

CHEMISTRY OF MATERIALS

VOLUME 17, NUMBER 13

JUNE 28, 2005

© Copyright 2005 by the American Chemical Society

Communications

Highly Conductive, Regioregular Alkoxy-Functionalized Polythiophenes: A New Class of Stable, Low Band Gap Materials

Elena E. Sheina, Sonya M. Khersonsky, Edward G. Jones, and Richard D. McCullough*

Department of Chemistry, Carnegie Mellon University,
Pittsburgh, Pennsylvania 15213

Received January 13, 2005
Revised Manuscript Received May 9, 2005

Electrically conductive polymers are entering a new era as devices and applications are beginning to enter the marketplace. Decades of revolutionary research has not only created exciting new science but also led to new plastic electronics.¹ Due to very high electrical conductivities, regioregular polythiophenes (rr-PTs) are being used in plastic photovoltaics, as the hole transport layer in OLEDs, in field effect transistors, and as conductive components in new coatings and bulk plastics.^{2,3} Alkoxy-substituted analogues

of PTs exhibit even more desirable properties, such as reduced band gaps, low oxidation potentials, and a highly stable conducting state.^{4–6} However, these materials possess rather low conductivities (1 S/cm) and are not very stable. A major breakthrough in the development of the commercially viable conductive polymers was the synthesis of poly(3,4-ethylenedioxythiophene) (PEDOT), which exhibited high stabilities in the oxidized state and conductivities up to 600 S/cm.^{7–9} Unfortunately, this material is generally only processible as a colloidal suspension in water and produces fairly low conductivities (10–50 S/cm), thereby limiting its usefulness in many commercial applications. Nevertheless, since the discovery of PEDOT in 1989, dioxythiophene chemistry has developed exponentially and has rapidly

* To whom correspondence should be addressed. E-mail: rm5g@andrew.cmu.edu.

- (1) (a) Chiang, C. K.; Fincher, C. R., Jr.; Park, Y. W.; Heeger, A. J.; Shirakawa, H.; Louis, E. J.; Gau, S. C.; MacDiarmid, A. G. *Phys. Rev. Lett.* **1977**, *39*, 1098. (b) Burroughes, J. H.; Bradley, D. D. C.; Brown, A. R.; Marks, R. N.; Mackay, K.; Friend, R. H.; Burns, P. L.; Holmes, A. B. *Nature (London)* **1990**, *347*, 539. (c) Gelinck, G. H.; Geuns, T. C. T.; de Leeuw, D. M. *Appl. Phys. Lett.* **2000**, *77*, 1487. (d) Kline, R. J.; McGehee, M. D.; Kadnikova, E. N.; Liu, J.; Frechet, J. M. J. *Adv. Mater.* **2003**, *15*, 1519. (e) Sirringhaus, H.; Tessler, N.; Friend, R. H. *Science (Washington, D.C.)* **1998**, *280*, 1741. (f) Drury, C. J.; Mutsaers, C. M. J.; Hart, C. M.; Matters, M.; de Leeuw, D. M. *Appl. Phys. Lett.* **1998**, *73*, 108. (g) Dodabalapur, A.; Bao, Z.; Makhija, A.; Laquindanum, J. G.; Raju, V. R.; Feng, Y.; Katz, H. E.; Rogers, J. *Appl. Phys. Lett.* **1998**, *73*, 142.
- (2) (a) McCullough, R. D. *Adv. Mater.* **1998**, *10*, 93. (b) Skotheim, T. A.; Elsenbaumer, R. L.; Reynolds, J. R. *Handbook of Conducting Polymers*, 2nd ed.; Marcel Dekker: New York, 1998; p 225.

