Synthesis and Characterization of New Processible Conducting Copolymers Derived from Thiophenes

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Various poly(3-decylthiophene-*co*-3,3′-dibutoxy-2,2′-bithiophene)s and poly(4,4′-didecyl-2,2′-bithiophene-*co*-3,3′-dibutoxy-2,2′-bithiophene)s have been chemically prepared using iron trichloride as oxidizing agent in chloroform. These copolymers should combine the excellent electrical properties of alkoxy-substituted polythiophenes with the good processibility of alkyl-substituted polythiophenes. All copolymers of the first series have shown a good solubility in chloroform but reduced electrical conductivities (10^{-3}–10^{-1} S/cm) when compared to the homolymers (5–140 S/cm). This behavior has been explained by an inhomogeneous distribution of the four different electroactive moieties (triads) found in these copolymers and, consequently, to a localization of the charge carriers created upon oxidation. In contrast, poly(4,4′-didecyl-2,2′-bithiophene-*co*-3,3′-dibutoxy-2,2′-bithiophene)s have exhibited both excellent processibility and electrical properties. Electrical conductivities up to 30 S/cm have been observed in some of these copolymers. At room temperature, alkoxy-rich polythiophenes showed also a good stability in the conducting state which can be partly related to their low oxidation potential. However, probably due to thermally induced steric interactions between the side chains and the counterions, an exothermic dedoping reation takes place at higher temperatures (>100 °C). On the basis of these results, it is proposed that alkoxy-substituted polythiophenes bearing ionic moieties should lead to processible and thermally stable conducting materials.

Introduction

During the past 20 years, a new class of organic polymers (e.g., polyacetylene, polypyrrole, polyaniline, polythiophene, etc.) has emerged which exhibit unusual electrical and optical properties.[1–5] However, characterization and processing of these conjugated polymers have been limited by their inherent insolubility and infusibility. This problem of processibility has been recently solved for polyaniline by using large counterions in the protonated (conducting) state.[6] The presence of such large counterions is believed to decrease the strong interchain interactions in the acid-doped state. The incorporation of relatively long and flexible side chains onto a rigid backbone is also a common technique to prepare fusible and/or soluble polymers and this concept was successfully applied to some alkyl-substituted polythiophenes.[7–10] Different methods of preparation were investigated, and it has been found that a

simple chemical oxidation of 3-alkylthiophenes with iron trichloride in chloroform gives soluble, high molecular weight, and conducting polymers in very good yields.[10,11] However, partly due to the relatively high oxidation potential (ca. 0.95 vs SCE) of these polymers, the stability of their oxidized (conducting) state is limited in air.

To develop processible, air-stable, and conducting polymers, alkoxy-substituted polythiophenes were recently synthesized since it was believed that the presence of the strong electron-donating alkoxy group should decrease the oxidation potential of the resulting materials. Indeed, stable and electroactive polymers with low oxidation potentials (0.2–0.3 V vs SCE) were obtained from the electrochemical or chemical oxidation of 3-alkoxythiophenes, but their molecular weight was very low.[12–14] It was also observed from spectroscopic analyses that the selectivity of the 2,5′ couplings during polymerization was not as good as that obtained with 3-alkylthiophenes and that can explain their lower molecular weight and lower electrical conductivities (ca. 10^{-3} S/cm instead of 10 S/cm). Therefore, to increase the regularity of the resulting alkoxy-substituted polythiophenes, 3,4-dibutoxythiophene was prepared and polymerized.[14] The resulting processible polymer is then perfectly regular (only 2,5′ couplings are possible), but it was found that the presence of two long substituents (e.g., butoxy) on every repeat unit increases the

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steric hindrance which causes a twisting of the main polymer chain and an increase of the interchain distance, resulting in a decrease of the electrical conductivity. Only cycloalkoxy 3,4-substituted polythiophenes gave highly conducting materials.[15] Moreover, with an oxidation potential around 0.0 V vs SCE, poly(3,4-ethylenedioxythiophene) shows an excellent stability in the conducting state. Although it is not soluble, this polymer is particularly promising for the development of antistatic and electromagnetic shielding layers.[16] It is also worth noting that the steric hindrance between neighboring cycloalkoxy 3,4-substituted monomer units in the polymer chain is not as severe as the case of cycloalkyl 3,4-substituted compounds.[17,18] All these results clearly show that the presence of alkoxy substituents instead of alkyl side chains gives a double advantage: it decreases the oxidation potential, but it also decreases the steric hindrance in the vicinity of the polymer chain which allows the formation of planar and highly conducting structures.

