

# Exciton Dynamics in Soluble Poly(*p*-phenylene vinylene)

By S. V. Frolov, M. Liess, P. A. Lane, R. K. Meyer, and Z. V. Vardeny  
University of Utah, Department of Physics  
Salt Lake City, UT 84112

## ABSTRACT

We report studies of poly(2,5-dioctyloxy paraphenylene vinylene) thin films and solutions by a variety of transient, steady state, and nonlinear optical techniques. The energy states and optical absorption of the dominant even and odd parity excitons have been determined. Photogenerated singlet excitons are characterized by strong stimulated emission and *two* photoinduced absorption bands. Triplet excitons are found to have a single absorption band; intersystem crossing time from the singlet to the triplet manifolds is estimated to be  $\sim 4$  ns in films and  $\sim 20$  ns in solutions.

## 2. Introduction

The most striking optical property of many  $\pi$ -conjugated conducting polymers is a bright photoluminescence (PL) band with high quantum efficiency, which can be chemically tuned to cover the complete visible spectral range [1]. Their application in optical emission devices such as light emitting diodes and, more recently, laser-active media has led to intensive investigations of conducting polymers, such as poly(*p*-phenylene-vinylene) [PPV] and its derivatives [2]. Attention has focused particularly on the properties of photogenerated excitons in neat films of these materials [3]. However, the exact spectral signatures of photoexcitations in PPV, i.e., singlet excitons, triplet excitons and polaron pairs, have remained unclear so far because of overlapping spectral features in the visible to near IR spectral range [3].

In this paper we concentrate on 2,5-dioctyloxy PPV [DOO-PPV] films and dilute solutions. We have elucidated the dynamics, absorption and emission properties of excitons in neat films and dilute solutions of DOO-PPV, using a variety of cw and transient ps optical techniques. We also identified and measured the absorption spectra of long-lived excitations, i.e., polarons, bipolarons, and triplet excitons. Linear absorption techniques used were transient and cw photomodulation (PM) measurements and photoinduced absorption detected magnetic resonance (PADMR). Nonlinear techniques used were two-photon absorption (TPA) and electroabsorption (EA) spectroscopies. We show that the photogenerated singlet excitons are the primary excitations in both neat films and solutions with an intersystem crossing time of order 5 ns. We prove that the singlet excitons are characterized by a stimulated emission (SE) band at 2.2 eV accompanied by phonon replicas, and two PA bands at 0.9 eV and 1.5 eV, respectively. The PA bands are due to optical transitions of the excitons to even-parity electronic states at 3.0 eV and 3.5 eV, respectively.

## 3. Experimental techniques

Transient PM measurements were performed using the pump-and-probe correlation technique employing two lasers synchronously pumped by a modelocked Nd:YAG laser [4]. The pump photon energy was fixed at 2.2 eV, whereas the probe photon energy was varied between 0.76 eV and 0.86 eV, using a color center laser, and from 1.25 to 2.2 eV, using a dye laser, respectively. The time resolution of the transient PM apparatus was 5-10 ps, as determined by a measurement of pump-probe cross-correlation. The transient PL decays were measured with a

streak camera having 10 ps time resolution in a synchroscan mode. Transient PM measurements were conducted at low exciton densities ( $N < 10^{17} \text{ cm}^{-3}$ ) to avoid significant exciton-exciton interactions.

The two photon absorption spectra were measured by the Z-scan technique [1]. Open and reduced-aperture Z-scans were conducted over a spectral range of 576 to 846 nm using various laser dyes in a three-stage dye amplifier system pumped by a Nd:YAG regenerative amplifier. Z-scan data were analyzed graphically to acquire the transmission changes. The nonlinear absorption,  $2$ , was calculated at the  $Z=0$  position by varying  $2$  to minimize the difference between the measured and calculated spectrum. The linear absorption spectra were obtained for DOO-PPV in a chloroform solution using a Perkin Elmer Lambda 9 spectrophotometer.

