Evidence for triplet interchain polaron pairs and their transformations in polyphenylenevinylene

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Photoluminescence of films of poly-(*p*-phenylenevinylene) (PPV), and changes of its intensity under conditions of electron spin resonance as a function of temperature and light intensity were studied. The experimental technique was based on the modulation of the spin state of paramagnetic species by resonant microwave transitions between Zeeman sublevels of dynamically spin-polarized pairs. Three types of resonant signals were found in the magnetic resonance spectrum: (i) a narrow (1.7 mT width at the half height), (ii) a broad (140 mT) enhancement signal at $g=2$, and (iii) the signal at $g=4$. The results permitted one to conclude that Coulomb bound polaron pairs are produced in PPV with high yield under 488-nm photoexcitation. The narrow signal is assumed to appear due to microwave-induced resonant transitions in triplet polaron pairs. This implies that the resonant transitions change the rate of geminate recombination of the pairs that leads to the formation of triplet intrachain excitons. Those excitons annihilate in the second-order reaction and show themselves in the intensity of the photoluminescence. The annihilation rate was found to be influenced by resonant transitions in triplet exciton pairs as well and resulted in broad and $g=4$ signals. The lifetime of triplet intrachain excitons was estimated from microwave modulation frequency dependence of resonant signal intensities. The results showed that the energy level of the lowest polaron pair state situated below that of singlet intrachain exciton can act as a sink of the excitation energy influencing the quantum yields of the photoluminescence, electroluminescence, and photoconductivity. [S0163-1829(97)04831-5]

I. INTRODUCTION

Studying the processes of photogeneration of free charge carriers in semiconducting polymers is important for a proper understanding of photoconductivity and related phenomena in these materials. The investigations of processes reverse to the above ones appear to have become even more attractive recently. It is connected with the observation of emission of light with a good quantum yield due to the recombination of charge carriers double injected into a polymeric film of poly-(*p*-phenylenevinylene) (PPV) from electrodes.[1] Investigations in this area meet inevitably a problem about the nature of states intermediate between free charge carriers and molecular electronic excited states. It is generally accepted for molecular crystals and for polymers with conjugated double bonds with a nondegenerate ground state of the chain that primary photoexcited states are intrachain excitations. Afterwards they may relax, producing light-emitting excitons or spend their energy on charge carrier production.[2] The low mobility of charge carriers in polymers prevents them from escaping from mutual Coulomb attraction, making charge carriers of opposite sign thermalize in the vicinity of each other. Low mobility [below 10^{-5} cm^2/V s (Ref. 3) at room temperature for PPV] is connected with hopping of charge carriers between conjugated segments of a polymer chain. Their mobility within the conjugation length, as one believes, is much higher. The intercharge distance in thermalized pairs is initially shorter than the Onsager radius:

$$r_{\mathrm{Ons}}=\frac{e^2}{\varepsilon k_B T}. \tag{1}$$

For $\varepsilon=6$ and $T=300$ K $r_{\mathrm{Ons}}=90$ Å. Those thermalized pairs either recombine geminately or dissociate into free charge carriers. The latter are known as polarons in polymers. The dissociation of polaron pairs is induced by interaction with phonons and becomes faster in high electric fields.

There exists, however, another point of view,[4,5] which is based on the assumption that Coulomb interaction is sufficiently well screened, and that free carriers are created upon photoexcitation. The authors claim that ''the singlet exciton is not a stable excited state, and the singlet exciton binding energy with respect to the single-particle continuum is less than k_BT.''[4] The results obtained in the present work interfere with such an assumption. The existence of the polaron pairs between free charge carriers and intrachain excitons makes the yield of free charge carriers (when exciting the photoconductivity) and the efficiency of electroluminescence (EL) [while injecting charge carriers into the light-emitting diode (LED) type samples] dependent on the properties of such pairs. That is why studying them is of importance. A hypothesis about the polaron pairs in conjugated polymers was suggested first on the basis of observation of magnetic field spin effect (MFSE) on the photoconductivity of polydiacetylene[6] and poly(arylenevinylene)s.[7] The authors[6,7] concluded that polaron pairs can be of two types, one as interchain charge transfer excitons, and the second as distant polaron pairs bound by Coulomb attraction and recombining geminately. Coulomb attraction was assumed to be not decisive for the geminate character of the recombination process in single crystals of polydiacetylene due to the quasi-one-dimensional character of charge-carrier motion. Gailberger and Bässler[8] considered the role of such states in the photo-

conductivity of PPV also. In the works of Hsu *et al.*[9] and Yan *et al.*[10] photoinduced absorption caused by polaron pairs was observed. A delayed fluorescence of PPV in the time domain of 50 ns has been reported,[11] and was speculated as being due to electron back transfer from polaron pairs. The energy levels of polaron pairs were calculated in Refs. 12 and 13, in accordance with transient absorption measurements.

The existence of geminate pairs, as mentioned above, gives rise to MFSE, which is based on the spin-dependent recombination processes. A change of recombination rate by an external dc magnetic field or by a resonant microwave magnetic field can be revealed as modulation of any parameters connected kinetically with the pairs. Photoconductivity, luminescence intensity, and induced absorption are usually used to monitor the changes.[7,14–20]

Polaron pairs should be taken into account when calculating the efficiency of EL, ϕ_{EL}. A simple point of view based on the spin statistics of free carriers and on the assumption that light-emitting excitons are formed directly in the charge recombination process gives the first estimate of ϕ_{EL} per one pair of recombining polarons:

$$\phi_{\mathrm{EL}} = \tfrac{1}{4}\phi_{\mathrm{PL}}. \tag{2}$$

Here ϕ_{PL} is the quantum yield of the photoluminescence (PL). Formula (2) does not seem to be true as long as the singlet exciton, which is supposed to emit the light, is created via the intermediate polaron pair state and which is subjected to a spin evolution. The value of ϕ_{EL} is thus expected to depend on kinetic parameters of the polaron pairs.

In the present paper we are using a technique based on the modulation of the spin state of polaron pairs by resonant microwave transitions between Zeeman sublevels of polarons that have a dynamic spin polarization. This is a technique that was introduced originally as reaction yield detected magnetic resonance.[14,15] The parameter used for monitoring the change of the reaction rate in this work is the luminescence intensity, so the term photoluminescence detected magnetic resonance (PLDMR) can also be used. A similar experimental approach to study electronic processes in PPV has been done in previous papers of Swanson *et al.*,[16,17] Wei *et al.*,[18] and in our laboratory.[19,20]

Experimental results obtained in the present paper do not contradict those reported in Refs. 16–19. However, additional data presented permitted us to come to conclusions that differ much from those made in the previous works, as will be discussed later on in this paper. Before going on to the description of experiments and discussion, we are listing the names of various types of excitations that take part in photophysical processes in conducting polymers, and are used in the present paper and papers in this branch of science. That may be helpful for readers who are not intimately involved with the subject.