On the basis of all these results obtained with alkoxy-substituted polythiophenes, it was then believed that the polymerization of 3,3′-dialkoxy-2,2′-bithiophenes or 4,4′-dialkoxy-2,2′-bithiophenes should lead to the preparation of well-defined and highly conducting polymers. These polymers have been prepared from chemical or electrochemical oxidation, and, as expected, air-stable conducting polymers have been obtained.[19,20] These polymers exhibit a very low oxidation potential (ca. 0.05 V vs SCE) and become nearly transparent in the conducting state (electrochromism). However, all these alkoxy-substituted polybithiophenes are only slightly soluble and show poor mechanical properties due to their low molecular weight. On the other hand, one may expect that a combination of both alkyl and alkoxy substituents on the same polymer chain should give excellent electrical and physical properties. This synergy was indeed achieved by polymerizing asymmetric bithiophenes.[20] Moreover, novel physical properties (formation of molecular quantum wells) were obtained from the combination of mixed thiophene units.[21,22] However, the preparation of these asymmetrically substituted bithiophenes is difficult and involves many synthetic steps. Therefore, in this study, we report the synthesis and characterization of various copolymers derived from alkoxy- and alkyl-substituted thiophenes and bithiophenes. These polymers should combine excellent electrical properties with a good processibility.

Results and Discussion

Poly(3-decylthiophene-*co*-3,3′-dibutoxy-2,2′-bithiophene)s. Several poly(3-decylthiophene-*co*-3,3′-dibutoxy-2,2′-bithiophene)s have been obtained from

Table 1. Structural Characterization and Electrical Conductivity of Poly(3-decylthiophene-*co*-3,3′-dibutoxy-2,2′-bithiophene)s

polymer no.	$f_1{}^a$	$F_1{}^a$	M_n	M_w	M_w/M_n	$\sigma_{max}{}^b$ (S/cm)
1	0	0	40000	230000	5.7	6
2	25	6	10000	95000	9.5	6×10^{-2}
3	50	46	7000	50000	7.1	3×10^{-3}
4	65	82	4000	5000	1.3	8×10^{-2}
5	75	90	3000	3500	1.2	2
6	100	100	4000	6000	1.5	140

^{a} f_1 and F_1 are in mole fraction of 3-butoxythiophene. ^{b} Maximum of conductivity from in situ measurements.
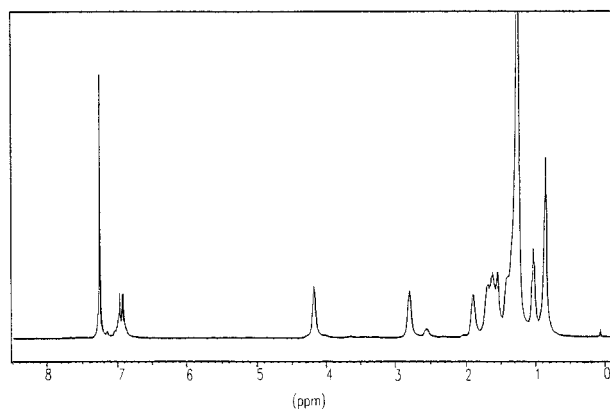

Figure 1. ^{1}H NMR spectrum of polymer **3** in CDCl$_3$.

chemical polymerization using iron trichloride as oxidizing agent. The various comonomer feed compositions f_1 (in mole fraction of 3-butoxythiophene unit) are reported in Table 1. The copolymer compositions F_1 (in mole fraction of 3-butoxythiophene unit) have been calculated from ^{1}H NMR data (see Figure 1). For this purpose, the ratio of the integration of the 4.18 ppm peak (characteristic of the methylene group attached to the oxygen atom of the butoxy substituent) over the integration of both 2.82 and 2.52 ppm peaks (characteristic of the methylene group attached to the thiophene units in head-to-tail and head-to-head structures[11]) have been used. As shown in Table 1, copolymers with less than 50% of alkoxy-substituted repeat units have relatively high molecular weights and, consequently, can give free-standing films. To prove that copolymers rather than a mixture of homopolymers have been indeed obtained, it is worth noting that all copolymers show a much better solubility in chloroform than poly-(3,3′-dibutoxy-2,2′-bithiophene). Moreover, a careful analysis of the ^{1}H NMR data has indicated that the head-to-tail content (related to the 2.82 ppm peak) goes from 80% in copolymer 2 to 95% in copolymer 5. This increasing head-to-tail content can be related only to the presence of mixed couplings along the backbone.

