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Structure–Property Relationships in Alkoxy-Substituted Polythiophenes

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ABSTRACT: Alkoxy-substituted polythiophenes have been synthesized in very good yields by chemical polymerization using iron(III) chloride as oxidizing agent. The effects of the alkoxy substituents on the physical properties of the resulting polymers were particularly studied. From the structural analysis of poly(3-butoxythiophene) and poly(3,4-dibutoxythiophene), it has been found that a good electrical transport can only be obtained with polymers having a regular α,α'-linked backbone and a planar or nearly planar conformational structure. Poly(3-alkoxy-4-methylthiophenes) meet both requirements, and, therefore, these processable materials exhibit a well-defined conjugated structure and high electrical conductivities (–1 S/cm). Moreover, due to the electron-donating effect of the alkoxy groups, relatively low oxidation potentials (0.60–0.64 V vs SCE) have been observed in these polymers which increase the stability of the conducting state.

Introduction

In the past decade, there has been great interest in the study of conducting polymers due to their potential applications in electrochemical and optical devices.[1] Different conjugated molecules have been investigated, and several aromatic polymers (poly(*p*-phenylene),[2] polypyrrole,[3] polythiophene,[4] etc.) have exhibited high electrical conductivities in conjunction with a good environmental stability. However, characterization and processing of this class of materials have been limited by the inherent insolubility of these compounds. Their rigid-rod nature combined with strong interchain interactions prevents the melting of these materials as well as their dissolution in common organic solvents.

The incorporation of relatively long and flexible side chains is a common technique for preparing soluble polymers having a stiff backbone,[5] and this concept was recently applied to some 3-substituted polythiophenes.[6-9] Indeed, poly(3-alkylthiophenes) have been synthesized and characterized as materials that are either melt or solution processable and highly conducting. Moreover, the design of new thiophene derivatives may be used for developing materials with improved electrical and optical properties. Electropolymerization of 3-alkoxythiophenes has also been studied, but only irregular low molecular weight products exhibiting reduced electrical conductivities were obtained.[10-12] Nevertheless, one advantage of the poly(3-alkoxythiophenes) comes from the electron-donating effect of the alkoxy group, which decreases the oxidation potential of these polymers and, consequently, stabilizes the conducting state.[11]

As shown with the unsubstituted polyacetylene,[13] a decrease of the structural defects (irregular couplings, branchings, cross-linking) is accompanied by an increase of the electrical conductivity. Polymerization of 3,4-disubstituted thiophenes is a convenient way to avoid α,β' couplings and should therefore lead to the synthesis of regular and highly conducting polythiophenes. On the other hand, steric interactions between the substituents and the polymer backbone have to be minimized for obtaining a good electrical transport.[14,15]

In order to get a better knowledge of the influence of the polymer structure on the physical properties of conjugated polymers, we describe here the chemical synthesis and characterization of some soluble alkoxy-substituted polythiophenes, namely, poly(3-butoxythiophene) (PBT), poly(3-butoxy-4-methylthiophene) (PBMT), poly[3-(octyloxy)-4-methylthiophene] (POMT), and poly(3,4-dibutoxythiophene) (PDBT). The poly(3-alkoxy-4-methylthiophenes) have been found to be particularly interesting since they are the first examples of soluble, stable, and highly conducting disubstituted polythiophenes.

Experimental Section

Monomers. Thiophene, 3-methylthiophene, and 3-bromothiophene were obtained from Aldrich Chemical Co. 3-Bromo-4-methylthiophene (bp 178–180 °C, 42% yield) and 3,4-dibromothiophene (bp 104–105 °C/12 mmHg, 20% yield) were synthesized from 3-methylthiophene and thiophene, respectively, following a two-step method developed by Gronowitz et al.[16] 3-Butoxythiophene (BT) was prepared from 3-bromothiophene and sodium butoxide in the presence of copper oxide and potassium iodide,[17] using conditions reported by Bryce et al.[18] This colorless liquid was purified by flash chromatography on silica gel using hexane as eluent (40% yield). The NMR spectra were in good agreement with those previously reported.[18]

