Factors Influencing Stimulated Emission from Poly(p-phenylenevinylene)

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We report measurements of stimulated emission (SE) in films of poly(p-phenylenevinylene) (PPV). SE is observed in the region of the cw photoluminescence, using 3.8 eV excitation, and 25% gain was obtained when a PPV film was incorporated into a microcavity structure. We show that photo-oxidation greatly reduces the SE. We demonstrate that singlet polaron excitons form a high proportion of the initially photoexcited states in pristine PPV, and consider that at the excitation density used here (3×10^{19} cm^{-3}) the fast decay of the SE is largely due to exciton-exciton annihilation. [S0031-9007(96)02258-2]

Poly(p-phenylenevinylene) (PPV) has been the proto-typical conjugated polymer with strong photoluminescence (PL) [1]. Despite recent progress in the fabrication of electroluminescent [2] and photovoltaic [3] devices from conjugated polymers, principally PPV and its derivatives, great controversy surrounds the nature of the photoexcited state and the efficiency of its generation. There is strong evidence [4] that electroluminescence and PL are due to recombination of coulombically bound electron-hole pairs in the form of singlet polaron excitons although this model is not universally accepted [5].

As a means of investigating the initial photoexcitations of conjugated polymers, time-resolved differential-transmission measurements have proved very fruitful but have raised further controversy [6–11]. Evidence for stimulated emission (SE) from PPV films has practical applications because of the potential for fabricating solid-state polymer lasers [12,13]. However, competition between SE and photoinduced absorption (PA) has been observed by Yan *et al.* [7] and has been cited as an obstacle to laser operation and also as evidence that singlet polaron excitons form only a small fraction ($\approx 10\%$) of the photogenerated species in these materials. The latter conclusion disagrees with measurements of absolute PL efficiencies and PL lifetimes [14].

We report sub-picosecond-resolution differential-transmission experiments on a PPV film which has been selectively photo-oxidized. We obtain strong SE in the region of the cw-detected PL spectrum, but this is reduced greatly in oxidized material. We show that the presence of defects caused by photo-oxidation may have influenced earlier time-resolved studies of PPV. Additionally, our measurements indicate that pristine PPV exhibits a considerably higher branching ratio, b (i.e., the efficiency of photogeneration of singlet polaron excitons), than the figure determined in some previous reports. We also demonstrate a new technique which allows access to the PA and SE dynamics in differential-transmission experiments by utilizing the pump-induced refractive-index change in a polymer microcavity structure. This technique also provides a novel method for measuring the nonlinear refractive index in polymer films.

A PPV film was fabricated by spin coating of the precursor solution onto a Spectrosil substrate followed by thermal conversion as detailed elsewhere [15]. The film (of thickness 400–500 nm) was then photo-oxidized in air by exposure to the 440 nm line of a Hg lamp for 4 hours. The photoluminescence excitation (PLE) line shape has been found to be a sensitive indication of the level of photo-oxidation of such films [15]. The PLE spectrum obtained when exciting the substrate side of this sample was identical to that of the pristine material indicating that the polymer was not photo-oxidized close to the substrate. All experiments were carried out under a dynamic vacuum of $\leq 10^{-5}$ mbar and at room temperature.

Pulses from a synchronously pumped dye laser operating at 650 nm with a pulse duration of 100 fs were amplified and then focused into a quartz plate to produce white-light continuum. This beam was split, with part being used as the probe beam; the rest was spectrally filtered to leave only the 650 nm component, amplified and frequency doubled in a β barium borate crystal. This beam at 325 nm (3.8 eV) acts as the pump and is focused onto the sample surface, coincident with the probe beam. Both beams were horizontally linearly polarized. Spectrally resolved measurements of the fractional change in probe transmission in the presence of the pump ($\Delta T/T$) were made using a Peltier-cooled CCD camera. Chirping of the probe pulses was numerically corrected using an empirical determination of the dispersion.