To characterize the electrochemical and electrical properties of these copolymers, cyclic voltammetry and in situ conductivity measurements have been performed. First, both homopolymers (polymers 1 and 6) have been analyzed and these results are shown in Figures 2 and 3. As already reported by many authors,[23–25] poly(3-decylthiophene) shows an oxidation

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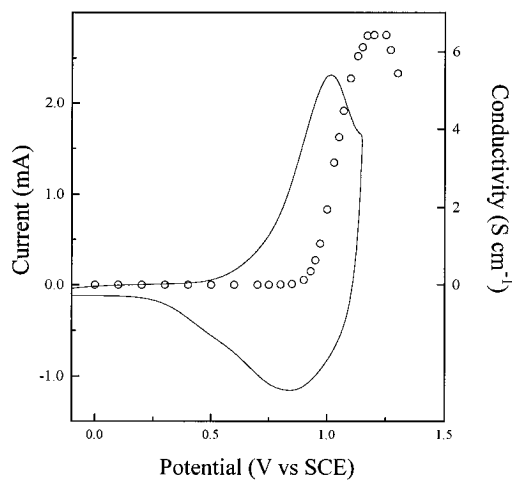
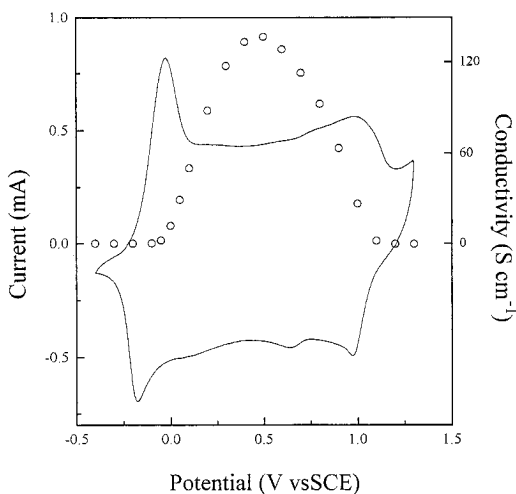**Figure 2.** Cyclic voltammetry (solid line) and in situ conductivity (open circles) measurements on polymer **1**.

Figure 3. Cyclic voltammetry (solid line) and in situ conductivity (open circles) measurements on polymer **6**.

Figure 4. UV−vis−NIR absorption spectra of polymer **1** at various electrochemical potentials.

Figure 5. UV−vis−NIR absorption spectra of polymer **6** at various electrochemical potentials.

potential around 1.0 V vs SCE with a maximum conductivity of about 6 S/cm at 1.2 V vs SCE. In contrast, poly(3,3′-dibutoxy-2,2′-bithiophene) exhibits two quasi-reversible redox processes. A first oxidation reaction occurs at 0.0 V vs SCE while the second one takes place around 1.0 V vs SCE. Between these two potentials, this polymer becomes conducting with a maximum of 140 S/cm at 0.5 V vs SCE. This high conductivity is in agreement with recent results reported for similar polymers.[26] It is also interesting to note that this conductivity level is higher than that we published for the same polymer from ex situ conductivity measurements,[19,20] and this clearly indicates the necessity to use in situ conductivity measurements to get a complete picture of the electrical properties of conjugated polymers. As reported by Ofer et al.[27] for other electroactive polymers, poly(3,3-dibutoxy-2,2′-bithiophene) has a finite window of conductivity, indicating that when the polymers are fully oxidized (which is marked by the second oxidation peak), the charge carriers are no longer mobile.

The formation of charge carriers modifies not only the electrical properties but also the optical features (elec-
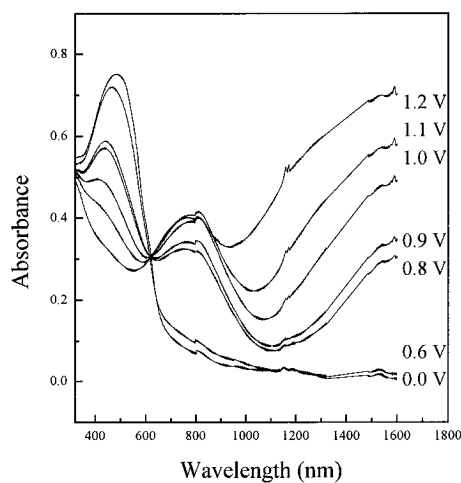
trochromism) of the polymers. As shown in Figure 4, the neutral poly(3-decylthiophene) has an absorption peak near 500 nm, whereas upon oxidation a new peak appears around 800 nm together with a large absorption band in the near-infrared range accompanied by a decrease of the intensity of the 500 nm peak. This redox process is then inducing a color change from a red-neutral form to a blue-oxidized conducting structure. Similarly, poly(3,3′-dibutoxy-2,2′-bithiophene) exhibits new absorption bands upon oxidation (near 1000 and 1500 nm), which leads to a dark blue to light gray color transition (Figure 5).

