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Light-induced luminescence quenching in precursor-route poly(p-phenylene vinylene)

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Abstract. We report the observation in partially converted precursor-route poly(p-phenylene vinylene (PPV) of a strong light-induced luminescence fatigue. Increasing the conversion towards the fully conjugated polymer results in a loss of the quenching effect. We discuss exciton annihilation at photoexcited charged polaronic states as a possible mechanism for this phenomenon.

1. Introduction

The preparation of PPV by in-vacuo thermal conversion of a sulphonium polyelectrolyte precursor is outlined in figure 1. Such a synthetic approach gives considerable flexibility in polymer processing and through a suitable choice of preparation conditions (see Bradley (1987b) for a recent review) high quality material of controlled morphology, crystallinity, orientation and length of uninterrupted conjugated sequences may be obtained. Of particular importance to the study reported here is the ability to vary the extent of the formation of conjugated sequences by controlling the temperature at, and time for which the conversion of the initially non-conjugated precursor (I) is carried out. 'Full conversion' to III (as judged by an absence of the precursor C–S stretching vibrational mode (632 cm^{-1}) from the infrared spectrum) requires heating at $300\text{ }^{\circ}\text{C}$. At lower conversion temperatures a copolymer (II) of conjugated and non-conjugated sequences is generated in which the degree of conjugation increases with the temperature and heating time (for further details see Bradley (1987b)). The corresponding expected increase in π -electron delocalisation is confirmed experimentally by electron energy loss dispersion (Fink *et al* 1987) and infrared intensity (Bradley 1987b and references therein) measurements.

The significance of the degree of conjugation in determining the relative importance of competing excited state relaxation pathways has previously been examined in terms of the luminescence efficiency and decay kinetics (Bradley *et al* 1987c, Friend *et al* 1987, Wong *et al* 1987). These earlier measurements showed that non-radiative recombination strongly increases with increasing precursor conversion and they identified processes with both monomolecular and bimolecular reaction kinetics. During the course of further investigations aimed at more clearly elucidating the nature of these processes we have observed a strong light-induced, low-temperature luminescence fatigue for samples

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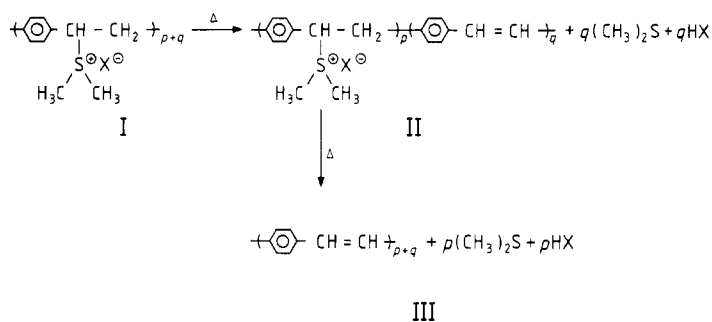


Figure 1. Thermal conversion of the sulphonium polyelectrolyte precursor polymer (I) to poly(p-phenylene vinylene) (PPV) (III). At intermediate stages of conversion (II) the material consists of a copolymer of conjugated and non-conjugated segments. (X = Cl, Br).

converted at 80 °C and 140 °C that is absent from the fully converted (i.e. heated to 300 °C) polymer (Bradley *et al* 1987c). In this paper we report the results of preliminary studies on the nature of the luminescence fatigue and we discuss a possible mechanism involving the photoexcitation of metastable charged polaronic states.

2. Experimental procedure

Photoluminescence was excited using the mechanically chopped (225 Hz) 457.9 nm (2.71 eV) output from a cw Ar⁺ laser (Coherent Innova 100). Following spectral dispersion by a grating monochromator (Spex Minimate), it was detected by a large area Si photodiode (RS 303-674) the output of which was fed to a lock-in amplifier (Ortec Brookdeal 9503-SC) triggered at the chop frequency. The emission was collected at right-angles to the excitation beam, with the sample set at 45°, and was focused onto the entrance slit of the monochromator. The excitation intensity incident on a sample area of 25 mm² was typically of order 30–40 mW. The samples were prepared as free standing films of order 5 μm thickness and were held in an optical access continuous-flow He gas cryostat (Oxford Instruments CF 204) under He exchange gas.

