

Bipolarons in poly(3-methylthiophene): Spectroscopic, magnetic, and electrochemical measurements

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In poly(3-methylthiophene), P3MT, charge is stored in spinless bipolarons at all but the most dilute doping levels. From the combination of magnetic and electrochemical measurements, we find definitive evidence of the reversed spin-charge relation expected for bipolarons with $N_s/N_{ch} < 10^{-3}$; from the spectroscopic data we find the two subgap absorptions indicative of self-localized bipolaron levels located nearly symmetrically within the gap. For charge injection below the principal injection threshold, one observes polaronlike features with a maximum number of spin-carrying species of approximately 0.2 mol % (one per 500 rings). Our results imply that these features result from defect states in the energy gap, but they are not the self-localized polarons which would be characteristic of a charge on a nondegenerate ground-state polymer such as a perfect P3MT chain. The conclusion that the bipolaron is the lowest-energy charge-storage configuration indicates that effective electron-electron Coulomb repulsion is relatively weak in P3MT.

I. INTRODUCTION

Polarons and bipolarons are expected to be the important nonlinear excitations and the dominant charge-storage configurations in conducting polymers (such as *cis*-polyacetylene, polythiophene, and polypyrrole) with a nondegenerate ground state.¹ Although the self-consistently generated structural distortion around a pair of like charges in the π system of such a polymer leads to the bipolaron (B^{2+}) as the lowest energy 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 be comparable. For weak electron-electron repulsion,

$$E_B < 2E_P \quad (1)$$

so that



where E_B and E_P are the bipolaron and polaron creation energies, respectively. In the case of relatively strong Coulomb interactions, the inequality in Eq. (1) would be reversed, and the reaction in Eq. (2) would proceed in the opposite direction.

In the case of polythiophene²⁻⁴ and the poly(3-alkylthiophenes),⁵ there is considerable evidence that upon doping or photoexcitation, charge is stored in spinless bipolarons. In the case of poly(3-methylthiophene), P3MT, however, Harbeke *et al.*⁶ concluded from detailed studies of the spectral changes induced by dilute doping that polarons are generated as well. The existence of polarons at very dilute concentrations going over to bipolarons at higher concentrations either means that the inequality in Eq. (1) is incorrect or that the

polaron-to-bipolaron reaction described by Eq. (2) is inhibited at very dilute concentrations⁷ (perhaps by disorder, finite chain length, etc.). In this context, we note that injection of a single charge *must* always occur via the formation of polarons, with bipolarons resulting from the reaction expressed in Eq. (2). Thus even in the case where the inequality holds (or when the two energies are comparable), polarons can be expected at very dilute concentrations, particularly in samples with a high degree of disorder and in samples with relatively low molecular weight (i.e., when the number of thiophene rings per chain is less than the dopant concentration per ring).

In this paper we present the results of a coordinated set of experiments on P3MT designed to address this problem. Visible-near-ir spectroscopy and electron-spin resonance (both carried out *in situ*) have been combined with electrochemical-voltage spectroscopy to determine the self-localized energy levels within the energy gap, the spin, and the injection energies relative to the gap edge associated with the charge carriers injected onto the P3MT chains by electrochemical doping. We find a maximum of $\approx 0.2\%$ polarons (with corresponding spectral and magnetic signatures) at energies near or below the principal charge-injection threshold; at higher doping levels we find that the charge is stored in spinless bipolarons.

II. P3MT FILM PREPARATION

Our measurements were performed on films prepared under strictly oxygen- and moisture-free conditions. By oxidative polymerization, freestanding films of polythiophene and its 3-alkyl (methyl, ethyl, butyl, hexyl, etc.) derivatives can be prepared with controlled thickness and having conductivities as high as 500 S/cm

(as a result of doping with anions of the supporting electrolyte). Tourillon and Garnier⁸ have noted, however, that nondegassed reaction systems (electrolytic solutions) result in film conductivities lower than those from carefully degassed systems. They attributed these lower values to the presence of chemical disorder (due, for example, to the introduction of carbonyl groups). Such disorder would be expected to obscure the physical properties of the polymer. With this in mind, we endeavored to improve the electrochemical-polymerization techniques for polythiophene and the poly(3-alkylthiophenes). In this paper we report on results obtained from the resulting P3MT films which showed an improved conductivity (doped, as-synthesized) of about 750 S/cm.