Figure 1(a) shows $\Delta T/T$ spectra for a range of time delays measured with excitation on the unoxidized side of the sample. The cw-detected PL spectrum is also shown for reference. The short absorbance length at 3.8 eV (60 nm) means that we probe pristine polymer in this case. (Some $\Delta T/T$ data close to 1.9 eV are not shown because of structure in the white-light spectrum in this region. Also, some noise is seen at 2.1 ± 0.05 eV due to low probe light). A positive $\Delta T/T$ signal is observed, centered at 2.29 eV, while PA occurs at lower energies.
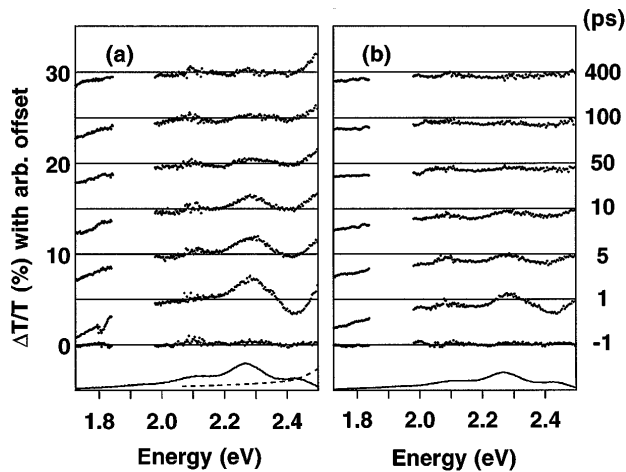
FIG. 1. $\Delta T/T$ spectra measured at a range of pump-probe delays for excitation of (a) the unoxidized side and (b) the photo-oxidized side of the film sample. The spectra are offset for clarity and the delays are shown on the right ordinate. The cw-detected PL spectra are shown as solid lines at the bottom of the figures and the dashed line at the bottom of (a) is the absorbance spectrum.

A further positive signal is present above 2.4 eV and is attributed to bleaching of the ground-state absorption because of its similarity to the steady-state absorption spectrum (shown as a dashed line at the bottom of the figure). Also apparent is a short-lived PA just below the bleaching. All of these features appear within the time resolution of the apparatus ($<$200 fs). Since there is no significant steady-state absorption at 2.29 eV, we attribute the feature at this energy to stimulated emission due to singlet polaron excitons. Note that spontaneous emission also occurs in this region, and we deduce from spectra taken at negative delays that this contributes $\sim$0.25% to $\Delta T/T$ at 2.29 eV. The spectra in Fig. 1 have not been corrected for this background. The SE spectrum should mimic that of the PL. Time-resolved PL measurements on PPV [16] have shown that the emission resembles the cw-detected spectrum, including its vibronic structure, within 200 fs of excitation (although the emission peak is blueshifted by up to $\sim$25 meV for the first few ps). However, although we expect to see SE over the whole PL spectral range, even after decay of the short-lived PA we see only a positive $\Delta T/T$ signal close to the main vibronic peak. We attribute the difference between the SE and PL spectra to the existence of PA across almost the whole spectrum of Fig. 1.

The broad extent of the PA is more apparent in Fig. 1(b) which presents $\Delta T/T$ spectra obtained for the photo-oxidized side of the sample. The SE component is substantially reduced on this side, but the PA is only slightly smaller. A consequence of this is that PA dominates the $\Delta T/T$ spectra at later times. The mechanism by which oxidation defects reduce the SE is not clear. There is good evidence [17] that photo-

oxidation of PPV introduces carbonyl groups and these are believed to quench exciton luminescence by the transfer of charge from the exciton to the carbonyl. Such charge transfer could occur extremely quickly; for example, we note that Kraabel et al. [18] have recently observed charge transfer within 200 fs from PPV derivatives to functionalized fullerenes.