3. Results and discussion

Figure 2 shows three emission spectra from a sample converted at 80 °C for 10 h, recorded during prolonged illumination at 14 K. As the illumination time increases the intensity of the emission shows a strong decrease, but the emission spectrum is otherwise unchanged. Since no significant decrease in intensity was observed when the emission was measured after keeping the sample for a similar length of time in the dark, we conclude that the observed luminescence fatigue is induced by the laser illumination. The invariance of the spectral profile, indicating that the emission centre is itself unaltered by the fatigue, allows us to rule out, as an origin, an irreversible chemical modification such as conversion to the fully conjugated polymer (III)[†] (conversion would indeed lead to a decrease in emission intensity but would be accompanied by a significant red shift of the

[†] Laser-induced conversion to III has been observed under conditions of high excitation intensity (achieved by focusing the laser beam) with the sample at or near to room temperature (Bradley 1987a).

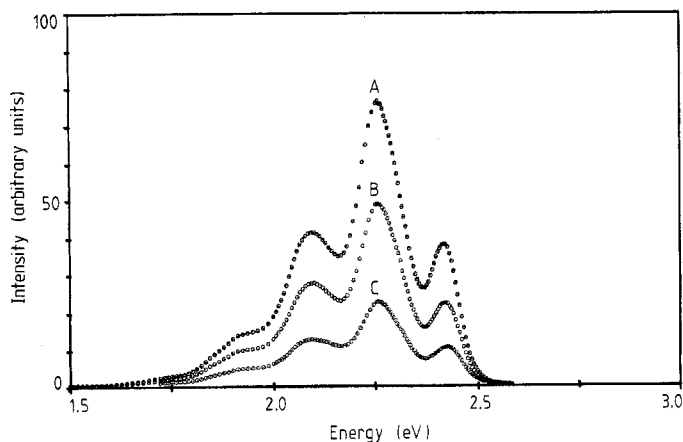


Figure 2. Luminescence emission spectra from a partially converted (80 °C for 10 h) PPV sample recorded during prolonged illumination by 457.9 nm (2.71 eV) laser light at 14 K. Curve A, initial spectrum; curve B, after 5 min; curve C, after 55 min.

spectrum (Bradley *et al* 1987c, Wong *et al* 1987)). This deduction is confirmed by recovery of the original luminescence emission intensity upon returning the sample to room temperature (see below) and by the absence of any changes in the infrared spectrum of the sample following repeated fatigue–recovery cycles. The invariance would also seem to preclude conformational (e.g. rod–coil) transitions as an origin, for which a spectral shift would again be expected to accompany the changes in emission intensity, as is the case in polydiacetylene (PDA) (Kanetake *et al* 1985) and poly(3-alkyl thiophene) (Yoshino *et al* 1988) polymers. It thus seems almost certain that the quenching effect arises through photogeneration of sites at which enhanced non-radiative recombination occurs (somewhat analogous to the well known Staebler–Wronski effect in amorphous silicon hydride (see e.g. Pankove 1987 and references therein) although here the fractional change in intensity is very much larger). The observed decrease (Wong *et al* 1987) in the measured luminescence decay time is consistent with this conclusion.

The time intervals between the three spectra in figure 2 were 5 minutes between the first and second and a further 50 minutes between the second and third, indicating that the fatigue has a very long characteristic time constant. The kinetics have not been fully investigated as yet, but preliminary experiments indicate non-exponential behaviour with a finite emission intensity asymptote (cf figure 3) at long times ($t \geq 1$ h). Associating the process responsible for the fatigue with photogeneration of non-radiative recombination sites implies that the sites must have a long lifetime at 14 K (significantly in excess of the 4.4 ms period of the optical chopper). This lifetime should be compared with a luminescence decay time that is measured to be less than 0.5 ns (Wong *et al* 1987). Clearly, the lifetime cannot be determined by interaction with the excitonic emission centres and hence it must be that the recombination sites are themselves unaffected by the quenching process.

