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Photoexcited states in poly(3-alkyl thienylenes)

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Abstract. We present a comparative study of the properties of two solution-processible alkyl-substituted polythienylenes, poly(3-hexyl thienylene), P3HT and poly(3-dodecyl thienylene), P3DT. Both show the onset of π - π^* interband absorption at 2 eV with the peak in absorption coefficient near 2.5 eV, and both show strong photoluminescence in an energy band extending from 1.3 to 2 eV. These properties are both due to intra-chain absorption across the π - π^* gap, with the photoluminescence arising from the radiative decay of the singlet exciton. For the case of P3HT, photoinduced absorption measurements show the presence of two sub-gap absorption bands, which are associated with the formation of charged bipolarons which require charge separation between chains. P3DT, in contrast, shows a single induced absorption band, at 1 eV, which shows very different temperature and frequency dependence from that of the bipolaron bands in P3HT. We consider that a triplet-triplet transition of the triplet intrachain exciton is a possible assignment for this band, and we consider that poorer contact between chains in P3DT over that in P3HT inhibits the transfer of charge between chains and thus prevents the formation of charged bipolarons in this polymer. We also discuss the role of the polymer structure in the stabilisation of the photogenerated bipolarons.

1. Introduction

The non-linear electronic excitations of the π -electron system in conjugated polymers distinguish the semiconductor physics of these materials from that of three-dimensionally-bonded inorganic semiconductors. The optical properties of these polymers provide clear evidence for the formation of intra-gap states associated with formation of self-localised polaron-like excitations, and also show the importance of the highly anisotropic motion of these excitations, with a clear distinction between intra- and inter-chain motion [1]. We report here a study of the optical excitations of two solution-processible alkyl-substituted polythienylenes, poly(3-hexyl thienylene), P3HT and poly(3-dodecyl thienylene), P3DT.

For the case of polymers which show a preferred sense of bond alternation, such as the polythienylenes, the characteristic family of excitations are the various charge states of the polaron, illustrated in figure 1 for the case of a poly(phenylene) chain. In the ground state the preferred sense of bond alternation is the aromatic conformation, but the excited states of the chain are stabilised as self-localised regions of the chain within which the bond alternation is shifted over to the alternative, quinoid conformation. Associated with this region of quinoid conformation, which has a lower π to π^* gap, states are pulled away from the band edges, to form the two gap states as shown in the

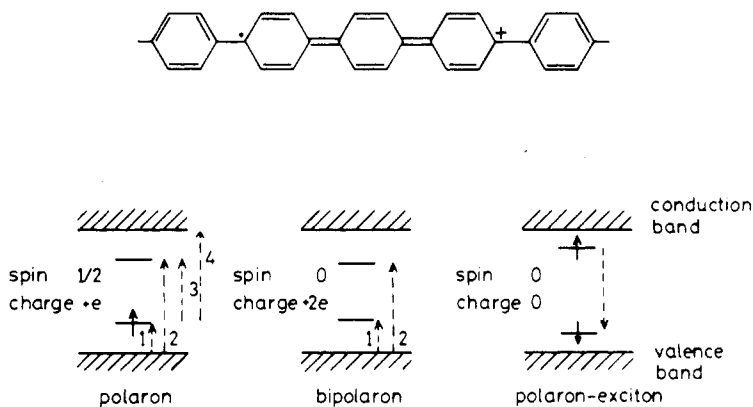


Figure 1. (a) Schematic diagram showing the formation of a positively-charged polaron on a polyphenylene chain. (b) Shows the energy level scheme and optical transitions for the positively-charged polaron and bipolaron, and also for the neutral polaron-exciton, shown in its singlet state, and which can decay radiatively as indicated by the transition between the two gap states.

figure. Quantum chemical calculations show that these self-localised states are extended typically over some 4 or 5 rings [2], and with this level of delocalisation it is appropriate to use the continuum models of Brazovskii and Kirova [3] and Fesser *et al* [4] (the FBC model).

Electron-hole pairs produced by photoexcitation across the band gap may either remain bound to form the neutral, intrachain polaron-excitation shown in figure 1. This excited state is naturally pictured as an intrachain exciton, and we consider that it is always the dominant product of photoexcitation. If formed in the singlet state, it is able to decay radiatively, with a Stokes shift for the luminescence of $2\Delta - 2\omega_0$, where 2Δ is the π - π^* gap for the chain in its ground state conformation, and $2\omega_0$ is the energy splitting between the two gap states. This decay channel is well established for the case of poly(phenylene vinylene), PPV, for which the quantum yield is several per cent [1, 5, 6]. In the case where the exciton is formed as the triplet, although slow luminescence has not been detected, sub-gap photoinduced absorption (at 1.45 eV in PPV) has been assigned to a triplet-triplet excitation [7, 8].

