Macromolecules **1995,** *28,* 2101−2102 **2101**

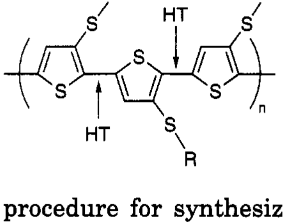
Synthesis of Regioregular Head-to-Tail Poly[3-(alkylthio)thiophenes]. A Highly Electroconductive Polymer

Xiaoming Wu, Tian-An Chen, and Reuben D. Rieke*

Department of Chemistry, University of Nebraska—Lincoln, Lincoln, Nebraska 68588-0304

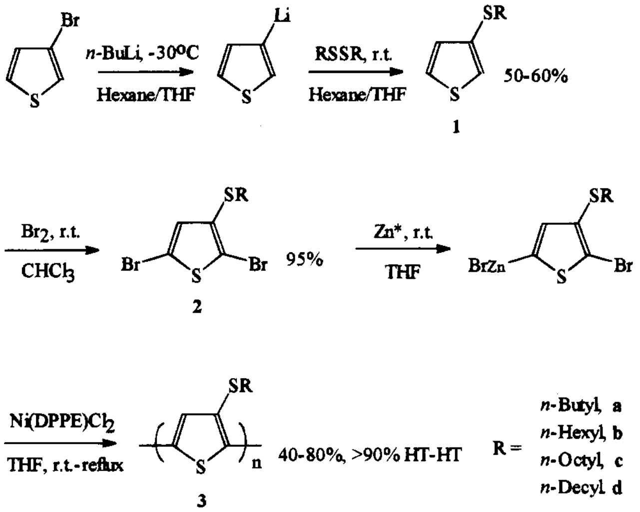
Received December 28, 1994

The introduction of long-chain alkyl groups into the 3-position of thiophene units in polythiophene converts the polythiophene into a class of identifiable, soluble, and processable conducting polymers.[1] The design and synthesis of specially structured poly(3-substituted thiophenes) has become an area of active interest. Recent research showed that the linkage regularity[2] of the poly(3-substituted thiophenes) and character of the substituents have a strong relationship on the physical properties of the polymers. Recently, we reported a regiocontrolled synthesis for regioregular head-to-tail (HT) poly(3-alkylthiophenes) (P3AT) *via* catalyzed polycondensation[3] of 2-bromo-5-(bromozincio)-3-alkylthiophenes. The organozinc reagents are readily prepared by oxidative addition of Rieke zinc[4] to 2,5-dibromo-3-alkylthiophenes. The regioregular head-to-tail poly(3-alkylthiophenes) (HT-P3AT)[3,5] displayed a variety of interesting physical properties and much higher electroconductivity over other P3AT's.[1,2,6] The variation of 3-substituents on the thiophene ring has a pronounced effect on the physical properties of the polythiophenes. The introduction of ether- or thioether-containing side chains onto the 3-position of thiophene led to the fine tuning of electrical and optical properties of polythiophenes;[5c,7] the crown ether group bestowed ionochromic activity on polythiophenes;[8] the chiral side chain resulted in an opitically active polythiophenes.[9] Since the physical properties (such as conductivity and band gap) of poly(3-substituted thiophene) were highly sensitive to the nature and regioregularity of the substituent, we have focused on the synthesis of novel regioregular head-to-tail poly(3-substituted thiophene) with new substituents, using our regiocontrolled synthetic methodology.[3] We report herein the synthesis and characterization of a new regioregular head-to-tail poly[3-(alkylthio)thiophene][7] in which the sulfur atom of the substituent is directly connected to the 3-position of the thiophene ring, and followed by a long alkyl chain:



