Chem. Mater. **1999,** *11,* 1541−1545 1541

Oxygen-Modified Poly(4-dicyanomethylene-4*H*-cyclopenta[2,1-*b*;3,4-*b*′]dithiophene): A Tunable Low Band Gap Polymer

Huan Huang† and Peter G. Pickup*

Department of Chemistry, Memorial University of Newfoundland,
St. John's, NF, Canada A1B 3X7

Received December 2, 1998. Revised Manuscript Received April 12, 1999

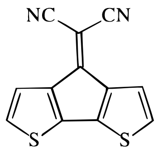
The reaction of n-doped poly(4-dicyanomethylene-4*H*-cyclopenta[2,1-*b*;3,4-*b*′]dithiophene) with O_2 at negative potentials (e.g., −0.60 V) produces changes in the polymer's electrochemistry, electronic spectrum, and conductivity profile that indicate a lowering of its band gap. Cyclic voltammetry of O_2-modified films shows increased currents in the voltage region corresponding to the band gap, between the original onsets of n and p doping. The onset of electronic absorption shifts from 0.8 eV to lower energies with increasing reaction time. In situ conductivity measurements show that the intrinsic conductivity increases by as much as a factor of 100 (to $\sim 10^{-6}$ S cm^{-1}), corresponding to a reduction of the band gap to ∼0.2 eV. Thus by controlling the reaction time with O_2 the band gap of the polymer can be tuned over the range of <0.2 to 0.8 eV. Raman spectra suggest that electrochemically driven substitution of the polymer with hydroxyl groups at the β-positions of the thiophene rings is responsible for the lowering of the band gap.

Introduction

π-Conjugated electroactive polymers have attracted considerable attention in the last two decades. In this field, the search for low band gap conducting polymers has become one of the central goals,[1] since band gap governs intrinsic electronic and optical properties. Low band gap polymers have high intrinsic electrical conductivities, and possibly even intrinsic metallic conductivities.[2] Also they are stable when doped, due to the lower p-doping potential and/or the less negative n-doping potential associated with their narrow band gap.[3,4]

A number approaches to the design and synthesis of low band gap polymers have been developed.[1] These include (a) increasing the contribution of the quinoid resonance structure to the ground state,[5−7] (b) use of alternating donor and acceptor moieties along a polymer chain,[8,9] and (c) introducing electron-withdrawing groups at a carbon bridging the β positions of bithienyl precursors.[10−12] Following these and other approaches, a significant number of conducting polymers with band gaps below 1 eV have now been reported.[1]

Among the known low band gap conducting polymers, poly(4-dicyanomethylene-4*H*-cyclopenta[2,1-*b*; 3,4-*b*′]-dithiophene)[11−16] (poly-**1**) has one of the lowest band gaps. We have investigated its in situ conductivity as a function of potential and shown that its intrinsic conductivity ($\sim 10^{-8}$ S cm^{-1}) corresponds to that prediced from its band gap (0.8 eV).[17] We have also shown that its band gap can be decreased to below 0.19 eV, and its intrinsic conductivity correspondingly increased to >7 × 10^{-3} S cm^{-1}, by making a copolymer with the donor thiophene, 3,4-ethylenedioxythiophene.[18] During the



1

---

* To whom correspondence should be addressed. E mail: ppickup@morgan.ucs.mun.ca.

† Current address: Department of Chemistry, University of Waterloo, ON, N2L 3G1 Canada. E mail: h4huang@sciborg.uwaterloo.ca.

(1) Roncali, J. *Chem. Rev.* **1997**, *97*, 173−205.

(2) Bredas, J. L.; Heeger, A. J.; Wudl, F. *J. Chem. Phys.* **1986**, *85*, 4673−4678.

(3) Arbizzani, C.; Catellani, M.; Mastragostino, M.; Mingazzini, C. *Electrochim. Acta* **1995**, *40*, 1871−1876.

