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1993 J. Phys.: Condens. Matter 5 247

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## Conformational effects in poly(p-phenylene vinylene)s revealed by low-temperature site-selective fluorescence

S Heun†, R F Mahrt†, A Greiner†, U Lemmer†, H Bässler†, D A Halliday‡, D D C Bradley‡, P L Burn§ and A B Holmes§

† Fachbereich Physikalische Chemie und Zentrum für Materialwissenschaften der Philipps-Universität, Hans-Meerwein-Strasse, D-W-3550 Marburg, Federal Republic of Germany

‡ Cavendish Laboratory, Madingley Road, Cambridge CB3 0HE, UK

§ University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW, UK

Received 10 August 1992

**Abstract.** Low-temperature site-selective fluorescence (SSF) spectroscopy is employed to study morphological effects on the conformation of poly(p-phenylene vinylene) (PPV) and its phenyl-substituted, soluble derivative poly(phenylphenylenevinylene) (PPPV). Samples of PPV prepared as spin-coated thin films and stretch-aligned free-standing films, and samples of PPPV prepared as cast films and as blends with poly(methylmethacrylate) and polycarbonate have been studied. The results that we present are consistent with the notion that each polymer sample consists of an array of ordered chain segments whose average length reflects the perfection of the local structure. The statistical distribution of the segment lengths is responsible for inhomogeneous broadening of the optical spectra (absorption and emission). The dominant electronic excitation created by photoexcitation across the  $\pi$ - $\pi^*$  energy gap is a singlet exciton that can execute a random walk among the chain segments. SSF spectroscopy allows us to distinguish the contributions to the apparent fluorescence Stokes shift that arise from energy relaxation through excitation migration (spectral diffusion) and from structural relaxation of the polymer chain (self-localization). The structural contribution to the Stokes shift approaches zero in well aligned PPV and reaches values of up to  $500\text{ cm}^{-1}$  in highly disordered PPPV films. The SSF method also provides a means of assessing the extent of phase separation that occurs in PPPV blends.

### 1. Introduction

There is currently much interest in the fundamental optical properties of  $\pi$ - and  $\sigma$ -conjugated polymers both for gaining greater insight into the mechanisms responsible for their non-linear optical properties (Abe *et al* 1992a, b, Hagler and Heeger 1992, Mukamel and Wang 1992) and for selection of materials suitable for electroluminescence application (Burroughes *et al* 1990, Burn *et al* 1992a, Bradley 1992). A central question in these deliberations is the role of electron-hole interactions, i.e. exciton formation. In general, the strength of coupling amongst the structural units of insulating solids, e.g. molecules in organic molecular crystals, chemical repeat units in polymer chains, and atoms in intrinsic inorganic semiconductors, determines whether their principal optical transitions are more appropriately described in terms of an exciton or a semiconductor band picture. Weak

inter-site coupling in conjunction with a low dielectric constant favours generation of strongly correlated electron-hole pairs (i.e. excitons) whilst strong inter-site coupling leads to the formation of weakly correlated electron-hole pairs that readily separate. It is clear that molecular materials like anthracene (Pope and Swenberg 1982) and polymers like polyvinylcarbazole (Rauscher and Bäessler 1990) have optical absorption spectra that are dominated by features appropriately described by an exciton picture and that inorganic semiconductors like Si are more appropriately described by a band picture (Smith 1978). The nature, however, of the absorption in conjugated polymers remains somewhat more controversial and both the band and exciton pictures have been used to describe different members of this class (Bloor *et al* 1974, Heeger *et al* 1988, Abe 1989, Wang and Mukamel 1992). The lowest-energy optical absorption of these  $\pi$ - or  $\sigma$ -conjugated polymers is often a more or less featureless peak and the maximum of fluorescence, if fluorescence occurs, is offset from the absorption maximum by an apparent Stokes shift of several thousand wavenumbers (several hundred meV). Such absorption and emission spectra have largely been interpreted in terms of transitions between the valence and conduction bands of a one-dimensional (1D) polymer chain (Heeger *et al* 1988) with the expected van Hove singularity broadened by disorder. The Stokes shift is then explained in terms of self-localization to form a 'polaron-exciton', a response characteristic of 1D one-electron band models (Heeger *et al* 1988). These simple models ignore both Coulomb and electron correlation effects. The former are known to be an essential ingredient in the description of at least one class of conjugated polymers, namely the polydiacetylenes (Bloor *et al* 1974, Lochner *et al* 1978, Sebastian and Weiser 1981), and are necessary to rationalize the observed discrepancy in poly(p-phenylene vinylene) (PPV) between the photoinduced bipolaron state intra-gap energy level separation and the energy of photoluminescence emission (Colaneri *et al* 1990). Electron correlation effects are held responsible for the reversal of the  $2^1A_g$  and  $1^1B_u$  excited state ordering in finite polyenes and *trans*-polyacetylene, and are thus used to explain the absence of dipole allowed fluorescence in these materials (Kohler 1990, Burna *et al* 1991). Such *ad hoc* inclusion or neglect of electron-electron and electron-hole interactions in discussions of different conjugated polymers is unsatisfactory and leads to unhelpful distinctions being made amongst them. It should be possible to fully describe within the same model the optical properties of both the polydiacetylenes and *trans*-polyacetylene and the many other polymers whose electronic structures link these two 'extremes'. This remains an important goal for theoretical studies.