Copolymers have been characterized using the same electrochemical and electrical techniques but gave very different results. As an example of this class of copolymers, the cyclic voltammogram of copolymer 3 exhibits four oxidation processes at 0.02, 0.27, 0.56, and 1.04 V vs SCE (Figure 6). In a first approximation, these four different redox processes could be attributed to the presence of four different triads along the polymer backbone. The first oxidation reaction at 0.02 V can be easily related to an alkoxy−alkoxy−alkoxy triad, while the last oxidation peak can be attributed to the oxidation of an alkyl−alkyl−alkyl triad (although the second oxidation peak observed for the homopolymer 6 must also contribute to the oxidation peak at 1.04 V). Consequently, the two intermediate redox processes could

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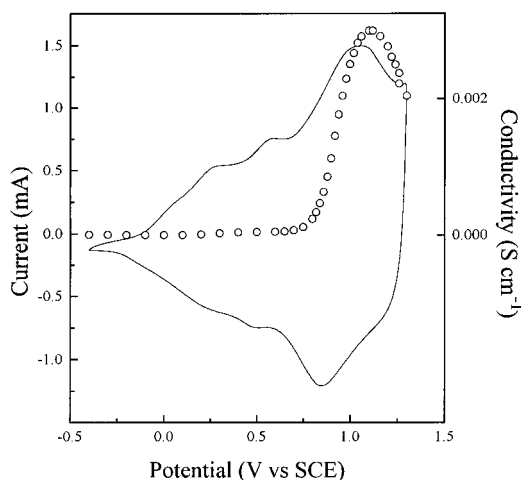
Figure 6. Cyclic voltammetry (solid line) and in situ conductivity (open circles) measurements on polymer **3**.

Table 2. Structural Characterization and Electrical Conductivity of Poly(4,4′-didecyl-2,2′-bithiophene-*co*-3,3′-dibutoxy-2,2′-bithiophene)s

polymer no.	$f_1{}^a$	$F_1{}^a$	M_n	M_w	M_w/M_n	$\sigma_{max}{}^b$ (S/cm)
7	0	0	30000	250000	8.3	6×10^{-1}
8	25	8	23000	72000	3.1	6×10^{-2}
9	50	16	11000	22000	2.0	2×10^{-1}
10	75	68	5000	14000	2.8	30
11	90	75	4000	9000	2.3	10
12	100	100	4000	6000	1.5	140

[a] f_1 and F_1 are in mole fraction of 3-butoxythiophene. [b] Maximum of conductivity from in situ measurements.

be related to the presence of two mixed triads. However, the electrical conductivity of this copolymer is much lower (most copolymers exhibit electrical conductivities around 10^{-3}–10^{-1} S/cm) which can be explained by a stronger localization of the charge carriers (see Table 1). These results could be attributed to an inhomogeneous distribution of the different triads along the backbone. Indeed, since both monomers have very different oxidation potentials (2.15 V vs SCE for 3-decylthiophene and 0.75 V vs SCE for 3,3′-dibutoxy-2,2′-bithiophene), it is highly probable that at the beginning of the polymerization reaction, the polymers are principally made of alkoxy-rich triads, whereas near the end of the reaction, alkyl-rich sequences are coupled.

