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Theoretical and Experimental Characterization of Small Band Gap Poly(3,4-ethylenedioxythiophene methine)s

**Wen-Chang Chen,*,† Cheng-Liang Liu,† Cheng-Tyng Yen,† Fu-Chuan Tsai,†
Christopher J. Tonzola,‡ Nicholas Olson,‡ and Samson A. Jenekhe‡**

*Department of Chemical Engineering and Institute of Polymer Science and Engineering,
National Taiwan University, Taipei, Taiwan 106, and Departments of Chemical Engineering
and of Chemistry, University of Washington, Seattle, Washington 98195-1750*

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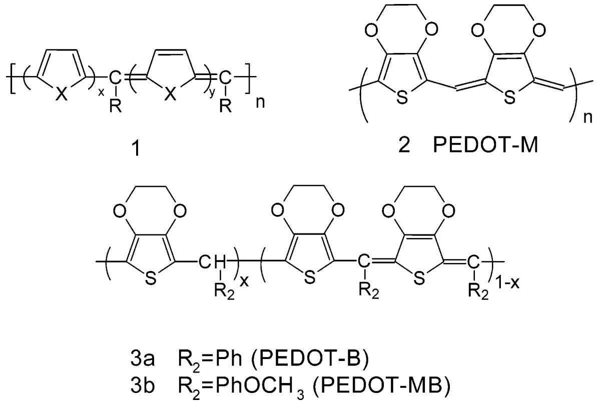
ABSTRACT: Theoretical and experimental characterization of relatively small band gap methine-bridged poly(3,4-ethylenedioxythiophene)(**PEDOT**) derivatives is reported. AM1 and the modified extended Hückel theory were used to explore the ground-state geometric and electronic structures of poly[(3,4-ethylenedioxythiophene-2,5-diyl) methine] (**PEDOT-M**). The bond length alteration in **PEDOT-M** was found to be smaller than that in the reported methine-bridged polythiophene, and this resulted in a significantly lower band gap of 0.48 eV in **PEDOT-M**. The structure and properties of the methine-bridged **PEDOT** were further verified by synthesis of poly[(3,4-ethylenedioxythiophene-2,5-diyl)-benzylidene] (**PEDOT-B**) and poly[(3,4-ethylenedioxythiophene-2,5-diyl)-(*p*-methoxybenzylidene)] (**PEDOT-MB**). These polymers were found to be highly dehydrogenated and to contain a conjugated backbone of alternating aromatic and quinoid ethylenedioxythiophene segments. The optical and electrochemical band gaps of **PEDOT-B** are 0.87 and 1.05 eV, respectively, while those of **PEDOT-MB** are 0.86 and 1.01 eV. The methoxy substitution of **PEDOT-MB** results in a smaller ionization potential and electron affinity than those of **PEDOT-B**. The theoretical and experimental results show that methine-bridged **PEDOT** is a small band gap polymer.

Introduction

Small band gap conjugated polymers have been extensively studied[1] because of their potential applications in organic optoelectronic devices,[2] such as photovoltaic cells,[2a,g] thin film transistors,[2b] light emitting diodes,[2c] nonlinear optical devices,[2d] electrochromic devices,[2e] and supercapacitors.[2f] The tuning of the band gap of conjugated polymers can be achieved through the molecular design of the bond length alternation, planarity, aromaticity, or donor/acceptor characteristics.[1] Representative small band gap polymers include poly(isothianaphthene) (PITN),[3] poly(thiophene methine)s (**PTMs**),[4] polysquaraines,[5] poly(thiopyrazine),[6] poly(cyclopentadithiophene),[7] poly(thieno[3,4,b]thiophene),[8] and ladder polymers.[9]