Separation of the electron-hole pair to form charged excitations requires that there is transfer of charge between chains [1]. These must initially be in the form of singly charged polarons. For this singly-charged, spin $\frac{1}{2}$, state, termed as a polaron, there is partial occupancy of one of the intra-gap states, with a single electron on the lower state for the positive polaron as shown in figure 1, P^+ , and a single hole on the upper state for the corresponding negative polaron, P^- . Within the FBC one-electron theory [4] the polaron is more strongly confined than the polaron-exciton, and the separation between the two gap states, $2\omega_0$ must be greater than $2\Delta/\sqrt{2}$, where 2Δ is the energy of the π to π^* gap. Electronic transitions involving the gap states and the band states are possible at the three energies shown in figure 1. It is also possible to accommodate two charges on the same self-localised excitation, to form a bipolaron. Figure 1 shows the positively charged bipolaron, BP^{2+} in which the two gap states are both unoccupied; for the corresponding negatively charged bipolaron, BP^{2-} , both gap states are fully occupied. There are now only two sub-gap optical transitions possible, from the valence band to each of the gap states for the BP^{2+} as shown in figure 1, and from each of the gap states to the conduction band for the BP^{2-} . Coalescence of two polarons of like charge is

energetically favoured in the one-electron, FBC theory, and it is found experimentally that only bipolarons are produced as long-lived excitations in several polymers, including PPV [1] and poly(thienylene), PT [9].

Poly(thienylene), (or polythiophene) is an example of a polymer with a non-degenerate ground state, and the formation of charged bipolarons, introduced either by chemical oxidation [10] or by photoexcitation [9] is well studied. It is not readily processed, being insoluble in common solvents and infusible, and there has therefore been very considerable interest in the properties of poly(3 alkyl thienylenes), which are solution processible for alkyl chains of butyl or longer [11, 12]. The presence of the alkyl side-chain appears to have rather little effect on the π -electron structure along the backbone, and the position of the optical absorption edge remains close to 2 eV for these materials in their low-temperature phase (there is a well-characterised thermochromism seen above room temperature, with a pronounced blue-shift of the absorption maximum, associated with a weakening of the π conjugation along the chain, at temperatures close to the melting transition [13]). However, we can expect that the presence of the alkyl chains will limit the contact between the conjugated π -electron systems on neighbouring chains, and that this will have a profound effect on those properties that involve inter-chain transfer of charge. There is inferential evidence for this in the observation of a decrease in electrical conductivity with increasing length of alkyl chain in fully oxidised films of these polymers [14].

2. Experimental details

The two polymers were prepared by oxidative coupling of the monomer units, and subsequent reduction to the neutral state as previously described [14, 15]. Thin films for optical experiments were obtained by spin-coating or solution-casting films onto sapphire or WF Spectrosil substrates from solution in chloroform. Polymer film thicknesses, of the order of 100 nm, were selected to give optical densities of about 1 in the region of the π to π^* absorption band.

Optical measurements were performed in an Oxford Instruments CF 204 optical-access helium cryostat, allowing temperature control between 10 K and room temperature. Thermal contact to the samples was provided by a helium exchange gas within the sample space. Absorption and induced absorption measurements were performed in the visible and near infrared spectral regions (0.4 eV–4 eV) using a tungsten halogen source, dispersed with a grating monochromator and measured with a photomultiplier tube, silicon photodiode, cooled germanium detector, or cooled indium antimonide detector.

Photoinduced absorption was measured using monochromated light from the tungsten halogen lamp as probe, and green, blue and ultraviolet lines from a Coherent Innova 100 argon ion laser as pump. Detection was performed with standard phase sensitive detection methods, with the pump beam mechanically chopped in the frequency range 5–4000 Hz.

3. Results

3.1. P3HT

The optical absorption and photoluminescence (PL) spectra for P3HT are shown in figure 2. The onset of the π - π^* absorption band is just below 2 eV, peaking near 2.5 eV. By

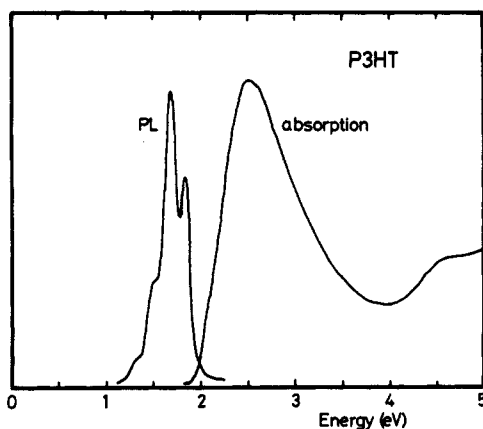


Figure 2. Optical absorption for a film of P3HT measured at room temperature, and photoluminescence spectrum measured with excitation at 457.9 nm and at a temperature of 40 K.

