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Polarons and triplet polaronic excitons in poly(paraphenylenevinylene) (PPV) and substituted PPV: An optically detected magnetic resonance study

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The X-band optically detected magnetic resonance (ODMR) of poly(paraphenylenevinylene) (PPV) and its dihexoxy derivative films and solutions is described and discussed. As in poly(3-alkylthiophenes) (P3AT), the photoluminescence (PL) -enhancing features include a narrow resonance at $g \cong 2.0023$, a broad triplet powder pattern around $g \sim 2$, and the $\Delta m_S = 2$ transition of this triplet at $g \cong 4.07$. The symmetric narrow resonance, attributed to intrachain "distant" polaron recombination, indicates that charge-conjugation symmetry violation is weaker in PPV than in P3AT. As in P3AT, its spectral dependence is similar to the PL spectrum, suggesting that the polaron levels are close to the band edges. Although the spectral dependence of the half-field resonance is similar, that may result from singlets generated by triplet-triplet collisions. A broad decrease in the ODMR intensity at $g \sim 2$, probably due to a PL-quenching resonance resulting from geminate singlet decay, is also observed at low temperatures.

Although numerous (semi)conducting polymers display strong photoluminescence (PL), the interest in their radiative decay channels has previously been shadowed by the transport and nonlinear optical properties of these systems.[1-3] Very recently, however, significant electroluminescence from poly(paraphenylenevinylene) (PPV) films was reported by Burroughes *et al.*[4] These films may therefore enable the development of low-cost large-area light-emitting diodes. A clear, fundamental picture of the radiative decay channels of PPV and its processible dialkoxy derivatives is therefore highly desirable.

In parallel with the recent developments in PPV, the radiative decay processes in poly(3-alkylthiophenes) (P3AT) were recently studied by X-band optically detected magnetic resonance (ODMR).[5-7] The PL-enhancing features included (i) a strong $\sim$15-G-wide asymmetric peak at $g \cong 2.003$, clearly resulting from narrow and broad Gaussians; (ii) a weak peak at $g \cong 4.07$; (iii) a $\sim$1200-G-wide axially symmetric ($E \cong 0$) triplet powder pattern at $g \sim 2$ below $\sim$50 K; and (iv) a $\sim$1200-G-wide triplet pattern of lower symmetry ($E \cong D/3$) above $\sim$50 K. Feature (i) was identical in all films from 5 to 300 K and in dilute CH_2Cl_2 solution, and its spectral dependence was similar to the PL spectrum. It was thus attributed to intrachain "distant" polaron recombination, from levels apparently close to the band edges. The g splitting and different linewidths of the two Gaussians therefore provided a quantitative measure of the charge-conjugation asymmetry in that system.[8] Features (ii) and (iii) were attributed to the radiative decay of intrachain triplet polaronic excitons resulting from the $\Delta m_S = 2$ and 1 transitions, respectively. Feature (iv), which could be observed in films up to 300 K, but not in solution, and of lower symmetry, was tentatively attributed to the decay of other triplet polaronic excitons.

Bradley and co-workers reached very similar conclusions on the nature of the radiative processes in PPV from essentially unrelated measurements and analyses.[9-11] Since the PL spectrum of PPV is similar to that of P3AT, a comparison of the ODMR of the two systems should yield valuable insight into the radiative decay channels of both. The ODMR study on PPV and its dihexoxy derivative (PDHOPV) described in this paper indeed yielded the following: (i) a narrow resonance at $g \cong 2.0023$, but of symmetric line shape, indicating weaker charge-conjugation-symmetry violation than in P3AT; (ii) the $E \cong D/3$ triplet polaronic exciton, but not the $E \cong 0$ one;[6,7] (iii) a relatively intense half-field resonance, of spectral dependence similar to the PL spectrum; this may result from decay via singlet generation from triplet-triplet collisions (but see below); and (iv) a broad decrease in $\Delta L/L$ around $g \sim 2$ at low temperature, suspected to result from a PL-quenching resonance. This feature, as well as other results,[12,13] may indicate that singlet geminate recombination is the dominant radiative decay channel from the photoexcited state.

