

Exciton dynamics in electroluminescent polymers studied by femtosecond time-resolved photoluminescence spectroscopy

G. R. Hayes, I. D. W. Samuel, and R. T. Phillips

Cavendish Laboratory, Madingley Road, Cambridge, CB3 0HE, United Kingdom

(Received 1 June 1995; revised manuscript received 11 August 1995)

We report measurements of the time-resolved photoluminescence from unoriented films of poly[2-methoxy,5-(2'-ethyl-hexyloxy)-*p*-phenylenevinylene] (MEH-PPV) and poly(*p*-phenylenevinylene) (PPV). An extremely rapid luminescence rise is observed over the entire spectral region measured. A broad high-energy luminescence tail can be seen for very short times after excitation. A redshift of the luminescence with time is also observed and is larger in MEH-PPV than in PPV. The measured decay times of the photoluminescence indicate that the nonradiative decay of singlet excitons is more rapid in MEH-PPV than in PPV, lowering its photoluminescence efficiency. We attribute the differences between the materials to the reduced crystallinity of MEH-PPV compared to PPV. This increases the density of conformational defects and thus reduces the effective conjugation length of the polymer chains. These defects also provide a more efficient nonradiative decay channel. Polarized measurements of the luminescence were performed and provide insight into the ultrafast dynamics of the excitons.

There has been considerable progress in recent years in the development of electroluminescent devices based on poly(arylenevinylene)s.¹ The addition of side chains onto the backbone of the conjugated polymer poly(*p*-phenylenevinylene) (PPV) enables the optical and electronic properties of these materials to be controlled chemically. An important derivative of PPV, due to its solubility and high electroluminescence quantum efficiency, is poly[2-methoxy,5-(2'-ethyl-hexyloxy)-*p*-phenylenevinylene] (MEH-PPV). Obtaining a detailed understanding of the dynamics of photoexcitations in MEH-PPV is therefore highly desirable for both fundamental and practical reasons.

Femtosecond photoluminescence spectroscopy is a very powerful tool for studying the ultrafast dynamics of excitations that decay radiatively. In PPV the luminescence has been attributed to the radiative recombination of the singlet polaron exciton. The luminescence is polarized parallel to the chain upon which the exciton recombines. Topological faults and impurities cause the effective conjugation length of the polymer to be much less than the actual chain length. This limits the extent along the chain to which an exciton can be delocalized. An extrapolation from the vibrational peaks observed in several well-defined oligomers of PPV (Refs. 2 and 3) and from PPV based polymers⁴ suggests that the conjugation length is about 15–20 repeat units for PPV samples prepared in a similar fashion to the ones studied in our experiment.

Several picosecond photoluminescence studies have been performed on PPV (Refs. 5 and 6) and MEH-PPV.^{6,7} More recently, subpicosecond⁸ photoluminescence spectroscopy has been employed on PPV to observe the energy relaxation of the excitons. The observed behavior has been explained by describing the polymer chain as a series of smaller subunits whose size depends upon the degree of chain alignment and sample purity. The broad absorption features seen in the polymer films are believed to be due to the range of effective conjugation lengths of chain segments that are initially excited. Exciton migration can occur prior to recombination,

via Förster transfer, from poorly conjugated and hence higher energy chain segments to more conjugated and thus lower energy chain segments.⁸ This results in a narrower emission spectrum. Subpicosecond photoinduced absorption spectroscopy has also been used to explore the ultrafast dynamics of excitations in PPV.^{9–11} These experiments enable the initial relaxation processes of both luminescent and nonluminescent excitations to be probed but the results can be complicated as they are a superposition of several nonlinear optical processes. Photoconductivity measurements¹² have been cited as evidence that initially polarons and subsequently bipolarons form the dominant excitation in PPV. However, recent results¹³ suggest that polarons are not generated immediately after photoexcitation but instead are created via the field-induced dissociation of excitons. Site-selective fluorescence measurements also suggest that excitons are the energetically favored photoexcitations in PPV.¹⁴ Recently, it has been suggested that up to 90% of the photoexcitations form “spatially indirect” singlet excitons that do not recombine radiatively.⁹ However, this has been found to be incompatible with photoluminescence quantum efficiency measurements.¹⁵

The MEH-PPV sample was synthesized via a direct dehalogenation route¹⁶ and then spin coated from chloroform solution onto a Spectrosil disk to form an optically thick film of physical thickness approximately 200–500 nm. For the PPV sample a soluble precursor polymer with a tetrahydrothiophenium leaving group was spin coated onto a Spectrosil disk and this was then converted to the final polymer.¹⁷ The samples were held in a cryostat under a dynamic vacuum of 8×10^{-6} mbar during the experiment and stored in a glovebox at other times.

