Excitation dynamics in conjugated polymers

H. Bässler (a), V. Brandl (a), M. Deussen (a), E.O. Göbel (b), R. Kersting (c), H. Kurz (c), U. Lemmer (b), R.F. Mahrt (a) and A. Ochse (b)

Fachbereiche Physikalische Chemie (a) and Physik (b) and Zentrum für Materialwissenschaften der Philipps-Universität, D-35032 Marburg and Institut für Halbleitertechnik II, RWTH Aachen, D-52074 Aachen (c), Germany

Abstract: High resolution cw photoluminescence spectroscopy, energy transfer studies, time and spectrally resolved fluorescence decay as well as quenching of photoluminescence by strong electric fields support the notion that photon absorption in PPV-type conjugated polymers creates neutral excitations. They undergo a random walk among segments of the polymer chain thereby relaxing energetically. In the presence of an electric field they can form off-chain geminate pairs acting as precursors for free charge carriers.

Introduction
Characteristic features of organic solids as compared to inorganic semiconductors such as silicon are their weak intermolecular coupling and low dielectric constants ranging from 3 to 4 only. As a consequence, transport bands for both charge carriers and excitons are narrow and the mean freepaths of elementary electronic excitations are of order of the intermolecular spacing, except at low temperatures. The importance of coulomb effects implies that the elementary optical excitations are excitons of the Frenkel type. Since their binding energy is of the order of 1 eV they cannot dissociate into free charge carriers except at interfaces or impurities acting as trap for one sort of carriers (1). Intrinsic photoconductivity requires the generation of charge transfer states either via direct charge transfer transition (2,3) or via autoionization of higher excites states (4). Recall that in an anthracene crystal the energy of a nearest neighbor charge transfer state is approximately 0.5 eV above the S_1-exciton (3). Electron-phonon coupling is usually weak as evidenced by both the fine structure of low temperature luminescence spectra and the absence of a Stokes shift (5).

Conjugated polymers have for long been considered as materials whose electronic properties are closer to those of a one-dimensional semiconductor than to a molecular crystal (6). Their fluorescence spectra are usually only weakly structured and off-set from the absorption by a Stokes-shift that varies from 0.2 to 1 eV. Instrinsic photoconduction starts at the absorption edge already (7-9). This has been taken as evidence that in conjugated polymers, such as polyphenylenevinylene (PPV), polythiophene and polyacetylene, the main absorption band results from a transition between valence and conduction band of the polymer backbone generating electron hole pairs that are only weakly bound by coulombic forces (10). However, there is one class of conjugated polymers, the polydiacetylenes, for which the excitonic nature of the lowest excited state remains unchallenged. Most of them are non-fluorescent because the lowest excited state is of A_g character (11) and acts as an efficient sink for singlet excitations. Photoconductivity sets in at an energy of about 0.4 eV above the absorption edge (12). This energy is likely to represent the exciton binding energy.

The different opto-electronic behavior of conventional conjugated polymers and polydiacetylenes has led to the conclusion that they differ with respect to the order of magnitude of the exciton binding energy. Support for this notion comes from the recent observation of rapid charge transfer in a C_{60}-doped PPV-derivative yet not in a C_{60}-doped polydiacetylene (13).

The purpose of this article is to reenforce the validity of the molecular approach for rationalising the opto-electronic properties of conjugated polymers, notably members of the PPV-family. The results of (i) high resolution cw-photoluminescence (PL) spectroscopy, (ii) energy transfer studies, (iii) time and spectrally resolved fluorescence, as well as (iv) studies of PL-quenching by electric fields form a

consistent body of experimental evidence in favor of the notion that the primary elementary excitations are neutral excitons. They migrate amongst the subunits of the polymer backbone comprising a statistically varying number of repeat units and considered to be the elementary absorbing units, i.e. chromophores in the sense of molecular spectroscopy.