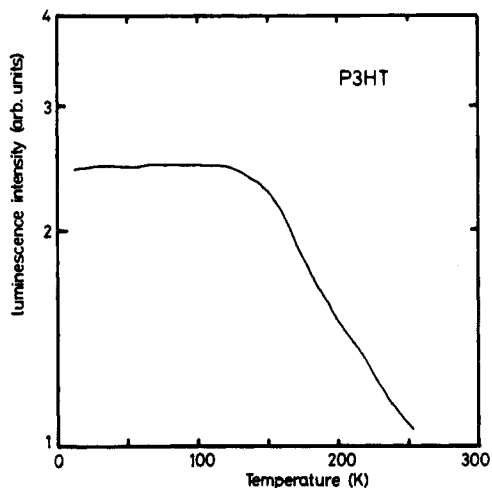


Figure 3. Temperature dependence of the photoluminescence intensity for P3HT. Experimental conditions as for figure 2.

contrast with the results reported for polythiophene, in the alkyl-substituted material the subgap region is free of absorption, and the band edge shows weak vibrational features spaced by about 0.18 eV. These differences have also been observed in the optical absorption spectrum of the insoluble 3-methyl derivative of polythiophene [17]. The PL intensity is moderately strong (though considerably weaker than for P3DT), and the structure in the spectrum is well-resolved at low temperatures, with an energy spacing between peaks of some 0.18 eV. As with other polymers such as PPV, the PL intensity is largest at low temperatures, saturating to a constant value below about 120 K, and falling steadily above this temperature, by a factor of two at room temperature, as shown in figure 3. We note that the PL intensity was reported by Yoshino *et al* [18] to rise at temperatures well above 300 K; this behaviour is associated with the change in polymer chain conformation as the melting temperature is approached. No significant changes in the spectral output of the PL, or in the form of the absorption edge, were seen for other excitation energies, and no differences were noticed for films prepared by spin-coating, after annealing, or prepared by casting.

In contrast, we find that the nature of the photoinduced absorption, PA, is strongly affected by the method of preparation of the film. PA for this polymer in the solid form has previously been reported by Kim *et al* [19], and in solution at room temperature by Spiegel *et al* [20]. Two sub-gap absorption bands were seen, and by association with the appearance of IR-active vibrational modes were shown to be due to charged photoexcitations [19]. The presence of only two absorption bands indicates that the charged excitations are bipolarons, with optical transitions between the gap states and the band edges as shown in figure 1. For a spin-coated film, prepared at room temperature and measured soon after preparation, we observe the PA spectrum shown in figure 4. We observe two sub-gap induced absorption bands, the upper with a peak at 1.1 eV, and the lower not fully resolved at the 0.5 eV cut-off for this experiment, but with indications that the peak is very close to 0.5 eV. Photoinduced bleaching (PB) is seen above 2 eV, with superimposed oscillations, with peaks at 2.09 eV, 2.26 eV and 2.43 eV. As we discuss below, these are associated with thermal modulation of the band-edge absorption. We find that the sub-gap structure of the PA is strongly modified for samples

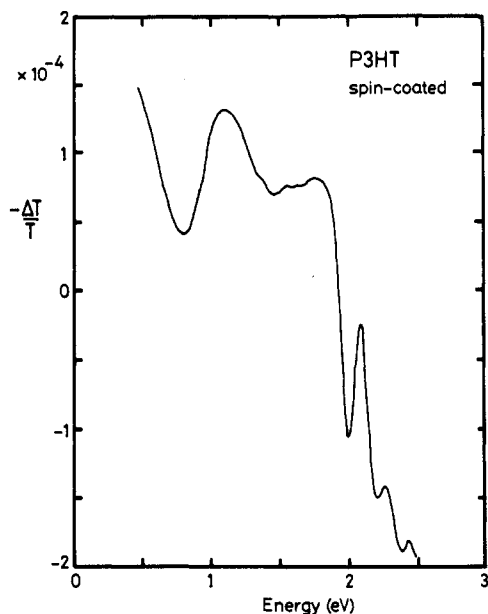


Figure 4. Photoinduced absorption spectrum for P3HT measured at 40 K with excitation at 457.9 nm. The film was prepared by spin-coating from solution in chloroform, and measurements were performed soon after preparation without thermal annealing.

