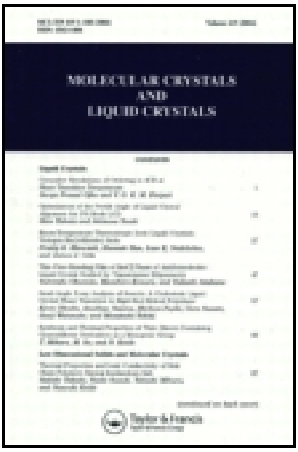

Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

Photogeneration of Polaron Pairs in Poly (Phenylene Vinylene)

Esther M. Conwell [a] [b] & Howard A. Mizes [a] [b]

[a] Xerox Webster Research Center, Webster, New York, 14580

[b] Center for Photoinduced Charge Transfer, University of Rochester, Rochester, New York, 14627

Version of record first published: 04 Oct 2006.

To cite this article: Esther M. Conwell & Howard A. Mizes (1994): Photogeneration of Polaron Pairs in Poly (Phenylene Vinylene), Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 256:1, 27-33

To link to this article: http://dx.doi.org/10.1080/10587259408039228

Mol. Cryst. Liq. Cryst. 1994, Vol. 256, pp. 27–33
Reprints available directly from the publisher
Photocopying permitted by license only

PHOTOGENERATION OF POLARON PAIRS IN POLY (PHENYLENE VINYLENE)

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

Abstract Photoinduced absorption measurements of poly (phenylene vinylene), PPV, made picoseconds after above-gap photon excitation, have been interpreted as showing that a majority of the photons create polaron pairs bound by Coulomb attraction. We have calculated the peaks and approximate widths of the absorption bands due to a polaron pair on adjacent chains in PPV, and find good agreement with the observed absorption.

INTRODUCTION

Picosecond photoinduced absorption (PA) measurements and other experiments have shown that, on exposure of PPV to photons of energy beyond the absorption edge, ~ 90% of the excitations created are neither excitons nor single polarons,[1-3] as would have been expected. It was suggested that they are pairs of polarons, P^+ and P^-, bound by Coulomb attraction[1-3]. The pair might be on adjacent chains, or side by side on the same chain, separated by a conjugation break.

There are several reasons why creation of such a pair is plausible. A P^+ - P^- pair may be considered a split exciton,[2] differing from the familiar singlet excitons in PPV in that two chains or two separate conjugation lengths are distorted rather than one. Production of an exciton by a photon of energy within some tenths of an eV of the absorption edge is not surprising. Preference for a split rather than a single chain exciton might be due to the existence in typical PPV samples of many conjugation lengths shorter than the singlet exciton length of ~ 6 or 7 monomers.[4] Upon confinement to a length shorter than a few monomers the exciton energy goes up very rapidly.[5] It could therefore be energetically advantageous for the electron and hole to be on separate conjugation lengths. If, for example, they move to adjacent chains, which are 4Å apart, they could decrease their total energy by the increase in Coulomb attraction due to smaller average separation. Less advantage can be expected from the electron and hole in different conjugation lengths on the same chain because the width of the polaron keeps the charges further apart. For photons with energy well beyond the absorption edge the photogenerated electron and hole are much less likely to completely separate than in a three-dimensional semiconductor like GaAs, for example. This is so because PPV is essentially an assembly of separate oligomers, the dielectric constant transverse to the chains is smaller by ~ a factor 5, and the carriers can more easily lose excess energy because they are strongly coupled to many, higher energy, optical modes.

