Macromolecules **1999,** *32,* 2397−2399

Heteroaryl Substituted Polythiophenes: Chemical and Electrochemical Syntheses and Characterization of Poly[3-(9-tris(ethylene glycol) monomethyl ether)carbazoylthiophene]

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Received November 12, 1998
Revised Manuscript Received February 17, 1999

In recent years, polythiophenes have attracted a great deal of research interest due to their electronic and electrochemical properties.[1] The thiophene and bithiophene[2] monomers are easily obtained and derivatized to give structurally diverse polythiophenes. Thiophene has been substituted in the 3-position with a wide variety of functional groups and polymerized to give the corresponding β-substituted polythiophenes. Polythiophenes substituted with alkyl,[3] alkoxy,[4] aryl,[5] chiral,[6] nucleobase,[2c] and redox[7] groups have been synthesized and studied. In particular, poly(3-arylthiophenes) are showing promise as electrode materials for redox supercapacitors due to their ability to undergo reversible electrochemical doping and dedoping.[5a,b,8] However, to our knowledge the poly(3-arylthiophenes) have been limited to derivatives of benzene.[5] Therefore, we have initiated studies with the aims of attaching aromatic and heteroaromatic moieties other than phenyl directly to the thiophene ring and of investigating the corresponding polymers made both chemically and electrochemically. Herein we communicate results on our first system, namely, poly-[3-(9-tris(ethylene glycol) monomethyl ether)carbazoylthiophene].

Carbazole, a synthetically versatile and electron rich heteroaromatic ring system, is an attractive candidate for study in polythiophene chemistry and allows comparison with the reported 3-aryl substituted polythiophenes.[5] The carbazole moiety is well-known for its photoconductive properties by enhancing hole migration in polymeric systems, and in this context, it has been employed in xerographic,[9] photorefractive,[10] and light-emitting[11] applications. Besides electrophilic aromatic substitution reactions available in the 3- and 6-positions of the ring system, substitution reactions are also easily executed in the 9-position, which allows further tailoring of bulk properties of a given polymer, including solubility and processability. With this strategy in mind, we chose to attach an tris(ethylene glycol) monomethyl ether (OEG) group to the carbazole ring. The OEG group enhances solubility and processability and has been used to make materials ionochromic and ion-conducting.[12] In addition, the carbazole ring system is thermally stable and should maintain the thermal stability of the resulting polythiophene.

The synthesis of the 3-substituted thiophene monomer is shown in Scheme 1 and began with the N-alkylation reaction between 3-iodocarbazole (**1**)[13] and OEG−OTs[12a] to give the novel 3-iodo-(9-tris(ethylene glycol) monomethyl ether)carbazole, **2**, in 82% yield as a colorless oil.[14] The use of OEG−OTs proved to be more reliable than the corresponding reaction with OEG−Br[12b] since a mixture of products was consistently obtained with the use of OEG−Br. The intermediate **2** is versatile in that it can be used in a wide variety of metal-mediated cross-coupling reactions. Palladium catalyzed cross-coupling of **2** and 3-thiophene boronic acid (Aldrich) under modified Suzuki conditions[15] gave 3-(9-tris(ethylene glycol) monomethyl ether)carbazoylthiophene, **3**, a colorless oil, in 40% yield.[16] The low yields for this type of reaction has been ascribed to the oligomerization of the coupled thiophene, since a dark red color always formed when the reaction was performed at 100 °C. Decreasing the temperature to 65 °C did not significantly slow the reaction but did retard the formation of the dark red color. Moreover, the use of the antioxidant 2,6-di-*tert*-butyl-4-methylphenol, BHT, was recently reported in Suzuki type couplings,[17] presumably to inhibit radical formation from dissolved trace oxygen. When BHT was added to the reaction mixture (5 mol %), in combination with lower temperatures, yields of 60% were obtained. Further enhancement of the yields are expected with ligand and catalyst optimization. Monomer **3** was then subjected to chemical and electrochemical polymerization.

