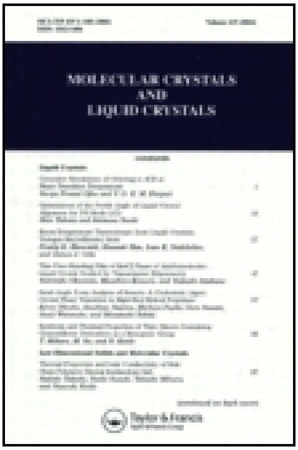

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In Situ Studies of Electrochemical Charge Transfer Processes in Conducting Polymers

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In Situ Studies of Electrochemical Charge Transfer Processes in Conducting Polymers

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Abstract

In situ techniques are described for studying the charge transfer doping reactions in conducting polymers. The development of such techniques and their unique application to conducting polymers has made it possible to determine the nature of the charge storage states as well as to monitor the kinetics of the charge transfer reaction.

INTRODUCTION

The discovery of electrochemical doping of conducting polymers[1] has opened the way for the development of a number of new and unique techniques for studying charge transfer processes in such systems. Electrochemical doping offers two specific advantages:

1) Precise control over the dopant concentration through external setting of the open-circuit voltage of the cell (with resolution of changes at the PPM Level).
2) In situ measurements carried out during the doping process.

In this paper we focus on the in situ measurements; including spectroscopy[2,3] and magnetic properties.[4] Such measurements have played a unique role in the development of the field of conducting polymes. They allow determination of the kinetics of doping,[5] and the nature of the charge storage state at dilute concentrations.[2,3,4] The continuous control of the dopant concentration makes possible precise determination of the concentration dependence of the relevant physical propeties. This is particularly important, for example, in investigating the nature of the evolution of such systems from semiconductor to metal[4] as the dopant concentration is increased.

EXPERIMENTAL TECHNIQUES[2,3,4]

The techniques utilized involve an electrochemical cell with the polymer under study as one electrode, a counter electrode, and appropriate electrolyte. The details of the cell design depend on the specific use. For example, in the case of in situ optical studies the cell is designed to minimize light scattering and to optimize light through-put (rectangular cell, semi-transparent, electrode, etc.) For _in situ_ electron spin resonance studies, the cell must fit inside a microwave cavity.

In Situ Opto-electrochemical Spectroscopy[2,3]

A Pyrex cell was designed and constructed so that the visible to near ir spectra of a conducting polymer (e.g. polyacetylene, polythiophene) could be recorded _in situ_ throughout the electrochemical doping and/or undoping process. A schematic diagram is shown in Fig. 1; the glass cell consists of two arms joined at the bottom containing a lithium-metal strip in one arm and the polymer sample on conducting glass in the other arm. The electrolytic solution, 0.5M $LiClO_4$ in propylene carbonate, extended into both arms, completing the internal circuit. The arm of the

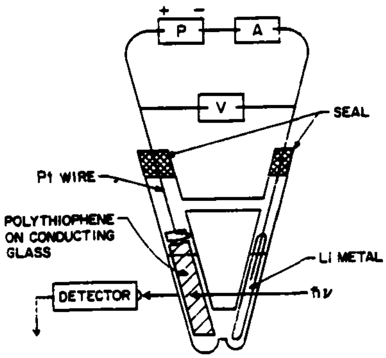

Fig. 1. Diagram of apparatus used for _in situ_ visible-ir absorption measurements during electrochemical doping.

cell which contained the polymer film was constructed of rectangular tubing in order to minimize scattered light, to prevent divergence of the beam, and to minimize the ratio of the electrolyte to polymer volumes. To maintain long-term stability of the cell, both arms were carefully sealed, with the wire contacts extending through the seals.

