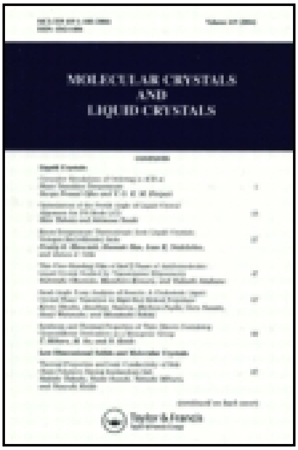

Molecular Crystals and Liquid Crystals

Charge Storage In Doped Poly(Thiophene): In-Situ Opto-Electrochemical Spectroscopy

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CHARGE STORAGE IN DOPED POLY(THIOPHENE): IN-SITU OPTO-ELECTROCHEMICAL SPECTROSCOPY

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Abstract An *in situ* study of the absorption spectrum during the electrochemical doping process has been carried out. In the dilute regime, the results are in detailed agreement with charge storage via bipolarons; weakly confined soliton pairs with confinement parameter $\gamma \simeq 0.1-0.2$. At the highest doping levels, the data are characteristic of the free carrier absorption expected for a metal.

INTRODUCTION

Polythiophene (PT) can be viewed as an sp^2p_z carbon chain in a structure analogous to that of *cis*-$(CH)_x$, but stabilized in that structure by the sulfur, which covalently bonds to neighboring carbons to form the heterocycle. Polymers such as poly(thiophene) are of current theoretical interest since the two structures sketched in Fig. 1 are not energetically equivalent. Thus, the coupling of electronic excitations to chain distortions (inherent in such linear conjugated polymers) will lead to polarons and bipolarons as the dominant charged species.[1-4]

In this paper, we summarize the results of an *in-situ* study[5] of the absorption spectrum during the electrochemical doping process and as a function of the dopant concentration for doped polythiophene, $[T^{+y}(ClO_4^-)_y]$, where T designates the thiophene ring (see Fig. 1). In the dilute regime, the results are in agreement with charge storage in bipolarons (confined soliton pairs).

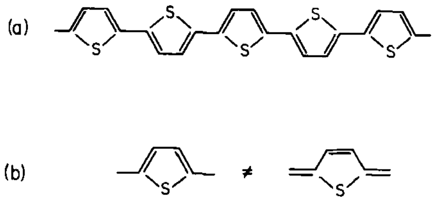

FIGURE 1 a. Chemical structure diagram of poly(thiophene)
b. Two inequivalent structures for the thiophene heterocycle in poly(thiophene).

IN-SITU SPECTROSCOPY (VISIBLE-NEAR IR) OF POLYTHIOPHENE

A pyrex cell was designed and constructed so that the visible-near i.r. spectra of polythiophene could be recorded *in-situ* throughout the electrochemical doping and/or undoping process. The cell containing the polythiophene 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). Details of the experimental techniques can be obtained from ref. 5.

Figure 2 shows a series of absorption spectra taken during the doping cycle at different applied voltages: 3.6 V (y = 2.8%), 3.65 V (y = 4%), 3.7 V (y = 5.4%), 3.8 V (y = 9.6%), 3.85 V (y = 12%), 3.9 V (y = 14%), 4.05 V (y = 20%). In each case the cell was allowed to come to quasi-equilibrium before taking the spectra. Doping levels were obtained from direct electrochemical measurements for V_{app} vs. Q in a parallel experiment using Electrochemical Voltage Spectroscopy.[5]

As the doping proceeded via the oxidation reaction,

(1)