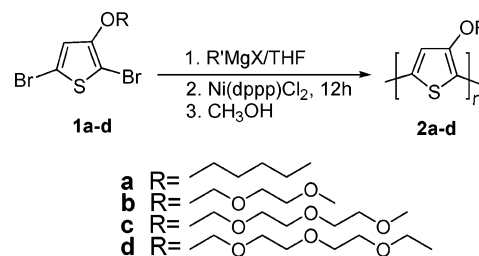
- (3) (a) McCullough, R. D.; Lowe, R. D. *J. Chem. Soc., Chem. Commun.* **1992**, 70. (b) McCullough, R. D.; Lowe, R. D.; Jayaraman, M.; Anderson, D. L. *J. Org. Chem.* **1993**, *58*, 904. (c) McCullough, R. D.; Tristram-Nagle, S.; Williams, S. P.; Lowe, R. D.; Jayaraman, M. *J. Am. Chem. Soc.* **1993**, *115*, 4910. (d) Chen, T. A.; Wu, X.; Rieke, R. D. *J. Am. Chem. Soc.* **1995**, *117*, 233.
- (4) (a) Jen, K. Y.; Eckardt, H.; Jow, T. R.; Shacklette, L. W.; Elsenbaumer, R. L. *J. Chem. Soc., Chem. Commun.* **1988**, 215. (b) Eckardt, H.; Shacklette, L. W.; Jen, K. Y.; Elsenbaumer, R. L. *J. Chem. Phys.* **1989**, *91*, 1303. (c) Van Dort, P. C.; Pickett, J. E.; Blohm, M. L. *Synth. Met.* **1991**, *41*, 2305.
- (5) (a) Leclerc, M.; Daoust, G. *J. Chem. Soc., Chem. Commun.* **1990**, 273. (b) Daoust, G. J.; Leclerc, M. *Macromolecules* **1991**, *24*, 455. (c) Faïd, K.; Cloutier, R.; Leclerc, M. *Macromolecules* **1993**, *26*, 2501.
- (6) Chen, S. An.; Tsai, C. C. *Macromolecules* **1993**, *26*, 2234.
- (7) (a) Bayer AG, Eur. Patent 339 340, 1988. (b) Jonas, F.; Schrader, L. *Synth. Met.* **1991**, *41*, 831. (c) Heywang, G.; Jonas, F. *Adv. Mater.* **1992**, *4*, 116. (d) Dietrich, M.; Heinze, J.; Heywang, G.; Jonas, J. J. *Electroanal. Chem.* **1994**, *369*, 87. (e) Winter, I.; Reece, C.; Hormes, J.; Heywang, G.; Jonas, F. *Chem. Phys.* **1995**, *194*, 207.
- (8) (a) Skotheim, T. A. *Handbook of Conducting Polymers*; Marcel Dekker: New York, 1986. (b) Heuer, H. W.; Wehrmann, R.; Kirchmeyer, S. *Adv. Funct. Mater.* **2002**, *12*, 89. (c) De Paoli, M. A.; Nogueira, A. F.; Machado, D. A.; Longo, C. *Electrochim. Acta* **2001**, *46*, 4243. (d) Groenendaal, L. B.; Zotti, G.; Aubert, P. H.; Waybright, S. M.; Reynolds, J. R. *Adv. Mater.* **2003**, *15*, 855. (e) Scrosati, B. *Applications of Electroactive Polymers*; Chapman & Hall: London, 1994.

become the frontier of PT-based inherently conductive polymers (ICPs). The pioneering work of Reynolds has led to regiosymmetric PXDOTs including the first soluble, very stable dialkylated poly(3,4-propylene dioxythiophenes) (ProDOT-R₂) that exhibit moderate conductivities (e.g., 7 S/cm, for chemically prepared samples) and possess excellent redox and electrochromic properties.¹⁰ Despite these discoveries, generating materials that possess high carrier mobilities and long-term stabilities in the oxidized state and are easily processible remains a great challenge. Here we present the synthesis and unique physical properties for a new class of regioregular 3-alkoxy functionalized polythiophenes that exhibit high electrical conductivities and very good stabilities when doped with iodine vapor followed by exposure to ambient conditions. In addition, we present air doping of the polymers by atmospheric oxygen.