One of us first proposed poly(heteroarylene methines) (**1**, in Chart 1), which directly incorporates both aromatic and quinoid isomers in the same polymer chain.[4a] The band gap of the different **PTMs** varied from 1.14 to 1.91 eV, depending on the block size and the side group at the methine carbon. Theoretical calculations on the electronic structures of the **PTMs** showed that they exhibited small band gap ranging from 0.75 to 1.21 eV.[10] These are intermediate between the known theoretical band gap limits of 0.19 and 1.84 eV for the quinoid and aromatic polythiophene, respectively.[10c] The small band gap of the **PTMs** has stimulated new attempts on other polythiophene derivatives. Wudl and co-workers synthesized poly(isothianaphthene methine) (PITNM) with a band gap of 1.2 eV, which showed good reversible electrochromic properties.[11a] Akagi and co-workers reported new methine-bridged PITN with a liquid crystalline side chain, which had a band gap similar to that of PITNM.[11b] Poly(3,4-ethylenedioxythiophene) (**PEDOT**) has a band gap of 1.5−1.6 eV,[12] which is smaller than that of its parent polythiophene. Hence, it would be interesting to compare the band gap of methine-bridged **PEDOT** (**PEDOT-M**, **2**, in Chart 1) to that of **PTMs**. Sannicolo and co-workers recently reported a small band gap polymer obtained by the electrochemical polymerization of bis[2-(3,4-ethylenedioxy)thienyl]methine, which has a structure similar to that of **PEDOT-M**.[13] An electrochemical onset band gap of 0.4 eV was obtained from their studies. However, the molecular structure of the electropolymerized polymer has not been fully explored yet because of insolubility.[13] Besides, a theoretical understanding of the electronic structure of **PEDOT-M** could provide insight on the design of small band gap polymers.

Chart 1


1

2 PEDOT-M

3a R_2=Ph (PEDOT-B)
3b R_2=$PhOCH_3$ (PEDOT-MB)

In this study, theoretical calculations based on AM1 and modified extended Hückel theory (EHT) were performed to obtain the ground-state geometry and

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* To whom correspondence should be addressed. Phone: 886-2-23628398. Fax: 886-2-23623040. E-mail: chenwc@ntu.edu.tw.

† National Taiwan University.

‡ University of Washington.

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electronic structure of **PEDOT-M**. Two methine-bridged **PEDOT** derivatives were prepared for verifying the small band gap characteristics, including **PEDOT-B** (**3a**) and **PEDOT-MB** (**3b**). They were prepared by the acid-catalyzed polymerization of 3,4-ethylenedioxythiophene (EDOT) with benzaldehyde or *p*-anisaldehyde (**3**, in Chart 1). The bulky side group at the bridge carbon of polymer **3** could solve the insolubility problem of **PEDOT-M**. Indeed, the **PEDOT** derivatives **3** are highly dehydrogenated, which is consistent with both methylene and methine linkages in the main chain. The polymer structures, thermal, optical, and electrochemical properties of polymers **3** were investigated. Hence, a comparison of the electronic structures of polymers **2** and **3** is provided in the study.

Theoretical Analysis

The ground-state geometric structures of the **PEDOT-M** trimer (where the terminal α-carbons carry a single hydrogen atom) were obtained after optimization at the semiempirical AM1 (Austin Model 1 for MNDO)[14] level of theory performed on Gaussian 98.[15] For all of the geometry optimizations, the system of the EDOT trimer was supposed to be planar because it is well known that the AM1 method is unable to determine dihedral angles that are satifactory.[16] The central part (the second unit) of the optimized trimer was used as the input geometry for band structure calculations with the modified extend Hückel theory (EHT) performed on YAeHMOP.[17]

Experimental Section

Materials. 3,4-Ethylenedioxythiophene (EDOT, Aldrich), benzaldehyde (98%, Acros), *p*-anisaldehyde (98%, Aldrich), *p*-dioxane (99%, Aldrich), sulfuric acid (96.1%, Baker), tetrahydrofuran (THF, 99.9 wt %, Acros), methanol (ACS, Mallinckrodt), hexane (95%, Grand), and dimethyl sulfoxide-d_6 (D, 99.9%, CIL) were used for the synthesis of the polymers. Acetonitrile (>99.9%, HPLC, TEDIA), silver nitrate (≥99.8%, Acros), tetrabutylammonium tetrafluoroborate (electrochemical grade, >99.9%, Fluka), and ferrocene (98%, Acros) were used for the electrochemical experiments. Iodine (resublimed, ≥99.5%, Acros) was used for iodine doping.

Polymer Synthesis. Poly[(3,4-ethylenedioxythiophene-2,5-diyl)benzylidene] (PEDOT-B, 3a). The polymerization reaction was carried out with procedures similar to those reported previously.[4b,c] 3.84 g (27 mmol) of 3,4-ethylenedioxythiophene, 3.30 g (31.45 mmol) of benzaldehyde, and 0.919 g (9 mmol) of sulfuric acid were dissolved in 35 mL of *p*-dioxane. The solution mixture was placed in a 250-mL three-necked flask under a nitrogen atmospheree and was stirred at 85 °C for 24 h. A dark red product was recovered in 500 mL of methanol, filtered out the THF-soluble fraction, redissolved in THF, recovered in hexane, and dried in a vacuum oven at 45 °C for 24 h. The solid polymer product was further purified by the Soxhlet extraction with hot methanol. The polymer was then collected and dried in a vacuum oven at 45 °C overnight. The yield was about 50%. Anal. Calcd for $[(C_{13}H_{10}S_1O_2)_{0.32}(C_{26}H_{18}S_2O_4)_{0.68}]$ based on the THF-soluble fraction: C, 68.07; H, 4.01; O, 13.96, S, 13.96. Found: C, 65.47; H, 4.54; O, 16.27; S, 13.27.

