Singlet Intrachain Exciton Generation and Decay in Poly(p-phenylenevinylene)

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We present excitation spectra, picosecond decay time, and quantum efficiency measurements of the photoluminescence (PL) signal in poly(p-phenylenevinylene) (PPV). In pristine PPV we observe a constant efficiency with excitation wavelength for singlet intrachain exciton generation, which we model to be close to unity. In contrast, photo-oxidized PPV samples contain a distribution of quenching centers following the profile of the absorption depth, which causes the PL efficiency to decrease with increasing excitation energy, and the PL efficiency and decay time to be no longer simply related. [S0031-9007(96)00969-6]

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The photophysics of conjugated polymers has been of interest for some time, [1] particularly since the discovery of electroluminescence (EL) in the polymer poly(p-phenylenevinylene) (PPV) in a light-emitting diode (LED) structure [2]. Since the initial observation of green electroluminescence from PPV, LED's with various colors of emission [3–7] and improved efficiencies [8] have been reported.

Much research has centered on the arylene-vinylene-based polymers, of which PPV is the simplest and most studied. However, there is still controversy surrounding the nature of the primary photoexcitation in these materials. Debate has often centered on the binding energy of the photoexcited state which can arise from both Coulombic and lattice distortion contributions. If this is small then description within a band model may be appropriate [9–11]; in contrast, if the electron and hole are strongly bound, they form an intrachain exciton [12–15]. We consider *vide infra* that an exciton model is more appropriate. However, it has also been suggested that nonemissive spatially indirect excitons ("bound polaron pairs" [12]) are the primary photoexcited species in these materials [16–19]. Luminescence in PPV is due to radiative decay of the intrachain singlet exciton, and measurements of photoluminescence (PL), provide important information about the nature of the photoexcitations. There is a discrepancy apparent between high values of PL efficiency (up to 0.27) reported recently [20] and the estimates for the quantum yield of "polaron pairs" [16–19]. A high quantum yield of a nonemissive species such as polaron pairs also invalidates the presumed relationship [20,21] between PL quantum efficiency and lifetime. Furthermore, conventional estimates of maximum LED efficiencies of 25% of the PL quantum yield [22] may be too low if photoexcitation forms polaron pairs with high efficiency, but electrical injection does not [17,19]. A resolution of these contradictory results is essential for a greater understanding of photophysical processes in conjugated polymers, and of great importance to the development of LED's based on these materials.

We have addressed these issues through measurements of photoluminescence excitation spectra, PLE, PL quantum yield, and PL transient decay on pristine and photo-oxidized samples of PPV. We find that the pristine material shows efficient photogeneration of intrachain singlet excitons, but the oxidized samples show lower efficiencies. The relationship between PL efficiency and decay time is no longer simple in an oxidized sample, and the PLE spectrum depends in a very sensitive way on the degree of photo-oxidation.

In a PL experiment, assuming there is a branching ratio b for the production of emissive singlet excitons from the initial excited state, with a fraction $(1 - b)$ forming, for example, charge separated excitations, then the PL quantum efficiency Q (defined as the number of emitted photons/number of absorbed photons) is given by [20]

$$Q = bk_r/(k_r + k_{nr}), \tag{1}$$

where k_r and k_{nr} are radiative and nonradiative decay rates for a singlet exciton. Estimates based on measurements of PL quantum efficiency and PL decay times, and results of the photovoltaic response of PPV/C_{60} photocells give values of $b = 1$ [20,23]. However, the literature results which show Q decreasing at higher excitation energies [19,24–26] strongly suggest that b decreases with increasing excitation energy. Measurements of picosecond photoinduced absorption, and PL decay dynamics make by Yan *et al.* [17,18] have been interpreted as showing that $b \approx 0.1$, with the majority of photoexcitations forming bound polaron pairs. The size and excitation energy dependence of b is a primary concern of this Letter.