A standard steady-state PM set-up was used for the cw optical measurements [1]. The pump was a modulated beam from an Ar<sup>+</sup> laser and the probe was an incandescent lamp. For the PADMR spectra, the sample was placed in an S-band  $\pi$ -wave cavity between the pole pieces of a superconducting electromagnet. We measured the changes in PA induced by resonant absorption of modulated  $\mu$ -waves [7]. Magnetic field swept H-PADMR data (at fixed probe wavelength) are presented, as well as  $\lambda$ -PADMR data (at fixed H with a swept probe wavelength). A similar set-up was also used for the EA measurements [1], where  $\Delta T$  is caused by a modulated electric field in the polymer film, of order  $10^5 \text{ V/cm}$ .

#### 4. Results and discussion

The transient PM spectra of DOO-PPV films at 300K are shown in Fig. 1 for time delays  $t=0 \text{ ps}$  and  $1.2 \text{ ns}$ , respectively. Above  $1.7 \text{ eV}$ , we measured  $\Delta T > 0$ . As DOO-PPV has no absorption in this energy range, this band must be due to SE rather than photobleaching of the absorption [3,]. We observed two PA bands with  $\Delta T < 0$ , peaking at  $\approx 0.9 \text{ eV}$  (PA<sub>1</sub>) and  $1.5 \text{ eV}$  (PA<sub>2</sub>), respectively. The SE band contains several phonon replicas at  $\sim 1.8$ ,  $1.98$  and  $2.15 \text{ eV}$ , respectively, which are very similar to those in the cw PL spectrum (see below). The decay dynamics of the SE, PA<sub>1</sub> and PA<sub>2</sub> bands are compared to that of the PL band in the inset of Fig. 1. Except for PA<sub>2</sub>, all show a single exponential decay dynamics with lifetime  $\tau_s = 240 \text{ ps}$ . We note that so far this  $\tau_s$  is the longest SE lifetime that has been measured in conducting polymer films [9]. PA<sub>2</sub> initially follows the same exponential decay dynamics up to  $\sim 300 \text{ ps}$ , then it deviates and becomes much slower, dominating the PM spectrum at longer times. The PM spectrum at  $t=1.2 \text{ ns}$  contains only a single asymmetric PA band, which is slightly blue-shifted from PA<sub>2</sub>, while PA<sub>1</sub> and SE are barely detectable at  $1.2 \text{ ns}$ .

We observed similar PM spectra in DOO-PPV dilute solutions, shown in Fig. 2. PA<sub>1</sub>, PA<sub>2</sub> and SE can be again identified at the same probe photon energies as those in films. The excitons in solution are longer-lived ( $\tau_s \approx 440 \text{ ps}$ ), and PA<sub>2</sub> deviates from a single exponential dynamics at much longer times ( $> 1 \text{ ns}$ ). As the polymer chains in dilute solutions are isolated from each other, the formation of polaron pairs is suppressed. The primary excitations in DOO-PPV dilute solutions must therefore be singlet excitons. Then from the similarity of the PM spectra and their decays in DOO-PPV films and dilute solutions, we conclude that the primary excitations in DOO-PPV films are also singlet excitons [4,]. We can thus calculate the radiative quantum efficiency,  $\eta$ , in films and solutions from the relation  $\eta = \tau_s / \tau_0$  [4], where  $\tau_0$  ( $\sim 1 \text{ ns}$  in PPV-based polymers [1]) is the exciton natural radiative lifetime. Using this relation and the measured  $\tau_s$ , we estimate for DOO-PPV films  $\eta = 24\%$ , and for solutions  $\eta = 44\%$ , respectively. Such a high PL quantum efficiency indicates that DOO-PPV is a high quality polymer material, suitable for electrooptics and laser action applications [1].

SE can be used to prove that PA<sub>1</sub> and PA<sub>2</sub> bands are due to transitions of singlet excitons [5]. Between the pump and probe beams, a third beam is focused onto the sample. The "dump" pulse causes SE, reducing the population of singlet excitons. At the same time, the intensities of both the PA<sub>1</sub> and PA<sub>2</sub> bands are markedly diminished. This proves that these bands must be due to optical transitions of singlet excitons.

