Design of Novel Electroactive Polybithiophene Derivatives

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Received September 25, 1992; Revised Manuscript Received February 8, 1993

ABSTRACT: Various derivatives of polybithiophene were synthesized and characterized. Poly(3,3′-dibutoxy-2,2′-bithiophene) and poly(4,4′-dibutoxy-2,2′-bithiophene) were found to be conducting upon doping but only partially soluble in common organic solvents. The oxidation potential of poly(4,4′-dibutoxy-2,2′-bithiophene) was only +0.05 V vs SCE, one of the lowest values for a polythiophene derivative. This low oxidation potential allows then the formation of a stable conducting state in the polymer. Moreover, upon oxidation, thin films of poly(dialkoxybithiophenes) became nearly transparent. Asymmetric disubstitution gave poly(3-butoxy-3′-decyl-2,2′-bithiophene) and poly(4-butoxy-4′-decyl-2,2′-bithiophene) which were completely soluble in chloroform. Their properties were intermediate between those of poly(alkylthiophenes) and poly(dialkoxybithiophenes).

Introduction

Conducting polymers have attracted considerable attention during the last decade due to their potential applications in electrochemical, electronic, and optical devices.[1] Among the numerous structures that have been investigated, polythiophenes have emerged as one of the most promising groups of materials. However, nonsubstituted polythiophene is insoluble and infusible, limiting drastically both its characterization and its processing. The incorporation of a long and flexible alkyl substituent in the β-position leads to polymers soluble in common organic solvents with a high conductivity in the oxidized state.[2–5] However, the physical properties of these polymers are affected by the regiochemistry of the couplings.[6,7] Although, the presence of substituents in the β-position reduces the possibility of wrong linkages (α–β, β–β) giving rise to more regular polymers with enhanced crystallinity and conductivity, the presence of head-to-head couplings increases the steric hindrance in the vicinity of the thiophene backbone, inducing the twisting of adjacent units. For instance, investigations on poly(3,3′-dialkyl-2,2′-bithiophene)[6] and poly(4,4′-dialkyl-2,2′-bithiophene),[8] in which the head-to-head interactions are maximized, have revealed materials with reduced conjugation length and conductivity.

Various ways were followed to overcome this problem of steric hindrance. McCullough et al.[9] reported the regioselective synthesis of poly(3-alkylthiophenes) which provided highly ordered materials with average conductivities of 600 S cm^{-1} and a UV–visible absorption maximum in $CHCl_3$ at 450 nm. Another approach that has been used was the synthesis of α-terthienyl, n-alkylated in the β-position of the central ring.[10] The polymerization of these starting materials leads to polymers soluble in organic solvents, but failed to produce free-standing films when cast from these solutions. Zerbi et al.[11] have also reported the polymerization of 3,3″-dihexyl-2,2′:5′,2″-terthiophene, in which the alkyl side chains have been suitably positioned in order to avoid the occurrence of head-to-head couplings. The resulting polymer was highly conjugated, as indicated by the UV–visible absorption maximum (455 nm in $CHCl_3$ solution and 530 nm in the solid state). Other solutions have consisted of the synthesis of poly(3-ethoxythiophene-ylvinylene)[12,13] and poly(3,4-dibutoxythiophene-ylvinylene),[14] where the vinylene group can act as a "conjugated spacer" in order to reduce the steric interactions of substituents on successive thiophene rings. The doped films are nearly optically transparent and have conductivities of 1 S cm^{-1}.

The polymerization of alkoxy monosubstituted thiophenes has also been carried out owing to the fact that the strong electron-donating effect of the alkoxy group should reduce the oxidation potential of the resulting polymers. However, only low molecular weight products with reduced electrical properties have been obtained.[15–17] The presence of an alkoxy group in the 3-position seems to decrease also the selectivity of the α–α' couplings during the polymerization processes, requiring that the 4-position be blocked by a substituent as small as possible in order to get a regular and conjugated structure. We have recently synthesized poly(3-alkoxy-4-methylthiophenes)[18,19] and found that these polymers have a conductivity after doping of around 1 S cm^{-1}. In comparison with poly(3-alkyl-4-methylthiophenes), their oxidation potential was also lowered significantly (2 V vs 0.6 V), thus increasing the stability of the conducting state. To our knowledge, they were the first examples of highly conducting disubstituted polythiophenes. However, the study of poly(3,4-dibutoxythiophene) showed that the presence of two long alkoxy substituents on the thiophene ring resulted in materials of low conductivity.[19] The presence of two bulky substituents on each thiophene ring leads to a nonplanar conformation of the backbone which is, moreover, surrounded by the insulating side chains. This conformational structure of the polymer leads to poor interchain contacts by keeping the chains away from one another, reducing thereby the probability of charge carrier hoppings.[20]

Our approach to the problem of improving the physical properties of polythiophenes was to design novel bithiophene derivatives with an adequate choice of the nature and positions of the substituents. The addition of side groups with low steric hindrance and the modulation of their electronic effects allowed us to prepare regular, soluble, and highly conducting polymers. For instance, we recently reported the synthesis of poly(3,3′-dibutoxy-2,2′-bithiophene) which gives nearly transparent conducting films upon doping.[21] The oxidation potential of this polymer was only +0.07 V vs SCE and the conductivity was 2 S cm^{-1}. These results encouraged us to prepare 4,4′-dibromo-2,2′-bithiophene and 3,3′-dibromo-2,2′-bithiophene which were further modified to give 4,4′-dibutoxy-2,2′-bithiophene, 4-butoxy-4′-decyl-2,2′-bithiophene, or 3-butoxy-3′-decyl-2,2′-bithiophene (Figure 1). In this paper, we present the synthesis and the