Since PPV is insoluble, samples for PL and ODMR measurements were processed as free-standing films. The chopped-microwave ODMR system was previously described.[5,6] The microwave field H_1 was normal to the dc field H_0, which was determined by an NMR gaussmeter. The 4880-Å excitation power was 50 mW or less.

The observed line shape of the narrow resonance at $g = 2.0023$ (Fig. 1) could be fit by either a single Lorentzian or two Gaussians. Yet the asymmetric double-Gaussian shape of this resonance in P3AT indicates that

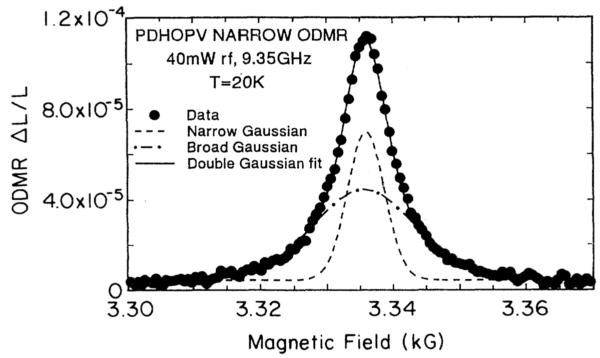

FIG. 1. Main narrow total-PL ODMR at $g=2.0023$. Although excellent agreement is obtained by fitting this ODMR to either a single Lorentzian or two Gaussians, the asymmetric double-Gaussian shape of this resonance in P3AT (see Refs. 5 and 6) favors the latter. Neither component, however, could be saturated by up to 810 mW microwave power.

the latter is the more plausible of the two. Neither component, however, could be saturated with microwave power up to 810 mW, inhibiting the unambiguous verification of a double-Gaussian structure.

The broad ODMR of PDHOPV at 20, 50, and 100 K, excited by 16 mW at 4880 Å, is shown in Fig. 2. Its shape above 100 K closely resembles the powder pattern of an $E \cong D/3$ exciton.[6,7] However, a broad decrease in $\Delta L/L$ near $g \sim 2$ in PDHOPV, possibly due to the appearance of a quenching resonance, becomes prominent at 20 K.

Figure 3 displays the half-field resonance at $g \cong 4.07$ resulting from the $\Delta m_S = 2$ transitions of this exciton, as well as the simulated resonance calculated from the parameters used to fit the full-field triplet powder pattern (see below).

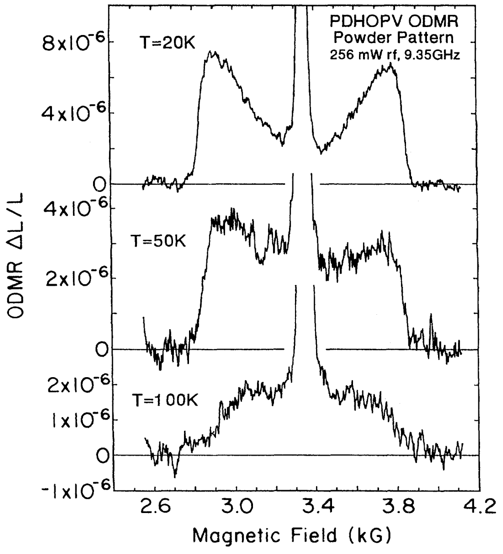

FIG. 2. Broad triplet powder pattern ODMR of PDHOPV at 20, 50, and 100 K, excited by 16 mW at 4880 Å.

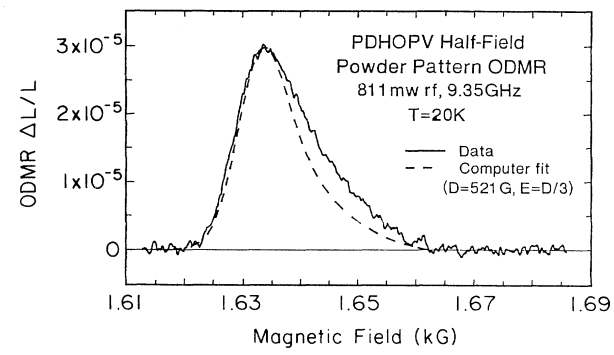

FIG. 3. Half-field resonance at $g \cong 4.07$ resulting from the $\Delta m_S = 2$ transitions of the triplet polaronic exciton producing the full-field pattern shown in Fig. 2. The dashed line was calculated using the parameters determined from the full-field pattern.

