

On the role played by polaron pairs in photophysical processes in semiconducting polymers

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Abstract

In this contribution, we consider the main manifestations of polaron pairs in: (i) Generation of the free charge carriers; (ii) delayed luminescence; (iii) intra-chain triplet exciton generation; (iv) recombination of free charge carriers; (v) persistence of the photoconductivity; (vi) displacement current in the transient photoconductivity experiments; (vii) spin-dependent reactions. New results on the photoluminescence of films of poly(*p*-phenylene vinylene) (PPV), and changes of its intensity under conditions of electron spin resonance as a function of temperature and light intensity are described. Models describing the connection between the resonant transitions and changes of experimentally measured parameters are discussed. These models are: The fluorescence quenching, ground state repopulation, free-polaron fusion, triplet exciton annihilation. Experimental results permitted to conclude that Coulomb bound polaron pairs are produced in PPV under photoexcitation. Microwave induced resonant transitions in triplet polaron pairs change the rate of formation of triplet intra-chain excitons at geminate recombination of these pairs. Those excitons annihilate in the second order reaction and show themselves in the intensity of the photoluminescence. The mechanism suggested was checked on PPV samples converted from the precursor polymer at different temperatures. Results showed that energy levels of the lowest polaron pair state in PPV, situated below that of singlet intra-chain exciton can act as a sink for the excitation energy influencing the quantum yields of the photoluminescence, electroluminescence and photoconductivity. © 1998 Elsevier Science B.V.

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1. Introduction

Polaron pairs in conjugated polymers are considered as an important intermediate state in the photophysical processes initiated by absorption of the light or by injection and recombination of free charge carriers.

1.1. Definition of polaron pair state

Polaron pairs are intermediate states between electronic molecular excitation and free charge carriers. They are formed inevitably at excitation of photoconductivity of polymers and other molecular solids as well as at combination of free charge carriers of different signs injected into the polymer. In the present paper, we discuss the main manifestations of pairs of polarons of opposite signs in non-equi-

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librium electronic processes which occur in the conjugated polymers with non-degenerate ground state.

Due to their key role in the processes of the electronic energy transformation in semiconductors, their properties have to be taken into account when describing the most of the photo- and electrophysics related parameters of the polymers.

According to present state of knowledge the photoexcitation of conjugated polymers generates intra-chain singlet excitons. Radiative decay of the excitons results in fluorescence (for poly(*p*-phenylene vinylene) (PPV) 0–0-transition being localized at 2.37 eV [1,2]). Alternatively, primary singlet excitations can produce triplet intra-chain excitons by intersystem crossing, or transfer an electron to the neighbouring chain or to the next conjugated segment of the same chain. The latter process forms charge-transfer (CT) inter-chain or inter-conjugation excitons, or polaron pairs. From next-neighbouring-chain sites, movable polarons can hop to further chain sites still belonging to the pair which is now called distant polaron pair. Distant polaron pair conserves the main property of the pair, to have recombination rate within the pair competing with the dissociation. Interplay between recombination and dissociation determines the life time of the pair. In simple monomolecular model, which is valid under Coulomb interaction within the pair, the pair can be treated as a quasi-particle with the life time τ_{pair} :

$$\tau_{\text{pair}}^{-1} = k_{\text{rec}} + k_{\text{diss}} \quad (1)$$

Hypothesis about the polaron pairs in conjugated polymers was suggested firstly on the basis of observation of magnetic field spin effect (MFSE) on the photoconductivity of polydiacetylene [3] and poly(arylene vinylene)s [4]. Authors [3,4] came to the conclusion that polaron pairs could be of two types, one as inter-chain CT-excitons, and second, as distant polaron pairs bound by Coulomb attraction and recombined geminately. The role of such states in the photoconductivity of PPV was considered in [5], too. In the works [6,7], a photoinduced absorption caused by polaron pairs was observed. A delayed fluorescence of PPV in the time domain of 50 ns has been seen in [8], speculated as being due to electron back transfer into polaron pairs. Energy levels of polaron pairs were calculated in [9,10]

being in accordance with transient absorption measurements.

1.2. Photogeneration of free charge carriers

The primary response of the molecular solids on a photoexcitation consists in the appearance of the electronic excited states. As a rule, they are delocalised over a conjugated segment of the polymer chain. As far as there is an overlap of the electron clouds of neighbour molecules having different donor–acceptor properties, the separation of the charges takes place, and inter-chain polaron pair (or CT–exciton) is formed. In such a pair, both Coulomb and a small exchange interactions coexist. The probability of dissociation of such a pair is usually small, that results in a low yield of free charge carriers. The yield can be significantly improved by applying of an electric field. High increase of the yield of free carriers is known to be achieved by doping of the polymer by electron acceptor molecules. Addition of C₆₀ molecules to PPV leads to quenching of the fluorescence of the polymer and to appearance of high photoconductivity [11,12]. Even higher increase of the photoconductivity can be achieved by adding molecular oxygen to the polymer [13], though photochemical reactions with O₂ destroy the material soon. These facts may be described as superfast formation of pairs of the (D⁺ ... A⁻)-type which have a high rate of dissociation and small rate of recombination. Formation of (Polaron⁺ ... C₆₀⁻)-pairs was evidenced by the observation of sensitivity of photoinduced absorption of light to magnetic resonant transitions [14]. Such a sensitivity can be expected only due to existence of dynamically polarised polaron pairs.

1.3. Pairs formed at the combination of free charge carriers

Formation of polaron pairs at combination of free charge carriers may be speculated as an approach to account for the so called persistent photoconductivity in PPV doped by electron acceptor molecules. The persistence was assumed in [15] to be connected with bipolarons.

It is known that a direct recombination of polarons in molecular solids depends on the polaron mobility μ , and is expected to occur with the rate constant

$$k_{0\text{rec}} = \frac{4\pi e}{c} \mu \quad (2)$$

At the mobility $\mu = 10^{-4} \text{ cm}^2/\text{V s}$ and dielectric constant $\epsilon = 6$, formula (2) gives $k_{0\text{rec}} = 3 \times 10^{-12} \text{ cm}^3/\text{s}$, i.e. fairly high. Taking the dissociation of the pair into account, we obtain the smaller value of k_{rec} :

$$k_{\text{rec}} = Ak_{0\text{rec}}, \text{ where } A = \frac{k_1 + 3k_3}{4k_{-1} + k_1 + 3k_3} \quad (3)$$

k_{-1} is the pair dissociation rate constant, and k_1 and k_3 are pair recombination rate constants into singlet and triplet channels, respectively. A much lower recombination rate is expected at $k_{-1} \gg k_1$ and k_3 . The question about the nature of slow recombination of charges within the pair for the case of an electron localised on an acceptor molecule remains open.