Poly(4,4′-didecyl-2,2′-bithiophene-*co*-3,3′-dibutoxy-2,2′-bithiophene)s. To adjust the oxidation of both starting materials and since copolymerization of 3-decylthiophene and 3-butoxythiophene gave always almost pure poly(3-decylthiophene), it was then decided to copolymerize two bithiophene derivatives as starting materials. For this purpose, 4,4′-didecyl-2,2′-bithiophene (oxidation potential at 1.20 V vs SCE) has been copolymerized with 3,3′-dibutoxy-2,2′-bithiophene. Several copolymers have been prepared by chemical oxidation and the comonomer feed compositions (f_1, in mole fraction of 3-butoxythiophene unit) are reported in Table 2. Once again, the copolymer compositions, F_1, have been easily determined by the use of ^{1}H NMR. With poly(4,4′-didecyl-2,2′-bithiophene), only alkyl head-to-head couplings are present, and this explains why the first methylene group attached to the thiophene rings gives only one signal at 2.56 ppm. In the case of the copolymers, as shown in Figure 7, two signals are found at 2.80 and 2.56 ppm. The low-field peak is attributed to head-to-tail couplings which can result only from
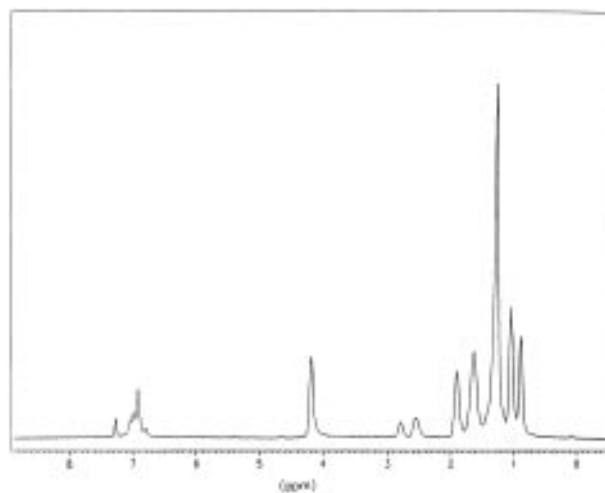

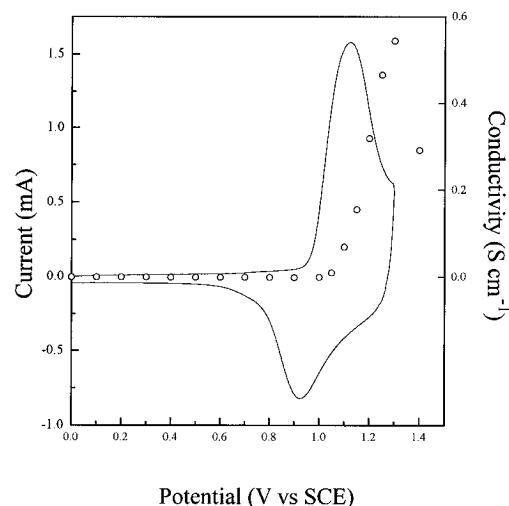**Figure 7.** ^{1}H NMR spectrum of polymer **10** in CDCl₃.

Figure 8. Cyclic voltammetry (solid line) and in situ conductivity (open circles) measurements on polymer **7**.

mixed couplings. The ratio of head-to tail couplings goes from 2% in copolymer 8 to 55% in copolymer 11.

Due to the presence of alkyl head-to-head couplings, poly(4,4′-didecyl-2,2′-bithiophene) is less conjugated than its geometric isomer (i.e., poly(3-decylthiophene) and exhibits an oxidation potential at 1.12 V vs SCE (Figure 8) and an absorption peak in the neutral state near 400 nm (Figure 9). However, upon doping, poly-(4,4′-didecyl-2,2′-bithiophene) can adopt an oxidized quinoid structure similar to that found in doped poly-(3-decylthiophene), and this explains their comparable absorption spectra in the oxidized state as well as the relatively high conductivity of poly(4,4′-didecyl-2,2′-bithiophene).[28,29]

All copolymers are very soluble in chloroform and most of them have a high molecular weight which can lead to the preparation of conducting free-standing films (see Table 2). The electrochemical, electrical, and optical properties of these copolymers have been also investigated, and very interesting features have been found. For instance, the cyclic voltammogram of copolymer 9 shows three oxidation processes (at 0.30, 0.70,

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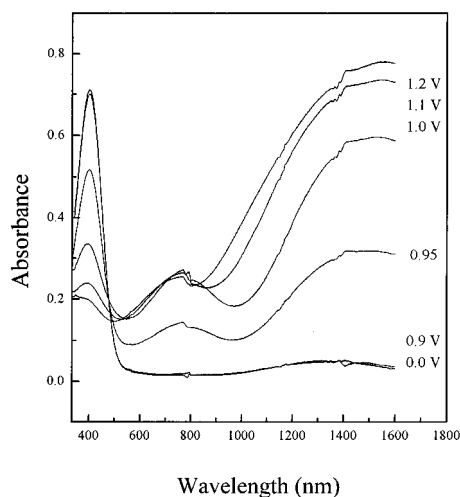
Figure 9. UV−vis−NIR absorption spectra of polymer **7** at various electrochemical potentials.
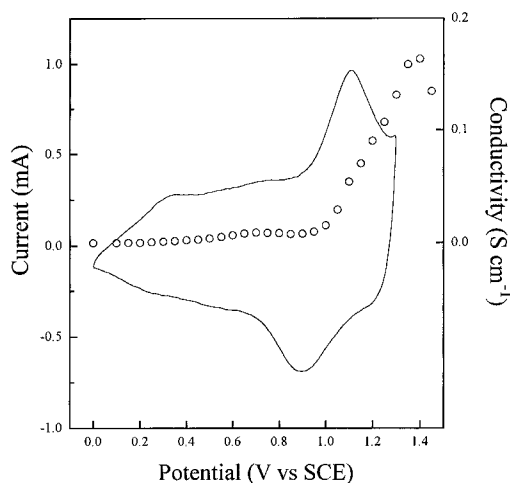