To prepare the films, 3-methylthiophene (Aldrich Chemical Co.) was dried over a molecular sieve and distilled under dry nitrogen. Nitrobenzene was distilled over phosphorous pentoxide under a reduced pressure of about 0.05 Torr. Tetrabutylammonium perchlorate (Thiokol Co.) was recrystallized from methanol-water (1:1 by volume), dried at 100°C under a reduced pressure of about 0.05 Torr for 20 h, then precipitated from dichloromethane into diethylether. The precipitate was collected by filtration and dried again in the same way. Reagent-grade methanol, deionized water, dry distilled dichloromethane, and diethylether were used. The monomer, solvent, and electrolyte were stored under dry argon for further use.

Polymerization was carried out in a closed glass cell equipped with a stopcock and ground-glass joint. By maintaining a rigorously oxygen-free and moisture-free environment during film preparation, we were able to obtain a significant increase in the conductivity of the resulting polymer. To this end, the cell and electrodes were evacuated and flame heated for 15 min prior to use. An electrolytic solution of the monomer (0.2M), electrolyte (0.02M), and solvent was then introduced into the cell in a dry-nitrogen environment. The cell was lowered to liquid-nitrogen temperature and evacuated to a pressure of about 2×10^{-3} Torr for 2 h. Dry nitrogen was then reintroduced through the stopcock and the cell temperature allowed to rise to 5°C. At this temperature poly(3-methylthiophene) films were deposited onto indium-tin oxide (ITO) electrodes by applying a constant current density of 2 mA/cm² for periods ranging from 40 s to 40 min. The resulting film thickness was proportional to the polymerization time, with a deposition rate of approximately 5 nm/s. The as-grown films, heavily doped with ClO₄⁻ ions, were undoped to the neutral state immediately after synthesis by reversal of the cell polarity.

III. SPECTROSCOPIC, MAGNETIC, AND ELECTROCHEMICAL MEASUREMENTS

For optical-transmission measurements, films with a thickness of about 0.2 μm were deposited on ITO electrodes on glass substrates. We used the technique employed by Chung *et al.*² in their study of polythiophene to measure, *in situ*, the visible-ir-absorption spectrum of P3MT during electrochemical doping. Inside a sealed

thin rectangular glass cell, the polymer electrode and lithium-metal counterelectrode were suspended in an electrolytic solution of 0.5M LiClO₄ in propylene carbonate. The cell was rigidly mounted in the beam of the broadband light from a Newport 780 tungsten halogen lamp. Light transmitted through the sample was dispersed by a McPherson EU700 monochromator and monitored by either a photomultiplier or an IR Industries Si/PbS two-color detector using standard light chopping and lockin-amplifier techniques. The monochromator-grating drive and detector electronics were interfaced to an IBM PCXT which collected and stored the data. By adjusting the cell voltage between 2.5 and 4.0 V, it was possible to reversibly dope (and undope) the polymer, and simultaneously measure the visible-ir-absorption spectrum.

In Fig. 1 we present four absorption spectra taken as the polymer was electrochemically reduced from maximum doping to the neutral state. Equilibration times were typically ~2–3 h. The spectrum of the neutral polymer (at 2.5 V versus Li) shows an interband transition peaking at 2.4 eV. The onset of absorption (i.e., the three-dimensional energy gap) is relatively sharp at about 1.9 eV. By comparison with the results from polythiophene^{2,4} and polyacetylene,^{9,10} we infer that the one-dimensional (1D) energy gap (E_g^{1D}) is about $E_g^{1D} \approx 2.2$ eV.

At the higher doping levels (above about 3 V versus Li) two subgap absorptions are clearly visible with maxima at $\hbar\omega_1 \approx 0.65$ eV and $\hbar\omega_2 \approx 1.6$ eV. In contrast to observations in polythiophene,² these spectral features remain even at the highest doping levels, never evolving into a smooth broadband ir absorption like that from free carriers in a metal. This is in contrast to observations reported by Sato *et al.*¹¹

Below about 3 V (versus Li) a weak feature near $\hbar\omega = 1.2$ eV appears in the spectrum. If the electrochemical cell is held at 2.5 V for several days, this peak gradually diminishes in intensity, but never entirely van-