1.4. Polaron pairs as a source of delayed fluorescence

Recombination of polarons inside a polaron pair can result in formation of intra-chain electronically excited states. The requirements are a suitable energy position and conservation of the spin. If the electron in the pair is localised on acceptor molecule, the energy level of the pair is lower than that of intra-chain singlet exciton, and only non-radiative decay of singlet state of the pair is possible. A delayed fluorescence of PPV in the time domain of 50 ns has been observed in [8], accounted for as due to electron back transfer in polaron pairs. MFSE on the photoluminescence (PL) was observed in [16] and explained as originated from spin-dependent recombination in polaron pairs. Energy level of a polaron pair lies in most cases higher than that of the triplet intra-chain exciton, and their formation is allowed.

The present work deals with delayed fluorescence connected with recombination of triplet polaron pairs, formation of intra-chain triplet excitons and their annihilation.

1.5. Polarisation of polaron pairs in an external electric field

In experiments on excitation of transient photoconductivity by pico-to-nanosecond light pulses, polaron pairs are expected to show themselves as an appearance of the electric current due to electric polarisation of the pairs (displacement current). Though the polarisation of polaron pairs formed in electric field proceeds extremely fast (about 10^{-14} s), electric response will be delayed by RC time of the electric circuit. The response is expected to look very similar to that induced by a drift of the free charge carrier with the lifetime $\tau \approx RC$, and values of the total charge Q transferred into the external circuit due to these two kinds of species can be comparable:

$$Q_{\text{pair}} = \frac{\alpha V}{d^2} N_{\text{pair}} \quad (4)$$

for N_{pair} pairs with the polarisability α ,

$$Q_{\text{free}} = \frac{e\mu\tau V}{d^2} N_{\text{free}} \quad (5)$$

for N_{free} free carriers with the mobility μ and the life time before trapping τ ; V is the voltage applied, and d is the gap between electrodes of the sample. Polarisability α of polaron pairs in conjugated polymers is expected to be high due to the possibility to shift the electron density along the conjugated part of the polymer chain. Estimation for α can be made by using the formula:

$$\alpha \approx \frac{1}{30} L^2 \frac{e^2}{E_c} \quad (6)$$

where L is conjugation length, and E_c is the energy of an excess electron on the polymer chain. If a conjugated segment of polymer is treated as a potential box of the length L , then

$$E_c = \frac{h^2}{8mL^2} \quad (7)$$

and at $L = 50 \text{ \AA}$, the polarisability α along the chain direction can be as high as 10^{-20} cm^3 .

One can expect that the signal caused by the polarisation will not depend on the temperature and will depend on the light intensity and the electric field strength linearly. Photocurrent signals with such

properties were observed in works [17,18], though described as originated from free charge carriers produced by inter-band light absorption. Further studies are necessary in order to find out their nature unambiguously.

1.6. Magnetic field spin effect on polaron pairs

The effect takes place when the life time of the pairs is shorter than spin-lattice relaxation time T_1 (T_1 is about 10^{-7} s for molecular solids). Under this condition, the motion or evolution of spin of the pair depends on the magnetic fields only, and is not subjected to the thermal energy fluctuations of the lattice. A scheme of energy levels of a polaron pair in a magnetic field and main processes within pairs are shown in Fig. 1. Pairs are produced from their precursors in the pure singlet state. But during their life time spins evolve, and in zero external magnetic field all four spin states of the pair (one singlet and three triplets) become populated. Spin evolution takes

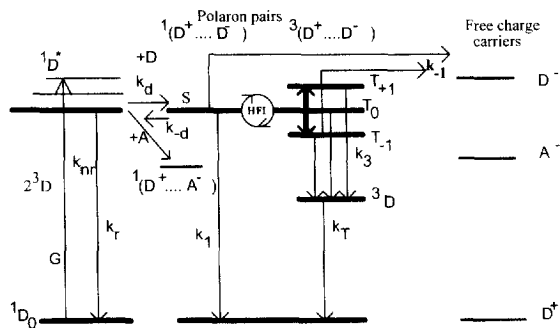


Fig. 1. Scheme of the processes responsible for the MFSE and PLDMR. G is an excitation rate, k_d is a rate constant of a singlet polaron pair formation from intra-chain singlet excitons $1D^+$; k_{-d} is an electron back transfer rate constant leading to singlet exciton formation; k_r and k_{nr} are rate constants for radiative and non-radiative transitions; k_1 and k_3 are electron back transfer rate constants leading to the ground state for singlet and triplet polaron pairs; k_{-1} is a rate constant of a polaron pair dissociation; k_T is a rate constant of monomolecular decay of an intra-chain triplet exciton $3D$; HFI means a hyperfine interaction. Magnetic sub-levels of the triplet polaron pair $3(D^+ \dots D^-)$ are shown splitted by an external magnetic field. Microwave induced resonant transitions in the triplet polaron pair are shown by bold arrows. Triplet-triplet annihilation path is marked by 2^3D . Formation of a CT-exciton state $1(D^+ \dots A^-)$ with an acceptor molecule A is also shown. Arbitrary energy scale is used in different parts of the scheme.

place due to hyperfine interaction of a polaron spin with magnetic nuclei (protons), which causes mixing, or periodical transitions, between singlet and triplet states of the pair. An external magnetic field lifts the degeneracy of the triplet state, and thus prevents mixing of the singlet and T_{+1} , T_{-1} sub-states. Only singlet and T_0 -substate are mixed now. Singlet and triplet pairs have different rates of geminate recombination, k_1 and k_3 . Thus, an external magnetic field can affect the relative amount of triplet and singlet pairs. Rates of kinetically connected processes, such as dissociation of pairs into free charge carriers, geminate recombination into singlet and triplet channels, and delayed fluorescence are changed as well. It is important to emphasise, that MFSE can take place only due to the mixing of singlet and triplet pair states by magnetic interaction (hyperfine or/and Zeeman interaction). The same is valid for microwave induced resonant transitions between magnetic sublevels of the triplet polaron pair, which are shown by bold arrows in Fig. 1. (No absorption of microwave energy is possible by singlet polaron pairs.) Resonant transitions act in the opposite direction to that of the action of permanent magnetic field. At saturating microwave power, all spin substates become mixed again, as they were before switching-on the magnetic field.