The cell containing the polymer was rigidly mounted in the light path so that a single area was in the beam throughout the doping-undoping cycle, thus allowing quantitative in situ comparison of the spectra for each voltage (i.e. each dopant concentration). The voltage across the cell is then changed to the next desired value, and the cell is allowed to come to equilibrium. During this time, the monochromator is set at λ_{max}, and the strength of the band-gap transition $\alpha(\omega)$ is monitored by the computer along with the cell current. Initially, after stepping the external voltage, current flows and then decays steadily with time as the cell appraoches equilibrium. Correspondingly, the absorption coefficient changes continuously after a voltage step and approaches a steady value characteristic of the new dopant concentration. By monitoring the approach to equilibrium through $\alpha(T)$ one can obtain direct information on the kinetics of the charge transfer reaction. After these parameters had reached steady state, a spectrum is taken.

In Situ Electron Spin Resonance[4]

A schematic diagram of the electrochemical cell used for in situ ESR measurement is sketched in Figure 2. To fit into (and be compatible with) the microwave cavity, the polymer sample (e.g. trans-$(CH)_x$) the electrolyte and the

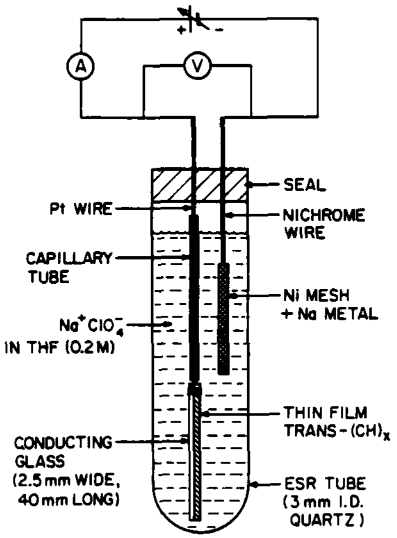

Fig. 2. Diagram of electrochemical cell used for _in situ_ esr measurements.

counter electrode must be assembled inside a 3 mm ESR tube. The glass can be sealed across the electrical contacts which are connected externally to a variable voltage supply. The ESR tube (electrochemical cell) is mounted with the tip inside the microwave cavity of a standard ESR spectrometer. To avoid having the metal counter-electrode and Nickel mesh inside the cavity, the counter electrode is mounted above the polymer film. The glass capillary tube (around the platinum wire leading to the polymer electrode) is included to minimize background currents.

EXPERIMENTAL RESULTS: IN SITU SPECTROSCOPY OF TRANS-$(CH)_x$ AND POLY(THIOPHENE)[2,3]

Figure 3 shows a series of absorption spectra for polyacetylene taken during the doping cycle at different applied voltages. In each case the cell was allowed to come to diffusion equilibrium as described above. As doping proceeds, a single mid gap absorption appears, centered near 0.75-0.80 eV, with an intensity which increases monotonically in proportion to the dopant concentration. These data were obtained with 1M $Li^+ClO_4^-$ in propylene carbonate; the series of curves correspond to p-type doping; i.e. to successively higher degrees of oxidation of the polymer to form $[(CH)^{+y}(ClO_4^-)_y]_x$.

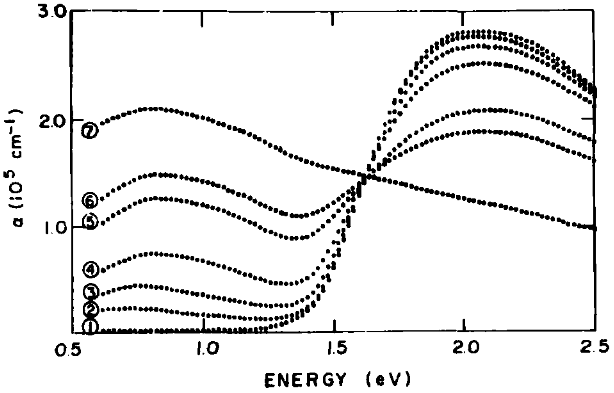

Fig. 3. Absoprtion spectra taken during the doping cycle at differnt voltage: Curve 1 -- 2.2 V (y=0). Curve 2 -- 3.28 V (y=0.003). Curve 3 -- 3.37 V (y=0.0065). Curve 4 -- 3.46 V (y=0.012). Curve 5 -- 3.57 V (y=0.027). Curve 6 -- 3.64 V (y=0.047). Curve 7 -- 3.73 V (y=0.078).