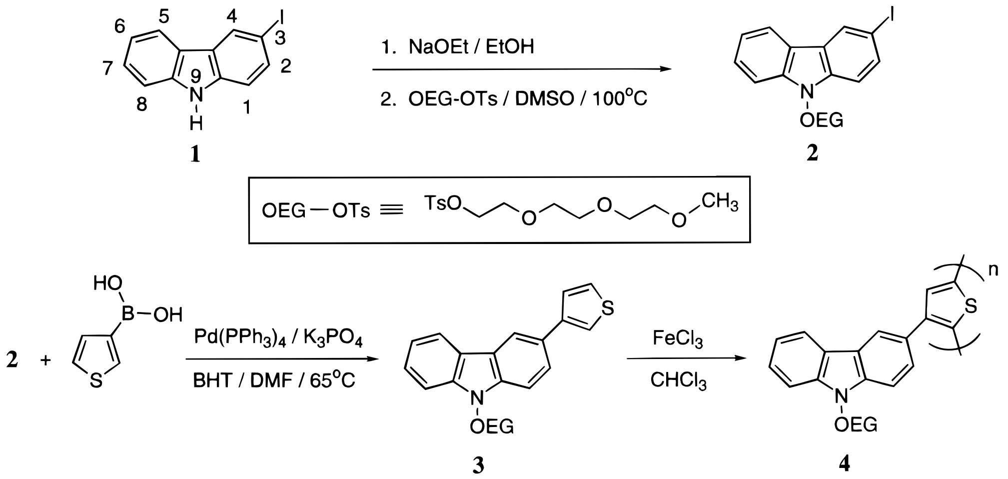
Chemical polymerization was carried out according to the method of Pomerantz and co-workers[3c] using 4 molar equiv of $FeCl_3$ in $CHCl_3$ at 50 °C under a slow purge of dry air, and gave poly[3-(9-tris(ethylene glycol) monomethyl ether)carbazoylthiophene], **4**, in 30% yield. These conditions have not yet been optimized for this system and alternative conditions[18] are being studied. The polymer was formed in the doped state and was dedoped using concentrated ammonia.[3c] Dedoped polythiophene **4** was readily soluble in common organic solvents allowing complete characterization.[16a,19]

The molecular weight of polymer **4** has been studied using gel permeation chromatography vs polystyrene standards. Using a refractive index detector, polymer **4** gave $M_w = 13\,731$ and $M_n = 4047$, a polydispersity of 3.2, and a degree of polymerization of about 35. Although it has been shown that polystyrene standards give lower molecular weight results (M_n and M_w) than light scattering analyses[3c] or NMR end-group analyses[12c] the molecular weights obtained are very promising in light of the considerable steric bulk that the carbazole moiety presents in the polymerization reaction. The electronic absorption spectra of monomer **3** and polymer **4** in tetrahydrofuran are shown in Figure 1. Polymer **4** shows $\lambda_{max} = 426.7$ nm, corresponding to the polythiophene backbone. A shoulder around 350 nm may be due to electronic interactions between the carbazole ring system and the polythiophene backbone as the two strong absorptions at 293.3 and 268.6 nm are due to the carbazole ring system. Thermal analysis of polymer **4** shows a 10% weight loss at 460 °C with 60% of the retained weight at 620 °C under a nitrogen atmosphere.[16a]

Electrochemical polymerization of monomer **3** was studied under a variety of conditions. All experiments were performed in a single-compartment, three-electrode assembly using glassy carbon as the working electrode, a platinum wire as the counter electrode, and Ag/Ag^+ as the reference electrode. Potentiostatic polymerization in acetonitrile (0.1 M NBu_4BF_4, 0.01 M **3**)

10.1021/ma981760l CCC: $18.00

Scheme 1



was unsuccessful. However, **3** did electropolymerize in CH_2Cl_2 under similar conditions, as shown in Figure 2. The electrodeposited films were obtained on the glassy carbon electrode, rinsed thoroughly with dry acetonitrile, and subjected to cyclic voltammetry in a fresh electrolyte solution containing no monomer **3**. The cyclic voltammograms are shown in Figure 3. The p-doping process is pseudo-reversible and varies linearly with the scan rate. It is interesting to note that the films obtained in this manner cannot be reversibly n-doped. Similar effects have been seen with poly(isothianaphthene)[20] where n-doping was reported to be unstable. The conditions for electropolymerization are important because preliminary results from galvanostatic electrodeposition repeatedly gave films which could be reversibly n-doped.