To identify the PL band responsible for the main narrow and half-field ODMR, the spectral dependence of their intensity ΔL was measured coincidentally with the PL for PDHOPV. Figure 4 shows that ΔL is proportional to the PL intensity L except for a slight enhancement of the narrow resonance at long wavelengths.

The temperature dependence of the ODMR intensity $\Delta L/L$ was highly unusual and similar to P3AT, where it decreased as $\exp(-T/T_0)$. Yet it varied from region to region of the same sample and depended on the thermal history of the film. Thermal cycling of the PDHOPV

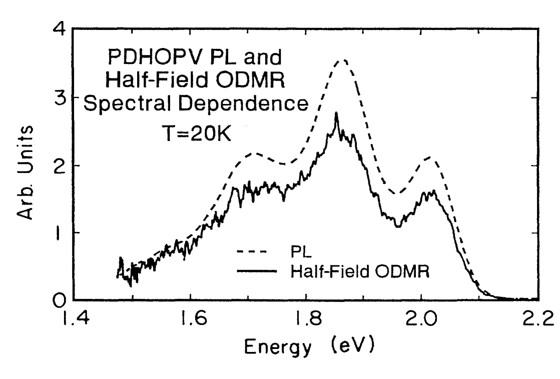

FIG. 4. Spectral dependence of the intensity ΔL of the main narrow and half-field ODMR. The spectral dependence was measured coincidentally with the PL. Note that ΔL is proportional to the PL intensity L, except for a slight enhancement of the main narrow resonance at long wavelengths.

powder samples over the 20–300-K range increased the intensity of the triplet exciton resonance. It is suspected that chain morphology, e.g., conjugation length and interchain coupling, is important in determining the ODMR intensity by controlling various decay and transport channels.

In light of the identical asymmetric shape of the main narrow ODMR in all P3AT samples,[5–7] its identical symmetric shape in all PPV and PDHOPV samples over a wide temperature range (Fig. 1), and a spectral dependence similar to the PL spectrum, it is attributed to intrachain "distant-pair" polaron recombination. The symmetric line shape then implies that PPV and PDHOPV are significantly more charge-conjugation symmetric than P3AT, where the main narrow resonance is distinctly asymmetric ($g_1=2.0019$, $g_2=2.0032$). The larger symmetry violation in the P3AT is suspected to result from the role of the sulfur atom, which increases the asymmetry between the highest occupied and lowest unoccupied molecular orbital states of the excited polymer, as compared to the identical carbons in the aromatic rings of PPV.

In P3AT, accelerated quenching of the ODMR intensity $\Delta L/L$ during photoinduced oxidation was observed. The absence of an observable ODMR in some P3AT solutions, which yield relatively intense PL spectra, was also noted. These results and the temperature and position dependence of $\Delta L/L$ mentioned above suggest that a significant portion of the PL is due to a nonresonant channel, probably the relatively short-lived (≤ 400-ps) geminate pair or singlet exciton decay.[13] Since all of the channels emitting near the band edge are expected to exhibit similar vibronic structure, it is not surprising that this channel yields a PL spectrum similar to that of the resonant channels. Within the continuum single-chain model, charge-conjugation-symmetry violation is required for nonradiative decay.[8] The high level of symmetry in PPV and PDHOPV is then consistent with the higher PL quantum yield of this system ($\sim 10\%$) compared to P3AT films ($\sim 1\%$).