Femtosecond upconversion spectroscopy was employed to resolve temporally the luminescence. A mode-locked Ti:sapphire laser was utilized that produced pulses of approximately 120 fs duration at an energy of 1.53 eV and a repetition rate of 76 MHz. A beam splitter was used to create a reference pulse and a sample pulse. The sample pulses were frequency doubled in a nonlinear optical crystal of

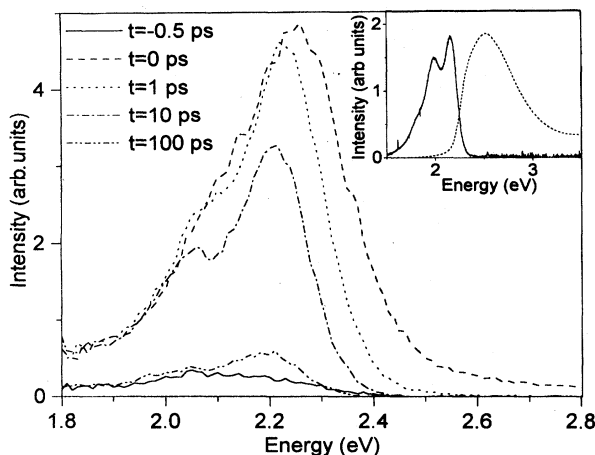


FIG. 1. Time-resolved photoluminescence spectra of MEH-PPV after excitation with 200 fs pulses at 3.06 eV. Inset: Solid and dashed lines are the cw emission and absorption of MEH-PPV at room temperature.

LiIO₃ to produce light pulses at 3.06 eV with a duration of about 200 fs. These were used to excite the samples. The polarization of the incident light was controlled by a waveplate and a polarizer. The spot size on the sample was 120 μm and the excitation power was reduced to 1 mW when performing the experiments on MEH-PPV and 2 mW on PPV to prevent laser-induced sample degradation. Luminescence produced after photoexcitation was collected by a non-dispersive mirror arrangement and focused onto a nonlinear optical crystal of BBO. The reference pulse was passed through a delay stage and then used to upconvert the luminescence in the BBO crystal. The crystal orientation was such that only vertically polarized luminescence was upconverted. The upconverted light was dispersed by a monochromator and detected by a photomultiplier tube employing single-photon counting. The temporal resolution of the experiment depends upon the pulse width of the laser and the group velocity dispersion in the BBO crystal and was calculated to be 150 fs at 1.8 eV increasing to 300 fs at 2.8 eV. The spectral resolution of the experiment was 18 meV. Spectral calibration of the system was performed by upconverting light from a tungsten-filament lamp of known temperature.

Figure 1 shows the room-temperature photoluminescence spectrum of MEH-PPV at various times after photoexcitation with the incident light polarized parallel to the detected luminescence. There are three main features of the time-resolved data that we wish to highlight. The first is the extremely rapid rise in the luminescence extending across the entire spectral region. After this, a rapid decay of the high-energy luminescence tail is observed within a few hundred femtoseconds and a slower redshift and narrowing of the luminescence peaks, which occurs on a picosecond time scale. The recognizable vibronic structure seen in cw experiments becomes apparent within a few picoseconds. Thirdly, the overall decay of the luminescence can be seen.

The ultrafast luminescence rise is attributed to the formation of excitons followed by their subsequent vibrational relaxation onto the lowest vibrational level of the first excited

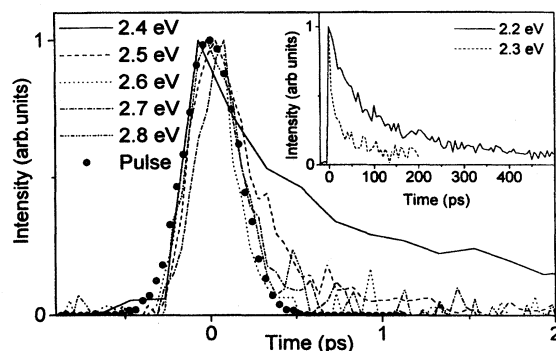


FIG. 2. Short-time evolution of the photoluminescence in MEH-PPV monitored at several luminescence energies. Also shown is the cross correlation of the sample pulse with the reference pulse. Inset: Longer-time evolution of the photoluminescence in MEH-PPV monitored at two different luminescence energies.

