Photogeneration of polaron pairs in conducting polymers

E. M. Conwell and H. A. Mizes

Wilson Research & Technology Center, Webster, New York 14580
and Center for Photoinduced Charge Transfer, University of Rochester, Rochester, New York 14627
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It is usually assumed that when photogeneration in a conducting polymer results in an electron and hole on separate chains they form negative and positive polarons that can move independently of each other. We show, on the basis of the small carrier yield per photon seen in picosecond photoconductivity, the different behavior of photoinduced absorption (PA) in dilute solution and thin films, and the spectral distribution of the PA in thin films, that photogenerated positive and negative polarons in poly(p-phenylene vinylene), polythiophene, and polyacetylene are, for the most part, bound in pairs by their Coulomb attraction. We also show that PA data give evidence for a gap of 2.8 eV, and thus an exciton binding energy of 0.4 eV, in poly(p-phenylene vinylene).

I. INTRODUCTION

Photoinduced charge transfer between a pair of like or unlike organic molecules to form a complex that is stable in the excited state, although not in the ground state, has been studied extensively by chemists for some 40 years. Typically a shallow local minimum of energy is found when the distance between the molecules is 3–4 Å, the overlap between π orbitals being relatively small.[1] Such charge transfer complexes may be formed between a pair of molecular functional groups, e.g., phenyls, that happen to be parallel and at the right distance even though they are parts of different polymer chains randomly oriented. Recently it was suggested that such a charge transfer complex is formed between portions of chains of the conducting polymer poly(p-phenylene vinylene) (PPV) by 80–90 % of photons above the absorption edge impinging on a PPV sample.[2] We have shown that the long-lived (ns) photoinduced absorption (PA) found in PPV can be explained by the formation of such a complex or polaron pair.[3,4] In the following we present evidence that such complexes are formed in polythiophene (PT) and polyacetylene $(CH)_x$ as well, thus demonstrating that complex formation is a common phenomenon in this group of conducting polymers. Interestingly, the polymer sample need not be oriented for this pair formation to take place. The observation of photoinduced dichroism in unoriented samples indicates "significant chain extension and chain alignment in microscopically random material."[5,6]

In the following we first present the experimental evidence for polaron pairs in these materials. We will then present the calculations we have carried out for polaron pairs in PPV and $(CH)_x$ and compare with experiment. Although we have not carried out calculations for PT, we will show that the PA results for this case can be deduced from those for PPV. Finally we will discuss the question of whether the polaron pair is an excimer. In our terms an excimer is a charge transfer complex in which the state of the electron or hole is a superposition of a polaron state and an exciton state.

II. EVIDENCE FOR POLARON PAIRS

Picosecond photoinduced absorption has been widely used to identify the excitations generated by light in conducting polymers. Picosecond PA experiments on unoriented $(CH)_x$ verified the predicted subpicosecond photogeneration of solitons.[7] When the ps PA measurements were carried out on oriented $(CH)_x$ they showed different behavior depending on whether the light was polarized parallel or perpendicular to the chains. For both orientations there was a large initial rapid rise of PA, identified by its absorption spectrum as due to solitons which decayed within 1–2 ps.[8] For the perpendicular polarization, however, there was in addition a sizable tail, corresponding to 40% of the excitations, which persisted for more than a ns.[8] Based on the prediction that for perpendicular polarization the electron and hole could be generated on separate chains,[9,10] after which each would evolve into a polaron, it was suggested that the photoinduced tail is due to individual polarons on separate chains.[8] As noted earlier, a sizable PA tail with a similar long lifetime, although quite a different spectrum, has been found also in PPV.[2] A similar PA tail has been found for PT.[11] We begin by summarizing some of the experimental evidence that the photogenerated excitation in these materials are polaron pairs.

