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Photoinduced absorption and photoluminescence in poly(2,5-dimethoxy-*p*-phenylene vinylene)

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We report a study of the photoexcited states in the conjugated polymer poly(2,5-dimethoxy-*p*-phenylene vinylene). Photoluminescence due to radiative recombination of singlet excitons is observed at energies just below the onset of the π-π^* absorption band at 2.1 eV. Photoinduced absorption at 80 K shows bands peaking at 0.68, 1.35, and 1.80 eV. The features at 0.68 and 1.8 eV are associated with the same excited state which we propose is a doubly charged bipolaron, while the third at 1.35 eV is unrelated. We assign this 1.35-eV absorption to a triplet-triplet transition of a triplet exciton. The bipolarons are long lived with significant numbers surviving in excess of 100 ms at 80 K, and have a weak temperature dependence such that photoinduced absorption is readily detectable even at room temperature. The triplet exciton has a lifetime of order 2.5 ms at 80 K but this falls rapidly at higher temperature and the response is not detected at room temperature. We contrast these results with those obtained previously for the related poly(arylene vinylene) polymers poly(*p*-phenylene vinylene), and poly(2,5-thienylene vinylene) and for other conjugated polymers, and draw attention to the important role played in the photophysics of these materials by neutral excited states.

I. INTRODUCTION

Expertise in synthesis and processing of conjugated polymers has now evolved to the point where high-quality samples in a variety of forms can be prepared for a range of polymers. Concomitant with this evolution, interest in conjugated polymers for applications now extends to include electronic devices [Schottky diodes, metal-insulator-semiconductor (MIS) diodes, MIS field-effect transistors (MISFET's) (Refs. 1 and 2)], electro-optic devices (MIS, MISFET, and dc Kerr effect optical modulators, electroluminescent structures[1-5]), and all-optical nonlinear elements (third-harmonic generators, ac Kerr effect modulators, and couplers).

The poly(arylene vinylene) polymers, of which poly-(*p*-phenylene vinylene) (PPV),[6,7] poly (2,5-dimethoxy-*p*-phenylene vinylene) (PDMeOPV), and poly (2,5-thienylene vinylene) (PTV) (Ref. 8) are the most widely studied examples, can be prepared by a "precursor route," with the synthesis of a solution processible, nonconjugated precursor polymer that can be readily converted to the conjugated material by an appropriate thermal treatment. Fabrication into the desired sample form (e.g., high optical quality, fully dense, homogeneous thin films) is carried out prior to the thermal conversion step, thus allowing the processing of a material which in its final state is intractable. Moreover, since chemical modification of the arylene group or its replacement by a heteroarylene group results in a systematic variation in electronic structure, the poly(arylene vinylene) polymers provide a range of materials well suited to detailed investigations of the novel physical properties of conjugated polymers.[9] Many such investigations have already been reported by us and by others and in the present paper we report photoinduced absorption and photoluminescence measurements on PDMeOPV.

The recent demonstration by some of the authors that PPV can be used as the emissive layer in an electroluminescent device[4,5] gives added weight to the importance that we have previously placed[6,7,10] upon an understanding of the role of neutral excited states (singlet and triplet excitons). With the exception of work on the polydiacetylenes, there has been greater interest in charged excitations such as the charged soliton and polaron states formed following self-localization of the lattice around charges added by doping, by photoexcitation, or by carrier injection. Part of the reason for this is that the signatures of the neutral excited states, principally the radiative decay of the singlet exciton, are very weak in many conjugated polymers. However, luminescence is readily observed in carefully prepared conjugated polymers, particularly those with larger band gaps, and is well studied in PPV (Refs. 6 and 7) and also the poly(3-alkyl thienylenes).[10] There is clear evidence that extrinsic factors can be important in producing this variation of luminescence quantum yield. For example, the presence of nonradiative recombination sites, which include any self-localized charge carriers that arise through unintentional doping, can strongly reduce the lifetime of the neutral excited states[3,11] and may cause them to decay too quickly to be readily detected. In PDMeOPV, as reported below, well-defined signatures of neutral excited states, namely a luminescence emission arising from radiative decay of singlet excitons and a photoinduced absorption that we associate with triplet-triplet transitions of triplet excitons, are observed. In addition, we also find signatures of long-lived charged excitations which we identify as doubly charged bipolarons.