electronic state as has been suggested for PPV.^{8,10} Our results show that this formation and vibrational relaxation occur in less than 300 fs. The broad high-energy luminescence tail that exists at very short times after photoexcitation is believed to be caused by the recombination of excitons from short-conjugated chain segments. The rapid removal of this high-energy luminescence tail is explained by exciton migration from higher-energy sites that occurs on a subpicosecond time scale due to the presence of a large density of lower-lying sites to which the exciton can hop.⁸ Recent results have shown that the exciton can migrate to sites in three dimensions in a derivative of PPV.¹⁸ This migration then becomes a slower diffusion because as the excitons lose more and more energy there are fewer and fewer energetically available sites to which the exciton can migrate. The migration causes the redshift and narrowing of the luminescence peaks. We can discount sample heating due to light absorption followed by subsequent cooling due to phonon decay as the cause of the observed redshift because of the small amount of energy present in each pulse. In Fig. 2 the short-time evolution of the photoluminescence monitored at several energies is shown. This highlights the rapid rise and decay of the high-energy luminescence tail that occurs within 300 fs after photoexcitation. In the inset of Fig. 2 the longer-time evolution at lower energies is shown. At lower energies the decay time increases significantly because exciton migration ceases to be the dominant cause of the luminescence decay. At an energy of 2.2 eV the luminescence decay can be fit roughly to an exponential with a time constant of 145 ps, which is comparable to the value of 180 ps obtained by Samuel *et al.*⁶ The luminescence decay at this energy is no longer caused principally by exciton migration but by radiative and nonradiative recombination. We observed almost identical decay curves as the initial excitation density was reduced by a factor of 8 and can therefore discount bimolecular effects as a cause of the nonradiative decay.

The room-temperature photoluminescence spectrum of PPV at various times after photoexcitation is displayed in Fig. 3. We again observe a very short-lived high-energy luminescence tail as well as a redshift and narrowing of the luminescence peaks with time. The vibronic structure is ap-

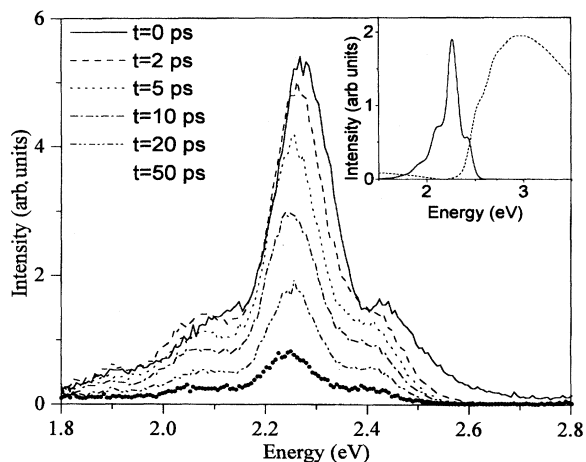


FIG. 3. Time-resolved photoluminescence spectra of PPV after excitation with 200 fs pulses at 3.06 eV. Inset: Solid and dashed lines are the cw emission and absorption of PPV at room temperature.

parent even at $t=0$. In Fig. 4 we have plotted the measured redshift of the main vibronic peak of PPV versus time. A similar time dependence is seen for the vibronic peaks adjacent to the main peak. Also shown is the temporal evolution of the main luminescence peak of MEH-PPV. This clearly shows that the redshift is larger in MEH-PPV than in PPV. The change in energy of an exciton that hops from a site with an effective conjugation length of B repeat units to one of $B+1$ repeat units is larger if B is smaller. The larger redshift obtained for MEH-PPV suggests that it is less conjugated than PPV. We attribute this feature to an increased concentration of defects in the MEH-PPV film compared to the PPV film. The time constant for the decay of the luminescence at an energy of 2.25 eV, which is near the cw peak in PPV, was measured to be 300 ± 30 ps. If we assume that the radiative

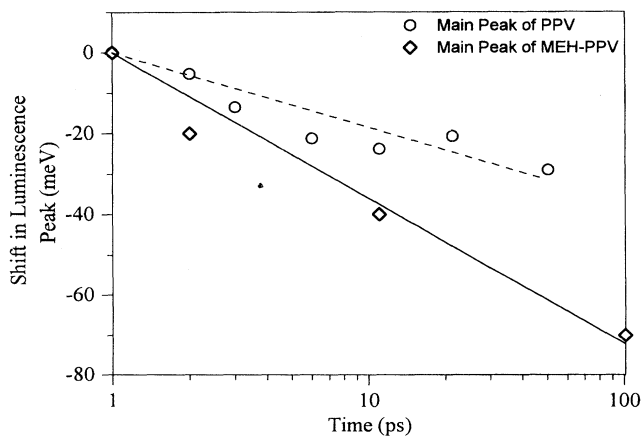


FIG. 4. Position of the peak of the main emission band of PPV and MEH-PPV versus time. The solid and dashed lines are guides to the eye that highlight the increased redshift seen in MEH-PPV. $t=0$ ps has been offset by 1 ps for clarity.