The general procedure for synthesizing the poly[3-(alkylthio)thiophenes] (**3**) is shown in Scheme 1. 3-Bromothiophene was used as the initial starting material. The metal−halogen exchange reaction of *n*-butyllithium with 3-bromothiophene in hexane/THF (10:1) mixed solvent at −30 °C led to a room-temperature-stable 3-lithiothiophene.[10] 3-Lithiothiophene reacted with different alkyl disulfides at room temperature under argon to offer related 3-(alkylthio)thiophenes (**1**) in 50−60% yield. 2,5-Dibromo-3-(alkylthio)thiophenes (**2**) were prepared by bromination of respective 3-(alkylthio)thiophenes (**1**) with Br$_2$ in chloroform. Rieke zinc (Zn*)[4] rapidly underwent oxidative addition to 2,5-dibromo-3-(alkylthio)thiophenes (**2**) in the 5-position of the dibromothiophene with a regioselectivity of >95% at room temperature. The 2-bromo-5-(bromozincio)-3-(alkylthio)thiophenes were then polymerized utilizing Ni(DPPE)Cl$_2$ (0.5% equiv) under argon to produce the polymers (**3**) in 40−80% yield.[7] Poly[3-(octylthio)thiophene] (**3c**), for example, was synthesized as follows: 2,5-dibromo-3-(octylthio)thiophene (**2c**) (1.93 g, 5.0 mmol, in 10 mL of THF) was added via a cannula to the newly prepared Zn*[4] (5.5 mmol, in 20 mL of THF) at 0 °C. The mixture was stirred for 1 h at this temperature. Ni(DPPE)Cl$_2$ (0.5 mol %, 13.2 mg, 0.025 mmol, in 10 mL of THF) was added via cannula at 0 °C. The mixture was allowed to warm to room temperature and then refluxed for 4 h. A dark-purple precipitate was formed gradually during this period. The mixture was poured into a solution of MeOH (50 mL) and 2 N HCl (25 mL), and the resulting dark precipitate was filtered and washed with MeOH and 2 N HCl. The polymer was reprecipitated from a hot chloroform solution upon addition of methanol. Repurification of polymer by Soxhlet extractions with MeOH for 24 h and then with hexane for 24 h afforded 0.62 g (54.8% yield) of poly[3-(octylthio)thiophene] (**3c**).[11]

Scheme 1. Typical Synthsis Procedure for HT Regioregular Poly[3-(alkylthio)thiophenes]



The poly[3-(alkylthio)thiophenes] are black−brown solids. They are soluble in carbon disulfide at room temperature and have poor solubilities in chloroform, THF, xylene, etc., at ambient temperature, but they are soluble under reflux. The solutions of the polymers in organic solvents are dark red. The solubilities of the polymers decrease with the increasing molecular weight and increase with increasing length of the alkyl side chain. Poly[3-(butylthio)thiophene] (**3a**) is hardly soluble in any organic solvents mentioned above.

The structure of poly[3-(octylthio)thiophene] (**3c**) was also characterized by FTIR and ^{1}H NMR. The FTIR spectrum displayed aromatic C−H stretching and out-of-plane vibrations at 3056 and 819 cm^{-1}, respectively; the aliphatic C−H stretching vibrations were present at 2954, 2923, and 2852 cm^{-1}. The peaks at 1411−1525 cm^{-1} originate from the ring stretching vibrations, and a strong peak at 628 cm^{-1} indicates the existence of a S−C stretching vibration.[12] ^{1}H NMR of a poly[3-(octylthio)thiophene] (**3c**) solution in carbon disulfide using CDCl$_3$ as the external reference shows a sharp peak at δ 7.54 ppm. This singlet aromatic H peak suggests more than 90% HT−HT linkage of the units

0024-9297/95/2228-2101$09.00/0

along the polymer chain based on proton NMR integration.

The UV–vis spectra of poly[3-(octylthio)thiophene] (**3c**) was obtained in the solid state and in dilute CHCl$_3$ solutions. Three major peaks were observed at 263, 324, and 513 nm, as well a shoulder at 605 nm in a CHCl$_3$ solution; the most intense maximum peak was at 513 nm. The solid-state UV–vis spectrum shows three almost equally intense maximum peaks at 520, 554, and 600 nm. The onset of the $\pi-\pi^*$ electronic transition corresponded to a band gap of 1.8 eV.

