ORGANIC LETTERS

2004
Vol. 6, No. 19
3381−3384

New Regiosymmetrical Dioxopyrrolo- and Dihydropyrrolo-Functionalized Polythiophenes

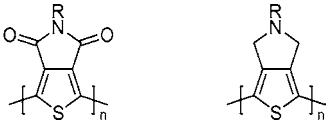
Christian B. Nielsen[†] **and Thomas Bjørnholm***

Nano-Science Center, University of Copenhagen, Universitetsparken 5,
DK-2100 Copenhagen, Denmark

tb@nano.ku.dk

Received July 13, 2004

ABSTRACT



We present the synthesis of two N-alkylated poly(dioxopyrrolothiophene)s and two N-alkylated poly(dihydropyrrolothiophene)s with potential application in the field of conducting polymers. The polymers are synthesized from the corresponding 2,5-dibromothiophenes by an Ullmann-type polymerization and a Stille-type polymerization, respectively. The two N-alkylated poly(dihydropyrrolothiophene)s are the first examples of amino-functionalized polythiophenes built from regiosymmetrical thiophene monomers.

Polythiophenes appear as one of the most important classes of π-conjugated polymers, primarily because they meet the essential requirements of solubility and processibility and a wide variety of functionalities can be incorporated through substituent modifications.[1] The early work in this field dealt primarily with unsymmetrical thiophene units substituted in the 3-position, and pioneering work by McCullough and others[2,3] has clearly shown that control of regiochemistry is decisive for the conductive properties of polythiophene thin films.[4,5] The discovery of the symmetrical poly(3,4-ethylenedioxythiophene) (PEDOT) as a new modified polythiophene with a high chemical stability, and a high electrical conductivity in the doped form, launched numerous investigations into the development of new regiosymmetrical thiophene-based polymer systems; these investigations primarily focused on systems closely related to PEDOT.[6−8]

In an effort to identify new systems that encompass the advantage of symmetrical thiophene units as well as the possibility of grafting solubilizing chains onto the polymer without disrupting the symmetry we have studied new symmetrical members of the polythiophene family; the approach has been to fuse a five-membered ring with a trivalent central atom (i.e., B, N, or P) to the thiophene unit.

This strategy has resulted in the synthesis and characterization of two new regiosymmetrical poly(dihydropyrrolothiophene)s (PolyDHPTs),[9] which to the best of our knowledge are the first polythiophenes of this type presented in the literature. We furthermore present the synthesis and characterization of the two related regiosymmetrical poly(dioxopyrrolothiophene)s (PolyDOPTs)[10] and for the first time report on electrochemical properties and structural

---

[†] Present address: Department of Chemistry, Imperial College of Science Technology and Medicine, Exhibition Road, South Kensington, London SW7 2AZ, UK. E-mail address: c.nielsen@imperial.ac.uk.

(1) *Handbook of Conducting Polymers*, 2nd ed.; Skotheim, T. A., Elsenbaumer, R. L., Reynolds, J. R., Eds.; Marcel Dekker: New York, 1998.

(2) McCullough, R. D.; Lowe, R. D. *J. Chem. Soc., Chem. Commun.* **1992**, *1992*, 70.

(3) Chen, T.-A.; Rieke, R. D. *J. Am. Chem. Soc.* **1992**, *114*, 10087.

(4) McCullough, R. D. *Adv. Mater.* **1998**, *10*, 93.

(5) Sirringhaus, H.; Brown, P. J.; Friend, R. H.; Nielsen, M. M.; Bechgaard, K.; Langeveld-Voss, B. M. W.; Spiering, A. J. H.; Janssen, R. A. J.; Meijer, E. W.; Herwig, P.; de Leeuw, D. M. *Nature* **1999**, *401*, 685.

(6) Jonas, F.; Schrader, L. *Synth. Met.* **1991**, *41−43*, 831.