Primary excitations are electronically and vibrationally excited states of the conjugated part of a polymer chain produced as a result of light absorption. *Intrachain excitons* are relaxed primary electronic excitations. They can be in singlet and triplet states. Singlet exciton is assumed to be delocalized over the conjugated length of the single polymer chain, whereas the triplet exciton is localized on the phenylene ring.[16] *Polarons* are negative or positive charge carriers that polarize the media around them; they are delocalized over the conjugated segment of the polymer chain. *Polaron pairs* are two polarons, positive and negative, which interact with each other and have their spins correlated. They can be in singlet and triplet states. Polaron pairs are called geminate if originated from ionization of the same molecule. Recombination of polarons within the pair is spin dependent. Polaron pairs situated not on the neighboring polymer chains are often called distant polaron pairs. *Interchain charge transfer (CT) excitons* are excited species having positive and negative charges, each of them being delocalized onto one of two neighbor polymer chains. Synonyms are spatially indirect excitons and bound polaron pairs. CT excitons may be in singlet and triplet states also. *Two-triplet, or triplet-triplet pairs,* are two triplet intrachain excitons with correlated spins. These pairs can be in singlet, triplet, or quintuplet states.

We have studied PL of films of PPV and changes of its intensity under conditions of electron spin resonance as a function of temperature, light intensity, and microwave power modulation frequency. Three types of signals have been revealed and further investigated in the magnetic resonance spectrum, i.e., narrow (1.7 mT width at the half height), broad (140 mT) signals, and the signal at $g=4$. The results obtained let us conclude that Coulomb bound polaron pairs are produced with a high yield under the 488-nm photoexcitation, and that the energy of the populated at low temperature pair state is lower than the energy of the singlet intrachain exciton level. The detailed mechanism of the spin-dependent recombination responsible for the ESR signals detected is proposed to be as follows. The narrow signal appears due to a microwave-induced resonant transition in triplet polaron pairs. This implies that the resonant transitions change the rate of geminate recombination of the pairs that leads to the formation of triplet intrachain excitons. Those excitons annihilate in the second-order reactions showing themselves as the change of the PL. The annihilation rate was found to be influenced by resonant transitions in triplet exciton pairs as well, resulting in the broad and half-field signals. The lifetime of triplet intrachain excitons was estimated from the modulation frequency dependence as 1.25 ms.

II. EXPERIMENT

PPV is an unmeltable and insoluble polymer and can be processed via a precursor route.[21] Thin films were cast from a methanol solution of the prepolymer by a doctor blade machine. A glass plate of 1 mm thickness and an area of $4 \times 4\ \mathrm{mm}^2$ was used as a substrate. The prepolymer films on the substrates were thermally converted in an oil bath. The use of the oil bath allowed constant temperature conditions over a long time range. Short time temperature variations were of the order 0.1 °C. In normal case the glass container with the substrate was filled with Ar gas under slight overpressure. The oil bath was heated to temperatures between 120 °C and 190 °C. After the heatup phase of about 30 min duration the temperature was kept constant for 2 h. In the last few minutes of cooling down the tube was flooded with nitrogen. After thermal conversion the thickness of the PPV films was about 300 nm.

All experiments presented in this paper were carried out in a homemade spectrometer, which is described elsewhere.[19] The synchronous changes of PL on square-wave amplitude modulated microwaves were measured with a lock-in amplifier. The sign of the measured signal was deduced from the change of the phase angle when sweeping through the resonance. To exclude the artifacts in the line shape due to the passage effects, the magnetic field could be also swept from high to low values of the magnetic field. During the measurements at 1.6 K the samples were immersed in pumped liquid helium in a bath cryostat, whereas at 120 K the temperature was directly measured by a thermocouple mounted near the sample. A second detection channel with a Keithley DMM 199 allowed one to measure the PLDMR spectrum and the PL intensity simultaneously. Both channels were built up symmetrically to ensure that both are measured under exactly the same conditions.

Experiments were performed at an excitation wavelength of $\lambda = 488$ nm from an Ar^+ laser. The laser light was transmitted to the sample via a quartz fiber. The intensity of the light was changed by varying the current and monitored by the intensity of the PL. The latter was checked to be proportional to the light intensity. The absolute value of the intensity was measured by a power meter placed at the same position as the sample. The maximum intensity used was about 2×10^{19} quantum/cm^2 s, an illuminated area was 1 mm^2. The absorption coefficient $\varepsilon = 10^5$ cm^{-1} is used for the estimation of the light absorption rate.

In order to study the kinetics of radiative recombination the frequency resolved spectroscopy method has been applied.[22] In conventional form, frequency-resolved spectroscopy is the phase shift spectroscopy technique in which the phase shift between pulsed microwave power and the resonant change of PL is measured to deduce the time constants of processes contributing to the recombination. By varying the modulation frequency of the microwave power the *in-phase* and *out-of-phase* (quadrature) output signals of the lock-in detector were measured. Considering a sine-shaped modulation of the excitation, $V(t) = V_0\sin(\omega t)$, the time-dependent response of the system is

$$I(t,\tau) = \int_{-\infty}^{t} \tau^{-1}\exp\left[-\frac{t-u}{\tau}\right]V_0\sin(\omega u)\,du$$

$$= \frac{V_0}{1+(\omega t)^2}[\sin(\omega t) - (\omega\tau)\cos(\omega t)]. \qquad (3)$$

Generally, the lock-in output can be written as

$$S(\omega,\tau) = \frac{\omega}{2\pi}\int_0^{2\pi/\omega} I(t,\tau)R(t)\,dt. \qquad (4)$$

In the case of *in-phase* detection, the reference $R(t) = \sin(\omega t)$, and the integration yields

$$\mathrm{Re}S(\omega,\tau) = V_0\frac{1}{1+(\omega t)^2} \qquad (5)$$

for the real part of the signal. For the imaginary part, $R(t) = -\cos(\omega t)$, the lock-in signal is

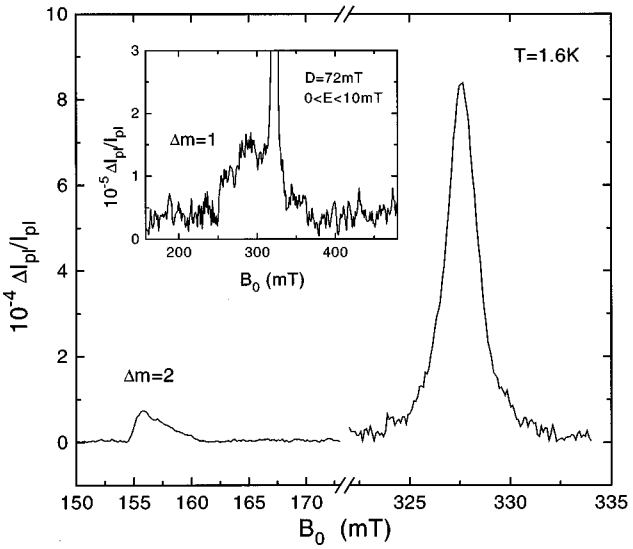

FIG. 1. Magnetic resonance spectrum of PPV, detected by photoluminescence. Three types of resonant signals can be seen: (i) a narrow signal at $g = 2.0$ with a full width at half maximum equal to 1.7 mT, (ii) a triplet powder pattern at $g = 2.0$, and (iii) a triplet signal at a half resonant field, corresponding to $\Delta m_S = \pm 2$ transitions. $T = 1.6$ K; $\lambda_{exc} = 488$ nm; light intensity 10^{19} quantum/cm^2 s; $\lambda_{det} = 568$ nm. The triplet powder spectrum is shown in the inset.

$$\mathrm{Im}S(\omega,\tau) = V_0\frac{\omega\tau}{1+(\omega t)^2}. \qquad (6)$$

The maximum of the imaginary part is reached when $\omega\tau = 1$. Therefore, a measurement of the frequency dependence of the *out-of-phase* signal yields the response time of the system by evaluating the maximum position. Note that because of its high quality factor ($Q_{\mathrm{unload}} \leqslant 10^4$), the *X*-band microwave cavity becomes the most inertial element in the measuring circuit for values of $t \leqslant 2\times10^{-7}$ s.