BT: Anal. Calcd: C, 61.5; H, 7.7; S, 20.5. Found: C, 61.9; H, 7.6; S, 20.8. ^{1}H NMR (300 MHz, CDCl$_3$, ppm): 1.00 (3 H, t, *J* = 7.3 Hz), 1.52 (2 H, m), 1.79 (2 H, m), 3.97 (2 H, t, *J* = 6.5 Hz), 6.25 (1 H, dd, *J* = 1.5, 3.1 Hz), 6.78 (1 H, dd, *J* = 1.5, 5.2 Hz), 7.18 (1 H, dd, *J* = 3.1, 5.2 Hz). ^{13}C NMR (75.4 MHz, CDCl$_3$, ppm); 13.68, 19.09, 31.16, 69.70, 96.70, 119.35, 124.31, 157.89.

3-Butoxy-4-methylthiophene (BMT) (35% yield) and 3-(octyloxy)-4-methylthiophene (OMT) (38% yield) were also prepared by this method using 3-bromo-4-methylthiophene as starting reagent.

BMT: Anal. Calcd: C, 63.5; H, 8.3; S, 18.8. Found: C, 63.9; H, 8.0; S, 18.9. ^{1}H NMR (ppm): 1.01 (3 H, t, *J* = 7.4 Hz), 1.53 (2 H, m), 1.80 (2 H, m), 2.13 (3 H, s), 3.97 (2 H, t, *J* = 6.4 Hz), 6.16 (1 H, d, *J* = 3.3 Hz), 6.83 (1 H, m). ^{13}C NMR (ppm): 12.50, 13.72, 19.20, 31.23, 69.62, 95.83, 119.56, 129.16, 156.23.

OMT: Anal. Calcd: C, 69.0; H, 9.8; S, 14.1. Found: C, 68.6; H, 10.2; S, 14.2. ^{1}H NMR (ppm): 0.92 (3 H, t, *J* = 7.4 Hz), 1.35 (8 H, m), 1.48 (2 H, m), 1.81 (2 H, m), 2.12 (3 H, s), 3.95 (2 H, t, *J* = 6.5 Hz), 6.15 (1 H, *J* = 3.3 Hz), 6.83 (1 H, m). ^{13}C NMR (ppm): 12.56, 14.00, 22.56, 25.99, 29.12 (two carbon atoms), 29.25, 31.72, 69.87, 95.71, 119.54, 129.11, 156.18.

Following a similar procedure, 3,4-dibutoxythiophene (DBT) was synthesized from 3,4-dibromothiophene and purified by fractional distillation under reduced pressure. 3,4-Dibromothiophene and 3-butoxy-4-bromothiophene were first distilled off, and, finally, 3,4-dibutoxythiophene was recovered (bp 110–111 °C/2.7 mmHg, 22% yield).

DBT: Anal. Calcd: C, 63.1; H, 8.8; S, 14.1. Found: C, 63.3; H, 8.6; S, 14.2. ^{1}H NMR (ppm): 0.98 (3 H, t, *J* = 7.3 Hz), 1.49

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(2 H, m), 1.81 (2 H, m), 3.99 (2 H, t, $J = 6.7$ Hz), and 6.17 (2 H, s). ^{13}C NMR (ppm): 13.61, 19.01, 30.94, 70.03, 96.80, 147.44.

All alkoxy-substituted thiophenes were stored under a nitrogen atmosphere in the dark.

Polymers. The alkoxy-substituted thiophenes were always repurified, as described above, immediately prior to polymerization. These monomers were polymerized by chemical oxidation using anhydrous iron(III) chloride (Fisher Scientific Co.) according to a procedure similar to that of Sugimoto et al.[8] In a 100-mL three-neck flask, 24 mmol of iron(III) chloride was dissolved in 30 mL of chloroform under nitrogen to which a solution of 6 mmol of monomer in 20 mL of chloroform was added dropwise. The mixture was stirred for 24 h at room temperature. The solution was then precipitated into methanol (1 L), and the blue-black precipitate was collected on a Büchner funnel and washed with methanol. Polymers were subsequently washed by Soxhlet extractions using methanol and then dried under reduced pressure. Undoped polymers were obtained by reduction with an aqueous solution of hydrazine (Fisher Scientific Co.). These neutral polymers were redissolved in chloroform, and then the solvent was slowly evaporated under reduced pressure in order to produce thin polymer films. These polymers were washed again by Soxhlet extractions using methanol and finally dried under vacuum (40–60% yields).