Picosecond to nanosecond PA in poly(2-methoxy-1,4 phenylene vinylene) (M-PPV) over the range investigated (0.2–0.5 and 1.2–2.3 eV) consists of two broad absorptions, peaked at ~0.5 and ~1.5 eV, the latter containing a weak secondary peak at 2.15 eV.[2] For PPV the two main peaks are at about the same locations, but the secondary peak is shifted to 2.3 eV.[12] The existence of the infrared absorption, with the same dynamics as the visible absorption, eliminates the possibility of the excitations being triplet excitons.[2] The possibility of their being singlet excitons is eliminated by the observed time dependence of luminescence, which shows that these excitons decay in a time much shorter than ns in both PPV (Ref. 2) and PT.[11] Although the PA in the range 0.2–0.5

eV, and at 2.15 eV in M-PPV, 2.3 eV in PPV, could be due to single polarons on chains with a variety of lengths, calculations of polaron levels cannot provide an explanation for PA in these materials around 1.5 eV.[13] An even stronger argument against the excitations being polarons comes from photoconductivity, as will be discussed. Finally, the fact that the PA is seen as early as fs and persists with little change to ns in both PPV (Ref. 2) and PT (Ref. 11) is evidence that the excitations are not bipolarons.

A most significant piece of evidence is provided by the cases where soluble forms of the polymers are available. A soluble form of PPV is poly(2-methoxy-5-(2'-ethylhexyloxy)-p phenylene vinylene), abbreviated MEH-PPV. For PT a soluble form is poly(3-octylthiophene), abbreviated P3OT. For both MEH-PPV and P3OT the long-lived PA was found in thin films but not in dilute solutions.[14,15] In the case of the MEH-PPV solution the PA dynamics match those of the photoluminescence, indicating that the PA is due to singlet excitons.[14] In MEH-PPV thin films, however, the photoluminescence shows different, overall more rapid, dynamics than the PA, which displays the long plateaulike tail seen in the other PPV's.[14] Similar behavior was found for P3OT.[15] The fact that the long-lived PA is not seen in dilute solutions rules out the suggestion that the excitations are biexcitons,[16] which require only a single chain.

Picosecond transient photoconductivity (PC) in these materials provides a cogent argument against the long-lived excitations being individual polarons, as suggested in Ref. 8. For polyacetylene with the E vector of the light parallel to the chains the rapid decay of the photogenerated soliton pairs led to the conclusion that only ~1% of the photons create photocarriers.[17,8] Additional evidence for the correctness of this conclusion is that the mobility deduced from this number of photocarriers and the measured PC is a few cm^2/V s, in agreement with the ps mobility deduced from the decay of the light-induced dichroism[6] and from the calculated mobilities of drifting polarons and solitons in (CH)$_x$.[18] For the E vector perpendicular to the chains, if the 40% of the excitations with ns lifetime were individual polarons, the PC would be very much greater than the PC resulting from the parallel E vector, which produced only short-lived soliton pairs. However, the PC for the $\perp E$ vector was only 1.7 times as large as that for the $\|E$ vector.[19] The discrepancy is resolved if the polarons created by the $\perp E$ vector are mainly bound in pairs by their Coulomb attraction and thus unable to contribute to PC.[20]

For oriented samples of PPV it was also found that the ps photocurrent was almost independent of the direction of polarization of the light source relative to the chain direction[21] even though photoinduced absorption was larger by about a factor 3 for light polarized perpendicular to the chains.[2] With the peak photocurrent comparable to that in (CH)$_x$ and the carrier mobility also expected to be comparable, it was similarly concluded for this case that only about 1% of the photons absorbed create free polarons.[21] A similar conclusion can be reached from photoconductivity data for derivatives of PT.[22]

III. THEORETICAL CALCULATIONS FOR PPV

The first theoretical calculations of the properties of excitations in conducting polymers were carried out for polyacetylene with the Su-Schrieffer-Heeger (SSH) Hamiltonian, taking into account electron-phonon interactions but neglecting electron-electron interactions.[23] These calculations gave sufficiently good agreement with experiment to encourage further calculations. Detailed calculations of the properties of polarons in (CH)$_x$ were carried out with the SSH Hamiltonian.[24] The results were considered to be in fair agreement with experiment for many conducting polymers except for the lower level in the gap for bipolarons.[25] The poor result of that case was judged to be due to the charge-conjugation symmetry of the SSH Hamiltonian,[25] as well as the neglect of electron-electron repulsion. Unfortunately the possibility for detailed comparison with experiment is limited, one important reason being that the polaron energy levels are quite conjugation-length dependent for the typical conjugation lengths found in these polymers.[26,13] A second reason, if the contention of this paper is correct, is that creation of isolated polarons by light absorption is relatively infrequent compared to pair creation.