III. RESULTS

Figure 1 shows the ESR spectrum of a PPV film ($d = 300$ nm) measured via PL intensity at 1.6 K. The PL increases in resonance by the factor of 9×10^{-4}. The full width at half maximum of the signal is about 1.7 mT. This signal is due to the microwave-induced transition within the pair of negative (p^-) and positive (p^+) polarons. It is inhomogeneously broadened, slightly asymmetric, and did not show any saturation effects for the microwave power used in experiment (160 mW).

The PLDMR spectrum displayed in the Fig. 1 contains additional features. The low-field part of the spectrum shows the PL enhancement by a factor of 8×10^{-5} in a field corresponding to the $\Delta m_S = \pm 2$ transition in a triplet exciton. The $\Delta m_S = \pm 2$ triplet ESR can be observed in an assembly of *randomly oriented* molecules, even if the high-frequency field is not parallel to the static magnetic field. The presence of the triplet powder pattern due to $\Delta m_S = \pm 1$ transition is expected too. The inset to Fig. 1 shows a broad asymmetric PLDMR signal that could originate from the $\Delta m_S = \pm 1$ transition in the triplet exciton. It corresponds to an enhancement of the total PL by factor of 1.5×10^{-5}, and was measured by accumulating several records. Similar features were previ-

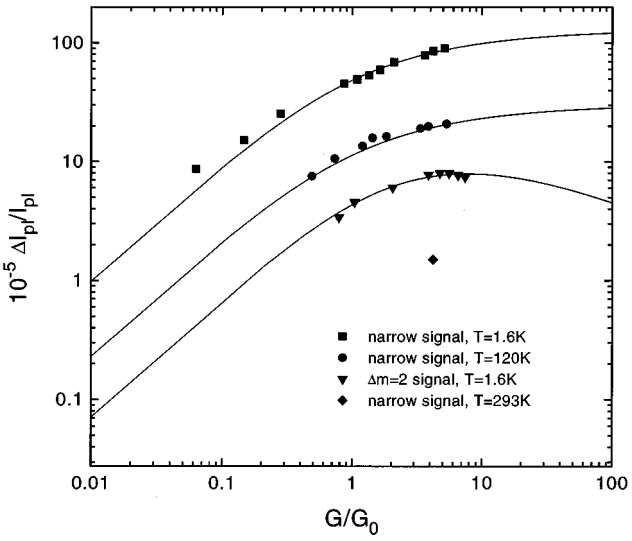

FIG. 2. Dependencies of magnitude of the resonant signals on the intensity G/G_0 of the exciting light. $G_0=2\times10^{23}$ quantum/cm^3 s. The solid lines are the fit by Eqs. (13) and (15), as explained in the text. Only one point is shown for room temperature.

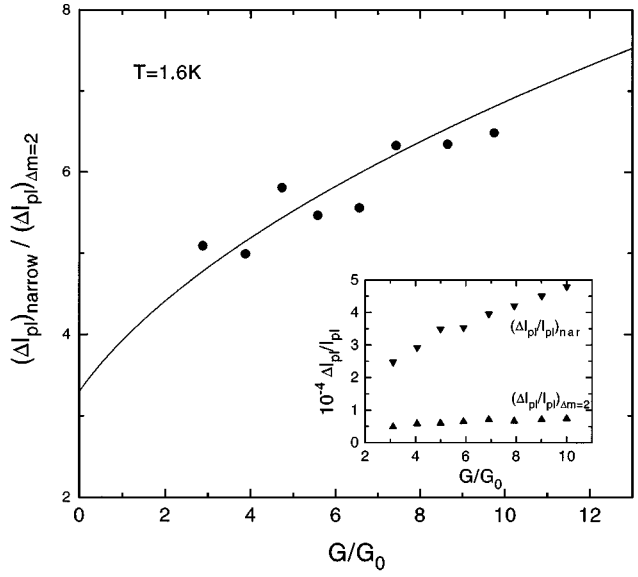

FIG. 3. Demonstration of different dependencies on the light intensity of magnitudes of the narrow signal at $g=2$ and the signal with $\Delta m_S=\pm2$. Solid line is the fit by the Eq. (17). See Discussion for explanation.

ously observed in PPV and other conjugated polymers.[16–18,20]

By varying the excitation intensity the rate of the polaronic pair generation can be varied. All signals were found to be strongly dependent on the intensity of exciting light and on the temperature of the sample. Figure 2 displays relative changes of the PL intensity $\Delta I_{pl}/I_{pl}$ as a function of the excitation intensity G/G_0 ($G_0=2\times10^{23}$ cm^{-3} s^{-1}) for a narrow signal at 1.6 and 120 K, $\Delta m_S=\pm2$ signal at 1.6 K. The value of $\Delta I_{pl}/I_{pl}$ for the narrow signal at room temperature is also shown. Due to the small amplitude of the signal it was not possible to study the excitation dependence on the narrow line at room temperature and on the triplet powder pattern. It is seen that when increasing the light excitation, the intensities of both signals, narrow (squares are measurements at 1.6 K, circles are those at 120 K) and $\Delta m_S=\pm2$ (inverted triangles), increase. Similar dependence for the narrow line in soluble polymer poly-(*p*-phenyl-phenylene-vinylene) was previously observed in Ref. 20 and interpreted as the polaron pair lifetime effect. It is seen that at higher excitation intensities the $\Delta m_S=\pm2$ signal starts to saturate, whereas the narrow signal keeps growing. To check this difference, we carried out the comparative measurements of both signals at the same experimental conditions in the same magnetic field sweep. The experimental points measured at higher excitation intensities are shown in the inset to Fig. 3 (note the linear scale) . The ratio of intensities of narrow and $\Delta m_S=\pm2$ signals is displayed in the Fig. 3. As will be discussed later in this paper, the reason for the above-mentioned saturation of $\Delta m_S=\pm2$ is that the triplet-triplet annihilation tends to become the main decay channel of triplet intrachain excitons at higher generation rate. In this case $n_T\rightarrow\sqrt{G/\gamma}$, and ΔI_{pl} gets proportional to I_{pl}.

By setting the magnetic field onto the resonant position and varying the modulation frequency of microwaves, one can measure the response time of the processes involved. Figure 4 displays the imaginary part (out-of-phase output of the lock-in) of the narrow (filled circles) and $\Delta m_S=\pm2$ (open circles) PLDMR signals in the frequency range from 60 to 6×10^5 rad/s. Both curves show maxima that can be used to determine the time constants of the processes contributing to the PL.