Physical Measurements. The elemental analyses were performed by Guelph Chemical Laboratories Ltd. NMR spectra were obtained in deuterated chloroform or methylene chloride solutions on a 300-MHz Bruker pulsed Fourier transform instrument. Infrared spectroscopy was performed by using a Perkin-Elmer 1430 apparatus, and UV–visible spectra were recorded on a Varian DMS 100 instrument. UV–visible absorption measurements were taken from neutral polymers dissolved in chloroform and from neutral polymer films cast on quartz plates. Cyclic voltammetry was carried out in an one-compartment cell using an EG&G PAR (Model 273) potentiostat/galvanostat. These measurements were performed in dry acetonitrile with tetrabutylammonium hexafluorophosphate (0.1 M), using platinum foils as working and auxiliary electrodes. The oxidation potentials of the monomers were determined at a scan rate of 100 mV/s versus a saturated calomel electrode (SCE). Voltammograms of the chemically prepared polymers were obtained by casting thin films of reduced polymers on platinum electrodes. They were recorded at a scan rate of 20 mV/s versus SCE. Finally, four-probe conductivity measurements were carried out on pressed pellets of the doped polymers at room temperature in air. Chemical doping was performed by soaking the neutral polymers in a nitromethane solution of iron(III) chloride (0.1 M).

Results and Discussion

Chemical oxidation of the alkoxy-substituted thiophenes by iron(III) chloride gave blue-black doped polymers in relatively good yields (40–60%). Soxhlet extractions with methanol induced a "dedoping" of PDBT, which turned brown-red. A similar effect was previously observed with poly(3-alkylthiophenes)[19] which could be explained by the instability of the doped state due to a relatively high oxidation potential.[20] In contrast, PBT, PBMT, and POMT remained partially doped in similar conditions, and a complete reduction of these polymers was obtained by chemical means using an aqueous solution of hydrazine. After this treatment, these three polymers became red-violet, and all neutral polymers were found to be soluble in common organic solvents such as chloroform, tetrahydrofuran, and methylene chloride. Uniform free-standing films of PBMT and POMT can be easily cast from chloroform solutions. Undoped PBT is unstable in air and is slowly oxidized, whereas neutral PDBT, PBMT, and POMT are quite stable in air.

The chemical structure of these neutral alkoxy-substituted polythiophenes was analyzed by ^{1}H NMR, and some of these NMR spectra are reported in Figures 1–3. From the ^{1}H NMR spectrum of PBT, we can deduce that this polymer has a low molecular weight and a relatively irregular chemical structure. Indeed, peaks at 6.15 and 6.80 ppm are clearly observed, which are characteristic of the hydrogen atoms at the 2- and 5-positions, respectively. Moreover, at least four peaks are found near 7.0 ppm, and these peaks can be related to hydrogen atoms in the 4-position having inequivalent chemical environments. The presence of multiple peaks for this aryl proton was previously related to structural defects such as α,β' couplings and branchings.[19] Finally, it must be noted that two peaks at 4.2 and 3.9 ppm are observed for the methylene group in α-position of the oxygen atom which can be attributed to a mixture of head-to-tail and head-to-head linkages along the polymer chain.[10,19,21]