Many calculations have taken into account electron-electron interactions by adding to the SSH Hamiltonian terms including on-site Coulomb repulsion U and near-neighbor terms characterized by Coulomb repulsion V. These calculations have generally either used $U \simeq 11$ eV, the difference between the ionization potential and the electron affinity of a neutral C atom,[27] or taken U and V as parameters to be chosen to fit the experimental value of the quantity being calculated. The latter procedure generally led to U of a few eV.[28] Neither of these procedures is satisfactory. In our calculations for the energy levels of polarons and polaron pairs in PPV we have chosen to use a tight-binding Hamiltonian similar in spirit to the SSH Hamiltonian, with the only Coulomb interactions explicitly included those between the positive and negative polarons on separate chains. We expect the results to be reasonably accurate for the energy levels, and for the optical transitions on a single chain, but not necessarily so for interchain transitions, as will be discussed further below.

The Hamiltonian we use for the polaron pair calculations is the sum of a single-chain tight-binding Hamiltonian

$$H = \sum_{m=1}^{M} \sum_{\langle ij \rangle} [-(t_0 - \alpha u_{\langle ij \rangle}) c_i^+ c_j$$

$$+ \tfrac{1}{2} K (u_{\langle ij \rangle} - C)^2 + \text{H.c.}] , \qquad (1)$$

the Coulomb potential at site i on the chain due to the excess charge at each site on the other chain arising from the polaron on that chain,

$$V_i = -\sum_k e e_k / \varepsilon_\perp [(d_\parallel)_{ik}^2 + (\varepsilon_\parallel / \varepsilon_\perp)(d_\perp)_{ik}^2]^{1/2} , \qquad (2)$$

and the interchain coupling

$$H_\perp = \sum_{i,j,k} (t_\perp)_{i,j,k}(c_{i,j}^+ c_{i,k} + c_{i,k}^+ c_{i,j}) \ . \qquad (3)$$

Here M is the number of monomers in the chain and $\langle ij \rangle$ indicates one of the pairs of nearest neighbors in the monomer. The sum in (1) is taken over all nine pairs in the monomer. t_0 is the electronic coupling or transfer integral between neighboring π orbitals on the same chain and $u_{\langle ij \rangle}$ is the change in length of the $\langle ij \rangle$ 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.[3] In Eq. (2) e_k is the charge on the kth site on the other chain (determined self-consistently), $(d_\parallel)_{ik}$ and $(d_\perp)_{ik}$ the parallel and perpendicular components, respectively, of the distance between the site i and the site k, and $\varepsilon_\parallel$ and $\varepsilon_\perp$ the dielectric constants parallel and perpendicular to the chain direction, respectively. For the PPV calculations $\varepsilon_\parallel$ was taken as 8, $\varepsilon_\perp$ as 3. The summation is to be taken over all sites on the other chain. For Eq. (3) $t_\perp$ of each pair was determined by apportioning the local-density functional (LDF) calculated splitting due to interchain coupling[29] among the eight atom pairs of a pair of monomers according to the distance between the atoms in each pair.[13]

The parameters t_0, α, and K were chosen so that calculation with Eq. (10) for a single chain yielded correct values for three quantities: (1) the difference between single bond length, 1.474 Å, and double bond length, 1.355 Å, of the vinyl group as determined by MNDO (modified neglect of differential overlap); (2) the valence bandwidth, 5.47 eV, obtained by local-density-functional theory;[29] (3) the energy gap, 2.8 eV.[30] The values that satisfy the criterion just given were $t_0 = 2.66$ eV, $\alpha = 10.29$ eV/Å, and $K = 99.0$ eV/Å^2.[13] Larger values than those familiar from polyacetylene[23] are expected because the band gap is twice as large, and the vinyl dimerization is 40% larger.

