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Polaron-pair generation in poly(phenylene vinylenes)

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The effects of weak magnetic fields on the photoconductivity of poly(*p*-phenylene vinylene) (PPV) and two derivatives, poly(1,4-phenylene-1,2-dimethoxyphenyl vinylene) (DMOP-PPV) and poly(2-phenyl-1,4-phenylene vinylene) (PPPV), were observed within the temperature range 130–350 K. These effects are attributed to the formation of interchain pairs involving a negative polaron and a positive polaron. A polaron pair is formed as a result of interchain electron transfer from a molecular exciton. The lifetime of a pair is estimated to be within the range of 10^{-8}–10^{-9} s. Thermal dissociation of a polaron pair produces free charge carriers, and recombination of the pair regenerates a singlet or triplet exciton on a single conjugated segment of a chain.

INTRODUCTION

Since the discovery of the precursor route for obtaining poly(*p*-phenylene vinylene) (PPV) films of good quality,[1-4] this polymer has been extensively investigated. Studies of photoconductivity,[5,6] photoluminescence,[7-11] photoinduced absorption,[7,9] and others provided information on the nature of photogenerated excited states in this polymer. Recently, the electroluminescence of PPV (Refs. 10 and 12) and a derivative polymer, poly[2-methoxy,5-(2′-ethylhexoy)-1,4-phenylene vinylene] (MEH-PPV) (Ref. 13) was observed. This report stimulated further studies on PPV and other poly(arylene vinylene)s (see, for example, Ref. 14).

According to these recent results, the transformations of photon energy in PPV can be described as follows: Absorption of photons of any polarization generates short-lived (≤ 300 ps at room temperature) singlet excitons, which are the intrachain states.[7-9] Radiative decay of singlet excitons leads to fluorescence of PPV with a quantum yield of about 0.1, the 0–0 transition being located at 2.37 eV.[7-9,11] Nonradiative decay of the singlet excitations generated initially results from charge transfer with acceptor species[11] or from an intersystem crossing and formation of triplet excitons.[9] The acceptor species can be either impurities or conjugated chain segments different from that of the site of the photogenerated singlet excitations. Transfer of electrons onto the next chain should generate metastable interchain charged photoexcitations, geminate electron-hole pairs among them, and finally generate long-lived charged photoexcitations which, in some cases, are supposed to be bipolarons.[7,9] However, injection of charge carriers of opposite signs into PPV films followed by their bimolecular recombination also produces intrachain singlet excitons.[10,12,13] Most generally, the above charge transfer can be between different conjugated segments, whether or not they are on the same chain. Consequently, the term *intrachain* means "within the same conjugation length" and the term *interchain* can be expanded to mean "between different conjugation lengths, whether or not these conjugation lengths are on the same chain or on different chains."

Although some information concerning the nature of singlet and triplet intrachain exciton states in PPV and its derivatives has been reported, the mechanism of photogeneration of charge carriers is not clearly established. This deficiency is especially true in the case of room-temperature phenomena, for which many effects, such as photoinduced absorption, are negligible;[7,9] as a consequence, limited experimental data are available. Thus, we decided to use the magnetic-field-effect (MFE) method to clarify the nature of intermediate paramagnetic species possibly involved in photogeneration of charge carriers in PPV and its derivatives. This method has already been used successfully for investigating the mechanism of photoconductivity for polydiacetylene (PTS) crystals[15-17] and other polymers and low-molecular-weight organics (see Refs. 18, and 19, and references cited therein).

Herein, we prove experimentally that negative-

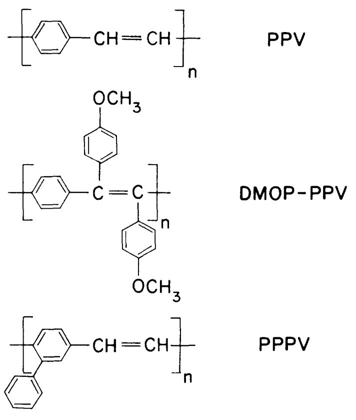

FIG. 1. Chemical structures of poly(phenylene vinylene) (PPV), poly(1,4-phenylene-1,2-dimethoxyphenyl vinylene) (DMOP-PPV), and poly(2-phenyl-1,4-phenylene vinylene) (PPPV).

polaron–positive-polaron pairs are formed in the process of charge-carrier photogeneration in PPV, poly(1,4-phenylene-1,2-dimethoxyphenyl vinylene) (DMOP-PPV), and poly(2-phenyl-1,4-phenylene vinylene) (PPPV) films. (For chemical structures of polymers, see Fig. 1.) The lifetime of the pairs is estimated to be within the range of $10^{-8}-10^{-9}$ s. The pairs are formed in the thermally activated process of interchain electron transfer from singlet excitons, and they may exist in the singlet as well as in the triplet state. Recombination of polarons within the pairs (geminate recombination) leads to the formation of singlet and/or triplet molecular excitons, whereas their thermal dissociation produces charge carriers, namely, polarons.