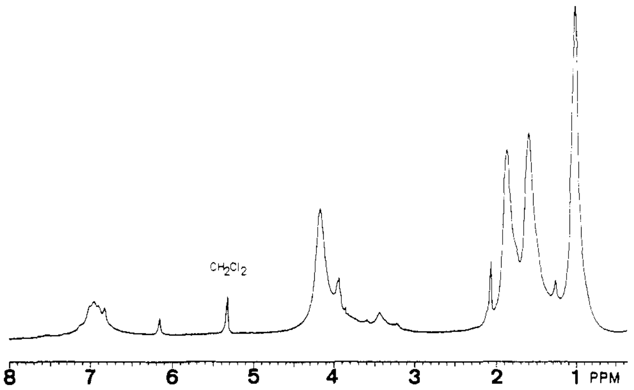

Figure 1. ^{1}H NMR spectrum of poly(3-butoxythiophene) (PBT) in CD_2Cl_2.

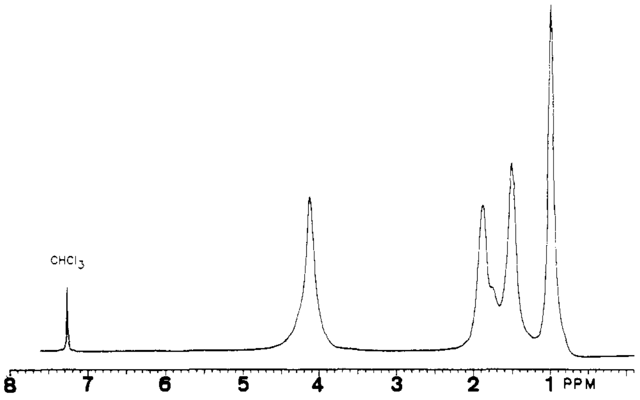

Figure 2. ^{1}H NMR spectrum of poly(3,4-dibutoxythiophene) (PDBT) in $CDCl_3$.

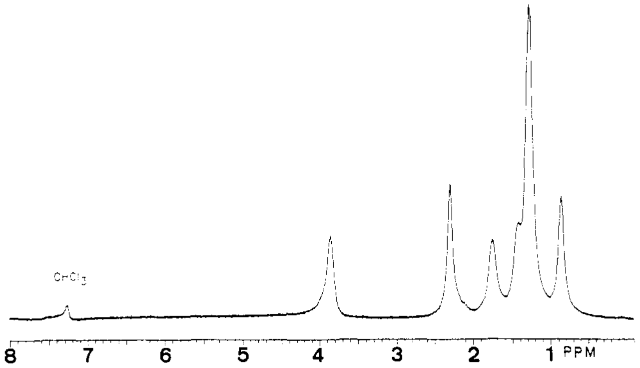

Figure 3. ^{1}H NMR spectrum of poly[3-(octyloxy)-4-methylthiophene] (POMT) in $CDCl_3$.

On the other hand, as shown in Figures 2 and 3, the ^{1}H NMR spectra of PDBT and POMT do not exhibit any peak between 6.0 and 7.0 ppm, indicating a linear and high molecular weight structure. A regular chemical structure was also observed by ^{1}H NMR for PBMT. PDBT

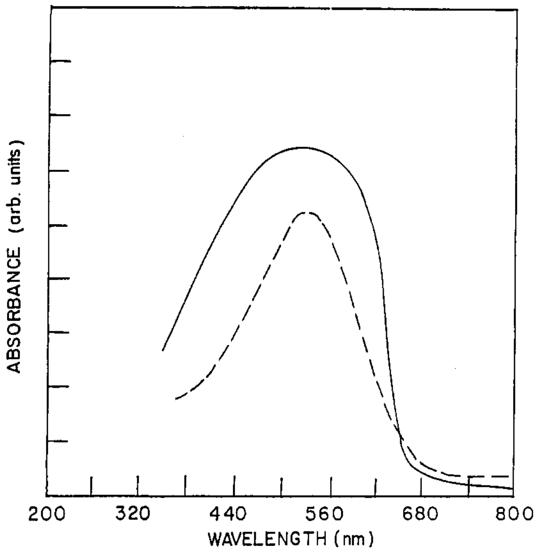

Figure 4. UV-visible absorption spectrum of neutral poly(3-butoxythiophene) (PBT) in the solid state (—) and in chloroform (- - -).