IV. DISCUSSION

A. On the nature of states responsible for resonant signals

The results obtained show for certain that there is a connection between states responsible for magnetic resonant transitions and PL. The first and the most important question is about the nature of those states. The position in the spectrum ($g=2.0$) and the half-width (1.7 mT) of the narrow

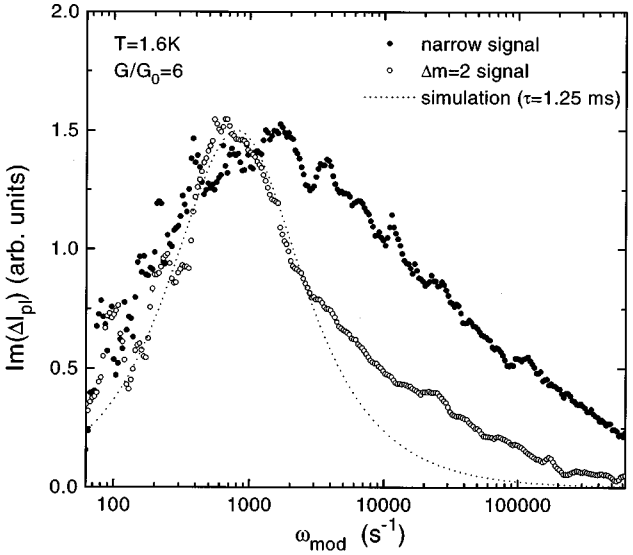

FIG. 4. Dependence of the resonant signals on the frequency of modulation of the microwave power. Dotted line is a simulation by the function Eq. (6) with τ_T = 1.25 ms.

TABLE I. Comparison between the relative changes of the recombination rate of the thermalized polarons $\Delta p_S/p_S$, as calculated by using Eq. (7), and the relative changes of the magnitude of the narrow ODMR signal $\Delta I_{\rm pl}/I_{\rm pl}$ at three temperatures (see Fig. 2).

T (K)	1.6	120	293
$\Delta p_S/p_S$ calc. by Eq. (7)	4.6×10^{-2}	1.3×10^{-5}	2×10^{-6}
$\Delta I_{\rm pl}/I_{\rm pl}$ exper. data	10^{-3}	2×10^{-4}	1.5×10^{-5}

signal correspond to transitions in doublet paramagnetic species, the magnetic sublevels of which are slightly broadened. The straightforward suggestion is about free polarons. However, at least two points are against it. First, free polarons may hardly be created at such a low temperature as 1.6 K, as the Coulomb attraction between them needs to be overcome. Second, even assuming the existence of free polarons, one has to consider their recombination into two channels, singlet and triplet ones, so that the change of the recombination probability due to the microwave-induced change of spin polarization may occur. Free polarons are assumed to be thermalized, and the change Δp_s of the recombination rate p_s into the singlet channel cannot be higher than that given by the formula

$$\frac{\Delta p_s}{p_s}=\left(\frac{1-e^{-g\mu_B B_0/kT}}{1+e^{-g\mu_B B_0/kT}}\right)^2, \tag{7}$$

where g is the g factor, μ_B is the Bohr magneton, and B_0 is the value of static magnetic field in the resonance. $\Delta p_s/p_s$ is the maximum achievable (at complete saturation) relative change of free polaron recombination rate caused by resonant transitions at thermal equilibrium. Its values for three operating temperatures are listed in Table I. The experimental values of the relative magnitudes of the narrow signal $\Delta I_{\rm pl}/I_{\rm pl}$ in the resonance are also shown in the table. Note that $I_{\rm pl}$ is the total PL collected. The relative change of the PL in ESR will become even larger if we take into account that we were working at microwave power of about one order of magnitude below saturation limit, and that only a small part (less than 5% in Ref. 11) of the total PL intensity stems from electronic processes other than prompt radiative decay of singlet intrachain excitons.

In order to overcome this difficulty one must consider polarons belonging to geminate pairs. The underlying mechanism was suggested earlier,[6–13] and consists in the formation of a CT exciton (or lowest state of a polaron pair) as a result of interchain electron transfer from intrachain singlet excitation. CT is possible in conjugated polymers due to the prominent overlap of π-electron clouds of two neighboring polymer chains and may become more pronounced due to the presence of a defect such as a carbonyl group.[23]

Only singlet CT states are populated initially, and only those states were considered in Refs. 8–13. Hyperfine interaction (HFI) of the electron spin with magnetic moments of protons is generally accepted as an effective mechanism of intersystem crossing in polaron pairs.[6,7,14,24] In the absence of exchange interaction between positive and negative parts of the CT exciton, HFI is known to mix all four spin substates of the pair with the frequency corresponding to hyperfine magnetic field, i.e., about 1–2 mT, or 10^9 s^{-1}. In a strong external magnetic field ($B_0 \gg B_{\rm HFI}$), T_{+1} and T_{-1} sublevels become separated from the mixed $S-T_0$ state.

As long as the population of magnetic substates stems from the singlet precursor only (geminate case), the triplet pairs become spin polarized in magnetic field. Such a dynamic polarization makes microwave transitions in triplet pairs very effective. For a detailed description of the mechanisms of spin-dependent processes and their dependence on external magnetic field and microwave resonant transitions in pairs of paramagnetic species in molecular solids see Ref. 24.

B. Kinetic connection between magnetic resonant transitions and luminescence intensity

One can imagine that an interchain CT process that creates the singlet CT exciton is reversible, and a delayed PL may appear due to the electron back transfer from the CT state. It is quite plausible to think so, and the electron back transfer is assumed to be the main step in the EL. However, let us remember the sign of the narrow resonant line in the PLDMR spectrum (see Fig. 1). It is positive, i.e., corresponding to the enhancement of the light intensity. If the PL would originate from the electron back transfer also, the resonant transitions from the more populated T_0 sublevel of the triplet pair (mixed with the S state) can only result in the negative sign of the narrow resonant line. Further, the back transfer is only possible in the case of free ($S-T_0$) mixing, i.e., in the absence of an exchange interaction in the pair. We therefore conclude that the electron back transfer forming the intrachain singlet exciton cannot be the main channel connecting magnetic resonance transitions with PL.

A great help in understanding of the mechanism comes from the observation that the *absolute* magnitude of the narrow line in the PLDMR spectrum, $\Delta I_{\rm pl}$, varies superlinearly with the intensity of the exciting light, and, second, that there are triplet exciton signals at $g=2$ and $\Delta m_S=\pm2$ in the PLDMR spectrum. This permits us to assume that a triplet recombination channel is operative, and triplet intrachain excitons are generated as a result of electron back transfer from triplet CT exciton pair. This is exactly the same process that produces triplet excitations in photosynthetic reaction centers.[25] The formation of triplet intrachain excitons in PPV was observed before in experiments via photoinduced absorption,[25] PLDMR,[16,17,20] and absorption detected ESR (ADMR).[18] These excitons were assumed to be produced by intersystem crossing from singlet intrachain exciton.