EXPERIMENT

All the experiments utilized pristine films. Free-standing, unoriented PPV films were obtained by the precursor route.[3,4] DMOP-PPV (mol. wt. 9000) (Ref. 20) and PPPV (mol. wt. 19 200) were synthesized in the Friedrich-Schiller University at Jena and Philipps University at Marburg (both in Germany), respectively. DMOP-PPV and PPPV films were cast onto quartz supports from chloroform solutions. The dc surface photoconductivity was measured in vacuum or in an atmosphere of inert gas, using Ag electrodes for PPV and Al electrodes for DMOP-PPV and PPPV. Photoconductivity was produced by excitation of the polymers in their main absorption band, using a constant light source. Measurements were done in the temperature range 130–350 K, using dc magnetic fields in the range $H=0-3$ kOe. The details of the experimental setup are published elsewhere.[15,16]

RESULTS

The magnetic-field effect on the photoconductivity of all three polymers was observed, i.e., photocurrent i increased and reached a new level when the external magnetic field was applied. A typical $i(H)$ dependence is shown in Fig. 2, the shape of the curves being the same for all three polymers. As shown in Fig. 3, the MFE values, i.e., the relative change of the photocurrent in the magnetic field, $\Delta i/i=[i(H)-i(0)]/i(0)$, were strongly temperature dependent. The temperature dependence of the $\Delta i/i$ curves differs dramatically from that of the $i(T)$ curves, the latter having Arrhenius temperature dependence corresponding to activation energies of about 0.17, 0.3, and 0.23 eV for PPV, DMOP-PPV, and PPPV, respectively. The MFE measurements were made within the linear or nearly linear range of photocurrent dependence on the applied electrical field and on the intensity of excitation. The MFE on the dark conductivity of all three polymers was less than 0.1% within the temperature range investigated. This result proves that the MFE on photoconductivity is due to the influence of the magnetic field on the rate of photogeneration of charge carriers rather than on their drift mobility.

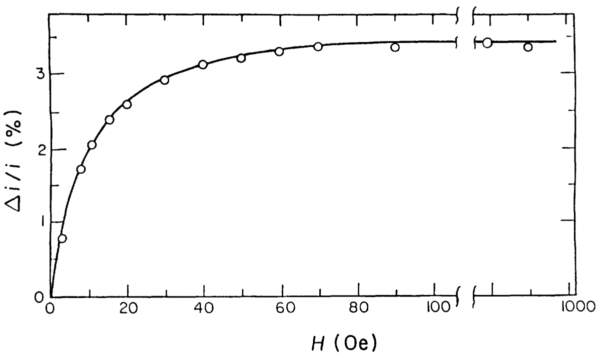

FIG. 2. Typical dependence of the photocurrent i on the magnetic-field strength H for films of PPV, DMOP-PPV, and PPPV. The data deputed here are for PPPV film.

DISCUSSION

The experimental data can be understood within the framework of the following model: After the photogeneration of a singlet molecular exciton $^1M_1$ from the

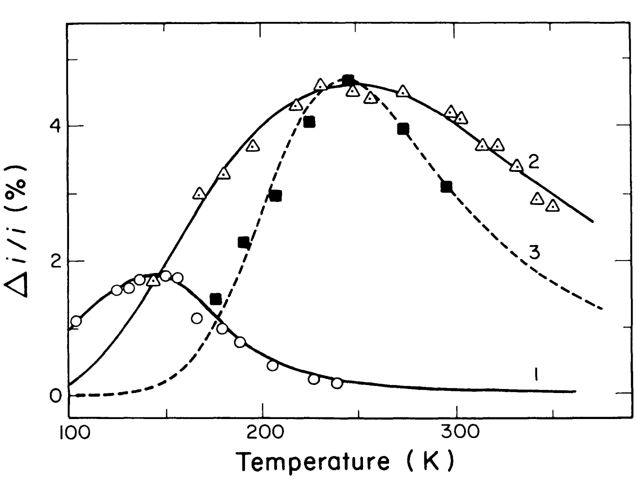

FIG. 3. Temperature dependence of the MFE ($H=1$ kOe) on photoconductivity for (1) PPV, (2) DMOP-PPV, and (3) PPPV. The solid lines are calculated by using Eq. (4).