The Hamiltonian that is the sum of (1)–(3) yielded π and π^* energy levels shown schematically in Fig. 1 for the case that the polarons are stationary and exactly opposite each other.[3,4] It is seen that 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 localized. The resulting energy difference E_1 between the top P^- level and the band edge is sufficient to make the lower P^- level merge with the valence band. On the chain with P^+ levels are moved up due to the repulsion of P^-. The upper P^+ level has merged with the conduction band and the lower P^+ level is at energy E_1 above the valence band. The introduction of interchain coupling was found to have little effect on the energy levels because $t_\perp$ is small.[3,4] The spacing between the P^- and P^+ levels in the gap is denoted E_2. The energies E_1, E_2, and E_3 as well as E_g are dependent on chain length, the dependence of the latter two, shown in Refs. 3 and 4, being much larger.
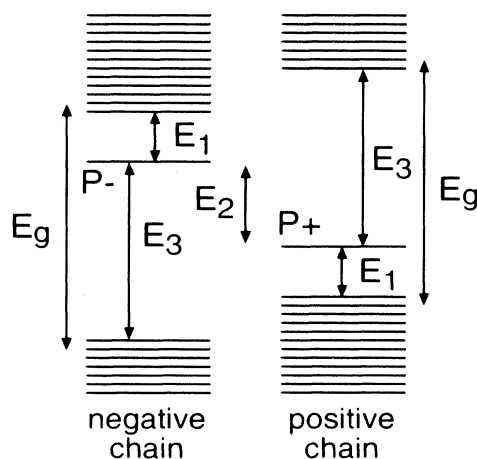

FIG. 1. Energy levels for a polaron pair in the region around the gap (schematic).

IV. COMPARISON WITH EXPERIMENT FOR PPV, P3OT

For chains seven monomers long, generally considered an average conjugation length for PPV, we found $E_1 = 0.45$ eV. If the opposite sign polaron were moved to infinite distance the energy interval E_1 would be 0.31 eV for this chain length. Thus we can account for the infrared PA peak at ~ 0.5 eV as due to transitions between the P^+ or P^- level and the nearest band edge. The weak PA peak found experimentally in PPV at 2.3 eV (Ref. 12) can be identified with the transition from the P^+ level to the conduction band. As is clear from Fig. 1, the experimental finding of PA peaks at 0.5 and 2.3 eV is independent evidence for a gap of 2.8 and, given the absorption edge at 2.4 eV, for an exciton binding energy of 0.4 eV. For M-PPV the absorption edge is at 2.2 eV rather than 2.4 eV and the gap, if we assume the same exciton binding energy as for PPV, is 2.6 eV. It is apparent from Fig. 1 that if E_1 were the same for PPV and M-PPV, which is reasonable to assume, E_g being 0.2 eV smaller for the latter would move the transition from the P^+ level to the conduction band down by 0.2 eV, to 2.15 eV, where in fact it is seen experimentally.[2]

The energy difference between P^+ and P^- levels is calculated to be 1.41 eV. This is close to the observed photoinduced peak in optical absorption at 1.5 eV. However, the final state in this transition has a negative bipolaron on the P^- chain and a positive bipolaron on the P^+ chain. To correctly calculate the energy of the final state in the transition would require taking into account the Coulomb repulsion of the like sign carriers for each other. If we look at the P^- level for specificity, the Coulomb repulsion due to the second electron would tend to raise this level. However, this effect would be at least partially canceled by the creation of the second positive charge on

the other chain due to the transition. In the absence of an exact calculation it is not possible to say how close the cancellation is, thus exactly what the energy E_2 is. We note also that a calculation of the bipolaron levels, made by adding two electrons to a PPV chain using the Hamiltonian (1) with the parameters described, led to a value for the upper bipolaron level in good agreement with experiment.[13] We conclude that it is hard to believe the optical transition would be more than a few tenths of an eV different from the calculated value, 1.4 eV, for E_2.