Figure 3 shows the temperature dependence of the equilibrium emission intensity. The data were obtained by cooling the sample to 14 K and fatiguing under steady laser illumination until the emission intensity showed no further change. Then, under the same illumination and whilst the luminescence was being continuously monitored, the sample was slowly warmed up. A heating rate of 10–15 K h⁻¹ was used to ensure that we

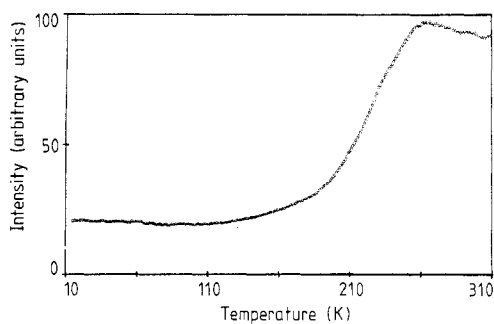


Figure 3. Temperature dependence of the equilibrium luminescence emission intensity from a partially converted (80 °C for 10 hrs) PPV sample excited by laser light at 457.9 nm (2.71 eV). The data were obtained following an initial fatigue at 14 K by warming the sample at a rate of 10–15 K h⁻¹.

indeed probed the thermal effect on the luminescence intensity *at equilibrium*. Taking the sample through several such fatigue–recovery cycles gives the same behaviour each time with a return to the same room-temperature emission intensity. The data show an initial apparently activated increase in emission intensity with temperature (E_a of order 20 meV), but at about 230 K the dependence weakens and above 260 K the intensity starts to decrease with increasing temperature. This behaviour indicates the presence of at least two contributions to the temperature dependence. In order to separate these contributions, a useful comparison may be made with the temperature dependence observed for fully converted samples (i.e. heated at 300 °C) (Bradley *et al* 1987a) in which, as noted above, the luminescence fatigue has not been observed. There, as seen in figure 4, the emission intensity shows a nearly exponential *decrease* with increasing temperature (E_a of order 5 meV for $T \geq 50$ K), matching (at least qualitatively) the behaviour seen above 260 K in figure 3. Hence we deduce that the process responsible for the fatigue has an approximately activated temperature dependence with a decrease in quenching efficiency as the temperature increases. In the case of photogeneration of non-radiative recombination centres this most probably arises either through a decrease in the equilibrium number density of such centres due to a reduction in their lifetime or alternatively through an increase in the escape probability for the polaron-exciton. However, since the luminescence decay time (of order 0.5 ns, Wong *et al* 1987) is very much less than the time required to establish an equilibrium emission intensity, it seems clear that the former (i.e. a reduced recombination-centre lifetime) provides the best explanation. The activation energy should then correspond to that required for annihilation of the recombination sites.

Although the nature of the non-radiative recombination centres cannot be deduced directly from the above results, a comparison with reports of dopant-induced quenching of the luminescence and photo-induced absorption measurements in this (Gu *et al* 1987, Bradley 1987a, Bradley *et al* 1987a, b, Friend *et al* 1987) and other polymers (Hayashi *et al* 1987, Kim *et al* 1988, Pratt *et al* 1987a, b) allows us, as will be discussed below, to propose an assignment to photogenerated charged polaronic states. The addition of charges to the polymer chain produces a localised lattice distortion (involving an increase in the quinoid character of the bond alternation) that causes the energy levels of the polaron or bipolaron state to reside within the gap of the previously uncharged polymer. Their precise positions are determined by the degree of confinement (characteristic of the asymmetry of the bonding along the carbon backbone) and by their occupancy (not simply the difference in occupancy of the two levels as predicted within one-electron models (Fesser *et al* 1983); see Friend *et al* (1987) for further discussion). The presence

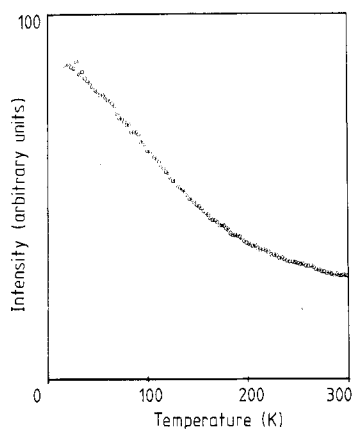


Figure 4. Temperature dependence of the luminescence emission intensity from a fully converted (i.e. 300 °C heated) PPV sample excited by laser light at 457.9 nm (2.71 eV).

