In Situ Conductivity and Spectroelectrochemistry of Asymmetrically Disubstituted Polybithiophenes: A Multistep Behavior

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The electrochemical behavior of polythiophene and some of its derivatives has been the subject of many investigations with "contradictory" results. The electrooxidation of thin films of these polymers led usually to only one wave[1,2] while a "prepeak" was sometimes observed.[3-5] On reduction, two ill-resolved waves have been usually reported. The apparition of this "prepeak" has been attributed to the presence of different conjugation lengths[6] or to the consecutive formation of polaron and bipolaron states.[7] Swelling effects[3] and resistivity changes[8] have also been reported to affect the aspect of polythiophene cyclic voltammogram. Moreover, the nature of the charge carriers in the oxidized polythiophenes was quite uncertain, since polarons, bipolarons,[3,9-11] and dimerized polarons[12-16] have been considered. The recent report of the synthesis of symmetric and asymmetric disubstituted polybithiophenes[17] has shown that the control of the nature and position of the substituents allowed a fine tuning of the polymers properties. For example, it has been found that the incorporation of alkoxy groups leads to polymers with very low oxidation potentials and interesting electrical properties. This study has also revealed the occurrence of two redox processes in asymmetric polybithiophenes which were tentatively attributed to the consecutive formation of polaronic and bipolaronic species. It was believed that an asymmetric substitution pattern leads to a localization and, therefore, to a stabilization of the polarons. To shed some light on this feature, we report here some electrical and spectroscopic measurements on an asymmetrically disubstituted polybithiophene, namely, poly(4-bromo-4′-(octyloxy)-2,2′-bithiophene) [PBOBT].

The synthesis of poly(4-bromo-4′-(octyloxy)-2,2′-bithiophene) was carried out following a procedure described in a previous publication.[17] On the basis of SEC measurements (in THF, calibrated with polystyrene standards), this soluble polymer has a weight-average molecular weight of 4200. The electrochemical study of thin film of PBOBT revealed two oxidation processes, one at +0.60 V and the second at +1.00 V vs SCE (with a weak shoulder near 0.90 V) associated with two cathodic processes at +0.43 V and +0.83 V vs SCE [Figure 1]. These redox processes are similar to those reported previously for poly(4-butoxy-4′-decyl-2,2′-bithiophene),[17] the higher redox potentials being related to the presence of the electron-attracting bromine substituent. In situ conductivity measurements were also performed on thin-cast films of PBOBT [Figure 1]. The electrical conductivity remains very low until the potential reaches +0.5 V vs SCE where it starts to increase slowly and with a maximum around +0.6 V. Near +0.7 V, the conductivity increases almost linearly, with a marked inflexion at +0.95 V, and goes through another maximum around +1.05 V. It should be noticed that the position of the two maxima corresponds to the two oxidation waves of the polymer, while the inflexion point in the conductivity curve could be related to the occurrence of a shoulder in the cyclic voltammogram. In situ spectroelectrochemical investigations of thin films of PBOBT [Figure 2] have also revealed the successive formation of different species generated upon oxidation. A first set of absorption peaks appears at low oxidation potentials and is characterized by two bands around 750 nm (1.65 eV) and 1350 nm (0.92 eV). Increasing the oxidation potential, a new absorption band at 615 nm (2.02 eV) increases gradually while the large absorption band near 1350 nm is slightly blue shifted. When the oxidation potential reaches +1.00 V, a large new band finally appears around 1000 nm (1.24 eV). To our knowledge, it is the first time that a multistep redox behavior has been observed in a polythiophene derivative and can be related to the occurrence of different charge carriers. However, the resolution and definition of the different processes are poor due to the solid-state nature of the film.

To get a better resolution of these absorption bands, chemical oxidation of PBOBT was performed with iron trichloride solution in chloroform. As shown in Figure 3, this process leads to the occurrence of various and successive well-defined absorption bands. The first set of absorption bands appear at 785 nm (1.59 eV) and 1350 nm (0.92 eV) at low oxidation levels. Increasing further the oxidation level, a new absorption band appears at 620 nm (2.00 eV) accompanied by a slight blue shift of the 1350-nm band to 1300 nm (0.95 eV). Upon further oxidation, the intensity of the first set of bands decreases while a third band emerges at 917 nm (1.35 eV).

