Optically Detected Magnetic Resonance Study of Polaron and Triplet-Exciton Dynamics in Poly(3-Hexylthiophene) and Poly(3-Dodecylthiophene) Films and Solutions

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The X-band optically detected magnetic resonance of poly(3-hexylthiophene) and poly(3-dodecylthiophene) films and solutions are described and discussed. The photoluminescence-enhancing features include (i) a strong, ~15-G-wide, asymmetric peak at $g \cong 2.003$; (ii) a weak peak at $g \cong 4.07$; and (iii) a weak, ~800-G-wide structure around $g \cong 2$. It is believed that feature (i) results from polaron recombination, and the others from the decay of two distinct intrinsic triplet polaronic excitons. The levels of all are apparently close to the band edges.

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Five-membered polyheterocycles in general, and polythiophene (PT) and its 3-alkyl derivatives (P3AT's) in particular, are prototypical weakly nondegenerate ground-state π-conjugated semiconducting polymers.[1] They can be oxidatively doped to conductivities exceeding 1000 S/cm,[2] exhibit a striking nonlinear optical response,[3] and are also soluble, processible, and stable in air.[4] The nonradiative decay channels of photogenerated e-h pairs into polarons within less than a picosecond, and of polarons into bipolarons from $\sim 10^{-9}$ to $\sim 10^{-3}$ sec, are well established.[1,5-7] Similar processes are observed during oxidative p doping.[1,6-9] The intrachain character of the long-lived radiative decay and the enhanced photoluminescence (PL) in solutions and short conjugation-length segments, due to suppression of interchain bipolaron generation, have also been established.[10-12] Yet the nature of the radiative process itself has not been settled. Kaneto and co-workers[10] attributed the PL to exciton decay. Early optically detected magnetic resonance (ODMR) results, however, were tentatively attributed to polaron recombination.[13] Similar PL spectra in polyparaphenylenevinylene (PPV) were interpreted in terms of "polaronic excitons."[7] The preliminary ODMR studies yielded only one PL-enhancing ODMR at $g \sim 2.003$, partially resolved into two components[13,14] possibly due to positive and negative polarons. This work provides new evidence supporting the polaronic nature of the main ODMR previously observed, and describes and discusses new ODMR features in films and solutions. These include a weak, broad PL-enhancing ODMR at $g \sim 2.0$ attributable to the $\Delta m_s = 1$ transitions of a triplet exciton, and a resonance at $g \sim 4.07$ resulting from its $\Delta m_s = 2$ transitions. The temperature dependence of the various resonances suggest the presence of two different intrinsic triplet polaronic excitons. We note that a recently detected photoinduced absorption peak in poly(3-dodecylthiophene) (P3DT) was tentatively assigned to a triplet-triplet transition of a polaronic exciton.[15]

Poly(3-hexylthiophene) (P3HT) and P3DT samples were processed from free-standing films as described elsewhere.[10,14] Dilute solutions of P3HT and P3DT in CCl_4, toluene, and CH_2Cl_2 were also similarly prepared, but only the CH_2Cl_2 solutions yielded a stable ODMR. The chopped-microwave ODMR system was also previously described.[14] 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, to prevent sample heating and optical saturation.

The total-PL ODMR spectra observed in P3HT and P3DT films are similar and consist of five features, all but one of which are enhancing. (i) The strong narrow resonance at $g = 2.003$ (Fig. 1), (ii) a broad pattern about $g \sim 2$ below 50 K (Fig. 2), (iii) a different broad pattern about $g \sim 2$ above 50 K (Fig. 2), (iv) a narrow weak signal at $g \sim 4.07$ (Fig. 3), and (v) weak PL-quenching wings observable below ~50 K at $\sim 3.3 \pm 0.3$ kG (i.e., symmetrical about $g \sim 2.0$) (Fig. 2).

The narrow resonance (Fig. 1) is the sum of wide ($\Delta H_{1/2} \cong 12$ G) and narrow ($\Delta H_{1/2} \cong 5$ G) Gaussians at $g = 2.0032$ and 2.0019 (± 0.0005), respectively, independent of temperature. The observed shape could not be synthesized by Lorentzians.[14] The components saturate at different microwave powers,[14] indicating distinct

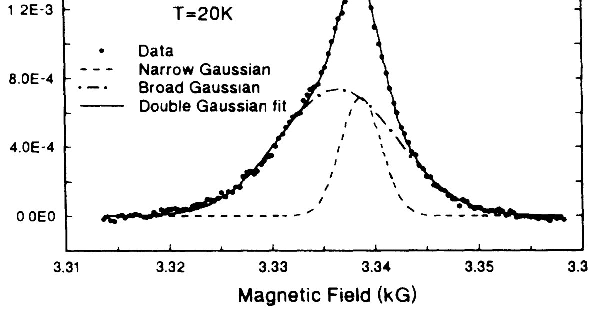

FIG. 1. The main narrow ODMR in poly(3-hexylthiophene) and poly(3-dodecylthiophene) films and solutions. It is dependent on microwave power P (see Ref. 16) but not on temperature.