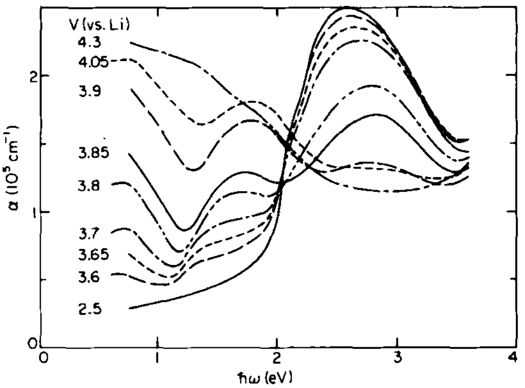

FIGURE 2 *In-situ* absorption curves for polythiophene during electrochemical doping with $(ClO_4)^-$. The applied voltages (vs. Li) are shown on the left. The corresponding concentrations were obtained from EVS measurements (see ref.) and are as follows (in mole % per thiophene ring): V_{app} = 3.60 V, y = 2.8%; V_{app} = 3.65 V, y = 4%; V_{app} = 3.70 V, y = 5.4%; V_{app} = 3.80 V, y = 9.6%; V_{app} = 3.85 V, y = 12%; V_{app} = 3.90 V, y = 14%; V_{app} = 4.05 V, y = 20%.

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) polyacetylene.[6-8]

Better accuracy was obtained by analyzing the difference spectra from the sample. Two examples are shown in Figure 3a (V_{app} = 3.65 V, y = 1% per carbon) and Figure 3b (3.85 V, y = 3% per carbon). In each case the spectrum was taken at the appropriate applied cell voltage (vs. Li), and the neutral point spectrum (2.5 V, y ≈ 0) was used as the reference. The two dopant induced infrared bands are seen clearly with peaks at $\hbar\omega_1$ = 0.65 eV and $\hbar\omega_2$ ≈ 1.5 eV. As noted above, $\hbar\omega_1$ is essentially independent of dopant concentration whereas $\hbar\omega_2$ increases with increasing frequency. Examination of Figures 2 and 3 indicates that the oscillator strength of these two dopant induced ir absorption bands is comparable to that of the mid-gap absorption in polyacetylene.[8,9] We conclude,

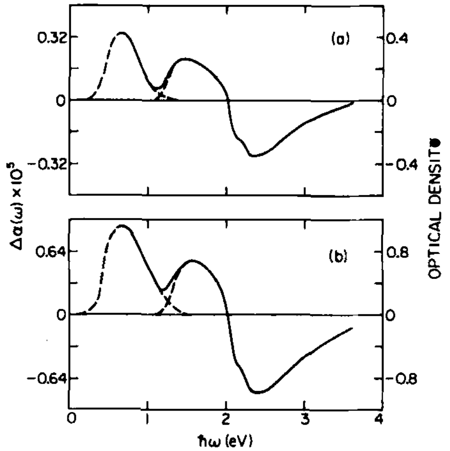

FIGURE 3 Difference spectra obtained from the data of Fig. 2.
a. V_{app} = 3.65 V, y = 4% (or 1% per carbon)
b. V_{app} = 3.85 V, y = 12% (or 3% per carbon)
In each case the neutral point spectrum (V_{app} = 2.50 V) was used as the reference. The dashed curves are extrapolations which attempt to separate the contributions from the two absorption peaks.

therefore, that these two absorption features arise from electronic transitions between the valence band and two localized energy levels which appear in the gap upon charge transfer doping.

The difference spectra of Figure 3 show that the oscillator strength which appears below the gap edge comes primarily from the interband transition. In contrast to trans-polyacetylene,[8,9] the loss of interband oscillator strength is not uniform but is greatest for frequencies near the band edge.