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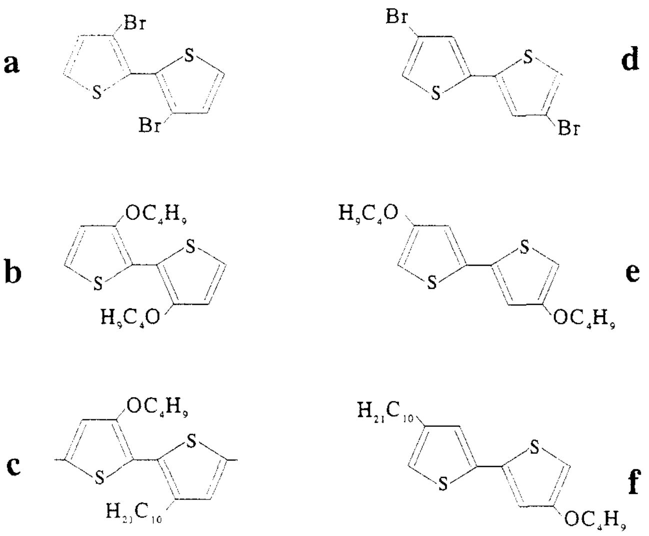


Figure 1. Chemical structure of various disubstituted bithiophenes: (a) 3,3′-dibromo-2,2′-bithiophene; (b) 3,3′-dibutoxy-2,2′-bithiophene; (c) 3-butoxy-3′-decyl-2,2′-bithiophene; (d) 4,4′-dibromo-2,2′-bithiophene; (e) 4,4′-dibutoxy-2,2′-bithiophene; (f) 4-butoxy-4′-decyl-2,2′-bithiophene.

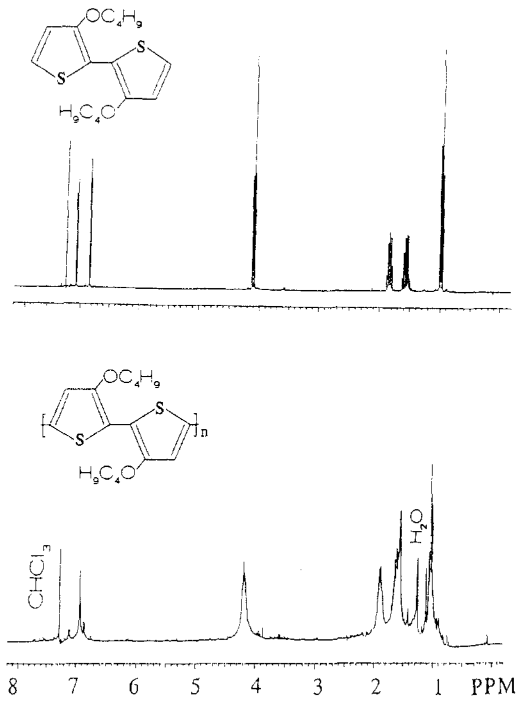


Figure 2. ^{1}H NMR spectra of 3,3′-dibutoxy-2,2′-bithiophene (top) and poly(3,3′-dibutoxy-2,2′-bithiophene) (bottom) in $CDCl_3$.

characterization of these various bithiophene derivatives as well as their corresponding polymers.

Results

Poly(3,3′-dibutoxy-2,2′-bithiophene). Chemical oxidation of 3,3′-dibutoxy-2,2′-bithiophene by iron(III) chloride gave a doped polymer which was reduced with an aqueous hydrazine solution. The undoped poly(3,3′-dibutoxy-2,2′-bithiophene) was found to be partially soluble (30–40%) in organic solvent such as chloroform and tetrahydrofuran while it remained almost completely insoluble in the doped state.

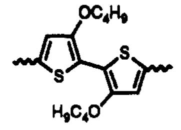
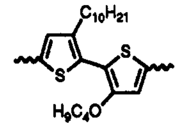
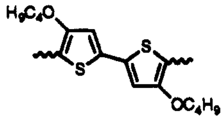
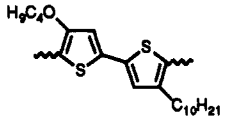
The chemical structure of soluble poly(3,3′-dibutoxy-2,2′-bithiophene) was analyzed by ^{1}H NMR (Figure 2). From the ^{1}H NMR spectrum of the soluble fraction, we can deduce that this fraction has a low molecular weight. Indeed, peaks at 6.84 and 7.08 ppm are clearly observed, which are characteristic of the hydrogen atoms at the 5,5′- and 4,4′-positions in 3,3′-dibutoxy-2,2′-bithiophene. The comparison of the area of these peaks to that of the alkyl peak gives a calculated degree of polymerization of approximately 10. However, regular structure was obtained, as indicated by the presence of a unique sharp peak at 6.92 ppm for the hydrogen atom in the β-position.[19,22] The soluble neutral poly(3,3′-dibutoxy-2,2′-bithiophene) exhibits a maximum absorption at 582 nm in the solid state and 545 in $CHCl_3$ solution (Table I). The poly(3,3′-dibutoxy-2,2′-bithiophene) was electroactive and exhibited an oxidation peak at +0.07 V vs SCE which is a very low value for a polythiophene derivative and similar to that observed for electrochemically prepared poly(4,4′-dimethoxy-2,2′-bithiophene).[23] Upon chemical doping with iron(III) chloride in nitromethane, conductivities up to 2 S cm^{-1} were obtained. Moreover, this polymer revealed a stable conductivity value under electrolysis conditions (application of a constant dc potential and monitoring the current) for months. These results are consistent with an electronic conduction mechanism, since in the case of an ionic mechanism a decrease of the conductivity level is expected as the ionic charge carriers are purged from the system.

