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EVIDENCE FOR BIPOLARONS IN PYRROLE POLYMERS

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Abstract Polypyrrole is an example of a conjugated polymer with a non-degenerate ground state. It has therefore been suggested that the stable defect states formed upon doping are bipolarons: doubly charged, spinless bound states of two holes with associated deformation of the molecule. ESR, transport, photoelectron spectroscopy and optical absorption data from pyrrole polymers are presented as evidence that indeed polarons and bipolarons are formed upon doping. Electron spin resonance reveals that the conduction mechanism in heavily doped samples involves charge carriers which possess no spin. At doping levels of order tenths of one percent a narrow ESR signal appears, indicating the presence of isolated polarons, but at higher concentrations of oxidant the spin concentration drops again as the polarons bind in pairs to form diamagnetic bipolarons. The transport properties of polypyrrole indicate hopping among localized states, but the data cannot be described in any of the conventional models of disordered semiconductors. The optical absorption spectrum reveals several states within the gap which can be correlated, on the basis of energy level calculations, with polaron states at low doping levels, and bipolaron states at high doping.

I. INTRODUCTION

The number of conjugated polymers which have been found to become electrically conducting upon doping with electron donors or acceptors contin-

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ues to grow: *cis* and *trans*-polyacetylene¹ (*c*-PAC, *t*-PAC), polypyrrole² (PP), poly-*para*-phenylene³ (PPP), polythiophene⁴ (PT) and others.⁵ The majority of these materials have the common feature of a non-degenerate ground state; namely, when the positions of the double and single bonds are reversed, an inequivalent structure, with a different energy, results. *t*-PAC is the exception. In this context, *c*-PAC would be the "prototypical conducting polymer," having the simplest chemical structure, and also being relatively crystalline. However, its detailed study is hampered by the disadvantage that it is unstable to isomerization into the *trans* form, either thermally or by doping. The other polymeric materials listed above are, in general, highly disordered or amorphous, and contain many different types of structural and electronic defects. In spite of these difficulties, there is an accumulation of experimental evidence that polarons and, more especially, bipolarons are the primary species created during doping of conjugated polymers with non-degenerate ground states.⁶

In this paper, we review those experiments which have led to this picture. PP is used as the primary example, since the most complete body of data exists for it, but reference is made also to the results which have been obtained on PPP and PT. Since all of these results are either already published, or have been presented for publication elsewhere, the present paper is written in the form of a review article.

In section II is given a phenomenological description of the relevant theory, and its predictions. Section III contains a brief description of the physical properties of PP, and outlines why conventional theories of charged defects and transport fail. In section IV, we summarize the experiments which demonstrate the validity of the bipolaron picture. Finally, section V is a discussion of the role which bipolarons play in the electrical conductivity of these polymers.

II. PHENOMENOLOGY OF POLARONS AND BIPOLARONS

The idea of a polaron is familiar in solid state physics:⁷ it consists of an electron (or hole) localized to a deformed region of the lattice. It is the Coulomb interaction between the electron and the ions which is responsible for the lattice distortion, and the breaking of the translation symmetry results in a localized wavefunction occupied by the electron in question. We say that the electron is "self-trapped."

The situation is similar in linear conjugated polymers. In this case the lattice deformation consists of a tendency for the double bonds to become longer, more like single bonds, and *vice versa*. Two localized states are formed, one split off from the top of the valence band, and one from the bottom of the conduction band.^{6,8,9} (See fig. 1b) If the defect is formed by removal of an electron, then the lower state is singly occupied and we have a hole-polaron, as shown in the figure. Electron injection results in the single occupation of the upper level, while the lower state remains fully occupied.

In either case, there is a net charge of one unit (positive or negative) on the chain, and the odd electron contributes spin $\frac{1}{2}$.

The energetics of polaron formation require the consideration of the elastic energy which it costs to form the lattice distortion, and the gain in electronic energy. Brédas¹⁰ has described this gain, in a most illuminating way, as the reduction in ionization energy (or increase in electron affinity) of the structure which has the double and single bonds reversed relative to the stable ground state configuration.

Restricting the remainder of the discussion to the case of acceptor doping (oxidation), which is relevant to the experimental situation in PP,¹¹ further charge transfer from the polymer chain with one hole-polaron, may then proceed either by formation of another polarons, or by removing the single electron in the lower polaron level. The former process costs additional elastic energy, while the latter involves the Coulomb energy of two charges in the same region of space. In all of the materials of interest it is found to be favorable to form the doubly charged species: the lattice deformation increases slightly, further lowering the electronic energy, and the Coulomb energy is largely compensated by the effect of the nearby counterion.¹⁰ The doubly-charged spinless species which results is called a bipolaron (fig. 1c).