(4) Arbizzani, C.; Mastragostino, M.; Meneghello, L.; Paraventi, R. *Adv. Mater.* **1996**, *8*, 331−334.

(5) Wudl, F.; Kobayashi, M.; Heeger, A. J. *J. Org. Chem.* **1984**, *49*, 3382−3384.

(6) Pomerantz, M.; Chalonergill, B.; Harding, L. O.; Tseng, J. J.; Pomerantz, W. J. *Chem. Commun.* **1992**, 1672−1673.

(7) Kitamura, C.; Tanaka, S.; Yamashita, Y. *Chem. Mater.* **1996**, *8*, 570−578.

(8) Havinga, E. E.; Hoeve, W. ten; Wynberg, H. *Synth. Met.* **1993**, *55−57*, 299−306.

(9) Zhang, Q. T.; Tour, J. M. *J. Am. Chem. Soc.* **1997**, *119*, 5065−5066.

(10) Lambert, T. L.; Ferraris, J. P. *Chem. Commun.* **1991**, 752−754.

(11) Ferraris, J. P.; Lambert, T. L. *Chem. Commun.* **1991**, 1268−1270.

(12) Ferraris, J. P.; Henderson, C.; Torres, D.; Meeker, D. *Synth. Met.* **1995**, *72*, 147−152.

(13) Toussaint, J. M.; Bredas, J. L. *Synth. Met.* **1993**, *61*, 103−106.

(14) Ferraris, J. P.; Lambert, T. L.; Rodriguez, S. U.S. Patent 5,510,438, 1996.

(15) Bakhshi, A. K.; Deepika. *Solid State Commun.* **1997**, *101*, 347−350.

(16) Beyer, R.; Kalaji, M.; Kingscote-Burton, G.; Murphy, P. J.; Pereira, V. M. S. C.; Taylor, D. M.; Williams, G. O. *Synth. Met.* **1998**, *92*, 25−31.

(17) Huang, H.; Pickup, P. G. *Acta Polymer.* **1997**, *48*, 455−457.

10.1021/cm9811038 CCC: $18.00

course of these studies, we found that the electrochemistry of poly-**1** coated electrodes changed significantly when they were cycled through the n-doped (reduced) state in the presence of O_2. These changes suggested a lowering of the band gap, and further investigation has confirmed this.

In this paper, we show by electrochemical, spectroscopic, and conductivity studies that the reaction of n-doped poly-**1** with O_2 leads to a structural modification that lowers its band gap in a controllable way. We provide evidence that this modification involves substitution of carbonyl/hydroxyl groups at free β-positions along the polythiophene chain (structure **2**).

Experimental Section

4-Dicyanomethylene-4*H*-cyclopenta[2,1-*b*;3,4-*b*′]dithiophene was donated by Philips (The Netherlands). Nitrobenzene (Fisher, ACS) was first distilled following addition of diluted H_2SO_4 to remove most of the impurities, and redistilled after it was dried over $CaCl_2$. The middle fraction of the second distillate was collected and stored under Ar. Acetonitrile (Aldrich, HPLC grade) and Bu_4NPF_6 (Fluka, puriss) were used as received.

A Pine Instruments RDE4 Potentiostat, $x-y$ recorder, and conventional three-electrode cell were used for electrochemical experiments. Polymer-coated Pt disks (5.2×10^{-3} or 1.3×10^{-4} cm^2) were used as working electrodes, with a Pt wire counter electrode, and a SCE reference electrode.

Poly-**1** films were synthesized galvanostatically on Pt electrodes, at 0.1 mA/cm^2 for 800 s, from 5 mM solutions of monomer **1** in nitrobenzene containing 0.1 M Bu_4NPF_6. These conditions produce a ~0.4 μm thick film of poly-**1** on the electrode.[17] Electrochemical measurements on the polymer coated electrodes were carried out in a monomer-free acetonitrile solution containing 0.1 M Bu_4NPF_6. For cyclic voltammetry, the solution was purged with argon, while for electrochemically driven modification of the polymer it was saturated with dry air.