The detailed description of the spin-dependent mechanism of free carrier generation can be found elsewhere [4,19,20]. Below is a simple formula describing the MFSE on the free-carrier generation rate g_e within the framework of the hyperfine mechanism [4]:

$$\frac{\Delta g_e}{g_e} = \frac{k_3 - k_1}{2k_1 + 2k_3 + 4k_{-1}} \quad (8)$$

The same formula is valid for changes of g_e caused by saturating resonant transitions in triplet polaron pairs, but with the opposite sign. Here, k_1 is the rate constant for geminate recombination of a singlet pair, k_3 is that of a triplet pair, k_{-1} is the dissociation rate constant of any pair. The sign of the MFSE on the carrier generation rate depends on the relative value of recombination rate constants k_1 and k_3 , as it follows from the above formula. Experiments on photoconductivity of PPV [4] showed increased photoconductivity in the magnetic field, i.e., positive MFSE, that means $k_3 > k_1$. Accordingly, the

effect of the resonant microwaves on the photoconductivity was found to be negative [21,22].

It is important to understand why polaron pairs recombine faster being in the triplet state. The factor which limits the rate of recombination can be dissipation of the energy released at the recombination, ΔE . The dependence of the type $k_{\text{rec}} \propto \exp(-\Delta E/kT)$ can be expected. Triplet intra-chain excitation can be suggested as a possible product of triplet pair recombination. The release of the energy in such a case is expected to be much lower than for singlet pairs. Similar process of triplet excited chlorophyll molecule formation is known to occur in photosynthesis reaction centres [23]. More evidences on validity of such a process in recombination of polaron pairs in PPV are presented in experimental part of the present contribution.

In the present work, we are using the technique based on the modulation of the spin state of geminate pairs by resonant microwave transitions between Zeeman sublevels of the pairs that have a dynamic spin polarisation. This is a technique that was introduced originally as reaction yield detected magnetic resonance (RYDMR) [24,25]. The parameter used for monitoring the reaction rate change is the luminescence intensity, so the term photoluminescence detected magnetic resonance (PLDMR) can be used also. Similar experimental approach to study electronic processes in PPV has been used in previous papers [21,22,26–28]. Experimental results obtained in the present paper do not contradict to those reported previously. However, additional data of the present work and those reported in [29,30] have permitted to come to conclusions that differ from those made in the previous works, as it will be discussed later on in this paper.

We have studied photoluminescence of films of PPV converted from precursor at different temperatures, and changes of its intensity under conditions of electron spin resonance as a function of temperature, light intensity. Two types of signals have been revealed in the magnetic resonance spectrum, namely, a narrow (1.7 mT width at the half height) and broad (120 mT) ones. The results obtained have permitted to conclude that Coulomb bound polaron pairs are produced with a high yield under the 488 nm photoexcitation. The narrow signal was shown to appear due to microwave induced resonant transitions in

triplet polaron pairs. The resonant transitions change the rate of geminate recombination of the pairs that leads to formation of triplet intra-chain excitons. Those excitons annihilate in the second order reactions showing themselves as delayed fluorescence. Annihilation rate was found to be influenced by resonant transitions in triplet exciton pairs as well. Delayed character of the processes followed from [29,30]. A prominent variation of the resonant signals in films prepared at different prepolymer conversion temperatures was found to be consistent with the model suggested. Results show that the energy level of the lowest pair state is situated below that of singlet intra-chain exciton, and therefore can act as a sink of the excitation energy influencing the quantum yields of the photoluminescence, electroluminescence and photoconductivity.

2. Experimental

PPV is an unmeltable and insoluble polymer and can be processed via a precursor route. Thin films were cast from a methanol solution of the tetrahydrothiophene prepolymer by a doctor blade technique. The prepolymer films on glass 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 variations were of the order of 0.1°C. The oil bath was heated to temperatures between 120 and 190°C. After the heat-up phase of about 30 min the temperature was kept constant for 2 h. After thermal conversion the thickness of PPV films was about 300 nm.

All experiments presented in this paper were carried out in the set-up which was described elsewhere [22]. The synchronous changes of the intensity 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. A second detection channel allowed to measure the PLDMR spectrum and the PL intensity simultaneously.

Experiments were performed at excitation wavelength of $\lambda = 488$ nm from Ar⁺-laser. Laser light was transmitted to the sample via the quartz fibre. The intensity of the PL was checked to be propor-

tional to the light intensity in the whole excitation power range used. 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/cm² s, illuminated area was 1 mm². Absorption coefficient $\epsilon = 10^5$ cm⁻¹ is used for estimation of the light absorption rate.

3. Results

3.1. Changes of the PL intensity under resonant conditions

Fig. 2a shows the ESR spectrum of a PPV film (thickness of 300 nm) measured via PL intensity at

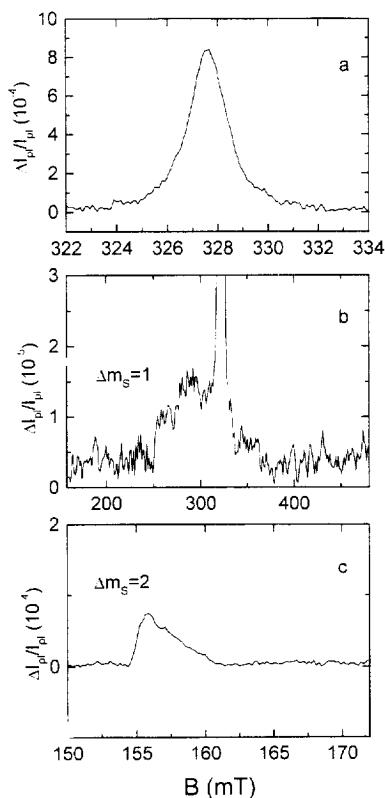


Fig. 2. Magnetic resonance spectrum of PPV, detected by PL: (a) narrow signal at $g = 2.0$, (b) a triplet powder pattern at $g = 2.0$, and (c) a triplet signal at a half resonant field, corresponding to $\Delta m_S = \pm 2$ transitions. $T = 1.6$ K; excitation at $\lambda_{\text{exc}} = 488$ nm; light intensity 10^{19} quantum/cm² s; detection at $\lambda_{\text{det}} = 568$ nm.

