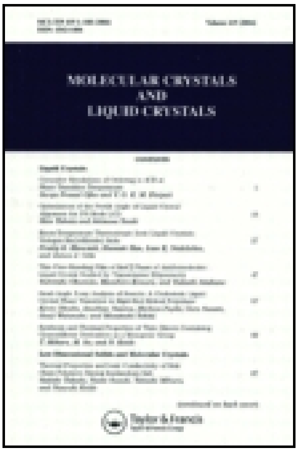

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Excited Energy States in Poly(P-Phenylenevinylene)

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EXCITED ENERGY STATES IN POLY(*P*-PHENYLENEVINYLENE)

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Abstract We have studied electronic excited states in films of poly (*p*-phenylene vinylene) using picosecond transient and steady state (cw) photoinduced absorption (PA) and photoluminescence (PL) as well as their excitation spectra (ES). The ps transient PA spectrum consists of two PA bands both with the same transient dynamics, one band peaks at ~0.5 eV and the other peaks at 1.7 eV; neither of them can be related to the cw PA bands. Since the transient PL decay is correlated with the transient decay of both PA bands up to 200 ps, we conclude that the photoexcitations for t < 200 ps are radiative singlet excitons; they relax in about 200 ps and the radiative quantum efficiency substantially decreases thereafter. From the ES spectra of the cw PA band ES we tentatively assign the important excited electronic states in PPV such as the mA_g exciton and the continuum band.

INTRODUCTION

Recent interest in the nature of the main electronic bands in conducting polymers such as PPV has caused furious debates. The central question is whether the electronic structure of PPV is of excitonic origin or can be described by a band theory. Our recent report[1] on the picosecond photoinduced absorption (PA) in PPV suggests that the photoexcitations are predominantly excitons, consistent with recent subpicosecond photoluminescence (PL) measurements[2]. Furthermore, steady-state PA spectroscopy, its excitation spectrum and electroabsorption spectrum revealed that the continuum band is higher in energy than the exciton level by about 0.7 eV. It is certainly of critical importance as to how we understand this new type of exciton experimentally and theoretically. In this paper, we have extended our picosecond photomodulation measurements to the infrared region (1.5 - 1.8 μm) using a color center laser. The new data confirm our prediction of a new transition from $1B_u$ to mA_g state[1]. Using a phase space filling model used by Greene *et al.*[3,4] in polydiacetylene PTS, we estimate the exciton size to be on the order of 20-30 Å.

EXPERIMENTAL

The picosecond PA was studied by the pump and probe correlation technique using two dye lasers synchronously pumped by a frequency-doubled mode-locked Nd:YAG laser at a repetition rate of 76 MHz with 5 ps resolution, and by a streak camera with 10 ps resolution of the PL transient. Transient spectra of photoinduced changes ΔT in transmission T were obtained by fixing the pump wavelength at 570 nm (2.17 eV) and varying the probe wavelength between 1.2 and 2.2 eV. The probe photon energy was recently extended to the infrared region with a color center laser[5] between 1.5 - 1.8 μm. For the cw PA measurements the excitation was an Ar^+ laser beam modulated at frequency f between 20 Hz and 1 MHz by an acousto-optic modulator, and the probe beam source was a premonochromatized tungsten lamp. For the excitation depedencies of the PL and various bands in the PA spectrum we used a premonochromatized 300 W Xenon lamp modulated at 150 Hz. The excitation intensity was normalized by the absorption, reflection, and the detection setup to yield a quantum-efficiency spectrum per absorbed photon. The PPV sample was a film polymerized on a sapphire substrate with thickness of about 30 μm.

EXPERIMENTAL RESULTS

The transient PA ($-\Delta T/T$) spectrum at 300 K obtained with the synchronously pumped laser system at t =0 is shown in Fig. 1. We observed a broad PA band (labeled EX), which differs substantially from the cw PA bands (also shown in Fig. 1). We believe that our less ordered PPV film gives rise to the bipolaron bands (ω_1 and ω_2) at 300 K, while the low temperature (80 K) PA is dominated by triplet transitions (T) at 1.5 eV. The cw PA above 1.9 eV at both 300 K and 80 K are due to heating effect. The EX band peaks at 1.75 eV and remains essentially unchanged up to 3 ns. For example, the PA spectrum at 1 ns (open sqaures) is compared to that at t = 0 (open circles) in

Fig. 1. The small redshift of the PA peak at longer times to about 1.7 eV may be due to exciton relaxation or diffusion, but does not show a drastic change in the photoexcitation properties. We conclude therefore that the dominant photoexcitations at 3 ns are the same as those generated at t = 0.