ground state $^1M_0$, an electron can be transferred to a neighboring (preferably, next-neighbor) chain,[7,9] forming with its parent hole a geminate interchain polaron pair $^1(\mathrm{P}\cdot^{+}\cdots\mathrm{P}\cdot^{-})$. Polarons within the pair are bound by the Coulomb interaction and thus do not contribute to the dc photoconductivity. Dissociation of the pairs into charge carriers (unbound polarons) is a thermally activated process, the activation energy being dependent on the initial separation of polarons within the pair. According to the spin-conservation rule, polaron pairs are formed initially in the singlet spin state $^1(\mathrm{P}\cdot^{+}\cdots\mathrm{P}\cdot^{-})$. However, the interchain polaron pair can also exist in a triplet state, $^3(\mathrm{P}\cdot^{+}\cdots\mathrm{P}\cdot^{-})$, the recombination of which leads to the formation of an intrachain molecular triplet exciton. The hyperfine interaction (HFI) in one or in both pair members mixes the singlet and triplet states, the degree of mixing being dependent on the external magnetic field.[18,19] Figure 4 shows the mixing as an intersystem crossing between the $^1(\mathrm{P}\cdot^{+}\cdots\mathrm{P}\cdot^{-})$ and $^3(\mathrm{P}\cdot^{+}\cdots\mathrm{P}\cdot^{-})$ states occurring at frequency $\omega(H)$. The spin state of the pair is determined by the Hamiltonian in the form:[18,19]

$$\hat{H}=2g\hat{S}H+\hbar a_1I\hat{S}_1+\hbar a_2I\hat{S}_2-\hbar J(r)(\tfrac{1}{2}-2\hat{S}_1\hat{S}_2)\ , \tag{1}$$

where the $2g\hat{S}H$ term describes the Zeeman interaction of two polarons ($g\equiv g_1=g_2$), the $a_1I\hat{S}_1$ and $a_2I\hat{S}_2$ terms describe the hyperfine interactions, a_1 and a_2 are the HFI constants, and the $J(r)(\frac{1}{2}-2\hat{S}_1\hat{S}_2)$ term relates to the exchange interaction provided by a separation-dependent exchange parameter $J(r)$. The solution of the Schrödinger equation with the Hamiltonian in form (1) includes the wave function of four spin states of the pair with the energy levels for $H=0$ and $J=0$ being located as shown in the upper part of Fig. 4. It is assumed that pure singlet and triplet spin states are characterized by the effective rate constants of recombination (k_S^{eff} and k_T^{eff}, respectively) and by the spin-independent dissociation rate (k_{-1}).

The mixing of the singlet and triplet states occurs if the following conditions are met: the energies of the mixing states have equal values and the pair lifetimes in the singlet state (t_S) and in the triplet state (t_T) are long enough for spin evolution

$$t_S=(k_S^{\mathrm{eff}}+k_{-1})^{-1}\ ,$$
$$t_T=(k_T^{\mathrm{eff}}+k_{-1})^{-1}>1/a=4\times10^{-9}\ \mathrm{s}$$

(Refs 18 and 19). One additional condition must be fulfilled for the MFE to be significant: $t_{\mathrm{ST}}<T_1\sim10^{-7}$ s, where t_{ST} is the lifetime of the mixed singlet-triplet states and T_1 is the spin-lattice relaxation time. If the exchange interaction is negligible, for $H=0$ all four spin states of a polaron pair are mixtures of the singlet (S) and triplet (T_+, T_0, T_-) states and their lifetime is $t_{\mathrm{ST}}^0=(k_S^{\mathrm{eff}}+3k_T^{\mathrm{eff}}+4k_{-1})^{-1}$. In a high-field limit, $H\gg a_1,a_2$, only the S and T_0 states are mixed; their lifetime is $t_{\mathrm{ST}}^H=(k_S^{\mathrm{eff}}+k_T^{\mathrm{eff}}+2k_{-1})^{-1}$, and the T_+ and T_- states remain pure triplet states that are not populated. Using the expression for t_{ST}, it is possible to calculate the changes in the total pair population N when the magnetic field is turned on. Here we assume that the polaron pairs are populated via the singlet channel and that the rate of free-carrier (polaron) formation G is proportional to the total pair population:

$$G=k_{-1}\sum_{j=1}^{4}N_j\ .$$

Because the photocurrent value i is proportional to G, the high-field limit of the MFE on photocurrent is

$$\begin{aligned}\Delta i/i&=\Delta N/N\\&=(k_T^{\mathrm{eff}}-k_S^{\mathrm{eff}})/(2k_S^{\mathrm{eff}}+2k_T^{\mathrm{eff}}+4k_{-1})\ .\end{aligned}\tag{2}$$

To use the notation of Fig. 4, we must substitute $k_\downarrow k_S/(k_S+k_\uparrow)$ for k_S^{eff} and $k_\downarrow k_T/(k_T+k_\uparrow)$ for k_T^{eff}. Equation (2) can then be rewritten as

$$\frac{\Delta i}{i}=\frac{1}{2}(k_T-k_S)\left[\frac{2k_Sk_T}{k_\uparrow}+(k_S+k_T)+\frac{2k_{-1}(k_S+k_\uparrow)(k_T+k_\uparrow)}{k_\uparrow k_\downarrow}\right]^{-1}\ . \tag{3}$$

The MFE not only for static fields but also for the resonant one can be obtained for paramagnetic pairs. In this latter case, a microwave magnetic field is applied in addition to the static one. At the resonant condition, the microwave field pumps the transitions between the magnetic sublevels with different spin projections of paramagnetic species, exactly as it does in ESR measurements, thus changing the total population of the magnetic sublevels of the pairs. If these pairs take part in the reaction, producing, for example, fluorescing excitons or charge carriers, one can obtain a magnetic-resonance signal by detecting the yield of the reaction. This method, originally named by its authors as RYDMR (reaction yield detected magnetic resonance),[18,19,21] was used recently to confirm the existence of polarons and triplet excitons in PPV (Refs. 22–24) and solitons in polyacetylene.[24] [One should take into the consideration the fact that the triplet signal obtained for PPV (Refs. 22–24) might originate

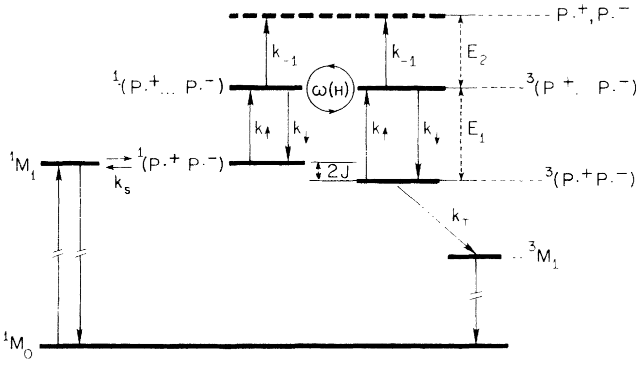

FIG. 4. The proposed energy-level diagram and associated rate constants relevant for the transformations of photogenerated excitons and polarons. $(\mathrm{P}\cdot^{+}\mathrm{P}\cdot^{-})$, $(\mathrm{P}\cdot^{+}\cdots\mathrm{P}\cdot^{-})$, and $\mathrm{P}\cdot^{+},\mathrm{P}\cdot^{-}$ denote short-range polaron pairs, long-range polaron pairs, and well-separated (i.e., free) polarons, respectively. The dashed line corresponds to the energy level of free polarons. Arbitrary scale is used for energy: the energy range for polarons is nonlinear. See text for details.

from the resonant transitions within polaron pairs; see Ref. 18, and references cited therein.]