PROPERTIES OF SINGLE POLARONS

To study the properties of polaron pairs in PPV we first need a Hamiltonian suitable for describing single polarons in that material. We set up a tight-binding Hamiltonian in the spirit of the SSH Hamiltonian[6], which has been used extensively to treat polarons in polyacetylene, specifically:

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

Here M is the number of monomers in the chain and <ij> indicates one of the pairs of nearest neighbors in the monomer. The sum is taken over all 9 pairs. t_0 is the electronic coupling or transfer integral between neighboring 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 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[7]. The parameters t_0, α and K were chosen so that calculations with Eq. (1) gave values within 1% for 3 quantities: (1) the difference between single bond length, 1.474 Å, and double bond length, 1.355Å, of the vinyl group as determined by MNDO; (2) the valence band width, 5.47 eV, obtained by Local Density Functional theory[8]; (3) the energy gap, 2.8 eV.[9] The values that satisfy the criterion just given are $t_\sigma = 2.66$ eV, $\alpha = 10.29$ eV/Å and $K = 99.0$ eV/Å^2. Larger values than those familiar from polyacetylene,[6] $(CH)_x$ were expected because the band gap is twice as large, and the vinyl dimerization is 40% larger.

From a self-consistent calculation [7] with the Hamiltonian (1) and the parameters just specified, the distance of the polaron energy from the band edge on a long chain of PPV ($\geq$ 20 monomers) was found to be 0.18 eV. It is larger, of course, for short chains.[10] The full width at half maximum of the polaron is ~ 4 monomers or ~ 26Å, and its mass, calculated from the kinetic energy of a moving polaron,[6] 1.8 m_e where m_e is the free electron mass. Determining whether the polaron is stable in the presence of interactions is more complicated than for $(CH)_x$ because the interchain distance is different for every C atom in the monomer. To obtain an order of magnitude approximation, we took the total interchain coupling for a monomer from the interchain coupling induced splitting of the bands at the band edge[8], and divided this up among the pairs of atoms according to their distance apart.[10] The over all coupling is smaller than in polyacetylene and the polaron in PPV was found to be stable under this coupling. However, as in polyacetylene, the interchain coupling resulted in a portion, $\geq$ 10%, of the polaron being shifted to the coupled chain.[11]

PROPERTIES OF A POLARON PAIR

To treat the case of a polaron pair on adjacent chains we added to Eq. (1) the term giving the potential at the i th atom on one of the chains due to the charge on the other chain:

$$V_i = -\sum_j e e_j/\varepsilon_\perp [(d_\parallel)^2_{ij} + (\varepsilon_\parallel/\varepsilon_\perp)(d_\perp)^2_{ij}]^{\frac{1}{2}} \qquad (2)$$

where the summation is over all the sites on the other chain, e_j is the charge on the j^{th} site (determined self-consistently) $(d_\parallel)_{ij}{}^2$ and $(d_\perp)_{ij}{}^2$ the parallel and perpendicular components, respectively, of the distance between the site i and the site j, $\varepsilon_\parallel$ and $\varepsilon_\perp$ the dielectric constants parallel and perpendicular to the chain direction, respectively. For the calculations $\varepsilon_\parallel$ was taken as 8, $\varepsilon_\perp$ as 3. Interchain coupling was also included, with the coupling $(t_\perp)_{ij}$ between the atoms i and j determined as described earlier.

The resulting Π and Π* energy levels for the situation that the polarons are stationary and exactly opposite each other are given in Fig.1 for 10 monomer long chains. It is seen that, as expected, the levels on the chain with P- are pulled down due to the attraction of P+. The polaron levels are pulled down more than the conduction or valence band levels because their wave functions are loocalized, the distance of the top P- level from the band edge thus increasing from 0.2 to 0.4 eV. For a 5 monomer chain the distance increases to 0.54 eV. The lower P- level has moved into the valence band. On the chain with P+ the levels are moved up due to the repulsion of P-. The upper P+ level has moved into the conduction band and the lower P+ level is 0.54 eV above the valence band. The introduction of the interchain coupling is seen to have little effect on the energy levels. The spacing between the P- and P+ levels in the gap is 1.39 eV for 10 monomer chains, 1.42 eV for 5 monomer chains. As is seen by comparison with Fig. 2, the transition between the P- level and the conduction band edge, or between the valence band edge and the P+ level, matches closely the experimental peak in the infrared, while the transition between the P- and P+levels matches closely that of the visible PA. A slightly better match is obtained for the 5 monomer length, which is in any case likely to be closer to the average conjugation length in the sample.