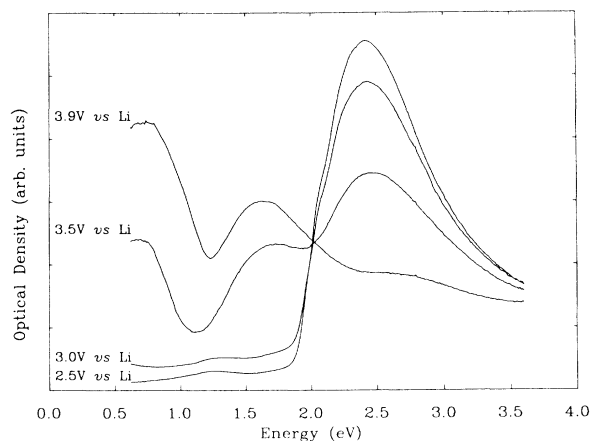


FIG. 1. Absorption spectra (optical density vs photon energy) taken as the polymer was electrochemically reduced from maximum doping to the neutral state (for calibration of the cell voltages, see Fig. 4).

ishes. To obtain better resolution of this feature, we made use of the technique of Harbeke *et al.*⁶ and measured the transmission of a much thicker film ($\approx 4 \mu\text{m}$) at dilute doping levels in the spectral range below the gap ($\hbar\omega < 2 \text{ eV}$). In this case the electrochemical cell was assembled with a doped film. Because of the thickness of the film, the doping kinetics were extremely slow. A series of spectra, recorded as the P3MT film was reduced from 3.3 V versus Li, are presented in Fig. 2. These thick-film observations essentially reproduce those of Harbeke *et al.*⁶

To determine whether the species introduced on doping carry spin, we conducted parallel *in situ* electron-spin-resonance (ESR) measurements during doping. The samples for these studies were thin films ($\approx 2 \mu\text{m}$) grown on ITO electrodes on quartz substrates. These were mounted in electrochemical cells as described by Chen *et al.*³ using lithium-metal counter-electrodes and LiClO_4 as the electrolyte in propylene carbonate. Magnetic resonance measurements were performed as a function of cell voltage on an IBM Instruments Bruker 200D Electron Spin Resonance Spectrometer interfaced with an Apple IIe computer for data acquisition and analysis. In this case, the cell was allowed to equilibrate for 24 h before measurement. Magnetic susceptibility versus cell-voltage data are presented in Fig. 3. At about 2.5 V versus Li, in the neutral polymer, a weak ESR signal with $\approx 6\text{--}8 \text{ G}$ linewidth is observed corresponding to an integrated magnetic susceptibility of $\approx 2 \times 10^{-6} \text{ emu/mol}$. This corresponds to about 0.2 mol %, i.e., about one spin per 500 thiophene rings, or about one spin per 2000 carbons along the conjugated backbone (a value comparable to that found in *trans*-polyacetylene¹²). If the cell voltage is held at 2.5 V for extended periods, χ slowly decreases by as much as an order of magnitude. If at this point the cell voltage is stepped to $\sim 3 \text{ V}$; the narrow line reappears, and χ increases back to $\approx 10^{-6} \text{ emu/mol}$.

As the cell voltage is slowly raised, the line narrows; at about 3.2 V versus Li, the 4-G wide line corresponds

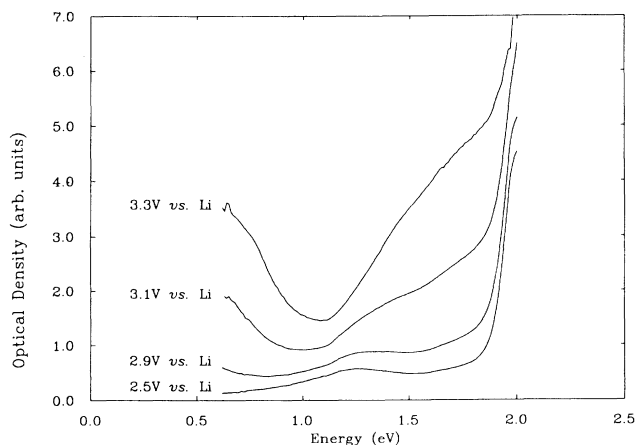


FIG. 2. Absorption spectra (optical density vs photon energy) of a thicker film at dilute doping levels in the spectral range below the gap ($\hbar\omega < 2 \text{ eV}$).

