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Absorption, luminescence and Raman spectroscopy of poly(p-phenylene vinylene) at high pressure

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Optical absorption, photoluminescence and Raman spectra of poly(p-phenylene vinylene) have been recorded as a function of pressure to 50 kbar. Both absorption and emission spectra are observed to red shift with pressure. The photoluminescence spectrum is observed to decrease in integrated intensity and lose vibronic structure with increasing pressure. Possible explanations of the observed results are discussed. In particular the possible role of intermolecular effects is highlighted. Copyright © 1996 Elsevier Science Ltd.

INTRODUCTION

Conjugated polymers are characterized by a highly delocalized π-electronic structure lying along the polymer backbone. When suitably doped, these materials can display metallic conductivities and historically much attention has been focused on developing these 'conducting' polymers[1]. Undoped conjugated polymers behave as semiconductors with band gaps typically in the range 2-3 eV. Recently, considerable interest has been directed towards undoped conjugated polymers as replacements for conventional semiconductors, particularly in optical devices[2-5].

Poly(p-phenylene vinylene) (PPV) is an important example of these semiconducting polymers. It was with this material that polymer electroluminescence was first demonstrated[2] in 1990. Since that time, considerable scientific and technological interest had been focused on PPV and related materials, largely driven by the promise of cheap, readily processible light-emitting diodes, TVs, computer screens, etc. Significant progress has been made in improving the efficiency[6-9] and range of available emitted colours[7-10] from these devices; many of the fundamental physical processes in these materials, however, are not well understood.

The nature of the excitation that leads to the electroluminescence is a critical element in a full understanding of the physics of these materials. Of particular interest are routes by which the excitation may lose its energy non-radiatively, thus reducing the efficiency of electroluminescent devices.

The optical properties of PPV may be summarized in *Figure 1*. A broad featureless optical absorption (OA) is observed with its low-energy edge lying at approximately 2.4 eV. This absorption is considered to be the π-π* transition, leading to the formation of a singlet exciton[11-13]. The energy of the π-π* transition is dependent on the extent of the π-electron delocalization (the 'conjugation length'). In relatively disordered polymers such as PPV, the extent of the delocalization tends to be limited by kinks and defects in the polymer chain leading to a range of π-π* energies for a given sample. The lack of vibronic structure in the absorption spectra is thus attributed to inhomogeneous broadening due to a range of conjugation lengths within the sample. If PPV is photoexcited at energies within the absorption band then the exciton may decay radiatively via a symmetry allowed transition, giving rise to photoluminescence (PL), or alternatively decay non-radiatively via a number of possible mechanisms. The PL spectrum is generally Stokes shifted from the absorption spectrum and the spectrum has clearly resolved vibronic structure. These observations have been explained by migration of the photo-generated excitons to the lower energy (longer conjugation length) chain segments before radiative decay has time to occur[12-15]. Thus, the observed emission originates solely from the lowest energy segments leading to the observed Stokes shift and reduced inhomogeneous broadening when compared with the absorption spectra.

A key observation is that the electroluminescence emission from PPV is essentially identical to the photoluminescence spectrum. It may thus be concluded that both emissions arise from the same type of excitation and that study of the PL of the material should provide valuable information about the electroluminescence process as well.

The application of high pressures was selected as a means of systematically influencing the electronic structure of the polymer without the complication of chemical modification of the material. In particular, the application of hydrostatic pressure would be expected to reduce intermolecular separation, thus amplifying any contribution of the intermolecular interactions to the optical properties.

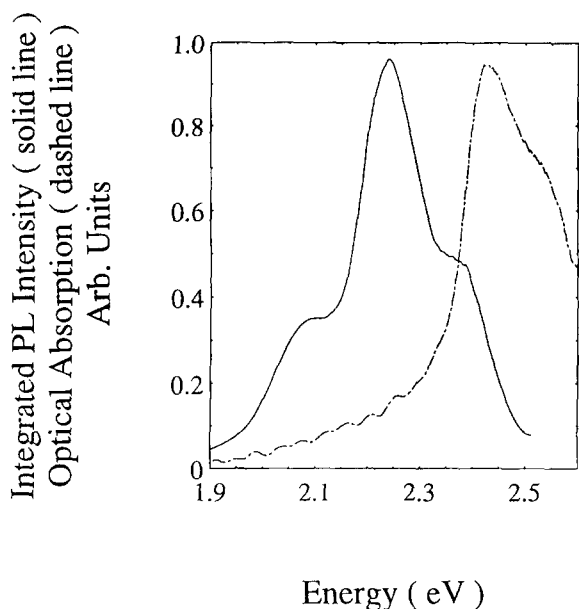
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Figure 1 Optical absorption and photoluminescence spectra of PPV: ———— PL; — · — OA

Optical absorption, photoluminescence and Raman spectra of PPV have been recorded as a function of applied hydrostatic pressure. The results are presented and the observed effects are discussed.

EXPERIMENTAL

The PPV sample was supplied by the Chemical Laboratory at the University of Cambridge. It was prepared via the sulfonium precursor route[16-18], with the precursor being spun onto PTFE to form a thin film. This was dried and then peeled off the PTFE and sandwiched between glass slides before undergoing thermal conversion to the fully conjugated PPV in a vacuum oven. Small, free-standing flakes of PPV were thus produced which were suitable for inclusion in the high pressure cell. The flakes were approximately 0.5–1 μm thick with significant variation in the thickness across the area of each flake.

Hydrostatic pressure was applied to the polymer using an opposed diamond anvil cell (DAC)[19-21]. The sample was contained in a preindented steel gasket[22] and surrounded by either silicone oil or a 4/1 mixture of methanol–ethanol[23]; this method produces a near hydrostatic pressure environment. The pressure inside the cell was determined by observing the shift of fluorescence from a number of small ruby chips contained within the sample volume[24-29]. The wavelength vs. pressure shift of the ruby fluorescence has previously been calibrated[26-28]. The use of multiple ruby chips and the use of a least squares fitting routine to determine the fluorescence peak positions improved the accuracy of the pressure measurement.

