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Exciton formation and decay dynamics in electroluminescent polymers observed by subpicosecond stimulated emission

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We observe stimulated exciton emission and Raman gain in stretch oriented poly(paraphenylenevinylene) (PPV) films with 200 fs resolution. The kinetics of stimulated emission of excitons show that excitons form and equilibrate within 200 fs after 500-nm photoexcitation with 100-fs laser pulses. Stimulated emission is not observed when higher energy photons are used to excite the polymer. The measured polarization and excitation wavelength dependence provide insight into the probability of exciton formation in PPV.

The strong coupling of electronic excitations to the lattice causes the optical and electrical properties of the conjugated polymers to differ greatly from those of inorganic semiconductors.[1] The understanding of lattice stabilized photoexcitations in these polymers is of fundamental and practical interest. The luminescent family of poly(*p*-phenylene vinylene)s (PPV) synthesized via a sulphonium precursor route has been of particular interest for electroluminescent devices and nonlinear optical applications.[2,3] The photoluminescence has been assigned to singlet "polaron excitons" which are delocalized over around six unit cells.[4] The emission exhibits vibrational structure with an energy spacing of 0.17 eV corresponding to the frequency of polymer backbone vibrations.[5] Electroluminescence from PPV is observed to have the same luminescence spectrum and is presumably due to the same species as photoluminescence.

In this paper, we present measurements of femtosecond stimulated emission from PPV films. This enables us to study exciton dynamics on timescales faster than typically accessible by photoluminescence. These data also allow us to identify the photoinduced absorption which is the competing loss mechanism and is relevant to the fabrication of lasers from conjugated polymers.[6] We observe both stimulated emission by excitons and transient stimulated Raman scattering from lattice vibrational modes and document these with both spectral and dynamical measurements. We find that the lattice stabilized exciton is formed within 200 fs after photoexcitation and its gain spectrum already matches that of cw luminescence indicating rapid equilibration. The majority of singlet excitons decay within 25 ps and we show that, even at high excitation densities, exciton-exciton interactions are negligible. We also observe a large photoinduced absorption which is spectrally overlapped with the emission band and turns the gain into absorption on timescales less than 100 ps. The assignment of this absorption and its implications for polymer lasers will be discussed.

The femtosecond time-resolved absorption spectrometer is based on an amplified CPM ring dye laser which produces 100 fs pulses at 620 nm with 100 μJ energies at 20 Hz repetition rate.[7] The amplified pulses are used to generate white continuum. A portion of this continuum is spectrally filtered and amplified in a coumarin dye cell pumped by the third harmonic of a Nd:YAG laser. In this way, blue light pulses (200 fs, 1 μJ) suitable for photoexcitation of PPV films are generated. The remaining white light is used as a probe pulse, part of which goes through the sample excitation region and part of which does not. These two portions are dispersed onto two diode arrays for spectroscopic studies. Differential absorption spectra at fixed delay times between pump and probe can then be obtained for each probe pulse to enhance sensitivity. The delay time between the pump and probe pulse was achieved by varying path-length delay with a translation stage in the pump leg. The probe white light pulse covers a broad wavelength range from 400 to 1200 nm (1–3 eV), and the pump pulse source was tuned using interference filters from 500 to 540 nm (2.3–2.5 eV). The time resolution was about 200 fs across the entire spectrum. Streak camera photoluminescence measurements with 6 ps resolution (Hamamatsu synchroscan) are made using the same samples and pump pulses and are also included for comparison with the gain. The samples are fully converted free-standing PPV films mounted between pieces of glass. The polymer has about a 8:1 stretch ratio and 5 μm thickness. The polymerization method has been reported elsewhere.[8]

Figure 1 depicts the photoinduced transmission change at various delay times with probe wavelengths from 530 nm to 640 nm after photoexcitation with 520 and 530 nm