Poly[(3,4-ethylenedioxythiophene-2,5-diyl)(*p*-methoxybenzylidene)] (PEDOT-MB, 3b). 3.84 g (27 mmol) of 3,4-ethylenedioxythiophene, 4.24 g (30.5 mmol) of *p*-anisbenzaldehyde, and 0.919 g (9 mmol) of sulfuric acid were dissolved in 35 mL of *p*-dioxane. The polymerization and purification procedures were the same as those of **3a**. A dark red product was obtained, and its yield was about 23%. Anal. Calcd for $[(C_{14}H_{12}S_1O_3)_{0.30}(C_{28}H_{22}S_2O_6)_{0.70}]$ based on the THF-soluble fraction: C, 64.82; H, 4.31; O, 20.47; S, 12.35. Found: C, 62.87; H, 5.01; O, 20.56; S, 11.56.

Characterization. Infrared spectra of the polymers **3** cast on NaCl windows from THF were recorded at room temperature by a DIGILAB FTS-3500GX spectrophotometer. ^{1}H nuclear magnetic resonance (NMR) data were obtained on a Bruker AV 500 MHz spectrometer. Elemental analysis was done by Heraeus VarioEL III-CHNS at the National Science Council (NSC) instrumental center at National Taiwan University (Taipei, Taiwan). The molecular weight distribution of the prepared materials was determined by gel permeation chromatography (GPC) equipped with PLgel 5 μm MIXED-C and D columns, a RI detector, and the elution solvent of THF at 1 mL/min.

Thermal analyses, thermogravimetric analysis (TGA), and differential scanning calorimetry (DSC) were performed under nitrogen flow using a Dupont model 951 thermogravimetric analyzer and a DuPont model 910S differential scanning calorimeter at a heating rate of 20 and 10 °C/min, respectively. Electronic absorption spectra were obtained in the range of 200−1600 nm using a Jasco model UV/VIS/NIR V-570 spectrophotometer at room temperature.

The electrochemical properties of the polymers in the solutions were carried out on Eco Chemie PGSTAT30 with a 0.1 M acetonitrile solution containing tetrabutylammonium tetrafluoroborate ($TBABF_4$) as the electrolyte. Platinum wire and rod-tip electrodes were used as counter and working electrodes, respectively. Silver/silver ion (Ag in 0.1 M $AgNO_3$ in the supporting electrolyte solutions) was used as a reference electrode. The polymers **3** were added into the electrolyte solution directly (the concentration of the polymers was roughly 1−2 wt %). The cyclic voltammetry in solution was then estimated by the three-electrode cell. The reference electrode was calibrated through running the cyclic voltammetry of ferrocene without any polymer added into the solution. The potential values obtained versus silver/silver ion were converted to versus saturated calomel electrode (SCE) by adding a constant of 0.0763 V to them. The gas-phase ionization potential (IP) and the electron affinity (EA) of the polymers were estimated using the following relations: $[E_{on}]^{ox} = \mathrm{IP} - 6.3$ and $[E_{on}]^{red} = \mathrm{EA} - 6.3$, where $[E_{on}]^{ox}$ and $[E_{on}]^{red}$ are the onset potentials for the oxidation and reduction of the polymers versus SCE. Solid-state IP and EA values were obtained by subtracting the polarization energy, 1.9 eV, from the gas-phase values.[18−20]

Iodine doping of the **PEDOT-MB** (**3b**) film was done as the following procedure. The polymer film was cast on the glass substrate by dip coating and then was placed into a jar containing iodine vapor and sealed for 15 min. The polymer films were then placed in a vacuum oven at 60 °C for 2 h to remove the excess iodine which covered the film.