All spectroscopic measurements were performed with a Renishaw Raman imaging microscope[30]. This was suitably adapted to enable PL and OA spectra to be recorded. Excitation of the PL spectra was provided by the 477 nm output of an argon ion laser. Excitation intensities were kept less than 0.1 mW to avoid photo-induced damage in the sample. Raman spectra were recorded using ∼ 5 mW of 633 nm radiation; at this wavelength the samples were nearly transparent.

RESULTS

Optical absorption

When viewed in transmitted light, the PPV was observed to gradually change from its yellow colour at ambient pressure, through orange to a deep red colour as the pressure was increased to 50 kbar. The optical absorption spectrum of PPV was recorded as a function of pressure. Independent experiments were performed using silicone oil and 4/1 methanol–ethanol as the pressure transmitting fluid. The PPV OA spectrum is shown in *Figure 2* at a range of pressures.

The position of the absorption edge, as judged by eye, was observed to red shift as a function of pressure as illustrated in *Figure 3*. Below about 30 kbar the data may be well fitted by a linear function; however, over a wider pressure range, the shift is clearly sublinear. A quadratic function was least squares fitted to the data and this is shown as the solid line in *Figure 3*. This has a linear coefficient of -5.4 ± 0.2 meV kbar^{-1} and a quadratic coefficient of 0.030 ± 0.004 meV kbar^{-2}. There is also an
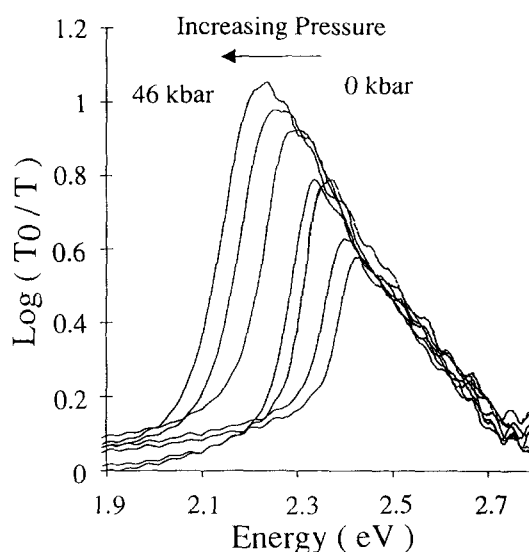

Figure 2 PPV optical absorption spectrum at a range of applied hydrostatic pressures. T_0 is the transmission through the DAC, to one side of the sample at a given pressure; T is the transmission through the PPV sample at a given pressure
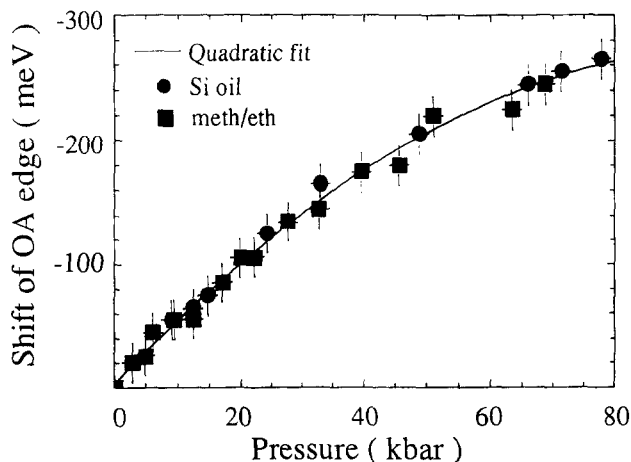

Figure 3 Shift of PPV optical absorption edge as a function of pressure: ● with silicone oil pressure transmitting fluid; ■ with methanol–ethanol; ———— quadratic fit to both sets of data

apparent increase in the absorption of the sample with pressure. All the reported effects of pressure on the OA of the PPV appear to be reversible with no observable hysteresis. The reported effects are independent of whether silicone oil or methanol/ethanol is used as the pressure transmitting fluid.

Photoluminescence

The photoluminescence spectrum of PPV at a range of applied pressures is presented in *Figure 4*. The intensity scale in this figure is the fractional value relative to that at ambient pressure. The main observations from *Figure 4* are: a general red shift of the spectrum; a loss of vibronic structure; a dramatic decrease in the integrated intensity; and a possible slight shift of the weighting of the intensity to lower energy (higher vibronic modes). The latter observation is however by no means clear.