For in situ conductivity measurements, the dual electrode voltammetry technique was employed.[19] In this technique the outer surface of a polymer film on a Pt disk (1.3×10^{-4} cm^2) electrode is connected to an adjacent Pt disk by a thin porous gold film. The assembly is inserted into an electrochemical cell (containing acetonitrile + 0.1 M Bu_4NPF_6 in this work) and a fixed potential difference ($E_{\mathrm{Pt-Au}} = 20$ mV) is maintained between the polymer-coated Pt electrode and the gold film while the potential of both is slowly scanned (1 mV s^{-1}) relative to a reference electrode (SCE). The conductivity (σ) as a function of potential (vs SCE) can be calculated from the steady-state current (I) vs potential curve by using the following equation:

$$\sigma = \frac{Id}{A\Delta E_{\mathrm{Pt-Au}}}$$

where d is the thickness of the polymer film and A is the electrode area.

Spectroelectrochemical measurements were carried out using an ITO electrode (0.8 cm^2, 10−20 Ω/cm^2, Donnelly Corp.) coated with the polymer, a Cary 5E UV−VI−NIR spectrometer, and a thin-layer quartz electrochemical cell containing acetonitrile + 0.1 M Bu_4NPF_6.

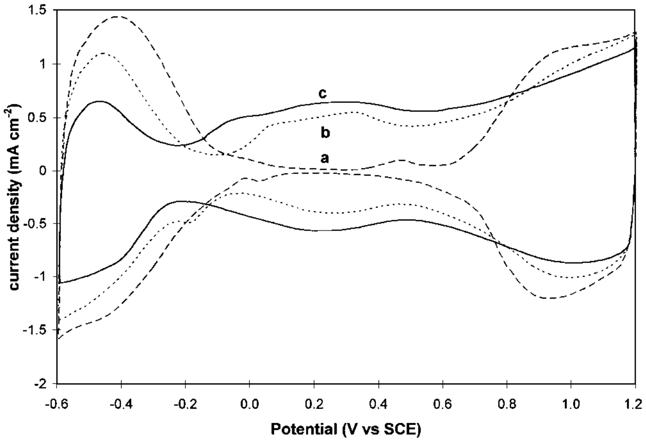


Figure 1. Cyclic voltammograms (100 mV/s in acetonitrile containing 0.1 M Bu_4NPF_6) of unmodified poly-**1** (a) and poly-**1** modified with O_2 at −0.6 V for 2 min (b) and 6 min (c). Electrode area: 0.0052 cm^2.

Raman spectra were recorded using a Reneshaw Raman Imaging Microscope System 1000 with a CCD31 detector and the 633-nm red line of an argon laser. The Raman spectrum of poly-**1** was measured for its neutral (undoped) state, while spectra of O_2-modifed films, whose n- and p-doping waves overlap, were obtained (ex situ) after holding their potential at the current minimum in their voltammogram.

All experiments in this work were carried out at room temperature (21 ± 2 °C)

Results and Discussion

Electrochemistry. Curve a in Figure 1 shows a cyclic voltammogram of an unmodified poly-**1** film. The p-doping peak potential of +0.99 V is similar to that for unsubstituted polythiophene,[20] while the n-doping peak occurs at −0.50 V, which is much higher than for unsubstituted polythiophene.[21] This substantial anodic shift of the n-doping region causes poly-**1** to be reasonably stable when n-doped. The electrochemical band gap, between the onsets of p doping and n doping, is ~0.8 V.