Figure 11. Cyclic voltammetry (solid line) and in situ conductivity (open circles) measurements on polymer **10**.

Figure 10. Cyclic voltammetry (solid line) and in situ conductivity (open circles) measurements on polymer **9**.

Figure 12. UV−vis−NIR absorption spectra of polymer **9** at various electrochemical potentials.

and 1.15 V vs SCE; Figure 10) which, in agreement with the previous results, can be attributed to the oxidation of alkoxy−alkoxy−alkyl, alkoxy−alkyl−alkyl, and alkyl−alkyl−alkyl triads. In the conductivity curve, a first weak conductivity maximum (0.005 S/cm) appears near 0.70 V vs SCE, while a second conductivity maximum (0.16 S/cm) occurs at 1.4 V vs SCE. This conductivity level is at least 1 order of magnitude higher than that obtained with a similar copolymer prepared from the oxidation of 3-decylthiophene and 3,3′-dibutoxy-2,2′-bithiophene. With a better distribution of the different triads, copolymer 10 exhibits four well-defined redox processes with a maximum conductivity of 30 S/cm around 0.7 V vs SCE (Figure 11). This copolymer has a large conductivity window and, in contrast to poly-(3,3′-dibutoxy-2,2′-bithiophene), copolymer 10 is highly soluble in chloroform and can give free-standing films.

Spectroelectrochemical experiments have been performed for all copolymers, and, as an example, the results obtained with copolymer 9 are shown in Figure 12. As mentioned above, the presence of alkyl head-to-head couplings gives rise to a localized twisting of the backbone which decreases the conjugation and induces a strong blue shift of the UV−visible absorption. Consequently, alkylated triads should have a completely different absorption behaviour in the UV−visible range and this can explain the optical features of the neutral
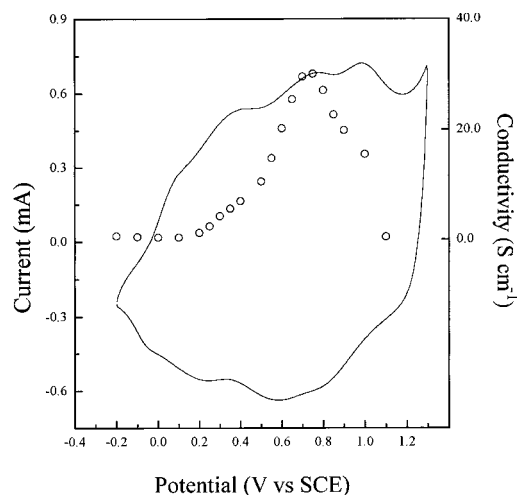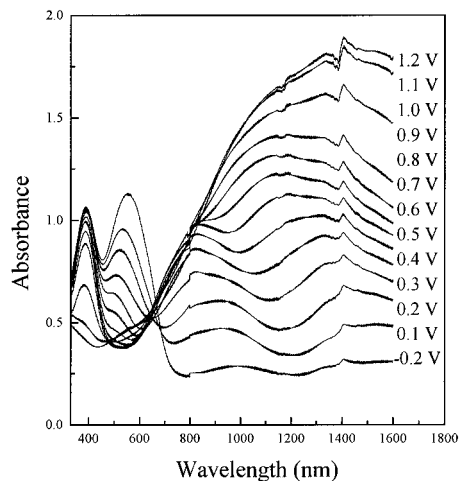
(at −0.2 V vs SCE) copolymer 9 which shows two absorption peaks at 394 and 560 nm. Upon oxidation, the intensity of the 560 nm band first decreases while two new absorption bands appear around 950 and 1450 nm. Upon further oxidation (up to 0.6 V vs SCE), the intensity of the 560 nm is still declining, whereas the absorption bands in the near-infrared range are slightly blue-shifted to 800 and 1200 nm. Between 0.6 and 0.9 V SCE, these two bands merge into one large absorption band whereas at potentials higher than 0.9 V vs SCE, the intensity of the 393 nm band is decreasing rapidly indicating the oxidation of the alkyl−alkyl−alkyl triads. On the other hand, it has been recently shown that the presence of different moieties with different oxidation potential can lead to the formation of quantum wells along the backbone.[21,22,30] Similarly, the presence of different triads with their own redox potential could lead to the controlled formation of localized paramagnetic radical cations (polarons) instead of the diamagnetic dications (bipolarons) observed usually in symmetrically substituted polythiophenes. However, all optical features observed in these copolymers can be described as a combination of the absorption bands observed in the parent homopolymers and, consequently, can be described as the results of the formation of bipolarons. In
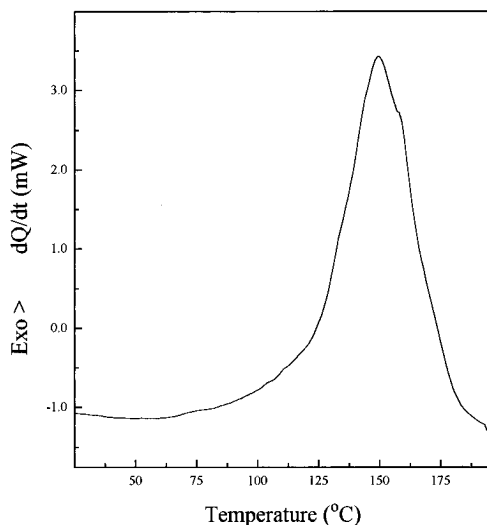
(30) Demanze, F.; Yassar, A.; Garnier, F. *Adv. Mater.* **1995**, *7*, 907.

