AN OPTICALLY DETECTED MAGNETIC RESONANCE STUDY OF RECOMBINATION MECHANISMS IN POLYTHIOPHENE

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ABSTRACT

From detailed optically detected magnetic resonance measurements in polythiophene, we show that the g=2.003 signal is luminescence enhancing, and that the signal comes from a broad photoluminescence band peaking near 1.65 eV. This band is tentatively assigned to the radiative recombination of polarons, with lifetimes between 10^{-8} and $5x10^{-5}$ sec.

INTRODUCTION

Polythiophene (PT) is a representative of the large class of conjugated polymers with a nondegenerate ground state, where polarons and bipolarons, rather than solitons, are the expected charge carriers upon injection by doping or photoexcitation [1].

Photoinduced absorption experiments [2] give evidence that spinless bipolarons are the dominant long-lived photoexcitations in PT for excitation photon energies above the energy gap, although polarons (s=1/2) are expected to play a transient role in the formation of bipolarons. Doping of PT at low concentrations [3] also proceeds in an essentially spinless manner, although some studies [4,5] have shown an increase in the susceptibility followed by a subsequent decrease as the dopant concentration increases; this is interpreted as a transition from polaron to bipolaron regimes.

Band-edge photoluminescence (PL) in PT, peaking at 1.95 ± 0.05 eV, has been reported by several groups [6-9]. Phonon sidebands are evident in some studies [6,8], but others [7,9] report only a single broad band. As in cis-$(CH)_x$, the PL quantum efficiency is $\sim10^{-5}$, and is nearly temperature independent. Picosecond studies [7] show a decay time of less than 9ps. In the excitation profile [6] the PL quantum efficiency exhibits a sharp step-like rise at 1.95 eV, which is the zero phonon band of the PL. The absence of phonon sidebands in the excitation profile and the lack of a Stokes shift between excitation and emission energies suggests that the band-edge PL is due to the recombination of excitons [6].

In this paper we report the first detailed study of optically detected magnetic resonance (ODMR) in PT. Preliminary results were reported by Shinar el al [10] and Vardeny et al [6]. By observing changes in the PL intensity as electron spin resonance conditions are met, we can study the role of polarons and other paramagnetic species in radiative and nonradiative recombination in neutral PT.

EXPERIMENTAL PROCEDURE

Two types of samples were studied: a pressed KBr pellet (sample c-PT) containing approximately 0.25 wt. % PT powder obtained by condensation polymerization of 2, 5-diodothiophene [11] (the same sample studied in ref. 6 & 10), and PT films (samples e-PT) electrochemically polymerized from dithiophene [12].

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For all measurements, the samples were mounted in a helium gas flow cryostat fitted to an X-band ESR cavity. The experimental apparatus and methods for the ODMR are similar to that described in [6]. The PL was usually excited by the 5145Å argon line. For excitation profile experiments other argon lines as well as krypton and R6G dye laser lines were used. The PL was collected by lenses, dispersed by a grating monochromator with 30 meV resolution, and detected by a silicon detector. Slits in the cavity face provided optical access for ODMR experiments. The spectral dependence of the ODMR was obtained by setting the magnetic field to a peak in the ODMR derivative spectrum, and monitoring the strength of this peak as the monochromator setting was scanned across the PL band.

EXPERIMENTAL RESULTS

PL band

In Fig. 1 we show the normalized spectra of PT (sample c-PT) at 20K and 290K; these have been corrected for monochromator and detector response, but not for reabsorption. The PL exhibits phonon sidebands at both temperatures,with the zero-phonon line near 1.95 eV, and with spacing of about 0.18 eV, as previously reported [6]. However, when proper corrections are taken into account, the PL peaks at about 1.65 eV, rather than near 2.0 eV.

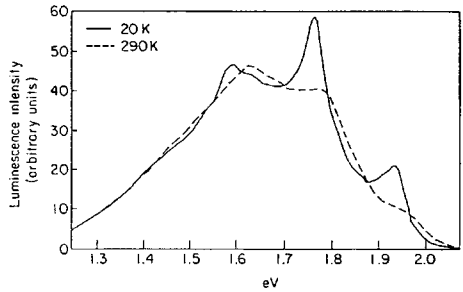

Fig. 1. Corrected PL spectrum of PT (sample c-PT).

The integrated PL intensity decreases only slightly and shifts to higher energies with increasing temperature. However, the intensity of the phonon sidebands decreases considerably relative to the broad peak.

ODMR Measurements

The derivative ODMR spectrum for the c-PT sample at 35K is shown in Fig. 2a. In the previous reports of the ODMR in PT [6,10], the phase (or sign) was compared with the derivative signal of a-Si:H, and a direct measurement could not be attempted. We therefore determined the sign of the ODMR by extensive signal averaging of direct measurements of the PL intensity vs. magnetic field. As clearly seen in Fig. 2b, the change is PL enhancing, and represents a total relative change in intensity ($\Delta L/L$) of about 1.5×10^{-3}.