Site selective fluorescence spectroscopy

The technique of site selective fluorescence (SSF) spectroscopy was originally developed to allow the spectra of chromophore molecules matrix-isolated in low-temperature glasses to be observed subject only to homogeneous broadening (14). It involves the use of a spectrally narrow laser, which makes it possible to excite selected chromophores from amongst a large ensemble contributing to an inhomogeneously broadened absorption. Only those whose transition energy is accidentally resonant with the laser are excited and, provided that excitation is into the $S_1 \leftarrow S_0$ 0-0 line, the resulting emission spectrum is a homogeneously broadened emission that provides information on the true molecular Stokes shift and on electron-phonon coupling. An additional requirement to observe homogeneously broadened spectra is that any inter-chromophore interaction be vanishingly small. The latter is not usually fulfilled when studying conjugated polymer films for which it is the segments of a polymer chain that have the role of chromophores. In polymers, rapid energy transfer is likely to occur along a chain or between chains for excitation of all but the lowest-energy segments, from which transfer is blocked on energetic grounds, there being very few if any nearby sites of lower-energy to transfer to. These latter segments contribute to the absorption at longest wavelengths and thus form a low-energy tail in the density of states (DOS). Only for excitation energies lying within this tail will it be possible to measure spectra subject only to homogeneous broadening. One can define a threshold ν_{loc} that separates states that participate in energy transport from those that do not. Exciting at $\nu_{ex} > \nu_{loc}$, even at low temperature, will therefore result in fluorescence spectra that are inhomogeneously broadened due to electronic energy relaxation occurring through migration of the excited state. These spectra will also be virtually independent of ν_{ex} since the emission is subsequent to the energy migration process. For $\nu_{ex} \leq \nu_{loc}$ a turnover to resonant or quasi-resonant (if a Stokes shift occurs) behavior is expected and the spectra should show only homogeneous broadening since absorption and emission are then expected to be from the same polymer segment. Thus spectra recorded with excitation below ν_{loc} can allow measurements of the true Stokes shift that arises from structural relaxation after photoexcitation, unaffected by spectral diffusion effects associated with energy transfer (15). They are consequently able to probe the extent of any self-localization to form a 'polaron-exciton' that may occur, and hence they provide an experimental test of the predictions of 1D one-electron band models.

The length of the segments, henceforth referred to as effective conjugation length L_{eff}, is much less than the total chain length (6,7). L_{eff} is a statistical quantity giving rise to inhomogeneous broadening, the entire absorption band then being identified as a singlet ($S_1 \leftarrow S_0$) electronic transition with a superimposed vibronic progression. The chain segments are delineated by chemical defects, configurational imperfections, and conformational disorder, including dynamic motions of the polymer chain. The elementary excitations generated by photoexcitation with $\nu_{ex} > \nu_{loc}$ execute an incoherent random walk among the chain segments thereby relaxing in energy within the DOS until they reach a segment from which they cannot escape within their lifetime. Analytic theory (18) has shown that the relaxation process occurs on a logarithmic time scale, i.e. it slows down as relaxation proceeds.

A family of SSF spectra recorded upon scanning a spectraly narrow excitation laser across the tail of the inhomogeneously broadened absorption spectrum of a substituted PPV, poly(2-tetrahydrothiophene-p-phenylenevinylene) is shown in Fig. 1.
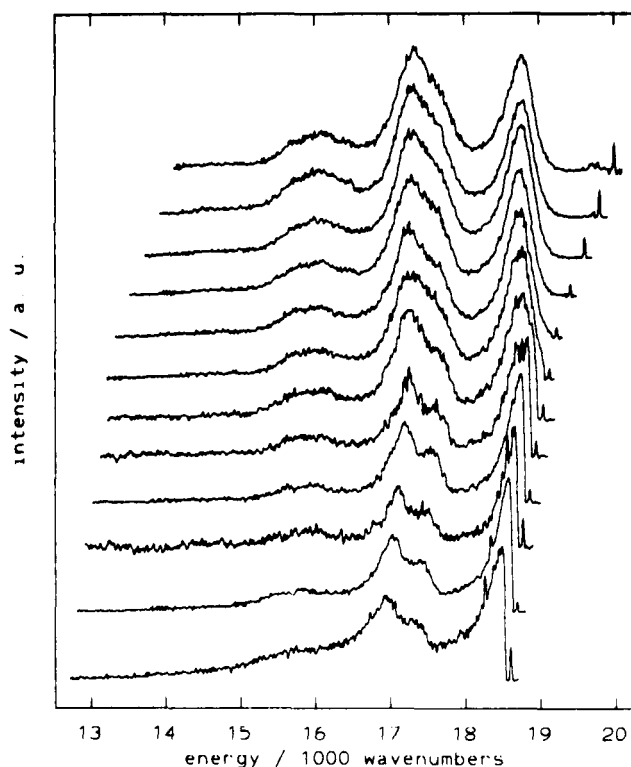
Fig.1 A series of fluorescence spectra of poly(2-tetrahydrothiophene-p-phenylenevinylene) parametric in excitation energy. The high energy spike marks the laser energy.

