ORGANIC LETTERS

2002
Vol. 4, No. 4
607−609

Thieno[3,4-*b*]-1,4-oxathiane: An Unsymmetrical Sulfur Analogue of 3,4-Ethylenedioxythiophene (EDOT) as a Building Block for Linear π-Conjugated Systems

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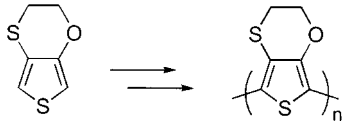
Received December 10, 2001

ABSTRACT



An unsymmetrical analogue of 3,4-ethylenedioxythiophene (EDOT) has been synthesized by transetherification of 3,4-dimethoxythiophene. Electropolymerization leads to a stable electroactive polymer with electrochemical and electronic properties intermediate between those of the two symmetrical parent polymers poly(EDOT) and poly(3,4-ethylenedithiathiophene). Experimental work shows that the 2- and 5-positions possess a different reactivity, thus opening the possibility of synthesizing regioregular oligomers or polymers.

The unique combination of high electrical conductivity, optical transparency, and stability of the doped conducting state of poly(3,4-ethylenedioxythiophene) (PEDOT) has generated a considerable currrent interest in relation to its use in a number of technological applications as, e.g., an antistatic coating, or a finishing layer for ITO electrodes for light-emitting or photovoltaic diodes.[1] On the other hand, the strong electron-donating properties of EDOT (**1**) and its excellent aptitude for electropolymerization have given rise to a rich chemistry focused on the design of hybrid conjugated oligomers and polymers.[1−3] While preventing the formation of the conjugation defects associated with $\alpha-\beta'$ linkages, the presence of two strong electron-donating alkoxy groups at the 3- and 4-positions of the thiophene ring produces a significant decrease of the polymerization potential and a considerable negative shift of the redox potential of the polymer, from 0.70 V for poly(thiophene) (PT) to ca. 0.0 V for PEDOT.[1] It is well known that in the thiophene series, alkylsulfanyl groups are stronger donors than alkoxy ones.[4] Thus, the disulfur analogue of EDOT ethylenedithiathiophene (EDTT) (**3**) shows an oxidation potential 0.18 V lower than that of EDOT (Table 1). However, these stronger electron-releasing effects are not reflected by the electronic properties of the resulting polymer, which exhibits a much higher oxidation potential and band gap than poly(**1**).[5] This shortening of the effective conjugation length can be attributed to the distortion imposed to the π-conjugated backbone by steric interactions among adjacent monomer

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[1] Groenendaal, L. B.; Jonas, F.; Freitag, D.; Pielartzik, H.; Reynolds, J. R. *Adv. Mater.* **2000**, *12*, 481.

[2] (a) McQuade, D. T.; Pullen, A. E.; Swager, T. M. *Chem. Rev.* **2000**, *100*, 2537. (b) Roncali, J. *J. Mater. Chem.* **1999**, *9*, 1875. (c) Mohanakrishnan, A. K.; Hucke, A.; Lyon, A. L.; Lakshmikantham, M. V.; Cava, M. P. *Tetrahedron* **1999**, *55*, 11745.

[3] (a) Raimundo, J.-M.; Blanchard, P.; Frère, P.; Mercier, N.; Ledoux-Rak, I.; Hierle, R.; Roncali, J. *Tetrahedron Lett.* **2001**, *42*, 1507. (b) Raimundo, J.-M.; Blanchard, P.; Brisset, H.; Akoudad, S.; Roncali, J. *Chem. Commun.* **2000**, 939. (c) Turbiez, M.; Frère, P.; Blanchard, P.; Roncali, J. *Tetrahedron Lett.* **2000**, *41*, 5521.

[4] Roncali, J. *Chem. Rev.* **1992**, *92*, 711.

[5] Wang, C.; Schindler, J. L.; Kannewurf, C. R.; Kanatzidis, M. G. *Chem. Mater.* **1995**, *7*, 58.