(7) Groenendaal, L.; Zotti, G.; Jonas, F. *Synth. Met.* **2001**, *118*, 105.

(8) Groenendaal, L.; Jonas, F.; Freitag, D.; Pielartzik, H.; Reynolds, J. R. *Adv. Mater.* **2000**, *12*, 481.

(9) IUPAC nomenclature: 5,6-dihydro-4*H*-thieno[3,4-*c*]pyrrole.

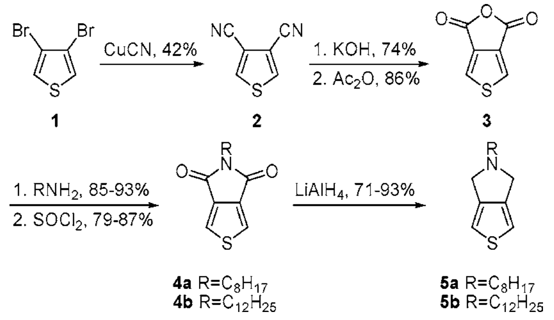
(10) IUPAC nomenclature: thieno[3,4-*c*]pyrrole-4,6-dione.

10.1021/ol048659n CCC: $27.50

characteristics obtained from X-ray diffraction for this newly discovered type of polymer.[11]

The thiophene monomers were synthesized as depicted in Scheme 1. 3,4-Dibromothiophene (**1**) was converted to 3,4-dicyanothiophene (**2**) by a Rosenmund−von Braun reaction with cuprous cyanide,[12] whereupon the cyclic anhydride (**3**) was obtained via the dicarboxylic acid through basic hydrolysis and subsequent ring closure.[13,14] Conversion of **3** to the unsubstituted cyclic imide (DOPT-H) surprisingly proved to be very troublesome, and instead the N-alkylated imides (**4a**,**b**, DOPT-alkyl) were synthesized via the 4-carbamoylthiophene-3-carboxylic acid; the second amide bond did not form spontaneously, and this step was hence forced with thionyl chloride afterward. The N-alkylated imides (**4a**,**b**) were easily reduced to the corresponding N-alkylated amines (**5a**,**b**, DHPT-alkyl) with lithium aluminum hydride.

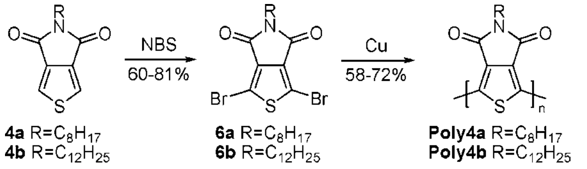
Scheme 1. Synthesis of DOPT and DHPT Monomers



Polymerization of the regiosymmetrical monomers (**4a**,**b** and **5a**,**b**) was initially attempted by both electrochemical and chemical oxidation (FeCl$_3$),[15,16] but neither DOPT-alkyl (**4a**,**b**) nor DHPT-alkyl (**5a**,**b**) showed signs of polymerization under these conditions, in the case of DOPT-alkyl (**4a**,**b**) most likely due to an increased oxidation potential because of the electron-withdrawing imide-substituent. For DHPT-alkyl (**5a**,**b**), the explanation could be that oxidation occurs at the nitrogen atom and not at the α-position relative to sulfur; other rationalizations encompass a low reactivity as a consequence of formation of a highly stable radical cation or an unfavorable complexation between iron species and the nitrogen atom.