The time evolution of the PA at 1.75 eV is identical for both sides of the sample, and, where SE and short-lived PA are negligible, we find the same dynamics across the spectrum, as reported previously [7,10]. Hence, it appears that the same species is responsible for PA in both oxidized and unoxidized PPV. Therefore, by comparing the PA magnitude at long times to that at 1 ps for both sides of the sample, we can correct for its effects and deduce that the pure gain obtained at 2.29 eV (corrected for spontaneous emission) in unoxidized PPV is 3.7% at 1 ps. (A similar figure was also obtained from a 20 nm pristine PPV film). The PA correction does not account for the possible influence of the short-lived PA feature; if this is significant we will obtain a larger value of pure gain. Yan et al. obtained 5% gain [7] using excitation at 2.43 eV. These authors also showed that the PA contribution increased with the pump photon energy, and at 2.7 eV the SE was overwhelmed by PA after only 1 ps. Yan et al. inferred that this effect prevents the observation of gain using UV excitation, but Fig. 1(a) contradicts this conclusion. We also note that the $\Delta T/T$ dynamics at 2.29 eV in oxidized material (a short-lived positive signal that evolves to net PA after a few ps) is the behavior seen by Yan et al. for pumping above 2.6 eV. This indicates that photo-oxidation defects may play a role in the pump-tuning dependence described by Yan et al. However, differences in polymer synthesis and processing may also influence the outcome of these experiments, and we believe that refinements to these explain why we observe SE, but only PA was detected in earlier experiments at Cambridge [19].

Comparison of the pure gain magnitude at early times and the pump fluence has been used by Yan et al. [7] to determine the branching ratio. They also used the ratio of pure gain to PA at their respective peak wavelengths as a further estimate for b and obtained a value of about 0.1 with both methods. Using the same analysis, we determine for unoxidized material values of $b = 0.5$ and 0.7 from the two methods, respectively. The latter figure is believed to be more accurate (with an error of $\pm$0.2) since it does not depend on the accuracy of the fluence measurement. Thus, we can conclude that the branching ratio is significantly larger in our unoxidized material than has been reported by Yan et al. A high value of b is also implied by PL lifetime and efficiency measurements made on this sample (giving 156 ps and 0.14, respectively) [15] yielding $b = 1.1 \pm 0.2$ for its unoxidized side.

Recently, a great deal of attention has been given to whether the spectral coincidence of PA and SE in PPV,

as seen in Fig. 1, prevents adequate gain to allow the production of lasers from this polymer or its analogs [6–8]. To address this point, we have fabricated microcavity structures [20], each containing a ~100 nm thick, pristine PPV film sandwiched between silver mirrors (of thicknesses 35 and 45 nm) as shown as an inset to Fig. 2. Figure 2(a) displays the $\Delta T/T$ spectra at 1 and 800 ps obtained from a typical microcavity which had a single mode with a transmission FWHM of 40 meV, centered at 2.23 eV. The spectra at short times after photoexcitation consist of two components [12]: the first is a derivative-like line shape caused by the intensity dependence of the refractive index. The sign of this line shape indicates that the cavity mode is blueshifted by photoexcitation and this is consistent with the refractive-index change (Δn) being caused by the PA feature. The other component in the spectra is a positive signal caused by SE. The SE is negligible at 800 ps, and we have deduced the SE component at shorter times by subtracting the scaled 800 ps spectrum from the earlier spectra. The scaling was chosen so that the resulting SE spectrum returned to the baseline away from the cavity mode. In Fig. 2(b), we show the "corrected" SE spectrum for 1 ps after excitation along with the cw-detected PL from the structure. The SE is considerably enhanced in this structure, displaying a peak value of 25%. As expected, the SE spectrum coincides with the PL although there is a small (4 meV) blueshift at 1 ps; this shift is absent at later times.

