Spin and Spinless Conductivity in Polypyrrole. Evidence for Mixed-Valence Conduction

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In situ conductivity of polypyrrole (as tosylate) as a function of oxidative doping level attains a maximum at three-quarters the total oxidation charge, and the relevant in situ ESR signal corresponds to an equal concentration of spin-carrying (polaron) and spinless (bipolaron) species. Results are explained on the basis of mixed-valence conduction. Bipolaron conduction, taking the place of polaron-bipolaron conductivity at higher oxidation levels, accounts for persisting conductivity in the high-oxidation state.

Introduction

The identification of the carriers responsible for electrical conduction in polyconjugated conducting polymers is still a controversial point. Although spinless species such as solitons in a degenerate polymer (e.g., polyacetylene) and bipolarons in a nondegenerate polymer (e.g., poly-*p*-phenylene) have previously been accepted as carriers,[1] in the case of polypyrrole the former identification of bipolarons as carriers[2] has been questioned by the discovery that polarons (spin-bearing species) are stable intermediates.[3,4] Although polypyrrole is oxidized reversibly in a single redox process, in which one positive charge is distributed over approximately three pyrrole rings,[5] it has been shown that this process results from the merging of two subsequent closely spaced redox processes.[3,4,6] The small potential difference between them (0.07 V) gives 6×10^{-2} for the equilibrium constant of disproportionation of the intermediate polaron species into neutral and bipolaron species, and this value is sufficiently low to provide the polaron species with a concentration as high as 80% of the redox sites at 50% oxidation.[6] This finding prompted further studies on the ability of polarons to act as carriers in polypyrrole.[7]

In the course of our recent investigations on the performance of a simple, reusable two-band (two-probe) electrode for direct (dc) and in situ determination of electronic conductivity of conducting polymers,[8] we found that polypyrrole shows a pronounced maximum at intermediate oxidation levels. To elucidate this result and for better understanding of the conduction mechanism in this material, we made an in situ investigation of the relationship between concentration of spin carriers and conductivity in polypyrrole using a simple dc conductivity device instead of complex ac impendance techniques and selecting polypyrrole as tosylate salt, i.e., the best ordered form of the polymer known so far.[9]

Experimental Section

Chemicals and Reagents. Pyrrole (C. Erba, Italy) was used as received. Acetonitrile was distilled twice over P_2O_5 and once over CaH_2. The supporting electrolyte tetraethylammonium *p*-toluenesulfonate (TEATos) was previously dried under vacuum at 70 °C. All other chemicals were reagent-grade products and used as received.

Apparatus and Procedure. Experiments were performed at 25 °C under nitrogen in three-electrode cells. The counter electrode was platinum; reference electrodes were a silver/0.1 M silver perchlorate in acetonitrile (0.34 V vs SCE) for film electrodeposition, cyclic voltammetric, and in situ conductivity experiments and a silver wire (0.05 V vs SCE) in ESR spectroelectrochemistry. In any case all quoted potentials are referred to the Ag/Ag^+ reference electrode. The voltammetric apparatus (AMEL, Italy) included a 551 potentiostat modulated by a 568 programmable function generator and coupled to a 731 digital integrator.

Polypyrrole films were electrodeposited from 0.1 M TEATos + acetonitrile containing pyrrole in 0.1 M concentration at an applied potential of 0.9 V. After washing with acetonitrile, the electrodes were inserted in the cell containing blank solution (solvent + electrolyte) and cycled between the neutral (−1.0 V) and the oxidized (0.2 V) states to condition the polymer. The relevant reversible charges were reproducible and stable, which guaranteed regularity of deposition and absence of degradation processes such as overoxidation.[10]

The working electrode used in in situ conductivity experiments and the relevant apparatus and procedures have previously been described in detail.[8] It was a two-band platinum electrode (0.3 cm × 0.01 cm each) with interband spacing of 20 μm, typically polymer-coated with the passage of 5 mC, corresponding to a thickness of ca. 2 μm, which ensured stable yet not heavy bridging of the bands. Measurements were performed following the method of Wrighton et al.,[11] i.e., bringing the deposit to the desired (gate) potential with the three-electrode potentiostat and applying a small-amplitude (typically 10 mV) dc (drain) voltage with an additional potentiostat in the two-electrode configuration. After equilibrium was attained, (zero gate current), the stable drain current was then recorded. Results obtained from different films indicated good reproducibility.

ESR in situ measurements were performed as previously reported in detail.[12] The working electrode was a Pt wire (0.05 cm^2) polymer-coated to a thickness of ca. 0.1 μm with the passage of 2.0 mC. The ESR signal was recorded on a Bruker ER 100D X-band spectrometer. Reproducibility was also good for these measurements.