When the poly-**1** film was maintained at −0.60 V in an O_2-saturated solution first for 2 min, and then for an additional 4 min, the cyclic voltammograms shown in Figure 1 as curve b and c, respectively, were obtained. In comparison with the original polymer, the p- and n-doping peaks of the modified film are both lower and are slightly shifted to higher and lower potentials, respectively. A new redox wave appears within the band gap between the original onsets of n-doping and p-doping and grows with increasing treatment time. This new redox process lowers the band gap of the polymer to values that are too low to estimate by cyclic voltammetry since the onsets of the original p- and n-doping waves overlap with the new wave. On the basis of conductivity profiles (see below), the new wave can be assigned to a new p-doping process in the modified polymer. The band gap of the modified polymer therefore corresponds to the current minima at approximately −0.1 to −0.2 V in its voltammograms.

The formal potentials for p doping of the modified polymer were +0.32 V ($E^{0'}_{\mathrm{p1}}$) and +1.02 V ($E^{0'}_{\mathrm{p2}}$), while for n doping the formal potential ($E^{0'}_{\mathrm{n}}$) was −0.51 V, which is slightly negative compared to the original film ($E^{0'}_{\mathrm{n}} = -0.47$ V). All peak potentials were virtually independent of scan rate up to at least 100 mV s^{-1}, and

---

(18) Huang, H.; Pickup, P. G. *Chem. Mater.* **1998**, *10*, 2212−2216.

(19) Ochmanska, J.; Pickup, P. G. *J. Electroanal. Chem.* **1991**, *297*, 211−224.

(20) Roncali, J. *Chem. Rev.* **1992**, *92*, 711−738.

(21) Mastragostino, M.; Soddu, L. *Electrochim. Acta* **1990**, *35*, 463−466.

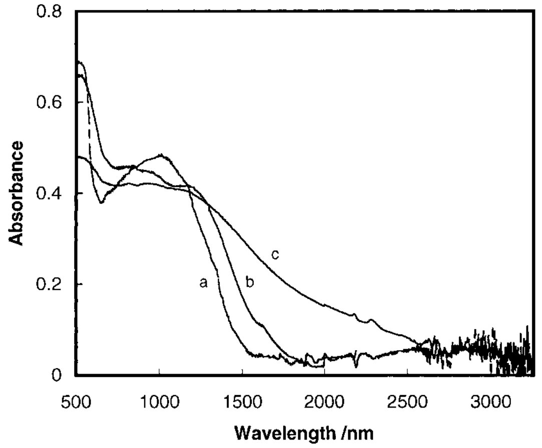


Figure 2. Electronic absorption spectra of unmodified poly-**1** (a) and poly-**1** films modified with O_2 at −0.6 V for 2 min (b) and 6 min (c). Films on ITO electrodes in acetonitrile containing 0.1 M Bu_4NPF_6 were held at a potential corresponding to the middle of their band gap.

peak currents increased linearly with increasing scan rate. Both the n-doping and p-doping processes of the modified poly-**1** exhibit good stability during multiple scans under argon.

In contrast to the results described above, maintaining a poly-**1**-coated Pt electrode at a high positive potential (e.g., +1.40 V) in the presence of O_2 does not lead to a low band gap polymer. It produces two obvious prepeaks, which grow and separate with time at the high potential. We have not fully investigated these effects, but assume that they are the result of nuleophilic attack on the oxidized polymer by trace H_2O (overoxidation), which has been well-documented for polythiophenes and most other conducting polymers.[22]

Electronic Absorption Spectroelectrochemistry. ITO electrodes coated galvanostatically (0.1 mA/cm^2) with a thin layer of poly-**1** were used for electronic absorption spectroelectrochemistry. The measurements were carried out in acetonitrile containing 0.1 M Bu_4NPF_6 with control of the potential of the poly-**1**-coated ITO electrode. For the original poly-**1** film the potential was set at +0.20 V so that the polymer was in its neutral state, while for the O_2 modified films, the potential was kept at the value corresponding to the polymer's minimum doping level (approximately −0.1 to −0.2 V). Vis−NIR absorption spectra of the original polymer, and following reaction with O_2 for 2 and 6 min are shown in Figure 2 as curves a, b, and c, respectively. The optical absorption onset for the original polymer is ~1520 nm, corresponding to a band gap of 0.82 eV. Following reaction with O_2 for 2 and 6 min, it shifts to ~1850 nm (0.67 eV) and ~2600 nm (0.48 eV), respectively, showing a significant reduction of the band gap, in good agreement with the new features seen in cyclic voltammetry (Figure 1). With controlled O_2 treatment, the band gap can be tuned down to values (<0.4 eV) that are too low to measure with our spectroelectrochemistry system.