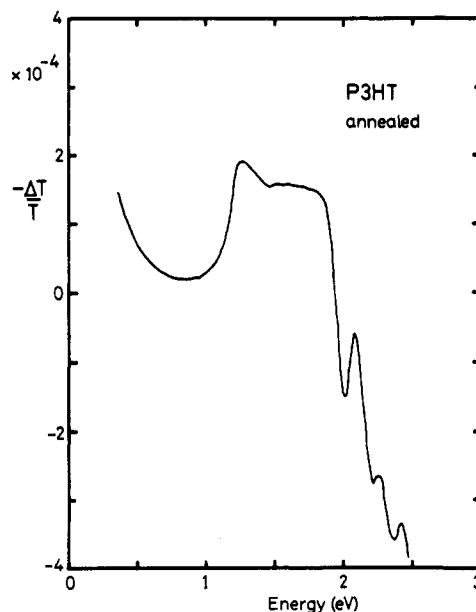


Figure 5. Photoinduced absorption spectrum for P3HT measured at 40 K with excitation at 457.9 nm. The film was prepared by spin-coating from solution in chloroform, and stored in an inert atmosphere for one week at room temperature before use.

prepared by solution casting or by spin-coating but subsequently aged or annealed, for example by storage at room temperature in an inert atmosphere for a period of one week. A typical PA spectrum for a cast film is shown in figure 5; it is very similar to that reported by Kim *et al* [19]. Note that the sub-gap absorptions are shifted away from the centre of the gap, with the upper feature increasing to 1.3 eV and the lower feature falling to energies outside the range of our measurement (measured to be at 0.35 eV by Kim *et al* [19]).

We associate the shoulder at just below 2 eV and the oscillations superimposed on the PB above 2 eV with thermal modulation of the absorption edge, on the basis of the temperature and frequency dependence we report below, and the directly-measured TM spectrum. The positions and spacing (0.17 eV) of these peaks suggest that they are associated with the vibrational structure in the band edge. The thermal modulation spectrum for an annealed sample, measured directly by ratioing the optical transmission, T recorded at different temperatures (60 and 40 K) as $(T(60 \text{ K}) - T(40 \text{ K}))/T(60 \text{ K})$, is shown in figure 6. We note that it reproduces most of the features of the PA spectrum in figure 5 above 1.5 eV, with both the negative feature peaking near 1.9 eV and the oscillations at higher energies.

The temperature dependence of the PA response for a sample prior to annealing at photon energies of 0.9 eV, and at 2.16 eV is shown in figure 7. At the lower energy, where we expect the PA response to be due only to induced absorption associated with the photoexcited gap states, we observe a weak temperature dependence up to about 120 K, and a rapid fall above this temperature. In contrast, the temperature dependence at 2.16 eV is much weaker, with a slow rate of decrease above 150 K, and a readily

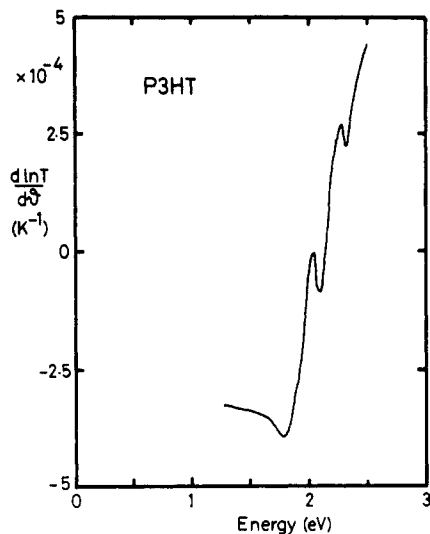


Figure 6. Thermal modulation spectrum for an annealed sample of P3HT, $\partial \ln T / \partial \theta$ measured directly from the optical transmission, T , recorded at 60 and 40 K.

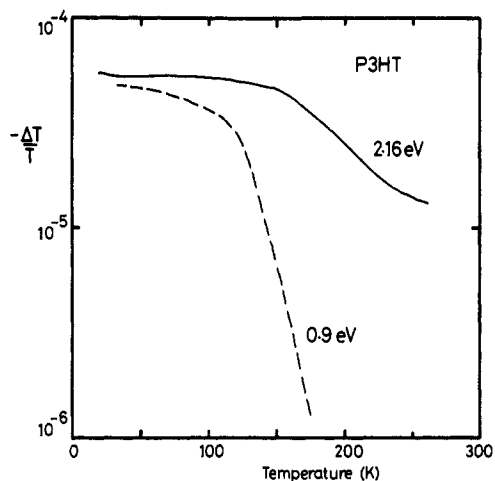


Figure 7. Temperature dependence of the photoinduced absorption signal in an unannealed film of P3HT, measured at photon energies of 0.9 eV and 2.16 eV. Excitation (200 mW cm^{-2} at 457.9 nm) was chopped at 110 Hz.

measurable signal at room temperature. The differences in behaviour at the energies clearly demonstrates that the two features have different origins; this allows us to discount electromodulation [21] of the band-edge as the origin of the PA response at 2.16 eV since this scales with the concentration of charged excitations and hence with the low-energy PA response [22]. Furthermore, electromodulation typically generates peaks shifted in energy and opposite in sign relative to those due to thermal modulation [21].