The energy shift of the high energy component of the photoluminescence spectrum, as judged by eye, is plotted as a function of pressure in *Figure 5*. Also plotted is the corresponding shift of the optical absorption edge. It can be seen from *Figure 5* that both the optical absorption and photoluminescence of PPV shift at essentially the same rate as a function of pressure. The integrated intensity of the PPV PL is plotted as a function of pressure in *Figure 6* for both the methanol–ethanol and silicone oil compressive media. The uncertainty of the
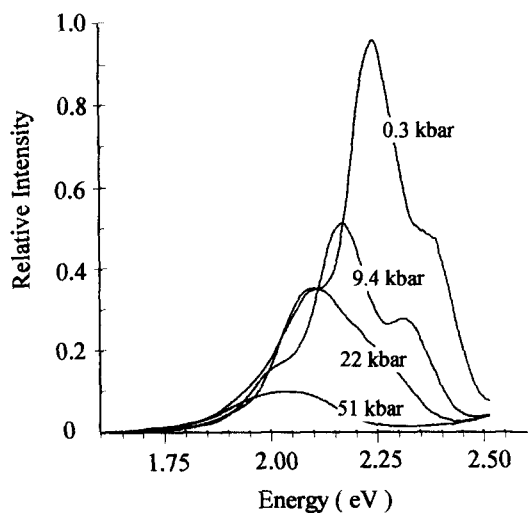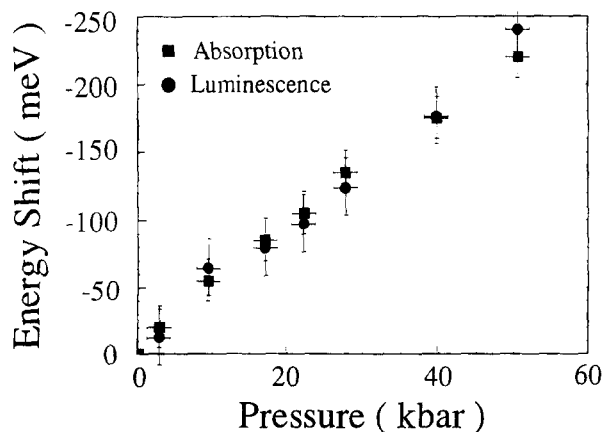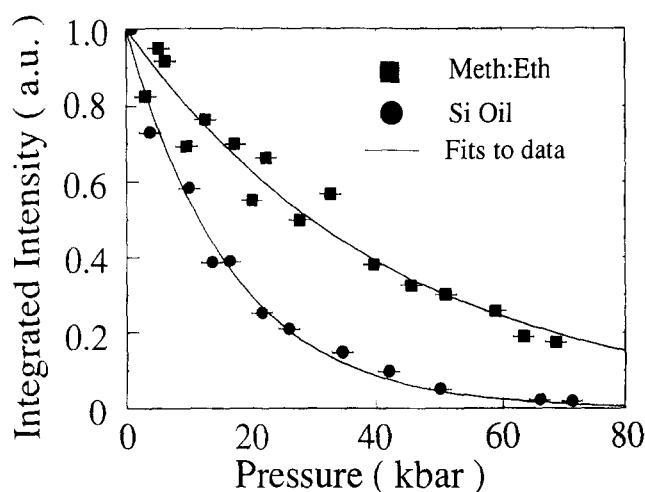

Figure 6 Integrated intensity of PPV PL as a function of pressure; ■ data with methanol–ethanol pressure transmitting fluid; ● with silicone oil; —— exponential fits to data

intensity data varied from experiment to experiment due to slight differences in sample morphology. In the worst cases this uncertainty could be as much as ±10% although better than ±5% was more typical. Simple exponential functions were fitted to the data and these are included in *Figure 6*. The fitted functions were $I = \exp(-0.061 * P)$ and $I = \exp(-0.024 * P)$ for the methanol–ethanol data and the silicone oil data respectively.

The choice of pressure transmitting fluid used in the DAC appeared to have no effect on the rate of red shift or change in shape of the PL spectrum as a function of pressure. The rate at which the PL was extinguished as a function of pressure was, however, dramatically affected by the choice of fluid as illustrated in *Figure 6*. It can be seen that the PL intensity is reduced far more rapidly as a function of pressure if silicone oil is used rather than the methanol–ethanol mixture. All the observed effects of pressure on the PL spectrum of PPV appear to be reversible with no observable hysteresis, irrespective of the choice of pressurizing fluid.

Raman

The Raman spectrum of PPV at a range of applied pressures is presented in *Figure 7*. The vibrational modes were observed to increase in frequency as a function of pressure. A Lorentzian curve fitting routine was used to determine the centre frequencies of the Raman bands and these are plotted as a function of pressure in *Figure 8*. The estimated uncertainty in determining the relative positions of the Raman bands is ±0.2 cm^{-1} and the uncertainty in the pressure measurement is ±1.6 kbar. Both of these uncertainties are too small to be shown on the figure.

An additional observation was an increase in intensity of the Raman bands and an increase in fluorescent background at elevated pressures. The fluorescent background has been subtracted in *Figure 7*; the increase in fluorescent background manifests itself as an apparent increase in the noise level of the Raman spectra in this figure. Interference from the 1332 cm^{-1} Raman band of the diamond anvil became less prominent at higher pressures as the PPV spectrum increased in intensity.

High pressure X-ray structural data are required to couple with the Raman data reported here to allow further interpretation.
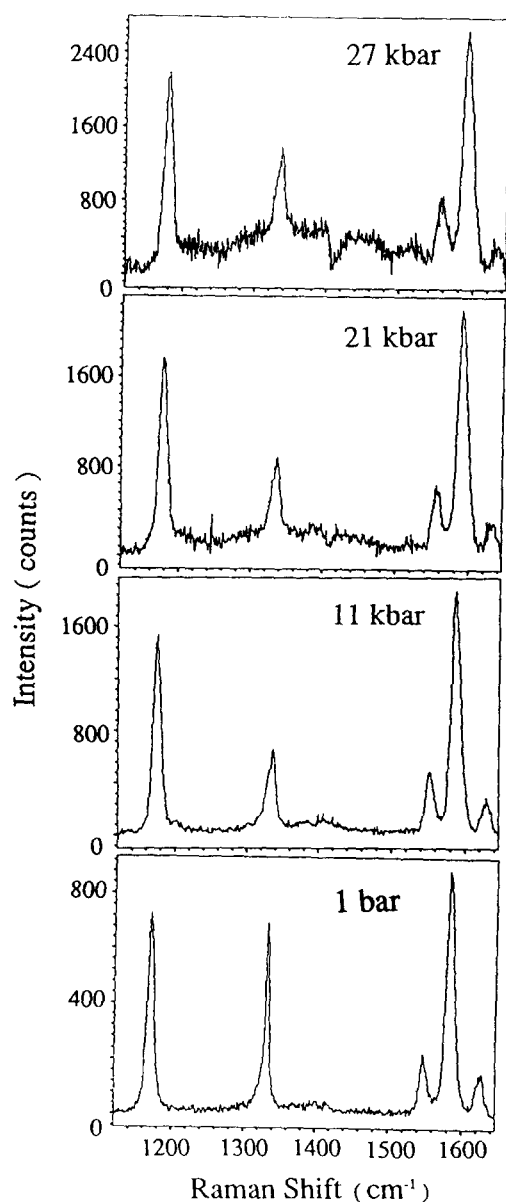