Results and Discussion

Geometric and Electronic Structures of PEDOT-M. To explore the electronic structure of the methine-bridged **PEDOT**, a theoretical analysis on the geometric and electronic structure of the **PEDOT-M** was performed. Figure 1 shows the optimized unit cell geometry of the **PEDOT-M**, where the geometric and electronic parameters are shown in Table 1. The bond lengths between the bridged methine and two α carbons of the thiophene rings ($R_{(C1-CM)}/R_{(C3-CM)}$) are 1.427/1.345 Å, while those of the carbon bond lengths in the aromatic ($R_{(C1-C2)}/R_{(C2-C2)}$) and quinoid ($R_{(C3-C4)}/R_{(C4-C4)}$) thiophene rings of the **PEDOT-M** are 1.370/1.437 and 1.453/1.367 Å, respectively. Hence, the bond length alternation in the aromatic thiophene ring is 0.067 Å, which is smaller than that (0.086 Å) of the quinoid thiophene ring. The geometric structures of the **PTM** reported by Bredas and his co-worker[10c] are also shown in Table 1: the ($R_{(C1-CM)}/R_{(C3-CM)}$), ($R_{(C1-C2)}/R_{(C2-C2)}$), and ($R_{(C3-C4)}/R_{(C4-C4)}$) are 1.450/1.356, 1.379/1.451, and 1.467/1.361 Å, respectively. The bond length alternation of the **PTM** also shows the same trend as that of the **PEDOT-M**:

Table 1. Geometric and Electronic Parameters of the PEDOT-M and PTM

	bond lengths (Å)[c]			electronic parameters		
	$R_{(C1-CM)}/R_{(C3-CM)}$	$R_{(C1-C2)}/R_{(C2-C2)}$	$R_{(C3-C4)}/R_{(C4-C4)}$	IP (eV)	EA (eV)	E_g (eV)
PEDOT-M[a]	1.427/1.345	1.370/1.437	1.453/1.367	4.49	4.01	0.48
PTM[b]	1.450/1.356	1.379/1.451	1.467/1.361	4.46	3.41	1.05

[a] This work. [b] Reference 10c. [c] The numbering of carbon atoms is shown in Figure 1.

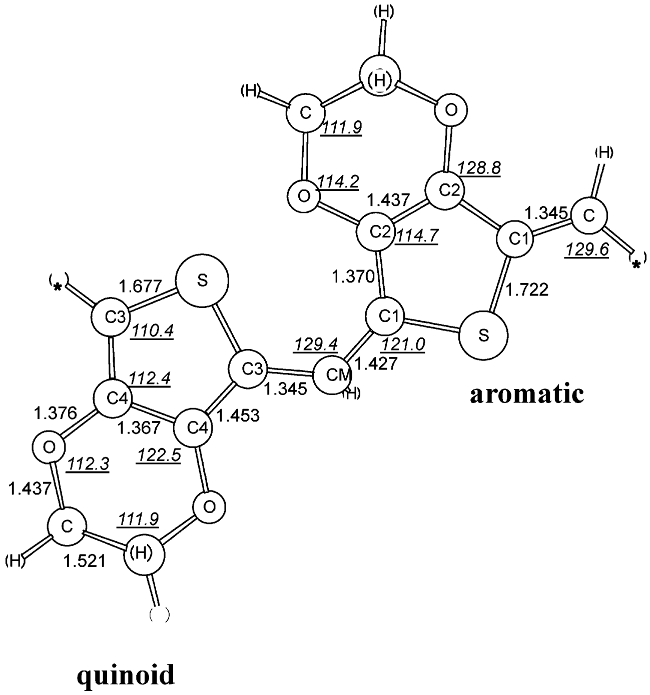

Figure 1. The optimized unit cell geometry of the **PEDOT-M**, where the geometric and electronic parameters are shown in Table 1.

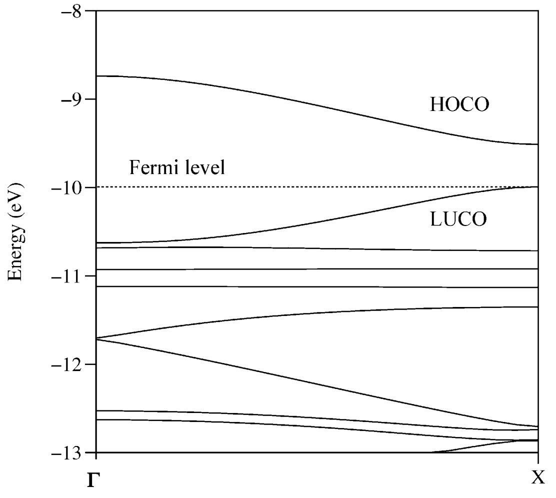

Figure 2. The band structure of the **PEDOT-M** obtained by the modified extend Hückel theory (EHT).

