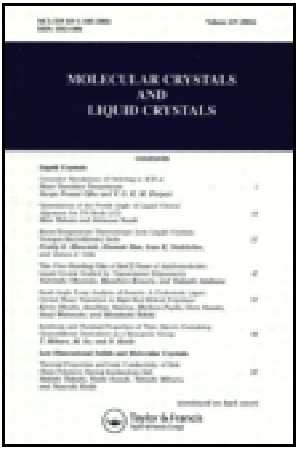

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Charge Storage in a Soluble Conducting Polymer

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ESR measurements and spectroscopic studies have been carried out on films of a soluble conducting polymer, poly (3-hexylthiophene) [P3HT], *p*-doped electrochemically. The nature of the lowest energy charge storage configurations, determined by these studies, are found to be spinless bipolarons for both doping methods. The results, when contrasted with similar studies performed on P3HT (in solution) and on polythiophene, suggest that the long alkyl substituents on the thiophene unit of the P3HT are responsible for some kind of localization phenomenon prevailing in the β-substituted systems. At temperatures below about 150 K, spins become localized.

Keywords: P3HT, conducting polymers, charge storage, doping.

1. INTRODUCTION

The mechanism of charge storage has been extensively investigated for conducting polymers, such as trans-$(CH)_x$ and polythiophene, through transport, magnetic and spectroscopic studies.[1] These studies have revealed the existence of an unusual reversed spin-charge relationship for both degenerate and nondegenerate ground state conducting polymers. The soliton (or bipolaron) and polaron picture, developed for these quasi-one dimensional systems, have gained considerable support both experimentally and theoretically.

Although the self-consistently generated structural distortion around a pair of like charges in the π-system of a nondegenerate ground state polymer leads to bipolarons (B^{2+}) as the lowest energy charge storage configuration, Coulomb repulsion favors two separated polarons (P^+). Thus, depending on the relative strength of the electron-phonon and electron-electron interactions, the polaron and bipolaron creation energies could become comparable so that the following equilibrium relation

$$B^{2+} \rightleftharpoons P^+ + P^+ \tag{1}$$

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must be considered. For the thiophene-based polymers, stabilization of polarons have been experimentally observed at very low doping levels for P3MT[2] and for P3HT (doped in solution).[3] Injection of single charges occurs via the formation of polarons—perhaps due to the presence of disorder or finite chain lengths, etc. For P3MT, a maximum of ≈0.2% polarons (with corresponding spectral and magnetic signatures) at energies near or below the principal charge injection threshold was found. For P3HT doped in solution, the polaron-bipolaron reaction could be altered by changing the ionic strength of the medium, to which the chains are subjected, to a more ionic background favoring the stabilization of spins (or polarons). Nevertheless, at higher doping levels, the dominant charge storage configurations were found to be spinless bipolarons. Analytical calculations have shown that two bipolarons (or solitons) on a chain repel each other with an exponential interaction whose range is smaller than that of the polaron-polaron attraction. Consequently, the ground state of a nondegenerate system at intermediate doping level is a bipolaron (or soliton) lattice.

At higher dopant concentrations, the energy difference between the bipolaron (or soliton) and the polaron is thought to be reduced through delocalization of electrons in the gap states into subbands. This causes a crossover of the energies, at a critical dopant concentration y_c from a non-metallic bipolaron (or soliton) lattice ($y \leqslant y_c$) to a novel metallic state ($y \geqslant y_c$). For several conducting polymers, this first order phase transition (at $y = y_c$) has been observed; occurring at ≈6% doping for trans-(CH_x) and ≈14% for polythiophene, for example. Below this transition, solitons and bipolarons have been identified as the lowest energy charge storage configurations for doped trans-$(CH)_x$ and polythiophene, respectively. Magnetic data should then reveal a temperature dependent magnetic (Curie) susceptibility below the transition and a temperature independent magnetic (Pauli) susceptibility above the transition. These observations have been confirmed for the model compounds: trans-$(CH)_x$ and polythiophene. However, the question of the dominance of the charge storage above the transition is yet to be understood.

