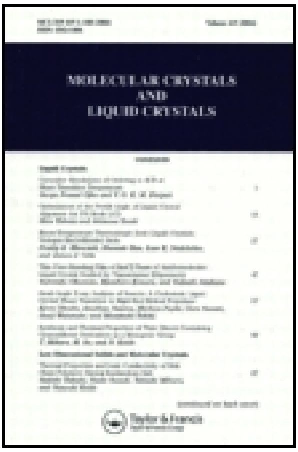

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Howard A. Mizes [a b] & Esther M. Conwell [a b]
[a] Xerox Webster Research Center, Webster, New York, 14580
[b] Center for Photoinduced Charge Transfer, University of Rochester, Rochester, New York, 14627

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POLARONS AND THEIR STABILITY IN POLY (P-PHENYLENE VINYLENE)

HOWARD A. MIZES AND ESTHER M. CONWELL
Xerox Webster Research Center, Webster, New York 14580
and Center for Photoinduced Charge Transfer,
University of Rochester, Rochester, New York 14627

Abstract We have parametrized a tight-binding description of the π electrons, with σ bond compressibility, on a poly (p-phenylene vinylene), PPV, chain by fitting the valence band width, the band gap and the chain geometry to better than 1%. With the resulting Hamiltonian we found that for long chains the polaron forms a localized state 0.18 eV from the band edge. Interchain coupling was described by using the results of ab initio electronic structure calculations and the actual separations of the atoms with the closest interchain contacts. It was found that interchain coupling does not destabilize the polaron in PPV.

INTRODUCTION

Potentially important applications of conducting polymers are to light emitting diodes and display panels.[1] These devices rely on the recombination of electrons and holes injected at the contacts. To understand, and possibly improve, operation of these devices it is necessary to know whether the injected carriers propagate as stable polarons and, if so, what are their properties. To study the polaron in PPV we have set up a Hamiltonian similar in spirit to the SSH Hamiltonian[2]. The latter was widely used for studying polaron properties in polyacetylene, as well as other properties where electron-phonon coupling is more important than Coulomb effects.

THE HAMILTONIAN

For the calculations the backbone was assumed to be planar, which should be essentially true in the solid. The Hamiltonian was taken in the form

$$H = \sum_{m=1}^{M} \sum_{<ij>} \left[-(t_0 - \alpha u_{<ij>}) c_i^{+} c_j + \tfrac{1}{2} K (u_{<ij>} - C)^2 + H.C. \right] \qquad (1)$$

Here M is the number of monomers in the chain and $<ij>$ indicates one of the pairs of nearest neighbor carbons in the monomer. The sum is taken over all 9 pairs. t_0 is the electronic coupling, i.e., the transfer integral, between adjacent π orbitals and $u_{<ij>}$ is the change in length of the $<ij>$ bond, referred to an imagined initial state with all bonds equal in length. α is the ratio between the electronic coupling change and bond length change, and K is the effective spring constant due to the σ bonds. C is a stiffness constant adjusted to give the correct chain length in a self consistent calculation.[3] In principle α and K should be different for different bonds, but we were not successful in obtaining a set of α's and K's that led to physically reasonable results. As indicated earlier, the parameters t_0, α and K were determined by fitting three properties of PPV. One of these properties was the valence band width, 5.47 eV, obtained by Local Density Functional (LDF) theory.[4] A second was the energy gap, taken as the sum of the absorption edge and the calculated exciton binding energy.[5] The third was the dimerization of the vinyl group. MNDO calculations, known to give a good representation of ground state geometry, gave the double bond as 1.355Å, the single bond as 1.474Å. The difference of 0.116 Å is almost 40% larger than the 0.08Å difference found in polyacetylene, but less than the difference between double and single bonds in nonconjugated polymers and other organics. The values of the parameters that result in the Hamiltonian giving results for the valence band width, gap and dimerization within 1% of those specified above are: $t_0 = 2.66$ eV, $\alpha = 10.29$ eV/Å and $K = 99.0$ eV/Å^2. Larger values of the parameters than those for polyacetylene were expected because the band gap is twice as large, the vinyl dimerization 40% larger, and the valence band width 10% larger. With the values of t_0, α and K obtained the features of the LDF electronic structure and MNDO geometric structure that were not specifically fitted are matched fairly well.