But the triplet intrachain excitons cannot affect the PL intensity directly, e.g., because of the energy. We may assume that it is the bimolecular triplet-triplet annihilation process that produces singlet intrachain excitations. Such a process is well known in molecular crystals[27] and can be expressed by the following reaction:

$$T+T \overset{1,3,5}{\rightleftharpoons} (T\ldots T) \overset{k_S}{\rightarrow} {}^1S^*+S_0. \tag{8}$$

An alternative process connecting resonant transitions in triplet pairs with PL intensity could be repopulation of the ground state from higher-lying metastable state. In this case the change of PL intensity will be observed in resonance too.

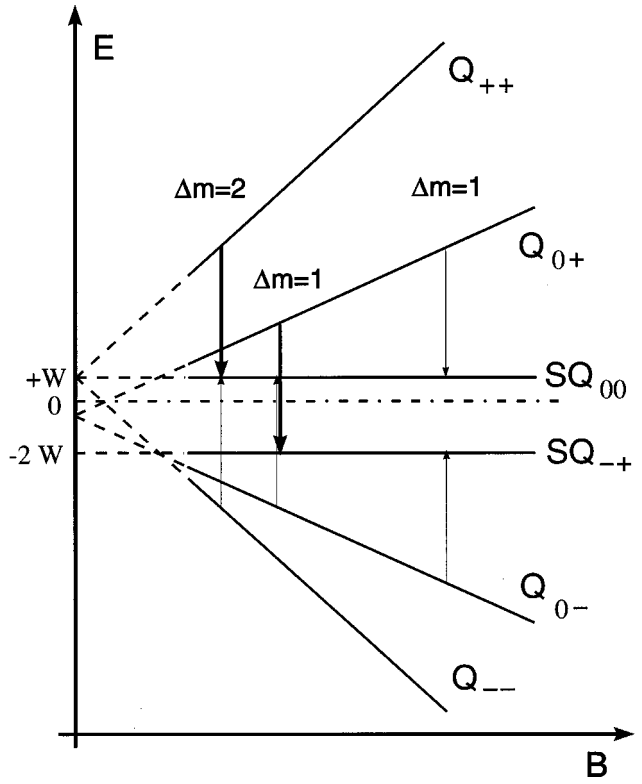

FIG. 5. Scheme of energy sublevels of a two-triplet exciton pair in magnetic field. Arrows show resonant transitions changing the population of singlet-containing central sublevels. Bold arrows correspond to more probable transitions. Only six magnetic sublevels containing quintuplet and singlet spin configurations are shown. Energy W depends on the D and E fine splitting parameters and on the orientation of the triplet axis in the magnetic field.

Let us consider the bimolecular annihilation mechanism first. Triplet-triplet pairs $(T\ldots T)$ [see reaction (8)] are known to be produced as intermediate states in singlet, triplet, and quintuplet magnetic substates, which are mixed with each other. Reactions of triplet excitons are spin dependent and competitive from the point of view of the yield of products with different multiplicity. An important feature of the two-triplet pair is a possibility to change its spin state under the action of external static magnetic field,[28] and of resonant microwave magnetic field.[29]

The structure of magnetic energy sublevels of the two-triplet pair in a strong magnetic field is shown in Fig. 5. Only six singlets and quintuplets containing levels are shown. The eigenstates of T-T pairs are obtained by the linear combination of the energies of the corresponding triplet eigenstates constituting the pair. For a pair of equivalent triplet excitons in a strong external magnetic field, i.e., $B_0 \gg D,E$, where D and E are fine splitting parameters, two out of nine spin sublevels will contain a singlet component. Those are levels $|00\rangle$ and $|+-\rangle$. The singlet components are mixed with quintuplet components. Upon exposure to a resonant microwave field, transitions that involve a change in the projection of the magnetic quantum number m_S by ± 1, and even ± 2 are possible. Transition from more populated quintuplet sublevels to singlet-containing sublevels of the pair will increase the rate k_S, at which singlet intrachain excitons are produced [see reaction (8)].

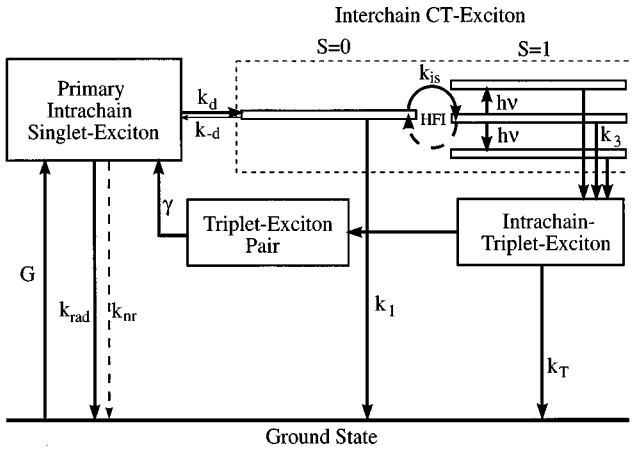

FIG. 6. Scheme of the processes participating in the PLDMR. k_d is a rate constant of interchain CT exciton formation from intrachain singlet excitons; k_{-d} is an electron back transfer rate constant into the singlet excited state; $k_{\rm rad}$ and $k_{\rm nr}$ are rate constants for radiative and nonradiative transitions; k_1 and k_3 are electron back transfer rate constants into the ground state; $k_{\rm is}$ is an intersystem crossing rate constant; HFI means the hyperfine interaction; k_T is a rate constant of the triplet monomolecular decay. Resonant transitions in triplet CT excitons are shown by arrows $h\nu$. Transitions in the two-triplet pair are shown in Fig. 5.

A rough estimation of the increase of the annihilation rate constant γ can be done by the next formula derived in Ref. 29:

$$\frac{\Delta\gamma}{\gamma} \approx \left(\frac{g\mu_B H_1}{\hbar}\tau\right)^2, \tag{9}$$

where H_1 is a microwave magnetic field strength, and τ is a lifetime of a two-triplet pair. Thus, one can expect for $H_1 = 0.1$ mT (in the rotating frame) and $\tau = 10^{-9}$ s $\Delta\gamma/\gamma \approx 4\times 10^{-4}$. The order of the magnitude of the latter value is typical for the magnitude of PLDMR signals observed in experiments.

We therefore suggest that the change of the PL may appear as a result of triplet-triplet annihilation, and the triplet powder spectrum of the positive sign is a result of resonant transitions within T-T pairs. Such transitions increase the rate of T-T annihilation with the formation of more singlet products. The scheme of the above processes is shown in Fig. 6.

At high enough intensity of the excited light, when a prominent part of the molecules in the ground state is converted into excitation products, any changes of the population of the latter can influence the intensity of the PL. As we show in the next section, the dependencies of the PL intensity and relative change of the PL in ESR on the intensity of the exciting light are different for different mechanisms.

C. Dependence of the magnitude of resonant signals on the light intensity

If one approves that T-T annihilation is the main bridge connecting CT pairs and radiative singlet excitons, then the origin of the dependence of the magnitude of the resonant signal on the intensity of the exciting light (Fig. 2) becomes clear.