Poly(4,4′-dibutoxy-2,2′-bithiophene). The chemical oxidation of 4,4′-dibutoxy-2,2′-bithiophene in chloroform by iron(III) chloride leads to a partially soluble polymer (15%) of a deep blue-violet color. The molecular weight of the soluble fraction of poly(4,4′-dibutoxy-2,2′-bithiophene) was around 3 times higher than that found for the soluble fraction of poly(3,3′-dibutoxy-2,2′-bithiophene). The UV–visible absorption maximum is around 600 nm in the solid state and 574 nm in $CHCl_3$ solution (Table I), values higher than that observed for the poly(3,3′-dibutoxy-2,2′-bithiophene) which is an indication of a more extended and conjugated structure. Moreover, an oxidation potential slightly lower than that of poly(3,3′-dibutoxy-2,2′-bithiophene), +0.05 vs +0.07 V/SCE, was also recorded (Figure 3 and Table I). The conductivity of the doped poly(4,4′-dibutoxy-2,2′-bithiophene) is similar (3 S cm^{-1}). A spectroelectrochemical study of a thin film of poly(4,4′-dibutoxy-2,2′-bithiophene) showed that, upon oxidation, nearly transparent films can be obtained (Figure 4).

Poly(4-butoxy-4′-decyl-2,2′-bithiophene). The chemical polymerization of 4-butoxy-4′-decyl-2,2′-bithiophene gave deep violet doped polymer which turned to red while dedoped with aqueous hydrazine. This polymer became then completely soluble in $CHCl_3$ solution. The UV–visible absorption maximum was at 500 nm in the solid state and at 480 nm in $CHCl_3$ solution (Table I). The ^{1}H NMR spectra (Figure 5) showed that a relatively high molecular weight material was obtained since no peak related to the terminal group was detected, suggesting a degree of polymerization at least equal to 50. This value is also supported by the fact that free-standing films have been prepared with this polymer.

The electrochemical behavior of this polymer was studied in acetonitrile and revealed two oxidation processes, one at +0.35 V/SCE and the second one at +0.75 V/SCE associated with two cathodic processes at +0.12 and +0.55 V/SCE, respectively (Figure 6). This behavior has been already observed in polythiophene by Zotti et al.[24] and in poly(di-2-thienyl-2,5-diheptoxyphenylene) by Reynolds et al.[25] These two oxidation steps seem to be related to the formation in the first stage of polarons and in the second one to the formation of bipolarons. However, Miller et al.[26] studied recently the oxidation of well-defined oligothiophenes and observed two redox processes that

Table I. Summary of Properties of Various Disubstituted Polybithiophenes

	λ_{max} in solid state (nm)	λ_{max} $CHCl_3$ solution (nm)	E_{ox} (V vs SCE)	σ (S cm^{-1})
	582	545	0.07	2
	506	460	0.41	1.3×10^{-2}
	600	574	0.05	3.25
	500	480	0.35	0.25

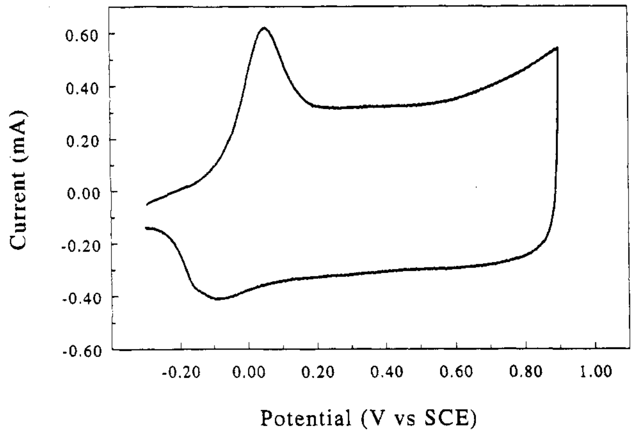


Figure 3. Cyclic voltammogram of poly(4,4′-dibutoxy-2,2′-bithiophene) film on a platinum electrode (potentials relative to SCE), sweep rate 100 mV s^{-1}.

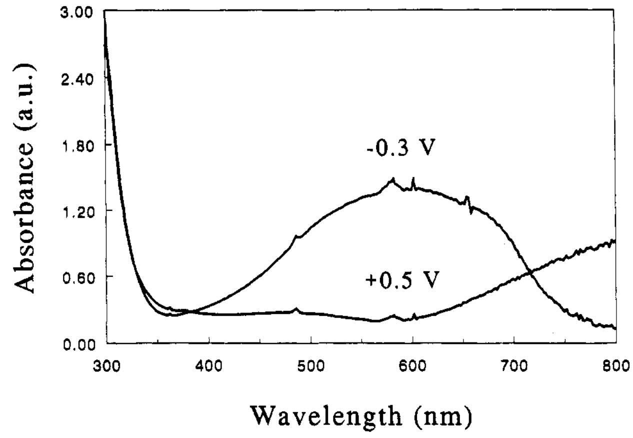


Figure 4. In situ spectroelectrochemical measurements of poly(4,4′-dibutoxy-2,2′-bithiophene) film on an ITO electrode (potentials relative to SCE).

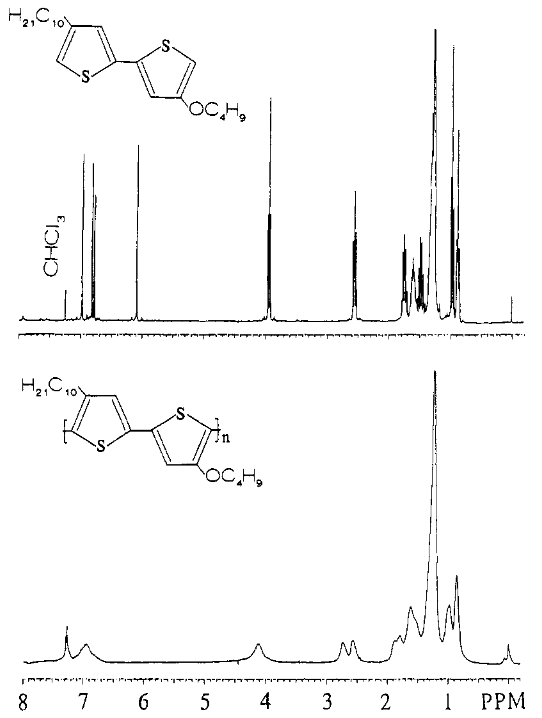


Figure 5. ^1H NMR spectra of 4-butoxy-4′-decyl-2,2′-bithiophene (top) and poly(4-butoxy-4′-decyl-2,2′-bithiophene) (bottom) in $CDCl_3$.

they attributed to formation of interchain π-dimers instead of bipolarons. Our results are also supported by the recent work of Guay et al.,[27] who found a similar behavior during the oxidation of a series of oligothiophenes.

