Structure/Properties of Conjugated Conductive Polymers. 2. 3-Ether-Substituted Polythiophenes and Poly(4-methylthiophene)s

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ABSTRACT: Two series of 3-substituted polythiophenes (PTs) and poly(4-methylthiophene)s (P4MTs) having the substituents containing 8 atoms in the backbone with oxygen as the first atom bonded to the thiophene ring, $C_7H_{15}O$–, $C_4H_9OC_2H_4O$–, and $CH_3OC_2H_4OC_2H_4O$– for the former series and having the first two substituents for the latter series were synthesized by chemical polymerization using ferric chloride as the oxidizing agent and characterized using thermal analysis, various spectroscopic methods, cyclic voltammetry, and conductivity measurement. For the first series, in comparison with poly(3-octylthiophene) (P3OT; λ_{max} = 480 nm), a replacement of the first carbon attached to the thiophene ring by an oxygen atom leads to a decreased band gap (λ_{max} = 580 nm) due to the electron-donating nature of the oxygen. Further substitution on the 4-position of the thiophene ring with the methyl group of the 3-substituted PT with the substituent $C_7H_{15}O$– leads to an increase in the band gap due to a decrease in conjugation caused by a steric hindrance of the methyl group as reflected in the change of λ_{max} from 580 to 420 nm. But its oxidation potential (0.76 V) is lower than that of P3OT (1.01 V) due to electron donation to the π system by the oxygen. Additional replacement of the third carbon atom by an oxygen atom in the side chain (giving $C_4H_9OC_2H_4O$–) improves the conjugation (as reflected by an increase in λ_{max} to 530 nm and a decrease in the oxidation potential to 0.6 V) due to a strong interaction between neighboring side chains, such that no thermochromism is observed before a decomposition of side chains.

Introduction

Polythiophene (PT) is an environmentally stable conjugated polymer in both neutral and doped forms having a conductivity as high as 500 S/cm[1] and therefore has been extensively investigated. Introducing a flexible side chain such as an alkyl group with carbon number four or more on the 3-position of the thiophene ring allows the polymer to become soluble in common organic solvents, fusible, and melt processable while retaining a rather high conductivity, about 30–100 S/cm, after doping.[2–4] In order to control optical, electrical, and electrochemical properties of poly(3-alkylthiophene)s (P3AT), introduction of various numbers of oxygen atoms at various positions in the side chain has been attempted.[5–12]

Incorporation of an alkoxy group with carbon number varying from 1 to 15 on the 3-position of the thiophene ring gives polymers with an optical absorption maximum at 475–530 nm comparable with those of P3ATs but with a lower conductivity of about 10^{-4}–10^{-2} S/cm after electrochemical doping due to lower molecular weight (MW) and with a lower oxidation potential due to electron-donating characteristics of the oxygen.[6–8] The polymers are soluble in organic solvents even after doping up to 20%. Further substitution on the 4-position with a methyl group leads to an improved conductivity of about 5–220 S/cm after electrochemical doping and an increased wavelength of the optical absorption maximum of about 530–550 nm.[6] But the polymers become insoluble after the doping. Both series of polymers are also environmentally stable. Comparison of these results from various research groups indicates that the solubility of doped poly(3-alkoxythiophene)s must result from their very low MW and perhaps defects due to α,β' coupling. The reason is that the steric hindrance due to the additional methyl group on the 4-position of the ring is expected to give a decreased conjugation and increased solubility, but the results are contrary to this expectation.

A disubstitution on the 3- and 4-positions of the thiophene ring with methoxy groups gives an amorphous material with an optical absorption maximum at 550 nm and a high conductivity of 64 S/cm after electrochemical doping, which is stretchable up to 1.2 times to give an increased conductivity of 120 S/cm along the stretching direction.[9] However, disubstitution with butoxy groups leads to a drop of the absorption maximum to 460 nm due to an increased steric hindrance introduced by the substituents which causes a decreased conjugation in the main chain.[10] Disubstituted thiophene with an ethylenedioxy group after polymerization with ferric chloride in poly(vinyl acetate) gives a very environmentally stable, chemically doped polymer dispersed in poly(vinyl acetate). The composite material has a surface resistance of 10^2–10^5 ohm (size of the sample was not specified) and has an environmental stability comparable with that of doped polypyrrole.[11]

As to the effects of the location of the oxygen atom in the side chain, replacing the second carbon atom with an oxygen atom in the poly(3-dodecylthiophene) gives a lower conductivity after doping than that at the third carbon. This was attributed to the electron-withdrawing effect of the oxygen located on the second position of the side chain.[12] For effects of the number of ethyleneoxy groups ($-C_2H_4O-$) on the same side chain terminated by a methyl group, the polymer with two ethyleneoxy groups has a higher conductivity after electrochemical doping than those with one and three ethyleneoxy groups.[12] However, if the first ethyleneoxy group is replaced by a methyleneoxy ($-CH_2O-$) group, the polymer with another two ethyleneoxy groups on the side chain has a much higher conductivity than the other two polymers.[13]