From the above discussion it is clear that polarons and bipolarons are characterized by two experimentally measurable properties: changes in optical absorption which result from the new energy levels created in the band-gap; and appearance of addition susceptibility due to the spin of the polaron. Specifically, we expect the following features in the optical spec-

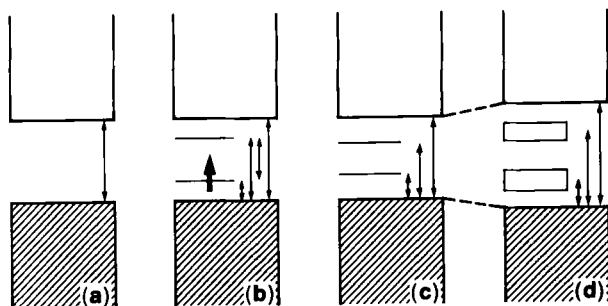


FIGURE 1. Energy level diagram of a conjugated polymer at increasing levels of acceptor doping (oxidation): (a) Neutral polymer, showing full valence (π) and empty conduction (π^*) bands. (b) After removal of a single charge a polaron is formed with spin $S=\frac{1}{2}$. Three new optical absorptions appear. (c) When a second electron is removed a bipolaron is formed; $S=0$, and there are only two optical transitions below the interband. (d) At heavier doping levels the bipolaron levels broaden into bands, and the gap between valence and conduction bands widens.

trum of polymers containing polarons (see fig. 1b): transitions from the valence band to each of the (1) lower and (2) upper polaronic levels, and (3) promotion of the electron from the lower level to the unoccupied upper level. When bipolarons are formed the last of these transitions is no longer possible because the lower state is unoccupied (fig. 1c). The other two transitions are basically unaffected, though they may shift in energy. Finally at high doping levels, the depletion of states from the valence and conduction band edges leads to a suppression of the intensity of the interband transition, as well as a blue shift.¹²

As doping of the neutral polymer proceeds, it is expected that the first species formed, at very low concentrations, will be polarons, detectable because of their spin susceptibility and three features in the optical spectrum. At heavier doping levels, more and more bipolarons will be formed, the susceptibility should decrease and the middle of the three optical sub-bandgap transitions should disappear.

III. PHYSICAL PROPERTIES OF POLYPYRROLE: FAILURE OF CONVENTIONAL MODELS

Polypyrrole is prepared in its doped, highly conducting form, by the simultaneous electrochemical polymerization and oxidation of the pyrrole monomer.^{2,11} It may be subsequently reduced, either chemically or electrochemically, to its neutral insulating form, and then redoped, again by chemical or electrochemical means. Prepared in this way, PP is very highly disordered, showing only diffuse X-ray scattering, and giving electron diffraction from only very local regions.¹³ The polymer is insoluble and infusible, so that conventional molecular weight determinations cannot be made, but Street and Nazzari¹⁴ have recently polymerized β -dimethylpyrrole, tritiated at the α -positions, and have used radio-assay techniques to obtain a determination of the degree of polymerization in excess of 100. IR¹⁵ and ¹³C NMR^{15,16} spectra indicate that the pyrrole ring structure remains intact during polymerization, in agreement with crystal packing models based on the electron diffraction pattern.¹³ However, the severe broadening of these spectra, as well as the appearance of additional NMR features and the extreme intractability of the material, indicate that chain branching and cross-linking occurs to a significant degree. Furthermore, in PP, as in every other conducting conjugated polymer with the exception of *c*-PAC, there is a large number (of order 1 per 100 monomers) of paramagnetic defects which contribute a Curie susceptibility.¹⁷

Before resorting to a description of conducting polymers in terms of the "exotic" model of bipolarons, one must first eliminate the more conventional pictures. In order to do so, consider, first, the electrical conductivity,

which was found to have the temperature dependence¹⁸

$$\sigma = \sigma_0 \exp [-(T/T_0)^{1/4}]$$

characteristic of three dimensional variable range hopping. Different samples give widely varying values of T_0 and σ_0 , but the results may be used to obtain a density of states at the Fermi surface of order 1 eV^{-1} per monomer, or greater.¹⁹ The thermoelectric power of the acceptor doped polymer is small, positive and linear in temperature, while the Hall coefficient is small, negative and weakly temperature dependent.¹⁸ Again these results are suggestive of properties expected for three-dimensional variable range hopping, and one may use Friedman's analysis²⁰ of the Hall effect to estimate a Fermi-surface density of states of 3 eV^{-1} per monomer. On the other hand, the temperature dependence of the magnetic susceptibility, as measured by ESR shows no detectable constant Pauli contribution, and one may place an upper limit on the density of states of 0.03 eV^{-1} per monomer.¹⁹ (Static susceptibility measurements on PPP doped with SbF_5 also revealed a vanishingly small Pauli contribution.²¹) A similar upper limit is deduced from the failure to observe a Fermi surface threshold edge in the photoelectron yield.²²

Thus, while the ideas of variable range hopping are consistent with the high degree of disorder known to exist in polypyrrole, it is impossible to obtain quantitatively consistent parameters on the basis of this model. It becomes necessary to consider other models for charge storage and charge transport.