of such states following both charge-transfer doping and photo-excitation has been confirmed experimentally for a number of conjugated polymers including PPV by the observation of the required absorption peaks in the sub-gap energy range arising from both their electronic and vibrational transitions (see Bradley 1987a, Bradley *et al* 1987a, b, Friend *et al* 1987, Gu *et al* 1987, Hayashi *et al* 1987, Kim *et al* 1988, Pratt *et al* 1987a, b and references therein). The first reports linking such states with luminescence quenching were by Yoshino and co-workers who studied the effect of electrochemical charge-transfer doping on the luminescence in PPV (Gu *et al* 1987) and polythiophene (PT) (Hayashi *et al* 1987). During doping, the luminescence of the polymer was strongly quenched, falling by 50% for a dopant (ClO_4^-) concentration of order 0.5 mol% and almost vanishing for about 5 mol%. The quenching was attributed to an interaction (unspecified in their reports, but see below for a possible mechanism) between the photo-excited polaron–exciton and dopant-induced charged polaronic states. The dopant concentration dependence of the luminescence quenching in PT was modelled phenomenologically in terms of an effective chain length occupied by the charge carrier (Hayashi *et al* 1987, Kaneto *et al* 1988). In order to fit the experimental data, a length of order 70 repeat units was required. This is too long to be the physical extent of the polaronic state but can be understood if allowance is made for motion of the polaron–exciton (the charge carrier is taken to be pinned by the presence of dopant ions in the neighbourhood of the chain). The distance will then correspond to the migration length of the exciton during its lifetime.

Photogeneration of charged polaronic states should clearly also give rise to the possibility of luminescence quenching. However, photogenerated polaronic states are transitory metastable excitations and are not pinned by dopant ions. Hence, the interaction processes leading to non-radiative annihilation of the polaron–exciton will be more complex and the lifetime and mobility of the charge carriers should also be considered. In order to confirm that photogenerated charged polaronic states are indeed responsible for the light-induced luminescence fatigue it should be demonstrated that they can have long lifetimes and a temperature dependence consistent with that shown in figure 3 (i.e. that the number of such states decreases strongly above 200 K). As yet, there are no measurements directly confirming this to be the case in partially converted PPV. However, it has been shown by photo-induced infrared (IR) absorption measurements using sampling times of up to 640 seconds that bipolarons with lifetimes as long as

hours at liquid nitrogen temperatures can be photogenerated in several polydiacetylenes [PDAs] (Pratt *et al* 1987a, b, Kim *et al* 1988) and that these states have an approximately activated temperature dependence (their number decreases with increasing temperature) with E_a of order 12 meV (Kim *et al* 1988). In preliminary measurements on fully converted PPV (Bradley *et al* 1987b) a photoinduced IR absorption signal was observed, indicating the presence of photogenerated charged states with lifetimes at liquid nitrogen temperatures that are significantly less than the sampling time of 6 s. This result is an agreement with previous estimates ($\tau \leq 1$ ms; Bradley *et al* 1987a, b, Friend *et al* 1987) for the bipolaron lifetime based upon photo-induced absorption arising from electronic transitions. In the case of partially converted PPV, however, no photo-induced IR absorption was observed in the long-time averaged signal (obtained from the ratio of the averages of 6000 scans with laser on and laser off) indicating either an absence of photogenerated charge carriers or that the lifetime of the carriers greatly exceeds the 6 s sampling time. An absence of photogenerated charge carriers is, however, seemingly at odds with other photo-induced absorption measurements in which electronic transitions have been observed (Bradley 1987a, Friend *et al* 1987) and we thus favour the latter explanation.

The temperature-dependence measurements of photo-induced absorption due to the electronic transitions of bipolarons in fully converted PPV samples show qualitatively (Bradley *et al* 1987a, b, Friend *et al* 1987) the required form to be consistent with figure 3. The photo-induced absorption signal (proportional to the number of bipolaron states) strongly decreases with increasing temperature but the agreement is, as expected, not quantitative; the signal does not persist to high enough temperatures (it vanishes for $T \geq 160$ K). The preliminary measurements on partially (140 °C) converted samples indicate that there the bipolaron states survive to higher temperatures, in better agreement with figure 3 (Bradley 1987a, Bradley *et al* 1987b). A fuller investigation and, in particular a more detailed study of the photo-induced IR absorption is clearly desirable, but present indications are that photogeneration of charged polaronic states is consistent with the observed luminescence fatigue.