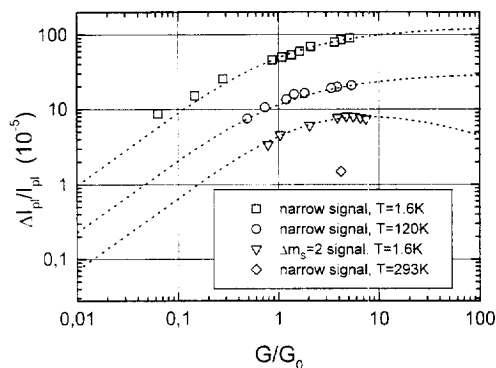


Fig. 3. Dependencies of magnitude of the resonant signals on the intensity G of the exciting light. $G_0 = 2 \times 10^{23}$ quantum/cm³ s. The solid lines are fits by Eqs. (20) and (23), as explained in the text. Only one point is shown for room temperature.

1.6 K. The PL increases in resonance by the factor of 9×10^{-4} . Full width at the half maximum of the signal is about 1.7 mT. It is inhomogeneously broadened, slightly asymmetric, and does not demonstrate any saturation effects at the microwave power used in the experiment (160 mW). The signal can not be saturated, and its intensity is proportional to B_1 -field inside the microwave cavity. Fig. 2b shows the PL enhancement by factor of 8×10^{-5} in a field corresponding to $\Delta m_S = \pm 2$ transition in a triplet exciton. Fig. 2c shows a broad asymmetric PLDMR signal originating 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 of several records.

3.2. Dependence of the PLDMR on the excitation intensity and the temperature

All signals were found to be strongly dependent on the temperature of the samples and the intensity of exciting light. By varying the excitation intensity the rate of the polaron pair generation can be varied. Fig. 3 displays the relative changes of the PL intensity $\Delta I_{\text{PL}}/I_{\text{PL}}$ as a function of the excitation intensity G (normalised to the value of $G_0 = 2 \times 10^{23}$ cm⁻³ s⁻¹) for the narrow signal at 1.6 K and 120 K, and $\Delta m_S = \pm 2$ signal at 1.6 K. The value of $\Delta I_{\text{PL}}/I_{\text{PL}}$ 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 $\Delta m_S = \pm 2$ (down triangles), increase. At higher excitation intensity the $\Delta m_S = \pm 2$ signal starts to saturate, whereas the narrow signal keeps growing. The PL intensity I_{PL} was checked to be proportional to the exciting light intensity in the whole intensity range used.

3.3. The influence of the thermal conversion of PPV precursor polymer on the intensity and spectral dependence of PLDMR

PL, narrow and broad PLDMR signals and spectral dependencies of their intensities were measured as a function of the temperature of the thermal conversion T_{conv} of the PPV prepolymer on a glass substrate. PL spectra recorded in a set of films converted at different temperatures are shown in Fig. 4. The intensities of all spectra are normalised to the height of the second peak. The spectra show partially resolved phonon structure due to the coupling of vibronic states to the excitonic transition. It can be

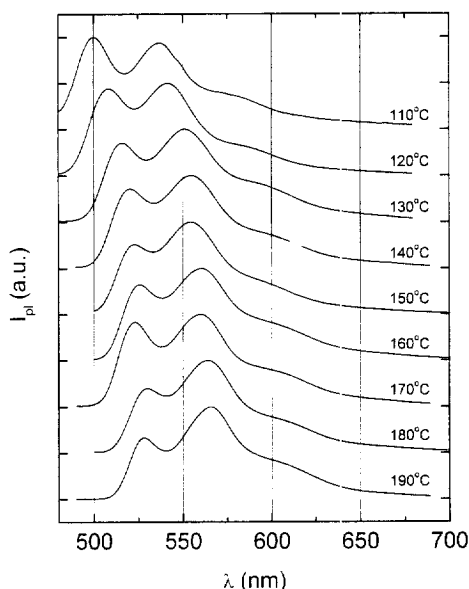


Fig. 4. PL emission spectra of PPV films converted at different temperatures. The intensities of the spectra are normalised to heights of the second peak. $d = 300$ nm, $T = 120$ K.

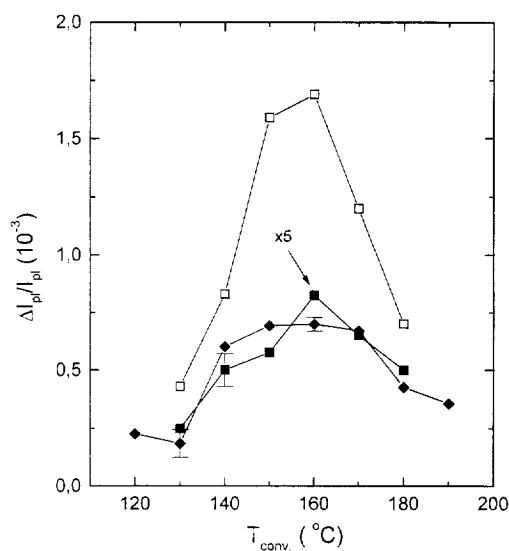


Fig. 5. Dependence of amplitudes of the narrow polaron resonant signal ($g = 2$) at 120 K (filled diamonds) and 1.6 K (open squares) and half-field resonant signal ($g = 4$) at 1.6 K (filled squares) on the prepolymer conversion temperature. $\lambda_{\text{exc.}} = 488$ nm.

seen that with increasing T_{conv} , the spectra are shifted to the longer wavelengths due to the higher degree of conjugation in the polymer. For conversion temperatures higher than 140°C the position of the spectra remains nearly constant.

Fig. 5 displays the dependence of the PLDMR amplitudes on the conversion temperature. By varying the conversion temperature one obtains a large variation in the amplitude $\Delta I_{\text{PL}}/I_{\text{PL}}$ of the narrow signal ranging from 10^{-4} to 10^{-3} . Neither the duration of the conversion, nor the atmosphere conditions at which the thermal conversion was carried out, have influenced the PLDMR signals. We did not find any differences in the PLDMR behaviour of PPV films converted on glass substrate and on indium tin oxide (ITO). The integrated PL intensity from the PPV converted on ITO, however, was found to be lower by a factor of two as compared to pristine PPV on glass.