In Fig. 3, the SE from the microcavity is shown as a function of time along with the $\Delta T/T$ (corrected for spontaneous emission) obtained at 2.29 eV from the unoxidized side of the film. The normalized PA from the film and Δn in the microcavity are also shown, the latter being just the scaling factor used in obtaining the SE spectra. The PA is well described by a power law as shown in Fig. 3. PL data from Ref. [15] are also shown for comparison. We note that the dynamics of the film PA and Δn are almost identical. Δn is related to the PA via the Kramers-Krönig relations [21] and the close agreement between the time evolution of these shows that the relationship amounts to a simple proportionality. We have calculated Δn at 1 ps by finding how much the transmission line shape must be shifted to give the magnitude of $\Delta T/T$ measured experimentally. Assuming the refractive index of PPV to be 2.1 [22], we obtain $\Delta n = 2.3 \times 10^{-3}$ yielding the nonlinear refractive index of PPV as 3×10^{-16} m^2 W^{-1} at 2.23 eV.

It is clear from Fig. 3 that the SE decays more quickly than the PL. This was also observed by Yan *et al.* [7,8] and was attributed to (80–90)% of the initially photoexcited species being coulombically bound interchain polarons. These are believed to yield PA with similar spectral position and line shape to that attributed to singlet excitons but are nonemissive. It was proposed that the PA from the interchain species causes the SE to decay more quickly than the exciton population. Although we also find significant PA in the vicinity of the SE, there is also evidence that, in our PPV films, the different PL
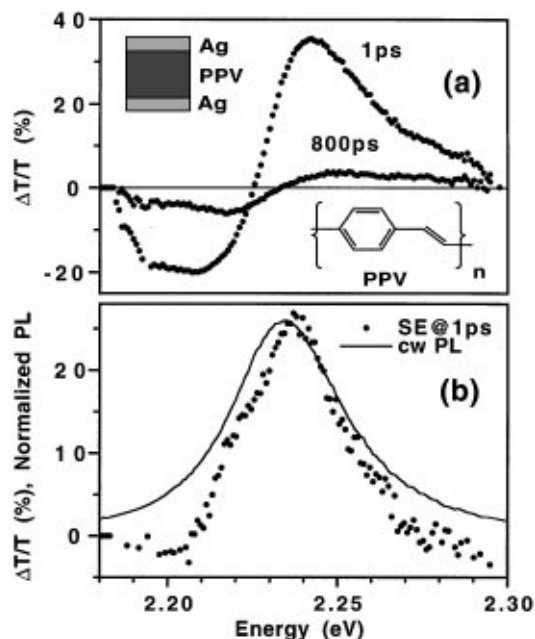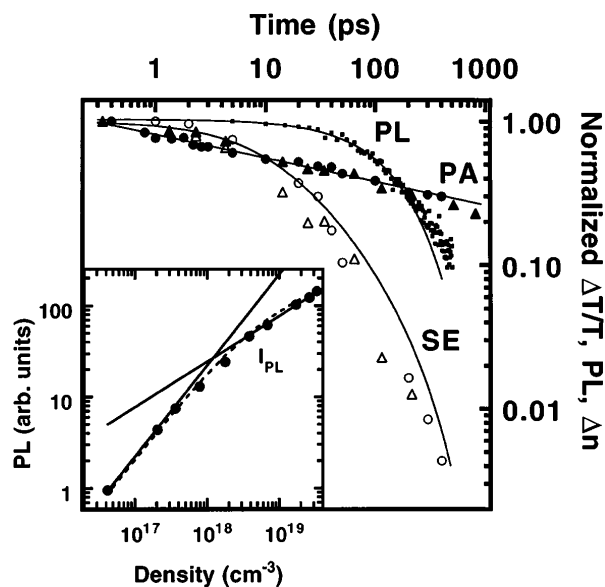
FIG. 2. (a) $\Delta T/T$ spectra measured on the microcavity structure at 1 and 800 ps after excitation. Insets: structure of microcavity and PPV. (b) Dots: corrected microcavity $\Delta T/T$ spectrum at 1 ps. Solid line: cw-detected PL from the structure.