Starting at high excitation energy ν_{ex} the emission spectra are inhomogeneously broadened and invariant against variation of ν_{ex}. Below a critical value of ν_{ex} (18900 cm) the spectra become narrower and begin shifting linearly with ν_{ex}. Most important, the spectra recorded under resonant conditions are virtually identical with the fluorescence spectrum of a 3-membered matrix isolated oligomeric model compound of PPV (19) if plotted relative to the laser energy. The main vibronic features occur at the same energy off-set from ν_{ex} indicating that the polymer spectrum is built on the same origin as the oligomer spectrum. The important message is that the true Stokes shift of the polymer spectrum is below the resolution of the detection systems indicating weak electron-phonon coupling and proving that the Stokes shift measured under conventional non-resonant conditions arises from spectral relaxation due to excitation migration rather than relaxation of the molecular skeleton, i.e. formation of an excitonic polaron. Previous work (17) has shown that this conclusion is valid for most members of the PPV family except those that contain a biphenyl-group in the backbone. It introduces strong coupling of the exciton to a torsional motion because the equilibrium conformation of the biphenyl moiety is twisted in the ground state yet planar in the excited state (20).

Energy transfer studies

Energy transfer is a prototypical phenomenon in molecular crystals, manifest in the quenching of the host luminescence by traces of inadvertant impurities or deliberately added dopants. It occurs via exciton migration (21). The trivial message of such experiments is that the excitations retain their identity as strongly bound electron-hole pairs until they decay radiatively at the trap. Performing a classic energy transfer experiment on PPV-type systems is thus a simple tool to check the nature of the excited state. In the course of such an experiment the emission intensity of the dopant (the "sensitizer") is recorded as a function of its relative concentration. Another manifestation of energy transfer is the shortening of the host fluorescence with increasing dopant concentration.

Figure 2 shows a series of cw-fluorescence spectra recorded with a 20:80 by weight mixture of poly-phenylphenylenevinylene (PPPV) and polycarbonate (PC) doped with the commercial dye 4-dicyanomethylene-2-methyl-6-(p-dimethyl-aminostyryl)-4H-pyran (DCM) upon exciting at 3.15 eV. The increase of the dye emission (with maximum at near 2.15 eV) at the expense of the host emission upon increasing the concentration of the former up to 2.35×10^{19} cm^{-3} is obvious. The PPPV emission shows vibronic structure the $S_1 \to S_0$ 0-0 peak being located at 2.5 eV. Fluorescence excitation spectra, reported by Ochse et al. (22) confirm that the guest emission is sensitized by the host. The luminescence decay, excited by 150 fs pulses of photon energy 3.1 eV of a mode-locked Ti:sapphire laser, was monitored employing a Streak camera with a time resolution of 30 ps. Figure 3 not only confirms the shortening of the host emission but also demonstrates the non-exponential character of the quenching process.
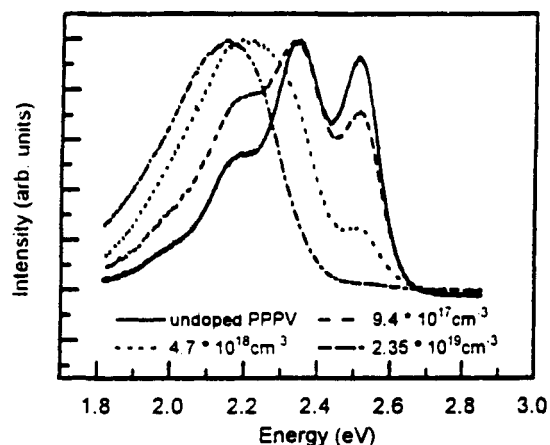

Fig.2 Low temperature fluorescence spectra of a 20% blend of PPPV with polycarbonate doped with various concentrations of DCM ($\nu_{ex} = 3.1$ eV).
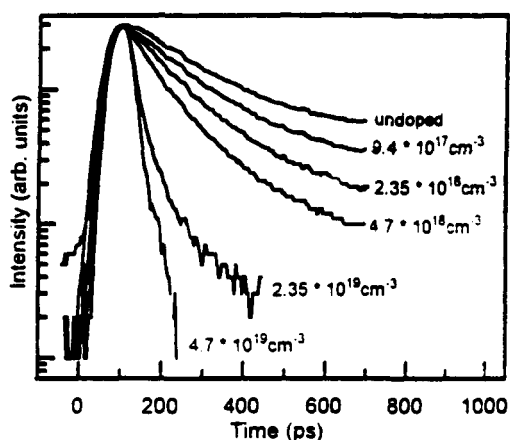
Fig.3 Decay of the PPPV-emission in PPPV/PC blends doped with various amounts of DCM