Owing to the position of the substituents on the bithiophene unit (4- and 4′-positions), head-to-head alkyl–alkyl, tail-to-tail alkoxy–alkoxy, and head-to-tail alkyl–alkoxy couplings are expected. Indeed, ^1H NMR of the poly(4-butoxy-4′-decyl-2,2′-bithiophene) (Figure 5) showed the presence of around 25% head-to-head alkyl–alkyl linkages, as indicated by the ratio of the signal at 2.56 ppm to that at 2.78 ppm, which are respectively characteristic of head-to-head alkyl–alkyl and head-to-tail alkyl–alkoxy linkages. These last assignments are based on results obtained with poly(3-alkylthiophenes).[23] This feature induces a slight rotation of the units and results in a lower conjugation length for the polymer chains. The occurrence of these alkyl–alkyl head-to-head linkages explains the reduction of poly(4-butoxy-4′-decyl-2,2′-bithiophene) properties and, in a more general way, of those of alkyl-substituted polythiophenes. Upon chemical doping with iron(III) chloride in nitromethane, the conductivity of poly(4-butoxy-4′-decyl-2,2′-bithiophene) was found to be 0.25 S cm^{-1}.

Poly(3-butoxy-3′-decyl-2,2′-bithiophene). The chemical oxidation of 3-butoxy-3′-decyl-2,2′-bithiophene by iron(III) chloride in chloroform gave an almost completely

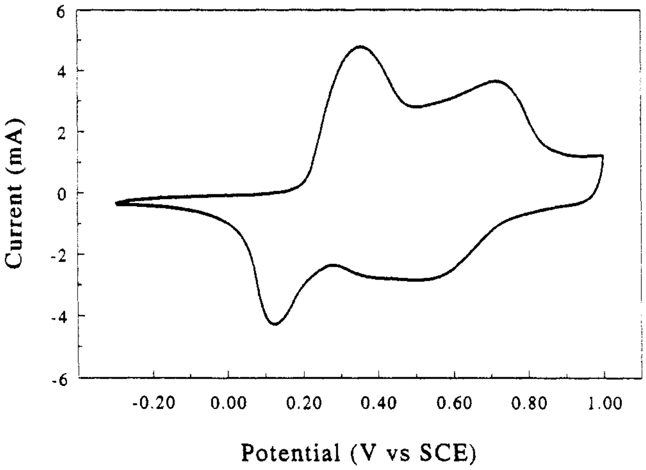


Figure 6. Cyclic voltammogram of poly(4-butoxy-4′-decyl-2,2′-bithiophene) film on a platinum electrode (potentials relative to SCE), sweep rate 200 mV s^{-1}.

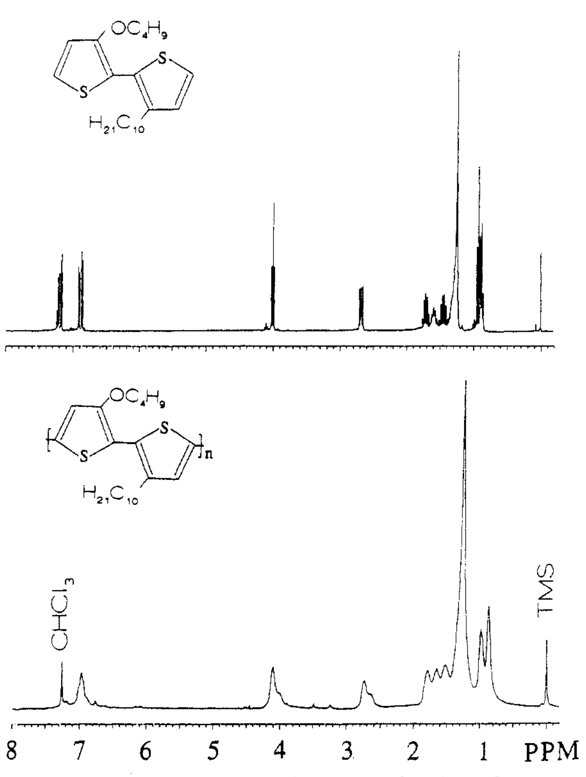


Figure 7. ^{1}H NMR spectra of 3-butoxy-3′-decyl-2,2′-bithiophene (top) and poly(3-butoxy-3′-decyl-2,2′-bithiophene) (bottom) in $CDCl_3$.

soluble polymer (90%) after dedoping with aqueous hydrazine solution. The maximum UV–visible absorption in the solid state was 506 nm and 460 nm in $CHCl_3$ solution (Table I). The ^{1}H NMR spectrum of the polymer (Figure 7) revealed that a relatively low molecular weight was obtained since peaks of terminal groups can be detected at 6.8 and 7.2 ppm. Moreover, the ^{1}H NMR of the soluble fraction of the poly(3-butoxy-3′-decyl-2,2′-bithiophene) revealed some splittings of the peaks at 4.0 and 2.8 ppm, which can be due either to the terminal groups or to different conformers. The electrochemical oxidation of poly(3-butoxy-3′-decyl-2,2′-bithiophene) showed the presence of two anodic processes at +0.41 and +0.89 V/SCE (Figure 8), values which are slightly higher than those observed in the case of poly(4-butoxy-4′-decyl-2,2′-bithiophene). Upon chemical doping with $FeCl_3$ in nitromethane, a conductivity of 1.3 × 10^{-2} S cm^{-1} was reached.