The poly[3-(alkylthio)thiophenes] with more than four carbon atoms in the side chain can form a copper-lustred film *via* the slow evaporation of a carbon disulfide solution of the polymer. The color of the thin films changes to dark blue after being doped in iodine vapor. The doped polymer films are highly electroconductive. Their conductivities, measured by four-probe methods, range from 450 to 750 S cm^{-1}. These conductivities are similar to that of the regioregular HT poly(3-alkylthiophenes)[3,13] and much higher than that of regio random poly[3-(ethylthio)thiophene].[7c]

The regioregular HT poly[3-(alkylthio)thiophenes] were found to be polycrystalline and self-orienting polymers.[3d,14] The cast films of the poly[3-(alkylthio)thiophene] solutions by simple air evaporation also showed a polycrystalline and self-organized lamellar morphology with three-dimensional ordering of the polymer chains. For instance, the X-ray diffraction pattern of poly[3-(octylthio)thiophene] (**3c**) film presented the strong first-, second-, and third-order reflections at 2θ angles of 4.1, 8.2, and 12.2°, which corresponded to a 21.54-Å interlayer *d*-spacing of well-organized lamellar structure. The *d*-spacing was 1.44 Å longer than that of regioregular HT poly[3-(octylthio)thiophene] which was 20.10 Å.[3d] This increase of the *d*-spacing was apparently due to the addition of the S atom between the thiophene ring and alkyl group in poly[3-(alkylthio)thiophenes].

The molecular weights of poly[3-(alkylthio)thiophenes] have not been fully determined due to their poor solubility in THF at room temperature. Poly[3-(octylthio)thiophene] (**3c**) was partially (ca. 10%) soluble in THF at room temperature. This part was, obviously, a low molecular weight fraction and had a weight-average molecular weight $\bar{M}_w = 4889$ and a number-average molecular weight $\bar{M}_n = 4417$, by GPC (gel permeation chromatography; relative to a polystyrene standard, with THF as eluant at room temperature). The majority of the poly[3-(octylthio)thiophenes] must have a molecular weight significantly higher than that of the soluble fraction of the polymer.

The regiocontrolled synthesis of polythiophenes provides a novel route to the highly electroconductive and regioregular HT poly(3-functionalized thiophenes) with a heteroatom S direct connection to the 3-position of the thiophene ring in the polymer units. Compared to the reported poly(3-alkoxythiophenes)[15] and regiorandom poly[3-(ethylthio)thiophene][7] which also have a heteroatom O or S at the 3-position, our regioregular poly[3-(alkylthio)thiophenes] have higher conductivities and longer λ_{max} UV absorption. The regioregular HT poly[3-(alkylthio)thiophenes] are self-organizing and polycrystalline polymers, whereas poly(3-alkoxythiophenes), synthesized by other methods, were amorphous[16] in their solid state. We are continuing to explore the synthesis of novel poly[3-(alkylthio)thiophenes] and study their physical properties.

Acknowledgment. This work is supported by the NIH (Grant GM35153). We thank Prof. C. H. Wang, Mr. Q.-R. Huang, and Mr. X. Q. Zhang for help with the MW determination. We also thank Mr. M. V. Hanson and Dr. N. G. Bhat for helpful discussions.

Supplementary Material Available: Analytical data of the monomers **1b–d** and **2a–d** and figures of ^{1}H NMR, FTIR, UV–vis spectrum, and X-ray diffraction pattern of poly[3-(octylthio)thiophene] (**3c**) (7 pages). Ordering information is given on any current masthead page.

References and Notes

(1) (a) Jen, K.-Y.; Miller, G. G.; Elsenbaumer, R. L. *J. Chem. Soc., Chem. Commun.* **1986**, 1346–1347. (b) Elsenbaumer, R. L.; Jen, K.-Y.; Oboodi, R. *Synth. Met.* **1986**, *15*, 169–174. (c) Hotta, S.; Rughooputh, S. D. D. V.; Heeger, A. J.; Wudl, F. *Macromolecules* **1987**, *20*, 212–215. (d) Sato, M.; Tanaka, S.; Kaeriyama, K. *J. Chem. Soc., Chem. Commun.* **1986**, 873–874. (e) Nowak, M.; Rughooputh, S. D. D. V.; Hotta, S.; Heeger, A. J. *Macromolecules* **1987**, *20*, 965–968.

(2) (a) Roncali, J.; Carreau, R.; Yassar, A.; Marque, P.; Garnier, F.; Lemaire, M. *J. Phys. Chem.* **1987**, *91*, 6706–6714. (b) Roncali, J.; Marque, P.; Garreau, R.; Garnier, F.; Lemaire, M. *Macromolecules* **1990**, *23*, 1347–1352. (c) Maior, R. M. S.; Hinkelmann, K.; Eckert, H.; Wudl, F. *Macromolecules* **1990**, *23*, 1268–1279. (d) Wei, Y.; Chan, C.-C.; Tian, J.; Jang, G.-W.; Hsueh, K. F. *Chem. Mater.* **1991**, *3*, 888–897. (e) Tour, J. M.; Wu, R.; Schumm, J. S. *J. Am. Chem. Soc.* **1991**, *113*, 7064–7066. (f) Pearson, D. L.; Schumm, J. S.; Tour, J. M. *Macromolecules* **1994**, *27*, 2348–2350. (g) Mao, H.; Holdcroft, S. *Macromolecules* **1992**, *25*, 554–558. (h) Mao, H.; Xu, B.; Holdcroft, S. *Macromolecules* **1993**, *26*, 1163–1169, 4457–4460.