the bond length alternation in the aromatic thiophene ring (0.072 Å) is smaller than the quinoid thiophene ring (0.106 Å). From the above analysis, the bond length alternation of the **PEDOT-M** is concluded to be smaller than that of the reported **PTM**.[10C]

Figure 2 shows the band structure of the **PEDOT-M** obtained by the modified extend Hückel theory (EHT). The band gap calculated for the **PEDOT-M** is 0.48 eV, which is much smaller than that of 1.05 eV for the **PTM**.[10C] The reduction of the band gap can be attributed to the smaller bond length alternation of the

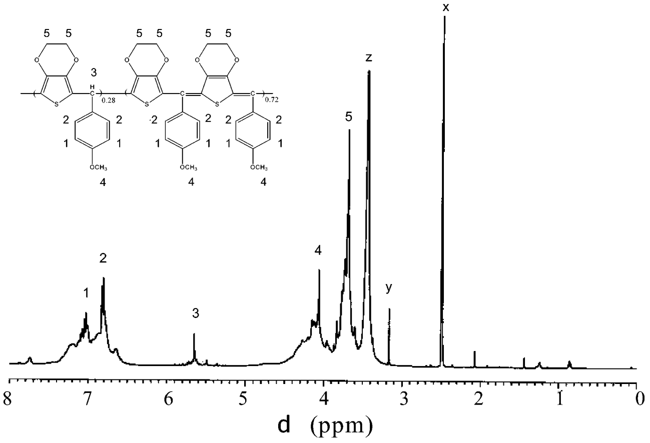

Figure 3. The ^1H NMR spectra of the **PEDOT-MB** in dimethyl sulfoxide-d_6 (DMSO). The peaks labeled as x, y, and z are assigned to the DMSO solvent, methanol residue, and water in DMSO-d_6, respectively.

PEDOT-M than the **PTM**. If the bond length alternation is small, the HOCO (highest occupied crystal orbital) antibonding interaction would be strengthened but the bonding interaction would be weakened. However, the case of LUCO (lowest unoccupied crystal orbital) shows a reverse trend from that of the HOCO: the bonding interaction would be strengthened, whereas the antibonding interaction would be weakened.[21] Hence, the HOCO level of the **PEDOT-M** is stabilized by only 0.03 eV, but the LUCO level of the **PEDOT-M** is stabilized by 0.6 eV relative to that of the **PTM**, giving a smaller band gap of the **PEDOT-M** than that of the **PTM**. The theoretical band gap of the **PEDOT-M** is similar to that reported for the electrochemical prepared poly{bi[(3,4-ethylenedioxy)thienylene]methine}.[13] It suggests that the approach of the conjugated polymers with alternating aromatic and quinoid moieties could achieve a relatively small band gap.

Polymer Synthesis and Structure. Although the **PEDOT-M** shows a relatively small theoretical band gap, it is an insoluble polymer and not able to be fully characterized. By inserting the bulky side group on the methine carbon, it could significantly improve the solubility. Hence, we prepared two methine-bridged PEDOT derivatives **PEDOT-B** (**3a**) and **PEDOT-MB** (**3b**). As reported previously on the synthesized **PTM** (**1**),[4c] the polymers obtained from the acid-catalyzed polymerization of the EDOT with aldehydes were highly colored because of dehydrogenation. The degree of dehydrogenation was determined from the methine hydrogen by ^1H NMR. Figure 3 illustrates the ^1H NMR spectra of the prepared **PEDOT-MB**, in dimethyl sulfoxide-d_6 (DMSO). The assignments of the peaks and integration are shown in the figure. The peaks labeled as x, y, and z are assigned to the DMSO solvent, methanol residue, and water in DMSO-d_6, respectively. The protons on the EDOT are at 3.5−3.9 ppm. The protons on the methoxy and phenylene side group are at 4.1 and 6.6−7.3 ppm, respectively. The small peak around 5.7 ppm is assigned to the methine-bridged

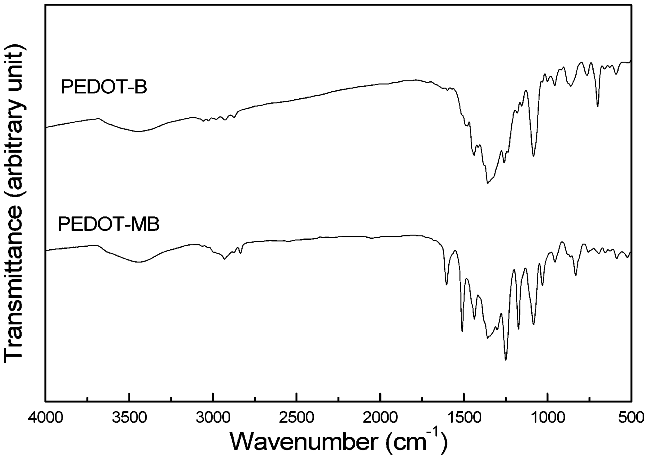

Figure 4. FTIR spectra of the **PEDOT-B** and **PEDOT-MB** in the range of 400−4000 cm^{-1}.