PROPERTIES OF THE PPV POLARON

The results of a self-consistent solution of the wave equation with one electron added to the chain are shown in Figure 1 for a wide range of chain lengths. The polaron levels are seen as discrete levels detached from a continuum only for chains of 20 monomers or more, whereas the average conjugation length is considered to be ~5 to 7 monomers. For the longest chains the distance of the polaron level from the band edge is 0.18 eV. It is seen that the location of the two polaron levels does not change much with decreasing chain length, but the distance between the polaron levels and the adjacent "band" levels increases quite considerably, reflecting the strong increase of energy gap with decreasing chain length. For 10 monomers the distance between the polaron level and the band level is 0.241 eV, while for 5 monomers it has increased to 0.454 eV. The only other determination of the isolated polaron energy level in the literature gave it as 0.32 eV away from the band edge in the long chain limit.[6] Although this value was determined using a Hamiltonian similar to (1), the t_0 and K values were taken from polyacetylene, and α then chosen to give the bipolaron energy level correctly. These choices could not be expected to give a good value for the polaron energy level.

As anticipated, we found that near the center of the polaron the single bonds become shorter and the double bonds longer while the top and bottom bonds on the ring decrease in length, making the ring slightly quinoidal. We

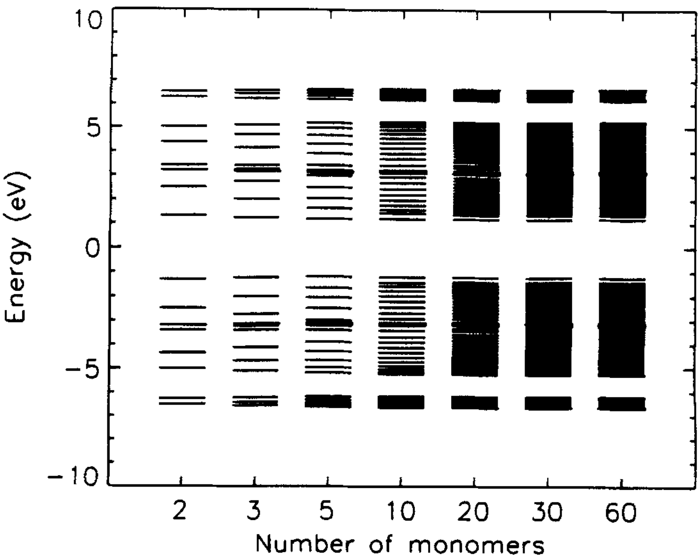

Figure 1 Calculated π band energy levels around midgap for PPV chains of various lengths.

also found that most of the charge resides on the vinyl group. The amplitude of the distortion falls to 10% at a distance 4.2 monomers from the center of the polaron, while 90% of the charge is contained within 5.8 monomers.

Calculation of the polaron geometry using MNDO gave results in poor agreement with those calculated using the Hamiltonian (1). The extent of the polaron from MNDO was only $\frac{1}{2}$ as large. The disagreement is not surprising because MNDO is known to have poor accuracy for open shell calculations. Significantly, a calculation of the polaron geometry using the unrestricted Hartree-Fock PM3 method gave results in good agreement with those from Equation (1) for the four central monomers of the chain. This agreement is additional evidence for the validity of our Hamiltonian.

POLARON STABILITY

It has been pointed out by various authors that interchain coupling in conducting polymers might be too strong for the polaron to be stable if the polymer sample were completely ordered.[7-11] Polarons in polyacetylene with the $P2_1/a$ structure were, in fact, shown to be unstable.[10-12] It was pointed out, however, that polarons can be stabilized by disorder,[11-12] in particular conjugation breaks.[12]

The quantities determining the stability of the polaron are usually taken to be $t_\perp$, the transfer integral between neighboring π orbitals in the direction transverse to the chains, and t_0. Just as does polyacetylene, PPV crystallizes in a herringbone structure with 2 nonequivalent chains in the unit cell. The nonequivalent chains have the stronger interaction, and it is usual to neglect the interaction between equivalent chains. The closest interchain contacts are between C atoms on one chain and H atoms on the neighboring chain. We assume that, as in polyacetylene,[10] the interactions of these closest C-H pairs are responsible for the interchain coupling. Unlike polyacetylene, however, each of the C atoms in a PPV monomer is at a different distance from its closest H atom. The coupling should be exponentially dependent on the C-H distance, and should therefore be dominated by the most closely spaced pairs. The three most closely spaced pairs in the $P2_1/a$ structure are shown in Figure 2. Note that because the chains are not in the same plane, but are in fact rotated in opposite directions away from the plane, the closest spaced atoms in the figure are not the closest in reality.