The monotonic shape of the experimentally observed dependence of the photocurrent on the magnetic-field strength (Fig. 2) confirms the proposal that spin evolution occurs in the states where the exchange constant J is essentially zero, i.e., at sufficiently large polaron-polaron distances.[18,19] But, it is exactly the exchange interaction that is responsible for the selection of the spin states during a short but close enough approach of their pair particles and that determines the different values of the rate constants k_S and k_T. Because the MFE value is proportional to the concentration of free charge carriers (polarons), upon particle approach and spin assessment in the region of the exchange interaction, the probability that the polaron pair will redissociate should become significant. Three regions of polaron-pair evolution can be identified (see Fig. 4): (1) The "exchange interaction region," in which relatively small distances exist between the polarons in the pair $(P\cdot^{+}P\cdot^{-})$; (2) the "$J=0$ region," where $J \ll V_{\mathrm{HFI}}$ in larger pairs $(P\cdot^{+}\cdots P\cdot^{-})$; and (3) the "free-polaron region," where pairs have already been dissociated into $P\cdot^{+}$ and $P\cdot^{-}$. Mixing of the S and T states of the pairs occurs only in region (2). In the polymers investigated, the process of polaron separation occurs within the Coulomb potential, and the energy level can be assigned to the polaron pair from each region (see Fig. 4).

Assuming that only the rate constants of the generation of polaron pairs $(P\cdot^{+}\cdots P\cdot^{-})$ $k_{\uparrow}$ and of their dissociation into charge carriers k_{-1} are thermally activated (see above): $k_{\uparrow}=k_{\uparrow}^{0}\exp(-E_1/kT)$, $k_{-1}=k_{-1}^{0}\exp(-E_2/kT)$, we can rewrite the expression for the MFE [Eq. (3)] in the form

$$\Delta i/i=K\{(1+A/k_{\uparrow})(1+Bk_{-1})+Bk_{-1}\}^{-1}, \tag{4}$$

where K, A, and B do not depend on the temperature. Here we assume also that $k_1,k_3 \gg k_{\uparrow}$. Computer simulation of the experimental dependence of the MFE on temperature (Fig. 3) allowed us to determine values for E_1 and E_2. Good agreement between experimental and calculated data was achieved for $E_1=0.03$ eV and $E_2=0.14$ eV for PPV, $E_1=0.07$ eV and $E_2=0.16$ eV for PPPV, and $E_1=E_2=0.15$ eV for DMOP-PPV. Qualitatively, the decrease of the MFE upon the increase of temperature could be explained by the decrease of the lifetime of polaron pairs as the probability of their dissociation increases. The same argument might explain the decrease of intensity of the RYDMR signal on fluorescence[22,23] in PPV at $T > 150$ K. At low temperatures, it takes a while for polarons to return from the distances where pairs have assessed their spin state. Thus, the diffusion time becomes larger than T_1, thereby decreasing the MFE value.

The average distance between polarons within $(P\cdot^{+}\cdots P\cdot^{-})$ pairs can be estimated as $L_{\mathrm{PP}}=e^2/\epsilon E_2$, which for typical values of $\epsilon \cong 3$ gives $L_{\mathrm{PP}} \cong 60$ Å. A lower limit for the distance between polarons within $(P\cdot^{+}\cdots P\cdot^{-})$ pairs is provided by the range of exchange interaction $r_{\mathrm{ex}}=e^2/\epsilon(E_1+E_2)$, which is ~27, 20, and 15 Å for PPV, PPPV, and DMOP-PPV, respectively. The microcrystalline structure of these polymers with at least one-dimensional ordering within the microcrystals[4,25] suggests, as was previously the case for polydiacetylene crystals,[17,26,27] that short-range polaron pairs $(P\cdot^{+}P\cdot^{-})$ with $J \gg V_{\mathrm{HFI}}$ are the charge-transfer (CT) excitons. In CT excitons, formed by the interchain electron transfer, the electron is delocalized on the chain next to the parent hole, and the size of the exciton is about $2r_{\mathrm{ex}}$. Experimentally, the existence of CT states could be confirmed by comparing the MFE measurements on polymers and their model monomers or oligomers. These experiments are now in progress.

The model presented above describes the processes that precede bipolaron formation via the meeting of two noncorrelated polarons of the same sign: $P\cdot^{\pm}+P\cdot^{\pm}\rightarrow BP^{2\pm}$. In principle, this latter reaction is also expected to be spin sensitive, but if so, it should cause an MFE on charge-carrier mobility. This effect has been observed for polaron-soliton reactions for polyacetylene[28] and for charge carrier–radical reactions for many other organic solids.[18,29] We have not observed this effect.

In conclusion, a modified scheme of the photoinduced processes in PPV and its derivatives was presented. The scheme includes the formation of polaron-polaron geminate pairs as a result of the interchain transfer of electrons. The pairs have a lifetime of 10^{-8}–10^{-9} s and are the precursors for free charge carriers, i.e., polarons and, then, bipolarons.

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