The appropriateness of the 1D one-electron band model for rationalizing the spectroscopy of members of the PPV family has recently been challenged on the basis of site-selective fluorescence (SSF) experiments (Rauscher *et al* 1990, Mahrt and Bäessler 1991). This technique was originally developed to allow the spectra of chromophore molecules matrix-isolated in low-temperature glasses to be observed subject only to homogeneous broadening (Personov 1983). 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  $\nu_{loc}$  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  $\nu_{ex}$  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) behaviour 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  $\nu_{loc}$  can allow measurements of the true Stokes shift that arises from structural relaxation after photoexcitation, unaffected by spectral diffusion effects associated with energy transfer (Bässler 1989). 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.

Earlier SSF spectroscopy measurements have shown that an exciton model provides the most appropriate description of the absorption and emission in PPV (Rauscher *et al* 1990). The polymer is visualized as an array of chromophores, identified as segments of the chain, each with an effective conjugation length  $L_{eff}$  much less than the total chain length (Rauscher *et al* 1990, Mahrt *et al* 1990, Woo *et al* 1992a).  $L_{eff}$  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 superposed vibronic progression. The chain segments are delineated by chemical defects, configurational imperfections, and conformational disorder, including dynamic motions of the polymer chain. An interesting question, yet to be answered fully, is whether or not the length scale for the exciton wavefunction is limited in real polymer samples by these extrinsic effects. The elementary excitations (singlet excitons) generated by photoexcitation with  $\nu_{ex} > \nu_{loc}$  execute an incoherent random walk among the chain segments relaxing in energy within the DOS until they reach a segment from which they cannot escape within their lifetime. This model of spectral diffusion is directly supported by recent time-resolved measurements that show a red shift in the emission spectrum with increasing time delay after pulsed photoexcitation (Samuel *et al* 1992).

The work reported here makes use of the SSF technique to optically probe morphological variations in films of PPV and its derivatives. The range of samples studied includes (i) a standard precursor route PPV spin-coated film, (ii) a stretch-oriented PPV film, (iii) a spin-coated PPV film with an increased extent of intra-chain order and correspondingly longer effective conjugation length, (iv) a phenyl-substituted derivative of PPV, namely poly(phenylphenylenevinylene) (PPPV), and (v) several blends of PPPV with poly(methylmethacrylate) (PMMA) and polycarbonate (PC). Apart from confirming the validity of the use of the exciton description to explain the spectra of the PPV family, the results elucidate the correlation between morphology

and the position and linewidth of the  $S_1 \leftarrow S_0$  0-0 band and demonstrate that the true molecular Stokes shift depends on the internal strain stored in a chain. The Stokes shift tends to vanish in well aligned PPV.

## 2. Experimental details

PPV samples were prepared from precursor polymers (Burn *et al* 1991, Burn *et al* 1992b, c). The standard tetrahydrothiophenium (THT) leaving-group precursor was used to prepare both a spin-coated film ( $\sim 100$  nm thickness) on a spectro-sil substrate (PPV sample 1) and a free standing film ( $\sim 1$   $\mu\text{m}$  thickness), that was subsequently stretch-aligned. The spin-coated film was converted by heating *in vacuo* at  $220^\circ\text{C}$  for 2 h. The stretch-oriented sample (PPV sample 2) was prepared by applying a uniaxial stress to the free-standing film held *in vacuo* within a home-built stretching apparatus whilst it was heated to  $100^\circ\text{C}$ . Following stretch orientation it was converted *in vacuo* at  $220^\circ\text{C}$  to affect the full conversion from the precursor to PPV. Stretch-oriented films show a high degree of crystallinity, though subject to paracrystalline disorder, and have uniaxial orientation function values of up to 0.96 even for relatively low degrees of elongation (Bradley 1987). A modified precursor route where the precursor polymer contains short conjugated segments (Halliday *et al* 1992) was also used to prepare a spin-coated sample (PPV sample 3) with an especially high degree of intra-chain order, corresponding to an enhanced extent of conjugation compared with samples prepared via the standard THT leaving-group precursor. The inter-chain order in these samples is still low and they thus represent an intermediate between standard spin-coated films and the stretch-oriented samples which possess high degrees of both inter- and intra-chain order.

PPPV was synthesized via a Heck reaction (Heitz *et al* 1988). The average molecular weight, determined by gel permeation chromatography against a polystyrene standard, was  $M_n \simeq 8000$  g mol $^{-1}$  which corresponds to a chain containing  $\sim 45$  repeat units. PPPV films, typically a few  $\mu\text{m}$  thick, were cast onto quartz substrates from chloroform solution. Blends were made by mixing PPPV with the desired matrix material (PMMA or PC) in a chloroform solution. These blends were then cast from solution onto quartz or alternatively precipitated with methanol and fibre-spun and stretched from the melt by extrusion through a thin jet.

Fluorescence measurements were made with the samples mounted on the cold finger of an He-flow cryostat at  $\sim 6$  K. The fluorescence was excited by tunable pulsed dye laser with spectral bandwidth  $< 1$  cm $^{-1}$  and Boxcar averaging techniques were employed for signal detection. The emission was dispersed through a motor-driven monochromator, with a spectral resolution better than 10 cm $^{-1}$ . A cut-off filter was used to block the laser line for energies offset from the laser line by  $\leq 30$  cm $^{-1}$ .