Samples were prepared on quartz substrates by spin-casting from a solution of precursor polymer (as described in Ref. [2]) and then thermally converting to fully conjugated PPV. The conversion conditions were 250 °C for 10 h under a vacuum of about 6×10^{-6} mbar, and the samples were stored in dry nitrogen. The PLE spectra were measured under vacuum in the range 2–5 eV with a monochromated 150 W xenon lamp as the excitation source. The results were corrected for incident photon

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flux, and thick samples (400–500 nm—optical density greater than 2 over the whole excitation range) were used so that all of the excitation light was absorbed (with no correction for reflection).

The PLE spectra were measured at ambient temperature, and only PL wavelengths longer than 590 nm (2.1 eV) were detected so that stray excitation light could be blocked with an appropriate optical filter (note that the emission spectrum does not vary with excitation energy above the edge of the optical absorption [14,27]). A spectrum was first measured on a sample of PPV in pristine condition. The sample was then photo-oxidized by exposure, in air, to the 440 nm (2.82 eV) Hg line at intensities of about 30 mW cm^{-2}. The sample was oxidized for progressively longer time periods, and PLE spectra were taken in between periods of oxidation. At the end of the experiment, and PLE spectrum was taken on the back of the sample through the substrate. This was found to be the same as the spectrum taken initially on the sample in pristine condition, showing that the sample had not been photo-oxidized all the way through. Measurements of absolute PL efficiency and PL decay time, τ, were then taken on the front (oxidized) and back (pristine) sides of the sample. Absolute efficiency was measured with an excitation energy of 2.7 eV in an integrating sphere [28]. PL decay time was measured in the range 0–500 ps with an excitation energy of 3 eV by femtosecond time-resolved spectroscopy employing the up conversion technique [29].

Figure 1(a) shows the PLE spectrum taken on the pristine back side of the sample, and spectra taken on the oxidized side at various exposures of the sample. The PL spectrum of PPV is shown for reference. The PLE spectrum of pristine PPV is broadly flat after the onset of the polymer absorption (at 2.5 eV). We note that a flat PLE spectrum has also been observed in a cyanoderivative of PPV [30], and in the molecular material aluminum-tris-quinolate [31]. In photo-oxidized PPV, it is clear that the quantum efficiency of PL in the sample *is* dependent on the excitation energy, and that the shape of the spectrum changes for different levels of oxidation.

PL decay data for the pristine and oxidized sides of the sample is shown in Fig. 2. A monoexponential decay with $\tau = 150$ ps describes the data for pristine PPV. The fit to the data for oxidized PPV derives from a model which is discussed below. Fitting a single exponential decay to these data (not shown) gives a time constant of $\tau = 115$ ps. Corresponding absolute PL efficiencies for the pristine and oxidized sides of the sample were $Q = 0.14$ and $Q = 0.05$.

It is clear from Fig. 1(a) that in pristine fully conjugated PPV the generation efficiency for singlet excitons is constant for excitation in the range 2–5 eV, and from this we conclude that b is constant over this range, in disagreement with other published results [19,24–26]. The values of $Q = 0.14$ and τ, a *monoexponential* 150 ps, are consistent with a value of $b = 1$, assuming a natural radiative lifetime for these materials of around 1 ns [20,21]. We consider, therefore, that decay channels of the optically prepared state, different from and parallel to relaxation to the thermalized exciton, are minor. We note that there is some of variability between different polymer batches, and comparisons of PL efficiency and decay time must be made on the same sample. However, our values are wholly consistent with $\tau \approx 320$ ps and $Q \approx 0.27$ measured by Greenham *et al.* [20]. These results, therefore, strongly support the model in which $b = 1$ at all excitation energies.