Let p_3 be the recombination rate of triplet polaron pairs. Then steady-state density of triplet intrachain excitons n_T can be calculated from the equation

$$\frac{dn_T}{dt}=p_3-k_T n_T-\gamma {n_T}^2=0 \tag{10}$$

as

$$n_T=\frac{k_T}{2\gamma}\left(\sqrt{1+4\frac{\gamma}{{k_T}^2}p_3}-1\right), \tag{11}$$

where γ is the T-T annihilation rate constant, and k_T is the rate constant for monomolecular decay of triplet excitons; the triplet polaron pair recombination rate is $p_3=G\phi_T$, here G is the rate of primary excitation generation, and ϕ_T is the quantum yield of triplet intrachain excitons in the recombination processes. The delayed PL intensity per unit volume is

$$(I_{\rm pl})_d\propto\frac{\phi_{\rm pl}}{9}\gamma {n_T}^2=\frac{\phi_{\rm pl}}{36}\frac{{k_T}^2}{\gamma}\left(\sqrt{1+4\frac{\gamma}{{k_T}^2}p_3}-1\right)^2, \tag{12}$$

where $\phi_{\rm pl}$ is a quantum yield of the PL. Magnetic resonant transitions cause changes $\Delta p_3 \ll p_3$ of the recombination rate of polaron pairs. Corresponding changes $(\Delta I_{\rm pl})_{\rm nar}$ of the luminescence intensity at the narrow signal resonance at $g=2.0$ may be calculated by differentiating Eq. (12) by p_3:

$$\frac{(\Delta I_{\rm pl})_{\rm nar}}{I_{\rm pl}}=AP_{\mu\omega}\left(1-\frac{1}{\sqrt{1+4(\gamma/{k_T}^2)p_3}}\right)=AP_{\mu\omega}\frac{x-1}{x}. \tag{13}$$

Here $P_{\mu\omega}\propto H_1^2$ is the microwave power in the cavity; $P_{\mu\omega}G\propto\Delta p_3$, where G is the exciting light absorption rate that is proportional to the light intensity and to the PL intensity; $x=\sqrt{1+4(\gamma/{k_T}^2)p_3}$; a coefficient A depends on the rate constants governing generation and recombination of polaron pairs. Using definitions shown in Fig. 6 one can obtain

$$A\propto\frac{k_d}{(k_{\rm rad}+k_{\rm nrad})(k_1+k_3+k_{-d})+k_d(k_1+k_3)}. \tag{14}$$

Corresponding formulas for the magnitudes of the triplet powder signal at $g=2$ and the signal at the half field ($\Delta m_S=\pm 2$) can be obtained by differentiating Eq. (12) by γ:

$$\frac{(\Delta I_{\rm pl})_{\rm pow}}{I_{\rm pl}}\propto\frac{x-1}{x(x+1)}. \tag{15}$$

Equations (13) and (15) predict different dependencies of the relative magnitudes of narrow and broad (powder pattern) signals on the light intensity, their ratio being equal to

$$\frac{(\Delta I_{\rm pl})_{\rm nar}}{(\Delta I_{\rm pl})_{\rm pow}}=x+1=\sqrt{1+4\frac{\gamma}{{k_T}^2}p_3}+1. \tag{16}$$

A comparison of calculated and experimental dependencies of the relative magnitudes of the narrow signal at $g=2.0$ and the triplet signal $\Delta m_S=\pm 2$ on the intensity of the exciting light is shown in Fig. 2. Experimental points were fitted by Eqs. (13) and (15), respectively. The fitting parameter was $B=4(\gamma/{k_T}^2)\phi_T G_0$ (ϕ_T is the quantum yield of triplet excitons formed in the recombination process). The best fit can be done with $B=1.5$ for the narrow signal, and $B=0.62$ for the signal with $\Delta m_S=\pm 2$. As can be seen from Fig. 2, both dependencies on the excitation intensity, for the narrow signal at $g=2$ and for $\Delta m_S=\pm 2$ signal, are different.

If the ground-state recovery mechanism is operative, one can show[30] that $\Delta I_{\rm pl}/I_{\rm pl}$ in ESR is proportional to $I_{\rm pl}$ at any intensity of excitation. That seems to be a general feature of the ground-state recovery mechanism. However, the experiment (see Fig. 2) demonstrates that $\Delta I_{\rm pl}/I_{\rm pl}$ saturates in conditions when the $I_{\rm pl}$ remains directly proportional to the excitation intensity.

A critical test of our model was done by measuring the magnitudes of the narrow and $\Delta m_S=\pm 2$ signals in the same magnetic field sweep at different exciting light intensities. The ratio of both intensities is shown in Fig. 3. The solid line is the fit by the function

$$\frac{\Delta I_{\rm pl}}{I_{\rm pl}}=a\left(1+\sqrt{1+B\frac{G}{G_0}}\right), \tag{17}$$

with $a=1.65$, $B=0.9$. The fit parameter B is not much different from values obtained from Fig. 2.

The mechanism of enhancement of triplet intrachain exciton formation caused by resonant transitions in polaron pairs should be discussed in more detail. To be effective the transitions should occur in triplet polaron pairs that are dynamically polarized in the process of their formation. As is known from MFSE experiments, the triplet polaron pairs may become polarized as a result of mixing of S and T_0 substates of the pairs by the HFI, if the generation of pairs originates from the singlet precursor.[7,24] Whether these substates in the bound polaron pairs remain mixed at low temperatures is questionable. The mixing of the substates (but not the formation of triplet pairs) will be hindered if the exchange interaction is strong enough in the pairs (stronger than the energetic width of sublevels), i.e., if polarons in the pair are localized on neighboring polymeric chains. Two alternative situations may be considered. First, the exchange interaction is small, and $S-T_0$ substates are mixed. Then the resonant transitions from the mixed $S-T_0$ state to empty $T_{\pm 1}$ sublevels open a new path of recombination of the pairs, which produces triplet intrachain excitons; the path is competitive with that via the singlet channel, and resonant transitions increase the rate p_3. In the second situation, the exchange interaction is strong enough and results in a gap between S and T_0. All triplet pairs formed recombine via the triplet channel, and resonant transitions between triplet sublevels do not change the rate p_3, since there is no competition with that recombination path. However, even in this case the triplet exciton density can be modulated by microwave transitions in the triplet polaron pairs. It will be the case if polaron pair recombination rates into $T_{\pm}$ and T_0 sublevels of triplet intrachain excitons are different, e.g., due to different monomolecular decay rates of the latter. Effectively the second case means that monomolecular decay rate constant k_T is modulated by microwaves. One can calculate the de-

pendence of the magnitude of the narrow signal on the intensity of the light, if k_T was modulated. By differentiating Eq. (12) by k_T one obtains

$$\frac{(\Delta I_{\rm pl})^{k_T}_{\rm nar}}{I_{\rm pl}} \propto \frac{x-1}{x(x+1)}. \tag{18}$$

The result is the same as that obtained for the intensity dependence of broad signals [see Eq. (15)]. Figure 2 (filled squares) demonstrates, however, a different behavior of the narrow PLDMR line. Therefore we interpret the latter as the modulation of the triplet exciton density due to microwave-induced changes of p_3. As follows from the experiment, the triplet-triplet annihilation prevails over the back transfer of an electron into the radiative singlet state (k_{-d} process) at all excitation intensities used in experiment, i.e., from 10^{22} to 10^{24} cm^{-3} s^{-1}, and temperatures from 1.6 to 120 K. It prevailed also at room temperature at the highest intensity of the exciting light.