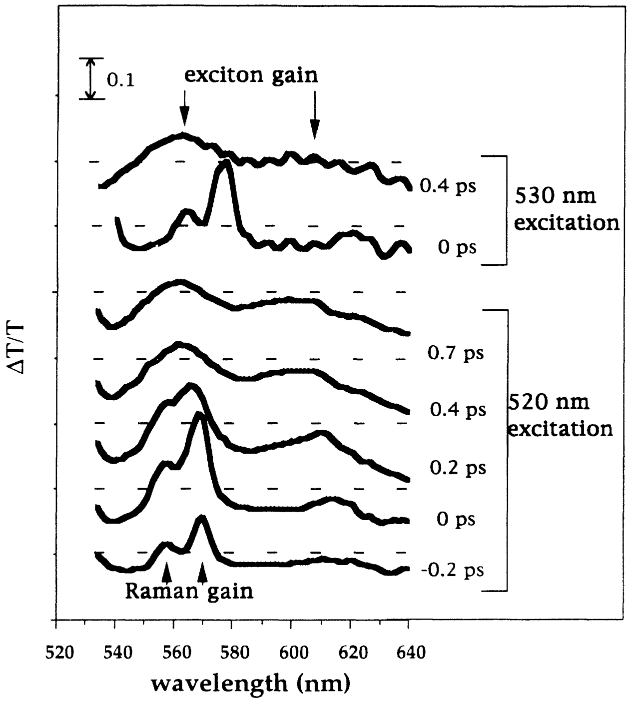

FIG. 1. Photoinduced change in probe transmission for several subpicosecond pump probe delays. Zero delay is defined to be temporally overlapped pump and probe. The bottom set is photoexicted at 520 nm and top one at 530 nm, both with excitation polarization parallel to the stretch direction. The curves are offset with a dashed line at $\Delta T/T=0$. The stimulated Raman and exciton gain are indicated.

pulses polarized parallel to the polymer chains. The polymer absorbs over 90% of the light at these wavelengths. The polarization of probe light is always fixed parallel to the chain. Since the probe wavelength range is below the π-π^* absorption edge, the transmission increase is due to stimulated emission rather than bleaching. The spectrum of the stimulated emission exhibits two sharp gain peaks when the pump and probe are temporally overlapped. These peaks clearly shift with the excitation wavelength and are due to transient Raman gain as has been previously observed in polydiacetylenes[9] and polythiophenes.[10] The frequency shifts of these two Raman bands are 1170 cm^{-1}, and 1560 cm^{-1}, which correspond to the two strongest Raman modes,[11,12] those modes assigned to the phenylene C-H bending vibration and ring stretch, respectively. This suggests that the lattice dimerization is distorted in the excited state. The magnitude of the nonlinear susceptibility describing the stimulated Raman gain, $\chi^{(3)\prime\prime}(\omega_2,\omega_1,-\omega_1,-\omega_2)$, is approximately 5×10^{-9} esu.

The photoinduced gain observed after 200 fs delay when pump and probe are no longer overlapped does not shift with pump wavelength. This gain spectrum agrees closely with the cw photoluminescence spectrum as shown in Fig. 2. This gain can therefore be associated with the same excitonic species responsible for the emission. It is noteworthy that it has already reached its "steady state" spectrum in 200 fs indicating that the requisite cooling and lattice relaxation are nearly complete by this time. This is consistent with the lattice relaxation times measured by Yoshizawa and co-workers in other conjugated polymers.[13] Lattice deformation on the order of the size of the excitation ($R\sim50$ Å) would be expected to take of order $t\sim R/v_s$ where v_s is the speed of sound, consistent with a 200 fs equilibration time. The rapid convergence of the emission spectrum to its "steady state" form indicates that substantial "self-trapping"[14] or exciton diffusion[15] on hundreds of picosecond timescales are negligible in our samples, in contrast to previous work.

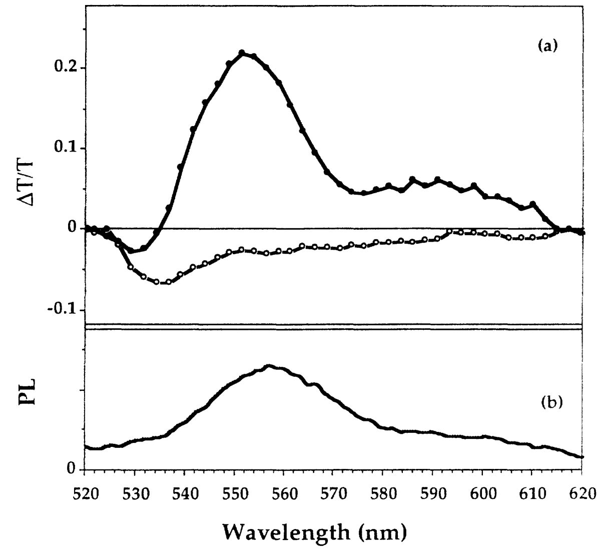

FIG. 2. (a) Spectrum of photoinduced change in probe transmission 200 fs after photoexcitation at 500 nm with polarization parallel (open circles) and perpendicular (solid circles) to the chain direction. (b) The steady-state (cw) photoluminescence (PL) spectrum for comparison.