For the first time, a series of soluble structurally regioregular alkoxy-substituted PTs (>98% head-to-tail (HT) couplings) of high molecular weights was synthesized through the Grignard Metathesis (GRIM) method,¹¹ which utilizes a chain-growth nickel complex-initiated cross-coupling reaction.¹² Previously, 3-hexyloxythiophene (HOT, **2a**) and 3-[2-(2-methoxyethoxy)ethoxy]thiophene (MEET, **2b**) monomers were polymerized via an oxidative chemical polymerization with ferric chloride (FeCl₃).⁶ However, the resulting materials were regioregular oligomers of low molecular weight (1387 and 860 for **2a** and **2b**, respectively). Furthermore, higher molecular weight fractions of these polymers were infusible and insoluble solids due to cross-linking via α,β' couplings between thiophene rings.

In this work, dibromoalkoxythiophenes monomers (**1a–d**) were synthesized in 80–90% yields first by copper (I) mediated substitution of 3-bromothiophene,¹³ followed by a modified NBS bromination¹⁴ in THF at cryogenic temperatures. The polymerization involved treatment of **1a–d** with a Grignard reagent R'MgX (e.g., MeMgBr) that resulted in magnesium bromine exchange, generating a mixture of regiochemical Grignard isomers.¹⁴ Investigation of the reaction mechanism employing kinetics revealed that, upon addition of Ni(dppp)Cl₂, the polymers were formed by

Scheme 1. Synthesis of Regioregular Alkoxy-Functionalized Polythiophenes by the Grignard Metathesis (GRIM) Method



first the selective coupling of 2-bromo-5-halomagnesio-3-alkoxy-thiophene followed by 2-halomagnesio-5-bromo-3-alkoxy-thiophene to afford HT-coupled regioregular polymers (**2a–d**) in good yield (e.g., 60–70%) (Scheme 1).¹⁵

The polymerization of **1a** generates PHOT (**2a**) in high yield (>80%). The fraction of **2a** that was soluble in chloroform was a rather low molecular weight ($M_n = 7200$; $M_w/M_n = 1.7$). Polymerization of **1b** yielded PMEET (**2b**) with a relatively high molecular weight ($M_n = 18000$; $M_w/M_n = 1.6$). Since the polymerization proceeded by a chain growth mechanism,¹² polymers of alkoxy-substituted thiophenes of varying molecular weights could be easily synthesized. Moreover, incorporation of several oxygen atoms in a polymer backbone (e.g., **2b–d**) resulted in polymers that were readily soluble in many common organic solvents relative to **2a**¹⁶ and possessed excellent film-forming abilities. As an example of characterization, the ¹H NMR spectra of PMEET (**2b**) revealed only one aromatic resonance with a chemical shift at $\delta = 6.98$ ppm, as expected for a regioregular PT¹⁷ and only four resonances ($\delta = 111.4, 112.9, 132.2, \text{ and } 153.2$ ppm) in the aromatic region in the ¹³C NMR spectrum. The UV–Vis data for PMEET (**2b**) showed a λ_{max} of 602 nm in CHCl₃ solution and λ_{max} of 685 nm ($E_g = 1.41$ eV) in the solid state as drop cast from CHCl₃. As a comparison, the λ_{max} values obtained for electrochemically prepared films of PEDOT were 580–610 nm ($E_g = 1.60$ eV).^{7d}

Thin films of **2a–d** were generated by the slow evaporation of CHCl₃ solutions and were doped with iodine. The conductive properties of the films stabilized over several weeks and remained more or less unchanged. The thin films of oxidized polymers were green initially, and upon diffusion of iodine from the polymer, the color changed to near transparent sky-blue. The films of PMEET (**2b**) exhibited very high average electrical conductivities of around 200 S/cm, with some samples exhibiting maximum conductivities of 650 S/cm (Figure 1).¹⁵ The SEM analyses revealed that the most conductive films were of exceptional quality and very dense.^{2,18} One of the most amazing findings was that PMEET (**2b**) is extremely stable to ambient conditions and remains highly conductive over long periods of time. The electrical conductivity of a cast film of **2b**, which was oxidized with iodine for 12 h followed by exposure to ambient conditions, was originally at 93 S/cm (Figure 1). Subsequently, a dramatic increase in conductivity (up to 650 S/cm) was observed within 24 h. Upon gradual diffusion of