proton, which suggests that the **PEDOT-MB** is not fully dehydrogenated. Integration of this resonance peak gives 0.28 proton, which suggests the **PEDOT-MB** consisted of 72% of conjugated and 28% of nonconjugated segments, respectively. A similar result is also obtained for the case of the **PEDOT-B**, which has a degree of dehydrogenation of 68%.

Figure 4 shows FTIR spectra of the **PEDOT-B** and **PEDOT-MB** in the range of 400−4000 cm^{-1}. The absorption band at 1080 cm^{-1} is assigned to the C−O−C stretching vibration band of the EDOT ring. The bands at 1440 and 1500 cm^{-1} of Figure 4 are assigned to the C=C symmetric and anti-symmetric stretching vibration bands of the EDOT ring. The absorption band at 1600 cm^{-1} is contributed from both the C=C stretching of the phenyl side group and the quinoid EDOT, which is similar to that reported previously on the IR spectra of **PTM**.[4d,e] The bands at 2900−3000 cm^{-1} are assigned to the C−H stretching vibration bands of the thiophene and phenyl rings, and those at wavenumbers higher than 3000 cm^{-1} are the C−H stretching vibrations of the ethylenedioxy moiety, undehydrogenated methylene moiety, or *p*-methoxybenzylidene. The absorption band at 1250 cm^{-1} in the spectrum of the **PEDOT-MB** is assigned to the C−O−C stretching vibration of the side group. The FTIR result suggests the prepared polymers have the proposed structures of **3** shown in Chart 1.

The obtained polymers **3** are soluble in the most common solvents such as THF, chloroform, and *N*,*N*-dimethylformaldehyde (DMF). The average molecular weights (M_n, M_w) measured by GPC with respect to polystyrene standard are (732, 1006) and (801, 1034), respectively. The repeating units of the **PEDOT-B** and **PEDOT-MB** are estimated to be 3.2 and 3.1, respectively, based on the GPC results. This result suggests that the prepared polymers are basically low molecular weight polymers or oligomers. However, optical quality films could be prepared from the polymers **3**. Hence, the actual molecular weights of polymers **3** are probably higher than those from the GPC results. The elemental analysis result on the **PEDOT-B** and **PEDOT-MB** shows a fair agreement with the theoretical values. The 1−2.6% difference in the expected carbon or sulfur content is due in part to the effects of the end groups (e.g., HSO_4) and low molecular weight of the synthesized polymers.

Because the degrees of dehydrogenation on the **PEDOT-B** and **PEDOT-MB** are 0.68 and 0.70, respectively, we attempted to further dehydrogenate the polymers by an oxidation agent, such as 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ). However, it was not successful in obtaining completely dehydrogenated polymer, which was probably due to the steric hindrance of the bulky side group or the methine hydrogen of the polymer end group.

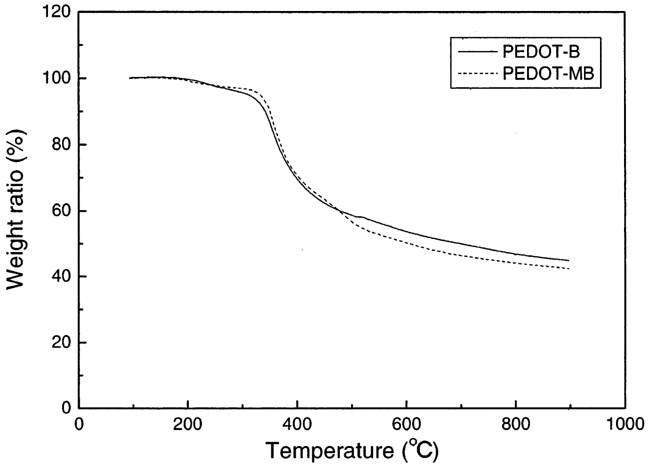

Figure 5. The TGA curves of the **PEDOT-B** and **PEDOT-MB** obtained in flowing N_2 at a heating rate of 20 °C/min.