FIG. 3. Normalized $\Delta T/T$ dynamics for the unoxodized side of the film at 2.29 eV (open circles) and 1.55 eV (solid circles) and the normalized SE (open triangles) and Δn in the microcavity (solid triangles). PL from Ref. [15] (for the unoxidized side of the film) is shown as small dots. Solid lines are curve fits to the film data: for PA and PL these are $t^{-\alpha}$ with $\alpha = 0.164$ and $\exp(-t/156 \text{ ps})$, respectively. The fit to the SE is $f(I, t)$ described in the text. Inset: I_{PL} (solid dots) vs injection density. The solid lines are I^1 and $I^{0.5}$ and the dashed line is the time integral of $f(I, t)$.

and SE decay rates reflect the injection densities used for these measurements (7×10^{16} and 3×10^{19} cm^{-3}, respectively). At high pump intensities, exciton-exciton annihilation occurs in PPV [1] and the resulting increase in the decay rate of the singlet-exciton population has been demonstrated recently [23]. The inset to Fig. 3 shows the time-integrated PL (I_{PL}) as a function of the injection density (I) using the same pulses as in our $\Delta T/T$ experiments. At 3×10^{19} cm^{-3} we observe that $I_{PL} \propto I^{0.5}$, indicating the dominance of bimolecular decay at this point. It is only below 2×10^{17} cm^{-3} that linear behavior is seen. Thus, we expect the exciton population to decay faster in the $\Delta T/T$ experiments than in the PL. The decay of the exciton population, n, is described by $dn/dt = -n/\tau - \beta n^2$ [1], where τ is the exciton lifetime and β describes the strength of bimolecular effects. The solution of this equation, $f(I, t)$, [1] has been fitted to the $\Delta T/T$ data using $\tau = 156$ ps, determined from the PL, and by varying β. The result, using $\beta = 2.4 \times 10^{-9}$ cm^3 s^{-1}, is shown as a solid line in the main part of Fig. 3. Substitution of $I = 7 \times 10^{16}$ cm^{-3} into $f(I, t)$ using the same values of τ and β yields a monoexponential decay that follows the PL. The dashed line in the inset of Fig. 3 is the time integral of $f(I, t)$. The excellent agreement between this calculated value and I_{PL} emphasizes the validity of this line shape and our value of β although we note that a larger figure was obtained recently by Kepler et al. (4×10^{-8} cm^3 s^{-1}) [23]. Our fit of $f(I, t)$ to the $\Delta T/T$ data at 2.29 eV does not account for the PA component at this energy. The PA is expected to increase the apparent SE decay rate, but comparison of PL, SE, and PA dynamics indicates that PA effects alone cannot produce the rapid $\Delta T/T$ decay seen at 2.29 eV. The sensitivity of our apparatus does not allow us to measure the SE lifetime in the low-intensity linear regime, but we note that recently reported $\Delta T/T$ measurements performed at $I \leq 10^{16}$ cm^{-3} on poly(2,5-dioctyloxy-p-phenylenevinylene) [24] show identical SE and PA dynamics up to 600 ps. Thus we believe that a large fraction of the PA is due to singlet excitons, consistent with the similar short-time behavior of the PA and SE, and that this species is the predominant product of photoexcitation. The source of the long-lived PA component is less clear. Interchain species have been discussed, but it is also possible that the products of exciton-exciton annihilation will introduce new features into the $\Delta T/T$ spectrum. Further work is required in order to clarify this point.

In summary, we have shown that SE can be obtained from PPV films using UV excitation but that it is greatly reduced in photo-oxidized material. Incorporating a PPV film into a microcavity enhanced the gain and we have recently obtained lasing from a similar structure [12], thus contradicting speculation that PA prevents the realization of laser devices from unblended conjugated polymers. We have also shown that singlet polaron excitons make up at least 50% of the initially created photoexcitations in pristine PPV and that exciton-exciton annihilation reduces the lifetime of these significantly in our $\Delta T/T$ measurements. We suggest that the products of exciton-exciton annihilation may contribute to the long-lived PA component although the presence of interchain species cannot be ruled out.

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