The results demonstrate conclusively the occurrence of energy transfer and, concomitantly, support the notion that the tranferred species is a neutral excitation rather than a charge carrier. The non-exponential character of host decay is an inherent feature of Förster type energy transfer in a system containing randomly distributed acceptors (23). The fact that the decay of the pure host luminescence is shorter than the decay of an isolated oligomer ($\simeq 1$ ns (24)) indicates that even the undoped material is contaminated with unidentified impurities (25). A crude data analysis in terms of Förster transfer yields a Förster radius of about 6 nm which is a reasonable value for a system with large spectral overlap, notably if one keeps in mind that the host excitation is delocalized among a few monomer units. The latter fact helps an excitation finding a trap.

Time resolved photoluminescence
Site-selective cw fluorescence spectra of PPV-type polymer, reported above, suggested that the polymer be considered as an array of chromophores with statistically varying excitation energy. At temperatures low enough to ensure that $\sigma \gg kT$, σ being a measure of the width of the distribution, excitations generated either statistically or energy-selectively at an energy above the demarcation energy ν_{loc} will relax energetically while hopping. The time dependent spectral diffusion can be monitored by measuring the PL spectrum within a narrow time window as a function of the delay time between generation and detection (26).

Figure 4 shows the inhomogeneously broadened steady state 10 K PL spectra of PPPV while Fig. 5 depicts the variation of the $S_1 \to S_0$ 0-0 section as a function of delay time on an expanded scale.
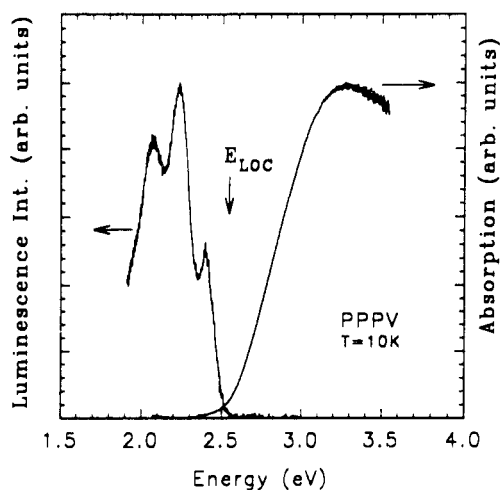
Fig.4 Absorption and steady state fluorescence spectra of PPV. E_{loc} denotes the localization energy as inferred from SSF spectroscopy (from ref. 26. By courtesy of Elsevier Publ.Co.).
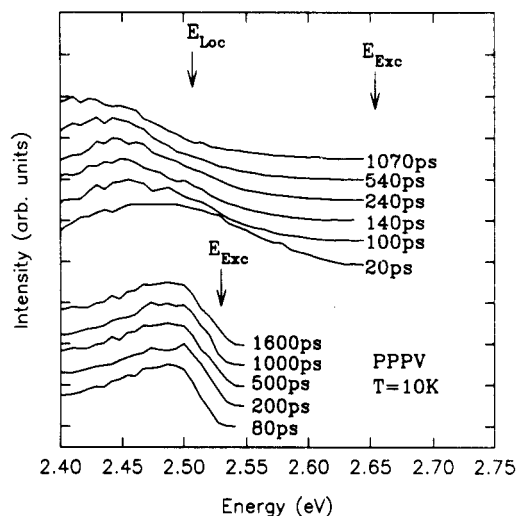
Fig.5 Gated fluorescence spectra of PPPV as a function of delay time and upon excitation either well above or close to the localization energy, respectively (from ref. 26. By courtesy of Elsevier Publ. Co.).

The latter spectra were recorded upon excitation with 7 ps pulses of a frequency-tripled Nd:YLF laser and employing Streak-camera recording techniques. Upon exciting above the localization energy the emission maximum shifts logarithmically towards lower energies with increasing delay time (Fig. 6) while no shift is observed upon exciting close to the localization threshold.
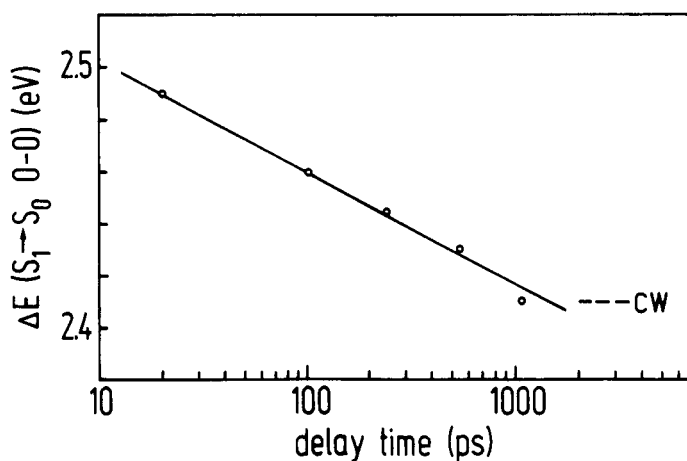

Fig.6 Temporal shift of the $S_1 \rightarrow S_0$ 0-0 emission maximum of PPPV as a function of delay time.