## 3. Results

Figure 1 displays a series of fluorescence spectra recorded for a highly intra-chain ordered PPV (sample 3) film upon scanning the laser excitation energy across the low-energy tail of its absorption spectrum. The latter has been measured in the form of a (total) fluorescence excitation spectrum and this is also shown in the figure. Fluorescence spectra measured following excitation near the centre of the

inhomogeneously broadened  $S_1 \leftarrow S_0$  electronic transition are invariant with respect to changes in excitation energy  $\nu_{\text{ex}}$  and are inhomogeneously broadened. Spectral narrowing occurs once  $\nu_{\text{ex}}$  has dropped to an energy 500–600  $\text{cm}^{-1}$  (62–74.4 meV) below the centre of the  $S_1 \leftarrow S_0$  0–0 band and the spectra then begin to shift linearly with  $\nu_{\text{ex}}$ . The latter phenomenon is illustrated in figure 2 where the high energy peak of the fluorescence spectrum, parametrized as  $\nu_{\text{em}}$ , is plotted as a function of  $\nu_{\text{ex}}$ . In addition to data for the intra-chain ordered PPV (sample 3) film, data are also presented for a standard PPV (sample 1) film and a stretch-oriented PPV (sample 2) film. Numerical data characterizing the inhomogeneously broadened absorption and emission spectra of these PPV films and also that of a PPPV film and of PPPV in a methyltetrahydrofuran (MTHF) glass are summarized in table 1. There is an  $\sim 100 \text{ cm}^{-1}$  (12.4 meV) red shift of the excitation-invariant emission for the stretch-oriented PPV (sample 2) film compared with standard PPV (sample 1) and intra-chain ordered PPV (sample 3) films. The quasi-resonant emission observed for  $\nu_{\text{ex}} \leq 19000 \text{ cm}^{-1}$  (2.356 eV) is, however, unaffected by the film morphology for these three samples and exhibits a maximum offset from the laser line of  $\sim 150 \text{ cm}^{-1}$  (18.6 meV). In a previous report (Rauscher *et al* 1990) we have attributed this peak shift to a genuine Stokes shift of the PPV emission indicative of structural relaxation in the excited state. Comparison of the fluorescence spectra of the intra-chain ordered PPV (sample 3) film with those of oligo-phenylenevinylenes (OPV) (Mahrt *et al* 1990) (see figure 3) leads us to revise this conclusion. The spectra of OPV(3) and OPV(4), containing respectively three (distyrylbenzene) and four (distyrylstilbene) phenyl/phenylene groups, reveal well resolved vibronic zero-phonon lines for vibrational energies of 160  $\text{cm}^{-1}$  (s), 320  $\text{cm}^{-1}$  (w), 1170  $\text{cm}^{-1}$  (s), 1340  $\text{cm}^{-1}$  (s), 1500  $\text{cm}^{-1}$  (w), 1570  $\text{cm}^{-1}$  (w), 1620  $\text{cm}^{-1}$  (s), 1670  $\text{cm}^{-1}$  (s) and 1790  $\text{cm}^{-1}$  (s); (s) and (w) standing, respectively, for strong and weak transitions. Except for some residual broadening the vibrational features in the 1000–2000  $\text{cm}^{-1}$  region are retained in the PPV spectrum indicating that the molecular vibrational modes are essentially unaffected by chain elongation, a conclusion in complete agreement with the results of resonance Raman studies and theoretical calculations (Lefrant *et al* 1989, Rakovic *et al* 1990, Tian *et al* 1991). Furthermore, this coincidence of vibronic energies in the oligomers and polymer suggests that the polymer spectrum is built on an electronic origin that is resonant with the laser i.e. for which there is a vanishingly small Stokes shift. The peak near 150  $\text{cm}^{-1}$  in the PPV spectrum is then ascribed to a superposition of the 160  $\text{cm}^{-1}$  vibronic feature and the tail of the  $S_1 \rightarrow S_0$  electronic transition. The relative oscillator strength of this zero-phonon line is, lying as it does so close to the laser line, sadly indeterminable on account of stray light effects. There is, however, an indirect indication that the  $S_1 \rightarrow S_0$  0–0 transition is in fact weaker than the vibronic satellites. In the inhomogeneously broadened spectra recorded with  $\nu_{\text{ex}} > \nu_{\text{loc}}$  the energy separation between the high-energy band and the dominant vibronic band appears to be the difference between the (average) vibrational energies and that of the 160  $\text{cm}^{-1}$  mode. The fluorescence spectrum of an intra-chain ordered PPV (sample 3) film can thus be explained in analogous fashion to that of a molecular chromophore subject to an electron–phonon coupling that is small enough to ensure non-vanishing zero-phonon features.

The above conclusion concerning the vanishing Stokes shift exhibited by a resonantly excited fluorescence spectrum is also valid (see figure 3) for PPPV dispersed in an MTHF glass (Rauscher *et al* 1989), but not for PPPV in the form of a cast film or as a blend with PC or PMMA (see below). An overview of emission spectra recorded

under non-resonant conditions is presented in figure 4. It is noted that the PPPV cast film spectrum is in fact blue shifted and broadened relative to the spectra for PPV in all its various morphological forms. The inhomogeneously broadened PPPV/PMMA blend spectrum appears at the same energy as that of the cast PPPV film but displays some additional broadening. PPPV/PC blend spectra are, however, blue shifted from the cast PPPV film spectrum by an amount that increases with decreasing PPPV content in the blend, but that is little affected by stretch orientation of the blend. Note that the reduction in the relative intensity of the high-energy emission feature in the spectra of the cast PPPV film and of the PPPV blends can be explained, at least in part, by self-absorption effects; these spectra were measured on optically thick samples.