IV. EXPERIMENTAL EVIDENCE FOR POLARONS AND BIPOLARONS

The first hint that polarons and bipolarons are formed during the doping of PP came from the results of an experiment to measure the ESR spectrum *in-situ* during oxidation with gaseous oxygen.¹⁷ As the doping started, an additional ESR intensity, above the normal background associated with defects formed on polymerization, was observed. However, at higher oxygen concentration this signal reached a maximum and then began to decrease. This is exactly the behaviour predicted (see section II) to occur, as first polarons then bipolarons are created at progressively higher doping levels.

It was also found¹⁷ that electrochemical cycling of PP films could reduce or remove the paramagnetic defect concentration, without affecting the electrical conductivity of the polymer, left finally in the fully doped state. This permits an even lower limit on the density of states, but more importantly shows that the species responsible for the conductivity of PP do not have spin.

The optical spectrum of PP, as a function of dopant concentration, was measured by Yakushi *et al.*²³ The spectra show three features below the interband absorption for lightly doped PP, and as the dopant concentration

increases the middle of these three features disappears while the interband transition itself weakens and shift to higher energy. Again, this is exactly the behaviour expected on the basis of the bipolaron model of PP doping.

The optical spectrum²⁴ of PT electrochemically doped with ClO_4^- , and the electron energy loss spectrum²⁵ of AsF_6^- doped PPP show two features below the interband transition which have also been associated with bipolaron states.

As final conclusive proof that the picture of polaron and bipolaron formation is really valid we considered it necessary to demonstrate that the central transition induced in the optical spectrum, attributed to polarons, is directly associated with the appearance of the additional spin concentration. To this end, two parallel experiments were performed *in-situ* on electrochemically oxidized/reduced PP: optical absorption and ESR.²⁶ The optical experiment is described in more detail by Kaufman *et al.* in these proceedings.²⁷ The results may be summarized as follows: whenever the electrochemical cell is displaced from equilibrium by changing the voltage, such that electrons are injected into, or removed from, the PP film, the middle optical transition grows in intensity, relative the those at lower and higher energy, and then decays with a characteristic time constant of order 10^3 sec., long after the current has stopped flowing. In the parallel ESR experiment, the PP electrode of the electrochemical cell was located in the microwave cavity of the ESR spectrometer. When the voltage was changed, additional ESR intensity was observed, and the characteristic time for the decay of this signal was the same 10^3 sec. These results may be interpreted as follows: the electrochemical oxidation or reduction of PP, removes or adds single electrons; removal of one electron forms a polaron, and the addition of one electron to a bipolaron converts it into a polaron; these non-equilibrium polaron defects persists for a time scale of hours until they find a partner with which to pair up, forming the more stable bipolaron.

Two further points may be made concerning these results. First, the intensity of the additional signal observed in the ESR experiment indicates that approximately one additional spin is observed for every 100 electrons transferred to or from the polymer. This means that there is a very fast recombination process in addition to the slow one which gives rise to the spins actually observed. Secondly, the very long persistence of the optical absorption and ESR signal is inconsistent with polaron (or electron) diffusion rates. We tentatively associate it with the diffusion of counterions, which must accompany the polarons in order to preserve local charge neutrality.

V. CHARGE TRANSPORT MECHANISMS

The arguments presented in the previous section prove only that the charge which is removed from the PP polymer chain during doping is stored in bipolaron states, and that therefore these states must be considered in any

model of the conduction process in this polymer. No clue is given as to the details of the charge transport mechanism itself. Little theoretical work has been done on the subject, but it is clear that there are two possible mechanisms which must be considered. The first is that the bipolarons themselves move as complete entities, carrying charge $+2e$ in a diffusive motion through the polymer. The second is that the bipolaron states provide only the necessary sites for the hopping of electrons, and that as the electrons move there is conversion of the states which they leave from polaron to bipolaron, while the target site is converted from bipolaron to polaron.

The latter mechanism requires a non-zero mean concentration of polarons, and is contrary to the observation that the conductivity is independent of the spin density.^{17,19} The former mechanism has been discussed by Chance *et al.*²⁸ in terms of a Franck-Condon effect for the interchain hopping of bipolarons. They compute a concentration dependent conductivity which saturates as all sites become filled with carriers, in agreement with experimental observation. Thus, at high doping levels, it is necessary that the bipolarons execute a correlated diffusive motion through the material. Using the Einstein relation for the mobility

$$\mu = qD/kT,$$

where $q=2e$ is the charge, and the measured room temperature conductivity of $10 \Omega^{-1} \text{ cm}^{-1}$, one may compute a diffusion constant for bipolarons: $D = 10^{-4} \text{ cm}^2 \text{ sec}^{-1}$, which is a small but not unreasonable value.

In summary, it has been shown that bipolarons are the charged species formed upon doping of conjugated polymers with non-degenerate ground state configurations. The details of the conduction mechanism involving these defects remain to be clarified. In particular, the role of disorder and the nature and effect, if any, of the ubiquitous paramagnetic defects must be understood.

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