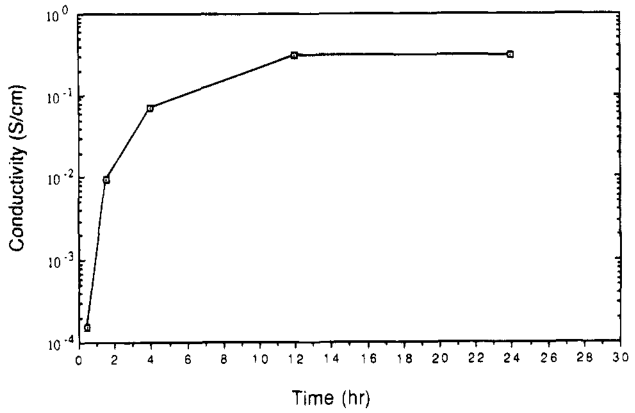

Figure 1. Conductivity of a thin film of **3** exposed to iodine vapor.

In summary, the well characterized polymer **3** can be oxidized to form electrically conductive films and solutions containing π-stacked oligothiophene cation radicals. Stacks in nonpolar solvent are unusual and may be important for applications. The conductivity is of fundamental interest because it cannot involve polarons/bipolarons. It is proposed that the conductivity involves the π-stacks.

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