Figure 8 shows the frequency dependence of the PA response measured at 0.41 eV with a sample temperature of 40 K. We observe a response that is empirically fitted by $\Delta T/T \propto \omega^{-1/2}$ over the whole frequency range measured. This indicates that there is no well-defined lifetime (there is probably a spectrum of decay times covering the whole frequency spectrum shown here). It also indicates that we are not able to work in the low-frequency limit, so that the temperature dependence of the PA measured at 110 Hz as shown in figure 7 is thus complicated by the effects of temperature-varying lifetimes.

3.2. P3DT

The room temperature optical absorption spectrum and low temperature PL spectrum (80 K) are shown in figure 9. The spectra are very similar to those shown for P3HT in figure 2, though there is a slight shift to lower energies for both PL and absorption for the P3DT. The PL response for the dodecyl derivative is noticeably stronger than in the hexyl derivative; under the experimental conditions used here we estimate that the quantum yield is a factor of 20–50 greater.

The PA spectrum P3DT is very different to that of P3HT, as can be seen in figure 10. In place of the two sub-gap bands seen in P3HT (figures 4 and 5) we observe only a single induced absorption band, peaking at around 1 eV. Also in contrast to P3HT, this PA band at 1 eV cannot be observed at temperatures above 100 K. Figure 11 shows the

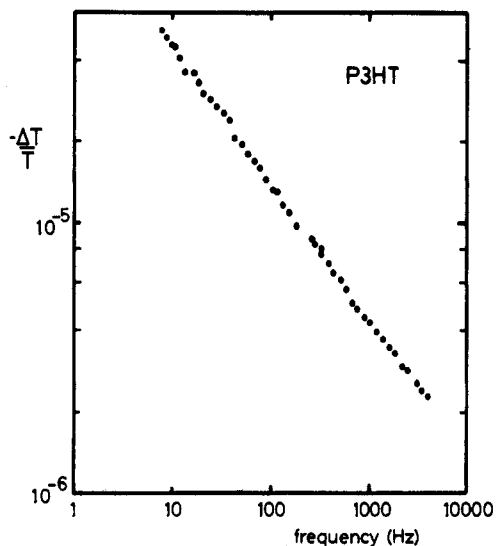


Figure 8. Frequency dependence of the PA signal at 0.41 eV for an annealed film of P3HT measured at 40 K.

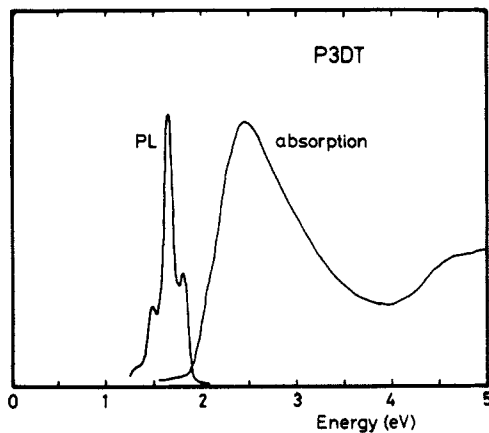


Figure 9. Optical absorption for a film of P3DT measured at room temperature, and photoluminescence spectrum measured with excitation at 514.5 nm and as a temperature of 80 K.

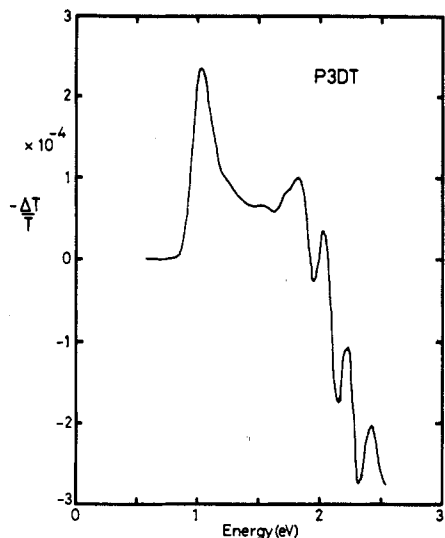


Figure 10. Photoinduced absorption spectrum of P3DT measured at 40 K with excitation at 457.9 nm, at an intensity of about 200 mW cm^{-2} .

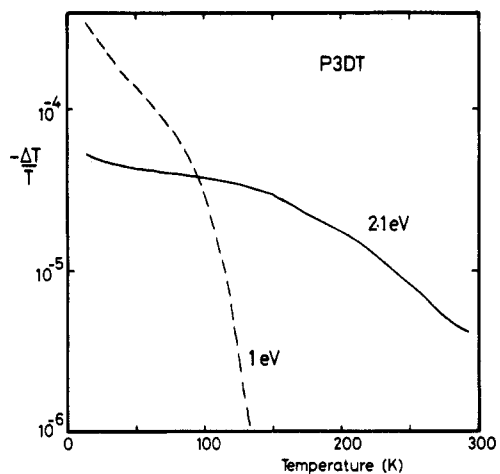


Figure 11. Temperature dependence of the PA response in P3DT measured at photon energies of 1 eV and at 2.1 eV. Experimental conditions were similar to those specified for figure 10.