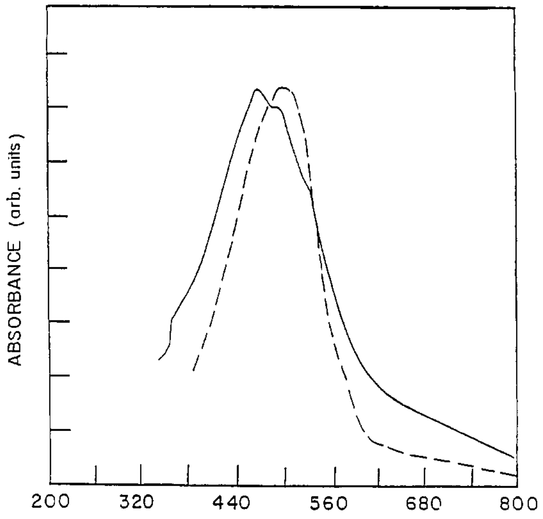

Figure 5. UV-visible absorption spectrum of neutral poly(3,4-dibutoxythiophene) (PDBT) in the solid state (—) and in chloroform (- - -).

has a symmetric structure, but, in addition to the main peaks at 4.15 and 1.90 ppm related to the methylene groups in α- and β-positions of the oxygen atom, two weak shoulders are observed near 4.30 and 1.75 ppm. These splittings could be related to different conformational structures (i.e., syn and anti conformations). A similar behavior is observed in the ^{1}H NMR spectra of POMT and PBMT (not shown here), but, in both cases, the analysis of these NMR spectra is complicated by the presence of different α,α' couplings (i.e., 2,2', 2,5', and 5,5' couplings). More complete investigations are presently being carried out to explain these splittings in the ^{1}H NMR spectra of alkoxy-substituted polythiophenes.

The optical properties of the neutral polymers were also analyzed, and their UV-visible absorption spectra in the solid state and in solution are reported in Figures 4-6. PBT exhibits a maximum of absorption at 520 nm in the solid state and at 530 nm in chloroform solution, which are characteristic of a highly conjugated backbone (a rodlike structure) in both conditions. Similar UV-visible absorption spectra were also observed for PDBT in the solid state and in solution, but, in this case, the absorption maxima occur at shorter wavelengths (460 and 480 nm, respectively) than those found for PBT. This higher band gap of PDBT in comparison with PBT might result from steric interactions between the substituents and the polymer backbone. These steric interactions induce a nonplanar conformation and, consequently, reduce the effective conjugation length. On the other hand, the absorption maximum of PBMT and POMT in the solid state is found at 545 nm, which indicates a highly conjugated backbone, whereas a smaller effective conjugation length (a coil conformation) for these polymers is observed in chloroform solution (420-440 nm). From these results, it seems that a coplanar or nearly planar structure is possible for 3,4-disubstituted polythiophenes in the solid state when the substituents are chosen in such a way that steric hindrance in the vicinity of the backbone is minimized.

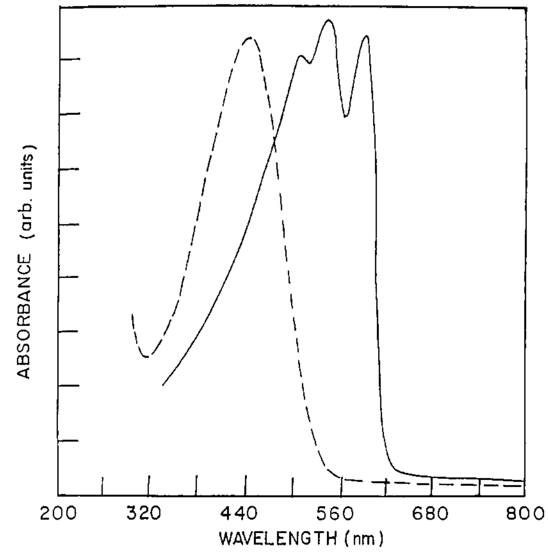

Figure 6. UV-visible absorption spectrum of neutral poly[3-(octyloxy)-4-methylthiophene] (POMT) in the solid state (—) and in chloroform (- - -).