From the work reviewed above, it is known that the locations and number of oxygen atoms in the side chain have significant effects on the optical and electrical properties of the substituted polythiophenes. However, only optical spectroscopy, cyclic voltammetry, and conductivity at room temperature were investigated. This

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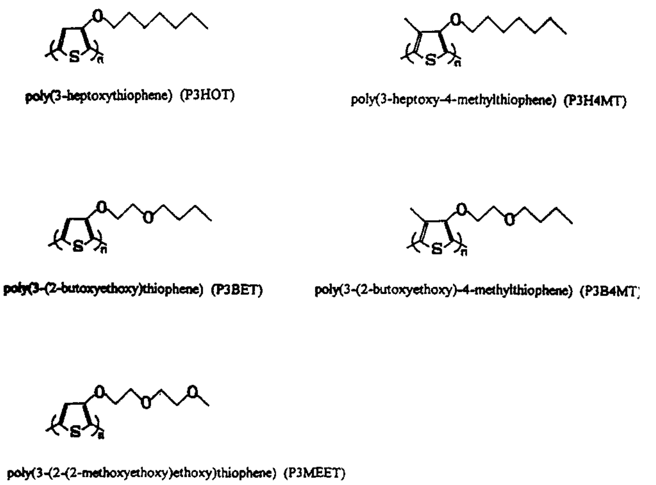

Figure 1. Chemical structures of the substituted polythiophenes investigated.

work is undertaken to investigate effects of the electron donation nature of the oxygen atoms attached to the ring on the band gap and oxidation potential and on the stereoregularity of the main chains for the two new series of 3-substituted polythiophenes and poly(4-methylthiophene)s with the substituents having the following chemical structures: $C_7H_{15}O-$, $C_4H_9OC_2H_4O-$, and $CH_3OC_2H_4OC_2H_4O-$. A comparison of the properties with those of poly(3-octylthiophene) (P3OT) is also made.

Experimental Section

1. **Synthesis of Monomers.** All of the monomers were prepared each starting from 3-bromothiophene or 3-bromo-4-methylthiophene by reaction with the reaction product of sodium with heptanol, 2-butoxyethanol, or 2-(2-methoxyethoxy)ethanol in the presence of copper oxide and potassium iodide as catalyst following the procedure reported by Bryce et al.[14] Identifications of the monomers using ^{1}H-NMR and mass spectrometry are reported below, which confirm the expected structures of the monomers.

3-Heptoxythiophene (3HOT): ^{1}H-NMR ($CDCl_3$, ppm) (3 H, t), 1.30–1.50 (8 H, m), 1.76–1.83 (2 H, m), 3.95 (2 H, t), 6.23 (1 H, dd), 6.78 (1 H, dd), 7.18 (1 H, dd); MS 198 (M^+).

3-(2-Butoxyethoxy)thiophene (3BET): ^{1}H-NMR ($CDCl_3$, ppm) 0.91 (3 H, t), 1.34–1.40 (2 H, m), 1.54–1.60 (2 H, m), 3.50 (2 H, t), 3.74 (2 H, t), 4.08 (2 H, t), 6.24 (1 H, dd), 6.76 (1 H, dd), 7.13 (1 H, dd); MS 200 (M^+).

3-[2-(2-Methoxyethoxy)ethoxy]thiophene (3MEET): ^{1}H-NMR ($CDCl_3$, ppm) 3.34 (3 H, s), 3.52 (2 H, t), 3.65 (2 H, t), 3.79 (2 H, t), 4.07 (2 H, t), 6.20 (1 H, dd), 6.72 (1 H, dd), 7.11 (1 H, dd); MS 202 (M^+).

3-Heptoxy-4-methylthiophene (3H4MT): ^{1}H-NMR ($CDCl_3$, ppm) 0.88 (3 H, t), 1.25–1.46 (8 H, m), 1.74–1.81 (2 H, m), 2.08 (3 H, s), 3.92 (2 H, t), 6.11 (1 H, dd), 6.80 (1 H, dd); MS 212 (M^+).

3-(2-Butoxyethoxy)-4-methylthiophene (3B4MT): ^{1}H-NMR ($CDCl_3$, ppm) 0.91 (3 H, t), 1.32–1.42 (2 H, m), 1.52–1.61 (2 H, m), 2.15 (3 H, s), 3.52 (2 H, t), 3.77 (2 H, t), 4.07 (2 H, t), 6.14 (1 H, dd), 6.80 (1 H, dd); MS 214 (M^+).