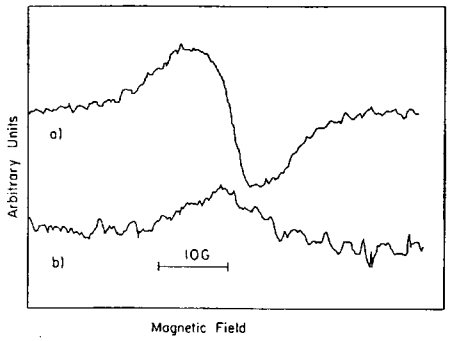

Fig. 2. ODMR in c-PT. a) Derivative (field modulated) spectrum. b) Direct observation of PL enhancing effect.

The ODMR signals for both c-PT and e-PT are centered at g=2.003, and have a peak to peak linewidth of about 10 gauss. ΔL/L decreases by two orders of magnitude between 4.5 and 250K (Fig. 3). The linewidth and g-value do not change over this large temperature range.

The ODMR efficiency (ΔL/L) shows a strong dependence on exciting laser wavelength. Fig. 4 shows that the efficiency increases by a factor of about 5 as the photon energy increases from 1.8 to 2.1 eV, the range covered by the krypton and dye lasers. We note that no correction for absorption or reflection factors is needed in ΔL/L. There is no observable change above 2.4 eV, as determined by using the argon laser lines.

The spectral dependence of the ODMR (ΔL) is shown in Fig. 5, together with the PL (L) which was measured under identical conditions. To improve the signal to noise ratio in the experiment, the monochromator slits were opened to four times their usual setting. Despite the poor resolution, this measurement clearly shows that it is the broad band, rather than the phonon sidebands, that gives rise to the ODMR.

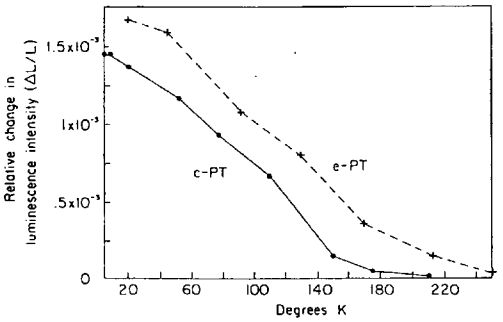

Fig. 3. Temperature dependence of the ODMR efficiency ΔL/L.

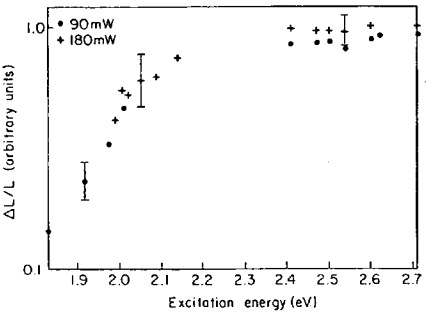

Fig. 4. Excitation dependence of the ODMR efficiency ΔL/L in c-PT at 20K. • and + denote the appropriate laser intensities.

DISCUSSION

PL

The PL band we observed in our samples is quite different from the published results [6-10], even though the c-PT sample is identical to the PT sample studied in refs. 6 and 10. The corrected PL peaks at 1.65 eV rather than near 2.0 eV, and the phonon sidebands are less pronounced. Although we have not yet performed a complete study of the excitation dependence of the PL itself, we have observed that the sharp step-like rise in the PL efficiency at 1.95 eV is not present in our samples. We conclude that changes in the sample due to ageing or laser irradiation (unfocused laser beam of up to 600 mW) have shifted the PL intensity from the excitonic spectrum that includes the phonon sidebands, to a broad peak that may underlie the spectra previously reported in ref. 6-10.

We note that the PL in e-PT (not shown) is very similar to that shown in Fig. 1, with a slight blue shift. These samples were made very recently, and should not show long term ageing effects. The nature of these differences is not known at the present time.

ODMR Studies

The observation of an ODMR signal gives indirect evidence that there are PL lifetimes much longer than the picosecond decay observed by Wong et al [7], which is attributed to fast nonradative decay in parallel with slower radiative decay. The observed ODMR derivative peak to peak width ΔH_{pp}=10G indicates, from lifetime broadening considerations, that some excitations involved in the PL have lifetimes exceeding 10^{-8} sec. However, we do not see a chopping-frequency (up to 1kHz) dependent phase shift of the PL with respect to the reflected laser light, and we conclude that the lifetime of the bulk of the PL is less than 50 μsec.

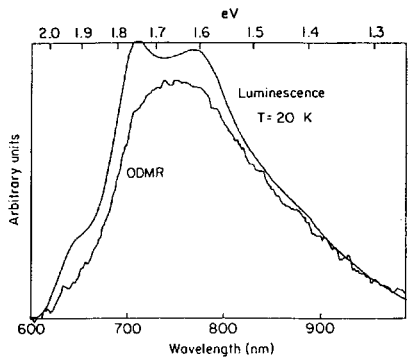

Fig. 5. Spectral dependence of the ODMR and luminescence at 20K in c-PT (uncorrected for response).