To summarize, one can distinguish three different doping regimes for which the nature of the charge storage configurations will be different:

i. $y << y_c$: (very low doping levels): here, singly injected charges are expected to form stable polarons.
ii. $y \leqslant y_c$: low (and intermediate) doping levels: the long range attractive interactions of polarons leads to the formation of solitons or bipolarons as the lowest energy charge-storage configuration.
iii. $y \geqslant y_c$: (high doping levels): the creation energies of the solitons (or bipolarons) and the polarons become comparable, so that a cross-over of the energies from a soliton (or bipolaron) lattice to a polaron lattice results.

P3HT, the so-called hexyl derivative of polythiophene, is soluble in common organic solvents. Because of this solubility, P3HT films can be made ultrapure with well-controlled and uniform thickness. In addition to its excellent processibility, P3HT can be doped in solution, thereby enabling uniform doping at a well-defined and accurately reproducible doping level. In this paper, we report optical and magnetic data for P3HT films doped electrochemically with $NaClO_4$. As with PT and P3MT, we find charges are predominantly stored in bipolarons. Qualitatively the same features for the different doping conditions are reproduced. The results demonstrate the spinless character of the doping-induced charge states and set an upper limit on the number of spins per ring of about 3.7×10^{-3}. This demonstration of reverse spin-charge relation proves that bipolarons are the lowest energy charge storage configurations in doped P3HT films (as for PT). From the magnetic data we find, in addition to a sharp increase in the number of spins (of at least 2–3 decades) at $y = y_c$. The spins present at $y \geqslant y_c$ become localized at low temperatures (below about 150 K). The results obtained here will be compared to those obtained for P3HT doped in solution (with $NOPF_6$).

2. EXPERIMENTAL

Details of the polymer synthesis and polymer characterization have been reported by several groups.[4] The *n*-hexyl derivative of polythiophene (P3HT) can be prepared as free standing films with high electrical conductivities (30–100 S/cm). High MW ($5-15 \times 10^4$) and high purity P3HT has been prepared; and characterized as 2,5 linked linear polythiophene chains by IR studies. Solution-cast films have spectral features essentially identical with those of the as-synthesized (electrochemically) films, both in the neutral state and after doping. Solutions were prepared by dissolving P3HT in spectral grade quality chloroform. Unless specified, the samples were handled under inert conditions.

In-situ optical and magnetic measurements were performed using $NaClO_4$ (ca. 0.25 M) as the electrolyte, propylene carbonate (freshly distilled) as the electrolytic solvent, and sodium metal as the counter and reference electrodes. Thin films were cast on conducting (indium/tin oxide coated) quartz/glass for ESR/optical studies. The optical spectra at different doping levels (corresponding to different applied potentials vs Na) were taken on a Perkin Elmer Model Lambda 9 absorption spectrophotometer. The ESR spectra were recorded using an IBM instruments E-2000 ESR spectrometer interfaced to an Apple IIe computer for signal averaging and data analysis; NBS ruby standards were used for calibration purposes. Measurements were taken after allowing the cells to come to equilibrium as monitored by the current flow (typically, for 24 hours).

3. RESULTS AND DISCUSSION

Figure 1 shows the absorption spectra of (in-situ) electrochemically doped P3HT film using $NaClO_4$. The π-π^* absorption of the neutral polymer has an onset which is relatively sharp at about 1.9 eV, a value comparable to that of PT and P3MT. The effect of doping is characteristic of non-degenerate ground state conducting polymers: the π-π^* transition is depleted with the oscillator strength shifted onto subgap features in the IR. Thus, below potentials of 3.0 V (vs Na), no doping occurs; while for applied potentials of 3.0 V to ca. 3.25 V, three features appear below the band gap at ca. 1.7–1.75 eV. ca. 1.25–1.3 eV and below 0.56 eV