On the basis of previous studies performed on polythiophenes[3,4] and oligothiophenes,[13-16] the first set of absorption bands, observed both in the solid state and in solution, can be related to the presence of polaronic species (radical cations). This feature is in agreement with preliminary ESR measurements which have revealed the formation of radical cations at low oxidation levels. The

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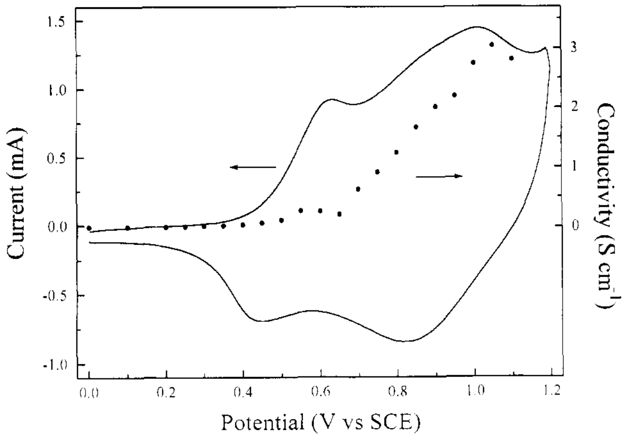

Figure 1. Cyclic voltammetry [solid line] and in situ conductivity [filled circle] of poly(4-bromo-4′-octyloxy-2,2′-bithiophene) on platinum electrode in acetonitrile/0.1M tetrabutylammonium hexafluorphosphate, at 25 °C, potentials relative to SCE.

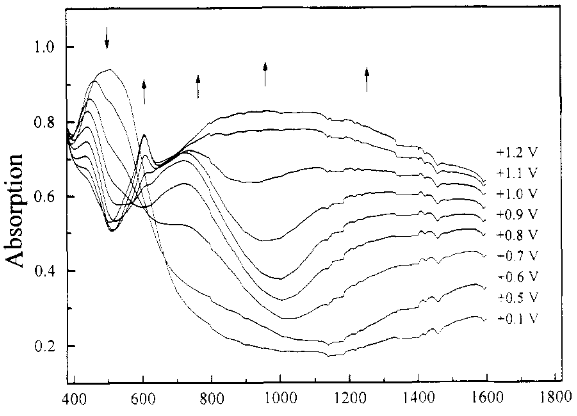

Figure 2. Spectroelectrochemistry of a thin film of poly(4-bromo-4′-octyloxy-2,2′-bithiophene) on an ITO electrode in acetonitrile/0.1 M tetrabutylammonium hexafluorophosphate, at 25 °C, potentials relative to SCE.

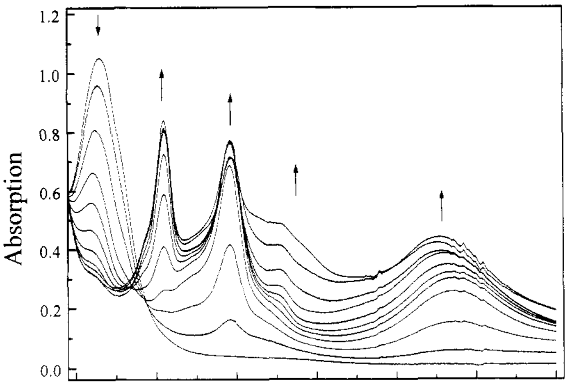

Figure 3. Evolution of the UV–vis–NIR absorption spectrum of poly(4-bromo-4′-octyloxy-2,2′-bithiophene) in chloroform with increasing oxidation levels, at 25 °C.