Also contributing to the PL are triplet polaronic excitons producing the resonances shown in Figs. 2 and 3. The full-field broad ODMR shape of PDHOPV changes with increasing temperature. The decrease in the pattern near the center at $g=2$ may be due to a separate quenching signal which has a stronger temperature dependence. We note, however, that this picture is not firmly established at present. Within this scenario, the broad pattern at $g\sim 2$ is attributed to two mechanisms: (i) PL-enhancing $\Delta m_s=1$ transitions of an $E\cong D/3$ triplet polaronic exciton (possibly requiring triplet-triplet collisions; see below) and (ii) PL-quenching $\Delta m_S=1$ transitions of (geminate) singlet excitons which result in longer-lived and possibly lower-energy triplet polaronic excitons. In any case, at $T=100$ K the pattern strongly resembles a triplet powder pattern given by the spin Hamiltonian[14]

$$\mathcal{H}=\beta\mathbf{H}\cdot\overleftrightarrow{g}\cdot\mathbf{S}+D(S_z^2-\tfrac{1}{3}\mathbf{S}^2)+E(S_x^2-S_y^2)\ , \tag{1}$$

with $E\cong D/3$ and $D/g\beta\sim 520$ G. Such a pattern has steps and shoulders at $H\sim(h\nu\pm D)/g\beta$ and a singularity at $H\sim h\nu/g\beta$. In PPV, $D/g\beta\sim 580$ G and the pattern is slightly asymmetric, possibly because of a weak quenching ODMR.[15]

The $E\cong D/3$ triplet powder pattern was also observed in P3AT (Refs. 6 and 7) and in derivatives of poly(paraphenyleneacetylene)[15] and is thus believed to be an intrinsic feature in nondegenerate ground-state (semi)conducting polymers. However, there are some differences in the distribution widths and average values of D among these polymers. In P3AT, an axially symmetric $E\cong 0$ exciton was prominent at low temperatures (≤ 50 K), whereas the $E\cong D/3$ exciton was dominant above ~ 75 K.

An upper bound on the spatial extent r_{UB} of an exciton may be calculated from

$$D=\tfrac{3}{4}(g\beta)^2\langle (r^2-3z^2)/r^5\rangle\ . \tag{2}$$

Since $\langle (r^2-3z^2)/r^5\rangle \leq \langle 1/r^3\rangle$,

$$r_{\mathrm{UB}}\cong(\tfrac{3}{4}g\beta)^{1/3}(D/g\beta)^{-1/3}\cong 24.1(D/g\beta)^{-1/3}\ \text{Å}\ . \tag{3}$$

For $D/g\beta\cong 520$ G, $r_{\mathrm{UB}}\cong 2.9$ Å, which is slightly larger than the diameter of a benzene or thiophene ring. In light of early electron spin resonance (ESR) and light-induced ESR studies of naphthalene and triphenylene,[16] the $E\cong 0$ powder pattern ODMR in P3AT is assigned to excitons pinned to thiophene rings with the axis of symmetry normal to the molecular plane. The $E\cong D/3$ triplet powder pattern is then suspected to be due to mobile "free" triplet polaronic excitons. This interpretation is consistent with the temperature dependence of the triplet powder pattern in P3AT: As the temperature is increased, the $E\cong 0$ excitons become depinned, mobile $E\cong D/3$ excitons. The absence of an $E\cong 0$ exciton from the ODMR in PPV and PDHOPV may possibly result from weaker pinning by the aromatic rings. We thus interpret the PPV and PDHOPV powder pattern as resulting from a mobile intrachain exciton of effective size $r_{\mathrm{UB}}\cong 2.9$ Å.