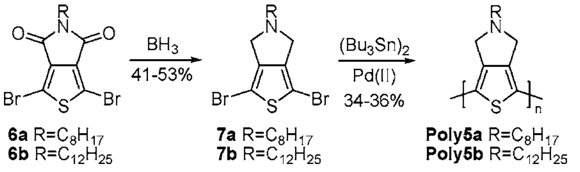
Instead, an Ullmann-type coupling proved to be successful for the polymerization of the DOPT-alkyls (Scheme 2). The DOPT-alkyls (**4a**,**b**) were initially dibrominated under harsh conditions with NBS in trifluoroacetic acid and sulfuric acid to afford **6a**,**b** after which the Ullmann-type polymerization was enforced with freshly activated cupper in DMF at 150 °C to give the PolyDOPT-alkyls (**Poly4a**,**b**) in fairly good yield; both PolyDOPT-alkyls appear as lustrous black solids. Polystyrene equivalent weight average molecular weights as determined from SEC are 2.2 kDa for **Poly4a** (DP 8, PDI 1.33) and 3.3 kDa for **Poly4b** (DP 10, PDI 1.48). ^{1}H NMR spectral end group analysis indicates a degree of polymerization (DP) of 8 for **Poly4a** and a DP of between 7 and 8 for **Poly4b**.

Scheme 2. Synthesis of DOPT Polymers



As illustrated in Scheme 3, a Stille-type coupling led to the successful polymerization of the DHPT-alkyls.

Scheme 3. Synthesis of DHPT Polymers



The dibrominated imides (**6a**,**b**) were reduced to the corresponding dibrominated amines (**7a**,**b**), which subsequently were converted to the PolyDHPT-alkyls (**Poly5a**,**b**) in moderate yields via the in situ-generated tributylstannyl-activated compounds.[17] Molecular weight characterization of **Poly5a** and **Poly5b**, which both appear as lustrous black solids, proved to be difficult. First, no end group protons were visible in the ^{1}H NMR spectra, probably due to preservation of the bromine atoms at the terminal positions. Second, size exclusion chromatograms showed severe tailing effects, indicating that the high-molecular weight fraction elutes in an unexpected way. This observation is evidently supported by the optical characteristics of the eluted main fractions, which have markedly blue-shifted absorption maxima relative to the crude polymer solutions. The very uncertain SEC weight average molecular weights are 1.9 kDa for **Poly5a** (DP 8, PDI 1.45) and 3.1 kDa for **Poly5b** (DP 11, PDI 1.55). The maximum of the UV−vis absorption of **Poly5b** situated at 533 nm (Figure 1) indicates a degree of

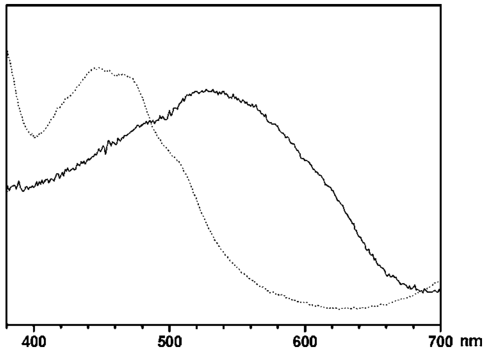


Figure 1. UV−vis absorption spectra of **Poly4b** (dotted line) and **Poly5b** (solid line) in thin films cast from chloroform.

polymerization that definitely exceeds the values obtained from SEC.

Comparison of the optical absorption data for the polymers in chloroform solution and as films cast from chloroform solution reveals a significant red-shift in all cases (Table 1).

Table 1. Summarized Characteristics of **Poly4a**,**b** and **Poly5a**,**b**

	Poly4a	Poly4b	Poly5a	poly5b
λ_{max} solution	424 nm	434 nm	494 nm	516 nm
λ_{max} film	460 nm	473 nm	508 nm	533 nm
ϵ_{max} [M^{-1} cm^{-1}]	4.2 10^3	7.0 10^3	1.7 10^3	2.5 10^3
film thickness[a]	60 nm	40 nm	60 nm	30 nm
E_{pa} †	1.39 V	1.56 V	1.39 V	1.67 V
E_{pc} [b]	−1.55 V	−1.65 V		
$d_{lamella}$	23.6 Å	27.8 Å	23.9 Å	
d_{stack}	3.45 Å	3.54 Å	4.5 Å	4.5 Å
density [g cm^{-3}][c]	1.42	1.43	0.96	