II. SAMPLE PREPARATION AND EXPERIMENTAL DETAILS

PDMeOPV was synthesized[12] according to the scheme in Fig. 1. Base-induced polymerization of the monomer, 2, 5-dimethoxy-1, 4-xylene-bis-(tetrahydrothiophenium chloride) (I) to yield the sulphonium salt precursor polymer (II) was achieved by the slow addition (30 min) of one equivalent of sodium hydroxide (0.4M) to an aqueous solution of the monomer at a temperature of 0 °C under an inert gas atmosphere. In the standard sulphonium polyelectrolyte precursor route as used in the synthesis of PPV, the next stage involves dialysis against water to remove low molecular weight material and ionic species. For PDMeOPV, however, the sulphonium salt precursor polymer has a tendency to gel during dialysis, most probably as a result of nucleophilic attack on the sulphonium moiety leading to substitution by hydroxy groups. To circumvent this difficulty, we have followed the modified route, due to Momii *et al.*,[13] in which the chloride counter anion is exchanged with a *p*-toluene sulphonate counter anion by addition of an excess of the sodium salt of *p*-toluenesulphonic acid to the reaction mixture. The product (III) precipitated and was recovered, dissolved in methanol, and on stirring for 12 h formed a second precipitate (IV), a modified precursor polymer with a methoxy leaving group. This polymer is soluble in dichloromethane and chloroform and was characterized by ^{1}H, NMR and infrared spectroscopy. Films for the optical measurements reported here were prepared either by drip casting (i.e., prepared by placing a drop of solution on the substrate and allowing the solvent to evaporate) onto polytetrafluoroethylene (PTFE), from which free-standing films can be lifted after the solvent evaporates, or drip casting onto spectrosil substrates. Conversion to PDMeOPV (V) was achieved by thermal treatment at 200 °C for 2 h under acidic flowing argon (bubbled through concentrated HCl prior to passing over the sample). Acid is required to catalyze the elimination of the methoxy leaving group attached to the benzylic carbon, a process that may be followed by infrared spectroscopy through loss of the band at 1093 cm^{-1} associated with a characteristic C-O-CH$_3$ in-plane bending mode.

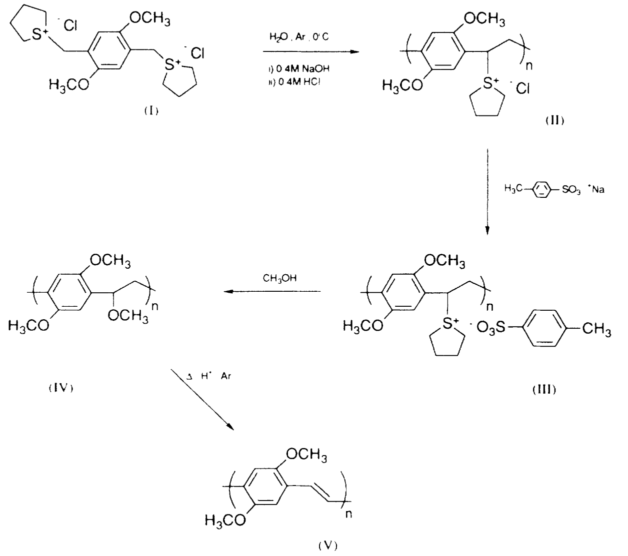

FIG. 1. Chemical synthesis of PDMeOPV (V) via the modified sulphonium polyelectrolyte precursor route.

Optical-absorption spectra were recorded using a Perkin Elmer Lambda 9 spectrophotometer. Steady-state luminescence and Raman spectra were measured using a double monochromator and cooled photomultiplier combination following excitation at 457.9 nm with an argon-ion laser. For measurements of photoinduced absorption the samples were mounted in a continuous flow optical access He cryostat (Oxford Instruments CF 204). A silicon diode thermometer mounted next to the sample on the cryostat insert was used to monitor the sample temperature. The sample transmission spectrum to light from a tungsten halogen lamp was measured, utilizing post-sample monochromation, with a Si or cooled InSb detector. Changes in the transmission due to mechanically chopped optical pumping by the 457.9-nm emission from a cw argon-ion laser were monitored by phase sensitive detection using a two-phase lock-in amplifier referenced to the chop frequency. The photoinduced absorption spectrum was normalized to the transmitted intensity in the absence of laser excitation. Measurements of photoinduced absorption were made over the frequency range from 10 to 3000 Hz, allowing us to detect only those metastable states that have lifetimes of between a few hundred μs and a hundred ms. Temperature dependence was studied over the range 20–300 K. As discussed below, in the energy range where photoluminescence can be detected in the photoinduced absorption measurement, there are then three overlapping contributions to the photoinduced response, namely the photoluminescence and two distinct photoinduced absorptions. In order to distinguish these responses we have recorded both the in-phase and quadrature components of the Si photocell output at a sufficiently high chop frequency that the photoluminescence and photoinduced absorptions are well separated in phase. This procedure allows separation of the different contributions by subsequent numerical manipulation of the phase information.