2. **Synthesis of Polymers and Preparation of Samples.** Neutral 3-substituted polythiophenes and poly(4-methylthiophene)s (Figure 1) were prepared from the monomers mentioned above following the chemical method used by Sugimoto et al.[15] for poly(3-alkylthiophene)s. A 0.1 M monomer was oxidation-polymerized in a 0.4 M $FeCl_3$ solution in chloroform at room temperature under a nitrogen atmosphere for about 24 h. The resulting mixture was then poured into methanol for precipitating out the polymer. This polymer was then washed several times with methanol and then extracted with methanol in a Soxhlet extractor in order to remove the residual oxidant and oligomers. Undoped polymer was obtained by reduction with an aqueous solution of hydrazine. The purified polymer, after dynamic vacuum pumping until a constant weight was retained, was ready for physical characterizations. Chemical doping of the polymers so obtained was performed by soaking the neutral powdery polymer (0.2–0.3 g) in 25 mL of a 0.1 M $FeCl_3$ solution in nitromethane for 1 h; the precipitate was washed with nitromethane and then dried under a dynamic vacuum until a constant weight was reached.

Table I
Solubility in Organic Solvents and Average Molecular Weight of the Substituted Polythiophenes[a,b]

polymer	solvent $CHCl_3$	 THF	 DMF	M_w	M_n	M_w/M_n
P3HOT	Δ	Δ	Δ	2164[c]	1387	1.6
P3BET	Δ	Δ	Δ	2711[c]	1420	1.9
P3MEET	Δ	Δ	Δ	1002[c]	860	1.2
P3H4MT	○	○	○	22777	5404	4.2
P3B4MT	Δ	Δ	○			

[a] P3HOT, poly(3-heptoxythiophene); P3BET, poly[3-(2-butoxyethoxy)thiophene]; P3MEET, poly[3-[2-(2-methoxyethoxy)ethoxy]thiophene]; P3H4MT, poly(3-heptoxy-4-methylthiophene); P3B4MT, poly[3-(2-butoxyethoxy)-4-methylthiophene]. [b] Δ, partially soluble; ○, soluble. [c] Average MW of oligomer fractions.

3. **Characterizations.** Gel permeation chromatography (Waters Model 201) with a UV detector at 400 nm and a column of Ultrastyragel linear P/N 10681 from Waters was used to measure the molecular weight distribution (MWD) relative to the polystyrene standards. The calibration curve was determined by use of 10 MW standards from a MW of 800–10^6. The carrier solvent used was tetrahydrofuran at a flow rate of 1 mL/min.

X-ray diffractions were measured using a Rigaku Model D/Max-2B diffractometer. The X-ray beam was nickel-filtered Cu Kα (λ = 0.1506 nm) radiation from a sealed tube operated at 30 kV and 20 mA. Data were obtained from 1° to 45° (2θ) at a scan rate of 1°/min with a smoothing number of 7.

A thermogravimetric analyzer (TGA; Perkin-Elmer Model TGS-2) was used to observe the weight loss of the polymers under a nitrogen atmosphere from 40 to 470 °C with a heating rate of 10 °C/min.

Ultraviolet–visible spectra (UV-vis) at −150 to +250 °C were recorded using an UV-vis-near-IR spectrophotometer (Perkin-Elmer Model Lambda 19). The spectrophotometer was equipped with a variable-temperature cell to allow measurement of the spectra under vacuum from −150 to +250 °C; the soaking time was 10 min at each specific temperature, and the heating rate used was about 1–2 °C/min during heating. The testing sample was prepared by coating the polymer solution in chloroform on a piece of glass and allowing it to dry to give a coated film.

Cyclic voltammetry was carried out in a one-compartment cell using an EG&G Princeton Applied Research (Model 173) potentiostat/galvanostat. These measurements were performed in dry acetonitrile with tetrabutylammonium hexafluorophosphate (0.1 M) as the electrolyte, using a platinum strip (1 × 3 cm) coated with the neutral polymer to be tested as a working electrode and a blank platinum strip of the same size as a counter electrode at a scan rate of 50 mV/s versus a standard calomel electrode (SCE).