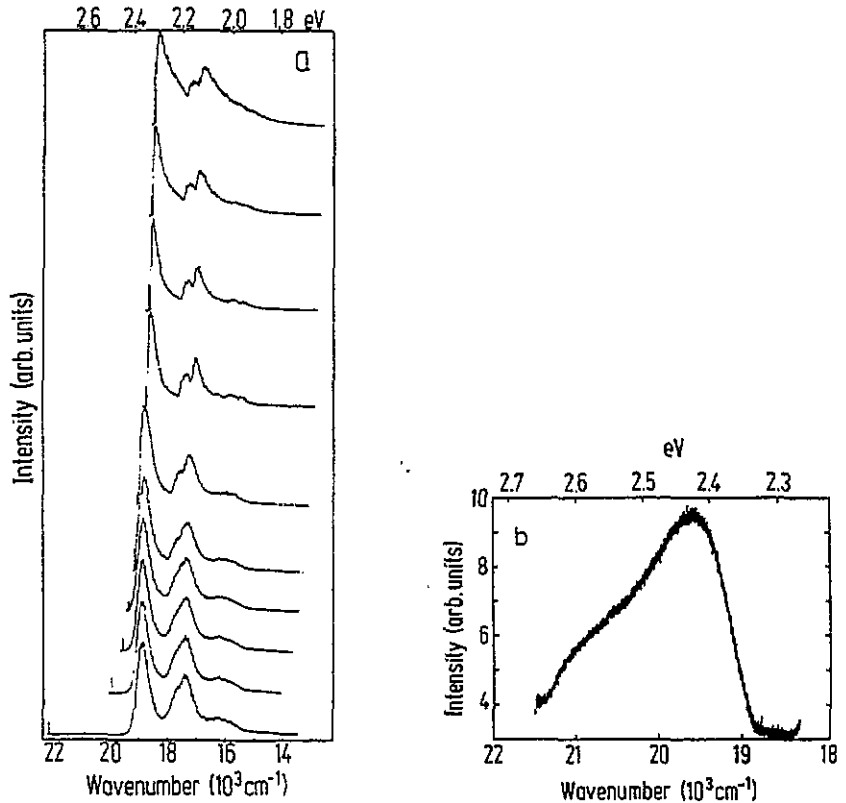


Figure 1. (a) 8 K fluorescence spectra of an intra-chain ordered PPPV (sample 3) film (see text for sample details). The different spectra (offset for clarity) were obtained by varying the excitation energy (indicated by the high-energy spike in the spectra), starting at the bottom far from resonance and moving into resonance going up the figure. (b) The low-energy portion of the absorption spectrum, recorded in the form of a fluorescence excitation spectrum, is also shown for comparison.

As shown in figure 5, the spectra of PPPV cast films reveal only minor spectral narrowing upon scanning  $\nu_{\text{ex}}$  across the absorption tail. The plot of  $\nu_{\text{em}}$  (the high-energy emission peak energy) versus  $\nu_{\text{ex}}$  exhibits a turnover to quasi-resonant behaviour for  $\nu_{\text{ex}} \leq 20\,200\text{ cm}^{-1}$  (2.505 eV) but a finite Stokes shift of about  $500\text{ cm}^{-1}$  (62 meV) persists down to the lowest excitation energies (see figure 6). The

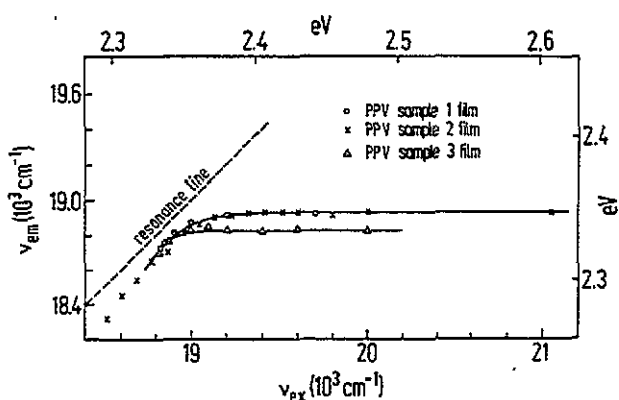


Figure 2. Emission versus excitation energies for various PPV samples (see text for sample details). The open circle data are taken from Rauscher *et al* 1990. Emission energies refer to the maximum of the high-energy emission peak.

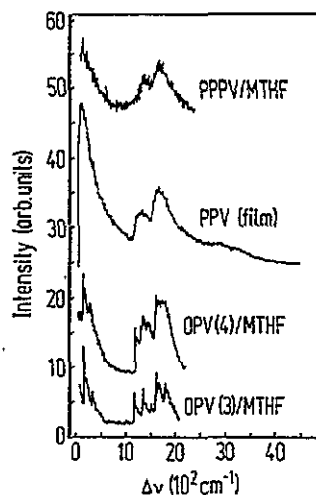


Figure 3. Comparison of resonantly excited fluorescence spectra of an intra-chain ordered PPV (sample 3) film (see text for sample details) with the spectra of PPPV and oligo-(phenylenevinylenes) in MTHF glasses (data for PPPV and OPV taken respectively from Rauscher *et al* (1989) and Mahrt *et al* (1990)). The abscissa scale is normalized to the laser excitation energy.