Having outlined the reasoning behind our proposed assignment, we now briefly consider a mechanism that leads to an enhanced non-radiative decay and that can explain the interaction between the overall neutral polaron–exciton and charged polaronic states (be they photo-excited or dopant-induced). As noted above, the lattice distortion around an added charge corresponds to an increasing resonance contribution from the quinoid chain geometry. Such a modification generates a localised region in which the effective band gap is reduced. Recalling that rapid exciton transfer from the larger to the smaller band-gap material in mixed molecular crystals is a well known phenomenon (see Lumb (1978), Davies *et al* (1983) and references therein) and that a similar process involving conjugated chain segments with different band gaps in PPV seems consistent with the sharpness of the emission spectrum and the dependence of the emission wavelength upon degree of conversion (Bradley *et al* 1987a, Friend *et al* 1987) we can expect that these sites are able to act as trapping centres for the polaron–exciton. The luminescence quenching is then easy to understand since it is found both theoretically (see Danielsen (1987) and references therein) and experimentally (Bradley 1987b, Bradley *et al* 1987c, Friend *et al* 1987, Wong *et al* 1987) that reductions in band gap lead to a heightened susceptibility to non-radiative decay. Thus, in summary, we propose that the photogeneration of charge carriers leads to centres at which the polaron–exciton can reduce its energy (leading to trapping) and at which the probability of non-radiative decay is enhanced. This simple mechanism is supported by the fact that (see above and Gu *et al*

(1987), Hayashi *et al* (1987)) the recombination sites are apparently unaffected (i.e. are not destroyed) by the quenching process. In addition, we note that the theoretical probability for non-radiative decay via multiphonon-emission and tunnelling processes shows a strong dependence upon band gap (decay rate $\propto \exp(-E_g)$) such that the reduction in effective gap energy need not be large in order to give a significant change in luminescence efficiency (Danielsen 1987).

The reason why light-induced luminescence fatigue should be so readily detected in partially converted PPV would seem to be a fortuitous combination of a long lifetime for the photogenerated charged polaronic states and a relatively high luminescence efficiency for the unfatigued material (the decay time is of order 0.5 ns at room temperature (Wong *et al* 1987)). Following full conversion, the lifetime of the photogenerated bipolarons is reduced and the overall luminescence efficiency is strongly decreased due to activation of additional non-radiative decay processes (the decay time is then of order 0.05 ns at room temperature (Wong *et al* 1987, Bradley *et al* 1987c, Friend *et al* 1987)). As a result the likelihood of interaction between the charge carriers and the polaron–exciton states is greatly reduced and the luminescence fatigue becomes correspondingly less significant. In the case of the dopant-induced effect, the lifetime of the charge carriers essentially becomes infinite and hence the quenching once more becomes important.

The apparent long lifetime for photogenerated polaronic charge carriers in partially converted PPV can be attributed, at least in part, in analogy with the case for PDAs (Kim *et al* 1988, Pratt *et al* 1987a, b) to the relative weakness of the interactions between the chains that results from the presence of bulky non-conjugated sulphonium moieties in the precursor polymer. The reduction in their lifetime on conversion then follows from an increase in interaction between the chains through elimination of the sulphonium side groups (Bradley 1987b). The very long bipolaron lifetime in PDA means that it may be possible to observe luminescence quenching in these materials, too. However, the very low overall luminescence efficiencies of the so-called ‘red forms’ of these polymers (with decay times less than 9 ps, see Wong *et al* (1985) and references therein) may well make such an observation difficult. The more disordered ‘yellow’ forms with their increased luminescence yields would seem to offer greater promise for study.

4. Conclusion

In this paper we have reported the presence of a strong low-temperature, light-induced fatigue of the luminescence emission from partially converted PPV samples. The effect is attributed to trapping and decay of the excitonic states at photogenerated non-radiative recombination centres. Comparison with luminescence quenching arising from electrochemical charge-transfer doping and with studies of photo-induced absorption arising from vibrational and electronic transitions leads us tentatively to identify these centres as charged polaronic states. A mechanism based upon local reductions in the effective band gap in the vicinity of such polaronic states is proposed and supporting evidence is presented.

Further experiments are planned in order to try to confirm our proposed origin and to probe the kinetics of the quenching effect, its intensity dependence and (using oriented samples) its dependence upon inter-chain processes. In addition, we intend to investigate other polymers including poly(4,4'-diphenylene diphenyl vinylene) (PDPV) which is already known to exhibit a luminescence fatigue (Bradley 1987a, Bradley *et al* 1987a)

and several more precursor-route poly(arylene vinylene)s such as poly(2,5-dimethoxy-p-phenylene vinylene).

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