Although these experiments prove the occurrence of spectral diffusion in bulk PPPV they also demonstrate that 20 ps after excitation a significant portion of the relaxation is already completed. Probing the initial relaxation of excitations therefore requires faster detection techniques. This has been achieved by applying the technique of fluorescence upconversion. The sample was excited at 3.12 eV by 150 fs laser pulses of a frequency doubled Ti-sapphire laser. The luminescence emitted from the sample is focussed dispersion-free onto an optically nonlinear crystal. Sum frequency light is generated if the emission and the reference pulse (1.50 eV) overlap temporally within the crystal. The

temporal evolution of the luminescence is mapped by delaying the reference pulse with respect to the pulse exciting the sample. At an emission energy of 2.8 eV the temporal resolution of the set-up is about 300 fs.

A series of PL decay signals probed at selected emission energies within the inhomogeneously broadened $S_1 \leftarrow S_0$ 0-0 absorption of a 1% blend of PPPV in PC, which centered at 2.83 eV and has a Gaussian width of $\sigma = 0.13$ eV, is presented in Fig. 7.
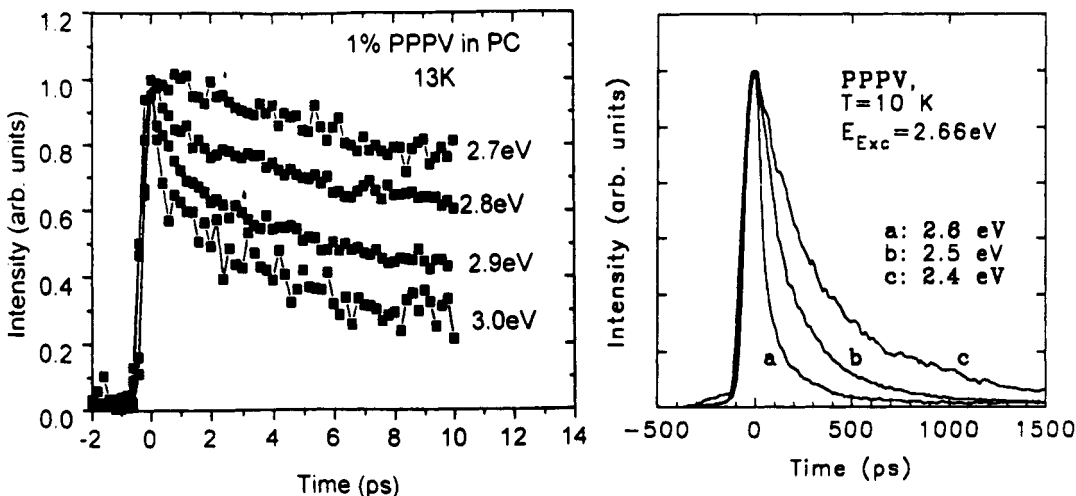
Fig.7 Decay of the photoluminescence of a 1% blend of PPPV in PC and a PPPV film, respectively, probed at various detection energies. Data were obtained using the upconversion (left portion) and the Streak camera (right portion) technique, respectively.