DISCUSSION AND ANALYSIS OF RESULTS: BIPOLARONS IN DOPED POLYTHIOPHENE

The absorption spectrum of neutral polythiophene is remarkably similar to that of trans-$(CH)_x$,[8,9] but blue-shifted by about 0.4-0.5 eV. Even the familiar structure on the leading edge, attributed by Melé to dynamical chain distortion following electron-hole pair creation,[10] is evident in the data. These similarities are suggestive that polythiophene can be viewed as similar to trans-$(CH)_x$, but with the ground state degeneracy lifted by a small amount due to the inequivalence of the two structures with opposite bond alternation. We emphasize the analogy between PT and $(CH)_x$ in the diagrams of Figure 4 where we redraw the polythiophene backbone structure, purposely leaving out the sulfur heteroatom. The resulting structure is that of an sp^2p_z polyene chain consisting of four carbon all-trans segments linked through a cis-like unit. In such a structure the ground state is not degenerate (as sketched in Figure 4). However, the energy difference per bond, $\Delta E/\ell$, might be expected to be small; i.e., greater than zero (as in trans-$(CH)_x$)but less than that of cis-$(CH)_x$. An obvious consequence of the lack of degeneracy is that the schematic PT structure of Figure 4 cannot support stable soliton excitations,[1-4] since creating a soliton pair separated by a distance d would

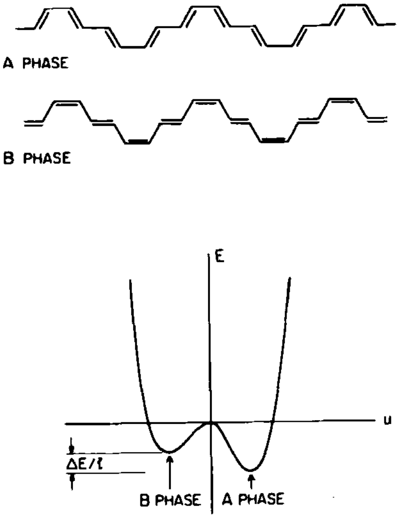

FIGURE 4 Schematic diagram of poly(thiophene) backbone structure leaving out the sulfur atoms (see Fig. 1). The two configurations (A phase and B phase) are nearly (but not precisely) degenerate as shown in the diagram at the bottom of the figure where we plot energy versus the distortion parameter, u (u = 0 when the bond lengths are equal).

cost energy $\sim d(\Delta E/\ell)$. This linear "confinement" energy leads to bipolarons as the lowest energy charge transfer configurations in such a chain.

Although this description of PT is admittedly schematic, there is experimental evidence that it represents an excellent starting point for a more detailed description of the doping processes in this system. The optical absorption data (Figures 2 and 3) indicate an energy level structure at dilute doping levels as shown in Figure 5 with $\hbar\omega_1 \approx$ 0.60-0.65 eV and $\hbar\omega_2 \approx$ 1.4-1.45 eV. We use values for $\hbar\omega_1$ and $\hbar\omega_2$ just below the peaks since the transitions involved are between a localized

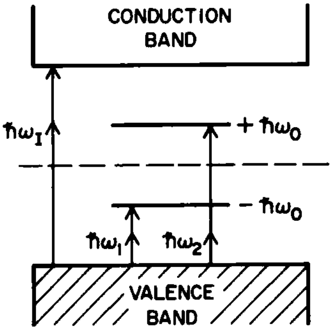

FIGURE 5 Energy level diagram for poly(thiophene) at dilute doping concentrations. The spectroscopic data of Figs. 2 and 3 imply the formation of the empty energy levels symmetric about the gap center.

gap state and the valence band density of states. The value for the interband absorption can be estimated from the data of Figures 2 and 3 to be $\hbar\omega_I \simeq 2.1$ eV. In this case, the joint density of states of the valence and conduction bands is involved in the absorption so that the point of steepest slope in $\alpha(\omega)$ (Fig. 2) or the crossover in the difference curves (Fig. 3) is used. Although there is surely some uncertainty in the assignment of the precise energies, the data from the dilute dopant concentrations yield

$$\hbar\omega_1 + \hbar\omega_2 \simeq \hbar\omega_I = E_g \qquad (2)$$

where $E_g \equiv 2\Delta_0$ is the energy gap. The results expressed quantitatively in Eqn. 2 indicate the existence of electron-hole symmetry in the doped polymer. Referring to Figure 5 , the two doping induced energy levels appear <u>symmetrically</u> with respect to the gap center at $\pm\hbar\omega_0 = 0.40 \pm 0.05$ eV. The existence of electron-hole symmetry implies that the schematic structure of and with the remarkable similarity of the shape of the absorption curves of neutral trans-$(CH)_x$ and neutral PT.