III. RESULTS

The room-temperature optical-absorption spectrum of a drip cast film of PDMeOPV is shown in Fig. 2(a) together with that for a spin-coated PPV sample prepared via the tetrahydrothiophenium precursor. At 300 K, the onset for π-π^* absorption in PDMeOPV is seen at 2.0 eV, some 0.35 eV (i.e., $\approx 15\%$) lower than for the PPV sample. This shift is ascribed to the electron donating character of the methoxy substituents attached to the phenylene ring which enhances the electron density along the polymer backbone. The absence of resolved structure on the absorption edge is in contrast to the clear structure seen for PPV and suggests that PDMeOPV films prepared via the methoxy leaving group precursor (IV) have a higher degree of conformational disorder that leads, through inhomogeneous broadening, to a smearing of the π-π^* absorption edge. There is a weak shoulder on the leading edge of the absorption which becomes stronger at 77 K [see Fig. 2(b)] and is more clearly seen in the numerically calculated second derivative of the spectrum. This feature appears for drip cast films but not spin-coated films (typically the polymer solution is applied to the substrate and immediately spun at 2000 rpm for 60 s).

The proposal that the absence of defined structure in the absorption edge arises from conformational disorder is consistent with the results of electron-diffraction studies which show a disordered material for drip cast and, particularly, for spin-coated films.[14] We expect a greater extent of random coiling in solution in the methoxy leaving group precursor (IV) than for the sulphonium salt presursors to PPV for which intrachain Coulomb interactions are expected to give a more chain-extended structure in solution. The lack of order found in these cast and spin-coated films of PDMeOPV is not, however, a characteristic feature of the polymer since upon stretch orientation, the samples of PDMeOPV show extremely high degrees of orientation and have a well-defined crystal structure with significantly less disorder than found in stretch-oriented PPV.[15]

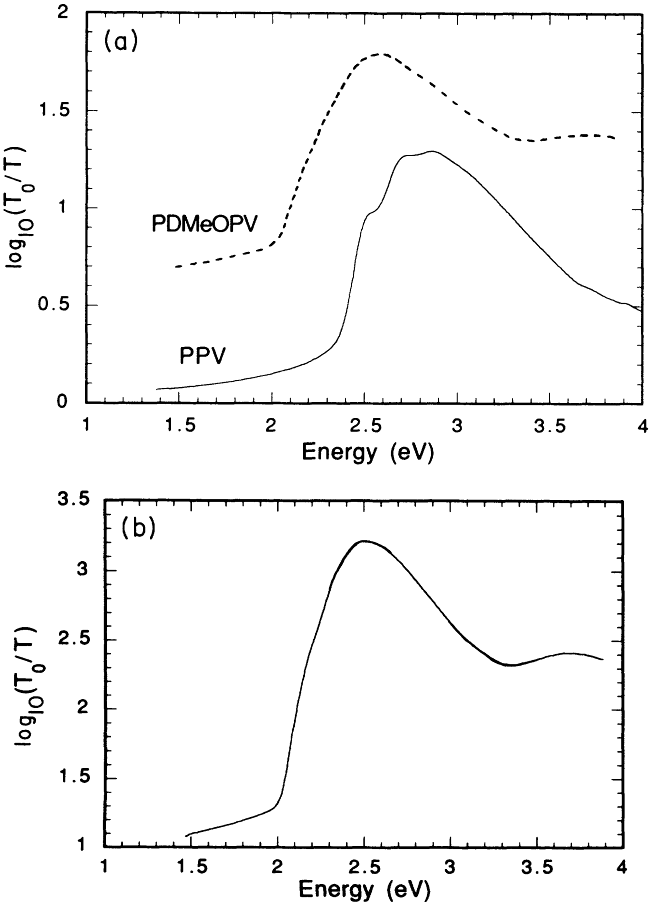

FIG. 2. (a) Room-temperature optical-absorption spectra of PPV and drip-coated PDMeOPV. (b) Low-temperature (80-K) absorption spectrum of same PDMeOPV sample.