Well-resolved data on the long-lived PA in the PT family have been obtained on poly(3 octylthiphene), P3OT.[15] The PA extends from ~ 1.1 to 2.0 eV with a maximum at ~ 1.2 eV and a smaller peak at 1.9 eV, just below the absorption edge at ~ 2 eV.[31] Somewhat similar data have been obtained for PT.[11] In principle a Hamiltonian of the type (1)–(3) could be set up to carry out calculations for PT similar to those done for PPV, but unfortunately calculations of the band structure and the exciton binding energy are not available to guide the choice of parameters. We can, however, make reasonable estimates of where the peaks should fall from the following considerations. First, it is reasonable that the distance of the polaron level from the nearest band edge, i.e., E_1, changes little when the band gap changes in this group of polymers, provided the chain length is kept the same. In support of this we note that the distance of the polaron level from the nearest band edge calculated for long chains of PPV with the Hamiltonian (1) is 0.19 eV,[13] agreeing closely with 0.2 eV obtained for a long chain of $(CH)_x$,[32] which has $E_g = 1.4$ eV. For poly(3 hexylthiophene) (P3HT) the polaron-to-band energy has been measured as 0.4 eV by observing the optical absorption due to electrons and holes injected at the contacts.[33] But it must be remembered that 0.4 eV does not apply to the polaron level in the long chain limit, but rather to that for the average conjugation length in the sample used. For PPV the polaron level is ~ 0.4 eV from the band edge for a conjugation length between six and seven monomers, thus ~ 40 Å.[13] This should be in the neighborhood of the conjugation length for the PT sample used for the measurements. The quantity E_1 includes a small additional shift of the polaron level from the band edge due to the Coulomb effect of the oppositely charged polaron. We expect this shift in PT to be similar to that for PPV because it depends essentially on the interchain distance and dielectric constants, which are quite similar for the different polymers in this group. If, on the strength of these arguments, we take the energy E_1 the same for P3OT as for PPV, and the difference in energy gaps as the difference in absorption edges of PPV and P3OT, 0.4 eV, the upper peak in P3OT would be shifted down relative to that in PPV by 0.4 eV, to 1.95 eV. This is in excellent agreement with 1.9 eV at which the peak is found.[15] The agreement suggests that the exciton binding energy in PT is also ~ 0.4 eV.[34] By the same arguments as given above it is reasonable to expect that the peak corresponding to E_2, at 1.5 eV in PPV, should also be decreased by the difference in band gaps, 0.4 eV. This gives the peak corresponding to E_2 for P3OT at 1.1 eV, quite close to the observed value of 1.2 eV.

V. PHOTOINDUCED ABSORPTION IN $(CH)_x$

Calculations of the energy levels due to a polaron pair in $(CH)_x$ were carried out using the SSH Hamiltonian and $C = 1.27\alpha/K$, $\varepsilon_\parallel = 11.0$, $\varepsilon_\perp = 3.0$, and other parameters as in Ref. 23. For a chain length of 100 CH's we found $E_1 = 0.39$ eV and $E_2 = 0.1$ eV. The small spacing between the P^- and P^+ levels compared to PPV or PT is due to the smaller gap of $(CH)_x$. In fact, the value of E_2 is quite close to the value obtained by a rigid shift downward of the levels on the P^- chain by the difference in band gaps. Specifically, in the long chain limit E_2 for PPV is found to be 1.4 eV. Subtracting from this the difference in energy gaps, $2.8 - 1.4$ eV, we obtain $E_2 = 0$, which is within 0.1 eV of the result calculated from SSH. This provides additional justification for our assumptions that E_2 and the downward shift of the energy levels on the P^- chain relative to those on the P^+ chain are essentially independent of E_g, being determined primarily by interchain distance and dielectric constants.

Measurements of ps PA in $(CH)_x$ are available only in the range 0.3–0.5 eV.[8] At 0.3 eV PA is low and increasing with increasing energy, and shows no evidence for a peak in the neighborhood of 0.1 eV. The PA is continuous in the range 0.3–0.5 eV but, unlike PPV, shows two local maxima in this range, at 0.35 and 0.45 eV,[8] the latter being somewhat higher. Around these maxima the PA is roughly symmetric over a few hundredths of an eV. Calculation of E_1 for a P^+P^- pair on adjacent chains in $(CH)_x$ using the SSH Hamiltonian plus Eqs. (2) and (3) gives the result that it ranges from 0.38 to 0.36 eV for chains from 200 sites down to ~ 100, and then increases with decreasing chain length to 0.6 eV at 30 sites. It is noteworthy that absorption and resonant Raman spectra in $(CH)_x$ have been well fitted using a bimodal Gaussian distribution of conjugation lengths, centered at chains of 30 CH's and 200 CH's with standard deviations 50% of the peak value.[35] According to our calculations, we can assign the local maximum at 0.38 eV to conjugation lengths from 200 down to ~ 100 sites. The maximum at 0.45 eV could be obtained with a Gaussian centered about 45 sites, larger than the 30 sites perhaps because the quality of $(CH)_x$ samples had improved in the six years between the two experiments. We can predict on the basis of our model that additional ps absorption should be found in $(CH)_x$ around 1 eV, corresponding to the transition between the P^+ level and the conduction-band edge on the same chain.