The interchain coupling has been quantified by using the results of Local Density Functional (LDF) theory for PPV. LDF calculations show splittings, due to interchain interactions, of what would otherwise be degenerate bands.[4] Because each chain has 4 nonequivalent chains as neighbors, we take the calculated splitting, W, at the band edge to be $4<t_\perp>$, $<t_\perp>$ being the average interchain transfer integral. The total interchain coupling for the 8 C atoms in a monomer, denoted by t_{mon}, is then $8<t_\perp>$ or 2W. We apportion t_{mon} among the three closest pairs shown in Figure 2 by the following procedure. The coupling for a pair of C atoms i, j is assumed to fall off exponentially according to

$$(t_\perp)_{ij} = Ae^{-\mu d_{ij}}$$

where d_{ij} is the distance between carbon i on one chain and the hydrogen bonded to carbon j on the other chain, μ the inverse decay length for the change in coupling with interatom distance d_{ij} and A an adjustable parameter chosen to satisfy $<t_\perp> = W/4$. We choose $\mu = 1.18\text{Å}^{-1}$, which is the rate that the wavefunction of an electron in a carbon p orbital decays. We assume that the wavefunction of an electron in a hydrogen p level, which is the orbital coupled to the carbon p orbital,[10] decays much less rapidly. The value chosen for μ leads to the $t_\perp$ values given in Figure 2 for the three atom pairs singled out. To complete the determination of $t_\perp$ we use W = 0.32 eV,[4] leading to $<t_\perp> = 0.08$ eV.

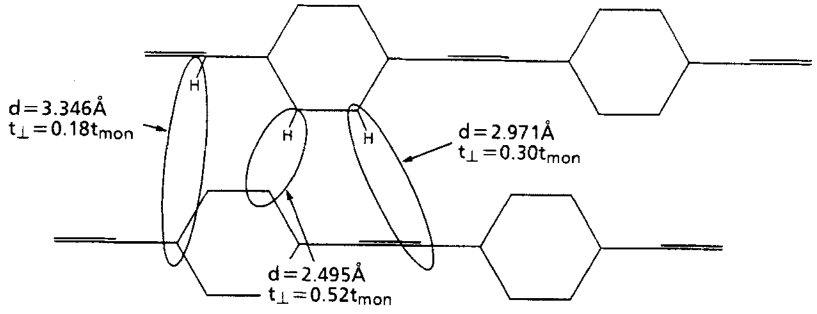

Figure 2 The three strongest interchain couplings for the $P2_1/a$ structure of PPV. The chain has been distorted for clarity.

To carry out the calculations for coupled chains we add to the Hamiltonian (1) the term

$$\sum_{ij\alpha\beta}(t_\perp)_{i\alpha,j\beta}\left(c^+_{i\alpha}c_{j\beta}+c^+_{j\beta}c_{i\alpha}\right) \tag{2}$$

when i, j are atom indices and α, β chain indices. The result of a self-consistent solution for two coupled 10 monomer chains is that the distortion and the charge are mainly on one chain. For the $t_\perp$ values used here the charge on one chain is 0.897 electrons, on the other 0.103 electrons. Further evidence from these calculations for the stability of the polaron in PPV is that the polaron level is clearly separated from the conduction band and valence band and the wavefunction for that level is clearly localized. However the spacing between the polaron level and the nearest band edge in the long chain limit is only 0.13 instead of the 0.18 eV it is for the single chain.

We conclude that the polaron is stable in PPV. The distance of the polaron level from the nearest band edge is 0.2 eV for chains of 10 monomers and longer, but increases rapidly as chain length decreases below 10 monomers.

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