Table 1. Numerical data characterizing absorption and non-resonant emission spectra of poly(p-phenylene-vinylenes) (see text for sample details). Data were taken at  $T < 10$  K unless otherwise stated.  $\sigma$ -values are Gaussian widths of inhomogeneously broadened bands.

	$S_1 \leftarrow S_0$ 0-0 transition energy ( $\text{cm}^{-1}$ )	$\sigma_{\text{abs}}^{\text{inh}}$ ( $\text{cm}^{-1}$ )	$S_1 \rightarrow S_0$ transition energy (1st max.) ( $\text{cm}^{-1}$ )	$\sigma_{\text{em}}^{\text{inh}}$ ( $\text{cm}^{-1}$ ) (high-energy peak)
Standard PPV (sample 1 film)	20 200 (295 K)	650 (295 K) 480 (8 K)	18 930	180
Stretch-oriented PPV (sample 2 film)			18 830	169
Intra-chain ordered PPV (sample 3 film)	19 580	310	18 930	173
PPPV cast film	23 000 (295 K)	1300	19 550	400
PPPV/MTHF glass	22 000	700		

PPPV/PMMA blend spectra show the same Stokes shift and differ from the spectra of the cast PPPV film only in that (i) the turnover to quasi-resonant behaviour occurs at somewhat higher energy ( $20\,400\text{ cm}^{-1}$ , i.e.  $2.53\text{ eV}$ ), and that (ii) inhomogeneous widths are larger, such that the uncertainty in the band maxima increases to



$\pm 100 \text{ cm}^{-1}$ . It is, however, remarkable that neither changing the PPPV concentration from 1% to 20% nor film stretching has an effect on spectral positions exceeding the experimental uncertainty (figure 7). A different behaviour is found for the PPPV/PC blend samples. Not only do the fluorescence spectra excited above  $\nu_{loc}$  exhibit a pronounced red shift by  $1050 \text{ cm}^{-1}$  (0.13 eV) upon going from a 1% PPPV/PC blend to a cast PPPV film (figure 8), there is also a reduction of the Stokes shift upon film stretching (figure 9), the effect being especially pronounced for the 1% film. For the latter sample the high-energy emission peak smoothly approaches the resonance line upon tail-state excitation whereas for an unstretched sample of the same composition there is a Stokes shift of about  $400 \text{ cm}^{-1}$  (49.6 meV). Note that to eliminate artefacts caused by reabsorption effects which depend in a complex way on optical density, concentration, and molecular Stokes shift the position of the high-energy emission peak has been inferred from that of the convolution of vibronic bands which appears as the second peak in the emission spectrum, and whose position is offset from the direct electronic transition energy by  $1500 \pm 50 \text{ cm}^{-1}$  (cf figures 3 and 4).

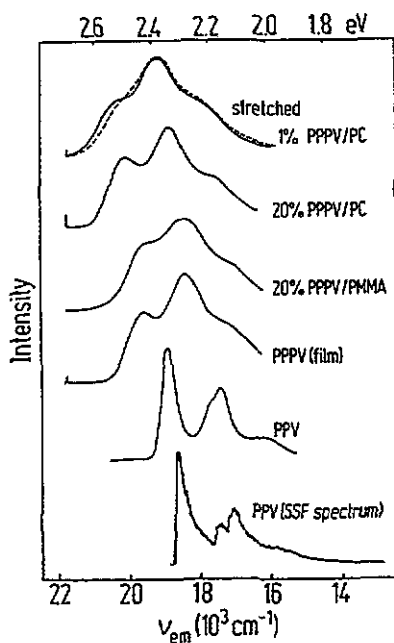


Figure 4. Non-resonant fluorescence spectra of an intra-chain ordered PPV (sample 3) film, PPPV cast film, and various PPPV blend films (see text for sample details). A resonantly excited (SSF) spectrum of an intra-chain ordered PPV (sample 3) film is also shown for comparison.

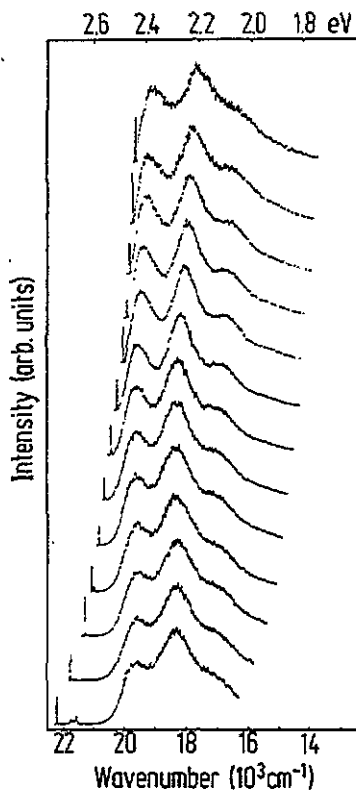
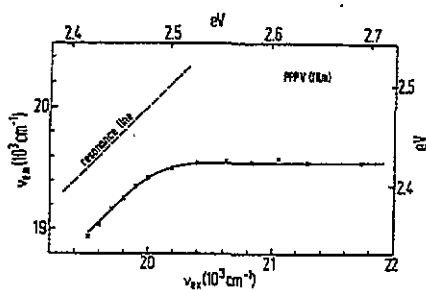
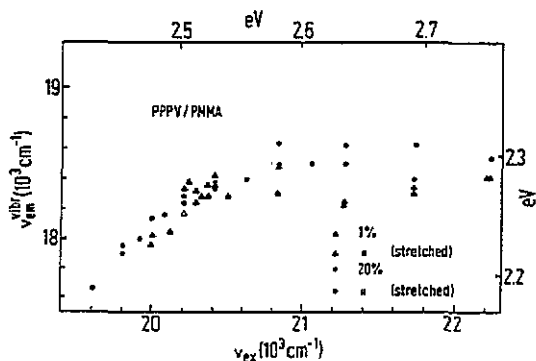