Our studies revealed the range of conversion temperatures where the most changes in all PLDMR signals occurred. They reached their maxima at the conversion temperature between 150 and 160°C .

A shift between longer wavelength maxima of the PL spectrum and that of the spectral dependence of

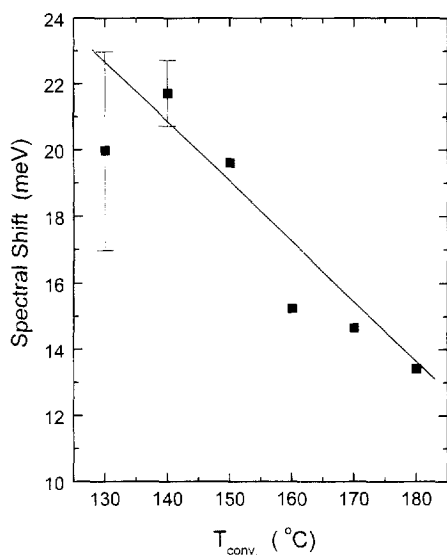


Fig. 6. Shift between emission spectra measured by total fluorescence intensity I_{PL} and by resonant changes ΔI_{PL} (narrow line at $g = 2$) as a function of prepolymer conversion temperature in PPV. Solid line is a guide for the eyes. $T = 1.6$ K, $d = 300$ nm.

amplitude of the narrow resonant signals was found in the present work. The spectral dependence of the narrow PLDMR signal appeared to be shifted to longer wavelengths. The shift is plotted as a function of the conversion temperature in Fig. 6. As it is seen, the shift is larger in the films converted at lower T_{conv} .

4. Discussion

4.1. Kinetic connection between magnetic resonant transitions and PL intensity

The problem is how to find out a mechanism of kinetic connection between microwave induced resonant transitions at $g = 2$ and 4 and the PL intensity. Changes of photo-induced absorption in similar conditions in absorption detected magnetic resonance (ADMR) are also known [31,32].

4.1.1. Recombination of free charge carriers

The model which is often applied to non-degenerate ground state polymers, assumes that free charge

carriers are generated via inter-band light absorption [33]. Microwave induced transitions in the magnetic field can act on polarons changing the rate of recombination of the latter and, hence, affecting their density. There is a possibility to connect changes of polaron density with PL intensity, say, by assuming a quenching of singlet excitations by polarons [32,34]. Let us consider the recombination in two different ways.

4.1.1.1. Direct recombination of free polarons. Singlet and triplet channels of recombination are operative at recombination. In an external magnetic field B_0 , populations of free polarons with spin up and spin down become non-equal, and rates of recombination into singlet and triplet channels changes. It is easy to show that relative change of recombination rate k_r into singlet channel decreases:

$$\left(\frac{\Delta k_r}{k_r}\right)_S = -\frac{1}{4} \left(\frac{g\beta B_0}{kT}\right)^2 \quad (9)$$

and that into the triplet channel increases:

$$\left(\frac{\Delta k_r}{k_r}\right)_T = \frac{1}{12} \left(\frac{g\beta B_0}{kT}\right)^2 \quad (10)$$

However, the total recombination rate of free polarons does not depend on the population of $+1/2$ and $-1/2$ -spin states of free polarons, and, hence, on the magnetic field and resonant microwaves. Of course, this is valid for the case when there are no spin-dependent restrictions for recombination of polarons.

Resonant transitions between Zeeman sublevels of free polarons, if the transitions are fast enough, make the population of the sublevels equal. They cause changes, signs of which are opposite to those followed from (9) and (10). One can estimate the magnitude of the changes expected, say, for the magnetic field induction $B_0 = 100$ mT. Values calculated for recombination into the singlet channel for different temperatures are listed in the next Table:

T/K	4	20	100	200	300
$-(\Delta k_r/k_r)_S$	2.8×10^{-4}	1.1×10^{-5}	4.5×10^{-7}	1.1×10^{-7}	5×10^{-8}

These values are useful when discussing the origin of MFSE and/or microwave induced resonant signals. Experimentally obtained values of relative changes of parameters such as intensity of PL, induced absorption, and photoconductivity are much higher than those shown in the Table. It means that the polarisation of magnetic substates is much higher than that in thermal equilibrium. In order to obtain a higher-than-equilibrium polarisation, the life time of the species responsible for resonance must be shorter than the spin-lattice relaxation time T_1 . Moreover, there must be some processes which populate or depopulate spin substates selectively. It is worth noting that in polaron pairs with the life time much longer than spin-lattice relaxation time T_1 , no dynamic polarisation is possible. Relative magnitudes of MFSE and microwave induced resonant signals in pairs at thermal equilibrium can not exceed those listed in the Table.

4.1.1.2. Recombination of free polarons via intermediate polaron pairs. It is natural to assume that polaron pairs can be formed at combination of free charge carriers. Probabilities of formation of pairs in singlet or triplet state in this case relate to each other as 1 to 3. Polaron pairs in the triplet state are just the species having a short life time and non-equilibrium dynamic polarisation. Microwave induced resonant transitions in such polarised pairs can be very effective. However, in order to be effective in influencing the free polaron density, the pairs must dissociate again reforming free charge carriers. This is hardly possible at low temperatures at which PLDMR signals are measured. Without the dissociation of pairs, the free polaron density does not depend on transitions within the triplet pairs.

However, the density of pairs themselves does depend on resonant transitions in triplet polaron pairs; it becomes lower when transitions take place. That opens the way for speculation connected with the quenching model. Weak points of that approach is an assumption about the population of pair states via free polarons, as far as at low temperature polarons appear to be immovable, that is evidenced by the negligible photoconductivity.

4.1.2. Quenching of singlet excitations by polarons

Most recent model derived in works [32,34] assumes a quenching of singlet intra-chain excitations

by polarons, free or belonging to pairs. Experimentally verified criterion of validity of such a model was the opposite sign of PLDMR and ADMR signals. There are no doubts that polaron density can be changed by resonant transitions in triplet polaron pairs. The decrease of polaron pair density can be predicted as by free polaron recombination model described above, and by more substantiated model which assumes formation of pairs from primary singlet excitations, but at the condition $k_1 < k_3$. The latter relation follows from the sign of MFSE on the photoconductivity [4].