Results and Discussion

1. **Molecular Weight and Solubility.** The 3-substituted polythiophenes and poly(4-methylthiophene)s so prepared were tested for their solubilities in the three organic solvents: chloroform, tetrahydrofuran (THF), and *N,N*-dimethylformamide (DMF). All the 3-substituted polythiophenes (PTs) are insoluble due to cross-linking by α,β' coupling between thiophene rings as reflected in the presence of a much weaker IR absorption peak at 824 cm^{-1} (due to C–H out-of-plane deformation of the thiophene ring) in comparison with that of the poly(3-octylthiophene) (P3OT), and only their oligomer fractions with a MW of a few thousand (Table I) are soluble. For the 3-substituted poly(4-methylthiophene)s (P4MTs), P3H4MT is soluble and has a MW of about 2×10^4 (relative to polystyrene standards), while P3B4MT is only partially

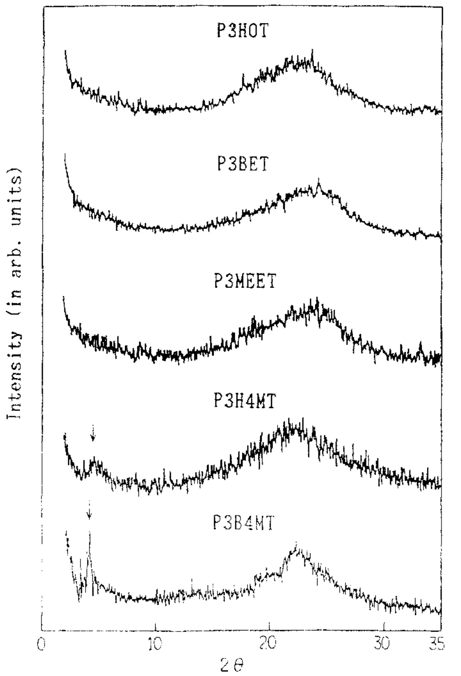

Figure 2. X-ray diffraction patterns of the substituted polythiophenes.

soluble in chloroform and THF but completely soluble in the highly polar solvent DMF. Thus the MW of P3B4MT is not measured (since DMF is not suitable to be used as a carrier solvent for the Ultrastyragel column) and is believed to be also on the order of 10^4. The solubility results indicate that introduction of more oxygen atoms in the side chain causes the polymer to become highly polar and only soluble in highly polar solvents.

2. X-ray Diffractions. X-ray diffraction patterns of the 3-substituted PTs and P4MTs are shown in Figure 2. Each of the three 3-substituted PTs is amorphous and has only a broad, single diffused scattering peak with a maximum intensity at about 22–24°, indicating that no crystallinity can be observed by the X-ray diffraction. For the two 3-substituted P4MTs, each has a broad, diffused scattering peak at a wide angle of about 22.5° and has a small peak at a low angle of about 4.5°. Besides, for P3B4MT, an additional peak with an appreciable intensity also appears at a wide angle of about 23°, and the peak at low angle is sharper than that of P3H4MT.

The above results for the 3-substituted P4MTs would indicate that introduction of an additional oxygen atom in the side chain leads to an increase in interplanar and intraplanar packing and therefore to an increase in crystallinity. The 3-substituted PTs are expected to have a better stereoregularity than the corresponding 3-substituted P4MT. The amorphous structure can be attributed to a cross-linking by α,β' coupling between thiophene rings.

3. Thermogravimetric Analysis (TGA). Thermogravimetric analysis (TGA) curves of the two neutral 3-substituted P4MTs are shown in Figure 3. The onset temperatures of weight loss are 133 and 164 °C for P3H4MT and P3B4MT, respectively. In both cases the weight losses increase rapidly from the onset temperature at about 130–160 °C up to about 390 °C and then slowly down above this temperature. P3B4MT has a weight loss *with a temperature* faster than P3H4MT.

The weight loss between the onset temperature and 390 °C is due to a cracking of the side chains as can be manifested by allowing the two polymers to stand at the typical side-chain decomposition temperatures 250 °C for P3B4MT and 280 °C for P3H4MT for 10 min under a nitrogen stream and then subjecting them to IR examination at room temperature. The IR absorptions at 1080 and 1035 cm^{-1} due to C–O vibration almost disappear in both cases (see the insets in Figure 3). The main-chain cracking is unlikely to occur below 390 °C since the onset temperatures of weight loss of P3ATs are about 400 °C.[16,17]

4. Ultraviolet–Visible Spectroscopy (UV–Vis). For the neutral 3-substituted PT oligomer solutions and 3-substituted P4MTs in chloroform the UV–vis spectra are shown in Figure 4. The absorption maxima for the former (580–590 nm) are higher than that of P3OT in chloroform (440 nm)[18] and in solid form (480 nm),[19] indicating that introducing an oxygen on the first position of the side chain leads to a lower band gap; even their MWs are very low and molecular chains are coillike. This can be attributed to the electron-donating nature of this oxygen atom, since their conjugating lengths are expected