Figure 3 shows the photoluminescence spectra of PDMeOPV at 80 and 300 K for the same drip cast sample shown in Fig. 2. The spectra are dominated by two strong peaks with a third, much weaker peak at lower energy. The two strong peaks are identified as zero- and one-phonon emission lines (S_1 to S_0 0-0 and 0-1 transitions) and the weak feature as a two-phonon emission line (S_1 to S_0 0-2 transition). At 300 K the 0-0 emission appears at 2.06 eV with the 0-1 line at 1.91 eV, i.e., some 0.15 eV to the red. On cooling to 80 K the emission shifts by about 0.08 eV to the red and the vibronic structure becomes more clearly resolved (the lines narrow) with greater weight transfered into the 0-0 line. The 0-0 peak is then seen at 1.98 eV with the 0-1 line at 1.80 eV showing a greater redshift. The spacing of the vibronic peaks by 0.15 eV at room temperature and 0.18 eV at 80 K is consistent with coupling of the exciton to symmetric C-C backbone stretching vibrations of the polymer chain, a common feature in fluorescent conjugated polymers.[6,7,16] The size of the redshift and the difference in behavior for the 0-0 and 0-1 lines on cooling is not however mirrored in the temperature dependence of the Raman spectrum. This points, as discussed further below, to a more complex electron-phonon coupling behavior than previously considered.

In Fig. 4 we show the Raman spectra recorded at room temperature and 80 K for the same sample as used to measure the photoluminescence shown in Fig. 3. The principle peaks appear at 1622, 1582, 1306, 1284, 1110, 964, and 598 cm^{-1}. All the peaks except that at 598 cm^{-1} can be assigned to in plane vibrations by comparison with valence-force-field calculations for PPV.[17]

Figure 5(a) shows the photoinduced absorption, recorded at a chop frequency of 317 Hz for a PDMeOPV sample at 80 K, in the energy range overlapped by photoluminescence, i.e., $\Delta \leq E \leq 2\Delta$ (where 2Δ is the π-π^* gap energy). There are two features in the spectrum which

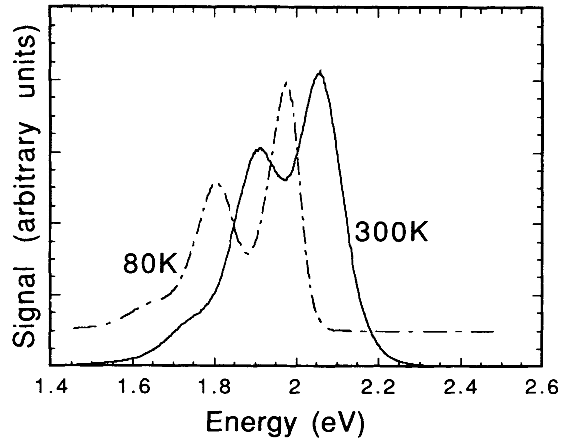

FIG. 3. PDMeOPV steady-state photoluminescence spectra recorded at room temperature (solid line) and 80 K (dash-dotted line), with excitation at 457.9 nm and using the same sample as that used for the optical-absorption spectra shown in Fig. 2. The spectra are offset the clarity.

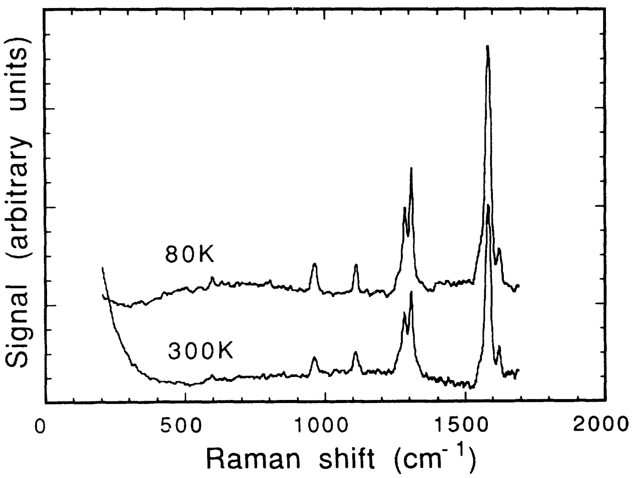

FIG. 4. PDMeOPV Raman spectra recorded at room temperature and 80 K, with excitation at 457.9 nm and using the same sample as that used for the optical-absorption spectra shown in Fig. 2. The spectra are offset for clarity.

have maximum intensities at significantly different phase angles relative to the maximum photoluminescence signal (taken, due to its very short decay time, to define the zero of phase in the measurements). The first is maximized at a phase retardation of 170° and peaks at 1.35 eV while the second is maximized at a phase retardation of 195° and peaks at 1.80 eV. This difference in characteristic decay time demonstrates that the two features are due to different excited states; this is readily confirmed, as discussed shortly, by the difference in temperature dependence.