Figure 4 PL spectra of PPV at a range of applied pressures

Figure 5 Shift of PPV PL and OA as a function of pressure: ■ OA; ● PL

Figure 7 PPV Raman spectrum at a range of applied hydrostatic pressures (fluorescence background subtracted)

Figure 8 Shift of PPV Raman bands as a function of pressure. The gradient each of the linear fits (solid lines) to each set of data is also shown

DISCUSSION

Effect of pressure on the PPV optical absorption spectrum

The low energy absorption of PPV has been identified previously as arising due to the formation of an exciton localized on the π-conjugated polymer backbone[11-13]. The energy of this absorption may be influenced by both the extent of the electron delocalization along the polymer backbone (conjugation length) and by the environment surrounding the exciton.

As the pressure is applied to the PPV, it will be compressed, effectively increasing the concentration of the molecules surrounding any photogenerated exciton, and therefore amplifying any environmental contributions to the exciton's energy. One of the most significant effects of increasing the concentration of material surrounding an exciton is expected to be the 'gas-to-crystal' shift[31-35]. This is the lowering of the exciton energy as a result of the polarization of the surrounding medium, neighbouring polymer molecules in this case. The reduction of the energy of an exciton energy as a
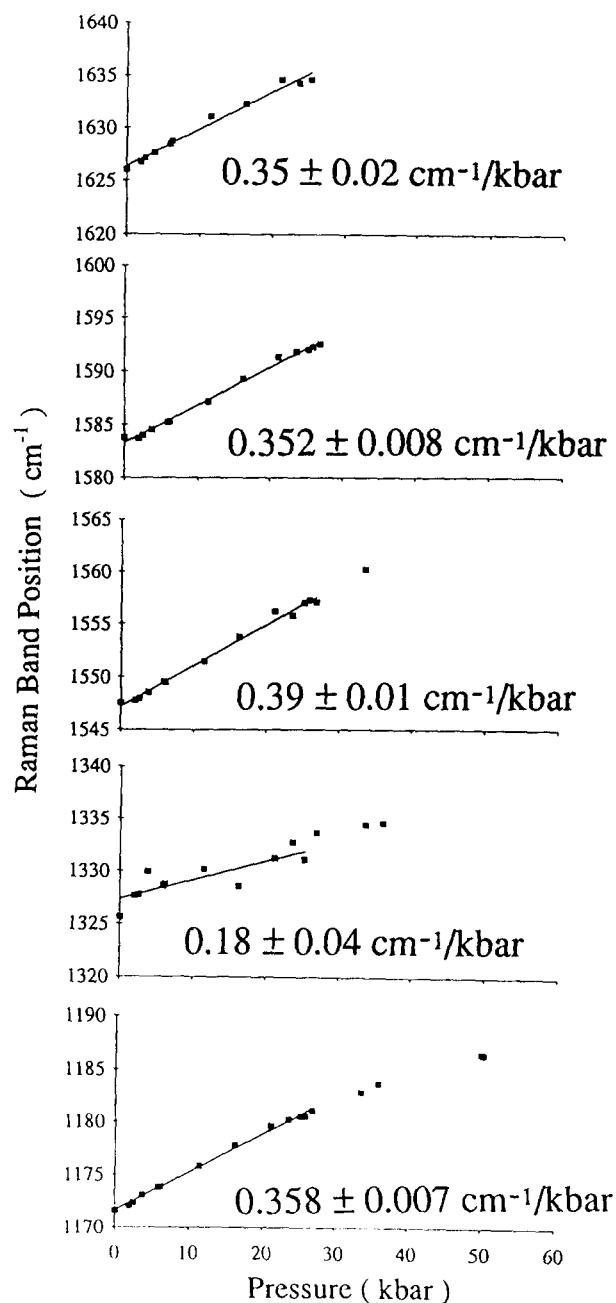
result of interaction with neighbouring non-polar solvent molecules has been demonstrated in a range of poly-enes[35] and a similar process is also quite plausible in the solid state. The gas-to-crystal shift has been previously used to explain a similar pressure-induced red shift of the optical absorption spectrum of a conjugated polydiace-tylene[32-34].

An alternative explanation for the origin of the pressure induced red shift of the PPV absorption spectrum might be that the application of hydrostatic pressure increases the conformational order of the polymer chains. This could lead to an increase in the average conjugation length of the polymer chains and consequently a lowering of the exciton energy (alternatively, the $\pi-\pi^*$ energy gap). This idea has been used previously in the literature to explain a number of phenomena[36-39]. It is noted here, however, that many of these phenomena could also, in principle, be explained

by an increasing contribution of the gas-to-crystal shift. Further, it is not clear why the disordered PPV used in this study would necessarily be expected to increase in conformational order upon the application of hydrostatic pressure. Indeed it is equally possible that hydrostatic pressure could decrease the conformational order of the PPV.

It is proposed here that the observed red shift of the optical absorption spectrum of PPV as a function of pressure occurs primarily as a result of increased intermolecular interaction, in the form of the gas-to-crystal shift. The possibility of a contribution from changing conformational order cannot, however, be discounted.

The apparent increase in the absorption coefficient of the sample with pressure in *Figure 2* is difficult to explain. Although there was some variability among the samples, probably due to non-uniformity, the general trend was always observed. An increase in the oscillator strength of the transition is expected with increasing energy of the transition[40]; this is insufficient, however, to explain the observed increase.