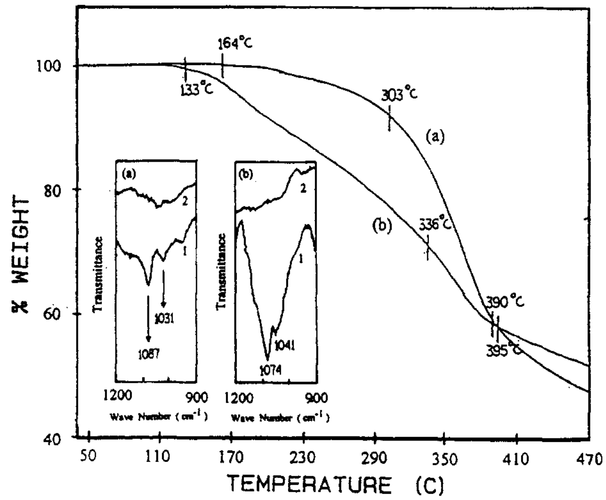

Figure 3. TGA curves of the 3-substituted poly(4-methylthiophene)s: (a) neutral P3H4MT, (b) neutral P3B4MT. The insets are IR transmittances in the range 900–1200 cm^{-1} of these two polymers before (curve 1) and after the heat treatment for 10 min (curve 2): (a) P3H4MT; (b) P3B4MT.

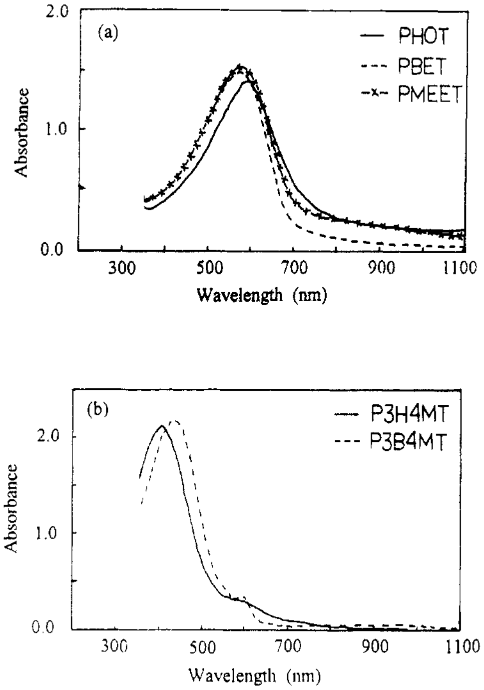

Figure 4. UV–vis absorption spectra of the substituted polythiophenes in $CHCl_3$ at room temperature: (a) the 3-substituted PTs; (b) the 3-substituted P4MTs.

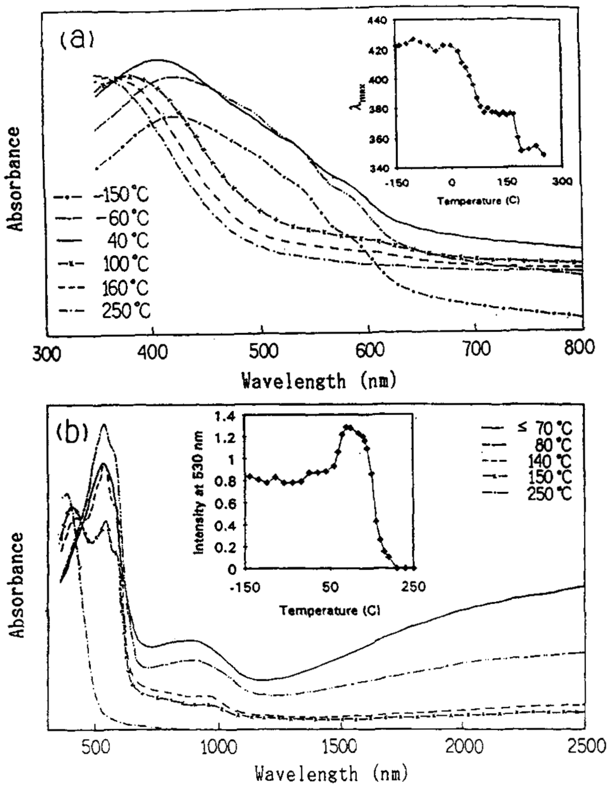

Figure 5. UV–vis absorption spectra of the 3-substituted poly(4-methylthiophene) thin films at various temperatures from −150 to +250 °C: (a) P3H4MT; (b) P3B4MT.

to be shorter than that of P3OT due to their amorphous characteristics in the solid state as reflected in the X-ray diffraction patterns above. For the latter series, the absorption maxima, 408 nm for P3H4MT and 436 nm for P3B4MT, are shorter than those of the former series and P3OT, indicating that the additional methyl substitution introduces a steric hindrance and results in a shorter conjugation length and higher band gap. While the longer λ_{max} of P3B4MT than P3H4MT might reflect a slight increase in conjugation by the additional replacement of the third carbon atom by an oxygen atom in the side chain of the latter, this oxygen atom (which gives no effect on the electron-donating nature of the first oxygen) might provide an enhanced side-chain interaction.