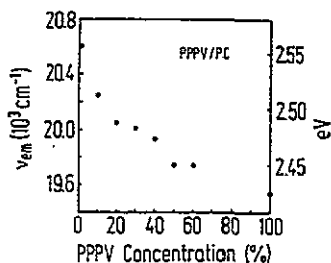
Figure 5. Site-selective fluorescence spectra of a PPPV cast film (see text for sample details). The high-energy spike marks the laser excitation energy.



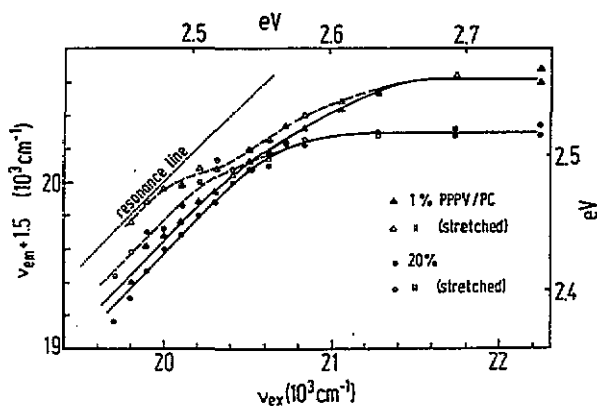
**Figure 6.** Emission (high-energy band) versus excitation energy for PPPV cast film (see text for sample details).



**Figure 7.** Variation of the peak energy of the dominant vibronic peak (a convolution of several vibronic transitions) with  $\nu_{ex}$  for unstretched and stretched PPPV/PMMA blends containing 1% and 20% PPPV (see text for sample details).



**Figure 8.** Variation with PPPV concentration of the high-energy emission peak of a non-resonantly excited PPPV/PC blend cast film (see text for sample details).



**Figure 9.** Emission versus excitation energy for unstretched and stretched PPPV/PC blend cast films containing 1% and 20% PPPV (see text for sample details). To eliminate the effects of any reabsorption on the apparent peak positions, the maximum of the  $S_1 \rightarrow S_0$  0-0 emission is inferred from the centre of the dominant (convolution) vibronic peak, which is offset from the electronic origin by  $1500 \pm 50 \text{ cm}^{-1}$ .

#### 4. Discussion

It has been previously shown (Bässler 1989, Rauscher *et al* 1990) that the fluorescence spectra of members of the PPV family can be understood in terms of the random walk of neutral excitations within a manifold of states associated with subunits of the polymer chains. The spectral red shift observed upon film stretching suggests identifying these subunits with ordered segments of the polymer backbone. This conclusion is supported by plotting, as in figure 10, the  $S_1 \leftarrow S_0$  0-0 transition

energies,  $E_{S_1 \rightarrow S_0}$ , of the OPV oligomers versus the reciprocal segment length,  $L^{-1}$ . The observed dependence suggests an inverse relationship between transition energy and  $L$  as has previously been observed for other conjugated systems (Baughman and Chance 1976, Wenz *et al* 1984). Although the molecules are not strictly linear, Kuhn's particle-in-a-box model (Kuhn 1958, Baughman and Chance 1976) appears to be at least qualitatively correct. Within the framework of this model the slope  $\delta(E_{S_1 \rightarrow S_0})/\delta(L^{-1})$  reflects the decrease of the level spacing as the chains get larger, and the ordinate intercept is a measure of the amplitude of a sinusoidal potential arising from bond alternation (Baughman and Chance 1976). Given the limitations of this model and the corresponding uncertainty of the extrapolation of the transition energy towards infinite chain length we are hesitant to derive absolute numbers for the average effective conjugation length ( $L_{\text{eff}}$ ) of the different polymer morphology samples from the position of the absorption or emission peaks. From the data for peak position and peak width listed in table 1 it is, nevertheless, obvious that the absorption and non-resonant fluorescence bands of the PPPV cast film and even the PPPV/MTHF glass are blue shifted relative to those of PPV films, indicating shorter  $L_{\text{eff}}$ . They are also significantly broadened relative to those of PPV films. The blue shift is particularly pronounced for the PPPV cast film, about  $3000 \text{ cm}^{-1}$  (0.372 eV). Stretch orientation of a PPV film on the other hand causes a red shift, i.e. segment elongation. These effects are rationalized in a straightforward manner by assuming that the ordered segments of the chain lengthen, i.e. the effective conjugation length increases, with increasing film order. Their length nevertheless remains finite even for the best ordered samples available (the extrapolation in figure 10 would suggest a lower limit of about 20 repeat units, i.e.  $\sim 120 \text{ \AA}$ , in good agreement with the estimate recently obtained from transient absorption measurements (Woo *et al* 1992b) and with estimates of the along chain crystallite sizes determined by x-ray and electron diffraction (Bradley 1987, Halliday *et al* 1992). In addition, the effective conjugation length is subject to a random variation that we believe is the main cause of the inhomogeneous broadening of the absorption and off-resonant emission profiles. A plausible explanation is that the deposition of a polymer film always introduces some disorder, e.g. in the form of entanglements or other chain defects, and that this disorder cannot be fully removed even upon film stretching. In PPPV films the bulky phenyl substituents hinder chain alignment with the consequence that ( $L_{\text{eff}}$ ) is reduced and the inhomogeneous broadening is increased relative to unsubstituted PPV. The less pronounced disorder (evidenced by a narrower inhomogeneous absorption line) for PPPV dispersed in an MTHF glass suggests that some chain ordering may occur in this matrix upon cooling.