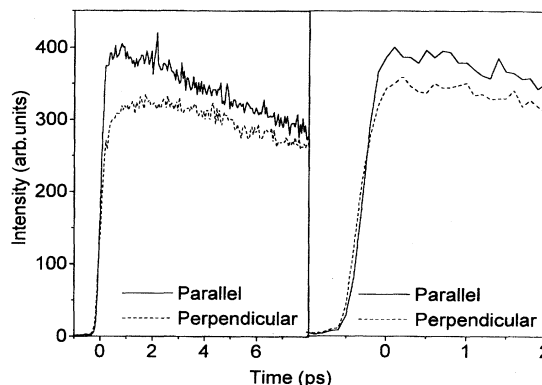


FIG. 5. Transient luminescence traces in MEH-PPV monitored at 2.2 eV (left) and PPV monitored at 2.4 eV (right) measured parallel or perpendicular to the incident light. The exact value of $t=0$ was not known when the measurements for the graph on the right were taken.

lifetime of the two polymers is of the order 1.2 ns which is what is observed in *trans-trans*-distyrylbenzene which is a model oligomer of PPV (Ref. 19) then this suggests that more efficient nonradiative decay channels, caused by defects, are present in MEH-PPV films. Recent experimental results¹⁵ have shown that the photoluminescence quantum efficiency of PPV films prepared by the same method as our samples is 0.27 ± 0.02 and for MEH-PPV films is in the range 0.10–0.15. These results are fully consistent with the decay times that we observe. Gettinger *et al.*²⁰ measured an increase in the photoluminescence efficiency of three PPV derivatives in solution as the degree of interchain order increased. They suggested that the increased ordering of the PPV derivatives reduced the number of conformational defects. MEH-PPV is less crystalline and has a lower glass transition temperature than PPV, which is a relatively crystalline polymer. The reduced crystallinity of MEH-PPV compared to PPV may be associated with the branched side chains present in MEH-PPV. The MEH-PPV film should therefore contain more topological faults than the film of PPV. Gromer and Reineker²¹ have considered the effect of bond disorder on the electronic properties of conjugated polymers within the model proposed by Su, Schrieffer, and Heeger.²² Electronic states can be generated within the energy gap between the π and π^* bands depending upon the type of bond distortion considered. This will significantly increase the rate of luminescence quenching by processes such as multiple-phonon emission, due to the creation of temporary states within the energy gap to which the exciton can first relax. It should be possible, therefore, to improve significantly the photoluminescence efficiency of MEH-PPV by making films with enhanced order. Thermally induced lattice defects may contribute to the bond disorder at room temperature. These are expected to be frozen out at low temperatures leading to an increased decay time and photoluminescence efficiency.

In Fig. 5 we show the evolution of the luminescence at ultrashort times when the incident light was polarized parallel or perpendicular to the detected luminescence. The luminescence takes slightly longer to rise when the polarization

of the incident and emitted light are crossed. Excitons are formed preferentially on chain segments oriented parallel to the incident light. Cross-polarized luminescence favors excitons that have migrated from chain segments oriented parallel to the incident light to segments oriented perpendicular to it. The observation of a very small delay in the luminescence rise is plausible since the coherence length is only 50 Å in this disordered material.²³ Further information should be obtainable from transient luminescence measurements of stretch-oriented samples.

In conclusion, we have measured the ultrafast time-resolved photoluminescence from PPV and its soluble derivative MEH-PPV. We observe an extremely rapid rise in the luminescence that is attributed to exciton formation and subsequent vibronic relaxation which occurs on a femtosecond time scale. A high-energy tail is seen in the photolumi-

nescence spectrum at early times after excitation. A redshift of the luminescence peak with time is also observed. These effects are explained by exciton migration from poorly conjugated and hence high-energy sites to longer-conjugated and thus lower-energy sites. The shorter decay time in MEH-PPV compared to PPV is considered to be due to nonradiative recombination and it is suggested that poorer structural order due to the reduced crystallinity of MEH-PPV compared to PPV may be the cause of this difference.

This work was supported by the EPSRC. I.D.W.S. thanks Christs College, Cambridge for financial support. We would like to thank CDT for the PPV sample, G. W. Spencer, S. C. Moratti, and A. B. Holmes for the MEH-PPV sample, and N. C. Greenham and R. H. Friend for helpful discussions.