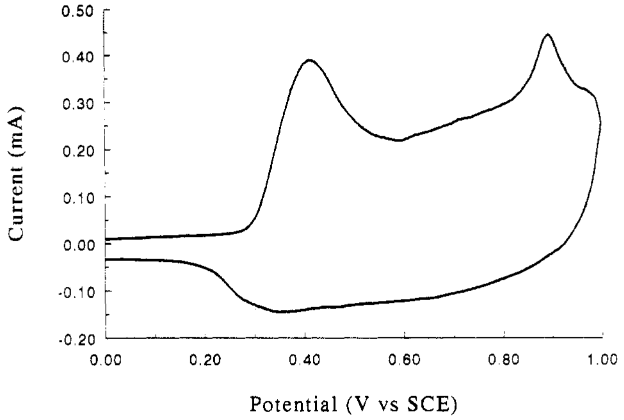


Figure 8. Cyclic voltammogram of poly(3-butoxy-3′-decyl-2,2′-bithiophene) film on a platinum electrode (potentials relative to SCE), sweep rate 100 mV s^{-1}.

Discussion

The polymerization of 3,3′-dibutoxy-2,2′-bithiophene has led to a polymer with a high conjugation length, as shown by its UV–visible absorption maximum, observed in the solid state and in $CHCl_3$ solution, and the high conductivity obtained upon doping. In contrast, the poly(3-alkoxythiophenes) were found to be of low conductivities[19] and this feature has been attributed to the formation of irregular couplings resulting from the presence of the alkoxy group which seems to decrease the selectivity of the α–α' couplings. The lower oxidation potential of the poly(3,3′-dibutoxy-2,2′-bithiophene) confirms the higher regularity of the material obtained when a disubstituted dimer unit is used instead of a monosubstituted monomer. Moreover, this fact was further confirmed when the 4,4′-dibutoxy-2,2′-bithiophene was used as the starting dimer. In this case, there is practically no possibility of having linkages other than in the α-positions because of the position of the substituents on the bithiophene which give a steric protection against couplings in the β-positions. In fact, as shown by the UV–visible maximum absorption (600 vs 582 nm in the solid state and 574 vs 545 nm in $CHCl_3$ solution), a higher conjugation length was obtained which results in a slightly higher conductivity level (3 vs 2 S cm^{-1}).

In the case of bithiophenes disubstituted with alkoxy substituents, the polymers obtained are both of high conjugation length and conductivity, showing that the presence of head-to-head alkoxy–alkoxy couplings does not affect the planarity of the chains. This is a clear indication that the steric hindrance induced by the head-to-head couplings of alkoxy groups is much smaller than that caused by alkyl substituents (van der Waals radius of the oxygen atom = 0.14 nm and that of the methylene group = 0.20 nm).[20] However, the presence of only alkoxy substituents on the thiophene rings does not promote the solubilization of the high molecular weight fraction, resulting in only partially soluble materials. Moreover, the use of longer substituents (octyloxy insteady of butoxy groups) has led to completely insoluble materials. This feature can be related to the very small difference found between the UV–visible absorption maxima obtained in the solid state and in solution (600 vs 574 nm). Indeed, the chains do not undergo any significant conformational changes in dilute solution which suggests that rigid-rod-like conformational structures prevail in both conditions. Therefore, there is no important gain in entropy upon dissolution and that may explain why it is difficult to solubilize the highest molecular weight fraction of these polymers. This feature is also supported by the fact that electrochemically synthesized thin films of poly(4,4′-dibutoxy-2,2′-bithiophene) were found to be completely insoluble even when fully dedoped. It is worth noting that similar results were reported for other alkoxy-substituted conducting polymers.[28] For instance it has been shown that poly(bis(octyloxy)phenylenevinylene) is poorly soluble in most common organic solvents. The authors have tentatively explained this low solubility by side chain interdigitation and side chain crystallization. Although no evidence of crystallinity has been found in our polymers, the synthesis of asymmetric poly(dialkoxybithiophenes), e.g. methoxy and butoxy groups, could be helpful to get a better understanding of these surprising results.

The need to improve the solubility of the polymers has led us to design monomers (i.e. 4-butoxy-4′-decyl-2,2′-bithiophene and 3-butoxy-3′-decyl-2,2′-bithiophene) in which both alkyl and alkyl substituents are present. Using such asymmetric dimers, the advantages of having an alkoxy substituent (lower oxidation potential and reduced steric hindrance) and an alkyl one (better solubility) are retained. In fact, the polymerization of such an asymmetric dimer has given a completely soluble polymer (i.e. poly(4-butoxy-4′-decyl-2,2′-bithiophene)) which exhibits interesting properties. However, the conjugation length is lower than that of poly(dialkoxybithiophenes) (λ_{max} = 500 vs 600 nm) and the conductivity is also slightly lower ($\sigma = 0.25$ vs 2 S cm^{-1}). These results can be related to the presence of about 25% head-to-head alkyl–alkyl couplings along the main polymer chain.