- (9) (a) Kumar, A.; Reynolds, J. R. *Macromolecules* **1996**, *29*, 7629. (b) Schottland, P.; Fitchet, O.; Teyssie, D.; Chevrot, C. *Synth. Met.* **1999**, *101*, 7. (c) Yamamoto, T.; Alba, M. *Synth. Met.* **1999**, *100*, 237. (d) Shiraishi, K.; Kanbara, T.; Yamamoto, T.; Groenendaal, L. B. *Polymer* **2001**, *42*, 7229.
- (10) (a) Welsh, D. M.; Kumar, A.; Meijer, E. W.; Reynolds, J. R. *Adv. Mater.* **1999**, *11*, 1379. (b) Welsh, D. M.; Kloeppner, J. L.; Madrigal, L.; Pinto, M. R.; Thompson, B. C.; Schanze, K. S.; Abboud, K. A.; Powell, D.; Reynolds, J. R. *Macromolecules* **2002**, *35*, 6517.
- (11) Loewe, R. S.; Khersonsky, S. M.; McCullough, R. D. *Adv. Mater.* **1999**, *11*, 250.
- (12) (a) Yokoyama, A.; Miyakoshi, R.; Yokozawa, T. *Macromolecules* **2004**, *37*, 1169. (b) Sheina, E. E.; Liu, J.; Iovu, M. C.; Laird, D. W.; McCullough, R. D. *Macromolecules* **2004**, *37*, 3526.
- (13) Keegstra, M. A.; Peters, T. H. A.; Brandsma, L. *Tetrahedron* **1992**, *48*, 3633.
- (14) Loewe, R. S.; Ewbank, P. C.; Liu, J.; Zhai, L.; McCullough, R. D. *Macromolecules* **2001**, *34*, 4324.
- (15) See Supporting Information for the experimental details on the synthesis, spectroscopic, and electronic characterizations.
- (16) Galazzi, M. C.; Castellani, I.; Marin, R. A.; Zerbi, G. *J. Polym. Sci., Part A: Polym. Chem.* **1993**, *31*, 3339.
- (17) Elsenbaumer, R. L.; Jen, K. Y.; Miller, G. G.; Eckhardt, H.; Shacklette, L. W.; Jow, R. *Electronic Properties of Conjugated Polymers*; Kuzmany, H., Mehring, M., Roth, S., Eds.; Springer Series in Solid State Sciences; Springer: New York, **1987**; Vol. 76, p 400.

- (18) McCullough, R. D.; Williams, S. P. *J. Am. Chem. Soc.* **1993**, *115*, 11608.

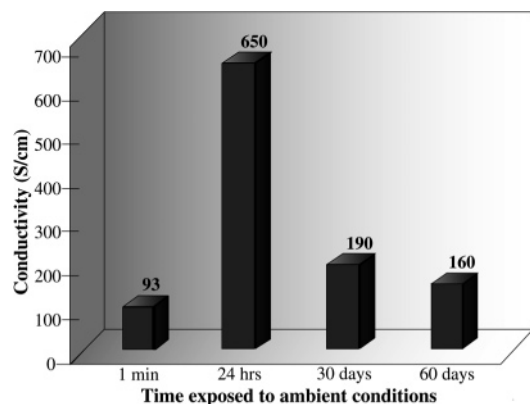


Figure 1. Time dependence of conductivity of iodine oxidized cast film of regioregular poly(3-[2-(2-methoxyethoxy)ethoxy]thiophene) (PMEET, **2b**) after exposure to ambient conditions.

Table 1. Conductive Stability of Iodine Oxidized, Cast Films of 3-Alkoxy-Functionalized Polythiophenes at Ambient Conditions for over 3 Years

	Conductivity (S/cm)			
	1 min	24 hrs	30 days	3 yrs
PHOT (2a)	0.1	3	2	0.15
PMEET (2b)	4	14	25	35

iodine from the polymer matrix, the conductivity remained almost constant at 150 S/cm after allowing the iodine adduct to stand at room temperature for over 2 months in air. Prior to optimization of film formation, we had prepared several iodine oxidized cast films of **2b** that were kept at ambient conditions for over 3 years and these films still had conductivities of 25–35 S/cm (Table 1).