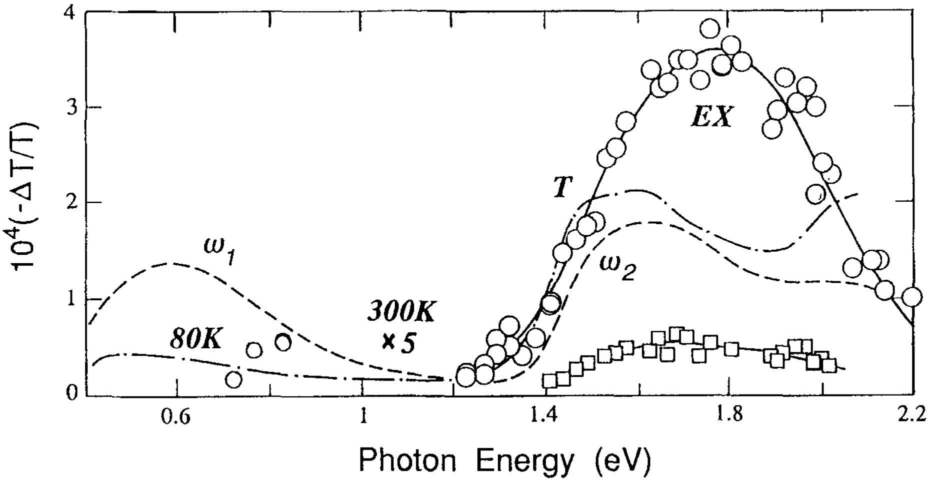

FIGURE 1 PA spectra of PPV in the ps time domain (open circles for t = 0, open squares for t = 1 ns) and cw at 80 K (dot-dashed line) and 300 K (broken line). The full lines through the ps data points are guides to the eye. Varies PA bands (EX, T, ω_1, and ω_2) are assigned.

The picosecond PA spectrum was extended to the ir spectral range. The PA signal was on the order of 5×10^{-5} and this is compared to the recent PA measurements in the ir range at 2.5 - 4.4 μm by Hsu *et al.*[6]. Their results seem to indicate a PA signal increase from 0.28 eV to 0.5 eV; then combining our ir ps PA data allows us to identify a new ir PA band which peaks at 0.5 - 0.6 eV.

The dynamics of the EX band from 10 ps to 3 ns are shown in Fig. 2 for a probe photon energy of 1.7 eV; the dynamics were the same for all probe wavelengths including the ir spectral range. The PA decay is very well fit by a formula based on monomolecular recombination caused by dispersive trapping in amorphous semiconductors[7]

$$n(t) = n(0)/(1 + (t/\tau)^{\beta}), \qquad (1)$$

where n(t) is the photoexcitation density [$-\Delta T/T \approx n(t)$], τ (=215 ps) is the trapping or recombination time, and β (=0.65) is the dispersion parameter characterizing the dispersion relaxation. This implies that the photoexcitations in the picosecond time domain recombine at recombination centers and their diffusion towards these centers is time dependent because of shallow traps. We suggest that the recombination of photoexcitations may be due to migration and thermalization of excitons within the inhomogeneous chain distribution[8]. The decay of the PA at 1.6 μm (0.78 eV) is also plotted in Fig. 2, showing the same dynamics.

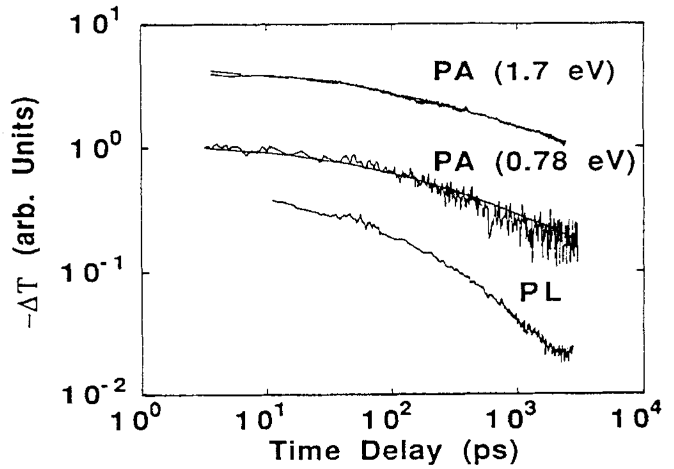

FIGURE 2 PA at 1.7 eV, PA at 0.78 eV, and PL decays.