[a] Film thicknesses were estimated from Lambert−Beer's law using the absorbance at λ_{max}, the extinction coefficient in solution, and the calculated density. [b] Electrochemical experiments were conducted under nitrogen in dry acetonitrile using tetrabutylammonium tetrafluoroborate (0.10 M) as the supporting electrolyte, an ITO glass plate as the working electrode, a coiled platinum wire as the auxiliary electrode, and an Ag/AgCl electrode as the reference system. [c] Densities were calculated from the XRD data using d_{stack}, $d_{lamella}$, and 7.6 Å as the three dimensions in a unit cell containing a dimeric thiophene unit.

This typical behavior for polythiophenes indicates that the degree of conjugation is increased in the dense thin films compared to solution due to ordering effects in the solid state. The red-shift, however, is not as significant as that seen for regioregular poly(3-alkylthiophene)s, indicating a certain degree of preaggregation in solution for **Poly4a**,**b** and **Poly5a**,**b**.[18] Corroborating the SEC data and the optical absorption maxima, we note that the extinction coefficient per monomer increases with increasing length of the alkyl chain for both presented polythiophene systems, which clearly indicates that the grafting of long dodecyl chains onto the monomers provides a higher degree of polymerization than what is observed with the shorter octyl substituents.

X-ray powder diffraction gives diffraction patterns typical for polythiophenes encompassing two to three rather broad peaks. At low angles, one typically observes a peak corresponding to the lamellar repeat distance between polymers. At higher angles, one observes one to two peaks corresponding to alkyl chain packing and/or π-stacking, respectively; these data are presented in Table 1.

Typical electrochemical behavior for polythiophene thin films is revealed by characterization of solution cast thin films of the PolyDOPTs (**Poly4a**,**b**) and PolyDHPTs (**Poly5a**,**b**) on conducting indium tin oxide (ITO) glass plates (Table 1). The oxidative behavior of **Poly4a**,**b** and **Poly5a**,**b** is very similar to poly(3-alkylthiophene)s, whereas thin films of **Poly4a**,**b** upon electrochemical reduction show a distinct reduction wave, indicating that PolyDOPTs could be potential carriers of negative charges.

Figure 2 illustrates a schematic packing motif, typical of polythiophenes,[19,20] which agrees well with all the observed data. In particular, the model shows that efficient π-stacking is only possible for the PolyDOPTs (**Poly4a**,**b**, Figure 2A), while the sp^3-hybridized carbon atoms in the five-membered ring seriously interfere with π-stacking, as evident by the absence of a diffraction peak corresponding to π-stacking for the PolyDHPTs (**Poly5a**,**b**, Figure 2B).