The study of poly(3-butoxy-3′-decyl-2,2′-bithiophene) revealed that this polymer has a lower molecular weight than that of poly(4-butoxy-4′-decyl-2,2′-bithiophene). This feature may be related to the lower reactivity of the 3,3′-disubstituted-2,2′-bithiophenes compared to that of the 4,4′-disubstituted-2,2′-bithiophenes. A similar behavior has been observed in the case of poly(dialkoxybithiophenes), as discussed above. The UV–visible absorption maximum of poly(3-butoxy-3′-decyl-2,2′-bithiophene) in the solid state was found to be slightly higher than that of poly(4-butoxy-4′-decyl-2,2′-bithiophene) (506 vs 500 nm), a value, however, much lower than that being expected because of the absence of any head-to-head alkyl–alkyl linkages. This low conjugation length may be related both to the low molecular weight of this polymer and to the possible presence of irregular couplings in the β-positions. In fact, around 10% insoluble material was obtained that may be cross-linked product. Moreover, this feature is supported by the lower conductivity of this polymer compared to that of poly(4-butoxy-4′-decyl-2,2′-bithiophene) (1.3×10^{-2} vs 0.25 S cm^{-1}).

It then appears that the careful molecular design of the starting bithiophene dimers, through the precise control of the nature and the position of the substituents, allows a fine tuning of the physical properties of the polythiophene derivatives. However, the presence of alkyl–alkyl head-to-head linkages in the case of poly(4-butoxy-4′-decyl-2,2′-bithiophene) gives rise to a reduction of the physical properties. The use of 3,3′-disubstituted bithiophene resulted in polymers with reduced conjugation length and properties due to the possibly lower reactivity of these dimers and to the higher possibility of irregular couplings. Finally, on the basis of these results, it therefore seems that 3-alkyl-4′-alkoxy-2,2′-bithiophene (Figure 9) would be very interesting starting materials since, in this case, there will be no possibility of head-to-head alkyl–alkyl couplings. Moreover the alkoxy substituent is in such a position that there will be very little possibility of irregular linkages. The study of these polymers is currently under investigation.

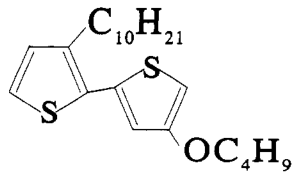


Figure 9. Chemical structure of 3-alkyl-4′-alkoxy-2,2′-bithiophenes.

Conclusion

The synthesis of 4,4′-dibromo-2,2′-bithiophene and 3,3′-dibromo-2,2′-bithiophene allowed the preparation of various symmetric and asymmetric substituted bithiophenes with a tight control of both the nature and the position of the substituents. The incorporation of alkoxy groups on bithiophenes and the polymerization of the resulting dimers led to polymers with very low oxidation potentials and high conjugation lengths. Upon doping, thin films of poly(3,3′-dibutoxy-2,2′-bithiophene) and poly(4,4′-dibutoxy-2,2′-bithiophene) became nearly transparent, opening the way to the fabrication of stable, nearly transparent, conducting materials.

However, the presence of only alkoxy substituents on the thiophene rings did not allow the solubilization of high molecular weight polymers. The design of asymmetric disubstituted bithiophenes has led to the synthesis of poly(4-alkyl-4′-alkoxy-2,2′-bithiophene) and poly(3-alkyl-3′-alkoxy-2,2′-bithiophene) which were found to be soluble in common organic solvents. The physical properties of these asymmetric polybithiophene derivatives were intermediate between those of poly(alkylthiophenes) and poly(dialkoxybithiophenes). Through the study of these various materials, it appeared that the incorporation of different substituents, such as alkyl and alkoxy groups, on bithiophenes allows a tight control of the polymer structure and gives a way to design new electroactive polymers with tunable properties.

Experimental Section

Thiophene, bromine, *n*-butyllithium (2.5 M in hexane), 2,3-dibromothiophene, and copper chloride ($CuCl_2$) were obtained from Aldrich Chemical Co. and used without further purification.

2,3,5-Tribromothiophene.[29] To a solution of thiophene (400 g, 4.76 mol) in dry chloroform (200 mL), bromine (2283 g, 14.28 mol) was added within 6 h. The reaction mixture was stirred overnight and then refluxed for 2 h. A solution of potassium hydroxide (400 g) in 95% ethanol (700 mL) was then added cautiously, and the reaction mixture was refluxed for 4 h and then poured into cold water (2 L). The suspension was filtered and the filtrate extracted with ether. The organic extract was washed with water, dried over magnesium sulfate, and concentrated. Distillation under reduced pressure gave 2,3,5-tribromothiophene (123–124 °C/10 mmHg; lit. 125 °C/10 mmHg), yield 78%. ^{1}H NMR (300 MHz, $CDCl_3$, ppm): 6.88. ^{13}C NMR (75.4 MHz, $CDCl_3$, ppm): 110.46, 111.89, 113.37, 131.89.

2,4-Dibromothiophene[30] **(DBT).** To a solution of 32 g of 2,3,5-tribromothiophene in 150 mL of anhydrous ether, cooled to −40 °C was added very quickly 39 mL of 2.5 M *n*-butyllithium in hexane, and the mixture was stirred for 5 min. The mixture was poured into cold water, and the organic layer was separated. The aqueous phase was shaken twice with ether, and the combined organic extracts were shaken with water and dried over magnesium sulfate. The solution was concentrated and distilled giving 2,4-dibromothiophene as the main fraction (74–76 °C/6 mmHg; lit. 83–85 °C/9–10 mmHg), yield 70%. ^{1}H NMR (300 MHz, $CDCl_3$, ppm): 7.15 (1H, d, J = 1.6 Hz), 6.98 (1H, d, J = 1.6 Hz).