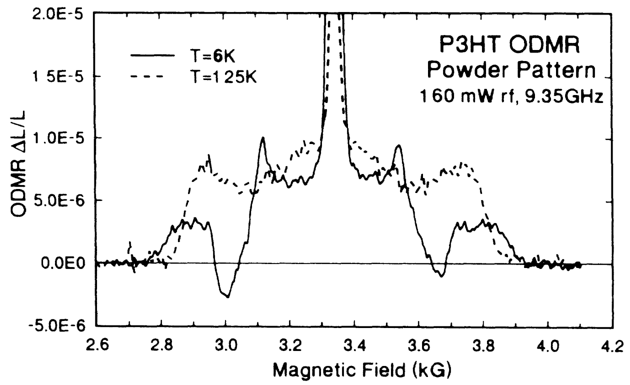

FIG. 2. The broad $\Delta m_s = 1$ triplet ODMR at 6 and 125 K.

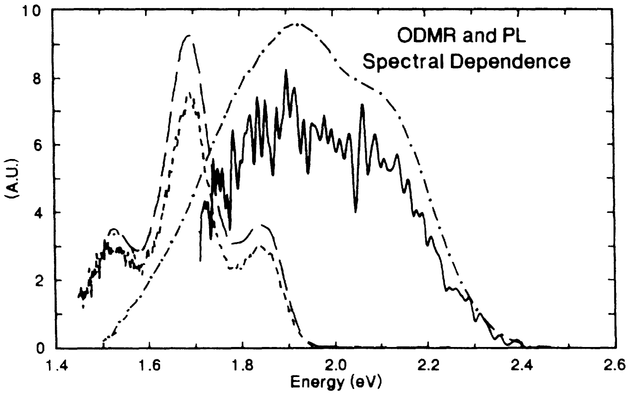

FIG. 4. The photoluminescence (PL) and spectral dependence of the main narrow ODMR in films at 20 K (— — — and ---, respectively) and CH_2Cl_2 solutions at 300 K (-··· and ——, respectively).

sources. Although the PL of the solutions (Fig. 4) is blueshifted by 0.3–0.5 eV and the ~0.17-eV phonon replicas are smeared due to radiative decay from chains widely distributed in length,[7,10,11,14] the main narrow ODMR is the same as in the films.

In order to identify the PL band responsible for the main ODMR, its spectral dependence was measured coincidentally with the PL in both films and CH_2Cl_2 solutions. Figure 4 shows that the ODMR intensity ΔL is everywhere proportional to the PL intensity L (i.e., $\Delta L/L$ is constant). Hence the entire PL spectrum contributes equally to the main ODMR.

Figure 2 displays the broad ODMR at 6 and 125 K. All other variables such as sample, microwave power, laser line, and power are identical. Note the obvious PL-quenching ODMR ~300 G above and below $g \cong 2.0$ at 6 K, and the changed pattern at 125 K. At 6 K the integrated ODMR intensity of the broad pattern is ~1.5 times that of the main narrow peak. The spectrometer sensitivity did not enable the detection of the broad pattern in solution, nor its spectral dependence in the films.

The integrated intensity ΔL of the weak half-field resonance (Fig. 3) is about $\frac{1}{35}$ that of the broad pattern at 6 K. These two features indicate the existence of a triplet polaronic exciton[7,15] contributing to the PL (see below).

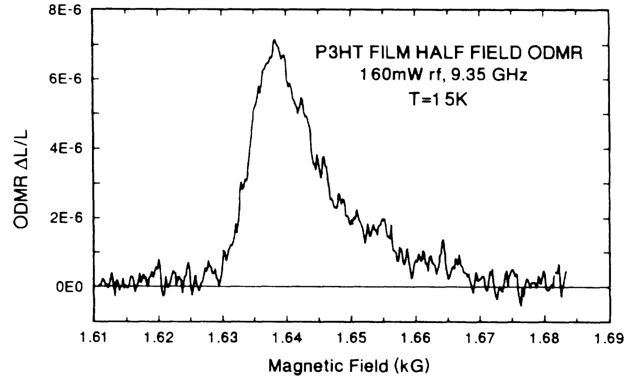

FIG. 3. The $\Delta m_s = 2$ triplet ODMR at 15 K. It is shifted 32 G downfield from $g = 2 \times 2.003$, and is reproducible from the triplet spin Hamiltonian [Eq. (2)], with the same D and E values as those of the low-T broad powder pattern shown in Fig. 2.