Experimentally the absorption was found to be much stronger for probe E vector parallel to the chain than perpendicular.[1,2] This is, of course, expected for the infrared band, which involves only a single polaron. For the visible band there is absorption for parallel E vector because the interchain coupling results in part of the P+polaron being on the P- chain and vice versa. This suggests that the intensity of the visible peak will be smaller than that of the infrared peak. Unfortunately the ratio of intensities of the two peaks is not known because, as seen in Fig. 2, the data for the infrared band were not carried far enough.

ABSORPTION OF POLARON PAIRS

In actuality the polarons are not stationary; each moves in the potential well due to the other, resulting in shifts of the energy levels and the frequencies absorbed. We determined the shape of the well as follows. The self-consistent solution of the wave equation for a pair of coupled chains with a positive charge on one, a negative charge on the other, is determined using the Hamiltonian of Eq. (1) plus Eq. (2). The resulting displacement of each C atom on one of the chains, representing a polaron on that chain, is then fitted by the function

$$u_{mn} = c_0(n) + c_1(n)\, sech\,[(m - c_3(n))/c_4(n)] \qquad (3)$$

where u_{mn} is the displacement of the n^{th} atom on the m^{th} monomer and the c's are parameters chosen for each atom in the monomer. The charge on each atom was fitted to a function of the same form. To displace the polaron, a constant was added to the argument of the sech function. This neglects any distortion of the polaron due to its moving away from the position opposite the other polaron, which is a secondary effect. The eigen-values of the system were then calculated for the new atom displacements and charges. With repetition of this procedure it was possible to map the total energy of the system as a function of the separation of the two polarons.

To a separation of ± 2 monomers the resulting well was found to be quadratic in the separation between the polarons, enabling the determination of the force constant k for simple harmonic motion in the well. The value of k is 1.30×10^{-3} eV/Å^2, which , with the polaron mass $m_p = 2.84$ m_e (in the presence of the other polaron) leads to the classical frequency of oscillation $\omega = (k/m_p)^{\frac{1}{2}} = 8.95 \times 10^{13}$/s. Using the simple harmonic oscillator wave functions we find that the probability of the polaron being x monomers away from the other polaron, which is kept stationary, is proportional to $\exp(-0.926\, x^2)$. If the other polaron is allowed also to execute zero point motion, the two polarons could on the average show greater separations. On a mean field basis we estimate the resulting probability of separation x as $\exp[(-0.926/2)\, x^2]$.

Plotting the probability of a given separation vs. the absorption frequencies characteristic of that separation for a pair of 10 monomer chains we obtain Fig.3. The plot for 5 monomer chains, which is a more realistic conjugation length for the samples concerned, is quite similar, with the peak for the infrared band at 0.54 eV, and for the visible band at 1.45 eV. Thus the peaks for the 5 monomer case agree quite well with the PA peaks of Fig. 2. Although the shape of the bands in Fig. 3 bears a distinct resemblance to the shape of the experimental bands, a number of corrections must be made before the ordinate actually represents photoinduced absorption. First, it is necessary to multiply the probability of each separation by the optical