Let us consider the model in more details. Quenching of intra-chain excitations $^1D^*$ can occur at collision with movable polarons:

$$\begin{aligned} \frac{dD}{dt} &= gN_0 - (k_r + k_{nr} + k_q p)D \\ \frac{dp}{dt} &= \eta gN_0 - k_f p \end{aligned} \quad (11)$$

Those rate equations are written for the case of independent generation of excitons $^1D^*$ (their density is D) and polarons p ; here gN_0 is the generation rate of $^1D^*$, η is a polaron generation quantum yield, k_q is the quenching rate constant. Free polarons density p can be changed by an increase of the rate constant k_f on Δk_f by some mechanism. Solution of the Eq. (11) gives the steady state PL intensity I_{PL} :

$$I_{PL} \propto D = \frac{gN_0}{k_r + k_{nr} + \frac{k_q \eta gN_0}{k_f}} \quad (12)$$

For the relative change of the PL intensity caused by an increase of k_f , one obtains:

$$\begin{aligned} \frac{\Delta I_{PL}}{I_{PL}} &= \frac{1}{D} \frac{dD}{dk_f} \Delta k_f \\ &= \frac{k_q \eta gN_0 \Delta k_f}{k_f^2 \left(k_r + k_{nr} + \frac{k_q \eta gN_0}{k_f} \right)} \propto I_{PL} \frac{\Delta k_f}{k_f^2} \end{aligned} \quad (13)$$

The formula (13) shows that applicability of the model for experimental results can be checked easily by comparison of dependencies of $\Delta I_{PL}/I_{PL}$ and I_{PL} on the excitation rate. They are expected to be

similar within the wide range of excitation rates. The same conclusion can be made for another case where polarons just occupy the sites otherwise available for singlet excitons. Results obtained in the present work show that the behaviour of the PLDMR signals and the PL intensity are not compatible with the above requirements.

4.1.3. Connection of polarons with fluorescence via ground state repopulation

This model connects polarons or polaron pairs with the total amount of ground state molecules N available for excitation. At high enough intensity of the exciting light, when a prominent part of the ground state molecules is converted into excitation products, any changes of the population of excited or charged species can deflect the amount of ground state molecules available for excitation, and hence the intensity of the PL. Simplified rate equations can be written for the formation of excitons ${}^1D^*$ and some product species P , the density of the latter being dependent on a rate constant k^* , which is assumed to be subjected to small changes Δk^* :

$$\begin{aligned} \frac{dD}{dt} &= gN - (k_r + k_{nr} + k_{12} + g)D; \\ \frac{dP}{dt} &= k_{12}D - k^*P; \quad D + P + N = N_0 \end{aligned} \quad (14)$$

Here, D denotes the exciton density, P is the density of product species, gN_0 is the excitation rate of ${}^1D^*$, k_r and k_{nr} are radiative and non-radiative decay rate constants of ${}^1D^*$, k_{12} is the rate constant for formation of products, and N_0 is the total density of ground state molecules in the absence of excitation, N is that one under excitation. Steady state solution of the system (14) gives:

$$I_{\text{PL}} \propto D = \frac{gN_0}{g\left(2 + \frac{k_{12}}{k^*}\right) + k_r + k_{nr} + k_{12}} \quad (15)$$

$$\begin{aligned} \frac{\Delta I_{\text{PL}}}{I_{\text{PL}}} &= \frac{1}{D} \frac{dD}{dk^*} \Delta k^* \\ &= \frac{gk_{12}\Delta k^*}{k^{*2} \left[k_{12} + k_r + k_{nr} + g\left(2 + \frac{k_{12}}{k^*}\right) \right]} \propto I_{\text{PL}} \frac{\Delta k^*}{k^{*2}} \end{aligned} \quad (16)$$

The result shows that the ground state recovery mechanism requires similar dependencies of relative changes of the PL and of the PL intensity on the excitation rate. That is not the case in our experiment, which shows saturation of $\Delta I_{\text{PL}}/I_{\text{PL}}$ and a linear dependence of I_{PL} on the intensity of exciting light.

4.2. Triplet excitons annihilation as a source of the delayed photoluminescence

One can imagine that the inter-chain charge transfer process, which creates the singlet CT-exciton is reversible, and a delayed fluorescence appears due to electron back transfer process. It is quite plausible to think so as the electron back transfer is the main step in the electroluminescence. MFSE on the PL intensity was attributed to the electron back transfer process, too [16]. However, let us remember the sign of the narrow resonant line in PLDMR spectrum. It is positive, i.e., corresponding to enhancement of the light intensity. If the PL originated from the electron back transfer also, the resonant transitions from the more populated sublevel T_0 of the triplet pair (mixed with singlet state) to less populated triplet sublevels T_{+1} and T_{-1} would reduce the population of the former, and thus would result in the negative sign of the narrow resonance line. Thus, the electron back transfer cannot be the main channel connecting magnetic resonance transitions with PL at our experimental conditions.

A great help in understanding of the mechanism comes from the observation that the absolute magnitude of the narrow line in PLDMR spectrum, ΔI_{PL} , changes superlinearly with the intensity of the exciting light, and that triplet exciton spectra are observed. Moreover, the spectral dependence of the PLDMR signal at $\Delta m_S = \pm 2$ is the same as the PL spectrum [21,22,26,27]. This permits to assume that a triplet recombination channel is operative, and triplet intra-chain excitons are generated from triplet polaron pairs as a result of electron back transfer process. This is exactly the process which produces triplet excitations in photo-synthetic reaction centres [23]. If so, the emission of the light appears as a result of triplet-triplet annihilation, and the triplet powder spectrum of the positive sign is a result of resonant transitions in T-T pairs. Such transitions

are known to increase the rate of annihilation of triplets with production of more singlet products, as was first discovered in RYDMR experiments in molecular crystals [24]. The triple: PLDMR signals in PPV were attributed to fusion of triplet intra-chain excitons in [27], too. The scheme of the processes responsible for the results obtained is shown in Fig. 1.

The formation of triplet intra-chain excitons in PPV was observed before in experiments via photoinduced absorption [6,7,35], PLDMR [21,26–28], and ADMR [31,32]. The main source of triplet excitons was suggested to be an intersystem crossing from the singlet exciton state.

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

If one approves that T–T annihilation is the main bridge connecting CT pairs and fluorescing excitons, then the origin of the dependence of the magnitude of the resonant signal on the intensity of the exciting light (Fig. 3) becomes clear.