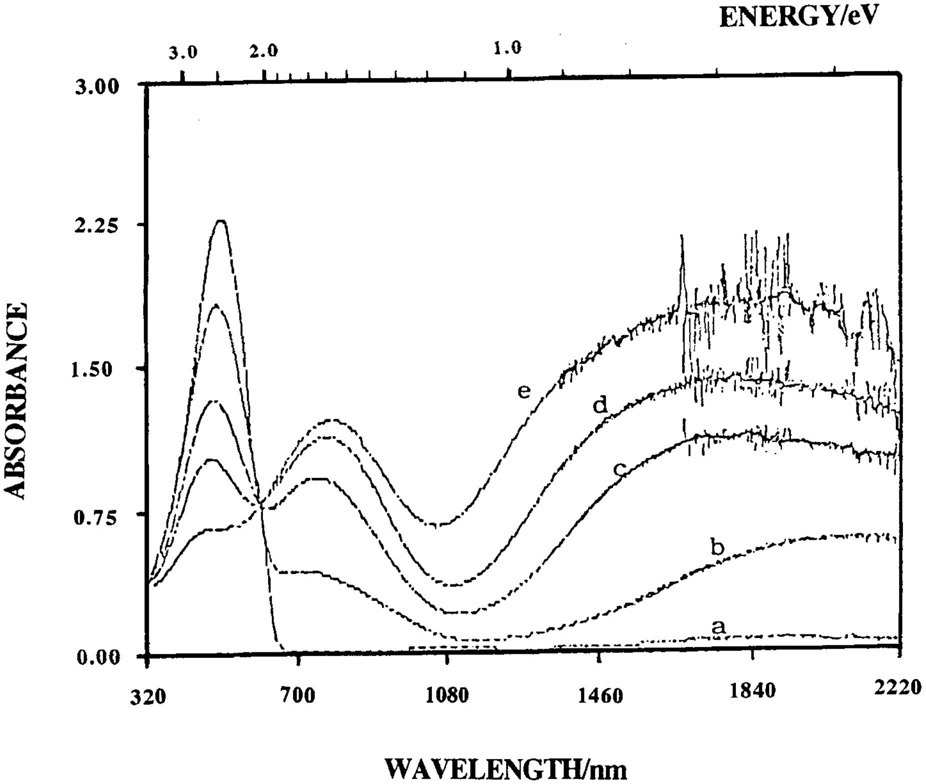

FIGURE 1 Series of in-situ visible-near infrared absorption spectra of poly 3-hexyl thiophene as a function of applied electrochemical voltage (vs Na)-Raw Data [(a) 2.95 V, (b) 3.20 V, (c) 3.35 V, (d) 3.45 V, (e) 3.55 V].

(probably peaking at ca. 0.45–0.5 eV)[3a]; consistent with charge storage predominantly in polarons. At higher doping levels, corresponding to potentials above 3.25 V, only two principal features become distinct, with maxima at 1.58 eV and 0.68 eV, consistent with charge storage predominantly in bipolarons. The occurrence of an isosbetic in the optical data implies the coexistence (and interconversion) of two species on a P3HT chain: neutral segments where the π-π^* transition is unchanged and localized sections surrounding the charge-storage configurations (polarons and bipolarons).

To confirm the nature of the charge storage species introduced upon doping, parallel in-situ ESR measurements were performed. The results lead to the conclusion of the predominance of spinless charged bipolarons; spins arising simultaneously on doping implying a small difference in the creation energies of polarons versus bipolarons, and hence, the shift in the equilibrium in the reaction 1 towards the polarons. Figure 2 shows the dependences of the magnetic susceptibility X and the linewidth H_{pp} on the chemical potential of the cell (vs. Na), respectively. A sharp increase in X is found on doping at around (V_c =) 3.1 V. Below this critical potential V_c, X was too small to be measured ($X << 10^{-8}$ emu/mole ring) for samples that were chemically treated with ammonia. For uncompensated samples