In addition to this absorption maximum at 545 nm (2.28 eV) for PBMT and POMT in the solid state, two other well-resolved absorption peaks are observed at 505 nm (2.46 eV) and 590 nm (2.10 eV). This energy difference of 0.18 eV (1460 cm^{-1}) from the main peak is consistent with a C=C stretching mode that would be expected to couple strongly to the electronic structure.[22] These vibronic peaks in the optical absorption spectrum are additional evidence for the presence of a linear and regular structure in PBMT and POMT. Moreover, as reported for poly(3-alkylthiophenes),[23] we have observed thermochromic and solvatochromic effects in poly(3-alkoxy-4-methylthiophenes). Thin films of these polymers are red-violet at room temperature, but when heated above 100 °C, they become yellow. This transition is reversible and on cooling, they slowly recover their initial color. On the other hand, dissolution of PBMT and POMT in chloroform gives clear yellow solutions, but, upon addition of a poor solvent (i.e., methanol), these solutions become red.

In order to obtain more information concerning the physical properties of these alkoxy-substituted thiophenes, cyclovoltammetric measurements were performed in acetonitrile with tetrabutylammonium hexafluorophosphate (0.1 M) as supporting electrolyte. Table I summarizes the electrochemical data of the different monomers and polymers. The oxidation potential of the monomers decreases in the order of 3-butoxythiophene, 3-(octyloxy)-4-methylthiophene, 3-butoxy-4-methylthiophene, and 3,4-dibutoxythiophene, which corresponds to the level of the

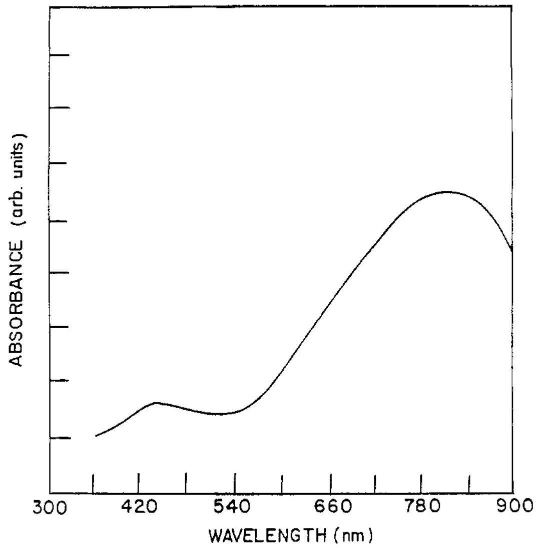

Figure 7. UV-visible absorption spectrum of oxidized poly[3-(octyloxy)-4-methylthiophene] (POMT) in the solid state.

Table I
Oxidation Potentials of Alkoxy-Substituted Thiophenes and Polythiophenes in 0.1 M Bu_4NPF_6/CH_3CN vs SCE

compd	E_{pa}, V	
	monomer	polymer
3-butoxythiophene	1.62	0.34
3-(octyloxy)-4-methylthiophene	1.59	0.64
3-butoxy-4-methylthiophene	1.50	0.60
3,4-dibutoxythiophene	1.44	0.70

Table II
Electrical Conductivity of Iron(III) Chloride Doped Polymers

compd	conductivity, S/cm
poly(3-butoxythiophene)	8×10^{-4}
poly[3-(octyloxy)-4-methylthiophene]	1
poly(3-butoxy-4-methylthiophene)	2
poly(3,4-dibutoxythiophene)	1×10^{-5}

electron-donating properties of the substituents. A quasi-reverse order is observed for the polymers, and this behavior can be explained by different conformational structures. Indeed, it has been shown that the presence of substituents may lead to a nonplanar conformation of the polymer chain which decreases the conjugation, thus giving a higher oxidation potential and band gap.[24,25] From the UV-visible measurements, it was already assumed that PDBT must adopt a nonplanar conformation in the solid state, and that could explain the high oxidation potential of this polymer. Following the same idea and combining the electrochemical and optical results, a nearly planar conformation seems to be possible for PBMT and POMT in the solid state, whereas a coplanar structure can be expected for PBT.