The random-walk concept implies that an excitation generated within an inhomogeneously broadened DOS at an energy above  $\nu_{\text{loc}}$  migrates incoherently, relaxing energetically as it does so. The model of choice for analysing the concomitant spectral diffusion is that of Rudenko *et al* (Rudenko and Bässler 1991, Arkhipov *et al* 1991). Based upon a master equation approach these authors calculated the occupational density of states (ODOS) that an ensemble of excitations at  $T = 0 \text{ K}$  relaxes to after being generated either randomly or at an energy much above  $\nu_{\text{loc}}$  within a Gaussian DOS of energetic width  $\sigma$ . The solution depends upon the topology of the system and, in the case of a 3D topology, on the number of neighbouring sites that an excitation is allowed to jump to. Figure 11 summarizes the results for 3D systems in which an excitation is allowed to jump either to the six nearest neighbours of a simple cubic lattice or to those six and in addition the 12 next-

nearest-neighbour sites at the face diagonals. It is in accord with intuition that the loss of electronic energy an excitation suffers by migrating in an energetically random system increases as the number of potential acceptor sites increases. At the same time the ODOS becomes narrower. Comparison with the experimental results from the PPV (sample 3) film, for which the low-energy peak of the fluorescence excitation spectrum (mapping the DOS) can be well approximated by a Gaussian of inhomogeneous width  $\sigma^{\text{inh}} = 310 \text{ cm}^{-1}$  (38 meV), indicates that the six-nearest-neighbour case provides a satisfactory description of the results (see figure 11). It is thus, to first approximation, sufficient to consider only jumps that result in transfer of the exciton to the adjacent segments of the same chain or to those of the nearest-neighbour chains. Longer-range jumps are not required to explain the energy relaxation and there is no evidence that Förster energy transfer processes contribute in any way.

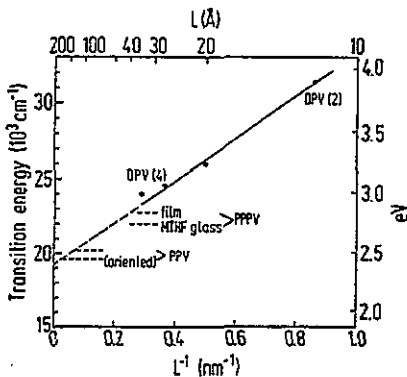


Figure 10.  $S_1 \leftarrow S_0$  0-0 transition energies for oligo-(phenylenevinylenes) (numbers labelling the number of phenyl rings) as a function of reciprocal chain length. (Data taken from Mahrt *et al.* (1990).) The dashed horizontal lines indicate the transition energies for several PPPV and PPV samples (see text for sample details). The PPV oriented sample is a stretch-aligned film.

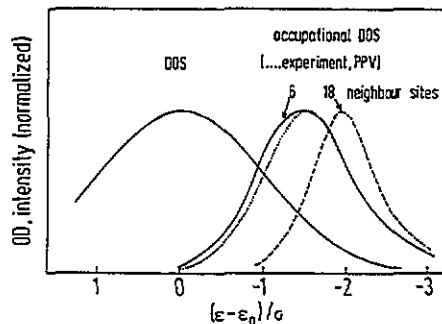


Figure 11. Result of the master-equation approach of Arkhipov *et al.* (1991) for the ODOS for excitations started randomly in a three-dimensional Gaussian DOS under the premise that jumps to the six nearest neighbours or 18 nearest plus next-nearest neighbours on a cubic lattice are allowed. The dotted spectrum is the high-energy wing of the non-resonant  $S_1 \rightarrow S_0$  0-0 emission band of an intra-chain ordered PPV (sample 3) film (see text for sample details), whose absorption tail is a Gaussian with standard deviation  $\sigma = 310 \text{ cm}^{-1}$ .

The random-walk model offers a simple and intuitively obvious way of relating the width and position of non-resonantly excited fluorescence spectra to the degree of disorder: the more perfect a structure becomes the more elongated the emitting segments will be and the more red-shifted the emission. At the same time the inhomogeneous widths of the emission bands decrease because (i) the relative variation of effective conjugation lengths decreases and (ii) with increasing motion of the excitation along a chain segment the effect of random variations in the van der Waals interaction energies with neighbouring chains becomes smeared out (i.e. motional narrowing). The vanishing Stokes shift in the resonantly excited fluorescence spectra is the signature of an absence of any major relaxation within a chain segment following photoexcitation, i.e. it argues against self-localization of the excitation as a 'polaron-exciton'. That this is a reasonable result is seen by realizing that the associated emission comes from the most extended chain segments sitting in a

well ordered local environment: these segments have less possibility for structural relaxation. Concerning the strength of the electron-phonon coupling we expect the situation to be similar to that for oligomeric model compounds. In fact, electron-phonon coupling appears to be somewhat stronger in PPV compared to the OPVs (as witnessed by the decrease in zero-phonon line strength), although the Huang-Rhys factor must still be close to unity, otherwise the vibronic emission lines should not be built onto the electronic transition energy that is identified by the laser excitation line.