D. Dependence of the resonant signals on the frequency of microwave power modulation

At this point we accept that the connection between processes within polaron pairs and emission of the delayed PL goes via triplet excitons formation. If so, the frequency dependence of PLDMR signals can give information about the lifetime of triplet excitons, as most long living species among intermediate excited states. One possibility is to modulate the triplet exciton formation rate p_3, which shows itself in the appearance of the narrow resonant signal at $g=2.0$. The modulated density of the triplet exciton will be described by the equation

$$\frac{dn_T}{dt} = p_3[1+\sin(\omega t)] - k_T n_T - \gamma {n_T}^2. \tag{19}$$

The solution is known at low density of excitons: the amplitude of the modulated part of triplet exciton density varies with the frequency ω in accordance with Eqs. (5) and (6). Another way is to modulate parameter γ. The triplet powder signal at $g=2.0$ and the signal with $\Delta m_S = \pm 2$ are expected to have a frequency dependence different from that of the narrow signal. Note that we measure not the triplet exciton density but the delayed PL, which is proportional to $(n_T)^2$. This means that all the times measured are one-half of the real lifetimes. Figure 4 shows that processes really involve an inertial part, which may be assumed to be triplet excitons with the lifetime distributed around the value of $\tau_T = 1.25$ ms. This value is typical for triplet excitons in PPV samples, measured by photoinduced triplet-triplet absorption.[26] But the τ_T obtained is shorter than the reciprocal monomolecular decay rate constant of triplet excitons k_T. This is because of the *T*-*T* annihilation process. Nevertheless, it is possible to estimate the constant k_T from the measured lifetime of triplet excitons by using the formula that gives the connection between them:

$$k_T = \frac{(1/\tau_T)_{\rm expt}}{1+\sqrt{1+[B(G/G_0)]_{\rm expt}}}. \tag{20}$$

The factor 2 mentioned above is taken into account here.

B is the parameter determined from the dependence of the intensity of narrow signal on the exciting light intensity, G/G_0 is the rate of excitation measured in relative units used in Figs. 2 and 3: $B=0.9$, $G/G_0=6$, $(1/t_T)_{\rm expt} = 8\times 10^2$ s^{-1}. Using the correction gives the next value for monomolecular decay rate constant: $k_T = 2.2\times 10^2$ s^{-1}.

The values of parameters B and k_T can be used for estimation of the product $\gamma\phi_T$. The quantum yield of polaron pairs in PPV was estimated from transient absorption measurements[10] as 0.9. It gives grounds for speculating that the yield of triplet excitons of recombination origin is also high enough. For estimations we put it equal to $\phi_T = 0.1$ (within an order of magnitude), and then one may obtain a rough estimation of the value of the annihilation rate constant:

$$\gamma = \frac{[B(G/G_0)]_{\rm expt}}{4\phi_T G} {k_T}^2 = \frac{10(2.2\times 10^2)^2}{4\times 0.1\times 2\times 10^{24}}$$

$$\approx 6\times 10^{-19}\ {\rm cm}^3\,{\rm s}^{-1}.$$

It corresponds to the diffusion coefficient D of triplet excitons, estimated from

$$D = \frac{\gamma}{4\pi R} = \frac{6\times 10^{-19}}{4\pi 10^{-7}} \approx 5\times 10^{-13}\ {\rm cm}^2\,{\rm s}^{-1}.$$

The size of the exciton was chosen arbitrarily as $R = 10^{-9}$ m.

Exciton hopping frequency ν may be estimated as

$$\nu = \frac{\gamma}{4\pi R^3} \approx \frac{6\times 10^{-19}}{4\pi 10^{-21}} \approx 50\ {\rm s}^{-1}.$$

All the estimations made, though being within an order of magnitude accuracy, show that triplet intrachain excitons are rather immovable species, their lifetime being comparable with reciprocal hopping frequency. This means that the annihilation occurs under formation of two excitons on the next neighbor or nearby lying chain segments, i.e., at high excitation levels.

The dependence of the magnitude of $\Delta m_S = \pm 2$ signal on the frequency of microwave power modulation (Fig. 4, open circles), though being also indicative on the role of long living species, cannot be described by Eq. (19). We speculate that the deviation is a sequence of modulation of γ rather than of the rate of formation. However, a fast response is expected as long as the change of γ is inertialess. The slow response observed may originate from delayed changes of density of triplet excitons caused by a changed value of γ.

Thus the experiment discussed above shows unambiguously that there exists an inertial step between resonant transitions in polaron pairs and the light emission. This would not be the case in the model describing the emission as originating directly from the recombination of polarons as assumed in Refs. 16, 17, and 19.

E. On the polarization of triplet excitons and temperature dependence of PLDMR

Triplet intrachain excitons that show themselves as a broad powder signal around $g=2$ (see inset to Fig. 1) seem to have a nonequal steady-state population of magnetic sublevels. It follows from a nonsymmetrical shape of the signal

with respect to the narrow line at $g=2$: the right part of the signal is less intensive than the left one. Energy sublevels of two-triplet exciton pairs, shown in Fig. 5, are populated at collisions of triplet excitons. On the other hand, we know that the intrachain singlet excitons can only be formed from states corresponding to sublevels $|+-\rangle$ and $|00\rangle$, which are the mixtures of quintuplet and singlet states. The resonant microwave transitions shown in Fig. 5 will increase the population of singlet-containing levels. We therefore suggest that the powder pattern asymmetry is a consequence of the higher population of the T_{+1} sublevel of triplet excitons as compared to the T_0 and T_{-1}. Moreover, the different populations of T_{+1} and T_{-1} sublevels are necessary for making transitions $\Delta m_S=\pm 2$ effective in the resonant enhancement of PL intensity. Bold arrows are used in Fig. 5 to show the most probable resonant transitions.

However, the origin of polarization of triplet excitons is not quite clear at the moment. Three possible reasons may be considered: (i) nonequal rates of population in the polaron recombination process, (ii) different monomolecular decay rates for different magnetic sublevels of the triplet exciton, with the lowest rate for $m=+1$ sublevel, and (iii) dynamic polarization in the T-T annihilation process. The second reason seems to be more probable.

The temperature dependence of the resonant signals is of importance. The magnitudes of all three resonance signals are increasing at lower temperature by about two orders of magnitude when cooling down from 300 K to 1.6 K. The factor A in Eq. (13) seems to be responsible for the increase. This may be due to a decrease of rate constants k_1 and k_3, or to longer lifetime of polaron pairs at low temperature.

F. Remarks on other spin-dependent recombination models and experiments

A comparison of the PLDMR results with the picture of spin-dependent processes developed on the basis of the MFSE on photoconductivity[7] has to be made. At higher temperatures polaron pairs are not confined in their lowest-energy state and spin evolution within distant polaron pairs becomes possible. Further, the experiments were performed at much lower excitation intensities than in our experiments. In the absence of triplet-triplet annihilation, the only connection of polaron pair states with singlet excitons will be a back transfer of the electron into the singlet pair state. It is a thermally activated process, but it may be assumed to be fast enough for higher-lying CT states, populated at higher temperatures. Hence, one would expect a negative PLDMR signal at room temperature and at low excitation intensities. This was not observed in experiment because of the sensitivity, however, the sign inversion is expected by us.