For thin solid films of the neutral 3-substituted P4MTs, the absorption maximum of P3H4MT (420 nm) is slightly higher than that in solution but is still much lower than those of the neutral 3-substituted PTs. Its UV–vis spectra at various temperatures from −150 to +160 °C (Figure 5a) show a drop of the wavelength at the absorption maximum by about 40 nm (see the inset in Figure 5a), indicating a very weak thermochromism. As the temperature further increases to above 160 °C, the absorption maximum drops rapidly. This is due to the cracking of side chains which results in a loss of the electron-donating "oxygen" atom (as indicated in the TGA selection above) and therefore in a rise in band gap. As an additional oxygen is added to replace the third carbon in the side chain which yields P3B4MT, the absorption maximum increases to 535 nm (Figure 5b), indicating an increase in the conjugation length, since this additional oxygen would not donate electrons to the thiophene ring. Polaron/bipolaron absorptions above 700 nm appear, indicating that a trace amount of dopant still remains in the sample even after Soxhlet extraction for several days. As temperature increases from −150 °C (no appreciable change in spectra as the temperature is varied from −150 to +70 °C) to 80 °C, thermal undoping starts and leads to a decrease in the polaron/bipolaron absorptions and an increase in the absorption due to π–π^* transition (see the inset in Figure 5b). Thus, the constant wavelength of the absorption maximum at 530 nm and the increase in the wavelength of the absorption maximum at solid state by 94 nm over that at solution state indicate an increase in conjugation due to a strong polar interaction between the side chains, as indicated in the enhanced X-ray diffraction intensities at low and wide angles due to an increased stereoregularity of the side chains and main chains. As the temperature further increases to 140 °C, the location of the absorption maximum still remains unchanged, but a new peak at a lower wavelength of about 470 nm is generated, resulting from a loss of parts of side chains due to thermal decomposition (as revealed in the TGA section). As the temperature increases to 250 °C, the original absorption maximum shifts to 450 nm. The retention of the original absorption maximum (at 535 nm) up to 140 °C is rather unusual, which was not observed for P3OT, for which a thermochromism (resulting from a rod-to-coil transition due to a melting of the ordered phase) occurs in the range of about 100–150 °C.[19-21] This means that no main-chain melting occurs before cracking of the side chains. Thus, a very strong mutual interaction between the neighboring side chains might exist, which prevents the main chains in the ordered phase from melting at the elevated temperature. The enhanced interaction between side chains due to introduction of the additional oxygen (P3B4MT) is also evidenced by its solubility in DMF and insolubility in THF and chloroform compared with the solubility of P3H4MT in all three of these solvents (Table I).

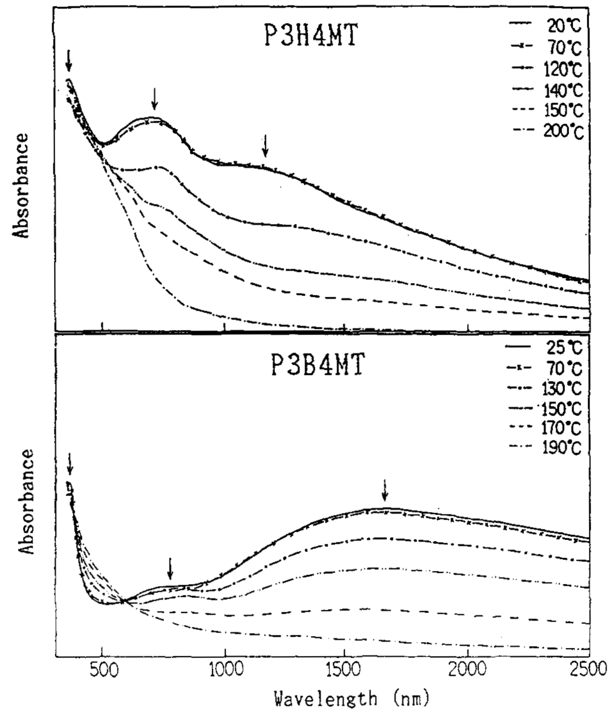

Figure 6. UV–vis absorption spectra of the $FeCl_3$-doped, 3-substituted poly(4-methylthiophene) thin films from room temperature to 200 °C.