Effect of pressure on the photoluminescence spectrum of PPV

Possible mechanisms that could lead to the pressure-induced quenching of PPV photoluminescence are discussed in the following sections. Where appropriate, reference is made to previously observed methods of quenching photoluminescence in conjugated polymers.

Multiphonon emission. The process of 'multiphonon emission' is defined here as internal conversion between electronic states followed by vibrational relaxation to the lowest vibrational level. This process will generally be rate limited by the internal conversion. The rate constant of internal conversion between two electronic states is critically dependent on the energy gap between the states, E_g[40,41]. The red shift of the optical absorption spectrum observed in this study shows that E_g is decreasing as a function of pressure; thus the rate of internal conversion will be expected to increase as a function of pressure. Additionally there is some indication (although this is not entirely clear) that the Franck–Condon weighting of the photoluminescence spectrum is shifting slightly to higher vibrational modes. This may be interpreted as an increase in the difference of the configurational co-ordinate in going from the ground to the excited state[40]. This would be expected to increase the Franck–Condon overlap of the wavefunctions of the lowest vibrational mode of S_1 (the first electronic excited state) and the higher S_0 (the ground electronic state) vibrational modes, thus increasing the rate of internal conversion[40]. If the S_1 curve were to move far enough, then the S_1 and S_0 surfaces could cross; this would lead to very rapid internal conversion.

The results presented in this study do indicate that the rate of internal conversion, and therefore multiphonon emission, may increase as a function of pressure. Whether this is an important mechanism in the observed pressure induced quenching of the photoluminescence yield in PPV will depend largely on how important multiphonon emission is as a mechanism of non-radiative decay as compared to other possible mechanisms. The non-radiative decay rate has been observed to increase as the band gap is reduced when the precursor is

converted to the polymer[38,39]. This, however, may equally be explained by a number of other mechanisms as discussed in the following sections.

If multiphonon emission is significant in PPV, it should be observable as an intrinsic rapid component in the time resolved fluorescence decay. However, Yan *et al.*[42] have reported that they have developed a means of synthesizing PPV such that its time resolved fluorescence decay displays a mono-exponential behaviour, with a time constant close to that expected for pure fluorescence in the absence of competing non-radiative decay mechanisms. This would argue against multiphonon emission being an important non-radiative decay route in PPV. A further suggestion that multiphonon emission is, at most, only one of a number of non-radiative decay mechanisms is the observation of the effect of the compressive media. Different fluids were observed to dramatically affect the decay of the photoluminescence as a function of pressure, yet the pressure dependence of E_g observed in the optical absorption remained unchanged. Also, there is no clear correlation between the ambient pressure E_g of other related materials and the quantum yield of their photoluminescence, suggesting that other factors are dominant in determining this yield[30].

Multiphonon emission is a common non-radiative decay mechanism in organic photo-physics and cannot be entirely ruled out. The balance of evidence, however, seems to suggest it is not the dominant factor in PL quenching in PPV.

Defect quenching and increased mobility to quenching sites. The presence of various sorts of defect in the PPV polymer chain can act as quenching sites for the photoluminescence. Such sites can include oxygen[42,43] and charged defects[44–47]. The efficiency with which such defects can quench the photoluminescence is determined by both the density of defects and by the ability of the singlet exciton to migrate to one of the defect sites. An increase in either would be expected to reduce the quantum yield of photoluminescence.

The application of hydrostatic pressure could potentially increase the mobility of the excitons to quenching sites in two ways: (a) As the pressure is increased, kinks and distortions in the disordered PPV may be 'pressed out'. This could increase the degree of conjugation (as previously suggested when discussing the optical absorption) and facilitate the motion of excitons along the polymer chains. Such a scheme has been suggested previously to explain the observed decrease in photoluminescence quantum yield with increasing conversion from the precursor polymer to the fully conjugated PPV[38,39,48,49]. Conversely, it has been shown that the photoluminescence quantum efficiency may be increased by limiting the degree of conjugation along the backbone, for example by producing co-polymers with non-conjugated segments to break up the overall conjugation[7,9]. (b) The overlap of the electronic wave functions of adjacent polymer chains is expected to increase with pressure as the chains move closer together. This will facilitate the motion of excitons between chains, thus giving greater access to quenching sites within a given three dimensional sphere, rather than just in one dimension along the chain. Interchain motion of excitons to quenching sites has previously been suggested[15,42], in particular to account for the

dramatic decrease in photoluminescence yield at very small defect concentrations.

A pressure induced increase in the mobility of photogenerated singlet excitons to quenching sites probably plays a significant role in the observed decrease in photoluminescence yield as a function of pressure. The exact nature of the quenching sites to which the excitons migrate is not entirely clear but oxygen, dopant induced charge defects and isolated charge defects are all likely candidates. The latter defects may be photogenerated, as will be discussed further below.

Cross-over of $1B_u$ and $2A_g$ excited states. Another interesting possible mechanism for the pressure induced quenching of the PPV photoluminescence may be a change in the ordering of the first two excited states, S_1 and S_2.

PPV has an idealized C_{2h} symmetry; the π-electronic states in this symmetry transform as A_g and B_u and have mutually exclusive selection rules for one and two photon processes in the dipole approximation. The ground state is an A_g singlet.

If the levels are ordered with the $1B_u$ below the $2A_g$ excited state, then following excitation an electron may return to the ground state by the dipole allowed $1B_u \rightarrow 1A_g$ transition, thus emitting a photon that will be observed as fluorescence. If, on the other hand, the levels are arranged with the $2A_g$ state below the $1B_u$ then the excited electron can make the small, dipole allowed transition down to the $2A_g$ state. From here a radiative transition down to the ground state is symmetry forbidden and so the excited electron will reside there until eventually it returns to the ground state via a non-radiative route. Therefore little or no fluorescence will be observed.