The half-field resonance resulting from the $\Delta m_S=2$ transitions of the triplet polaronic exciton is displayed in Fig. 4. The dashed line is the resonance calculated from the parameters $D^*=(D^2+3E^2)^{1/2}\sim 600$ G used to fit the full-field pattern for PDHOPV. The peak position and shape are thus in excellent agreement with the full-field signals. The half-field pattern has a singularity at

$$H=(h\nu/2g\beta)[1-\tfrac{4}{3}(D^*/h\nu)^2]^{1/2}\ . \tag{4}$$

It is difficult to determine the value of E from the half-field pattern alone. When $E=0$, there is a second singularity at $H=(h\nu/2g\beta)[1-(D/h\nu)^2]^{1/2}$. This singularity, however, could not be detected using the present ODMR system, where H_1 is normal to H_0.[6] The other critical points for $E\neq 0$ are smeared out by the triplet angular dependence. The shapes of the half-field resonances of both $E=0$ and $E\neq 0$ triplets are thus expected to be similar under these conditions. The full-field parameters, though, yield a reliable value of D^*. The half-field powder pattern will decrease to zero at

$$H\cong(h\nu/2g\beta)[1-2(E/h\nu)^2]\ , \tag{5}$$

in agreement with the ODMR.

As in P3AT, the spectral dependence of the main narrow ODMR of PPV and PDHOPV shows the polaron levels to be close to the band edges. In contrast to P3AT, the half-field resonance of PPV and PDHOPV was sufficiently intense to determine its spectral dependence too. As seen in Fig. 4, the narrow resonance is slightly enhanced in the red region. If the observed triplet ODMR is due to direct decay to the ground state, the observed spectral dependence would imply that the triplet levels are close to the band edges. If, however, the decay is due to triplet-triplet collisions resulting in generation of singlets, the observed dependence would simply reflect the singlet level. This scenario would then support the assignment of the triplet pattern to free excitons. However, it implies a quadratic dependence of the exciton ODMR intensity on the laser photon flux in the weak flux limit. Yet a sublinear behavior is actually detected, corresponding to optical saturation at a power density of $\sim 2\mathrm{W/cm}^2$. This corresponds to ~ 3000 photons per monomer per second and may indeed be too high to yield a quadratic dependence. Further measurements at lower excitation intensities are underway and are planned to be reported later.[15]

Another similarity between P3AT and PPV derivatives is the (presumably) PL-quenching ODMR of similar width. The shape of this resonance in P3AT is difficult to determine because of the relatively complex $E \cong 0$ powder pattern at $T = 20$ K. In PDHOPV, however, the PL-quenching ODMR appears to resemble a Gaussian with a full width at half maximum of ~ 500 G. Assuming a lifetime-broadened resonance, the lifetime of the spin pair is ~ 700 ps, probably due to geminate singlet or pair decay. Time-resolved PL measurements indeed show that, in PPV and its derivatives, most of the radiative decay in stretch-oriented films occurs within ~ 700 ps.[13] This decay rate may be less in the unoriented samples studied in this work, accounting for the weak quenching ODMR observed in PPV.[15] The observed PL-quenching ODMR would then be due to this geminate process. Then the very-long-lived (>10-ns) polaron and triplet polaronic exciton decay and the short-lived geminate decay would all be significant PL channels.

In summary, the optically detected magnetic resonance (ODMR) of poly(paraphenylenevinylene) (PPV) and its dihexoxy derivative (PDHOPV) was described and discussed in comparison with a previous ODMR study of poly(3-alkylthiophenes) (P3AT). The main narrow resonance, assigned to intrachain "distant-pair" polaron recombination, was found to be significantly more symmetric than that of P3AT. This implies considerably stronger charge-conjugation-symmetry violation in P3AT, probably due to the sulfur containing thiophene ring. As in P3AT, the spectral dependence of this resonance is similar to the photoluminescence (PL) spectrum, implying that the polaron levels are close to the band edges. As in P3AT, a broad triplet powder pattern resulting from the $\Delta m_S = 1$ transitions of a triplet polaronic exciton and its half-field $\Delta m_S = 2$ transitions was also clearly observed. The zero-field parameters of this triplet, believed to be a free intrachain exciton, indicate a spatial extent $r_{\mathrm{UB}} \cong 3$ Å. Although the spectral dependence of the half-field resonance is also similar to the PL spectrum, this may result from decay via singlet generation from triplet-triplet collisions; then the spectral dependence is that of singlet excitons. Finally, a broad decrease in the ODMR intensity at $g \sim 2$ at low temperature is suspected to result from the significant singlet geminate exciton decay.

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