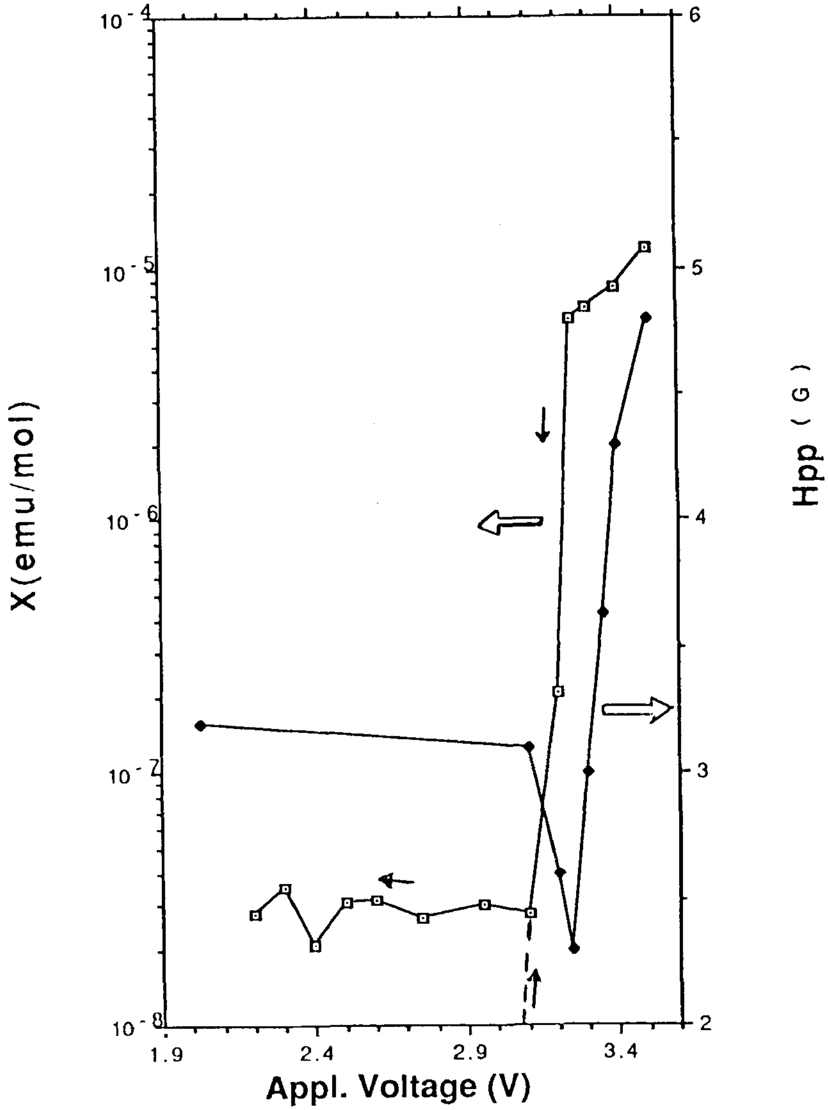

FIGURE 2 Magnetic susceptibility (X) and linewidths (H_{pp}) dependences upon the electrochemical voltage (vs Na). Arrows indicate direction of doping/undoping.

handled in air, the X measured was found to be ca. 1.5–3.0 × 10^{-8} emu/mole ring (depending on the sample) corresponding to about 1 spin for ≈0.4–0.8 × 10^5 rings. This suggests that the sample treatment is important; air oxidation contributes to the measured X values. This effect was found to be reversible since on exposure of a compensated sample to air the ESR signal reappears. After the dramatic increase in X above V_c, X saturates and takes a value of ca. 6–12 × 10^{-6} emu/mole ring. Thus, for compensated samples, the sharp increase in X at V_c must be more than 2–3 decades. From Figure 2, we see that the linewidth (H_{pp}) increases from ca. 2.0–3.0 G for undoped (uncompensated) samples to ca. 5.0–6.0 G for doped (uncompensated and compensated) samples. The magnitude and dependence of X and H_{pp} on doping were found to be comparable to chemically doped samples.[5]