In PPV at ambient pressure, the $1B_u$ excited state lies below the $2A_g$, thus facilitating a high fluorescence yield[50]. If the order of the excited states were to change as a result of applied pressure, then the fluorescence would effectively be extinguished.

Such a scheme is interesting since it has been suggested that it is the ordering of the excited states that differentiates between strongly fluorescing polymers such as PPV and weakly fluorescing polymers such as polyacetylene[50-55]. Thus the nature of S_1 sharply separates conjugated polymers into two classes: those where S_1 is a B_u state and so will be highly fluorescent and those where S_1 is an A_g state and so will be weakly fluorescent.

Theoretical studies have indicated that the ordering of the excited states is highly sensitive to the degree of bond alternation in a given polymer[51-54]. The degree of bond alternation is relatively small in polyacetylene and polydiacetylene (PDA) resulting in the $2A_g$ state lying below the $1B_u$ state with consequently low fluorescence[55]. In PPV the phenyl rings act to increase topological bond alternation. This places the $1B_u$ state below the $2A_g$ state, leading to strong fluorescence.

One and two photon absorption measurements appear to support the theoretical predictions of the excited state ordering. In PPV an even symmetry state has been identified lying $\sim 0.5\,eV$ above the S_1 state[50,56]. In PDA an even symmetry state has been located below the first odd symmetry state[55].

If the application of hydrostatic pressure were to decrease the degree of bond alternation, then it is conceivable that a change in the relative positions of the first odd and even states is the origin of the pressure quenching of the luminescence. Indeed a reduction of the degree of bond alternation might intuitively be expected as the single bonds are more compressible than the double bonds. Thus, the application of pressure will be expected to reduce the difference in the lengths of the single and double bonds. The similarity in the rate of frequency shift of the various Raman active modes with pressure, however, qualitatively suggests that there is in fact no dramatic change in the degree of bond alternation.

Formation of charge transfer (CT) excitons as a quenching mechanism. On the basis of photoinduced absorption measurements of PPV, Hsu *et al.*[57] have proposed the presence of what have been variously described as 'spatially indirect excitons' or 'bound polaron pairs'. In this paper these species shall be described as charge transfer (CT) excitons, indicating the analogy with the similar species sometimes formed in conventional molecular crystals.

The formation of CT-excitons in conjugated polymers may be described as follows: following photogeneration of a singlet excited state, the excited electron may transfer to a neighbouring polymer chain. This effectively leaves a hole on the original chain and an electron on the other which are therefore bound together by the Coulomb interaction. It is this bound electron–hole pair that constitute the spatially indirect exciton. The positive and negative charges on adjacent chains may be thought of as forming positive and negative polarons, leading to the alternative description as geminate interchain bound polaron pairs. The bound polaron pair may dissociate in certain circumstances to produce ordinary polarons and bipolarons.

The formation of these CT-excitons takes place before the excited state can relax into a potentially radiative singlet exciton and is thus a competitive process. Since the formation of these CT-excitons appears to preclude subsequent singlet exciton emission, the reformation of the CT-exciton as a singlet exciton appears to be largely forbidden due to some energy barrier. The exact nature of this barrier is, however, not entirely clear.

It can thus be seen that the formation of CT-excitons may play a crucial role in quenching the photoluminescence in conjugated polymers by reducing the number of singlet excitons formed and, therefore, available for emission. Additionally, it seems plausible that as the polymer chains move closer together, as is expected with increasing pressure, the overlap of the electronic wave functions of neighbouring chains will increase the probability of CT-exciton formation.

It has been suggested by Yan *et al.*[42] that CT-excitons are in fact the primary photogenerated species in PPV, with some 90% of absorbed photons leading to their generation and only 10% leading to the formation of singlet excitons. If this is the case, then CT-excitons will be absolutely critical to the observed quantum yield since only a small fractional increase in the probability of their formation will lead to a dramatic fractional decrease in exciton formation and so a dramatic decrease in photoluminescence quantum yield.

An additional interesting possibility is that the two charged polarons formed as part of the CT-exciton may act as quenching sites for any singlet excitons that do

form. Quenching of photoluminescence as a result of doping or electron injection has previously been observed in PPV and its derivatives[44-46].

Formation of excimer ('concentration quenching'). An idea related to the CT-exciton discussion is that the excited PPV chain may form an excimer with a neighbouring unexcited chain[58]. Such a species is stable as a result of resonance contributions from exciton and charge transfer configurations. The charge transfer configuration is essentially a CT-exciton/bound polaron pair. Excimers are a common origin of the quenching of excitonic emission, an effect commonly known as 'concentration quenching' or 'self quenching'[40]. Excimers are generally characterized by long radiative lifetimes and a broad, featureless emission that is red shifted from the emission of the isolated exciton[40]. The probability of excimer formation is dependent on the proximity of the neighbouring molecules and their relative orientation. It can thus be seen that the application of pressure could increase the probability of excimer formation through compression of the sample and possibly increased ordering of the sample.

In previous work[58], the formation of excimers has been proposed as being critical in reducing the PL quantum efficiency of other conjugated polymers. As part of this earlier work the PL quantum efficiency of the polymers was studied as a function of concentration in solution. We comment here on the remarkable similarity of the results of the concentration quenching in ref. 58 and the pressure induced quenching of PPV reported here. It is also noted that our pressure experiment removes the possibility of solvent effects.

If the observed pressure induced quenching of PPV occurs as a result of increased excimer formation, then the loss of vibronic structure, decrease in intensity and movement to red shifted emission of the PL emission could be explained as the transition from excitonic emission to excimer emission.