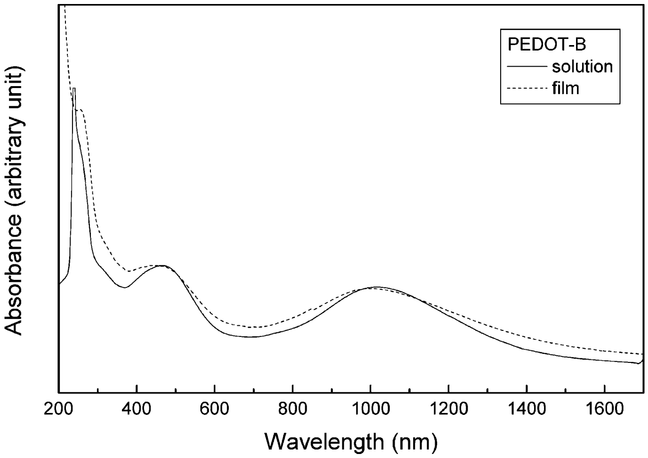

Figure 6. The UV−vis−NIR absorption spectra of the **PEDOT-B** solution in THF and its corresponding film on quartz.

Polymer Properties. Figure 5 shows the TGA curves of the polymers **3** under the nitrogen atmosphere. The thermal decomposition temperatures of the **PEDOT-B** and **PEDOT-MB** are 312 and 333 °C, respectively. This result suggests that the polymers **3** have a fairly good thermal stability. There is no observable glass transition point (T_g) observed in the DSC curves. However, there is a T_g in the previously reported **PTM** with the phenyl side group.[4d] This suggests that the **PEDOT-B** with the EDOT ring has a more rigid backbone than the previous reported **PTM** with the thiophene ring.[4d]

Figure 6 shows the UV−vis−NIR absorption spectra of the **PEDOT-B** solution in THF and their corresponding films on quartz. Both the spectra of the solution and the film show the absorption bands at similar positions. For the case of the polymer film, it shows three major absorption bands with the absorption maximum (λ_{max}) at 255, 437, and 1002 nm, respectively. The UV absorption band with the λ_{max} at 255 nm is assigned to the aromatic benzene or thiophene ring. The strong visible

Table 2. The Optical and Electrochemical Properties of the PEDOT-B and PEDOT-MB

	optical absorption (λ_{max})			oxidation (vs SCE)			reduction (vs SCE)			
polymer	solution (in THF)	film	E_g (eV)[a]	E_p (V)	E_{on} (V)	IP (eV)	E_p (V)	E_{on} (V)	EA (eV)	E_g (eV)[b]
PEDOT-B	241, 465, 1018	255, 437, 1002	0.87	0.48	−0.18	4.22	−1.52	−1.23	3.17	1.05
PEDOT-MB	245, 459, 1023	315, 483, 1053	0.86	0.03	−0.30	4.10	−1.60	−1.31	3.09	1.01

[a] Determined from the band edge of the optical absorption spectrum on polymer film. [b] Determined from the difference of IP − EA.

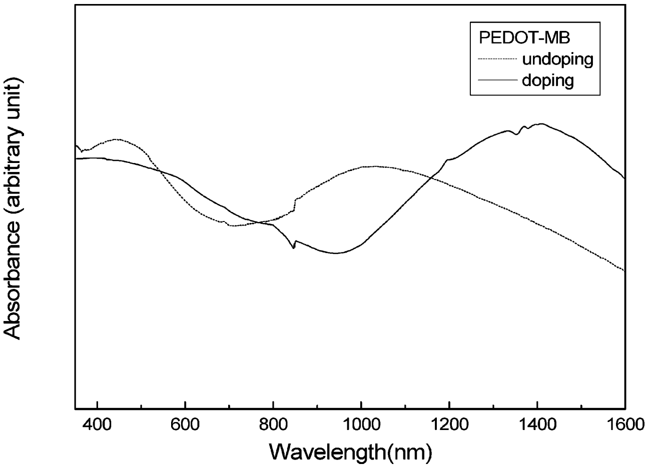

Figure 7. The UV−vis−NIR absorption spectra of the **PEDOT-MB** film before and doping with iodine.