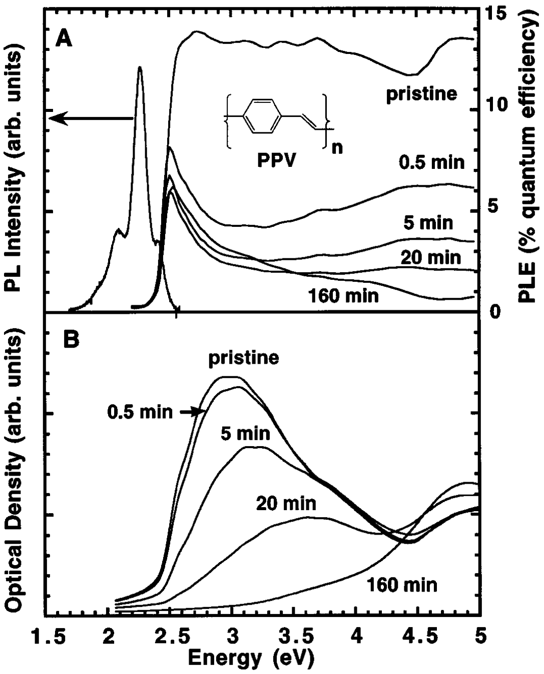

FIG. 1. (a) PLE spectra for the pristine (back) side of the sample, and the front side after photo-oxidation at 440 nm (2.82 eV) and 30 mW cm^{-2} for 0.5, 5, 20, and 160 min. Note that 1 min corresponds to about 2 J cm^{-2}. The heights are scaled from the measurements of absolute quantum efficiency made at 2.7 eV. The structure of PPV and its PL spectrum is shown for reference. (b) The optical absorption [shown as $-\log(\text{transmission})$, with no correction for reflection] of a thin (20 nm) sample of PPV in pristine condition, and after photo-oxidation for 0.5, 5, 20, and 160 min.

Figure 1(b) shows the bleaching of the optical absorption of a *thin* (20 nm) sample of PPV, oxidized in the same way as in Fig. 1(a). Modeling of the rate of bleaching indicates that oxidation is not diffusion limited, so that this thin film is uniformly oxidized. It is known that photo-oxidation of PPV [32–34], and high temperature PPV conversion [35] introduces carbonyl defects into the polymer which bleach the absorption, and act as effective exciton quenching centers. We find that the oxidized PPV PLE spectra can be modeled with an inhomogeneous depth profile of photogenerated defects which causes the characteristics of the PL signal to be

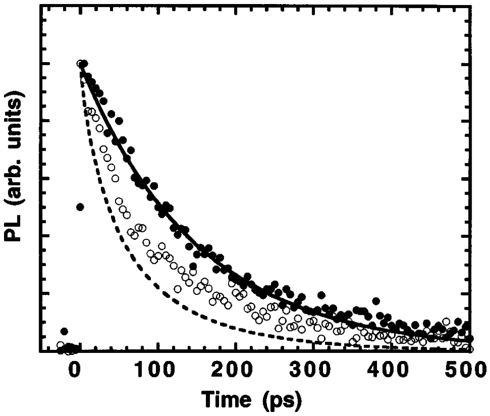

FIG. 2. PL decay dynamics for the pristine (filled circles) and oxidized (open circles) sides of the sample. The fits are $\exp[-t/(150\ \text{ps})]$ for the pristine side (full line), and a sum of exponentials as described in the text for the oxidized side (broken line).

strongly dependent on the penetration depth of the excitation light. Defect density profiles were modeled for a thick (500 nm) sample for various levels of oxidation, assuming the absorption coefficient, a, at the oxidation wavelength (440 nm = 2.82 eV) has the form

$$a = a_0(1 - nV_{\text{abs}})\,, \tag{2}$$

where a_0 is the pristine value ($1.9 \times 10^5\ \text{cm}^{-1}$ at 440 nm as measured here), n the photogenerated defect density, and V_{abs} the volume around a defect in which the absorption is bleached. The defect profiles were calculated over a series of time steps short compared to the time scale of the absorption bleaching. For low oxidation levels (times less than 20 min) we did not need to make any assumptions about the oxygen distribution in the sample, and set the defect generation rate equal to the amount of light absorbed by a region. For higher oxidation levels the fit to the PLE spectra obtained from the model could be improved by making some allowance for oxygen diffusion. We scaled the defect generation rate by a factor decaying exponentially with depth (this matches numerical modeling of the diffusion equation under the condition where the oxygen concentration is low at the back of the sample—note that the thick sample was never oxidized all the way through). This approach requires a diffusion constant of the order $10^{-14}\ \text{cm}^2\,\text{s}^{-1}$, which is low [36]. However, we note that the effective rate of diffusion of oxygen will be lowered if it is used in photo-oxidation reactions during its passage through the film.