Figure 3 shows the temperature dependences of X and H_{pp} of electrochemically-doped (3.35 V vs Na) P3HT samples. These plots show a temperature-independent (Pauli type) susceptibility above about 150 K and a temperature-dependent (Curie type) susceptibility below the temperature for highly doped P3HT samples. We note for PT, X is independent of temperature at high doping levels. Probably one can associate this difference to the extent of order/disorder in these systems. The

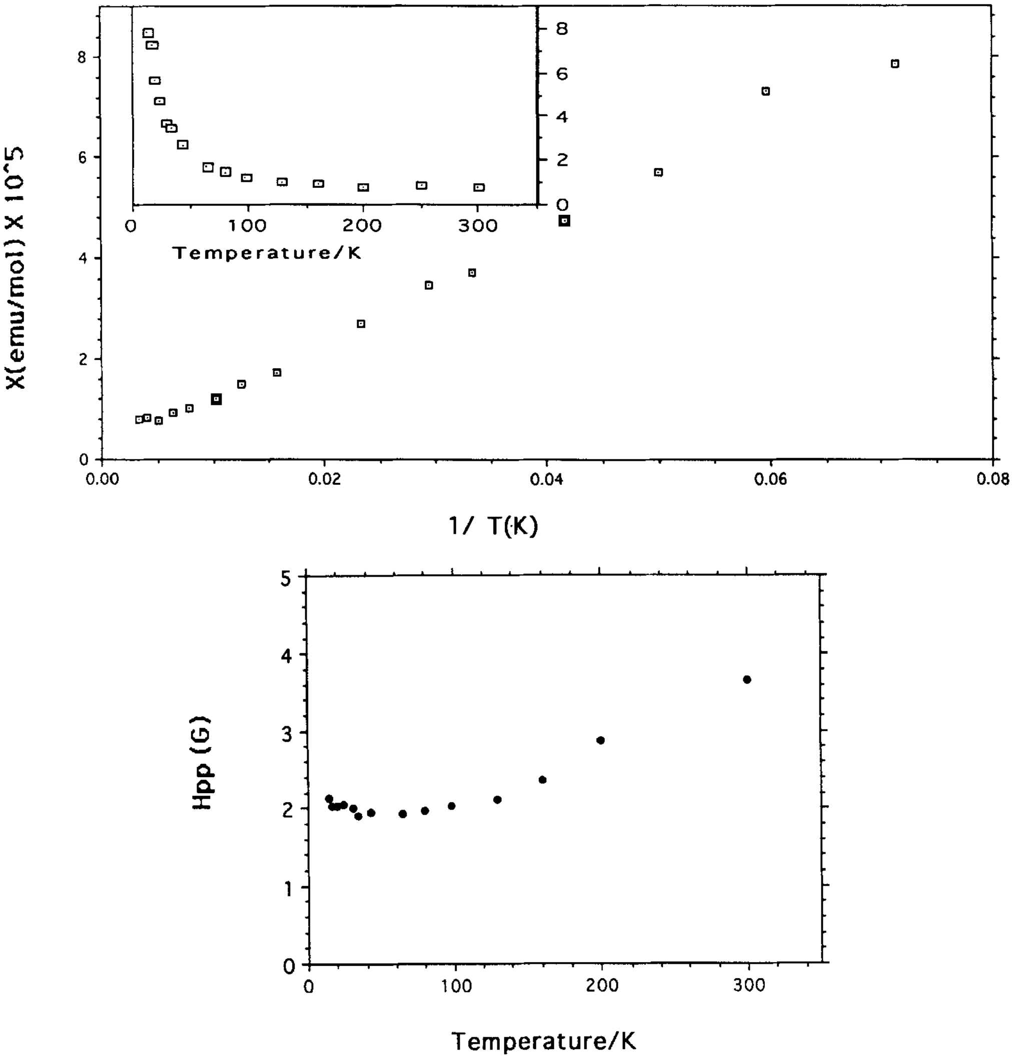

FIGURE 3 Temperature dependence of the magnetic susceptibility (X) and linewidths (H_{pp}) for P3HT sample doped at 3.35 V (vs Na).