The PL decay from 10 ps to 2 ns is also shown in Fig. 2. For t < 200 ps, we concluded[1] that PL ~ d(PA)/dt and consequently the dominant photoexcitations within 200 ps are radiative excitons. Beyond 200 ps we found that PL(t) deviates substantially from d(PA)/dt. This fact strongly suggest that initially (t < 200 ps) photoexcited excitons recombine mostly radiatively; at later time the excitons that migrate or relax are trapped by phenyl ring twists[9] and/or impurities, and their radiative quantum efficiency is substantially reduced.

Figure 3 shows the normalized quantum efficiency (QE) excitation spectra of the cw PL (PLE), triplet (TE), and BP (BPE) PA bands in the cw PM spectrum measured at 2.2, 1.45, and 0.55 eV, respectively, together with the PL spectrum and a typical optical density (OD) of PPV (measured with a thinner film). All three excitation spectra show a peak at 2.4 eV (a in Fig. 3), close to a prominent shoulder in the OD. Since this peak is very close to the 0-0 transition in the PL spectrum (Fig. 3, excited with an Ar$^+$ laser at 488 nm), we identify it as the level of the 1B$_u$ exciton in PPV. This is consistent with our picosecond results showing that the 1B$_u$ excitons are the primary excitations in PPV.

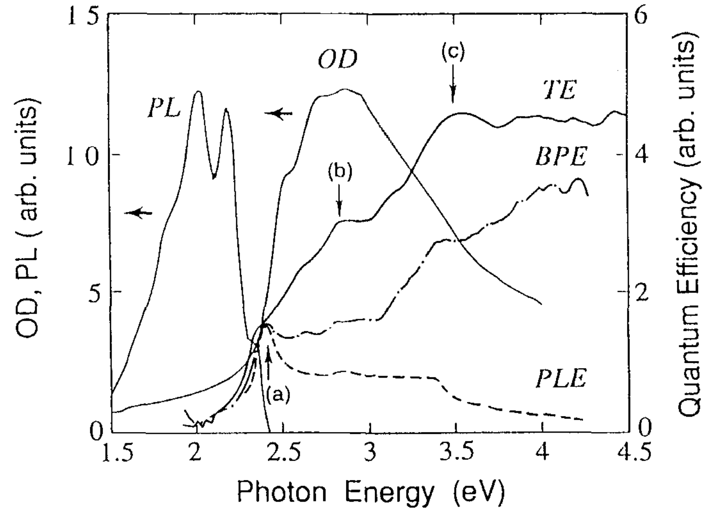

FIGURE 3 PPV ES of PL (PLE), BP$^{2\pm}$ (BPE), and triplets (TE).

MODELS AND DISCUSSIONS

From Fig. 3 we note that the TE spectrum starts to increase at 3.1 eV and reaches its plateau (maximum) at 3.5 eV. We assign the 3.1 eV QE increase as the CB threshold. It has been recently demonstrated[10] that the CB in conjugated polymers consists of closely spaced delocalized A$_g$ and B$_u$ levels, and inside the CB the triplet states are also degenerate. Intersystem crossing thus becomes most efficient within the CB. Further support for this assignment comes from the BPE spectra, which show a prominent increase also starting at 3.1 eV reaching a broad maximum at 3.5 eV. It is obvious that once the CB is reached, the quantum efficiency for charge separation leading to long lived BP is expected to increase dramatically. The above assignment is also supported by EA measurements[1]. The CB threshold at 3.1 eV gives a binding energy $E_b \cong 0.7$ eV for the $1B_u$ excitons. This large E_b for the $1B_u$ excitons in PPV is in reasonable agreement with the recently calculated $E_b = 0.4$ eV based on a model involving Wannier type excitons[11].