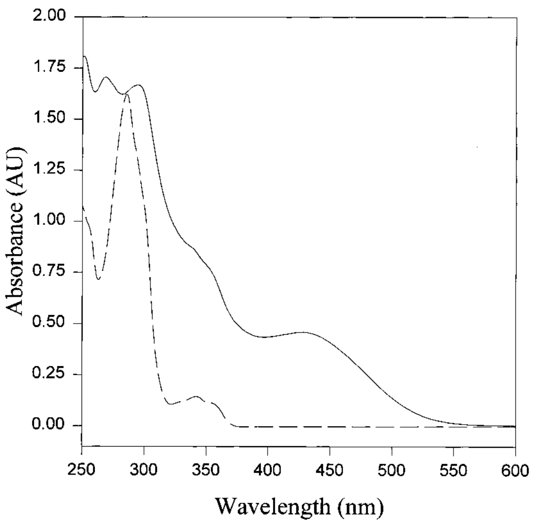


Figure 1. Electronic absorption spectrum of monomer **3** (dashed line) and polymer **4** (solid line) in tetrahydrofuran.

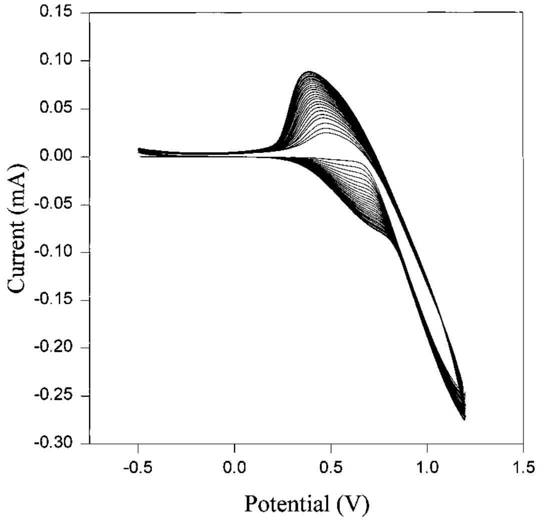


Figure 2. Potentiostatic polymerization of monomer **3** (0.01 M) in CH_2Cl_2 containing 0.1 M NBu_4BF_4 at 100 mV/s (vs Ag/Ag^+). The increase in current on each scan corresponds to the formation of polymer **4** on the electrode surface.

To make a comparison of the electrochemical properties of the chemically and electrochemically prepared polymers, chemically prepared polymer **4** was drop cast onto a glassy carbon electrode. The two films were then independently scanned in acetonitrile solution containing 0.1 M NBu_4BF_4, at 100 mV/s, using a Pt wire counter electrode vs Ag/Ag^+. As shown in Figure 4, the chemically prepared polymer film had an oxidation potential of 0.62 V compared to 0.85 V for the electrochemically deposited film.[2a,4b]

In conclusion, a new 3-substituted heteroaryl polythiophene has been synthesized by chemical and electrochemical methods. Spectroscopic data confirm the proposed structure. Other aromatic moieties such as

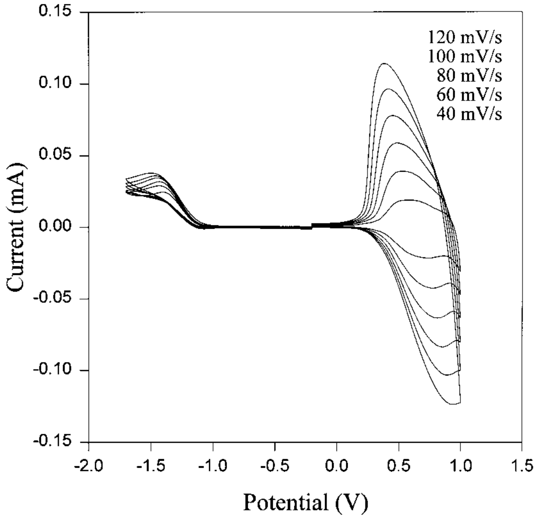


Figure 3. Cyclic voltammograms of polymer **4** film on glassy carbon, in CH_3CN containing 0.1 M NBu_4BF_4, taken at increasing scan rates (vs Ag/Ag^+).