4,4′-Dibromo-2,2′-thiophene was synthesized from 2,4-dibromothiophene by lithiation with butyllithium[31] followed by oxidative coupling with copper chloride.[32,33] To a solution of 19.5 mL of 2.5 M *n*-butyllithium in 90 mL of anhydrous ether at −70 °C was added dropwise a solution of 10 g of 2,4-dibromothiophene in 100 mL of ether. The solution was stirred at this temperature for 15 min after which 6.94 g of $CuCl_2$ was added in one portion. The mixture was stirred overnight while the temperature was allowed to reach slowly the ambient temperature. The suspension was filtrated, washed with water, and dried over calcium chloride. After evaporation, a yellow solid was obtained, which was purified by flash chromatography on silica gel using petroleum ether as the eluent. A yellowish solid was obtained which was further purified by sublimation to give white crystals, melting point 112 °C, yield 45%. ^1H NMR (300 MHz, $CDCl_3$, ppm): 7.15 (2H, d, J = 1.4 Hz), 7.08 (2H, d, J = 1.2 Hz). ^{13}C NMR (75.4 MHz, $CDCl_3$, ppm): 110.35, 122.09, 126.48, 136.86. Anal. Calcd for $C_8H_4S_2Br_2$: C, 29.65; H, 1.25; S, 19.78; Br, 49.32. Found: C, 30.06; H, 1.19; S, 19.51; Br, 48.89.

4,4′-Dibutoxy-2,2′-bithiophene. Sodium metal (2.0 g, 0.087 mol) was completely reacted with *n*-butanol (125 mL) under an atmosphere of nitrogen. Copper(II) oxide (1.25 g, 0.016 mol) and potassium iodide (50 mg, 0.3 mmol) were then added, followed by 4,4′-dibromo-2,2′-bithiophene (5.02 g, 15.5 mmol). The mixture was stirred at 100 °C for 3 days, more potassium iodide (20 mg) was then added, and the reaction is continued for an additional 2 days at the same temperature.[34] After filtration, the butanol solution was poured into distilled water and extracted with ether. The combined organic extracts were dried over magnesium sulfate, and the solvent was removed under reduced pressure. The residue was chromatographed on a silica gel column with petroleum ether (35–60 °C) as the eluent, melting point 46 °C, yield 49%. ^1H NMR (300 MHz, $CDCl_3$ ppm): 0.98 (6H, t, J = 7.3 Hz), 1.5 (4H, quin, J = 7.6 Hz), 1.75 (4H, quin, J = 6.7 Hz), 3.95 (4H, t, J = 6.4 Hz), 6.12 (2H, d, J = 1.6 Hz), 6.83 (2H, d, J = 1.6 Hz). ^{13}C NMR (75.4 MHz, $CDCl_3$, ppm): 13.69, 19.09, 31.11, 69.62, 96.14, 115.68, 135.84, 157.39. Anal. Calcd for $C_{16}H_{22}S_2O_2$: C, 61.89; H, 7.14; S, 20.65. Found: C, 61.46; H, 6.98; S, 20.38.

4-Butoxy-4′-decyl-2,2′-bithiophene. Sodium metal (322 mg, 14 mmol) was completely reacted with *n*-butanol (50 mL) under an atmosphere of nitrogen. Copper(II) oxide (550 mg, 7 mmol) and potassium iodide (20 mg, 0.12 mmol) were then added, followed by 4,4′-dibromo-2,2′-bithiophene (4.07 g, 12.56 mmol). The mixture was stirred at 100 °C for 3 days, more potassium iodide (20 mg) was then added, and the reaction was continued for an additional 2 days at the same temperature. After filtration, the butanol solution was poured into distilled water and extracted with ether. The combined organic extracts were dried over magnesium sulfate, and the solvent was removed under reduced pressure. The residue was chromatographed on a silica gel column with hexanes as eluent. 4-Butoxy-4′-bromo-2,2′-bithiophene was recovered as the main fraction, yield 45%. ^1H NMR (300 MHz, $CDCl_3$, ppm): 0.99 (3H, t, J = 7.3 Hz), 1.50 (2H, quin, J = 7.7 Hz), 1.76 (2H, quin, J = 6.6 Hz), 3.96 (2H, t, J = 6.5 Hz), 6.86 (1H, d, J = 1.6 Hz), 6.16 (1H, d, J = 1.7 Hz), 7.06 (1H, d, J = 1.4 Hz), 7.09 (1H, d, J = 1.4 Hz).

4-Butoxy-4′-bromo-2,2′-bithiophene (8.23 mmol, 2.6 g) was further reacted with an excess of *n*-decylmagnesium bromide (40 mmol) in 30 mL of dry diethyl ether containing a nickel catalyst, following the method described by Kumada et al.[35] The crude product was purified by chromatography on silica gel using hexane as eluent and crystallization in cold methanol. 4-Butoxy-4′-decyl 2,2′-bithiophene was recovered as a white solid, melting point 43 °C, yield 22%. ^1H NMR (300 MHz, $CDCl_3$, ppm): 0.88 (3H, t, J = 6.9 Hz), 0.98 (3H, t, J = 7.4 Hz), 1.35–1.20 (14H, m), 1.49 (2H, quin, J = 7.5 Hz), 1.58 (2H, m), 1.76 (2H, quin, J = 6.6 Hz), 2.57 (2H, t, J = 7.9 Hz), 3.95 (2H, t, J = 6.4 Hz), 6.09 (1H, d, J = 1.5 Hz), 6.79 (1H, d, J = 1.1 Hz), 6.82 (1H, d, J = 1.5 Hz), 6.98 (1H, d, J = 1.5 Hz). ^{13}C NMR (75.4 MHz, $CDCl_3$, ppm): 13.72, 14.01, 19.12, 22.58, 29.20 (two carbon atoms), 29.35 (two carbon atoms), 29.49, 30.26, 30.38, 31.14, 31.79, 69.63, 95.72, 115.66, 119.02, 124.71, 136.06, 137.06, 143.91, 157.39. Anal. Calcd for $C_{22}H_{34}S_2O$: C, 69.84; H, 8.99; S, 16.93; O, 4.23. Found: C, 69.90; H, 9.10; S, 17.04; O, 4.16.