- ¹P. L. Burn, A. B. Holmes, A. Kraft, D. D. C. Bradley, A. R. Brown, R. H. Friend, and R. W. Gymer, *Nature (London)* **356**, 47 (1992).
- ²H. S. Woo, O. Lhost, S. C. Graham, D. D. C. Bradley, R. H. Friend, C. Quattrocchi, J. L. Brédas, R. Schenk, and K. Müllen, *Synth. Met.* **59**, 13 (1993).
- ³B. Tian, G. Zerbi, R. Schenk, and K. Müllen, *J. Chem. Phys.* **95**, 3191 (1991).
- ⁴S. Heun, R. F. Mahrt, A. Greiner, U. Lemmer, H. Bässler, D. A. Halliday, D. D. C. Bradley, P. L. Burn, and A. B. Holmes, *J. Phys. Condens. Matter* **5**, 247 (1993).
- ⁵I. D. W. Samuel, B. Crystall, G. Rumbles, P. L. Burn, A. B. Holmes, and R. H. Friend, *Synth. Met.* **54**, 281 (1993).
- ⁶I. D. W. Samuel, B. Crystal, G. Rumbles, P. L. Burn, A. B. Holmes, and R. H. Friend, *Chem. Phys. Lett.* **213**, 472 (1993).
- ⁷L. Smilowitz, A. Hays, A. J. Heeger, G. Wang, and J. E. Bowers, *J. Chem. Phys.* **98**, 6504 (1993).
- ⁸R. Kersting, U. Lemmer, R. F. Mahrt, K. Leo, H. Kurz, H. Bässler, and E. O. Göbel, *Phys. Rev. Lett.* **70**, 3820 (1993).
- ⁹M. Yan, L. J. Rothberg, F. Papadimitrakopoulos, M. E. Galvin, and T. M. Miller, *Phys. Rev. Lett.* **72**, 1104 (1994).
- ¹⁰M. Yan, L. Rothberg, B. R. Hsieh, and R. R. Alfano, *Phys. Rev. B* **49**, 9419 (1994).
- ¹¹I. D. W. Samuel, F. Raksi, D. D. C. Bradley, R. H. Friend, P. L. Burn, A. B. Holmes, H. Murata, T. Tsutsui, and S. Saito, *Synth. Met.* **55-57**, 15 (1993).
- ¹²C. H. Lee, G. Yu, D. Moses, and A. J. Heeger, *Phys. Rev. B* **49**, 2396 (1994).
- ¹³R. Kersting, U. Lemmer, M. Deussen, H. J. Bakker, R. F. Mahrt, H. Kurz, V. I. Arkhipov, H. Bässler, and E. O. Göbel, *Phys. Rev. Lett.* **73**, 1440 (1994).
- ¹⁴U. Rauscher, H. Bässler, D. D. C. Bradley, and M. Hennecke, *Phys. Rev. B* **42**, 9830 (1990).
- ¹⁵N. C. Greenham, I. D. W. Samuel, G. R. Hayes, R. T. Phillips, Y. A. R. R. Kessener, S. C. Moratti, A. B. Holmes, and R. H. Friend, *Chem. Phys. Lett.* **241**, 89 (1995).
- ¹⁶F. Wudl and S. Hoger, U.S. Patent No. WO 94/20589 (1991).
- ¹⁷P. L. Burn, D. D. C. Bradley, R. H. Friend, D. A. Halliday, A. B. Holmes, R. W. Jackson, and A. Kraft, *J. Chem. Soc. Perkin Trans. 1*, 3225 (1992).
- ¹⁸U. Lemmer, R. F. Mahrt, Y. Wada, A. Greiner, H. Bässler, and E. O. Göbel, *Chem. Phys. Lett.* **209**, 243 (1993).
- ¹⁹I. B. Berlman, *Handbook of Fluorescence Spectra of Aromatic Molecules*, 2nd ed. (Academic, New York, 1971).
- ²⁰C. L. Gettinger, A. J. Heeger, J. M. Drake, and D. J. Pine, *J. Chem. Phys.* **101**, 1673 (1994).
- ²¹O. Gromer and P. Reineker, *Synth. Met.* **64**, 281 (1994).
- ²²W. P. Su, J. R. Schrieffer, and A. J. Heeger, *Phys. Rev. B* **22**, 2099 (1980).
- ²³K. Pichler, D. A. Halliday, D. D. C. Bradley, P. L. Burn, R. H. Friend, and A. B. Holmes, *J. Phys. Condens. Matter* **5**, 7155 (1993).