After doping with $FeCl_3$ in nitromethane, the UV–vis spectra of P3H4MT and P3B4MT thin films show typical polaron/bipolaron absorptions, having two characteristic peaks above 700 nm as shown in Figure 6. The absorption peak at 363 nm is due to the presence of the dopant counterion $FeCl_4$.[22] As the temperature increases from 20 to 190 °C, the polaron/bipolaron absorption characteristic peaks disappear gradually. Finally, only one

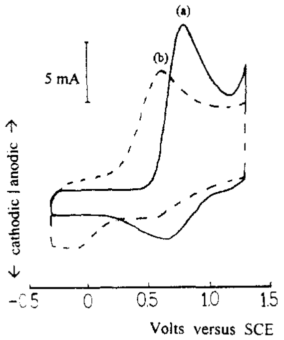

Figure 7. Cyclic voltammograms of the 3-substituted poly(4-methylthiophene)s at the scanning rate 50 mV/s in a 0.1 M Bu$_4$NPF$_6$ solution in acetonitrile with a standard calomel electrode (SCE) as the reference electrode: (a) P3H4MT; (b) P3B4MT.

Table II
Oxidation and Reduction Potentials of the Substituted Polythiophenes vs SCE at the Scanning Rate 50 mV/s in a 0.1 M Bu$_4$NPF$_6$ Solution in CH$_3$CN

polymer[a]	E_{pa}, V	E_{pc}, V
P3H4MT	0.76	0.65
P3B4MT	0.60	0.50
P3OT[b]	1.01	0.94

[a] Notations for the polymers are the same as those for Table I. [b] P3OT: poly(3-octylthiophene). Data taken from ref 23.

absorption peak at about 350 nm is observed for both polymers. The spectra of the doped polymers do not return to their original spectra before doping. This is due to the decomposition of side chains and perhaps main chains also, causing a serious disruption of the conjugation in the main chains. This is quite different from FeCl$_3$-doped P3OT, for which the absorption maximum after thermal undoping is 410 nm, which is lower than that of the neutral form by only 70 nm. In addition, a comparison of the polaron/bipolaron absorptions in both doped 3-substituted P4MTs (which were doped under the same conditions) exhibits that the doped P3B4MT has a bipolaron band having a lower gap with the valence band than that of P3H4MT as indicated in the presence of a broad absorption peak (1700 nm) with moderate intensity and a weak peak at 800 nm of P3B4MT. For P3H4MT the absorption peak at about 700 nm is significantly higher than that at 1200 nm (present as a shoulder), indicating a dominant polaron state. These observations from absorption spectra also support that the introduction of the additional oxygen atom in the side chain does improve the conjugation in the main chain.

5. Electrochemical Doping/Undoping (Cyclic Voltammetry). Potential scans on a P3H4MT- or P3B4MT-coated Pt strip as the working electrode versus a blank Pt strip as the counter electrode in an electrolyte solution of 0.1 M Bu$_4$NPF$_6$ in acetonitrile from −0.3 to +1.3 V versus SCE were carried out. Their cyclic voltammograms (CV) at the scanning rate 50 mV/s are shown in Figure 7. During the doping/undoping cycle, P3H4MT shows the color change orange-yellow → blue-green → orange-yellow, while P3B4MT has the change violet → green → violet. The oxidation and reduction potentials (E_{pa} and E_{pc}) in the potential scans are listed in Table II. As can be seen, E_{pa} values are in the order P3OT > P3H4MT > P3B4MT, indicating that E_{pa} decreases with an increase in the number of oxygen atoms in the side chain. Although the band gap of P3OT (λ_{max} = 480 nm) is higher than that of P3H4MT (λ_{max} = 430 nm), E_{pa} of the former is higher than that of the latter. In addition, the band gap of P3B4MT (λ_{max} = 530 nm) is lower than P3H4MT (λ_{max} = 430 nm) due to its higher conjugation in the main chain as revealed above. These results would indicate that E_{pa} depends not only on the band gap but also on the electron density in the π system due to the presence of the electron-donating oxygen atom on the first position of the side chain. Further substitution on the 4-position by a methyl group on the thiophene ring of the 3-substituted PT with the substituent C$_7$H$_{15}$O– leads to an increase in the band gap (as reflected in the change of λ_{max} from 590 to 420 nm) due to the decreased conjugation due to a steric hindrance caused by the methyl group. However, additional replacement of the third carbon atom by an oxygen atom in the side chain (giving C$_4$H$_9$OC$_2$H$_4$O–) improves the conjugation. Upon opening the circuit after the doping, self-undoping to some extent occurs, as can be observed from a color change of the polymer film on the electrode. For the doped P3B4MT, the conductivity of the film peeled off from the electrode is about 10^{-2}–10^{-3} S/cm as measured by use of the four-point method. The neutral P3B4MT has a conductivity of 10^{-7} S/cm.