Though hysteresis phenomena may sometimes prevent the attaining of equilibrium, we have previously shown[13] that, for polypyrrole-tosylate films up to 2 μm thick, responses independent of the direction of the potential change are obtained after a reasonable time delay. Thus our measurements were performed

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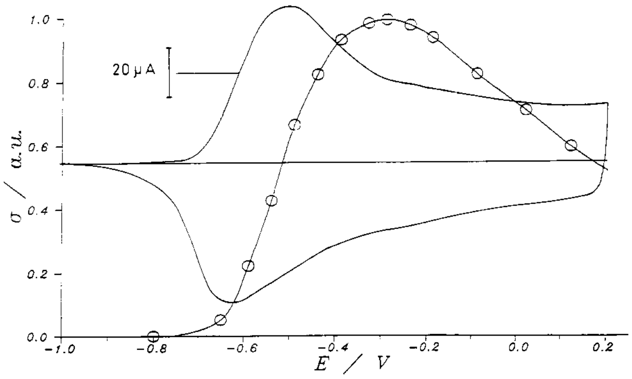

Figure 1. Conductivity vs potential for polypyrrole (○). Cyclic voltammogram for comparison (—) at 0.1 V/s on a polypyrrole film deposited with 2.0 mC at a 0.05 cm² electrode.

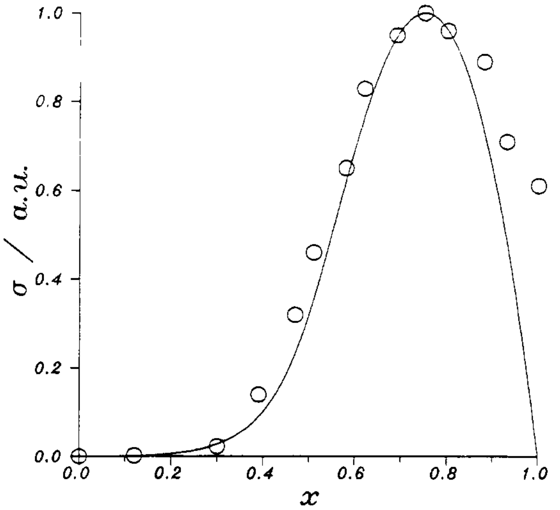

Figure 2. Conductivity vs fractional redox charge for polypyrrole: (○) experimental points; (—) theoretical curve for $K = 6 \times 10^{-2}$.

under true equilibrium conditions.

Results

As reported previously[8] and illustrated in Figure 1, the dependence of conductivity of polypyrrole on applied voltage E, instead of being sigmoidal as expected, shows a pronounced maximum at −0.3 V, i.e., with a conspicuous anodic displacement from the formal redox potential of the polymer ($E_0 = -0.6$ V). For poly(methylthiophene) a broad conductivity maximum was found with a width of 1.3 V, which correlated with the width of the valence band of the material, i.e., with the distribution of electrons available for conduction.[14] As the theoretical width for polypyrrole is ca. 1 eV wider,[15,16] given the measured low width (ca. 0.5 eV) and the fact that at more positive potentials the decrease in conductivity is slower, an analogous interpretation can be ruled out in our case.

The conductivity of polypyrrole was first investigated as a function of reversible oxidation charge q, driving the potential from −1.0 V up to a maximum of 0.2 V, i.e., a value high enough to decrease the concentration of residual spin-bearing (not fully oxidized) species to a negligible level (see Figure 4) without causing irreversible alterations of the polymer. The plot of conductivity σ vs fraction of reversible charge x ($x = q/q_{\text{tot}}$, $q_{\text{tot}} = q$ measured at 0.2 V, Figure 2), shows that conductivity increases supralinearly with charge attaining a maximum at $x = 0.75$. This result indicates that conductivity is not given by the intermediate polaron state, which attains its maximum concentration at 50% of the charge, as evidenced by ESR[3] and UV–vis spectroelectrochemistry.[6] Instead, the maximum at $x = 0.75$ suggests that the conditions most favorable for conduction occur when the oxidation level is intermediate between the polaron and bipolaron states, which clearly recalls the mixed-valence state and the behavior of redox polymers.[17] In this class of materials conductivity is explained on the basis of a mechanism of electron hopping between sites of different oxidation level, as in, for example, poly(vinylpyridine)–dipyridylosmium.[17] According to this model, conductivity increases with the probability of finding both sites occupied by electrons (donor sites) and electron-free sites (acceptor sites), so that conductivity is proportional to the product of the concentrations of the redox partners. Accordingly, the relationship between conductivity and fraction of reversible charge may be obtained as follows. If we call n_0, n_1, and n_2 the concentrations of neutral, polaronic, and bipolaronic sites, charge concentration q is given by