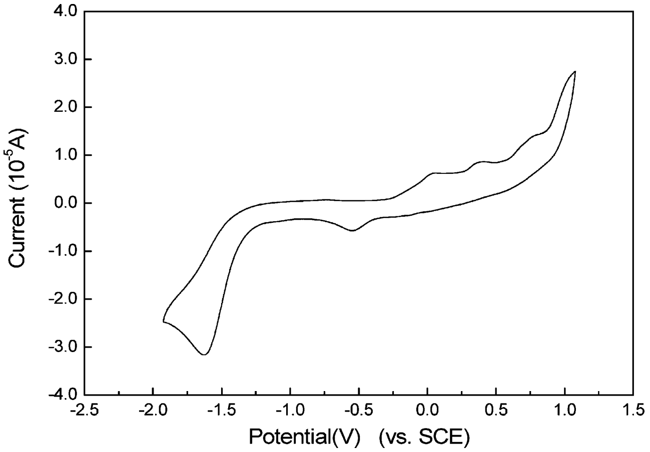

Figure 8. Cyclic voltammogram of the **PEDOT-MB** in 0.1 M TBABF$_4$/acetonitrile solution at a sweep rate of 50 mV/S.

and NIR absorption region indicates that there are highly conjugated moieties in the **PEDOT-B**. The difference between the visible and NIR absorption bands might be due to the different degree of conjugation in the polymer backbone. The **PEDOT-MB** also shows a feature on the absorption band similar to that of the **PEDOT-B**, as shown in Table 2. The estimated optical band gaps of the **PEDOT-B** and **PEDOT-MB** are about 0.87 and 0.86 eV, respectively. The slightly smaller band gap of the **PEDOT-MB** than that of the **PEDOT-B** is due to the electronic donating effect of the methoxy side group because their degrees of dehydrogenation are similar. The obtained optical band gaps of the polymers **3** are larger than the reported electrochemical band gap of 0.4 eV for the **PEDOT-M**.[13] It is probably due to the partially conjugated backbone or the steric hindrance from the bulky side group of the prepared polymers **3**. Figure 7 shows the UV−vis−NIR absorption spectra of the **PEDOT-MB** film before and after doping. By doping with iodine vapor, a new absorption band with the λ_{max} at 1409 nm is shown for the **PEDOT-MB**. The new band is assigned due to doping, which has a feature similar to that reported on the electrochemically prepared methine-bridged PEDOT.[13] The conductivities of the doped polymers **3** are around 10^{-6}∼10^{-7} S/cm. The relatively low conductivity might be due to the low carrier mobility, which comes from the low molecular weight of the prepared polymers.

The electronic structure and properties of the polymers **3** were further investigated by cyclic voltammetry. Figure 8 shows the cyclic voltammogram (CV) of the **PEDOT-MB** in the potential range from −2 to 1 V (vs SCE) at the sweep rate of 50 mV/S. The peak potentials (E_p) for the electrochemical oxidation and reduction of the **PEDOT-MB** are shown at +0.03 and −1.60 V, respectively. The onset potentials (E_{on}) for the oxidation and reduction of the **PEDOT-MB** are shown at −0.30 and −1.31 V, respectively, which correspond to an ionization potential (IP) of 4.10 eV and an electron affinity of 3.09 eV, respectively. Hence, the electrochemical band gap of the **PEDOT-MB** is 1.01 eV, which is higher than the optical band gap of 0.86 eV. However, both the electrochemical and the optical band gap confirm that the **PEDOT-MB** is a small band gap polymer. The electrochemical properties of both **PEDOT-B** and **PEDOT-MB** are listed in Table 2. As shown in Table 2, the IP of the **PEDOT-MB** is smaller than that of the **PEDOT-B**, which is due to the electron-donating methoxy substitution of the former. Besides, the electron-donating side group is expected to be more difficult to reduce, and thus the EA of the **PEDOT-MB** is smaller than that of the **PEDOT-B**. The electrochemical band gap of the **PEDOT-B** is estimated to be 1.05 eV, which again confirms the small band gap characteristic.

Conclusions

Both theoretical and experimental studies demonstrated the characteristics of the small band gap of the methine-bridged PEDOT. The theoretical analysis suggested that the small bond length alteration of the **PEDOT-M** resulted in a relatively low band gap of 0.48 eV. Soluble methine-bridged poly(3,4-ethylenedioxythiophenes) were successfully synthesized by the acid-catalyzed polymerization. The synthesized polymers were found to be highly dehydrogenated and resulted in the conjugated backbone of alternating aromatic and quinoid EDOT segment. The optical and electrochemical band gaps of the synthesized polymers were 0.86−0.87 and 1.01−1.05 eV, respectively. The present study suggests that the approach of incorporating both aromatic and quinoid moieties into the conjugated polymers could achieve a very small band gap polymer.

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Supporting Information Available: Cyclic voltammogram of the **PEDOT-B** in 0.1 M TBABF$_4$/acetonitrile solution. This material is available free of charge via the Internet at http://pubs.acs.org.

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