The PM spectrum of excitons in DOO-PPV is schematically explained in Fig. 3, which shows the ground and excited electronic levels and their associated optical transitions in a configuration coordinate (Q) diagram [1]. The pump beam induces transitions from the ground state ( $1A_g$ ) to the first allowed excitonic state ( $1B_u$ ). Following a relatively small relaxation ( $\sim 0.1 \text{ eV}$ ), SE can then occur between the relaxed  $1B_u$  and unrelaxed ("hot")  $1A_g$ . Since

the high-frequency phonon occupation of the "hot"  $1A_g$  state is negligibly small at room temperature, this leads to population inversion between  $1B_u$  and  $1A_g$  following photoexcitation. In addition to SE, PA from  $1B_u$  to higher energy levels occurs for two even-parity states, namely,  $mA_g$  and  $kA_g$  (Fig. 3).

We have directly measured the energies of these two  $A_g$  states in solution by two-photon absorption (TPA) spectroscopy and in film by electroabsorption (EA) spectroscopy. The linear and two-photon absorption spectra of a dilute DOO-PPV solution are shown in Fig. 4(a). Guides for the eye are included to accentuate feature suggested by the data points. The TPA spectrum exhibits a strong band at 3.2 eV and a weaker one at 3.5 eV. We assign the lowest energy band to the  $mA_g$  essential state. Although the 2 data for the other peak ( $kA_g$ ) is not as convincing as that for the  $mA_g$ , the dispersion in  $n_2$  [6] confirms its existence. We note that recent elegant theoretical calculations have identified  $mA_g$  as a charge transfer exciton and  $kA_g$  as a biexciton (bound state of two excitons) [1]. However, the exact character of these states cannot be inferred from our measurements.

The energy level diagram in Fig. 3 is further substantiated by the EA spectrum measured on a thin DOO-PPV film, shown in Fig. 4(b). The EA spectrum is composed of a derivative-like feature with zero-crossing at 2.25 eV, due to the quadratic Stark shift of the  $1B_u$  exciton at this energy [8], and bands at 3.0 and 3.5 eV, respectively. These bands are due to even parity states ( $mA_g$  and  $kA_g$ ), which become partially allowed in EA due to symmetry breaking caused by the strong applied electric field  $F$ . We successfully simulated the EA spectrum [Fig. 4(b)] by calculating the imaginary part of the third order optical nonlinear susceptibility [13],  $\text{Im}(\chi^{(3)}(\omega, -\omega, 0, 0))$ , where  $\Delta\alpha(\text{EA}) \sim \text{Im}(\chi^{(3)})F^2$ . Calculations were done using summation over the states shown in Fig. 3, and their strongly coupled vibrations using appropriate Frank-Condon overlap integrals [13]. The fitting parameters were  $1B_u$ ,  $mA_g$  and  $kA_g$  energy levels, their dipole couplings and relative configuration coordinate displacements,  $\Delta Q$ ; whereas the frequency of the strongest coupled C=C stretching mode (1600  $\text{cm}^{-1}$ ) was directly determined by Raman scattering. Using the fitting parameters of the EA spectrum, we were also able to calculate the PA spectrum from the relaxed  $1B_u$  exciton to the  $mA_g$  and  $kA_g$  levels using the Huang-Rhys approximation (Fig. 3). The calculated spectrum agrees very well with the experimental PA bands at  $t=0$  ps (Figs. 1,2).

The slower component of  $PA_2$  deviates from the respective SE and  $PA_1$  decays, which correspond to singlet excitons dynamics,  $N(t)$ , at about 300 ps in DOO-PPV films (Fig. 1, inset). This slower PA component can be measured at 300K by cw PM. The cw PM spectrum (Fig. 5) is dominated by a peak at 1.45 eV, for which there is no correlated PA band at 0.8 eV. From the modulation frequency dependence of the 1.45 eV PA band, we estimate a corresponding lifetime of about 5  $\mu\text{sec}$ . The spin signatures of this band can be readily obtained by low temperature PADMR measurements [7].