10.1021/ol017204k CCC: $22.00

Table 1. Electrochemical and Optical Data for Monomers and Polymers

monomer	Epa_{mon} /V[a]	Epa_{pol} /V[a]	λ_{max}/nm[b]
1	1.50	0.20	590
2	1.38	0.40	532
3	1.32	0.90	448

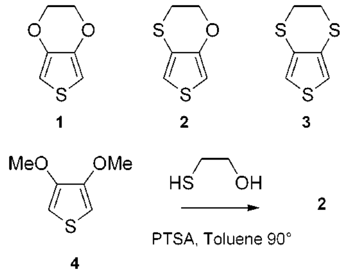
[a] Versus Ag•AgCl, in 0.1 M Bu_4NPF_6/MeCN, Pt working electrode (7.85×10^{-3} cm^2) 100 mV/s. Deposition charge 100 mC/cm^2. [b] Determined by spectroelectrochemistry on films grown on Pt disk electrodes of 5 mm diameter.

units. On the other hand, as shown by recent crystallographic and optical data, intramolecular interactions between the oxygen of the ethylenedioxy group and the sulfur atom of the thiophene ring play a key role in the planarization and rigidification of EDOT-based conjugated systems.[3]

In this context, it was interesting to synthesize the intermediate structure (**2**) in which only one oxygen atom of EDOT is replaced by sulfur in order to analyze the consequences of this modification on the structure and electronic properties of the linear π-conjugated systems based on this new building block.

Thieno[3,4-*b*]-1,4-oxathiane (**2**) was prepared in one step by transetherification of 3,4-dimethoxythiophene (**4**)[6] with 2-mercaptoethanol in the presence of a catalytic amount of *p*-toluenesulfonic acid in refluxing toluene (Scheme 1). This procedure has already been used for the preparation of 3-substituted or 3,4-disubstituted thiophenes.[7] Usual workup followed by distillation under reduced pressure afforded analytically pure **2** in 60% yield as a colorless oil.[8] Compound **3** was synthesized according to a known procedure.[5]

Scheme 1



A single potential scan applied to a 5 mM solution of **2** in 0.10 M Bu_4NPF_6/MeCN shows an irreversible oxidation peak at 1.38 V vs Ag•AgCl (Epa_{mon}). As expected, this value is intermediate between those obtained for EDOT (**1**) and EDTT (**3**) under the same conditions (Table 1).

Application of recurrent potential scans with a positive limit set at the foot of the oxidation wave of the monomer leads to the emergence of a new redox system centered around 0.50 V corresponding to the doping/undoping process of the growing polymer (Figure 1A). The electrochemical and optical properties of poly(**2**) have been investigated with respect to those of films of poly(**1**) and poly(**3**) prepared under the same experimental conditions.

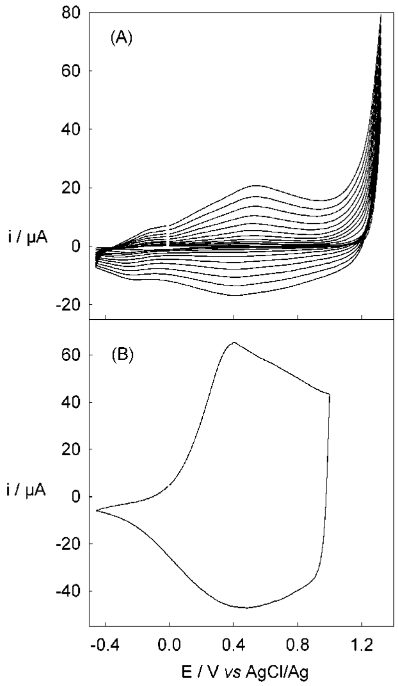


Figure 1. (A) Potentiodynamic electropolymerization of **2** (10 mM) in 0.1 M Bu_4NPF_6/MeCN at 0.1 V/s. (B) CV of poly(**2**) in 0.1 M Bu_4NPF_6/MeCN at 0.1 V/s.