The red shift of the resolved excitonic emission appeared to occur at the same rate as the OA spectrum. This is probably largely due to an increase in the gas-to-crystal shift, as discussed previously.

Effect of compressive fluid on PL quenching

The origin of the effect of the compressive fluid on the rate of pressure induced quenching of the PL is not easy to understand. One possible suggestion is that the methanol–ethanol somehow reduces the number of quenching sites. If this occurred then any pressure induced increase of the mobility of excitons to quenching sites would have less effect. Examples of how this might occur include the methanol–ethanol dissolving impurities in the sample or the polar fluid 'deactivating' quenching by, for example, any molecular oxygen present. The later effect is known in conventional organic photophysics[40].

The effect of the fluid is presumably concentrated at the surface of the sample which, following the above argument, would suggest a large proportion of defect sites lie at the surface of the sample and that the excitons can diffuse efficiently to them. Further, increasing pressure could increase the diffusion length of the excitons enabling them more readily to reach the surface.

The cause of the effect of the compressive fluid remains unclear and will require further investigation.

Effect of pressure on the Raman spectrum of PPV

The origin of the pressure induced shift of the PPV Raman bands is presumably due to anharmonic potential functions of the bonds in the polymer backbone (i.e. the spring constant of the bonds effectively increases at higher pressure). Similar shifts have been observed in another conjugated polymer and have been well explained by the idea of an anharmonic potential function[33].

The increase in intensity of the Raman bands may be explained by the pressure-induced red shift of the PPV OA, bringing E_g closer to the exciting photon energy, and hence causing an increase of the preresonant enhancement of the Raman signal. The apparent increase in the noise level of the Raman spectra with pressure is due to an increase in the background luminescence intensity that has been subtracted from the spectra presented in *Figure 6*.

CONCLUSION

Photoluminescence, optical absorption and Raman spectra of PPV have been recorded as a function of pressure. Perhaps the most important result is the observed pressure quenching of the PL. A number of possible origins for this have been discussed. These suggested origins are not mutually exclusive and could in principle all play a role in the observed effects. The results presented here do not allow the importance of each of these mechanisms to be unambiguously determined.

It is becoming increasingly evident, however, that intermolecular effects play a vital role in the photophysics of conjugated polymers and high pressure studies offer an excellent way of studying this. The results presented in this paper may be explained in terms of increased intermolecular interactions. For example, the decrease in energy gap with applied pressure can be explained by an increase in the gas-to-crystal shift while the decrease in PL may be explained by an increased probability of excimer formation with increasing pressure.

Further high pressure studies employing a wider range of spectroscopic techniques are currently underway to unambiguously identify the importance of the various quenching mechanisms in conjugated polymers.

REFERENCES

1   Feast, W. J. *RAPRA Rev. Rep.* 1987, 1
2   Burroughs, J. H., Bradley, D. D. C., Brown, A. R., Marks, R. N., Mackay, K., Friend, R. H., Burn, P. L. and Holmes, A. B. *Nature* 1990, **347**, 539
3   Bradley, D. D. C. *Adv. Mater.* 1992, **4**, 756

4   Friend, R. H., Bradley, D. D. C. and Holmes, A. R. *Physics World* 1992, **11**, 42
5   Braun, D. and Heeger, A. J. *Appl. Phys. Lett.* 1991, **58**, 1982
6   Greenham, N. C., Moratti, S. C., Bradley, D. D. C., Friend, R. H. and Holmes, A. B. *Nature* 1993, **355**, 628
7   Burn, P. L., Holmes, A. B., Kraft, A., Bradley, D. D. C., Brown, A. R., Friend, R. H. and Gymer, R. W. *Nature* 1992, **356**, 47
8   Brown, A. R., Marks, R. N., Burroughs, J. H., Greenham, N., Friend, R. H., Bradley, D. D. C., Burn, P. L., Kraft, A. and Holmes, A. B. *Appl. Phys. Lett.* 1992, **61**, 2793
9   Burn, P. L., Holmes, A. B., Kraft, A., Bradley, D. D. C., Brown, A. R. and Friend, R. H. *J. Chem. Soc. Chem. Commun.* 1992, **32**, 32
10   Grem, G., Leditsky, G., Ullrich, B. and Leising, G. *Adv. Mater.* 1992, **4**, 36
11   Furukawa, M., Mizuno, K., Matsui, A., Ruhoopth, S. D. D. V. and Walker, W. C. *J. Phys. Soc. Japan* 1989, **58**, 2976
12   Rauscher, U., Bassler, H., Bradley, D. D. C. and Hennecke, M. *Phys. Rev. B* 1990, **42**, 9830
13   Bassler, H., Gailberger, M., Mahrt, R. F., Oberski, J. M. and Weiser, G. *Synth. Met.* 1992, **49–50**, 341
14   Mahrt, R., Yang, J., Greiner, A., Bassler, H. and Bradley, D. D. C. *Macromol. Chem. Rapid Commun.* 1990, **11**, 415
15   Samuel, I. D. W., Crystall, B., Rumbles, G., Burn, P. L., Holmes, A. B. and Friend, R. H. *Synth. Met.* 1993, **54**, 281
16   Burn, P. L., Bradley, D. D. C., Brown, A. R., Friend, R. H. and Holmes, A. B. *Synth. Met.* 1991, **41–43**, 261
17   Burn, P. L., Bradley, D. D. C., Friend, R. H., Halliday, D. A., Holmes, A. B., Jackson, R. W. and Kraft, A. *J. Chem. Soc. Perkin Trans.* 1992, **1**, 3225
18   Halliday, D. A., Burn, P. L., Friend, R. H. and Holmes, A. B. *J. Chem. Soc. Chem. Commun.* 1992, **22**, 1685
19   Jayaraman, A., *Rev. Mod. Phys.* 1983, **55**, 65
20   Jayaraman, A. *Rev. Sci. Instrum.* 1986, **57**, 1013
21   Dunstan, D. J. and Spain, I. L. *J. Phys. E: Sci. Instrum.* 1989, **22**, 913
22   Dunstan, D. J. *Rev. Sci. Instrum.* 1989, **60**, 3789
23   Piermarini, G. J., Block, S. and Barnett, J. D. *J. Appl. Phys.* 1973, **44**, 5377
24   Forman, R. A., Piermarini, G. J., Barnett, J. D. and Block, S. *Science* 1972, **17**, 284
25   Barnett, J. D., Block, S. and Piermarini, G. J. *Rev. Sci. Instrum.* 1973, **44**, 1
26   Piermarini, G. J., Block, S., Barnett, J. D. and Forman, R. A. *J. Appl. Phys.* 1975, **46**, 2774
27   Mao, H. K., Bell, P. M., Shoner, J. W. and Steinberg, J. *J. Appl. Phys.* 1978, **49**, 3276
28   Mao, H. K., Xu, J. and Bell, P. M. *J. Geophys. Res.* 1986, **91**, 4673
29   Adams, D. M., Appleby, R. and Sharma, S. K. *J. Phys. E Scientific Instrum.* 1976, **9**, 1140
30   Webster, S. Ph.D Thesis, University of Leeds, 1994
31   Rice, S. A. and Jortner, J. in 'Physics of Solids at High Pressure' (Eds C. T. Tomizuka and R. M. Emrick), Academic Press, London, 1965