Either chemical or electrochemical doping of these alkoxy-substituted polythiophenes gave blue-black products. These doped polymers show broad absorption peaks at 400–500 and 800–850 nm (Figure 7), which are characteristic of the presence of bipolarons.[26] The electrical conductivities of these polymers doped by iron(III) chloride are reported in Table II. As previously found for electropolymerized poly(3-alkoxythiophenes),[10–12] chemically prepared PBT exhibits a relatively low electrical conductivity, which can be explained by its low molecular weight and irregular chemical structure. PDBT has a regular structure but, on the other hand, due to steric interactions, this polymer must adopt a nonplanar conformation, which combined with the presence of bulky substituents leads to poor interchain contacts, thereby reducing the electrical conductivity. From these results, it is clear that regular α,α' couplings and a coplanar or at least nearly planar conformation are important criterions for obtaining a good electrical transport. Poly(3-alkoxy-4-methylthiophenes) combine both properties and, consequently, exhibit high electrical conductivities.

These analyses also indicate that a 3,4-disubstituted structure is necessary for obtaining high electrical conductivities with alkoxy-substituted polythiophenes. The presence of an alkoxy group in the 3-position seems to decrease the selectivity of the α,α' couplings during the polymerization processes, and, therefore, the 4-position has to be blocked by a substituent as small as possible in order to get a regular and conjugated chemical structure. Similar effects can be observed in recent studies on electrochemically prepared alkoxy-substituted polythiophenes.[12,27,28] In contrast, we had previously found that only monosubstituted polythiophenes exhibit high electrical conductivities in the alkyl series.[15,19] On the other hand, despite the fact that poly(3-alkoxy-4-methylthiophenes) have only α,α' couplings along the polymer chain, whereas a low, but nonnegligible, amount of α,β' couplings has been found in chemically prepared poly(3-alkylthiophenes),[19] lower electrical conductivities are observed in PBMT and POMT. This particular feature may be explained by a slight deviation of the backbone from planarity and by a reduction of the mobility of the charge carriers due to a partial localization of the bipolarons on the oxygen atoms. Similar arguments were recently proposed to explain the low electrical conductivities observed in ethylthio-substituted polythiophenes.[21] Nevertheless, one main advantage of poly(3-alkoxy-4-methylthiophenes) over poly(3-alkylthiophenes)[9,19] comes from their lower oxidation potential (0.60–0.64 V compared to 0.95–1.00 V vs SCE), which increases the stability of the conducting state.

Conclusion

These studies on poly(3-butoxythiophene) and poly(3,4-dibutoxythiophene) have shown that regular α,α' couplings and a nearly planar conformation are important criterions for obtaining a good electrical transport. Poly(3-alkoxy-4-methylthiophenes) have both qualities, and, therefore, high electrical conductivities have been observed in these materials. In addition to their excellent electrical properties, poly(3-alkoxy-4-methylthiophenes) exhibit low oxidation potentials and band gaps, and these characteristics combined with their good mechanical properties make these materials quite interesting for applications in electrochemistry or nonlinear optics. Moreover, the structural parameters defined in these analyses on alkoxy-substituted polythiophenes may be used for designing new processable and electroactive polythiophene derivatives.

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Registry No. BMT, 124407-47-2; BMT (homopolymer), 124407-48-3; OMT, 130434-37-6; OMT (homopolymer), 130434-39-8; DBT, 126673-34-5; DBT (homopolymer), 126673-35-6; BT (homopolymer), 130434-38-7; $FeCl_3$, 7705-08-0; sodium butoxide, 2372-45-4; 3-bromo-4-methylthiophene, 30318-99-1; 1-octanol·Na, 17158-60-0; 3,4-dibromothiophene, 3141-26-2.