(3) (a) Chen, T.-A.; Rieke, R. D. *J. Am. Chem. Soc.* **1992**, *114*, 10087–10088. (b) Chen, T.-A.; Rieke, R. D. *Synth. Met.* **1993**, *60*, 175–177. (c) Chen, T.-A.; O'Brein, R. A.; Rieke, R. D. *Macromolecules* **1993**, *26*, 3462–3463. (d) Chen, T.-A.; Wu, X.; Rieke, R. D. *J. Am. Chem. Soc.* **1995**, *117*, xxxx.

(4) (a) Zhu, L.; Wehmeyer, R. M.; Rieke, R. D. *J. Org. Chem.* **1991**, *56*, 1445–1453. (b) Zhu, L.; Rieke, R. D. *Tetrahedron Lett.* **1991**, *32*, 2865–2866.

(5) (a) McCullough, R. D.; Lowe, R. D. *J. Chem. Soc., Chem. Commun.* **1992**, 70–72. (b) McCullough, R. D.; Lowe, R. D.; Jayaraman, M.; Anderson, D. L. *J. Org. Chem.* **1993**, *58*, 904–912. (c) McCullough, R. D.; Williams, S. P. *J. Am. Chem. Soc.* **1993**, *115*, 11608–11609.

(6) Roncali, J. *Chem. Rev.* **1992**, *92*, 711–738.

(7) Synthesis and characterization of regiorandom poly[3-(ethylthio)thiophene] was reported: (a) Ruiz, J. P.; Gieselman, M. B.; Nayak, K.; Marynick, D. S.; Reynolds, J. R. *Synth. Met.* **1989**, *28*, C481–C486. (b) Reynolds, J. R.; Ruiz, J. P.; Wang, F.; Jolly, C. A.; Nayak, K.; Marynick, D. S. *Synth. Met.* **1989**, *28*, C621–C628. (c) Ruiz, J. P.; Nayak, K.; Reynold, J. R. *Macromolecules* **1989**, *22*, 1231–1238.

(8) Swager, T. M.; Marsella, M. J.; Bicknell, L. K.; Zhou, Q. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1994**, *35*, 206–207.

(9) Bouman, M. M.; Meijer, E. W. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1994**, *35*, 309–310.

(10) Wu, X.; Chen, T.-A.; Zhu, L.; Rieke, R. D. *Tetrahedron Lett.* **1994**, *35*, 3673–3674.

(11) Poly[3-(octylthio)thiophene] (**3c**). Anal. Calcd for $-(C_{12}H_{18}S_2)-_n$: C, 63.68; H, 7.96; S, 28.36. Found: C, 63.61; H, 7.72; S, 27.78; Br, 1.20.

(12) Silverstein, R. M.; Bassler, G. C.; Morrill, T. C. *Spectrometric Identification of Organic Compounds*; John Wiley & Sons: New York, 1981; p 132.

(13) Reghu, M.; Yoon, C. O.; Moses, D.; Heeger, A. J.; Chen, T. A.; Wu, X.; Rieke, R. D., unpublished.

(14) McCullough, R. D.; Tristram-Nagle, S.; Williams, S. P.; Lowe, R. D.; Jayaraman, M. *J. Am. Chem. Soc.* **1993**, *115*, 4910–1911.

(15) (a) Blankespoor, R. L.; Miller, L. L. *J. Chem. Soc., Chem. Commun.* **1985**, 90–92. (b) Hagiwara, T.; Yamaura, M.; Sago, K.; Hirasak, M.; Iwata, K. *Synth. Met.* **1989**, *32*, 367–369.

(16) Chen, S.-A.; Tsai, C.-C. *Macromolecules* **1993**, *26*, 2234–2239.

MA946005W