Figure 13. DSC thermogram of FeCl$_3$-doped polymer **6** (heating scan).

Figure 14. Temperature-dependent UV−vis absorption spectra of polymer **6** (heating scan).

situ ESR measurements are in progress to give a better characterization of the charge carriers created upon oxidation.

All these results indicate that processible, conducting polymers can be obtained from the copolymerization of 4,4′-didecyl-2,2′-bithiophene and 3,3′-dibutoxy-2,2′-bithiophene. In particular, copolymer 10 seems to combine the best features of alkyl-substituted and alkoxy-substituted polythiophenes. Moreover, as already reported for poly(3,3′-dibutoxy-2,2′-bithiophene),[20] FeCl$_3$-doped copolymer 10 is stable and conducting for weeks at room temperature. However, at temperatures higher than 100 °C, these polymers seem to undergo an exothermic dedoping reaction (Figure 13). Very similar exothermic dedoping reactions have been observed for all polymers investigated in this study and have been observed in many other polythiophene derivatives.[31] Polymers with a high content of alkoxy−alkoxy−alkoxy triads (polymers 6, 11, and 12) show a room-temperature electrical conductivity of ca. 10^{-3} S/cm after thermal dedoping which is due to a partial reoxidation of the polymers by oxygen in air. First, explanations of the thermal dedoping of polythiophene derivatives were based on a twisting of the main chain (thermochromism) driven by a thermally induced disordering of the side chains, which leads to a reduction of the effective conjugation length and to an increase of the oxidation potential of the polymer.[32] However, it is important to note that poly(3,3′-dibutoxy-2,2′-bithiophene) is not thermochromic (Figure 14), which means that the thermally induced disordering of the side chains does not lead to any twisting of the main chain. On the basis of these results, it can be then considered that thermally induced steric interactions between the side chains and the counterions could be responsible for the dedoping reaction and not a twisting of the main polymer chain. Similar conclusions were drawn from experiments on partially substituted polythiophenes[31,33] and semiinter-penetrated polymer network.[34] To solve this problem
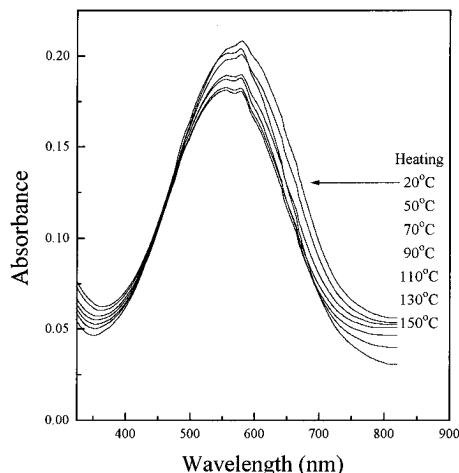
of thermal stability and processibility in conducting alkoxy-substituted polythiophenes, it could be interesting to prepare poly(3,3′-dialkoxy-2,2′-bithiophene)s bearing ionic moieties at the end of the side chains. These potentially water-soluble and conducting polymers[35] should exhibit a greater thermal stability in the doped state since a covalent link will attach the counterions to the polymers.