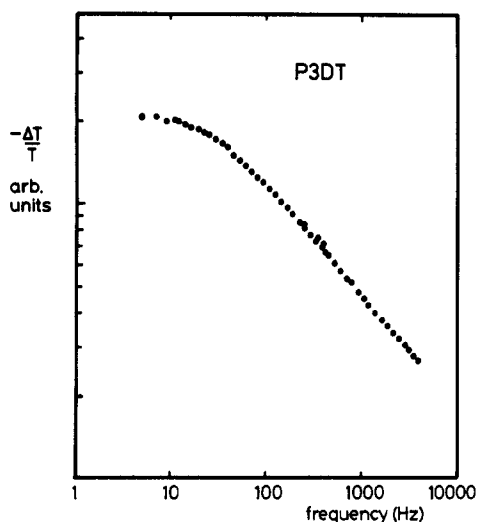


Figure 12. Frequency dependence of the PA response in P3DT at 40 K at a photon energy of 1 eV.

temperature dependence of the signal at 1 eV, illustrating the abrupt drop in signal strength between 40 and 100 K, by some two orders of magnitude. Figure 12 shows the frequency dependence of the PA response at 1 eV at 40 K. In contrast to the results for P3HT shown in figure 8, we observe here a clearly defined crossover from a low frequency regime where the response is independent of frequency, to a high frequency regime where the response falls, following the same $\omega^{-1/2}$ response seen for P3HT. The crossover at 40 Hz in figure 12 indicates that there is a time constant of 4 ms which characterises the long-time limit for the decay of this photoexcitation; however, since the response at higher frequencies does not fall as $1/\omega$, falling considerably more slowly as $\omega^{-1/2}$, we have to conclude that there is a spectrum of lifetimes, albeit with a maximum value set at 4 ms. As we discuss in section 4, we consider that the sub-gap PA response we observe for P3DT is not associated with the formation of charged photoexcitations. One possible assignment is to a triplet–triplet transition of a photoinduced triplet exciton.

As for P3HT, the structure in the band edge, including the apparent absorption peak at 1.9 eV, is assigned to thermal modulation of the band edge absorption. The temperature dependence of these features is typically of the form of the data shown in figure 11 for the PA response at 2.1 eV. As with the data of figure 7 for P3HT, the response at 2.1 eV decreases slowly on raising the temperature to 140 K, above which there is a much more rapid decrease. This temperature dependence is completely distinct from that of the PA at 1 eV, and therefore indicates that the band edge features and the 1 eV feature are unrelated.

4. Discussion

The use of two examples of poly(3-alkyl thienylenes) with different lengths of alkyl chain provides an interesting control for the study of the optical excitations of this class of conjugated polymer. Though the theoretical framework for the nature of the self-localised polaronic excitations of the chain is now well established, it is not straightforward to apply models developed in a one-electron theory for isolated chains to polymers for which Coulomb interactions are evidently important, which can show considerable levels of π to π interchain interaction, and which contain high con-

centrations of chain defects, both chemical and conformational. We consider these three issues in the discussion below. It is useful for the discussion that follows to first extend the discussion of polaron formation in non-degenerate ground state polymers.

In the continuum models of Brazovski and Kirova [3] and Fesser *et al* [4] (the FBC model), the preferred sense of bond alternation is introduced through an extrinsic contribution to the gap parameter, Δ , as

$$\Delta = \Delta_0 + \Delta_e \quad (1)$$

where Δ_0 is the contribution to the gap due to the Peirls mechanism, and Δ_e is the extrinsic contribution. It is useful to define a confinement parameter, γ , as

$$\gamma = \Delta_e / 2\lambda\Delta \quad (2)$$

where λ is the effective electron–phonon coupling constant, such that

$$\Delta = \Delta_0 \exp\{\gamma\} \quad (3)$$

The extent of the polaron along a polymer chain, together with the position in the gap of the localised energy levels, are determined in these one-electron models by the strength of γ . The case of near degeneracy allows the polarons to be relatively extended with electronic levels near the centre of the gap, while strong breaking of the degeneracy keeps them much more compact with levels near the band edges. Hence, the degree of non-degeneracy can be conveniently parametrised by an experimentally accessible ratio ω_0/Δ , where $2\omega_0$ is the separation between the intragap polaron levels and 2Δ is the energy gap. For the case of those polarons for which the occupations of the upper and lower intra-gap states are equal (the polaron-exciton and bipolaron in figure 1), ω_0 is related to γ through [4],

$$\gamma = (\omega_0/\Delta) \sin^{-1}(\omega_0/\Delta) / \sqrt{1 - (\omega_0/\Delta)^2} \quad (4)$$

For the case of the singly-charged polaron, the gap states are more closely tied to the band edges, with a limiting separation of $\pm\Delta/\sqrt{2}$ about the centre of the gap for $\gamma = 0$. The greater degree of relaxation of the bipolaron over the polaron stabilises the coalescence of two like-charged polarons to form a bipolaron.