The H-PADMR spectrum of DOO-PPV, measured at 1.45 eV and shown in Fig. 5 inset, shows an asymmetric band at 390 Gauss, due to  $\Delta m_s = \pm 2$  transitions between triplet sublevels. The triplet -PADMR spectrum (Fig. 5), measured at 390G, clearly shows that the slow component of  $PA_2$  is due to triplet excitons. In fact, the triplet  $\lambda$ -PADMR spectrum matches both the slow component of the ps transient PM (Fig. 1) and the cw PA at 1.45 eV (Fig. 5). We therefore conclude that the slower  $PA_2$  dynamics are due to intersystem crossing (ISC) from singlet to triplet excitons having a much longer lifetime (5  $\mu\text{sec}$ ). Assuming that  $PA_2$  is composed of contributions from both singlet and triplet excitons, we calculate for  $\Delta T$  at  $\lambda = 1.45$  eV:

$$\Delta T \propto \left[ e^{-t/\tau_s} + (\tau_s/\tau_{\text{ISC}})(1 - e^{-t/\tau_s}) \right] \quad (1)$$

From the  $PA_2$  dynamics (Fig. 1, inset),  $\tau_s/\tau_{\text{ISC}} = 0.06 \Rightarrow \tau_{\text{ISC}} \approx 4$  ns. The same analysis for  $PA_2$  decay in DOO-PPV solutions gives  $\tau_{\text{ISC}} \approx 20$  ns.

In summary, we found that photogenerated singlet excitons in DOO-PPV films and dilute solutions have a strong SE in the visible, and two associated PA bands in the NIR spectral ranges. In addition, we determined the ISC time into the triplet manifold to be of order 5 ns and solved the puzzle regarding  $PA_2$  at 1.5 eV [3]; we found that both singlet and triplet excitons strongly contribute to PA at 1.5 eV.

The work at the University of Utah was supported in part by the DOE, FG-03-96-ER 45490 and ONR grant no. N00014-94-1-0853.

Keywords: Conducting polymer, PPV, Exciton dynamics

---

## REFERENCES

- [1] D.D.C. Bradley, *Polymer International* 26, 3 (1991).
- [2] For a review of recent advances in polymer devices see: *Proc. Intl. Conf. Synth. Metals 94*, Seoul, S.Korea, 1994 (*Synth. Met.* 69-71 (1995)); *Proc. Intl. Conf. Synth. Metals 96*, Salt Lake City, Utah, 1996 (*Synth. Met.*, in press).
- [3] M.Yan et al., *Phys. Rev. Lett.* 72, 1104 (1994).
- [4] N.T.Harrison et al., *Phys. Rev. Lett.* 77, 1881 (1996).
- [5] S.V.Frolov, Ph.D. thesis, University of Utah, 1996 (unpublished).
- [6] R. K. Meyer et al., in Ref. [2]; and R. K. Meyer, Ph.D. thesis, University of Utah, 1996 (unpublished).
- [7] X.Wei et al., *Phys. Rev. Lett.* 68, 666 (1992).
- [8] S. A. Jeglinski et al., *Mol. Cryst. Liq. Cryst.* 256, 87 (1994).
- [9] M. Yan et al., *Phys. Rev. Lett.* 75, 1992 (1995); W. Graupner et al., *ibid* 76, 847 (1996); J. W. Blatchford et al., *ibid* 76, 1513 (1996); T. Pauck et al., *Chem. Phys. Lett.* 244, 171 (1995).
- [10] J. M. Leng et al., *Phys. Rev. Lett.* 72, 156 (1994).
- [11] I. D. W. Samuel et al., *Phys. Rev. B* 52, R11573 (1995).
- [12] S.V.Frolov et al., *Jpn. J. Appl. Phys.* 35, L1371 (1996).
- [13] M.Liess et al., in Ref. [2] and submitted to *Phys. Rev. B*.
- [14] M.Chandross et al., in Ref. [2] and submitted for publication.