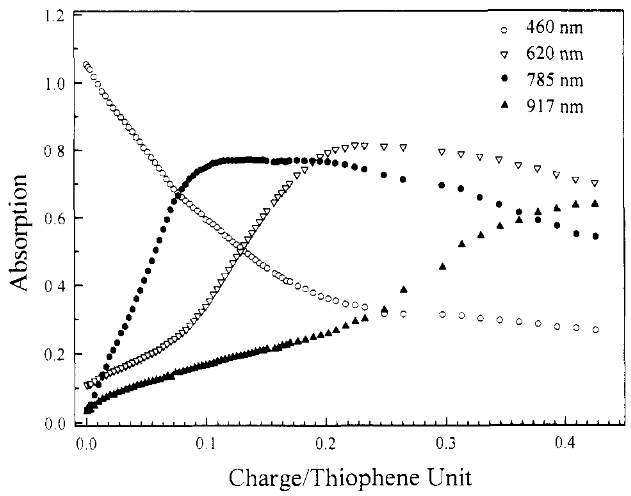

Figure 4. Evolution of the different absorption bands in poly-(4-bromo-4′-octyloxy-2,2′-bithiophene) upon chemical doping by iron trichloride in chloroform, at 25 °C.

second absorption band which appears at 620 nm could be related to the formation of dimeric radical cations as reported in the case of isomerically pure dialkylsexithiophene.[16] The formation of dimerized polaronic species during the oxidation of a polythiophene derivative has, to our knowledge, never been observed so far. Moreover, an equilibrium between the radical cation and the dimerized species exists in PBOBT solution. This equilibrium can be displaced by varying the temperature in a manner similar to that reported previously for oligothiophenes.[16] Finally the third band, around 950–1000 nm, could correspond to the formation of bipolarons (dications). The substitution pattern is believed to play an important role in the formation and stabilization of polarons, since similar properties have been observed in poly(4-butoxy-4′-decyl-2,2′-bithiophene) (weight-average molecular weight of 8700) while symmetrically disubstituted polybithiophenes (by alkyl or alkoxy groups) did not reveal a similar behaviour. This feature could be related to a localization and stabilization of the radical cations near the alkoxy-substituted units in the asymmetric polybithiophenes.

The evolution of these different species as a function of iron trichloride content during the oxidation process is shown in Figure 4. It must be noticed that the formation of the dimeric species (hollow triangles) is significantly taking place only when the concentration of the radical cations (filled circles) reaches a maximum and stabilizes, while the concentration of the undoped units (hollow circles) is continuously decreasing. The undoped polymer absorption band has almost completely disappeared after the addition of 0.2 charge/thiophene ring, while the concentration of π-dimers reaches a maximum. Consecutively, the bipolaron absorption band (filled triangles) appears while the concentration of the polarons is decreasing.

Moreover, from results shown in Figures 1 and 2, it is interesting to note that the first maximum in the conductivity curve (near 0.65 V vs SCE) is associated with the formation of around 50% of the polarons generated in the system. This feature is in agreement with previous studies[18–20] which have revealed a mixed-valence electrical transport (in this case, between oxidized and neutral units) in conjugated polymers. Moreover, by doubling the electrochemical charge transferred to the polymer (from +0.65 to +0.90 V vs SCE), the conductivity increases by a factor of 10, indicating that the simultaneous presence of different charge carriers (polarons, π-dimers, and

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bipolarons) is a more efficient pathway for the electrical transport. This proposed mechanism is currently analyzed in other polythiophene derivatives.

In conclusion, this study has shown that asymmetrically disubstituted polybithiophenes exhibit well-defined redox processes with are related to the successive formation of polarons, dimerized polarons, and bipolarons. It has been revealed also, for the first time, that an electrical transport involving neutral and oxidized (polarons) units can take place in this class of materials although a more efficient electrical transport is undergoing in the presence of dimerized polarons and bipolarons.

Experimental Section

In situ conductivity measurements have been carried out on a dual microelectrode, courtesy of Dr. G. Zotti (CNR, Padova, Italy), and the experimental setup was derived from the literature.[21] The working electrode was a two-band platinum electrode (0.3 cm × 0.01 cm for each band) with an interband spacing of 6 μm, coated by a thin polymer film of ca. 1 μm. The polymer film was then held under various electrochemical potentials while a small-amplitude (ca. 10 mV) dc voltage was applied between the bands. The current was recorded with a picoammeter (Keithley 485). The chemical oxidation of PBOBT was carried out by adding known quantities of iron trichloride solution in chloroform. The UV–vis spectra were recorded after homogeneization with a Cary 5 spectrophotometer. The in situ spectroelectrochemistry (on ITO glass) and cyclic voltammetry (on platinum) were carried out in a solution of 0.1 M tetrabutylammonium hexafluorophosphate in acetonitrile, and all potentials are relative to SCE.

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