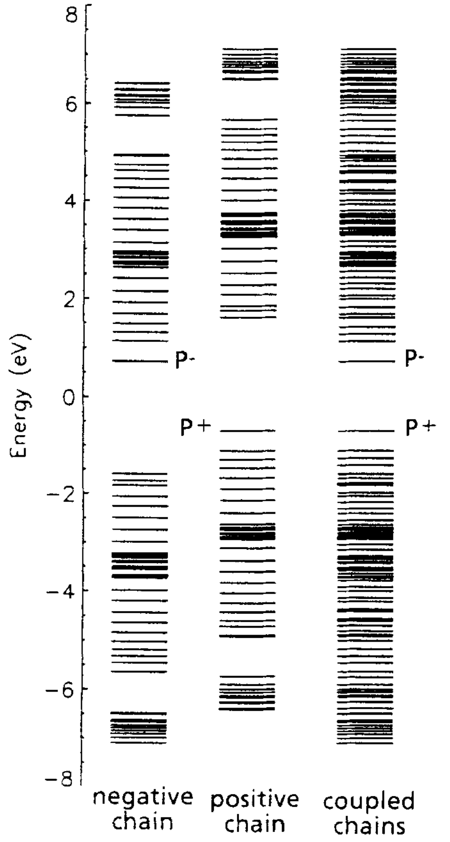

Figure 1 Energy levels for a polaron pair on 10 monomer long PPV chains. Zero on the scale is ~ at midgap.

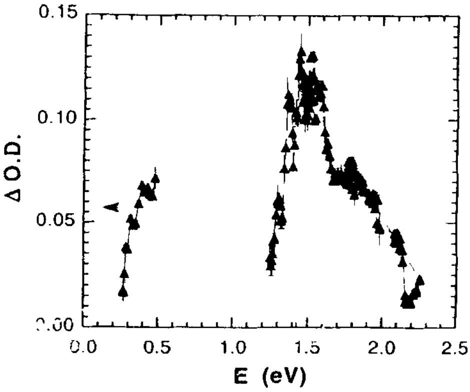

Figure 2 Experimental ps photoinduced absorption for methoxy PPV. The data for PPV are essentially the same. (Adapted from Ref.2)

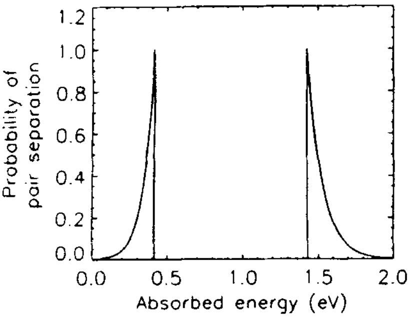

Figure 3 Probability of separation of polaron pair vs. energy of the absorption corresponding to that separation, for 10 monomer chains.

transition probability for that separation. This should make the bands of Fig. 3 somewhat narrower because the wave function overlap decreases as the polarons move apart. Second, the contributions of all different chain lengths must be included. As already noted, polaron pairs on longer chains will have absorptions at lower energies, while those in shorter chains will have absorptions at higher energies. Some absorption at higher energies will also come from transitions to higher levels, although these transitions should have much smaller matrix elements. Finally, polarons on separate conjugation lengths of the same chain, which cannot come as close as polarons on different chains, should give additional absorption not far removed from the absorption of isolated polarons. Their absorption in the visible band would be masked, being in the neighborhood of or beyond the absorption edge. However, in the infrared band the lowest frequency for which data were taken, ~ 0.25 eV, is close to the absorption frequency for an isolated polaron on a 10 monomer chain. We conclude that polaron pairs can account for the picosecond photoinduced absorption of PPV.

We are grateful to Dr. L.J. Rothberg for illuminating discussions.

References

1. L. Rothberg et al., SPIE Proc., 1910, 122 (1993)
2. J.W.P. Hsu et al., Phys. Rev., B49, 712 (1994)
3. M. Yan et al., Phys. Rev. Lett., in press
4. S.C. Graham et al., Synth. Met. 41, 1277 (1991)
5. R. Mahrt et al., Makromol. Chem. Rapid Commun. 11, 415 (1990)
6. W.-P. Su, J.R. Schrieffer and A.J. Heeger, Phys. Rev. 22, 2099 (1980)
7. S. Stafström and K.A. Chao, Phys. Rev. B30, 2098 (1984)
8. P. Gomes da Costa, R.G. Dandrea and E.M. Conwell, Phys. Rev. B47, 1800 (1993)
9. P. Gomes da Costa and E.M. Conwell, Phys. Rev. B48, 1993 (1993)
10. See H.A. Mizes and E.M. Conwell, this issue, for more complete discussion.
11. See, for example, H.A. Mizes and E.M. Conwell, Phys. Rev. Lett. 70,1505 (1993)