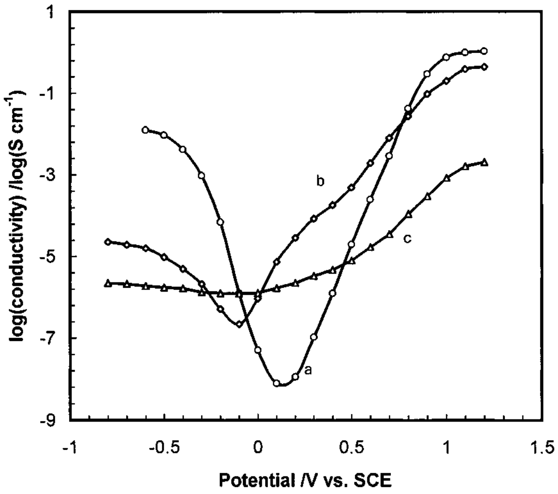


Figure 3. In situ conductivity profiles (in acetonitrile containing 0.1 M Bu_4NPF_6) of unmodified poly-**1** (a) and poly-**1** modified with O_2 at −0.6 V for 20 min (b) and 30 min (c).

Table 1. Electrical Properties of Original and O_2-Modified Poly-1 Films

reaction time with O_2 (min)	$\sigma_{max,p}$ (S cm^{-1})	$\sigma_{max,n}$ (S cm^{-1})	σ_{min} (S cm^{-1})	E_{min} (V)	$\sigma_{intrinsic}$ (S cm^{-1})	E_g (eV)
unmodified	1.1	1.2 × 10^{-3}	7.9 × 10^{-9}	0.18	1.0 × 10^{-8}	0.78
20	0.44	2.3 × 10^{-3}	2.2 × 10^{-7}	−0.05	8.0 × 10^{-7}	0.52
30	2.0 × 10^{-3}	2.2 × 10^{-3}	1.2 × 10^{-6}	−0.20	1.3 × 10^{-6}	0.22

In Situ Electronic Conductivity. In situ conductivity data on a log scale against potential are plotted in Figure 3. Curves a, b, and c are for an original poly-**1** film (0.37 μm) and films modified by reaction with O_2 at −0.60 V for 20 and 30 min, respectively. Longer times were needed to modify the polymer because of the porous gold coating needed for the conductivity measurements. Table 1 lists results from the conductivity measurements, including maximum conductivities for n doping ($\sigma_{max,n}$) and p doping ($\sigma_{max,p}$), minimum conductivities (σ_{min}) and their corresponding potentials (E_{min}), intrinsic conductivities ($\sigma_{intrinsic}$) and band gaps (E_g). The method for the intrinsic conductivity and band gap calculations has been described previously.[17,18]

In curve a of Figure 3, the p-type conductivity of the original poly-**1** rises to a maximum of 1.1 S cm^{-1} at +1.2 V. The n-type conductivity is ~90 times smaller, peaking at 0.012 mS cm^{-1} at −0.5 V. Further n doping to more negative potentials decreases the conductivity. The low n-type conductivity relative to the p-type conductivity is due mainly to the lower mobility or the n-type carriers[23] and in part to the lower doping level when the conduction band is half-filled during n doping.[17] The intrinsic conductivity and band gap are calculated to be 1.0 × 10^{-8} S cm^{-1} and 0.78 eV, respectively.