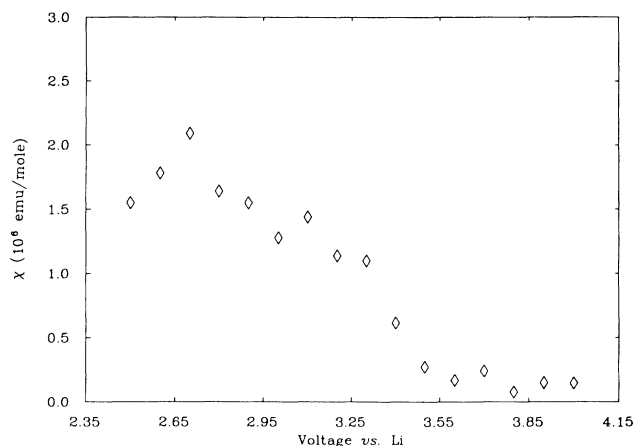


FIG. 3. Magnetic susceptibility vs cell voltage (or electrochemical potential); for calibration of the cell voltages, see Fig. 4.

in intensity to about one spin per 1000 thiophene rings. Above 3.4 V versus Li, the susceptibility drops to a value less than 10^{-7} emu/mol . If the cell voltage is lowered again, the small narrow line signal reappears for cell voltages between 3.4 and 3 V. This signal persists if the voltage is lowered to 2.5 V, slowly relaxing over the course of a week to its original magnitude and linewidth at that voltage.

Finally, a series of electrochemical-voltage spectroscopy¹³ (EVS) measurements were made to determine the relation of the above observations to charge injection and storage in the polymer. This technique involves slowly stepwise incrementing the voltage of the electrochemical cell and recording the charge removed from (or injected into) the polymer after each voltage step. For our EVS measurements, an Apple IIe was used to control a Hewlett-Packard 59501 digital-to-analog converter (DAC), which applied the cell voltages, and to monitor the cell current during the approach toward equilibrium after each voltage step. Typical data for a 2-mg sample cycled from 2.5 to 3.7 V (versus Li) and back in 0.05 V steps are shown in Fig. 4. This curve indicates a threshold for charge injection at 3.1–3.2 V versus Li. Coulomb efficiency of these films is excellent ($> 98 \%$). Cycling to higher voltages results in reduced Coulomb efficiency, but this can probably be attributed to breakdown of the propylene carbonate.

IV. DISCUSSION

Our EVS measurement indicates that most of the charge transfer to the polymer occurs in the range of electrochemical voltages in which the ESR data set an upper limit of 8×10^{-5} spins per thiophene ring ($\chi = 10^{-7} \text{ emu/mol}$). For example, as shown in Fig. 4, a cell voltage of 3.6 V corresponds to an injected charge of about 200 mC; i.e., approximately 10 mol % doping. Combining this with the number of spins determined at the same cell voltage leads to a spin-to-charge ratio of $N_s/N_{\text{ch}} \approx 8 \times 10^{-4}$, where N_s is the number of spins in

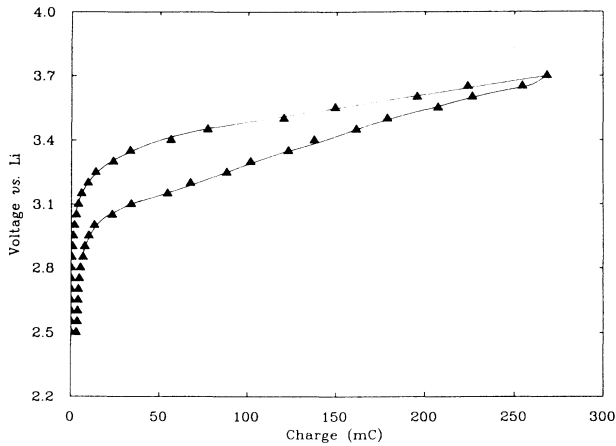


FIG. 4. Cell voltage vs charge for a 2-mg sample of P3MT.

the polymer resulting from N_{ch} injected charges. This is the smallest value reported for any polymer system and is a direct and unambiguous demonstration of the reversed spin-charge relation for the charge-storage species in P3MT.

In the same electrochemical range (cell voltage greater than 3.3 V versus Li), two strong subgap transitions are observed in the ir with energies that satisfy the familiar rule^{1(c)}

$$\hbar\omega_1 + \hbar\omega_2 = E_g^{1D}, \quad (3)$$

expected for the two bipolaron transitions in a polymer with nondegenerate ground state [see Fig. 5(a)]. The equality in Eq. (3) is satisfied by the two subgap features and the interband absorption to at least within about 0.2 eV, with the accuracy limited by uncertainty in the precise values to be taken from the spectra. We note that Eq. (3) is expected to be only approximate; including the electron-electron repulsion associated with the double charge on the bipolaron, and the binding energy of the charged bipolaron to the counterions ($2E_B$) (Refs. 3 and 4)