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

$$\frac{dn_T}{dt} = p_3 - k_T n_T - \gamma n_T^2 = 0 \quad (17)$$

as

$$n_T = \frac{k_T}{2\gamma} \left(\sqrt{1 + 4 \frac{\gamma}{k_T^2} p_3} - 1 \right) \quad (18)$$

where γ is T–T annihilation rate constant, and k_T is the rate constant for monomolecular decay of triplet excitons; triplet polaron pair recombination rate $p_3 = G\phi_T$, here G is the rate of primary excitation generation, and ϕ_T is the quantum yield of triplet intra-chain excitons in the recombination processes.

Delayed PL intensity per unit volume is:

$$(I_{PL})_d \propto \frac{\phi_{PL}}{9} \gamma n_T^2 = \frac{\phi_{PL}}{36} \frac{k_T^2}{\gamma} \left(\sqrt{1 + 4 \frac{\gamma}{k_T^2} p_3} - 1 \right)^2 \quad (19)$$

where ϕ_{PL} is a quantum yield of the PL.

Magnetic resonant transitions cause changes $\Delta p_3 < p_3$ of the recombination rate of polaron pairs. Corresponding changes $(\Delta I_{PL})_{nar}$ of the narrow signal at $g = 2.0$ can be calculated by differentiating Eq. (19) by p_3 :

$$\begin{aligned} \frac{(\Delta I_{PL})_{nar}}{I_{PL}} &= AP_{\mu\omega} \left(1 - \frac{1}{\sqrt{1 + 4 \frac{\gamma}{k_T^2} p_3}} \right) \\ &= AP_{\mu\omega} \frac{x - 1}{x} \end{aligned} \quad (20)$$

Here, $P_{\mu\omega}$ 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;

$$x = \sqrt{1 + 4 \frac{\gamma}{k_T^2} p_3} \quad (21)$$

a coefficient A depends on the rate constants governing generation and recombination of polaron pairs. Using rate constants shown in Fig. 1 one can obtain

$$A \propto \frac{k_d}{(k_r + k_{nr})(k_1 + k_3 + k_{-d}) + k_d(k_1 + k_3)} \quad (22)$$

Corresponding formulas for the magnitudes of the triplet powder signal at $g = 2.0$ and the signal at the half field ($\Delta m_S = \pm 2$) can be obtained by differentiating Eq. (19) by γ :

$$\frac{(\Delta I_{PL})_{pow}}{I_{PL}} \propto \frac{x - 1}{x(x + 1)} \quad (23)$$

Eq. (20) and (23) predict different dependencies of the relative magnitudes of narrow and broad (powder) signals on the light intensity, their ratio being equal to

$$\frac{(I_{PL})_{nar}}{(I_{PL})_{pow}} = x + 1 = \sqrt{1 + 4 \frac{\gamma}{k_T^2} p_3} + 1 \quad (24)$$

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. 3. Experimental points were fitted by Eqs. (20) and

(23), respectively. Fitting parameter was $B = 4\gamma / (k_T^2 \phi_T G_0)$ (Here, 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 it can be seen from the Fig. 3, the dependencies of the narrow signal at $g = 2$ and the signal $\Delta m_s = \pm 2$ on the excitation intensity are different.

The rate constant of monomolecular decay of triplet excitons was measured by frequency resolved spectroscopy as $k_T = 2.2 \times 10^2 \text{ s}^{-1}$ [29,30]. The quantum yield of polaron pairs in PPV was estimated in transient absorption measurements [6,7] as 0.9. It gives the ground 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:

$$\gamma = \frac{\left(B \frac{G}{G_0} \right)_{\text{exp.}} k_T^2}{4 \phi_T G} = \frac{10(2.2 \times 10^2)^2}{4 \times 0.1 \times 2 \times 10^{24}} \\ \approx 6 \times 10^{-19} \text{ cm}^3/\text{s}$$

It corresponds to the diffusion coefficient D of triplet excitons:

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

The size of the exciton was chosen arbitrarily as $R = 10^{-7}$ cm. Exciton hopping frequency ν may therefore be estimated as:

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

All the estimations made, though being within an order of magnitude accuracy, show that triplet intra-chain excitons are rather immovable species, their life time being comparable with reciprocal hopping frequency. It means that the annihilation occurs under formation of two excitons on the next neighbour or nearby lying chains, i.e., at high excitation intensities. Further, the T–T annihilation channel was found to prevail over direct back transfer of an electron leading to a singlet exciton at all excitation intensities used, i.e., from 10^{22} to $10^{24} \text{ cm}^{-3} \text{ s}^{-1}$, and

temperatures from 1.6 to 120 K. It prevailed also at room temperature at highest intensity of the exciting light. That is why we may conclude that the rate constant k_{-d} is small. However, the MFSE on the PL in PPV at temperatures higher than 150 K and intensities of the light below than $10^{20} \text{ quantum/cm}^3 \text{ s}$ was interpreted [16] as being completely due to the electron back transfer into singlet polaron pairs and not via T–T annihilation channel. Triplet excitons have low rate of annihilation at those conditions because of their low density, and back electron transfer in singlet polaron pairs becomes the main source of delayed fluorescence.

4.4. Dependence of the magnitude of the resonant signals on the frequency of microwave power modulation

At this point we accept that the connection between processes in polaron pairs and an emission of the delayed PL is provided by triplet excitons. If so, the modulation of parameters involved in the processes can give an information about life time of triplet excitons as most long living species among intermediate excited states. The simplest case is modulation of triplet exciton formation rate p_3 , which shows itself in the appearance of the narrow resonant signal at $g = 2.0$. It was found that the processes really involve an inertial part which may be assumed to be triplet excitons with the lifetime distributed around the value of $\tau_T = 1.25 \text{ ms}$ [29,30]. In similar experiments [34], $\tau_T = 39$ and $666 \text{ } \mu\text{s}$ were reported for ladder-poly(*p*-phenylene). Authors of Ref. [34] believed however that the inertiality was caused by long lived polaron pairs. Such a conclusion makes the possibility of dynamic spin polarisation in the pairs questionable, as a thermal equilibrium can be achieved in polaron pairs having such a long life time. These values of the life time are typical for triplet excitons in PPV samples, measured by photo-induced triplet–triplet absorption [35]. The experiments discussed above show unambiguously that there exists an inertial step between resonant transitions in polaron pairs and the light emission. It would be not the case in the model describing the emission which originates directly from the recombination of polarons.