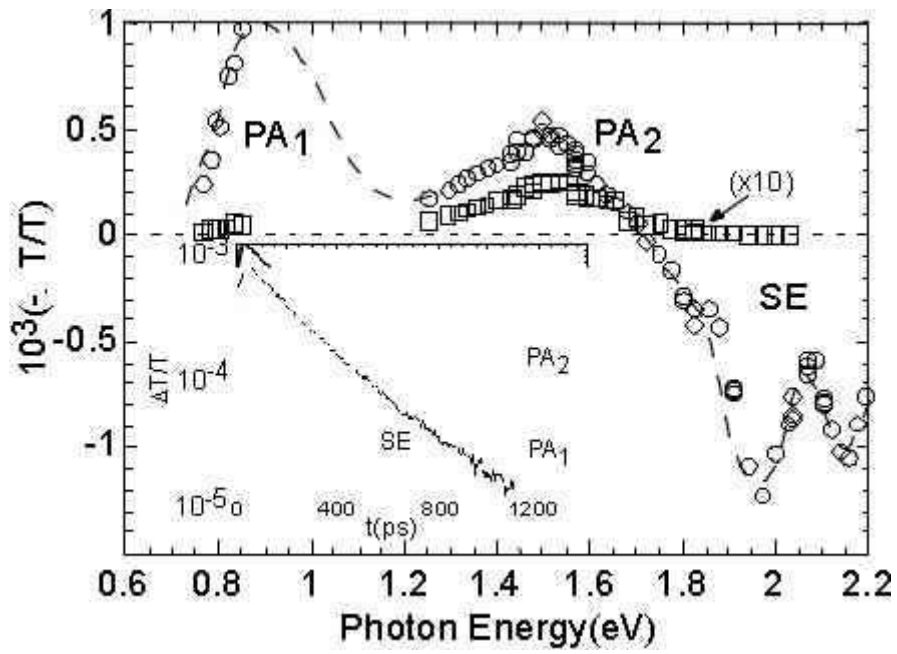


Figure 1

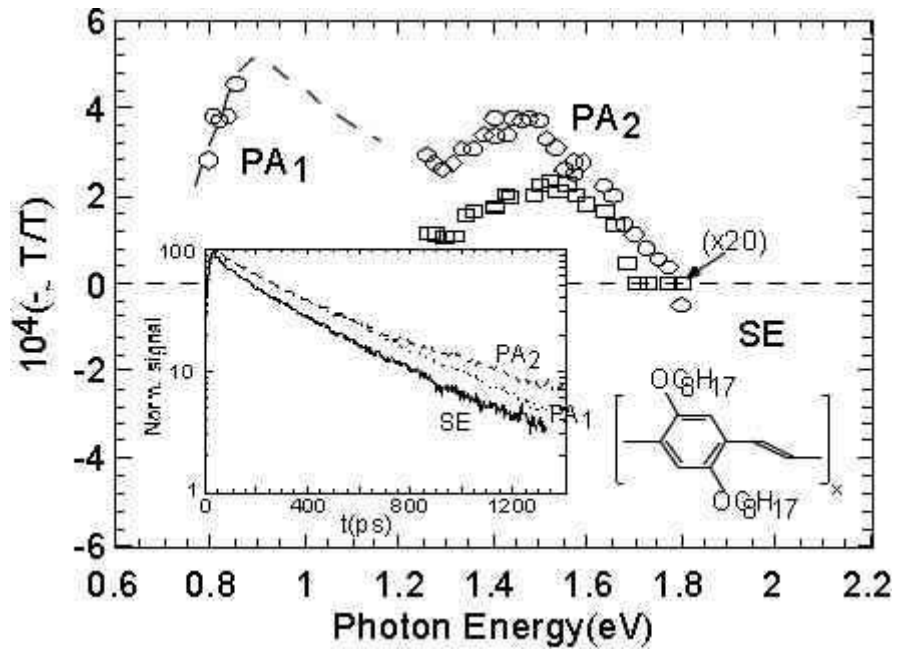


Figure 2

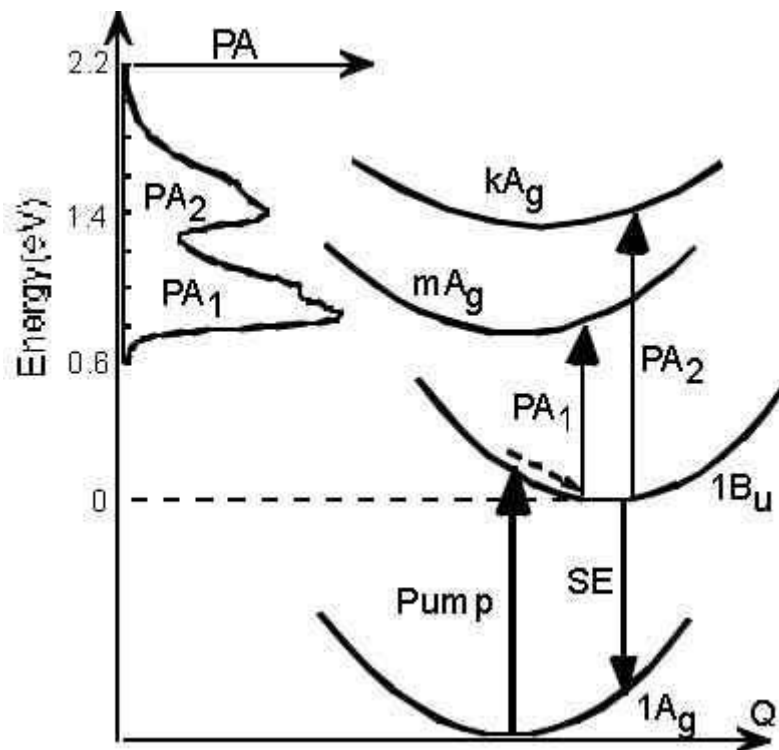