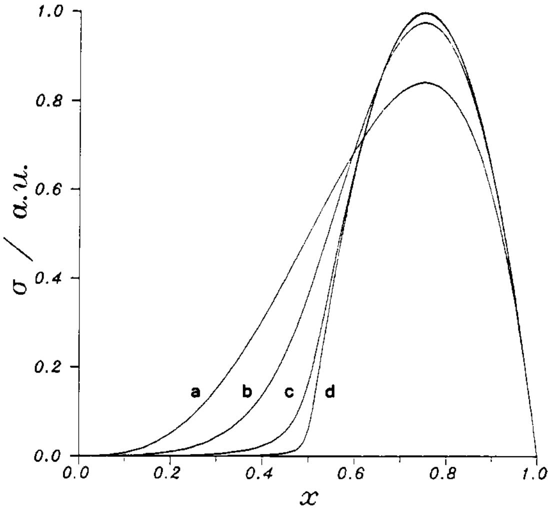

Figure 3. Theoretical curves of conductivity vs fractional redox charge for different K values: (a) $K = 1$; (b) 0.1; (c) 0.01; (d) 0.001.

$$q = F(n_1 + 2n_2) \tag{1}$$

With the normalizing condition

$$n_0 + n_1 + n_2 = 1 \tag{2}$$

the total charge concentration is

$$q_{\text{tot}} = 2F \tag{3}$$

so that fractional charge x is

$$x = q/q_{\text{tot}} = (n_1 + 2n_2)/2 \tag{4}$$

From eq 4 and the disproportionation constant

$$K = 4n_0n_2/n_1^2 \tag{5}$$

(4 in eq 5 is a statistical factor accounting for spin degeneracy[3]) the relationship between polaron concentration n_1 and fractional charge x, in implicit form, is

$$(2x - n_1)(2 - n_1 - 2x) = Kn_1^2 \tag{6}$$

The abovementioned proportionality of conductivity (in arbitrary units) with polaron and bipolaron concentrations

$$\sigma = n_1n_2 \tag{7}$$

and eqs 4 and 6 give the relationship $\sigma = f(x,K)$, illustrated

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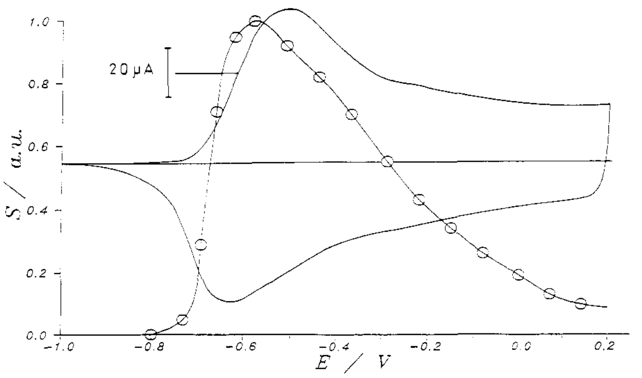

Figure 4. Spin concentration vs potential for polypyrrole (○). Cyclic voltammogram for comparison (—) with the conditions of Figure 1.

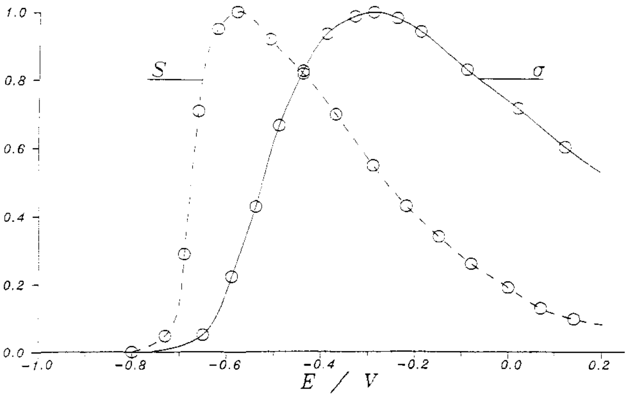

Figure 5. Conductivity (—) and spin concentration (- - -) vs potential for polypyrrole.

in Figure 3 for different K values. The close resemblance of the case for $K = 6 \times 10^{-2}$, which is the actual case for polypyrrole[6] with the experimental curve (Figure 2) is good confirmation of the proposed mechanism. Deviations at higher x values indicate the contribution from bipolarons alone.