The temperature dependence of the integrated $\Delta L/L$ of each resonance is plotted in Fig. 5. Note that for the main narrow ODMR, the $g \sim 4.07$ resonance, and the broad pattern above ~100 K,

$$\Delta L/L \propto \exp(-T/T_0)\,, \tag{1}$$

where $T_0 \cong 80$ K. The temperature dependence of the $g \sim 4.07$ resonance, resulting from the $\Delta m_s = 2$ transition of a triplet exciton, is similar to that of the main narrow resonance. Yet they are not related. If the main narrow ODMR were due to the $\Delta m_s = 1$ transitions of a triplet exciton, its zero-field splitting parameters[16] would be very small. The $\Delta m_s = 2$ transition of that resonance would then yield a strong Gaussian resonance at *very nearly* half field, of width similar to that of the main resonance. Yet the $g \sim 4.07$ resonance is shifted downfield by 32 G, and its shape is highly asymmetric. It is be-

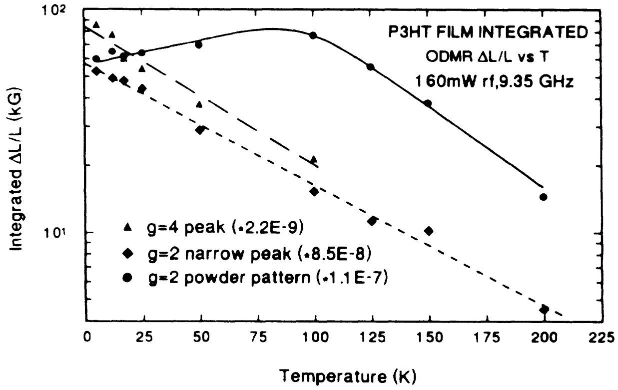

FIG. 5. The temperature dependence of the various photoluminescence-enhancing resonances shown in Figs. 1–3. Note the unusual dependence of $\Delta L/L$ on T [$\propto \exp(-T/T_0)$], where $T_0 \cong 80$ K.

lieved that this ODMR is related to the triplet exciton producing the low-T broad pattern (see below). The source of the main narrow ODMR at $g \sim 2.003$, clearly an intrinsic intrachain radiative channel identical in all P3AT films and solutions, is therefore not a triplet exciton. It is thus attributed to recombining "distant"[17] positive and negative polarons. At present it is not possible to determine which g value is that of the positive or negative polaron. If this assignment of the two Gaussian components of the main narrow ODMR is correct, however, it provides the first experimental evidence for (unexpectedly slight) charge-conjugation symmetry violation in a conducting polymer.[18]

The PL and the spectral dependence of the main narrow ODMR (Fig. 4) then clearly show that polaron recombination is responsible for much of the PL. More importantly, it indicates that the polaron levels are very close to the band edges. Although some previous studies have suggested that these levels are near the bipolaron levels,[1,9] these previous conclusions were debatable. Theoretical studies[6] and experimental results on PPV[7] are consistent with polaron levels that are close to the band edges.

Figures 2 and 3 show that polaron recombination is not the only source of the long-lived PL. We now focus on the polaronic excitons producing the broad ODMR at $g \sim 2$. Ignoring the PL-quenching ODMR wings and the main narrow ODMR, the low-T pattern strongly resembles a triplet powder pattern[19] given by the Hamiltonian[16]

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

It yields $E = 0$ and $D/g\beta \sim 560$ G. Such a pattern has steps at $H \cong (h\nu \pm D)/g\beta$, singularities at $H \cong (h\nu \pm D/2 - D^2/8h\nu)/g\beta$, and no shoulders. The observed positions of the singularities are shifted toward $h\nu/g\beta$, apparently by the quenching ODMR.

Although two singularities should be present in the $\Delta m_s = 2$ powder pattern, only that at $(h\nu/2g\beta)[1 - \frac{4}{3}(D/h\nu)^2]^{1/2}$ is detectable when H_1 is normal to H_0.[19] The transition probability vanishes for the other at $(h\nu/2g\beta)[1-(D/h\nu)^2]^{1/2}$ and decreases to zero at the step at $h\nu/2g\beta$, resulting in the observed extended tail.[20] When $E \neq 0$ the first-order transition probability vanishes for both singularities when H_1 is normal to H_0 and none is detectable by our spectrometer.[2] Indeed, the shape of the $\Delta m_s = 2$ resonance does not change with temperature and is thus assigned to the low-T $E = 0$ triplet polaronic exciton only.