Figure 2 also shows that photoinduced gain is *not* observed at 500-nm pump wavelength when the polarization of pump pulse was parallel to the polymer stretch direction. This is reminiscent of photoluminescence excitation spectra in oriented phenylenevinylenes where perpendicular excitation leads to more emission and both pump polarizations are more efficient in producing emission when excited near their respective absorption edges.[16] These facts are consistent with a picture where excitation onto the longest chain segments produces emission more efficiently and the reason for this is discussed in greater detail elsewhere.[17] For this reason, previous transient absorption measurements in PPV made with ultraviolet excitation[18] do not observe stimulated emission.

The kinetics of stimulated Raman and exciton gain are depicted in Fig. 3 for photoexcitation at 530 nm polarized along the chain direction. At a probe wavelength of 576 nm were stimulated Raman gain is observed (shown in open circles), the Raman gain is formed instantaneously and quickly decays within the 200 fs instrument resolution. This occurs because Raman gain is a four-mixing process which is only observed when the pump and probe

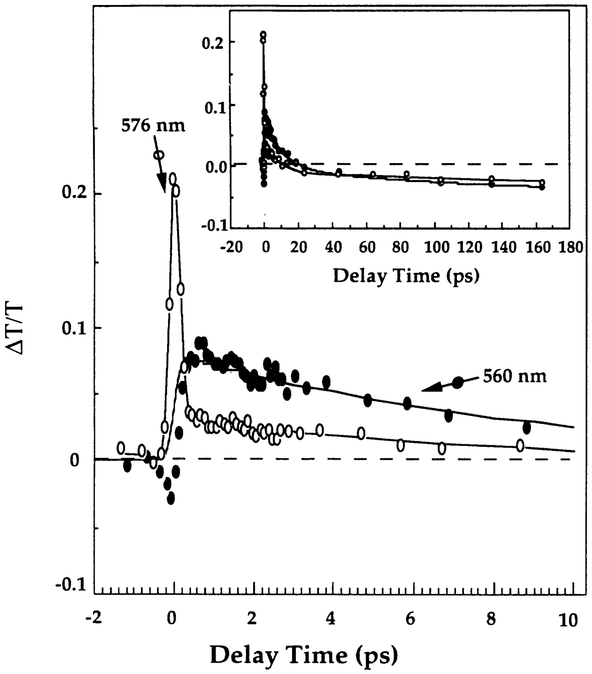

FIG. 3. The time-resolved photoinduced change in probe transmission at 560 nm and 576 nm after photoexcitation by 530 nm pulses polarized parallel to the chain direction. The inset displays a longer timescale. The solid lines are the fits to a biexponential decay with 10 ps and 100 ps components. The 576 nm trace also includes an instrumentally limited component describing stimulated Raman gain at 0 ps.

pulses temporally overlap. The relatively slow decay is due to the exciton gain and, at 560 nm (solid circles) where Raman gain is absent, is all that we observe. A very brief excited-state absorption ($<$ 100 fs) is detected at this probe wavelength which becomes the gain signal observed in Figs. 2 and 3 within 200 fs. For reference, the decay of excitation gain is fitted with two exponentials, the faster having a 10 ps time constant and the slower one at least 100 ps (see inset of Fig. 3). The dynamics cannot be fitted by a single exponential.

Note that the gain is overwhelmed after about 20 ps by a long-lived induced absorption which is apparently formed instantaneously.[7] The origin of this photoinduced absorption is controversial and has been discussed by several groups.[18,19] We wish to point out that, as is evident from the inset to Fig. 3, the dynamics of the photoinduced absorption and luminescence are *not* the same and that the absorption is therefore not due to singlet excitons, the emitting species. There is strong reason to ascribe the photoinduced absorption to polaron pair absorption as we have noted in previous work,[7,16,20] but that is out of the domain of the present paper. Regardless of its assignment, we believe that the induced absorption is intrinsic and that this precludes the fabrication of lasers from PPV films even though photopumped lasers have been demonstrated in solution from soluble members of the phenylenevinylene family.[6] We note that gain is not observed at all in our previous work on monomethoxy substituted PPV[16] because the side group spectrally alters the induced absorption and exciton emission independently. Thus there may be side groups where excited-state loss can be avoided or reduced.