In curve b, where the poly-**1** has been modified by reaction with O_2 for 20 min, maximum conductivities for both n and p doping decrease, and the potential of the maximum n-type conductivity moves negatively. However, the minimum conductivity at −0.1 V is increased by a factor of ~30. Further reaction with O_2 (curve c) decreases the maximum n-type and p-type conductivities further, and increases the minimum conductivity to 1.2 × 10^{-6} S cm^{-1}, which is ~150 times

---

[22] Pud, A. A. *Synth. Met.* **1994**, *66*, 1−18.

[23] Guerrero, D. J.; Ren, X. M.; Ferraris, J. P. *Chem. Mater.* **1994**, *6*, 1437−1443.

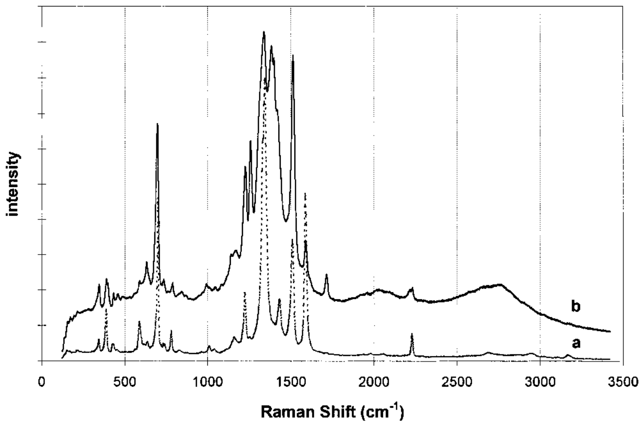


Figure 4. Raman spectra of unmodified poly-**1** (a) and poly-**1** modified with O_2 (b).

Table 2. Assignment of Raman Spectra of an Original Poly-1 Film and an O_2-modified Poly-1 Film

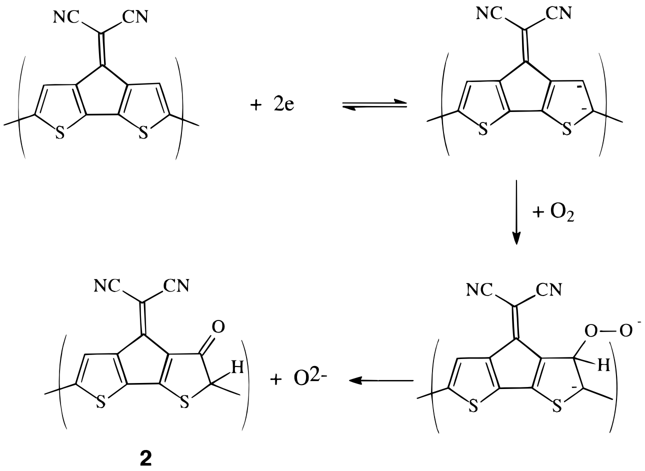
poly-**1**		O_2-modified poly-**1**	
bond	frequency (cm^{-1})^a	bond	frequency (cm^{-1})
C_β-H	3171	O−H	2759
C≡N	2230	C≡N	2230, 2217
C_β=O	1712		
$C=C(CN)_2$	1589	$C=C(CN)_2$	1587
$C_\alpha=C_\beta$	1511, 1434	$C_\alpha=C_\beta$	1511, 1417, 1396
$C_\beta-C_\beta$	1345	$C_\beta-C_\beta$	1381
=C−CN	1334	=C−CN	1335
C_β−OH	1256		
C_β−C=	1225	C_β−C=	1225
inter-ring $C_\alpha-C_{\alpha'}$	1161	inter-ring $C_\alpha-C_{\alpha'}$	1168
C−S−C	702, 782	C−S−C	695

higher than that of the original polymer. Intrinsic conductivities (Table 1) are increased similarly, and the band gaps calculated from these conductivies are decreased to 0.52 and 0.22 eV by 20 and 30 min of reaction with O_2, respectively.