The addition of Coulomb interactions to the problem introduces several new aspects to the behaviour. It is widely observed that where there are optical transitions associated with the two band to gap state transitions shown for the bipolaron in figure 1, the two transitions are approximately equal intensity. This, and their asymmetric displacement about midgap is inconsistent with the predictions of the non-interacting electron continuum model [3, 4]. Calculations of the effects of inclusion of on-site and inter-site electron–electron interaction terms in the model Hamiltonian [23, 24] show that weak on-site interactions do not alter much the predictions of the non-interacting model for the relative transition intensities and only when the strong coupling limit is approached can the theories obtain intensity ratios consistent with experiment. Weak interactions can, however, explain the asymmetric displacement of the levels. Within a perturbation theory treatment [23] the two bipolaron transitions are found at energies:

$$E_{\pm} = \Delta \pm \omega_0 - U_{\text{eff}} \quad (5)$$

where $U_{\text{eff}} = aU_0/3l$ with U_0 the bare Coulomb repulsion for two electrons on one p_z orbital, and l/a the length in units of carbon–carbon bonds for the bipolaron. An estimate of the interaction strength, U_{eff} , can thus be obtained from the observed difference between the gap energy and the sum of the two bipolaron transition energies.

4.1. Intrachain excitation

The optical processes that dominate the optical response of these polymers are those that are associated with intrachain excitation. Many of the non-degenerate ground state polymers, including PPV [1] and PT and its alkyl-substituted derivatives show strong PL, in contrast to polyacetylene for which PL is extremely weak [25]. The form of the absorption and the PL emission is very much as expected for the emission from any conjugated molecular system, with vibronic structure in the PL band due to vibrational quanta of the ground state system, and vibronic structure in the absorption band (best detected in derivative experiments such as the thermal modulation spectrum of figure 6), associated with vibrational quanta of the excited state. Within the standard treatment for molecular systems of this type, the excited state is relaxed at a different configuration coordinate of the molecular system from that of the ground state, and the involvement of the vibrational modes that couple to this configuration coordinate then follows according to standard Franck–Condon theory [26]. Within the formalism of the polaron models developed for the conjugated polymers, the relaxation of the configuration coordinate in the excited state pulls the two gap states away from the band edges, as shown in figure 1. The Stokes shift, $2\Delta - 2\omega_0$, is the energy difference between the zero-phonon transition to the excited state, which will be close to the peak in the absorption, and the transition from the vibrationally-relaxed state to the vibrationally relaxed ground state. The peak in absorption is near 2.5 eV for P3HT, and the high-energy band in the PL spectrum is at 1.85 eV, giving a Stokes shift of 0.65 eV, and a value for γ of 0.9 from (4). This value of γ is consistent with plausible estimates for the parameters of (2), and we consider the description of the PL given here is satisfactory.

The quantum yield for PL in many conjugated polymers is often very low. We do not have quantitative estimates for the quantum yield here, but consider that it is of order tens of per cent for P3DT, and fractions of a per cent for P3HT. It has been shown in the case of PPV that the effect of introducing good conjugation onto the polymer chain is to increase the effectiveness of non-radiative decay channels; this is considered to be due to the high mobility of the exciton and its rapid diffusion to centres at which non-radiative decay can occur (such as exciton–exciton collisions, and interactions with charged polarons) [1, 5, 6]. There are only small differences in the energies of the π -electron states for these two alkyl thienylene polymers, but there is a large difference in the quantum yield for PL. We consider that the difference in behaviour is due to the differences in the effectiveness of interchain motion of the excitons, and that this is considerably lower in the polymer with the longer alkyl-chain side-groups.

4.2. Interchain excitation

The processes by which metastable charged photoexcitations are produced are now understood to involve interchain motion of charge. The effect of varying the length of the alkyl side-chain must be to alter the structure of the polymer, and we consider that this controls the effectiveness of the interchain π -electron interactions. It is known that these polymers tend to crystallise in a layer structure, which allows close interaction between the conjugated backbone units within the plane of the lamellae [15, 27]. For P3HT this gives a spacing of about 3.8 Å between chains. This structure does therefore allow interchain contact of similar effectiveness to that found in PT, and it is perhaps therefore not surprising that the photogeneration of charged excitations is very similar for PT and P3HT. The increased length of the alkyl side chain in P3DT is largely taken up by an increased separation between the lamellae. However, whereas P3HT is rather

disordered, the longer side chains in P3DT can crystallise and P3DT is much better ordered [15]. This side chain crystallisation may force an unfavourable registry of the thiophenes on adjacent chains, and weaken the contact between them.