The signals bear out a fast initial rise which is limited by the resolution of the set-up except for the lowest detection energy (2.7 eV) and a subsequent decay that becomes progressively slower as the detection window is shifted towards lower energies. Upon further shifting of the detection window the PL decay becomes slow enough to be amenable to Streak camera probing (Fig. 7). Fig. 8 combines the PL decay data recorded with a 1% PPPV/PC blend and an undiluted PPPV-film, respectively, and plotted on a double logarithmic ln $I_0/I(t)$ versus t scale.
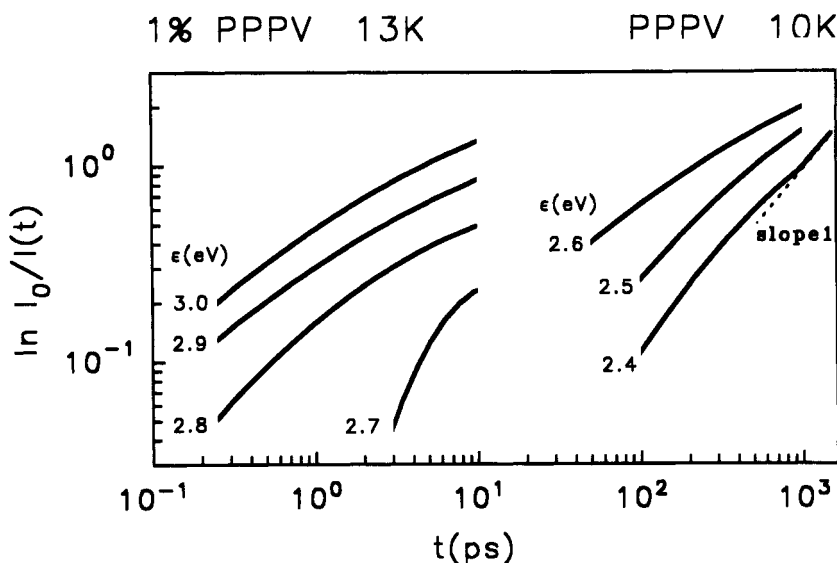
Fig.8 The smoothed decay profiles of Fig.7 plotted double logarithmically on a ln $I_0/I(t)$ versus time scale.

In this representation a decay profile that shows a stretched exponential dependence on time, $I(t) = I_0 \exp[-(t/t_0)^\beta]$ would reproduce as a straight line with slope β. The message contained in Fig. 8 is that (i) the decay pattern retains its character upon scanning the detection energy across the tail of the absorption band but shifts by 3 orders of magnitude towards longer times and (ii) there is an initial exponential decay process that merges into a stretched exponential law with $\beta \simeq 0.4$. The shortest extrapolated 1/e decay time of the initial decay portion is of order 1 ps. The result reported previously for PPV (27) is very similar to the present results except that the fastest decay time is shortened by a factor of 3. This reflects the increase of the number of nearest neighbors a chain segment in PPV has as compared to a 1% PPPV/PC blend.

Luminescence quenching by an electric field

If in a dielectric solid the absorption of a photon results in the production of an unbound electron hole pair the only effect an electric field can have is a modification of the oscillator strength of the transitions. Excitons, on the other hand, are, in principle, amenable to field-induced dissociation manifest in the quenching of luminescence. The latter effect has been studied in organic solids, notably phthalocyanines, by Popovic (28). It provides a handle on the primary process involved in the photogeneration of charge carriers. Studying PL-quenching of conjugated polymers by an electric field is, therefore, another tool to gain information on the nature of the primary excitations and their dynamics.

Electric field induced PL quenching was investigated for a blend of 20% PPPV and 80% PC sandwiched between an indium tin oxide (ITO) electrode and an Al contact employing cw as well as time-resolved techniques. The cw experiment showed that a static electric field of 2×10^6 V cm^{-1} reduces the luminescence intensity by approximately 30 percent, independent of the spectral detection window. The quenching effect is independent of polarity and, hence, of the cell current, which is characteristic of a rectifying diode, indicating that it is caused by the electric field rather than by the current flow. The time evolution of the quenching effect has been studied employing both fluorescence upconversion as well as Streak camera techniques. The result of the former experiment, portrayed in Fig. 9, indicates that PL-quenching is not an instanteneous effect caused, for instance, by field-induced reduction of the transition oscillator strength but rather is a secondary process starting at $\simeq 0.5$ ps. It extends into the 100 ps time domain as revealed by the Streak camera data (Fig. 10).
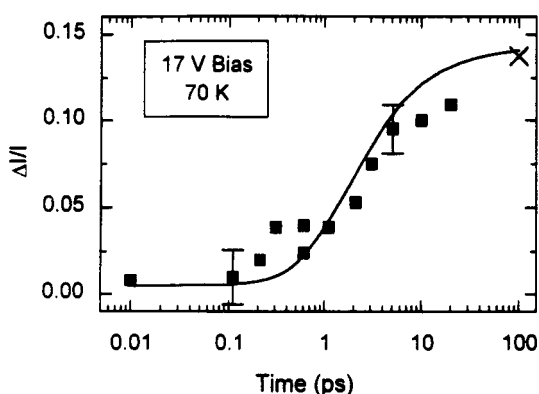
Fig.9 Time evolution of the quenching effect an electric field of 1.7×10^6 Vcm^{-1} has on the photoluminescence of a 20% PPPV/PC blend. The cross indicates the cw quenching efficiency.
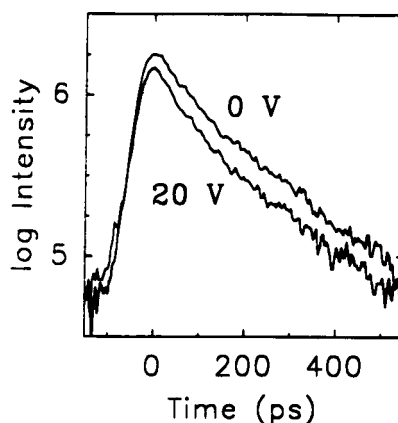
Fig.10 Semilogarithmic plot of the decay of the spectrally integrated fluorescence of a 20% blend of PPPV and PC at zero field and at a field of 2×10^6 V/cm, respectively.