Conclusions

Several poly(3-decylthiophene-*co*-3,3′-dibutoxy-2,2-bithiophene)s and poly(4,4′-didecyl-2,2′-bithiophene-*co*-3,3′-dibutoxy-2,2′-bithiophene)s have been chemically prepared by using iron trichloride as oxidizing agent in chloroform. All copolymers exhibit a good solubility in chloroform and most of them form free-standing films. Copolymerization of 3-decylthiophene with 3,3′-dibutoxy-2,2′-bithiophene has led to processible but poorly conducting materials due to a localization of the charge carriers. This behavior could be explained by a quasi-block structure with isolated electroactive moieties. On the other hand, poly(4,4′-didecyl-2,2′-bithiophene-3,3′-dibutoxy-2,2′-bithiophene)s showed a better distribution of the four different electroactive triads and, consequently, showed high electrical conductivities (up to 30 S/cm) upon oxidation. All alkoxy-rich conducting copolymers exhibit an excellent stability at room temperature but undergo a dedoping exothermic transition over 100 °C, which seems to be related to steric interactions between disordered side chains and the counterions. To enhance the thermal stability of the conducting state, ionic moieties (e.g., sulfonate, carboxylate groups) should be attached to the alkoxy substituents, leading to self-doped, water-soluble, alkoxy-substituted polythiophenes.

Experimental Section

Materials. 3-Decylthiophene,[24] 4,4′-didecyl-2,2′-bithiophene,[36] and 3,3′-dibutoxy-2,2′-bithiophene[20] have been polymerized and copolymerized by chemical oxidation using iron trichloride in chloroform.[10,11] All resulting oxidized polymers have been washed by Soxhlet extraction using methanol and dried under reduced pressure. Dedoped (neutral) polymers

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have obtained by reduction using an aqueous solution of hydrazine (Fisher). These neutral polymers have then dissolved in chloroform, and the solvent was slowly evaporated to produce free-standing films. These polymer films have been purified again by Soxhlet extraction using methanol and finally dried under reduced pressure (40−80% yields).

Physical Methods. NMR measurements were performed in deuterated chloroform on a 300 Bruker instrument. Different scanning calorimetry (DSC) analyses were carried out at 10 °C/min on a TA instruments thermal analyst (Model 2910) calibrated with ultrapure indium. Molecular weights were determined by size-exclusion chromatography (Waters 510) in tetrahydrofuran using ultrastyragel columns calibrated with polystyrene standards.

Cyclic voltammograms were recorded at a scan rate of 100 mV/s in solutions of 0.1 M tetrabutylammonium hexafluorophosphate in acetonitrile, and all potentials are relative to a saturated calomel electrode (SCE). The working and auxiliary electrodes were platinum foils and all electrochemical experiments were performed at 25 °C in a one-compartment cell. For spectroelectrochemical measurements, an indium tin oxide (ITO)-coated glass electrode (Applied Films) and a platinum wire were used as the working and auxiliary electrodes. UV−vis−NIR absorption spectra were taken using a Cary 5 spectrophotometer. All measurements were started at the reduced form and kept at the desired electrochemical potential for 2 min. Temperature-dependent UV−vis absorption spectra of the polymers were obtained using a Hewlett-Packard diode-array spectrophotometer (Model 8452A). A temperature control unit was installed to allow measurements between 25 and 250 °C with a maximum error of ±2 °C.

Four-probe (ex situ) conductivity measurements were carried out on $FeCl_3$-doped polymers at room temperature in air. Chemical doping was performed by soaking the neutral polymers in nitromethane solution of iron trichloride (0.1 M). In situ conductivity experiments were carried out with a two-band microelectrode[37] in solutions of 0.1 M tetrabutylammonium hexafluorophosphate in acetonitrile according to a procedure described elsewhere.[38] Plots of conductivity vs the electrochemical potential were calibrated using the conductivity value obtained from the four-probe technique with $FeCl_3$-oxidized polymers (ca. 1.10 V vs SCE). This method of calibration is based on the relative independence of the conductivity upon the nature of the counterion (PF_6^- vs $FeCl_4^-$) and can give accurate conductivity values within one order of magnitude.[38]

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