Figure 4 shows corresponding spectra for polythiophene (PT). As the doping proceeded (again using the $Li^+(ClO_4)^-$ in propylene carbonate as electrolyte) via the oxidation reaction

$$(PT)_x + xyLiClO_4 \rightarrow [(PT)^{+y}(ClO_4^-)_y]_x + xyLi$$

the intensity of the interband transition decreased continuously and the absorption peak shifted toward higher energy. In addition, two new absorption features appeared in the ir below the gap edge with intensities which increased as the dopant level increased. The lower-energy ir peak remains at a constant energy (∿ 0.65 eV), while the higher-energy one shifts toward higher energy as the dopant level is increased. At 4.3 V, the frequency-dependent absorption is characteristic of the free-carrier spectrum of the metallic state, similar to that found in heavily doped (either chemically or electrochemically) poly-

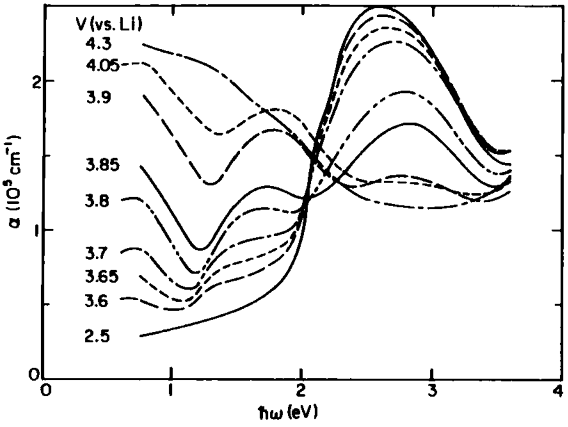

Fig. 4. PT spectroscopy data.

acetylene.

At dilute doping levels, the spectra of Figures 3 and 4 indicate the formation of localized states in the gap. For trans-$(CH)_x$, there is a single state located near the center of the energy gap; for polythiophene, the two peaks indicate the formation of two levels symmetric about the gap center. In either case, the charge is stored in these localized states of the π-electron system of the polymer. These localized states form as a result of charge transfer.

EXPERIMENTAL RESULTS: IN SITU ELECTRON SPIN RESONANCE[4] OF TRANS-$(CH)_x$

In Figure 5, we plot the electron spin contribution to the magnetic susceptiblity (χ) of trans-$[Na_y^+(CH)^{-y}]_x$ as a function of its electrochemical potential, μ (referenced to Na metal). Note that both χ and μ are intrinsic thermodynamic variables. The abrupt increase in χ at $\mu = +0.8$ eV (relative to Na) and the observation of hysteresis in χ vs. μ are indicative of a first order phase transition.

Data were taken by first setting the external voltage and monitoring the current while allowing the cell to come to equilibrium (typically 12 to 36 hours). At equilibrium, the measured external voltage is the open-circuit voltage, which is by definition the electrochemical potential of the doped polymer referenced to that of the Na counter electrode. After allowing the cell to come to equilibrium, the ESR signal was recorded using signal averaging to obtain the necessary signal-to-noise ratio from the thin film samples. The data were integrated twice to obtain the spin contribution to the magnetic susceptibility (χ). An NBS ruby standard was attached to the outside of the esr tube