Discussion

The variation of the characteristic decay time of the PL by three orders of magnitude upon red-shifting the detection window, the accompanied red-shift of the emission spectrum, and the non-exponential decay pattern combined with the independence of these effects on the pump intensity are characteristic features of neutral excitations executing an incoherent random walk within a density of localized states whose width is $> >$ kT. This conclusion is substantiated by a comparison of the results with theoretical studies of energy transfer along a random chain assuming Förster type coupling which will be published elsewhere (29). This indicates that the dynamics of excitations in PPV and PPPV is no different from that in a molecular glass such as benzophenone (30,31) except that in the latter systems the distribution of excitation energies of a chromophore is due to a variation of the local van der Waals interaction energy while in the former it results from a variation of the lengths of uninterrupted segments of a polymer chain.

Despite this similarity concerning the relaxation pattern of excitations in molecular and conjugated polymer systems there is one important difference. It relates to the size of the excited states. While in conventional molecular systems the excitations are tightly bound electron hole pairs forming Frenkel excitons in the respective crystals they resemble charge transfer excitons in conjugated polymers as evident from the large value of the polarizability inferred from electroabsorption spectra (32,33) and supported by recent theoretical calculations (34,35). The larger spatial extention of the excitation - in PPV it is about 17 Å, equivalent to two monomer repeat units - goes in hand with a reduced exciton binding energy. Moreover, since the interchain separation is about 7 Å, i.e. comparable to the Bohr radius of the exciton, the energies of an on-chain exciton and of an electron-hole pair localized on adjacent chains (off-chain or spatially indirect excitons (36)) should also be comparable. The important consequence is that excitons in conjugated polymers should be liable to dissociation into free charge carriers while (Frenkel) excitons in molecular crystals are not. This explains why in the former yet not in the latter intrinsic photoconductivity starts at the absorption edge. The latter cannot, therefore, be taken as argument in favor of an exciton binding energy E_b of order kT only. In that case exciton breaking by an electric field should not require an electric field of order 2×10^6 V cm^{-1}, equivalent to a drop of the electrostatic potential across an interchain distance of 0.14 eV. Picosecond transient pump and probe spectroscopy of PPV support this conclusion (37).

The combined set of experimental facts present above suggests the following scenario for the dynamics of optical excitations in PPV-type conjugated polymers. Photon absorption creates on-chain singlet excitations of chain segments that differ with regard to effective conjugation length and, hence, excitation energy. They couple weakly to phonons and relax energetically in course of a random walk and finally accumulate in tail states of the density of states. While migrating an excitation can (i) fluoresce, (ii) get trapped at impurities, or (iii) form off-chain geminate pairs as potential precursors for photoconductivity. The latter process is field assisted and continues after most of the energetic relaxation of the excitation has been completed.

References
1. M. Pope and C.E. Swenberg, *Electronic Processes in Organic Crystals,* Clarendon Press, Oxford (1982).
2. P.J. Bounds and W. Siebrand, *Chem.Phys.Lett.* **75**, 414 (1988).
3. L. Sebastian, G. Weiser, G. Peter, and H. Bässler, *Chem.Phys.* **75**, 103 (1983).
4. E.A. Silinsh, *Organic Molecular Crystals,* Springer Verlag, Berlin (1980).
5. E. Glockner and H.C. Wolf, *Chem.Phys.Lett.* **27**, 161 (1974).
6. A.J. Heeger, S. Kivelson, R.J. Schrieffer, and W.P. Su, *Rev.Mod.Phys.* **60**, 782 (1988).
7. S. Tokito, T. Tsutsui, R. Tanaka, and S. Saito, *Jpn.J.Appl.Phys.* **25**, 2680 (1986).
8. H.H. Hörhold, M. Helbig, D. Raabe, J. Opfermann, U. Scherf, R. Stockmann, and D. Weiss, *Z.Chem.* **27**, 126 (1987).