Figure 3

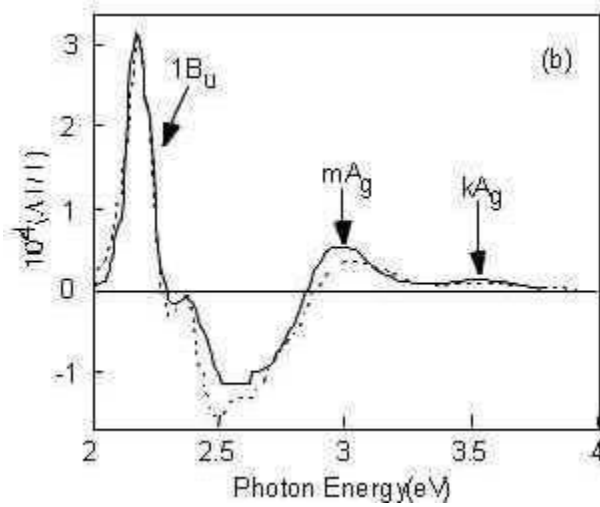


Figure 4

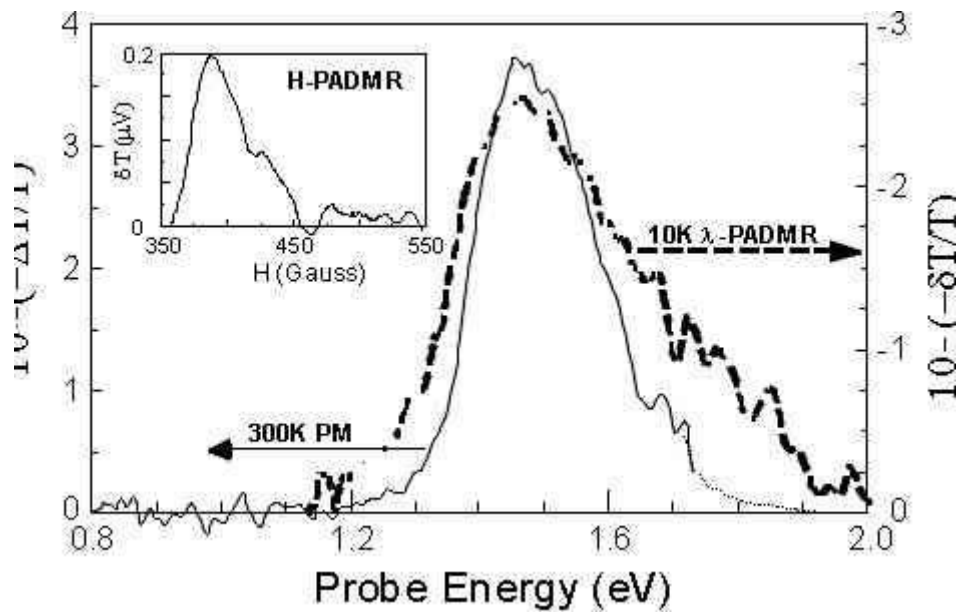


Figure 5