Transient photoluminescence as measured by a streak camera is displayed in Fig. 4. The excitation densities used ($\sim 10^{20}/\mathrm{cm}^3$) are comparable to those used in the time-resolved gain measurements and the observed gain and luminescence decay dynamics are essentially identical. Note that the decays do not depend much on excitation wavelength even though the absorption depths for these two pump colors vary by nearly an order of magnitude. Similarly, emission dynamics after perpendicular photoexcitation are also nearly indistinguishable. These indicate that density effects and two exciton bimolecular processes are unimportant in determining the decay dynamics, contrary to previous speculation.[5] Radiative decay could also not be responsible for the rapidity nor the nonexponential nature of the exciton disappearance. It would require an unphysically large oscillator strength in disagreement with the Einstein relation between A and B coefficients to explain such fast emission and one might expect much higher luminescence yields as well. We believe the dynamics are dominated by nonradiative quenching at defect centers as suggested by Kanner *et al.*[21] in polythiophene and, more recently, by Lemmer *et al.*[22] in phenylenevinylene polymers. There is therefore hope that higher emission yields can be achieved by elimination of these defect sites.

In summary, we report picosecond transient absorption measurements on oriented PPV and observation of stimulated gain in phenylenevinylene films. Lattice stabilized excitons are formed and equilibrate within 200 fs as observed by comparing transient stimulated emission and

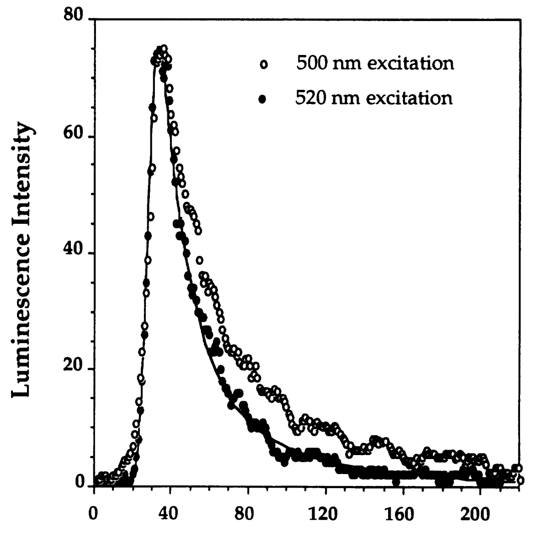

FIG. 4. Time-resolved luminescence at 570 nm after photoexcitation by 520 nm (solid circles) and 500 nm (open circles) pulses with polarization parallel to the chains. Fluency is 1×10^{16} photons/cm^2 in each case and emission intensity is scaled to match at the maxima. The solid line is a fit to a biexponential decay with 20 ps and 100 ps components.

cw photoluminescence. The agreement of the 200 fs spectra with later photoluminescence argues against the importance of self-trapping and exciton diffusion on longer timescales. Rapid nonexponential decay is observed on a few picosecond timescale which is likely due to nonradiative quenching by defects. A photoinduced absorption due to a different species competes with stimulated emission and overwhelms the gain in about 20 ps. This absorption precludes quasicontinuous lasing action in PPV films, but not necessarily substituted phenylene vinylenes. Remarkably, the stimulated exciton gain changes its amplitude dramatically but not its spectrum when the photoexcitation wavelength is varied. Similarly, anisotropy with respect to pump polarization of the transient magnitude but not the spectra is observed for the gain and photoinduced absorption. These results are both consistent with those observed in photoluminescence excitation[16] and are explained by the observation that gain only occurs near the absorption edge where the longest conjugation segments are excited directly. There, excitons are formed with the largest probability. In the case of electrical injection, electrons and holes (or their polaronic analogs) are most likely to meet on the longest conjugation (lowest energy) segments.[23] Electroluminescence device efficiency is therefore best compared to the photoluminescence yields for near band-edge excitation. Finally, we observe two stimulated Raman gain resonances when pump and probe pulse overlap in time. The Raman shifts of 1170 cm^{-1} and 1560 cm^{-1} correspond to vibrations which reflect excited-state distortions along those coordinates. Further work to study the photoinduced absorption spectroscopy and dynamics is in progress.

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