9. M. Gailberger and H. Bässler, *Phys.Rev.B* **44**, 8643 (1991-II).

10. C.L. Lee, G. Yu, and A.J. Heeger, *Phys.Rev.B* **47**, 15543 (1993).

11. D.E. Kohler, *J.Chem.Phys.* **93**, 5838 (1990).

12. K. Lochner, H. Bässler, B. Tieke, and G. Wegner, *phys.stat.sol.(b)* **88**, 653 (1978).

13. L. Smilowitz, N.S. Sariciftci, R. Wu, C. Gettinger, A.J. Heeger, and F. Wudl, *Phys.Rev.B* **47**, 13835 (1993).

14. R.I. Personov in: *Spectroscopy and Excitation Dynamics of Condensed Molecular Systems* (V.M. Agranovich and R.M. Hochstrasser, eds.), p.535, Elsevier, Amsterdam (1983).

15. H. Bässler in: *Optical Techniques to Characterize Polymer Systems* (H. Bässler, ed.), p.181, Elsevier, Amsterdam (1989).

16. U. Rauscher, H. Bässler, D.D.C. Bradley, and M. Hennecke, *Phys.Rev.B* **42**, 9830 (1990).

17. S. Heun, R.F. Mahrt, A. Greiner, U. Lemmer, H. Bässler, D.A. Halliday, D.D.C. Bradley, and A.B. Holmes, *J.Phys.Condens.Matter* **5**, 247 (1993).

18. B. Movaghar, M. Grünewald, B. Ries, H. Bässler, and D. Würtz, *Phys.Rev.B* **33**, 5545 (1986).

19. R.F. Mahrt, J. Yang, A. Greiner, H. Bässler, and D.D.C. Bradley, *Makromol.Chem.Rapid Commun.* **11**, 415 (1980).

20. R.F. Mahrt and H. Bässler, *Synth.Metals* **45**, 107 (1991).

21. H.C. Wolf and H. Port, *J.Lum.* **12/13**, 33 (1976).

22. A. Ochse, U. Lemmer, M. Deussen, J. Feldmann, A. Greiner, R.F. Mahrt, H. Bässler, and E.O. Göbel, *Mol.Cryst.Liq.Cryst.*, in press.

23. J. Klafter and A. Blumen, *J.Chem.Phys.* **80**, 875 (1984).

24. I.B. Berlman, *Handbook of Fluorescence Spectra of Aromatic Molecules*, 2nd Ed., Academic Press, New York (1971).

25. U. Lemmer, R.F. Mahrt, Y. Wada, A. Greiner, H. Bässler, and E.O. Göbel, *Appl.Phys.Lett.* **62**, 2827 (1993).

26. U. Lemmer, R.F. Mahrt, Y. Wada, A. Greiner, H. Bässler, and E.O. Göbel, *Chem.Phys.Lett.* **209**, 243 (1993).

27. R. Kersting, U. Lemmer, R.F. Mahrt, U. Leo, H. Kurz, H. Bässler, and E.O. Göbel, *Phys.Rev.Lett.* **70**, 3820 (1993).

28. see e.g. Z.D. Popovic, *J.Chem.Phys.* **78**, 1552 (1983).

29. B. Mollay, U. Lemmer, R. Kersting, R.F. Mahrt, H. Kurz, H.F. Kauffmann, and H. Bässler, *Phys.Rev.B*, submitted.

30. R. Richert and H. Bässler, *J.Chem.Phys.* **84**, 3567 (1986).

31. R. Richert, H. Bässler, B. Ries, B. Movaghar, and M. Grünewald, *Phil.Mag.Lett.* **59**, 95 (1989).

32. H. Sebastian and G. Weiser, *Chem.Phys.* **62**, 447 (1981).

33. A. Horvath, H. Bässler, and G. Weiser, *phys.stat.sol.(b)* **173**, 755 (1992).

34. H.X. Wang and S. Mukamel, *Chem.Phys.Lett.* **192**, 417 (1992).

35. S. Abe, in: *Relaxations in Polymers* (T. Kobayashi, ed.), World Scientific, Singapore (1993).

36. M. Yan, L.J. Rothberg, F. Papadimitrakopoulos, M.E. Galvin, and T.M. Miller, *Phys.Rev.Lett.* **72**, 1104 (1994).

37. J.M. Leng, S. Jeglinski, X. Wei, R.E. Benner, and Z.V. Vardeny, *Phys.Rev.Lett.* **72**, 156 (1994).