32   Lochner, K., Bassler, H., Sowa, H. and Ahgbahs, H. *Chem. Phys.* 1980, **52**, 179
33   Webster, S. and Batchelder, D. N. *Macromol Symp.* 1994, **87**, 177
34   Lacey, R. J., Batchelder, D. N. and Pitt, G. D. *J. Phys. C: Solid State Phys.* 1984, **17**, 4529
35   Longuet-Higgins, H. C. and Pope, J. A. *J. Chem. Phys.* 1957, **27**, 192
36   Colaneri, N. F., Bradley, D. D. C., Friend, R. H., Burn, P. L., Holmes, A. B. and Spangler, C. W. *Phys. Rev. B* 1990, **42**, 11670
37   Zheng, L. X., Hess, B. C., Benner, R. E., Vardeny, Z. V. and Baker, G. L. *Phys. Rev. B* 1993, **47**, 3070
38   Bradley, D. D. C. *J. Phys. D: Appl. Phys.* 1987, **20**, 1389
39   Wong, K. S., Bradley, D. D. C., Hayes, W., Ryan, J. F., Friend, R. H., Lindenberger, H. and Roth, S. *J. Phys. C: Solid State Phys.* 1987, **20**, L187
40   Gilbert, A. and Baggott, J. in 'Essentials of Molecular Photochemistry', Blackwell Scientific Publishers, Oxford, 1991
41   Danielson, P. L. and Ball, R. C. *J. Phys.* 1985, **46**, 1611
42   Yan, M., Rothberg, L. J., Papadimitrakopoulos, F., Glavin, M. E. and Miller, T. M. *Phys. Rev. Lett* 1994, **72**, 1104
43   Papadimitrakopoulos, F., Yan, M., Rothberg, L. J., Katz, H. E., Chandross, E. A. and Galvin, M. E. *Mol. Cryst. Liq. Cryst.* 1994, **256**, 663
44   Gu, H. B., Takiguchi, T., Hayashi, S., Kaneto, K. and Yoshino, K. *J. Phys. Soc. Japan* 1987, **56**, 3997
45   Bradley, D. D. C. and Friend, R. H. *J. Phys: Condens. Matter* 1989, **1**, 3671
46   Ziemelis, K. E., Hussain, A. T., Bradley, D. D. C., Friend, R. H., Ruhe, J. and Wegner, G. *Phys. Rev. Lett.* 1991, **66**, 2231
47   Friend, R. H., Bradley, D. D. C. and Townsend, P. D. *J. Phys D: Appl. Phys.* 1987, **20**, 1367
48   Pichler, K., Halliday, D. A., Bradley, D. D. C., Burn, P. L., Friend, R. H. and Holmes, A. B. *J. Phys. Condens. Matter* 1993, **5**, 7155
49   Friend, R. H., Bradley, D. D. C. and Townsend, P. D. *J. Phys. D: Appl. Phys.* 1987, **20**, 1367
50   Baker, G. J., Gelson, O. M. and Bradley, D. D. C. *Chem. Phys. Lett.* 1993, **201**, 127
51   Soos, Z. G., Galvao, D. S. and Etamad, S. *Adv. Mater.* 1994, **4**, 280
52   Soos, Z. G., Etamad, S., Galvao, D. S. and Ramasesha, S. *Chem. Phys. Lett.* 1992, **194**, 341
53   Soos, Z. G., Rameshesha, S., Galvao, D. S. and Etamad, S. *Phys. Rev. B* 1993, **47**, 1742
54   Soos, Z. G., Ramesesha, S. and Galvao, D. S. *Phys. Rev. Lett.* 1993, **71**, 1609
55   Lawrence, B., Torruellas, W. E., Cha, M., Sundheimer, M. L., Stegeman, G. I., Meth, J., Etamad, S. and Baker, G. *Phys. Rev. Lett.* 1994, **73**, 597
56   Lemmer, U., Fischer, R., Feldmann, J., Mahrt, R. F., Yang, J., Greiner, A., Bassler, H and Gobel, E. O. *Chem. Phys. Lett.* 1992, **203**, 28
57   Hsu, J. W. P., Yan, M., Jedju, T. M. and Rothberg, L. J. *Phys. Rev. B* 1994, **49**, 712
58   Jenekhe, S. A. and Osaheni, J. A. *Science* 1994, **265**, 765