Additional experimental data permitted us to describe PLDMR results with a model, the most important part of which is the interchain geminate polaron pair. Differences from the previous model[16,17,19] concern the origin of the narrow signal at $g=2.0$. It was assumed as being due to resonant transitions in polarons taking part ''in intrachain distant pair polaron recombination,'' the latter giving the excited intrachain singlet state, which emits the light. The detailed mechanism, however, remains unclear. If geminate pairs are considered, i.e., the T_0 sublevel is more populated because of the singlet precursor, then resonant transitions will produce a decrease of the singlet exciton production. The experiment shows, however, an increase of the PL intensity. In the nongeminate case, when pairs are formed from free polarons with noncorrelated spins, the sign of the PLDMR will depend on the relation between rates k_1 and k_3 (see Fig. 6). An increase of the PL intensity in ESR will occur only at $k_3<k_1$. However, as shown in Ref. 7, $k_3>k_1$. Furthermore, this case is not consistent with the inertial nature of the narrow signal, showing that the long-living states are involved.

The inconsistency of the ''free-polaron fusion'' model supports the recent paper by Graupner *et al.*[31] too. Instead, authors describe PLDMR data in a model[32] in which the interchain (or interconjugation segment-) trapped polaron pair acts as a singlet exciton quenching center and, as a consequence, is responsible for the appearance of the enhancing narrow PLDMR signal in PPP-type ladder polymers.

The model is aimed at resolving the contradiction between two observations: the emission from PPV's at $\tau > 50$ ns at 300 K is small,[11] whereas ''the lifetime of the antiparallel spin polaron pairs responsible for the resonance is longer than 10 μs'' (see Ref. 31 and references therein). The former observation concerns the ns-range component of the PL from ''interchain excitons which reform intrachain excitons.''[11] Our experiments demonstrate that energy levels of the pair state populated at low temperatures are situated below the level of the singlet intrachain exciton (no electron back transfer), hence, the radiative path should include T-T annihilation. (Note that the sign of the PLDMR is not sensitive to the relation between k_3 and k_1.)

The model we describe here is based on the assumption of the existence of a delayed component in the PL. However, to our knowledge, there are no data in the literature on any significant emission in PPV's in the μs–ms range. This is not surprising, since the PL component originated from the T-T annihilation process can hardly be expected in time-resolved experiments because of the very small γ, as estimated by us. It is about eight orders of magnitude smaller than that in molecular crystals. Hence, for bimolecular annihilation to occur, triplet excitons should be accumulated to high density, as achieved at high intensity cw excitation, which seems to be not the case when using the very short exciting light pulses in conventional time-resolved spectroscopy. We therefore believe that it is our results that show the very existence of magnetosensitive delayed fluorescence in the ms time domain at 1.6 K. The time scale of the underlying process follows from the frequency dependence of the ODMR signal measured via fluorescence (see also Ref. 31), and we have evidence that the signal is of bimolecular annihilation nature. Nevertheless, we believe that the applicability of the model presented has to be proved experimentally on every particular polymer, and the excitation dependence of the PLDMR signal is of extreme importance.

The source of triplet excitons was assumed in Refs. 16–20,26 to be an intersystem crossing from singlet intrachain excitons due to spin-orbit coupling. In the above discussion we did not take into account the generation of intrachain triplet excitons via intersystem crossing. This does not mean that this process is absent in PPV at all. In this work we found that at the excitation intensities and temperatures used, triplet excitons can be very effectively produced via recom-

bination of geminate polaron pairs. It is not only the case at low temperature, where the rate of intersystem crossing can be small due to an activation energy involved, as it is the case in anthracene crystals, but even at room temperature the generation of triplet excitons in PPV occurs via charge-transfer states, as it follows from the very existence of the narrow PLDMR line.

The enhancement of the PL intensity due to the microwave-induced increase of the triplet-triplet annihilation rate means that the density of triplet excitons will decrease. Indeed, as follows from differentiation of Eq. (11) by γ, a change of the triplet density Δn_T caused by a positive increase of $\Delta\gamma$ is negative. It is a direct consequence of a higher annihilation rate at the same generation rate of triplet intrachain excitons. A negative change of the triplet exciton density Δn_T in PPV at 1.36 eV, as detected in the ADMR experiment by Wei *et al.*,[18] Vardeny and Wei,[32] and identified as $\Delta m_S = \pm 2$ transitions in triplet species, can be of the origin discussed above. On the other hand, the resonant transitions in triplet polaron pairs increasing the PL intensity (narrow line in PLDMR spectrum), can lead, generally speaking, either to an increase, or to a decrease of the total density of triplet excitons produced. The sign of the ESR effect on the triplet-triplet absorption depends on rate constants governing the radiative and nonradiative paths of recombination of the triplet excitons. The general idea is worth explaining for the simple case of a two-state model.

Let the first state with radiative rate constant k_r be populated at the rate P_1. This state might be, for example, the singlet-containing level of the T-T pair (see Fig. 5). The second state, which is nonradiative with the rate constant $k_{\rm nr}$, is populated at the rate P_2. Initial total population of both states is

$$N_0 = \frac{P_1}{k_r} + \frac{P_2}{k_{\rm nr}}.$$

The resonant change of P_1 on ΔP at the expense of P_2 will lead to a change $\Delta N = N - N_0$. It is easy to see that

$$\Delta N < 0 \quad \text{for} \quad k_r > k_{\rm nr} \quad \text{and} \quad \Delta N > 0 \quad \text{for} \quad k_r < k_{\rm nr}.$$

Therefore the PLDMR results are consistent with any sign of the narrow line in the ADMR spectrum. Furthermore, a direct comparison of the PLDMR and ADMR spectra would help to bring about a deeper understanding of the mechanism of energy transformation in conducting polymers.

V. CONCLUSION

The results obtained permitted us to conclude that Coulomb bound polaron pairs are produced with a high yield under the 488-nm photoexcitation of PPV. Energy levels of the pair state populated at low temperatures are situated below the level of singlet intrachain exciton. Therefore, no electron back transfer producing an excited intrachain singlet state was observed. The results imply that the singlet exciton has a binding energy that is less than $k_B T$ not with respect to the single particle continuum, but with respect to CT exciton state. We conclude that triplet excitons are produced mainly by recombination of geminate polaron pairs. Triplet polaron pairs show themselves as a narrow resonant signal at $g = 2$. The resonant transitions change the recombination rate of triplet pairs and lead to the formation of triplet intrachain excitons. Those excitons annihilate in the second-order reaction showing themselves as the change of the PL. The annihilation rate was found to be influenced by resonant transitions in triplet exciton pairs as well. Lifetime and monomolecular decay rate constant of triplet intrachain excitons were measured by the modulation frequency dependence. Our results show that the energy level of the lowest polaron pair state can act as a sink of the excitation energy influencing the quantum yields of the PL, EL, and photoconductivity.

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