The CV of poly(**2**) in a monomer-free electrolytic medium exhibits a main anodic wave peaking at +0.40 V (Figure 1B). The polymer films are homogeneous and stable and did not exhibit any decrease in electroactivity (as indicated by the amount of charge reversibly exchanged under redox cycling) after 5000 cycles between −0.40 and +1.00 V. The CV data in Table 1 shows that whereas the stepwise replacement of oxygen by sulfur induces a negative shift of Epa_{mon}, the anodic peak associated with the oxidation of the polymer (Epa_{pol}) shifts in the opposite direction increasing from 0.20 V for poly(**1**) to 0.90 V for poly(**3**).

The optical properties of the three polymers have been analyzed by spectroelectrochemistry on films grown on a Pt disk electrode. As could be expected on the basis of CV data, replacement of oxygen by sulfur produces a progressive hypsochromic shift of the absorption maximum from 590

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(6) Gronowitz, S. *Ark. Kemi* **1958**, *12*, 239.

(7) (a) Zotti, G.; Gallazzi, M. C.; Zerbi, G.; Meille, S. V. *Synth. Met.* **1995**, *73*, 217. (b) Faïd, K.; Leclerc, M. *Chem. Commun.* **1996**, 2761. (c) Welsh, D. M.; Kumar, A.; Meijer, E. W.; Reynolds, J. R. *Adv. Mater.* **1999**, *11*, 1379. (d) Wegener, P.; Feldhues, M.; Litterer, H. (Hoechst, A. G.) German Patent, DE 3804522 A1, 1989; *Chem. Abstr.* **1990**, *114*, 98369f. (e) Goldoni, F.; Langeveld-Voss, B. M. W.; Meijer, E. W. *Synth. Commun.* **1998**, *28*, 2237. (f) Krishnamoorthy, K.; Ambade, A. V.; Kanungo, M.; Contractor, A. Q.; Kumar, A. *J. Mater. Chem.* **2001**, *11*, 2909.

(8) Compound **2**: bp 90−95 °C/0.3 mbar. ^1H NMR 500 MHz ($CDCl_3$) δ: 6.73 (d, 1H, $J = 3.6$ Hz), 6.47 (d, 1H, $J = 3.6$ Hz), 4.39 (m, 2H), 3.02 (m, 2H). ^{13}C NMR 125 MHz ($CDCl_3$) δ: 148.5, 115.9, 115.2, 102.2, 66.6, 24.4. EI MS *m/z* (I%): 158 ($M^{+\cdot}$, 100), 130 (23), 85 (40). Anal. calcd (found) for $C_6H_6OS_2$: C, 45.54 (45.29); H, 3.82 (3.73); O, 11.11 (10.84); S, 40.52 (39.66).

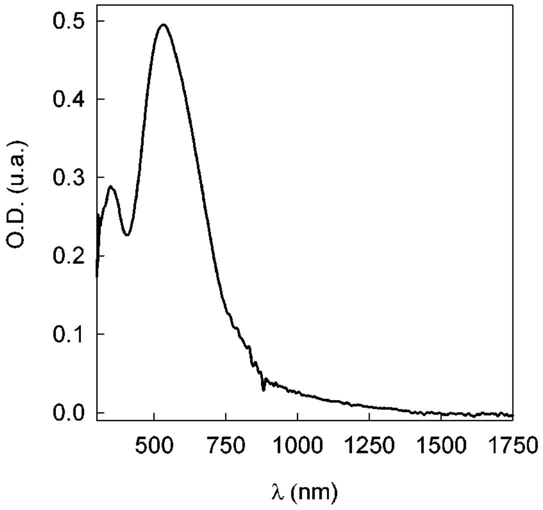


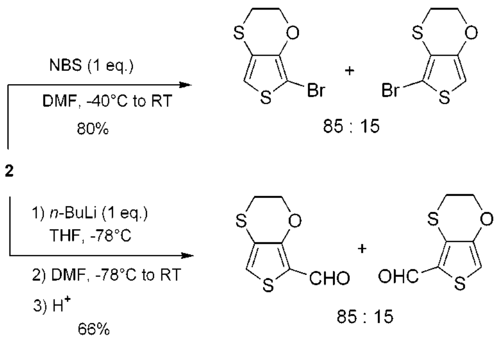
Figure 2. In situ optical spectrum of neutral poly(**2**) on Pt, applied potential = −0.40 V vs Ag·AgCl.

nm for poly(**1**) to 532 and 448 nm for poly(**2**) (Figure 2) and poly(**3**), respectively, indicating a parallel increase of the band gap.