magnetic data on P3HT suggest that the observed spins (or polarons) become delocalized at high temperatures. From the Curie part of the X dependence, we calculate about 3.1×10^{-3} spins/ring (1 spin for 325 rings); strongly implying the predominance of bipolarons in accord with the corresponding absorption data. Comparison of the magnetic and optical data suggests that the subgap features (and the associated bleaching beyond the energy gap) and spin (polaron) population evolve almost simultaneously on doping. Thus, the presence of small number of spins per ring and the appearance of the two subgap features in the absorption spectra (at doping levels corresponding to above 3.25 V) indicate bipolarons as the predominant charge storage configurations in the doped P3HT chains. Further support comes from the 1:1 correspondence of doping-induced and photo-induced spectral changes for this polymer.[6]

Optical and magnetic data of neutral and doped P3HT have been reported for this polymer in solution.[3] Again, on doping, oscillator strength from the main π-π^* transition is shifted onto two principal subgap features in the IR with maxima at 1.55 eV and 0.5 eV, consistent with charge storage predominantly in bipolarons. At high doping levels in dilute solutions nearly all the π-electron oscillator strength has been shifted into the two intense IR bands, implying the existence of a close-packed array of bipolarons on the P3HT chain (interdispersed with a small number of polaron defects). The maximum number of spins per ring is found to be ca. 0.04–0.05 (that is 1 spin for every 20–25 rings) at high doping levels (and at high concentrations). The polaron population is thus about a decade higher for polymer chains in solution than for chains in the solid state. The enhancement in the bipolaron population (as a result of two polarons attracting each other) in the films probably comes either from the greater order existing in the chains in the solid state or from the extent of the Coulomb screening prevailing in the media. In the more random conformation of the polymer chains in solution, the equilibrium reaction (1) is shifted toward polaron production since the energy difference between the creation energies of the polarons and the bipolarons becomes smaller.

4. CONCLUSION

Of the two charged states, the bipolaron is the favored species in calculations which exclude the electron-electron interactions. Addition of the Coulomb interaction clearly favors the polaron states. Consequently, the strength of the Coulomb interaction is the critical parameter in determining the lowest energy charge storage configuration in non-degenerate ground-state systems. Experiments on many conducting polymers in the solid state (e.g. for polyacetylene and many polyheterocycles) have been reported. The availability of processible conducting polymers has opened up the way for new and/or renewed investigations. For example, the soluble polymers have made possible studies as a function of polymer concentration and thus the extent of interchain interaction. Not surprisingly, the effect on the equilibrium between the two possible charge storage configurations (P^+ and B^{2+}) for doped chains (recall Equation 1) has also been possible. These studies have led us to the conclusion that this equilibrium can be disturbed by altering the ionic strength of the medium. The ability to stretch-align the processible polymers (like D-CH_x and PPV)[7] has made possible various studies of the anisotropic properties of these conjugated systems.

In-situ measurements have demonstrated the reverse spin-charge relationship, thereby proving that bipolarons are the lowest energy charge-storage configurations in doped PT. That this is also applicable to the β-substituted polythiophenes has been demonstrated here for the case of P3HT through both in-situ and ex-situ optical and magnetic measurements; the magnetic data setting an upper limit on the spins per ring $<5 \times 10^{-3}$. Further support of the bipolaron picture comes from the photo induced and doping-induced studies for this polymer. Similar conclusions have been reached for studies of P3HT doped in solution. Polarons have been seen to arise from singly injected charges (at very low doping levels) or due to the presence of disorder or defects on the chains or, in the case of polymers in solution, due to a change in the ionic environment of the medium at higher doping levels. Thus, the concept of nonlinear excitations, initially developed for conducting polymers in the solid state has now been extended to include soluble polymers.[3]

The magnetic susceptibility data shows that the spins, arising as a result of the shift in the equilibrium reaction (1), display an unusual temperature dependence. The results suggest that these spins become delocalized at temperatures above about 150 K and localized at lower temperatures. The cause of this localization phenomenon is unknown although one can speculate that it could be sidechain-induced.

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