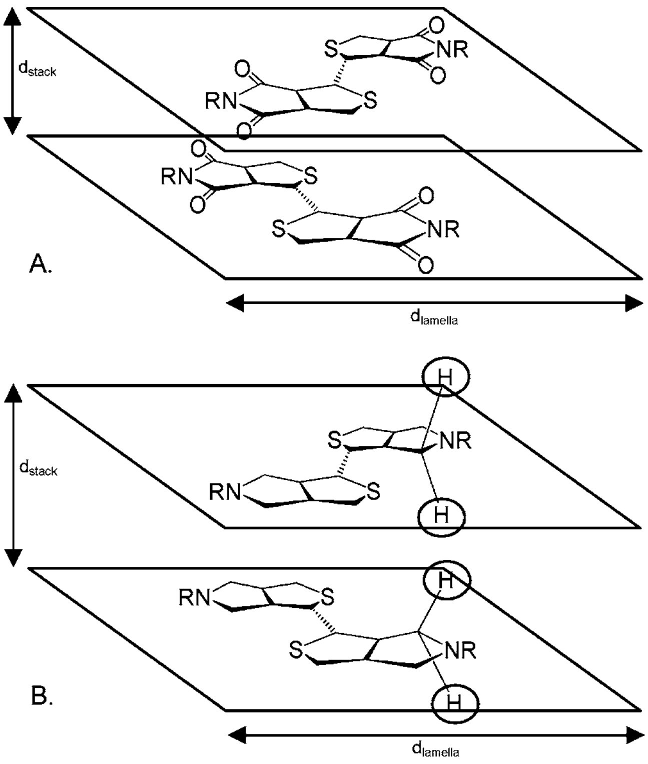


Figure 2. Schematic model illustrating the two packing motifs for PolyDOPTs (A) and PolyDHPTs (B).

Pomerantz has reported on ab initio calculations concluding that the most stable conformation of the DOPT-methyl dimer is the coplanar structure due to favorable electrostatic oxygen−sulfur interactions, while the most stable conformation of the DHPT−methyl dimer is characterized by a

---

(11) Pomerantz, M.; Amarasekara, A. S. *Synth. Met.* **2003**, *135−136*, 257.

(12) MacDowell, D. W. H.; Wisowaty, J. C. *J. Org. Chem.* **1972**, *37*, 1712.

(13) Muenster, P.; Freund, W.; Steiner, G.; Walter, H.; Westphalen, K. O.; Gerber, M. European Patent 407793, 1992.

(14) Sicé, J. *J. Org. Chem.* **1954**, *19*, 70.

(15) Roncali, J. *Chem. Rev.* **1992**, *92*, 711.

(16) Yoshino, K.; Hayashi, S.; Sugimoto, R. *Jpn. J. Appl. Phys. 2* **1984**, *23*, L899.

(17) Xu, J. M.; Ng, S. C.; Chan, H. S. O. *Tetrahedron Lett.* **2001**, *42*, 5327.

(18) Bjørnholm, T.; Greve, D. R.; Geisler, T.; Petersen, J. C.; Jayaraman, M.; McCullough, R. D. *Adv. Mater.* **1996**, *8*, 920.

(19) Prosa, T. J.; Winokur, M.; Moulton, J.; Smith, P.; Heeger, A. J. *Macromolecules* **1992**, *25*, 4364.

(20) Reitzel, N.; Greve, D. R.; Kjaer, K.; Howes, P. B.; Jayaraman, M.; Savoy, S.; McCullough, R. D.; McDewitt, J. T.; Bjørnholm, T. *J. Am. Chem. Soc.* **2000**, *122*, 5788.

dihedral angle of 36° between the two thiophene units, a twist caused by unfavorable interactions between sulfur and adjacent methylene groups.[21] A good consistency with our results is found with respect to the coplanar orientation of PolyDOPTs (Figure 2A); also, due to the increased π-stacking distance for the PolyDHPTs (Figure 2B), our results allow a certain degree of backbone twisting for this system as indicated by Pomerantz, although the X-ray data does not provide evidence for this hypothesis.

Preliminary measurements of electrical conductivity of iodine-doped thin films of the synthesized polymers give low values compared to those observed for poly(3-alkylthiophene)s. Work is in progress in our laboratories to further investigate the conductive, optical, and supramolecular properties of these polymers.

In summary, we have reported the synthesis and gross structural, optical, and electrochemical properties of two new members of the polythiophene family.

Acknowledgment. This work was supported by a research grant under The Danish Materials Research Program (MUP). Fruitful discussions with Professor R. D. McCullough are gratefully acknowledged.

Supporting Information Available: Experimental procedures and full characterization for compounds **1**−**7**, along with experimental procedures and ^{1}H NMR spectral data, powder X-ray diffractograms, and absorption spectra for polymers **Poly4a**,**b** and **Poly5a**,**b**. This material is available free of charge via the Internet at http://pubs.acs.org.

OL048659N

---

[21] Pomerantz, M. *Tetrahedron Lett.* **2003**, *44*, 1563.