Matching the measured bleaching at 2.82 eV [Fig. 1(b)] to that predicted by the model, absorption coefficients were obtained in the range 2–5 eV as a function of defect density. PLE spectra were then calculated for various levels of oxidation, assuming Q varied with n as

$$Q = Q_0 \exp(-nV_{\text{lum}})\,, \tag{3}$$

V_{lum} being the volume around a defect in which the PL is quenched, and Q_0 the value for pristine material (0.14 for our sample). The significant adjustable parameter is this model is the ratio $V_{\text{lum}}/V_{\text{abs}}$, and a value of about 4 gave good agreement between experimental and calculated PLE spectra for a low and high level of oxidation, as shown in Fig. 3. We stress that in our modeling of these spectra, we do not require b to vary from 1.

It is clear that the relation between PL efficiency (Q) and decay time (τ) which is established for pristine PPV is not valid for oxidized samples. The efficiency in these samples is low because much of the incident light is absorbed by regions in which the PL is quenched effectively. In a measurement of decay time, however, most of the observed PL signal comes from less oxidized regions of the sample which have longer decay times. Note that for an inhomogeneous (oxidized) sample a similar excitation energy should be used for both efficiency and decay time measurements to allow comparisons to be made (2.7 and 3 eV were used here). We attempted to model the oxidized-sample PL decay results by calculating τ for different depths in the sample using Eq. (1) with $k_r = 1/(1\ \text{ns})$. The result, however, showed too much decay at short (<20 ps) times. We therefore suggest that in regions of the sample with a high defect concentration, $b < 1$. We might expect photoexcitation very close to a defect such as a carbonyl group would give charge separation directly (with the electron transferring to the chain region with the carbonyl group) within the relaxation time to form a ground vibrational state exciton (≤200 fs [29,37]). In justification of this, we note that Kraabel *et al.* have observed electron transfer from conjugated polymers to a functionalized fullerene acceptor on a subpicosecond time scale [38]. We suggest that this is the origin of the transient absorption associated with interchain charge separation [16–19]. The data in Fig. 2

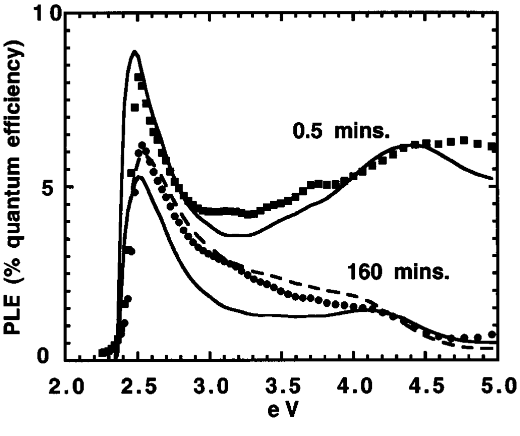

FIG. 3. PLE spectra for oxidation times of 0.5 and 160 min, with model fits without diffusion-limited oxidation (full lines) and with diffusion-limited oxidation (broken line). The absolute height of the diffusion-limited model prediction is scaled down by around 20%; note that this is within uncertainties in the measurements of the PL efficiency.

indicate that we need to include such a PL quenching process for regions of the sample with a high density of quenching centers, and we have modeled here the response when $b = 0.1$ for $\tau \leq 20$ ps. The reasonable fit obtained (using the diffusion-controlled model) is illustrative of the satisfactory way in which the discrepancy between Q and τ is accounted for in an inhomogeneously oxidized sample.

In conclusion, we have shown that b is independent of excitation wavelength in pristine PPV, and has a value close to unity. This is very important to our understanding of the photophysics of this family of conjugated polymers, and our results support estimates of maximum LED efficiencies of $Q/4$ [39]. In an oxidized sample we have shown that inhomogeneous depth profile of photogenerated defects causes the PL efficiency to be reduced at high excitation energies, and changes the relationship between the PL efficiency and temporal decay.

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