4.5. The influence of the thermal conversion of the prepolymer on recombination processes

As it was mentioned already, the PL quantum efficiency of the emitting material is one of the major factors which determine the electroluminescence. Since the PPV is prepared via the precursor route, the conditions of the elimination of the prepolymer to the conjugated polymer PPV may influence the quantum efficiency of the PL [36].

In our work we measured the amplitudes of PLDMR signals as well as the PL intensity for samples prepared at different temperatures of the prepolymer conversion. Remarkable is the behaviour of the PL (see Fig. 4). When the conversion temperature increases, the spectrum clearly shifts to lower energies (bathochromic shift). This is an indication of the increase of the conjugation length [37].

We found a strong variation of the relative changes $\Delta I_{\text{PL}}/I_{\text{PL}}$ with the conversion temperature, too. As it is shown in Fig. 5, all PLDMR signals reached their maxima in the conversion temperature range between 150 and 160°C.

As we assumed already, resonant signals detected via PL intensity were due to the triplet–triplet annihilations process. In Ref. [38], the energy of the singlet and triplet intra-chain excitons for different chain lengths was calculated. Authors found that the triplet exciton energy decreased with an increase of the molecule size from two to five phenyl rings, but not so strong as singlet exciton energy did. This is a sequence of localised character of the lowest triplet exciton. An important finding is that starting from the certain number of phenyl rings, the sum energy of two triplet excitons becomes not sufficient for the formation of a singlet exciton. This can lead to the situation in which the triplet–triplet annihilation becomes no more operative for small oligomers or polymers converted at low temperatures because of the energy reason. That explains the behaviour of the curves in Fig. 5 at lower T_{conv} . Above 180°C, PLDMR amplitudes strongly decreased also. This may be due to the formation of the crystalline regions in the sample, smaller overlapping of π -electron clouds, and lower rate of CT-state and polaron pair formation.

Limited energy of two triplet excitons explains also the origin of the shift between longer wave-

length maxima of the PL spectrum and that of the spectral dependence of amplitude of the narrow resonant signals (see Fig. 6). It appears because the energy of two triplet excitons is sufficient to form a singlet exciton on the polymer segment with longer conjugation, which results in emission of light of longer wavelength. The exciting light is able to excite all the distribution of polymer molecules by conjugation lengths. Of course, such an explanation implies that the energy of two triplets is less than the excitation energy quantum used in the experiment, i.e., 2.54 eV.

4.6. On the existence of a delayed fluorescence from T–T annihilation

Our experiments demonstrate that energy levels of the populated at low temperatures pair state are situated below the level of singlet intra-chain exciton. Hence, the radiative path should include T–T annihilation. (Note, the sign of the PLDMR is not sensitive to the relation between k_3 and k_1 .)

The generation of singlet intra-chain excitons in double injection regime (electroluminescence) occurs mainly not via lowest polaron pair state but from higher lying states produced at approaching of free polarons of different signs to each other. These states are higher than the energy level of intra-chain excitons, and they can populate the latter level at any temperature. This distinguishes PL-regime from EL-regimes markedly.

The model we describe is based on the assumption of the existence of delayed component in the PL. However, there are no literature data on any significant emission in PPVs in μs to ms range. It is not surprising, since the component of the PL originated from T–T-annihilation process can hardly be expected in time-resolved experiments because of the very small γ , as it is estimated by us. It is by 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 it was 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 magneto-sensitive delayed fluorescence in

ms time domain at low temperature. Though the model suggested may be important for a broad class of semiconducting polymers, we believe that its applicability has to be proven experimentally on every particular type of polymer. Excitation dependence of the PLDMR signal is of extreme importance for checking the validity of models used.

4.7. On the origin of triplet excitons

The source of triplet excitons was assumed in Refs. [26–29,35] to be an intersystem crossing from singlet intra-chain excitons due to spin-orbit coupling. In the above discussion, we did not take into account the generation of intra-chain triplet excitons via intersystem crossing. It does not mean that this process is absent in PPV at all. In this work, we found that at excitations intensities and temperatures used, triplet excitons could be very effectively produced via recombination of geminate polaron pairs, too. It is not only in low temperature experiments, 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.

4.8. Comparison of PLDMR and ADMR experiments

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 it follows from differentiation of Eq. (18) by γ , a change of the triplet density Δn_T caused by a positive increase $\Delta\gamma$, is negative. It is a direct consequence of higher annihilation rate at the same generation rate of triplet intra-chain excitons.

A negative change of the triplet exciton density Δn_T in PPV at 1.36 eV, as detected in ADMR experiment [31,32] and identified as $\Delta m_s = \pm 2$ transitions in triplet species could 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 pro-

duced. The sign of the ESR effect on the triplet–triplet absorption depends on rate constants governing the radiative and non-radiative paths of recombination of the triplet excitons. General idea is worth to be explained in a 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 T–T pair. The second state, which is non-radiative with the rate constant k_{nr} , is populated at the rate p_2 . Initial total population of both states is

$$n_0 = \frac{p_1}{k_r} + \frac{p_2}{k_{nr}} \quad (25)$$

The resonant change of p_1 on Δp_1 at the expense of p_2 will lead to a change $\Delta n = n - n_0$. It is easy to see that

$$\Delta n < 0 \text{ for } k_r > k_{nr} \text{ and } \Delta n > 0 \text{ for } k_r < k_{nr}$$

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

5. Conclusion

The results obtained permitted us to conclude that Coulomb bound polaron pairs were produced with a high yield under the 488 nm photoexcitation of PPV. Energy levels of the populated at low temperatures pair state were situated below the level of singlet intra-chain exciton. Therefore, no electron back transfer producing excited intra-chain singlet state was observed. The results imply that the singlet exciton has a binding energy which 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 were produced mainly by recombination of geminate polaron pairs. Triplet polaron pairs showed themselves as a narrow resonant signal at $g = 2$. The resonant transitions changed the recombination rate of triplet pairs and led to formation of triplet intra-chain excitons. Those excitons annihilated in the second order reaction and showed themselves as the change of the PL. Annihi-

lation rate was found to be influenced by resonant transitions in triplet exciton pairs as well. Our results show that energy level of the lowest polaron pair state can act as a sink of the excitation energy influencing the quantum yields of the PL, electroluminescence and photoconductivity.

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