Although these results may appear convincing, they are based on the determination of reversible charges, which might raise questions on the value of the total reversible charge and the selection of the relevant voltage. Thus, to confirm the proposed mechanism with a different and more direct measure of the redox species involved, we performed in situ ESR measurements of spin concentration S as a function of applied voltage E and correlated them with conductivity results.

Figure 4 illustrates the S/E relationship, which shows quite good correspondence of the maximum with the formal redox potential of the polymer, in agreement with previous results.[3,4] Spin and conductivity data, compared in Figure 5 vs potential, are mutually compared and plotted in Figure 6. In the latter relationship spin concentration is given as fraction of polaronic sites n_1, which attains a maximum value of 0.8.[6] It is clear that maximum conductivity is displayed at a spin fraction n_1 of 0.5 in the upper (oxidative) branch (50% polarons and bipolarons). Theoretical curves σ vs n_1 are obtained from eqs 2, 5, and 7, which provide the relationship $\sigma = f(n_1,K)$, given in implicit form in eq 8.

$$(K/4)n_1^4 + \sigma n_1^2 - \sigma n_1 + \sigma^2 = 0 \qquad (8)$$

The relationship $\sigma = f(n_1,K)$ for different K values is shown in Figure 7 and that for $K = 6 \times 10^{-2}$ in Figure 6.

The good fit with experimental values shows unambiguously what the relationship between conductivity and reversible charge had previously evidenced, i.e., that, in the course of oxidation of polypyrrole, mixed-valence conduction between half-oxidized (polaron) and fully oxidized (bipolaron) species operates before bipolaronic ("metallic") conduction sets in.

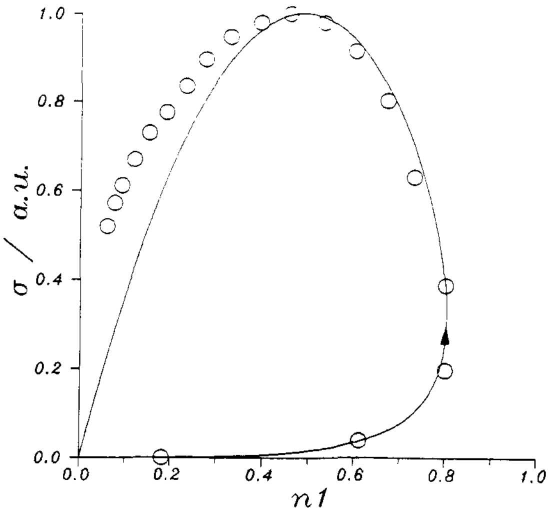

Figure 6. Conductivity vs polaron concentration for polypyrrole: (○) experimental points; (—) theoretical curve for $K = 6 \times 10^{-2}$. Arrow: direction from neutral to oxidized states.

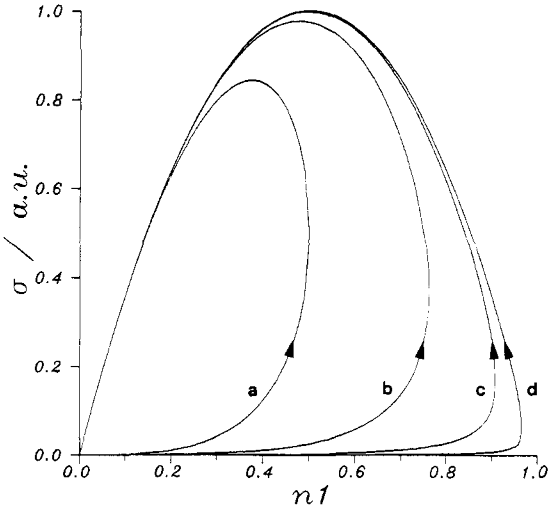

Figure 7. Theoretical curves of conductivity vs polaron concentration for different K values: (a) $K = 1$; (b) 0.1; (c) 0.01; (d) 0.001. Arrow: direction from neutral to oxidized states.

Discussion

A clear historical view to the question as to whether polarons or bipolarons are the carriers responsible for conductivity in polypyrrole has been given in a recent paper by Compton et al.[7] Briefly, former investigations, based on chemical doping by oxygen,[2] showed no correlation between conductivity and spin concentration, so that is was concluded that only spinless conductivity was operating. In their in situ investigation of polypyrrole conductivity, based on impedance measurements of polypyrrole with BF_4^- as doping anion,[7] Compton et al. give polarons and bipolarons an independent contribution to conductivity as carriers with the same mobility. However this conclusion was drawn from the observation that the conductivity/potential relationship had a sigmoidal shape with no maximum and that spin concentration followed conductivity before decreasing at potentials close to the attainment of limiting conductivity.