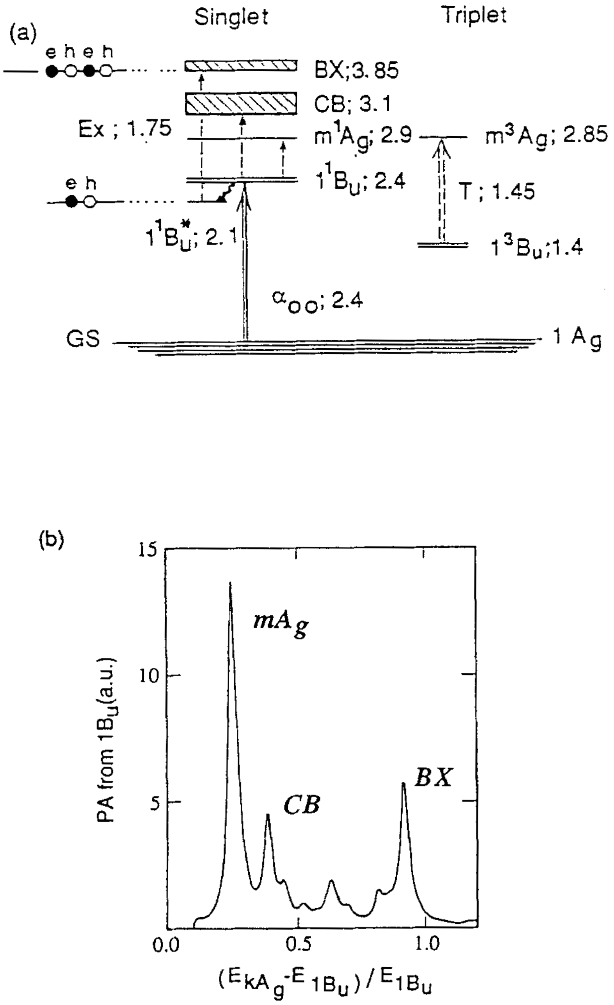

FIGURE 4 Excited state energy levels of PPV. $1B_u{}^*$ is the relaxed $1B_u$ exciton.

We assigned[1] the PA band EX in Fig. 1 as transitions into a BX state. Since EX peaks at 1.75 eV and the excitons were generated at 2.17 eV (570 nm), the BX state should be at 3.9 eV. We note that the excitons generated are actually in relaxed form as we denoted in Fig. 4 (a) as $1B_u^*$. This assignment is supported by our model calculation within an extended Hubbard Hamiltonian[10] with an on-site Coulomb repulsion U=3t, nearest neighbor interaction V=t, and δ=0.2t for a 16 site linear chain. Here t is the nearest neighbor hopping integral. Our purpose is to demonstrate that substantial optical transitions can occur from the 1Bu states to excited A_g states including the mA_g, CB threshold, and BX. In Fig. 4 (b) we have plotted the absorptions from the $1B_u$ to the higher excited A_g states. In spite of the finite size effect that raises the energy of the biexciton, strong absorption to a biexciton state is seen. From Fig. 4(a) and 4(b) we predicted[1] that optical transitions such as $1B_u \rightarrow mA_g$ might be dominant in the ir PA band. Indeed the ir results generated by the color center laser has verified our previous predictions (Fig. 1).

Greene *et al.*[3,4] have used a phase-space filling model to estimate the size of the excitons in 1-D polydiacetylene-toluene-sulfonate (PTS). The density of photoexcited excitons is a function of pump laser intensity (or absorbed photon density); then when the exciton density reaches such a high level that excitons start to overlap with each other (saturation occurs). This saturated exciton density N_s can be used to estimate the exciton length ξ_o (=$2/3N_s\sigma$), where σ is the cross-sectional area per chain. N_s is related to the experimental measurements by

$$N/N_s=-\chi^{(3)}E^2/\chi^{(1)}, \qquad (2)$$

here N is the exciton density, $\chi^{(1)}$ and $\chi^{(3)}$ are linear and third susceptibilities, respectively, E is electric field inside the sample. Bubeck *et al.*[12] have measured the ratio of $\chi^{(3)}/\alpha$ for PPV using the degenerate four wave mixing method and reported a value of $5\pm3\times10^{14}$ esu cm. Then from Eq. (2) we calculated N_s to be 1.1×10^{21} cm^{-3}. The structure of strectched PPV was measured by Chen *et al.*[13] as monoclinic. The cross-sectional area per chain was found to 20 Å^2. Since our sample is spin cast films on sapphire substrate (amorphous), we estimate[14] σ to be ~30 Å^2. Then the exciton size ξ_o (Bohr radius) is calculated to be 20-30 Å. We note that the exciton size estimated here is very close to that in PTS by Greene *et al.*[3,4] of 30-40 Å and that the binding exergy (E_b = 0.7) eV is also close to that in PTS (E_b=0.5 eV). Suhai[5] studied excitons in quasi 1D polymers from first principles. His calculations indicated that the 1D charge transfer type excitons can fulfill both large binding energy and intermediately large, Bohr radius, while Wannier type excitons only contribute up to 40 % of binding energy in PTS.

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