Figure 5 shows that the integrated ΔL of the broad powder pattern increases and its shape changes with T up to ~ 100 K, indicating changes in D and E. This change occurs within a narrow temperature range around ~ 50 K. The low-T satellite singularities disappear and are replaced by a broad singularity at the center superimposed on the main narrow resonance; shoulders occur at the step locations. For this high-T pattern, Eq. (2) yields $E = D/3$, a single singularity at $H \cong h\nu/g\beta$, and both steps and shoulders at $H \simeq (h\nu \pm D)/g\beta$.

It thus appears that the main narrow resonance, the $\Delta m_s = 2$ ODMR, and the low-T broad pattern all decrease similarly with increasing T (Fig. 5). Since the high-T broad pattern is distinct, we suggest that two different intrinsic triplet polaronic excitons exist simultaneously along with polarons, all contributing to the PL. Since the spectral dependence of neither the broad pattern nor the $g = 4.07$ resonance could be determined, their contribution L_i to the PL is not clear at present. Yet the integrated intensity $\Delta L_i/L$ of the broad ODMR is 1.5 times that of the main narrow resonance at 5 K, and much higher at 100 K. L_i is therefore insignificant only if $\Delta L_i/L_i$ is much higher, which appears improbable (see below) but is not ruled out. If $\Delta L_i/L_i$ is similar to that of the main narrow ODMR, then their spectral dependence should also be similar, i.e., mirroring the PL itself. This conclusion is also expected from the proximity of the polaronic exciton and polaron levels to the band edges and each other. Indeed, if their levels were significantly separated, their phonon replicas would smear each other.

The density of $E = D/3$ triplet polaronic excitons increases dramatically from 5 to 100 K, where it saturates and becomes essentially constant. At present we cannot determine if either of the excitons is free or pinned. It may be speculated that the lower-symmetry $E = D/3$ exciton is pinned at thermally generated conformational defects. Its rising intensity, and that of the PL from 5 to 100 K, would then be possibly due to an increasing density of such defects. Yet this scenario cannot explain the emergence of this high-T exciton within a narrow range above 50 K.

The PL intensity increases by $\sim 25\%$ from 6 to 100 K, and decreases by $\sim 20\%$ from 100 to 300 K, where its yield is $\sim 0.7\%$ in films and $\sim 7\%$ in solutions. The radiative yield is thus roughly constant below 300 K. We suspect that the $\exp(-T/T_0)$ behavior [Eq. (1)] is due to similar spin-lattice relaxation mechanisms. A calculation of the ODMR transition rate yields[20]

$$\Delta L/L \propto R_s T_1\,, \tag{3}$$

where R_s is the singlet recombination rate and $1/T_1$ is the spin-lattice relaxation rate. Equations (1) and (3) then yield

$$1/T_1 \propto \exp(T/T_0)\,, \tag{4}$$

clearly not a phonon-mediated mechanism.[21] Exciton-exciton collisions, established as dominant decay channels in some organic salts[16] and polysilanes,[22] and similar polaron-polaron and polaron-exciton collisions may possibly provide the spin-lattice relaxation in the P3AT's. As T is increased, the excitations will rapidly migrate to the longest conjugation-length segments of the chains. Their collision rate will increase as their density and mobility increases with T. This scenario is obviously speculative at present.

At present we can only wonder whether the nonradiative, spin-dependent decay of two spin-$\frac{1}{2}$ polarons into spinless bipolarons yields the observed PL-quenching ODMR. This resonance is not due to geminate singlet exciton decay, which would yield a very weak, several-kilogauss-wide line.

In summary, several distinct intrinsic radiative channels in poly(3-hexylthiophene) and poly(3-dodecylthiophene) films and solutions were identified by X-band ODMR. The photoluminescence-enhancing features included the following: (i) A strong narrow line partially resolved as two Gaussians at $g=2.0032$ and 2.0019 (± 0.0005) and attributed to positive and negative polaron recombination. (ii) A broad pattern at $g \sim 2$, observed at 5-50 K, was assigned to the $\Delta m_s = 1$ transitions of intrinsic $E \cong 0$, $D \cong 560$ G triplet polaronic excitons. (iii) The $\Delta m_s = 2$ transitions of these excitons were clearly observed at $g = 4.07$. (iv) A second intrinsic powder pattern, where $E = D/3$, emerging above 50 K, was assigned to a distinct triplet polaronic exciton. (v) Below 50 K, weak PL-quenching wings were observed at ± 300 G about $g \sim 2$. The spectral dependence of the main narrow ODMR and the temperature dependence of the various resonances suggest that the polaron and triplet polaronic exciton levels are close to the band edges. The temperature dependence of the resonances was also discussed in relation to exciton-exciton, polaron-exciton, and polaron-polaron collisions.

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