The increase in the conductivity over time was possibly due to either doping with atmospheric oxygen or the release of excess iodine from the polymer. Excess iodine could cause charge pinning or initial disruption of the conjugation system due to overoxidation, in which the placement of iodine ions along the chains could lead to distortion of the intermolecular order and reduction of interchain charge transfer, as previously reported by Reynolds.^{10b} Preliminary thermal stability tests indicated that iodine-doped PMEET (**2b**) was stable when exposed to 70 °C for 2 days under ambient light and atmosphere. Samples with conductivities of 20 S/cm showed only slight drops in conductivity to about 10 S/cm and then remained stable for months. In contrast, conductivities of iodine-doped poly(3-alkylthiophene) decrease by a factor of 1000 to 10000 over time. Due to their low oxidation potential, the polymer films could be oxidized by atmospheric oxygen. For example, “air-doped” PMEET (**2b**) exhibited conductivities of 0.1–10 S/cm in thin films (50–200 nm). Air doping was also reported by Elsenbaumer et al. for poly-

(3,4-dimethoxy-2,5-thienylene-vinylene), which had a conductivity of 10^{-3} S/cm.¹⁹ Air-doped samples remained conductive to date.

PHOT (**2a**) exhibited conductivities as high as 5 S/cm for thin films (e.g., 200 nm) and conductivities as high as 1 S/cm for thicker films (e.g., 10 μ m). The remarkable stability of iodine-doped PHOT (**2a**) can be seen in two samples that had conductivities of 1 S/cm after 5 days and 0.2 S/cm after more than 3 years of exposure to ambient conditions. Polymers **2c** and **2d** exhibited conductivities of up to 50 S/cm and up to 0.5 S/cm when iodine- and air-doped, respectively.

The polymers **2b** and **2d** were oxidized in solution with different dopants, such as I_2 , $NOPF_6$, and $ZnCl_2$. Upon successive additions of I_2 and $NOPF_6$, the π to π^* transition was depleted, giving rise to two lower energy transitions at 1100 nm and near 1600 nm, respectively. The neutral polymer solution of **2b** was dark purple (dark blue for **2d**) in color and, upon slow oxidation, the solution first turned blue, then sky blue, almost transparent, and eventually green. At high doping levels, the UV–Vis–NIR spectra exhibited a single strong electronic absorption, indicating formation of bipolarons and displaying characteristics of the free-carrier absorption of the metallic state.²⁰ One very interesting observation was that solutions treated with excess $ZnCl_2$ caused the polymer solution to become transparent and doped. It is possible that the zinc(II) could have been inserted within the alkoxy side chains, leading to a supramolecular organization of the polymer.²¹ It was noted that the polymers in their oxidized form could remain in solution for extended periods of time, allowing for the self-organization of the conjugated polymer backbones before being processed.^{8a}

These regioregular poly(3-alkoxythiophenes) are remarkable new materials that are very stable, processable, and highly conductive. It is our hope that they may bring further commercialization of conductive polymers closer to reality.

Acknowledgment. We gratefully acknowledge the NSF (CHE0107178) for support of the work. NMR spectra were obtained at the NMR Facility at Carnegie Mellon University. Partial funding for the facility was obtained from the NSF (CHE0130903).

Supporting Information Available: A complete description of the procedures for the synthesis of the monomers and the corresponding polymers are available (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

CM050083O

(19) Cheng, H.; Elsenbaumer, R. L. *J. Chem. Soc., Chem. Commun.* **1995**, 1451.

(20) Chung, T. C.; Kaufman, J. H.; Heeger, A. J.; Wudl, F. *Phys. Rev. B: Condens. Matter* **1984**, *30*, 2, 702.

(21) Boldea A.; Lévesque, I.; Leclerc, M. *J. Mater. Chem.* **1999**, *9*, 2133.