Conclusion

Chemically synthesized 3-substituted polythiophenes with C$_7$H$_{15}$O–, C$_4$H$_9$OC$_2$H$_4$O–, and CH$_3$OC$_2$H$_4$OC$_2$H$_4$O– as substituents are found to be insoluble (except their oligomers) in organic solvents due to cross-linking by α,β' coupling between thiophene rings. For the oligomers, a replacement of the carbon atom attached to the ring of poly(3-octylthiophene) (λ_{max} = 440 nm, in chloroform) by an oxygen atom can lower the band gap significantly (λ_{max} = 580–590 nm, in chloroform). Further substitution on the 4-position by a methyl group on the thiophene ring of the 3-substituted polythiophene with the substituent C$_7$H$_{15}$O– leads to an increase in the band gap (as reflected in the change of λ_{max} from 590 nm of the polymer in chloroform to 420 nm in solid film form) due to the decreased conjugation due to a steric hindrance caused by the methyl group. However, an additional replacement of the third carbon atom by an oxygen atom in the side chain (giving C$_4$H$_9$OC$_2$H$_4$O–) improves the conjugation (λ_{max} = 530 nm) due to a strong interaction between neighboring side chains such that no thermochromism is observed before a decomposition of side chains. The oxidation potential (E_{pa}) depends not only on the band gap but also on the electron density in the π system as reflected in the sequence of E_{pa} values P3OT > P3H4MT > P3B4MT.

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References and Notes

(1) Sato, M.; Tanaka, S.; Kaeriyama, K. *J. Chem. Soc., Chem. Commun.* **1985**, 713.
(2) Jen, K. Y.; Miller, G. G.; Elsenbaumer, R. L. *J. Chem. Soc., Chem. Commun.* **1986**, 1346.
(3) Rughooputh, S. D. D. V.; Nowak, M.; Hotta, S.; Heeger, A. J.; Wudl, F. *Synth. Met.* **1987**, *21*, 41.
(4) Rughooputh, S. D. D. V.; Hotta, S.; Heeger, A. J.; Wudl, F. *J. Polym. Sci., Polym. Phys. Ed.* **1987**, *25*, 1071.
(5) Winokur, M. J.; Spiegel, D.; Kim, Y.; Hotta, S.; Heeger, A. J. *Synth. Met.* **1989**, *28*, C419.
(6) Feldhues, M.; Kampf, G.; Litterer, H.; Mecklenburg, T.; Wegener, P. *Synth. Met.* **1989**, *28*, C487.
(7) Blankespoor, R. L.; Miller, L. L. *J. Chem. Soc., Chem. Commun.* **1985**, 90.

(8) Chang, A. C.; Blankespoor, R. L.; Miller, L. L. *J. Electroanal. Chem.* **1987**, 236.

(9) Hagiwara, T.; Yamaura, M.; Sato, K.; Hirasak, M.; Iwata, K. *Synth. Met.* **1989**, *32*, 367.

(10) Daoust, G.; Leclerc, M. *Macromolecules* **1991**, *24*, 455.

(11) Jonas, F.; Schrader, L. *Synth. Met.* **1991**, *41-43*, 831.

(12) Roncali, J.; Garreau, R.; Delabouglise, D.; Garnier, F.; Lemaire, M. *Synth. Met.* **1989**, *28*, C341.

(13) Bryce, M. R.; Chissel, A.; Kathirgamanathan, P.; Parker, D.; Smith, N. R. M. *J. Chem. Soc., Chem. Commun.* **1987**, 466.

(14) Bryce, M. R.; Chissel, A. D.; Smith, N. M. R.; Parker, D.; Kathirgamanathan, P. *Synth. Met.* **1988**, *26*, 153.

(15) Sugimoto, R.; Taketa, S.; Gu, H. B.; Yoshino, K. *Chem. Press* **1986**, *1*, 635.

(16) Gustafsson, G.; Inganas, O.; Nilsson, J. O.; Liedberg, B. *Synth. Met.* **1988**, *26*, 297.

(17) Chen, S. A.; Ni, J. M. *Polym. Bull.* **1991**, *26*, 673.

(18) Osterholm, J.-E.; Laakso, J.; Nyholm, P.; Isotalo, H.; Stubb, H.; Inganas, O.; Salaneck, W. R. *Synth. Met.* **1989**, *28*, C435.

(19) Inganas, O.; Gustafsson, G.; Salaneck, W. R. *Synth. Met.* **1989**, *28*, C377.

(20) Chen, S. A.; Ni, J. M. *Makromol. Chem., Rapid Commun.* **1992**, *13*, 31.

(21) Chen, S. A.; Ni, J. M. *Macromolecules* **1992**, *23*, 6081.

(22) Rabek, J. F.; Lucki, J.; Qu, B. J.; Shi, W. F. *Macromolecules* **1991**, *24*, 836.

(23) Roncali, J.; Garreau, R.; Yassar, A.; Marque, P.; Garnier, F.; Lemaire, M. *J. Phys. Chem.* **1987**, *91*, 6706.