While confirming the high conductivity of the spinless state, our investigation assigns polarons a quite different role in conductivity properties, i.e., that of partners in a mixed-valence (redox) mechanism. Features of the conductivity/potential relationship similar to ours, i.e., a maximum in conductivity shifted to an oxidation potential higher than that of maximum spin concentration, have also been observed in polyaniline.[18,19] The absence of these features in the results of ref 7 may be due to the fact that small inorganic anions (such as BF_4^-) give a much less ordered material than that produced by relatively large aromatic anions such as tosylate as shown by X-ray diffraction,[20] neutron scattering,[21] and cyclic voltammetry.[22] Thus, although relative order of materials is required for mixed-valence conduction, it may be a general case for conducting polyconjugated polymers.

Last, it must be noted that mixed-valence conductivity in polypyrrole operates between polaron and bipolaron states and not between neutral and polaron states. In fact theoretical investigations on polyconjugated polymers[23] show that conformational changes from twisted to planar configurations are expected from the undoped to the doped form and, since polarons and bipolarons are topologically quite similar,[24] it is conceivable that the major conformational change takes place at the neutral-to-polar transition. Thus, electron hopping is easier between polaron and bipolaron than between neutral an polaron as the similar planarity of the former couple of states implies lower conformational activation energy.

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Registry No. TEATos, 733-44-8; polypyrrole, 30604-81-0.

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Transition Metals Complexed to Ordered Mesophases.[1] Synthesis Characterization and Mesomorphic Properties of Binuclear Cyclopalladated Phenylpyrimidine Species. Crystal Structure of Bis{(5-(1-hexyl)-2-[(4′-methoxy)phenyl-2′-ato]pyrimidine-$N',C^{2'}$)-μ-acetato}dipalladium(II)

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To prepare new mesogenic materials, the dinuclear palladium(II) complexes $[Pd(L)(\mu\text{-}Cl)]_2$ have been synthesized by cyclometalation of the HL*n* species (HL*n* = 5-R-2-(4′-R′-phenyl)pyrimidine; HL1, R = C_6H_{13}, R′ = CH_3; HL2, R = C_9H_{19}, R′ = CH_3; HL3, R = C_6H_{13}, R′ = $C_{11}H_{23}$; HL4: R = C_9H_{19}, R′ = C_9H_{19}). With these complexes as precursors, a number of $[Pd(L)(\mu\text{-}X)]_2$ compounds (X = Cl, Br, I, OAc) have been obtained by metathetical reactions. The molecular structure of $[Pd(L1)(\mu\text{-}OAc)]_2$ has been determined by a single-crystal X-ray analysis. The crystals are triclinic, space group $P1$ with $Z = 2$. Unit cell parameters are $a = 10.454$ (1) Å, $b = 13.229$ (1) Å, $c = 14.674$ (2) Å, $\alpha = 80.20$ (1)°, $\beta = 79.97$ (1)°, $\gamma = 72.87$ (1)°, $V = 1894.5$ (4) Å^3, D(calcd) = 1.36 g cm^{-3} for mol wt 869.62. Each palladium(II) ion in a square-planar geometry is bonded to a nitrogen atom and to an ortho carbon of pyridine and phenyl rings respectively (Pd(1)–N(2) = 2.013 (6) Å, Pd(2)–N(4) = 2.011 (5) Å; Pd(1)–C(1) = 1.947 (7) Å, Pd(2)–C(18) = 1.950 (7) Å) and to oxygen atoms of two different acetato groups (Pd(1)–O(1) = 2.142 (5) Å, Pd(1)–O(2) = 2.045 (5) Å; Pd(2)–O(3) = 2.159 (5) Å, Pd(2)–O(4) = 2.044 (5) Å). The two palladium coordination planes are folded at 25.66 (2)° with a Pd–Pd separation of 2.871 (1) Å. The HL2–HL4 ligands are nematic liquid crystals, while their mesogenic cyclopalladated derivatives display smectic mesophases only.

Introduction

A new class of materials with liquid-crystalline properties has recently been obtained by incorporation of transition metals into an organic structure. These metallomesogens, organometallic or coordination compounds, when derived by complexation of metal atoms to appropriate thermotropic ligands usually display the mesomorphism at temperatures higher than those exhibited by their mesogenic parents.[2-11] On the other hand, to be of

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