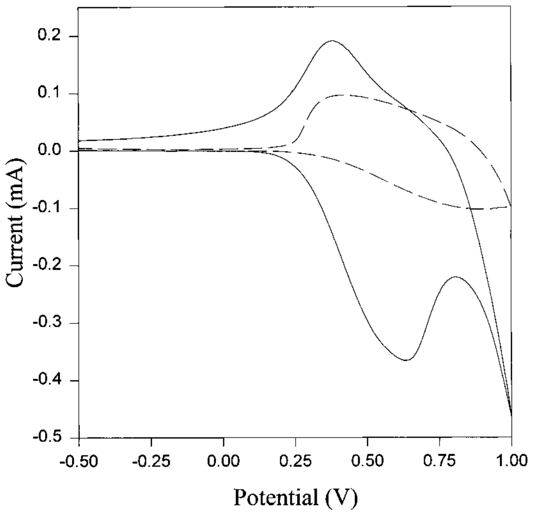


Figure 4. Cyclic voltammograms of polymer **4** prepared by chemical (solid line) and electrochemical (dashed line) polymerization.

naphthalene, pyrene, and indolizine have also been covalently attached to thiophene and polymerized chemically and electrochemically. Studies on these materials, along with the conductivity and electrooptical properties, such as electroluminescence of the carbazole-substituted polythiophene, are currently in progress.

Acknowledgment. This work is supported in part by the U.S. Army Research Office under Grant No. DAAH04-96-I-0130 and by an IIT-ERIF grant.

Supporting Information Available: Figures showing FT-IR, ^{13}C, and ^{1}H NMR spectra of monomer **3** and polymer **4** and the thermal analysis of polymer **4** under a nitrogen atmosphere. This material is available free of charge via the Internet at http://pubs.acs.org.

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(14) For **2**: FTIR (neat) 3052.7, 2874.4, 1623.6, 1590.7, 1472.2, 1453.4, 1350.9, 1331.5, 1275.3, 1215.8, 1108.6, 1021.5, 932.5, 875.5, 849.3, 796.8, 747.6, 722.1 cm^{-1}. ^{1}H NMR (300 MHz CDCl$_3$): δ 8.38 (s, 1H), 8.02 (d, 1H), 7.74−7.66 (m, 1H), 7.54−7.42 (m, 2H), 7.33−7.22 (m, 2H), 4.47 (t, 2H), 3.85 (t, 2H), 3.59−3.33 (m, 11H). ^{13}C NMR (300 MHz CDCl$_3$): δ 140.4, 139.7, 133.6, 128.9, 126.2, 125.3, 121.5, 120.3, 119.4, 111.1, 108.9, 81.4, 71.7, 70.9, 70.5, 69.2, 58.9, 43.2.

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(16) (a) See Supporting Information for spectra. (b) For monomer **3**: FTIR (neat) 3099.8, 3049.7, 2875.1, 1626.7, 1600.4, 1490.3, 1467.9, 1352.2, 1332.1, 1216.9, 1107.1, 932.8, 866.1, 834, 780.9, 748.9, 729.2 cm^{-1}. ^{1}H NMR (300 MHz CDCl$_3$): δ 8.30 (s, 1H), 8.12 (d, 1H), 7.72 (d, 1H), 7.55−7.40 (m, 4H), 4.53 (t, 2H), 3.90 (t, 2H), 3.60−3.40 (m, 6H), 3.34 (s, 3H). ^{13}C NMR (300 MHz CDCl$_3$): δ 43.2, 58.9, 69.2, 70.5, 70.9, 71.7, 109.0, 109.1, 118.0, 118.7, 119.0, 120.2, 122.9, 123.2, 123.6, 124.6, 125.8, 125.9, 126.6, 127.3, 139.9, 140.9, 143.2. HRMS: calculated for C$_{23}$H$_{25}$NO$_3$S, 395.1555; found, 395.1560.

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(19) For polymer **4**: FTIR (neat): 2873.8, 1600.2, 1468.8, 1352.6, 1281.4, 1249.9, 1215.6, 1106.8, 1023.9, 846.8, 806.6, 747.9 cm^{-1}. ^{1}H NMR (300 MHz CDCl$_3$): δ 7.7−6.7 (m), 4.6−4.3 (m), 3.7−3.0 (m). ^{13}C NMR (300 MHz CDCl$_3$): δ 140.2, 125.7, 122.9, 120.3, 109.1, 71.7, 70.4, 69.2, 58.9, 43.2.

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