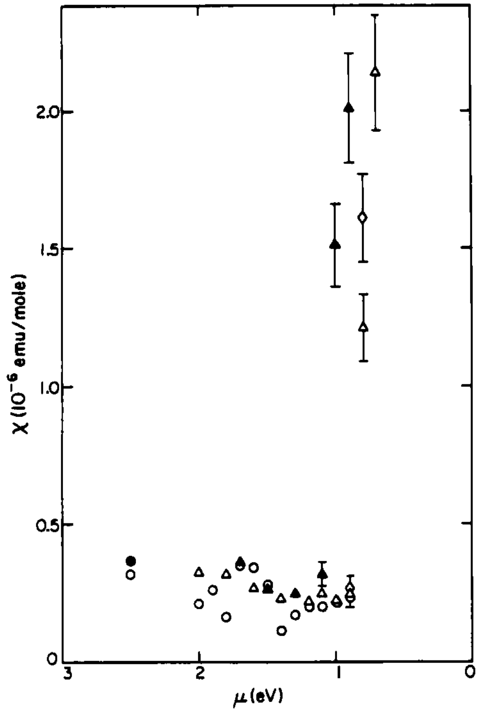

Fig. 5. Spin susceptibility of $[Na_y^+(CH)^{-y}]_x$ as a function of the chemical potential of the doped polymer (referenced to Na metal). The results were obtained by esr measurements carried out in situ during electrochemical doping; o - first cycle doping, o - first cycle undoping, Δ - second cycle doping, Δ - second cycle undoping, □ - third cycle doping.

(near the sample) for calibration of the absolute magnetic susceptibilities. Symmetric esr lines and accurate χ values were obtained since the sample thickness (≅ 0.5 μm) was much less than the microwave skin depth, even at the highest concentration.

The data of Figure 5 are qualitatively similar to the results for χ vs. y obtained from chemical doping[6] of $[Na_y(CH)^{-y}]_x$. In both cases, the two regimes are clearly defined with a sharp transition between them. In the chemical doping experiment,[6] detailed measurements of the temperature dependence demonstrated that the weak narrow line belowthe transition obeyed Curie's law ($\chi \sim 1/T$) indicative of a dilute concentration ($\sim 1.5 \times 10^{-4}$ per carbon) of localized magnetic states, whereas the large susceptibility above the transition was temperature independent indicative of the Pauli susceptibility (χ_p) of a metal.

CHARGE STORAGE IN CONDUCTING POLYMERS: SOLITONS, POLARONS AND BIPOLARONS

As a result of the Peierls instability, the dominant "electronic" exciations in conducting polymers are inherently coupled to chain distortions.[7] Thus quite generally, one anticipates that solitons, polarons and bipolarons will be the excitations of major importance in this class of one-dimensional polymer semiconductors. In particular, after charge transfer (at dilute dopant concentrations) the charge will be stored in the localized electronic states associated with the structural distortions.

For polyacetylene, trans-$(CH)_x$, the degenerate ground state leads to solitons as the important excitations and the dominant charge storage species.[8-11] The susceptibility results shown in Fig. 5 (and presented earler[6] for chemical charge transfer doping) demonstrate without ambiguity that for dopant levels below the first-order transition, charge is stored predominantly in a nonmagnetic configuration. This conclusion combined with the results of infrared studies[12] on doped and photoexcited trans-$(CH)_x$ demonstrate that doping occurs via the formation of spinless charged solitons, and that these solitons dominate the physical properties at all concentration below the sharp transition to the truly metallic state (characterized by a finite density of states at the Fermi energy and an associated Pauli spin susceptibility).

The in situ spectroscopy data shown in Figure 3 are fully consistent with this conclusion. The formation of a single state at the center of the energy gap (see Fig. 5a) is a central prediction of the theory.

For polythiophene, the ground state degeneracy is lifted.[3] As a result soliton pairs are "confined" into bipolarons.[7,11c,13-15] This confinement and the associated interaction between the two electronic states leads to a splitting of the mid-gap state into a symmetric pair. The in situ spectroscopy results for polythiophene are in detailed agreement with charge storage in bipolarons subsequent to charge transfer.

CONCLUSION

In situ studies of the charge transfer doping reactions have played an important role in clarifying the chemistry and physics of conducting polymers. For this growing class of polymers, the coupling of electronic excitations to nonlinear conformational distortions is an intrinsic and important feature of conducting polymers. This coupling and the degenerate ground state lead to the novel soliton excitations in trans-$(CH)_x$. Generalization of these concepts and application to the larger class of conjugated polymers has been an obvious goal of the field. The experimental evidence of electron-hole smmetry and weak confinement in polythiophene makes this polymer a nearly ideal example of a model systemin which the ground state degeneracy has been lifted. The study of bipolarons (or confined charged solitons) in poly(thiophene) has demonstrated that the concepts carry over in detail and that a quantitative understanding of the resulting phenomena is possible even for relatively complex systems.

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