$$\hbar\omega_1 + \hbar\omega_2 = E_g^{1D} - 2(U_B - E_B), \quad (4)$$

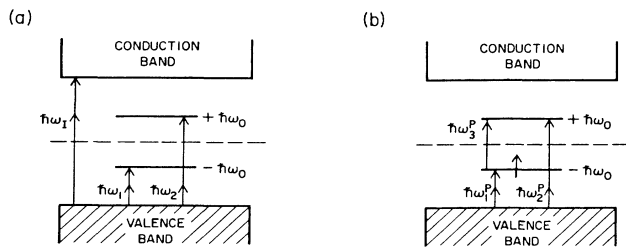


FIG. 5. (a) Band diagram showing the gap states and allowed transitions for a self-localized bipolaron. (b) Band diagram showing gap states and allowed transitions for a self-localized polaron.

where $2U_B$ is the difference in Coulomb energy between the initial state (double charge) and the final state (single charge). As for polythiophene, the close agreement of the observed transitions with Eq. (3) implies that $U_B \approx E_B$, and that both are small relative to the size of the energy gaps.^{3,4}

From these magnetic and spectroscopic data, we conclude that at least for doping levels above a few mol %, charge is stored in bipolarons. In the dilute doping regime the situation is less clear, for the appearance of the transition near ≈ 1.2 eV in the range of cell voltages below 3.2 V versus Li might indicate the presence of polarons. In this interpretation, the energy of this transition would be $\hbar\omega_3^p$ where^{1(c)}

$$\hbar\omega_2^p - \hbar\omega_1^p = \hbar\omega_3^p$$

and the transition energies $\hbar\omega_1^p$, $\hbar\omega_2^p$, and $\hbar\omega_3^p$ are defined in Fig. 5(b). The other two polaron peaks are not, however, evident at these doping levels. This may simply be the result of the breadth of the respective spectral features. Since $\hbar\omega_1^p$ and $\hbar\omega_2^p$ result from transitions from the valence band to the localized gap levels, the joint density of states would be broad, whereas the $\hbar\omega_3^p$ transition is between two sharp gap states and therefore narrower and easier to detect. In fact, the 1.2-eV peak is quite narrow by comparison with the width of the interband transition, which also depends on the joint density of states of the valence and conduction bands. Assuming that this transition and the corresponding magnetic signature (both of which occur at low doping levels) result from polaron formation, the maximum number of polarons is about 0.2 mol %. At higher doping levels the reaction described in Eq. (2) takes over, and the charge goes into bipolarons.

The assignment of the 1.2-eV transition and the corresponding ESR signal to self-localized polarons is, however, somewhat problematic. It is significant that these signals, which appear at very dilute doping, occur as the electrochemical potential of the polymer is swept through the region near the gap edge, below the principal threshold for charge injection, as indicated by the EVS data. Using the EVS data, one sees that in the range of cell voltages for which the new features appear the doping level is at most a few-tenths of a mol %, i.e., comparable to the number of spins observed for cell voltages between 3.0 and 3.3 V versus Li. We conclude, therefore, that the spectroscopic features and related ESR signals observed at the lowest cell voltages are due to defect states in the energy gap, localized perhaps by disorder. Although these features are genuine, they are not the self-localized polarons which would be characteristic of a charge added to a perfect P3MT chain.

V. CONCLUSIONS

We find that charge is stored in spinless bipolarons in poly(3-methylthiophene) at all but the most dilute doping levels. From the combination of magnetic and electrochemical measurements, we find definitive evidence of the reversed spin-charge relation expected for bipolarons with $N_s/N_{\text{ch}} < 10^{-3}$; from the spectroscopic data we find

the two subgap absorptions indicative of self-localized bipolaron levels located nearly symmetrically within the gap.

For charge injection below the principal injection threshold, one observes polaronlike features with a maximum number of spin-carrying species of approximately 0.2 mol% (one per 500 rings). Our results imply that these features result from defect states in the energy gap, but they are not the self-localized polarons which would be characteristic of a charge on a nondegenerate ground-state polymer such as a perfect P3MT chain.

The conclusion that the bipolaron is the lowest-energy

charge-storage configuration indicates that effective electron-electron Coulomb repulsion is relatively weak in P3MT; a conclusion which appears to be quite generally true for polythiophene and the poly(3-alkylthiophene) derivatives in solution as well as in the solid state.

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