The presence of two sub-gap absorption bands in the PA spectrum, and the associated infrared active vibrational modes, as established by Kim *et al* [19], demonstrates that bipolarons are formed as the long-lived metastable charged excitations of P3HT. Our results are in agreement with these assignments. We note that the time constants for the decay of the PA response due to the bipolaron transitions are rather longer for P3HT than usually found for conjugated polymers without side-chains, and we consider that this may be attributable to the weakened interchain contact in the alkyl-substituted polymer.

For P3DT we have no evidence for the presence of charged photoexcitations from the PA experiments we report here. Though we see in the PA spectrum of figure 10 some structure at 1 eV and above, we do not see the low-energy band to gap-state transition always expected from charged polarons or bipolarons. We emphasise that, under the experimental conditions that we use, we can only detect excitations which have a lifetime of the order of the modulation frequency used for the pump beam; in the limit where the excitations are short lived the signal is too weak to detect since it scales with lifetime, and in the limit where the lifetime is long, the response is too slow to give a response at the modulation frequency. The latter limit is considered to be obtained for polydiacetylenes where bulky side-groups can keep the chains apart [28, 29].

The structure in the PA at 1.9 eV and above can be trivially associated with thermal modulation of the band-edge absorption, but the PA peak near 1 eV is evidently due to a photoexcited state. We note that it shows a rather different temperature and frequency dependence to that of the sub-gap transitions in P3HT, falling away more quickly with increasing temperature and showing a faster time response. One possible assignment is to a triplet-triplet transition of the triplet exciton, as assigned to the PA feature in PPV at 1.45 eV [7, 8]; the fast fall off at temperatures above 40 K is similar to that seen in PPV, though the frequency response for P3DT is more complicated. Unambiguous assignment to the triplet exciton will require measurements of light-induced ESR or of the magnetic field dependence of the decay times [30].

4.3. Bipolaron confinement

The bipolaron is the charged excitation of lowest energy in one-electron models, but the effect of Coulomb interactions must be to destabilise it [31]. Where charge is introduced through doping, it is possible to invoke the Coulomb interactions between the charge on the chain and the dopant ions as a means of neutralising the Coulomb interaction between the two like-charges on the bipolaron, and there is clear evidence for P3HT in solution, from ESR studies as a function of dopant concentration, that the bipolaron is lower in energy than the corresponding pair of polarons [32]. Charges produced by photoexcitation of electron-hole pairs are not bound to dopant counter ions, so that the Coulomb interaction between the two charges is not screened. The presence of the Coulomb interaction is evident from the asymmetric positioning of the bipolaron bands about mid-gap, for example, for the annealed P3HT here, with values for E_- and E_+ of 0.35 and 1.3 eV and $2\Delta = 2.5$ eV, we estimate a value for U_{eff} of 0.42 eV through (5). In spite of this, the energies of the bipolaron formation are broadly comparable, with similar values for γ for chemical doping and photoexcitation [19].

The concentration of charged photoexcitations obtained under our experimental conditions is low, of the order 10^{17} to 10^{18} cm^{-3} , and it is important to consider whether

they reside on the 'defect free' regions of the chains or whether they are stabilised at chain defects. Photo-induced bleaching of the optical transitions associated with the states used to create the bipolarons is not easy to determine here because the band-edge PA is masked by strong thermal modulation of the absorption edge. However, the evidence gathered for other polymers, such as poly(thienylene vinylene) [33] is that the gap states are generated from band states, with bleaching of the interband transitions extending from the absorption edge deep into the band. For those polymers which can be well oriented, such as PPV, the induced absorption associated with the bipolarons is very strongly polarised along the direction of the polymer chain [1], and from this it is inferred that the bipolarons are situated on the long, straight sections of the chain, thus avoiding chain defects found in the less oriented regions of the polymer between the crystallites.

We observe here, however, that the positioning of the bipolaron absorption bands within the gap does vary according to the method of preparation of the polymer, although gross properties such as the band gap are unaffected. We note that in spite of very similar values for the band-gap, 2Δ , the splitting between the two bipolaron levels, 2ω , varies from as low as 0.6 eV for the unannealed P3HT, 0.8 eV for PT [9], and 0.95 eV for the annealed P3HT. Thus γ is not simply related to the gap through (2), and we consider that local structural defects on the chain may have a role to play in the stabilisation of photogenerated bipolarons. This range of values for $2\omega_0$ is much lower than the value of $2\omega_0$ determined for the polaron–exciton from the spectrum of the PL, and we emphasise that this is inconsistent with the predictions of the FBC model for which the positions of the states in the gap is determined by the difference in the occupations of the two gap states, and are thus the same for the polaron–exciton and for the bipolaron [4]. This discrepancy has been noted previously for other polymers [1, 5, 33] and is probably related to the effect of the Coulomb interaction and its influence on the stabilisation of the bipolaron.

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