VI. DISCUSSION AND CONCLUSIONS

The above discussion has dealt mainly with the peaks in the PA, which arise from the polarons being exactly opposite each other. In an earlier paper, treating PA only in PPV,[4] we showed that the zero-point motion of each polaron in its potential well causes a broadening of the absorption frequencies comparable to the observed spread in PA. To fit the PA in detail would require knowledge of the conjugation lengths and the probability of their occurrence in the sample. Other features of the

PA discussed briefly in Ref. 4 are the polarization and the relative intensities of the peaks. Experimentally, the PA was found to be much stronger for probe E parallel to the chains than perpendicular.[2] This is expected for the absorption bands corresponding to E_1 and E_3, which are each due to a single electron transition on a single chain. We account for the polarization at frequencies corresponding to interchain transitions by noting that the spatial part of the wave function must be symmetric (electron and hole spins are antiparallel), a superposition of P^+ on, say, the left-hand chain and P^- on the right with the equally probable situation of P^- on the left and P^+ on the right. Thus for the interchain transitions the components of the transition dipole perpendicular to the chains should largely vanish by cancellation. There is absorption for parallel E vector in the situation we have discussed because the interchain coupling results in part of each polaron being on each chain.[26] As discussed in Refs. 13 and 26, we believe the polaron is stable in PPV, which means that the major part of the polaron is on one chain, and only a minor part on the other. This suggests that the intensity of peak E_2 should be less than that of E_1 and E_3. The ratio of intensities of peak E_2 to E_1 is not known even in PPV because the experimental data for the infrared bands were not carried to high enough frequency. However, the data[2,15] indicate that the intensity of peak E_3 is less than that of peak E_2. This could indicate that polaron pairs are excimers, with some of the exciton state mixed in with the charge transfer state.[1] In this situation there would be a borrowing of oscillator strength from the exciton transition.[1] The admixture of exciton states with the states we have designated P^- and P^+ need not change their energy much because, as has been seen in the previous discussion, the exciton binding energy is comparable to the energy E_1. Our reason for designating the polaron pair state a charge transfer state, involving only polaron wave functions, rather than an excimer is that the latter are usually identified by their emission. Emission for the state responsible for the PA in PPV, PT, and $(CH)_x$ is weak if it exists at all. It is quite possible that the polaron pairs are excimers but the imperfections of the currently available samples of these polymers are such that the nonradiative lifetime is shorter than the radiative one.

A suggestion that the charge transfer states may be excimers in these polymers comes from a comparison with recent work on planarized poly(paraphenylene) (PPP). PPP has been made into a rigid structure by connecting four carbon atoms of each phenyl ring with neighboring rings.[36] The resulting PPP-type ladder polymer has been shown to have a high degree of intrachain order.[37] For one form of this ladder polymer, with CH_3 replacing a hydrogen atom at the bridge between two phenyls, the quantum yield of photoluminescence in solution was found to be very high, 85%.[38] The luminescence was blue. Increasing the concentration of this ladder polymer, denoted Me-LPPP, by incorporating it in poly(methyl methacrylate), or even more by making a pure Me-LPPP film, resulted in increasing amounts of a broad yellowish emission.[37] The finding of a lower-frequency emission which increases as the concentration of emitting units increases is clear evidence for excimer formation in the film. It is clear that the luminescent photogenerated excitations in the film are not singlet or triplet excitons, biexcitons, single polarons, or bipolarons. The fact that excimers are found for this conjugated polymer suggests that they would be found also in PPV, PT, etc. Although a high degree of interchain order may be necessary for observing emission from excimers, it may not be necessary for excimer formation. We note that the theory requires only short parallel sections of the polymer chains for formation of the polaron pairs. For PPV we have found that even with a chain length of only two monomers the energy E_2 is within 0.3 eV of its value for seven monomer chains and longer.

We conclude that the long-lived ps photoinduced absorption observed in PPV, PT, $(CH)_x$, and their derivatives can be ascribed to a photogenerated charge transfer state, or polaron pairs. More generally, the state may be an excimer due to the admixture of exciton wave function. Although some single polarons can be generated, for example, in situations where disorder or defects result in there not being an adjacent chain suitable to accommodate a polaron of opposite sign, we believe that photogeneration of polaron pairs rather than single polarons is common in this group of conducting polymers. We point out also that the experimental finding of PA peaks at 0.5 and 2.3 eV is independent evidence for a PPV gap of 2.8 eV and an exciton binding energy of 0.4 eV.

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