The situation is very different in a cast PPPV film. There the quasi-resonant emission spectra do show a significant Stokes shift of about  $500\text{ cm}^{-1}$  (62 meV) and retain an appreciable spectral broadening. This, taken in conjunction with the higher degree of disorder that is derived from absorption and non-resonant emission spectra, strongly suggests that long ordered chain segments are absent from such samples. It appears likely that upon casting a PPPV film from solution the chains become trapped in worm-like conformations, as previously proposed for polydiacetylenes in solution (Wenz *et al* 1984), that are subject to considerable mechanical strain. Upon excitation the chain segments may relax locally into new metastable conformations by coupling to intra- and/or inter-chain motions. Appearance of a Stokes shift is thus interpreted as a signature of the existence of chain conformations that are far from equilibrium.

#### 4.1. PPPV blends

The difference in behaviour between PPPV/PC and PPPV/PMMA blends can be understood in terms of phase separation. PPPV is expected to aggregate and to form clusters in a PMMA matrix, as is confirmed by scanning tunnelling microscopy. The independence of the non-resonant emission on both concentration and film stretching is the spectroscopic manifestation of the facts that (i) clusters are formed even in a blend containing only 1% of PPPV and that (ii) stretching does not disentangle the clusters. The emission band centre,  $\nu_{\text{em}}^{\text{inh}}$ , for PPPV/PMMA blends is slightly blue shifted in comparison to cast PPPV films indicating stronger disorder, consistent with the increase in inhomogeneous band width.

If, on the other hand, PPPV forms a solid solution within a polymer blend, a continuous red shift of  $\nu_{\text{em}}^{\text{inh}}$  is expected with increasing PPPV concentration because energy transfer and, concomitantly, electronic spectral relaxation should become more efficient. At low concentration excitation migration will be more or less restricted to individual chains and acquire 3D character only when inter-chain contacts become efficient channels for excitation transfer. This behaviour is observed for PPPV/PC blends (see figures 8–10) where independent evidence indicates that upon casting a PPPV/PC film from solution at room temperature a thermodynamically metastable solid solution is formed. Upon film stretching the individual, if coiled, PPPV chains will be elongated with a resulting increase of the effective conjugation length and a red shift of  $\nu_{\text{em}}^{\text{inh}}$  (see figures 8 and 9). A remarkable feature is the decrease of the Stokes shift leading to essentially resonant emission upon tail-state excitation of the stretched samples. Stretching clearly generates elongated chains that are no longer able to relax structurally after excitation and, therefore, behave in similar fashion to PPV.

## 5. Conclusions

The present comparative SSF study of members of the poly(p-phenylenevinylene)

family prepared with different morphologies confirms the notion that the elementary electronic excitations in these materials are singlet excitons that reside on chain segments delineated by disorder. On the basis of an extrapolation of oligomer transition energies one can estimate the average number of monomer repeat units within such a chain segment to range from about five in a PPPV cast film to more than 20 for stretch-oriented PPV. Variation of the length of these segments, i.e. the effective conjugation length, is the major origin of band shifts and inhomogeneous broadening upon structural manipulation. The segments act as hopping sites for the random walk of excitations generated above a certain energy, termed the localization energy,  $\nu_{loc}$ , within the tail of the DOS. The consequent electronic relaxation is the main origin of the 'Stokes shift' observed when performing broad-band fluorescence spectroscopy measurements (Colaneri *et al* 1990, Hagler *et al* 1991, Woo *et al* 1992a). The true Stokes shift measuring the structural relaxation of a segment after excitation depends primarily on how strained a chain segment is. It approaches zero for elongated or locally well ordered PPV chains.

Previous Monte Carlo simulations have indicated that at temperatures such that  $kT \ll \sigma$ , where  $\sigma$  is the Gaussian width of the DOS, thermally activated hopping of excitations is unimportant and the number of hops that an excitation, initially generated at an energy  $\nu_{ex} > \nu_{loc}$ , makes is small, typically  $\leq 5$  in the case of a 3D topology and  $\leq 2$  for a 1D topology. The excitation thus samples only a small volume and SSF spectroscopy can consequently be used as a simple microscopic-level probe of miscibility in polymer blends. It complements the technique of photochromic labelling that is often used to identify (based on energy transfer studies) structural modifications in polymer solutions or blends (Peterson *et al* 1989, Henker *et al* 1990, Winnik 1990, Lin *et al* 1990). The advantage of the SSF method is that it uses the spectral diffusion due to energy transfer among the subunits of the polymer itself, which has to be fluorescent, but does not then require the attachment of an additional label to the polymer or its incorporation within the blend.

## Acknowledgments

Financial support by the Deutsche Forschungsgemeinschaft and the Fond der Chemischen Industrie in Germany and the Science and Engineering Research Council in the UK is gratefully acknowledged. We also thank Dr J H F Martens for preparation of the stretch-oriented PPV film. PLB thanks Christ's College Cambridge for the provision of a Dow Research Fellowship.

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