Raman Spectroscopy. Figure 4 shows Raman spectra of an original poly-**1** film on a Pt electrode and another film after reaction with O_2 at −0.65 V for 8 min. Assignments of Raman shifts of both films are listed in Table 2.[24]

The most characteristic new feature in the spectrum of the modified polymer is the band at 1712 cm^{-1} that can be assigned to a carbonyl functionality. The most significant shifts of backbone resonances occur for the $C_\beta-C_\beta$ bond and one of the $C_\alpha=C_\beta$ bonds, suggesting that the carbonyl is at the 4-position of the thiophene ring (structure **2**). This is supported by the disappearance of the $C_\beta-H$ resonance at 3171 cm^{-1} in the spectrum of the original polymer and the shift of the $C_\alpha=C_\beta$ resonance at 1434 to 1396 and/or 1417 cm^{-1} (this band appears to have split). The new bands at 1256 cm^{-1} and ~2759 cm^{-1} are characteristic of an −OH, indicating that the carbonyl group is involved in a keto−enol tautomeric equilibrium. The low frequency of the −OH stretch (2759 cm^{-1}) and the splitting of the −CN stretch suggest that the enol −OH groups are strongly hydrogen bonded with some of the −CN groups. Vibrational frequencies of bonds remote from the proposed substitution site are almost unchanged.

Scheme 1



The proposed substitution of the polymer with =O at the 4-position (structure **2**) is consistent with the modification method and presumably occurs by electrophilic attack of O_2 on the n-doped polymer, as illustrated in Scheme 1. This scheme is obviously simplistic and is intended primarily to show the stoichiometry and proposed location of the reaction. The suggested dianion intermediates would be stabilized by delocalized over several monomer units. The extent of substitution is uncertain, but the weakness of the original Raman resonances associated with the outer β-position (at 1334, 1434, and 3171 cm^{-1}) in the spectrum of the modified polymers suggests that there is extensive substitution and perhaps some substitution at both outer β-positions.

The loss of conjugation caused by the keto tautomer shown in structure **2** explains the decrease in the maximum p- and n-type conductivities that accompany modification of the polymer. The decreased band gap presumably results from the donor character of the −OH group of the enol tautomer, since it has previously been shown that incorporating donor moieties into poly-**1** decreases its band gap considerably.[18] Overoxidation of poly-**1** would also be expected to produce structure **2**,[22] but although it leads to decreased maximum p- and n-type conductivities it does not decrease the polymer's band gap. This would suggest that overoxidation involves oxygen substitution at a different position on the thiophene ring, such as the sulfur as proposed by Barsch and Beck.[25]

A reviewer has suggested that the oxygen-modified polymer may have a two-phase structure in which modified and unmodified phases act as donor and acceptor components, respectively. This possibility seems unlikely, but cannot easily be discounted with the available data.

Conclusions

A tunable and extremely low band gap polymer has been obtained by the reaction of n-doped poly-**1** with O_2. Cyclic voltammograms of the O_2-modified polymer show a new p-doping wave within the band gap between the original onsets of n and p doping (−0.1 V to 0.7 V). The consequent decrease in band gap has been confirmed by optical and conductivity measurements. Near-

---

(24) Louarn, G.; Buisson, J. P.; Lefrant, S.; Fichou, D. *J. Phys. Chem.* **1995**, *99*, 11399−11404.

(25) Barsch, U.; Beck, F. *Electrochim. Acta* **1996**, *41*, 1761−1771.

IR spectra show that the band gap can be decreased from ∼0.8 eV to <0.5 eV, while in situ conductivity measurements show an increase in the intrinsic conductivity to $>10^{-6}$ S cm^{-1} corresponding to a band gap as low as 0.2 eV. Raman spectroscopy suggests that substitution of the polymer in the β-positions with hydroxyl groups, which are in equilibrium with a keto tautomer, is responsible for the lowered band gap.

Acknowledgment. This work was supported by the Natural Sciences and Engineering Research Council of Canada and Memorial University. We thank Dr. Dago Leeuw (Philips, Netherlands) for providing us with the monomer.

CM9811038