These two series of results show that replacement of oxygen by sulfur in the monomer structure results in a progressive increase of steric interactions between adjacent units of the π-conjugated polymer backbone. These interactions produce a departure from planarity that restricts the extent of the effective conjugation length. On the other hand, the data in Table 1 also show that replacement of only one oxygen atom allows the limitation of the steric crowding and, hence, the resulting distortion of the π-conjugated PT backbone. Furthermore, with the probable regiorandom structure of poly(**2**) taken into account, it may be anticipated, as suggested by CPK models, that a regioregular polymer could exhibit a lower band gap.

On the basis of the already discussed differences in the electronic effects of alkoxy and alkylsulfanyl groups, the dissymmetry introduced in the electronic structure of compound **2** could be expected to induce a difference in the reactivity of the 2- and 5-positions. To test this hypothesis, compound **2** has been submitted to two of the basic reactions involved in the synthesis of π-conjugated oligomers, namely, monobromination by NBS and monoformylation via lithiation followed by quenching with *N*,*N*-dimethylformamide and hydrolysis (Scheme 2).

Scheme 2



It is worth noting that, whereas monolithiation of EDOT poses no difficulty, monobromination requires the use of a 2-fold excess of EDOT compared to NBS in order to avoid the formation of a 2,5-dibromo derivative.[9] In contrast, reaction of **2** with 1 equiv of NBS produces 80% of the monobromo compound and less than 3% of the dibromo derivative. On the other hand, ^{1}H and ^{13}C NMR correlation studies revealed that for both bromination and lithiation, the regioisomer substituted at the 5-position of compound **2** was formed preferentially in an 85:15 ratio.[10] In addition, it was also possible to improve this regioselectivity up to 97:3 in the case of a monoiodination reaction by using I_2 (1 equiv) in the presence of $Hg(OAc)_2$.[11]

On the basis of these preliminary results, the synthesis of regioregular oligomers of **2** is now in progress and will be reported in future publications.

Acknowledgment. The authors thank the SCAS of the University of Angers for analytical characterizations. Financial support was provided by the CNRS for a research studentship to A.C.

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(9) Belletête, M.; Beaupré, S.; Bouchard, J.; Blondin, P.; Leclerc, M.; Durocher, G. *J. Phys. Chem. B* **2000**, *104*, 9118.

(10) 2-Formyl-3,4-(1-oxa-4-thiabutane-1,4-diyl)thiophene: ^{1}H NMR 500 MHz ($CDCl_3$) δ: 9.96 (s, 1H), 7.15 (s, 1H), 4.56 (m, 2H), 3.07 (m, 2H). 5-Formyl-3,4-(1-oxa-4-thiabutane-1,4-diyl)thiophene: ^{1}H NMR 500 MHz ($CDCl_3$) δ: 9.70 (s, 1H), 6.91 (s, 1H), 4.42 (m, 2H), 3.07 (m, 2H). 2-Bromo-3,4-(1-oxa-4-thiabutane-1,4-diyl)thiophene: ^{1}H NMR 500 MHz ($CDCl_3$) δ: 6.77 (s, 1H), 4.46 (m, 2H), 3.04 (m, 2H). 5-Bromo-3,4-(1-oxa-4-thiabutane-1,4-diyl)thiophene: ^{1}H NMR 500 MHz ($CDCl_3$) δ: 6.43 (s, 1H), 4.38 (m, 2H), 3.04 (m, 2H).

(11) 2-Iodo-3,4-(1-oxa-4-thiabutane-1,4-diyl)thiophene: ^{1}H NMR 500 MHz ($CDCl_3$) δ: 6.99 (s, 1H), 4.47 (m, 2H), 3.02 (m, 2H).