3,3′-Dibromo-2,2′-bithiophene[33] was synthesized from 2,3-dibromothiophene (Aldrich) by lithiation with butyllithium followed by oxidative coupling with copper chloride. To a solution of 33 mL of 2.5 M *n*-butyllithium in 30 mL of anhydrous ether at −70 °C, was added dropwise a solution of 15 g of 2,3-dibromothiophene (62 mmol) in 20 mL of ether. The solution was stirred at this temperature for 15 min after which 9.42 g of $CuCl_2$ were added in one portion. The mixture was stirred overnight while being allowed to reach the ambient temperature. The suspension was filtrated, washed with water, and dried over calcium chloride. After evaporation, a yellow solid was obtained, which was recyrstallized in hexane. A white solid was obtained which was further purified by sublimation to give white crystals, melting point 102 °C (lit. mp 102–104 °C), yield 38%. ^1H NMR (300 MHz, $CDCl_3$, ppm): 7.40 (2H, d, J = 5.4 Hz), 7.08 (2H, d, J = 5.4 Hz).

3-Butoxy-3′-decyl-2,2′-bithiophene was synthesized following the same experimental procedure that was used in the synthesis of 4-butoxy-4′-decyl-2,2′-bithiophene.

3-Butoxy-3′-bromo-2,2′-bithiophene: yield 32%. ^1H NMR (300 MHz, $CDCl_3$, ppm): 7.20 (2H, d, J = 2.5 Hz), 7.18 (2H, d, J = 2.3 Hz), 6.97 (2H, d, J = 5.4 Hz), 6.86 (2H, d, J = 5.6 Hz), 4.09 (2H, t, J = 6.4 Hz), 1.80 (2H, q, J = 3.5 Hz), 1.53 (2H, q, J = 3.1 Hz), 0.97 (3H, t, J = 2.3 Hz).

3-Butoxy-3′-decyl-2,2′-bithiophene: yield 28%. ^1H NMR (300 MHz, $CDCl_3$, ppm): 0.85–0.98 (6H, m), 1.25 (14H, m), 1.43 (2H, q, J = 7.3 Hz), 1.59 (2H, m), 1.71 (2H, q, J = 2.5 Hz), 2.68 (2H, t, J = 7.7 Hz), 4.00 (2H, t, J = 6.5 Hz), 6.85 (2H, d, J = 5.6 Hz), 6.90 (2H, d, J = 5.2 Hz), 7.16 (2H, d, J = 5.5 Hz), 7.20 (2H, d, J = 5.2 Hz). ^{13}C NMR (75.4 MHz, $CDCl_3$, ppm): 13.68, 13.99, 19.06, 22.58, 29.23, 29.29 (two carbon atoms), 29.37, 29.50 (two carbon atoms), 30.45, 31.56, 31.80, 71.51, 113.48, 117.45, 122.94, 124.22, 127.67, 128.68, 140.41, 153.44. The accurate mass spectra were determined by high resolution mass spectrometry: calcd, 378.61; found, 378.2073.

3,3′-Dibutoxy-2,2′-bithiophene.[21] A solution of 2.23 g of 3-butoxythiophene[34] in 50 mL of dry diethyl ether was prepared. Diisopropylamine (2.25 mL) (Aldrich) and 6.4 mL of 2.5 M *n*-butyllithium in hexanes were dissolved in 30 mL of anhydrous ether, and the solution was added dropwise to the first solution. The mixture was refluxed for 1 h under argon, and after being cooled to −78 °C, 2.4 g of $CuCl_2$ (Aldrich) was added in one portion, and the solution was stirred overnight while the temperature was allowed to reach the ambient temperature. The solution was acidified and extracted with ether. The organic phase was evaporated, and the crude bithiophene derivative was purified by flash chromatography (light petroleum–chloroform 80:20) on silica gel and finally recrystallized from *n*-hexane, melting point 98–99 °C, yield 33%. ^1H NMR (300 MHz, $CDCl_3$, ppm): 1.00 (6H, t, J = 7.4 Hz), 1.58 (4H, m), 1.84 (2H, m), 4.12 (4H, t, J = 6.5 Hz), 6.84 (2H, d, J = 5.6 Hz), 7.08 (2H, d, J = 5.6 Hz). ^{13}C NMR (75.4 MHz, $CDCl_3$, ppm): 13.76, 19.22, 31.70, 71.52, 114.00, 115.89, 121.46, 151.80. Anal. Calcd for $C_{16}H_{22}S_2O_2$: C, 61.89; H, 7.14; S, 20.65. Found: C, 61.89; H, 7.41; S, 20.62.

Polymerization. Polymers were obtained by chemical oxidation of the corresponding dimers using iron trichloride according to a procedure similar to that of Sugimoto at al.[5] In a 100-mL three-neck flash, 2 mmol of iron(III) chloride was dissolved in 10 mL of chloroform under nitrogen and 1 mmol of dimer in 15 mL of chloroform was added dropwise. The mixture was stirred for 24 h at room temperature. The solution was then precipitated in methanol (500 mL), and the precipitate was collected and washed further with methanol. The polymers were subsequently washed by Soxhlet extraction using methanol and then dried under reduced pressure. Undoped polymers were obtained by reduction with an aqueous solution of hydrazine (Fisher Scientific Co.).

Physical Measurements. The elemental analyses were performed by Guelph Chemical Laboratories Ltd. NMR spectra were obtained in deuterated chloroform solutions on a 300-MHz Bruker pulsed Fourier transform instrument. UV–visible spectra were recorded on a Hewlett-Packard diode array spectrophotometer (Model 8452 A), from neutral polymer film cast on quartz plates. Cyclic voltammetry was carried out in a 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 as working and auxiliary electrodes. 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).

Acknowledgment. This work was supported by grants from the Natural Sciences and Engineering Research Council of Canada (NSERC) and the Department of Education of the Province of Quebec (FCAR programs).

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