Since the ODMR is PL enhancing, these results do not support the model previously proposed [6,10] for the ODMR in PT. This model assumed quenching ODMR, and assigned the signal to the modulation of a nongeminate, nonradiative recombination channel through spin dependent capture of unthermalized photocarriers at the dark ESR centers (also near g=2.003).

A nonradiative channel could be responsible for an enhancing ODMR, if nonradiative **geminate** recombination of unthermalized spins, in competition with the radiative channel, is assumed. In this case most photoexcited electron-hole pairs do not separate, and are in their original antiparallel spin configuration. Then at spin resonance parallel spin pairs are created which cannot recombine quickly, allowing these pairs to dissociate. If this dissociation enhanced the probability of radiative recombination with other carriers, then spin resonance would increase the PL.

However, the excitation dependence of the ODMR shows increased efficiency with higher energy photons. We interpret this as the creation of hot photocarriers at higher energies, which would increase the probability of nongeminate recombination. This suggests that the ODMR describes a **nongeminate** recombination process. Then the enhancing signal implies that the radiative channel itself is spin dependent. If so, it is unlikely that the enhancing ODMR signal is due to the dark ESR centers, which should be located near the center of the gap [13] at ~1-1.1 eV for E_g~2.0-2.2 eV. Radiative capture at these centers would yield PL peaking at energies near half the band gap, as is seen in the g=2.0065 enhancing hole-dangling bond ODMR in amorphous silicon [14]. However, the spectral dependence shows that the ODMR in c-PT comes from a broad band peaking at 1.65 eV, which is ~0.8 E_g.

We note that in PT both the LESR [15] and the doping induced spins [5], assigned tentatively to the creation of polarons, have g-values very close but not equal to that of the dark ESR. The broad band PL in PT could be explained by the nongeminate radiative recombination of hole and electron polarons:

$$P^+ + P^- = 2P^o + h\nu. \quad (1)$$

Although pairs excited on the same chain are expected to recombine quickly because of the confinement potential [16], electron and hole polarons photoexcited on neighboring chains can easily drift away from each other. Indeed such a mechanism has been suggested [2] as a first step for the creation of bipolarons. Two such polarons of opposite charge could recombine radiatively when they appear on the same or neighboring chains.

The hole and electron polaron levels are separated in the gap by the energy $2\omega_{bp}$, the magnitude depending on the strength of the confinement potential and the occupation of the levels. Recent observation of bipolaron states in PT by photoinduced absorption [2] gives the bipolaron level splitting $2\omega_{bbp}$=0.8eV (i.e. $2\omega_{bbp}$=0.4 E_g). The level splitting, $2\omega_b$, is predicted to be always larger for polarons than for bipolarons, and in the calculations of Fesser et al [17], for a bipolaron level splitting of 0.4 E_g, the polaron splitting $2w_{op}$ is predicted to be 0.8 E_g, or 1.6-1.7 eV, which is at the peak of the broad PL band responsible for the ODMR. The width of this polaron PL band (~0.4 eV at half maximum) is comparable to the width of the photoinduced bipolaron absorption bands seen in the same c-PT sample [2].

Since charged polarons carry spin 1/2, the recombination of P^+ and P^- is spin dependent. P^+-P^- loosely bound pairs in the antiparallel spin configuration recombine rapidly, and in steady state the parallel pair population is much larger than the antiparallel one. We note that in a steady state ODMR experiment such as described here, changes in the PL intensity can occur only if there is a nonradiative channel (here assumed to be spin-independent) in competition with the radiative recombination. Enhancement of PL intensity occurs under resonant conditions, when parallel spin pairs are converted to antiparallel ones.

The large drop in the ODMR ($\Delta L/L$) between 4.5K and room temperature is probably due to a decrease in the spin-lattice relaxation time with increasing temperature; spin-phonon interactions act to thermalize spins so that resonant absorption of microwaves has a smaller relative effect on the PL magnitude. However, the model of thermally activated hopping or tunneling of spins between inequivalent sites proposed by Davidov et al [13] to account for the temperature dependence of the spin relaxation of the dark ESR does not explain the temperature dependence of the ODMR, since in their model one would not expect significant relaxation at temperatures much less than $kT \sim \Delta$, where Δ is the typical energy difference between the inequivalent sites. Davidov et al predict Δ~190K, whereas the spin-relaxation in the ODMR is significant at temperatures as low as 20K. This is additional evidence that the dark ESR does not account for the spin-dependent recombination channel observed in the ODMR.

CONCLUSIONS

In summary, we have shown that radiative electron and hole polaron recombination can account for the broad-band PL and ODMR in PT. Although spinless bipolarons are the dominant excitation at long times (~5ms) [2], ODMR studies of electron and hole polarons at intermediate times can provide valuable information about polaronic transport and recombination. Time-resolved ODMR, PL, and photoinduced absorption measurements will be particularly illuminating.

ACKNOWLEDGEMENTS

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