In the heavily doped limit (V_{app} = 4.3 V), all signs of the interband transition have disappeared, and the spectrum (Fig. 2) is dominated by the free carrier absorption in the infrared. In this regime, the optical properties of doped PT are those of a metal. The magnitude and spectral dependence of $\alpha(\omega)$ are similar to those reported earlier[9,10] for Na-doped trans-$(CH)_x$ where electrical conductivities in excess of 10^3 Ω^{-1} - cm^{-1} were inferred from the frequency dependent absorption in the ir and subsequently observed directly in dc measurements.[7] Thus, metallic doped PT can be expected to be an excellent conductor. Although previous conductivity measurements on electrochemically synthesized (and doped) PT have yielded values as high as 100 Ω^{-1} - cm^{-1},[8] the intrinsic values may in fact be much higher.

CONCLUSION

An in-situ study of the absorption spectrum during electrochemical doping has been carried out on polythiophene films polymerized electrochemically using dithiophene as the starting material. In the dilute regime, the results are in detailed agreement with charge storage in bipolarons; weakly confined soliton pairs with confinement parameter $\gamma \approx 0.1$-0.2. At the highest doping levels, the visible-ir data are characteristic of the free carrier absorption expected for a metal.

Previous studies of polyacetylene have demonstrated that the coupling of electronic excitations to nonlinear conformational changes is an intrinsic and important feature of conducting polymers. Although this coupling and the degenerate ground state lead to the novel soliton excitations in trans-$(CH)_x$,

Figure 4 represents an essentially correct point of view. The sulfur atoms stabilize the polyene chains in the configuration of Figure 4 through covalent bonding to neighboring carbon atoms. However, evidently, the sulfur is only weakly interacting with the π-electron system of the polyene backbone. If this were not the case, some of the transferred charge would reside on the sulfur, and the electron-hole symmetry implied by Figures 2 and 3 would not be present.

We assign the two energy gap states shown in Figure 5 to the two levels expected from charge storage in bipolaron states in doped PT.[1-4] This assignment is based on three facts:

1) The two transitions imply formation of two levels symmetric with respect to the gap center.
2) The observation of only two transitions implies that the two levels are not occupied. If there were electrons in the lower level (as would be the case for a "hole" polaron) then a third absorption would be evident arising as a transition between the two localized levels. This is not observed.
3) Analysis of the data leads to $(\omega_o/\Delta_o) \simeq 0.35$. This small value is inconsistent with polaron formation for which $(\omega_o/\Delta_o) \geq 0.707$.[1,2]

The small value inferred for (ω_o/Δ_o) implies weak confinement. Using the results obtained by Fesser, Campbell and Bishop (FBC)[2] in their detailed analysis of the bipolaron problem, we can extract values for the relevant microscopic parameters. The confinement parameter is defined as $\gamma = \Delta_e/\lambda\Delta_o$ where Δ_e is the constant external gap parameter, γ is the dimensionless electron-phonon coupling constant appropriate to the two-fold commensurate case, and Δ_o is the full gap parameter ($\Delta_o = \Delta_e + \Delta_i$). From Figure 4 of FBC, we obtain $\gamma \simeq 0.1$-0.2 using the experimental value for $(\omega_o/\Delta_o) \simeq 0.35$. This small value for γ, implying weak confinement, is consistent with the point of view expressed in Figure 4 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 symmetry and weak confinement in polythiophene makes this polymer a nearly ideal example of a model system in which the ground state degeneracy has been lifted. The study of bipolarons (or confined charged solitons) in poly(thiophene) presented in this paper 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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