In order to resolve the line shapes of the two features more clearly, we have numerically adjusted the phase to minimize, in turn, the contribution from each feature. This involves generation of the spectra in quadrature to those at which maximum intensities were obtained, i.e., at 260° and 105°. The results of this manipulation are shown in Fig. 5(b) after rescaling to the maximum peak values of Fig. 5(a). In Figs. 6(a) and 6(b) the manipulated spectra of the two features are shown for different temperatures, from which it is clear that the feature peaking at 1.35 eV has a much stronger temperature dependence. On warming up to 300 K the 1.35-eV feature is lost whereas that at 1.80 eV remains visible. On cooling from

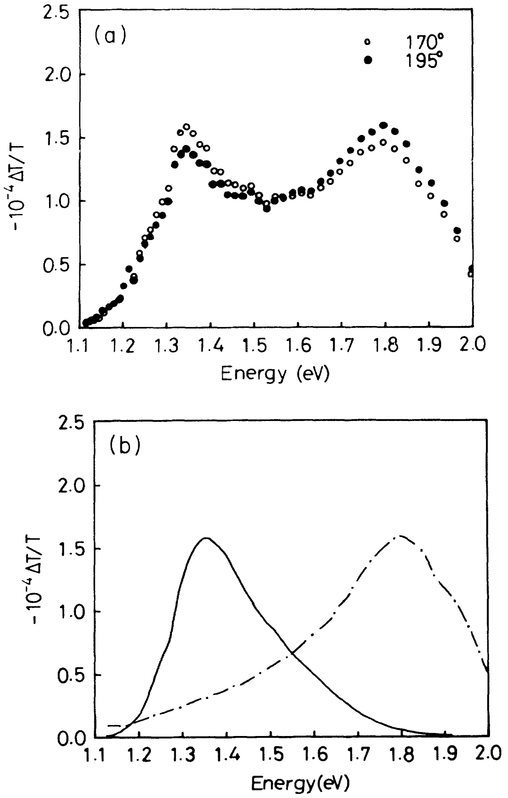

FIG. 5. (a) Photoinduced absorption in energy range $\Delta \leq E \leq 2\Delta$ recorded at a chop frequency of 317 Hz for a PDMeOPV sample at 80 K. The spectra are shown for phase angles of 170° and 195°, at which values the two features separately have maximum intensity. (b) More clearly resolved line shapes obtained by numerical adjustment of the phase to minimize, in turn, the contribution from each feature. The results have been rescaled to the maximum peak values of (a).

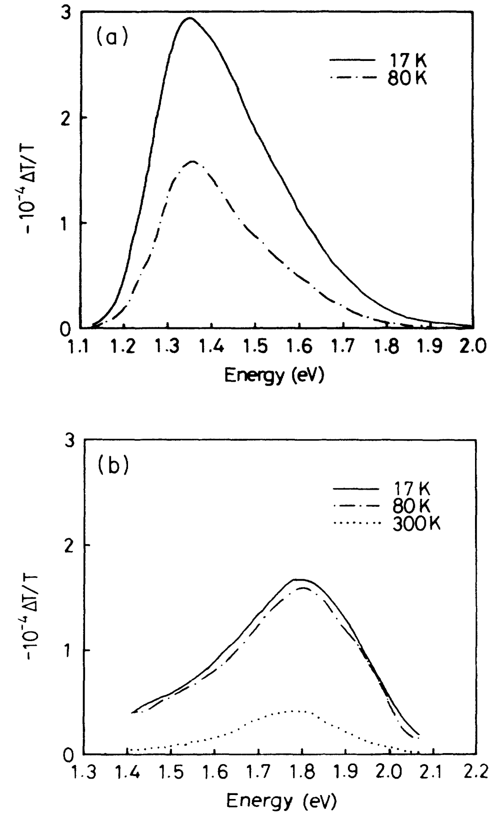

FIG. 6. (a) 1.35-eV photoinduced absorption feature recorded at 17 K (solid line) and 80 K (dashed-dotted line) for 317-Hz mechanically chopped excitation at 457.9 nm. (b) 1.8-eV photoinduced absorption feature recorded at 17 K (solid line), 80 K (dash-dotted line), and room temperature (dotted line) for 317-Hz mechanically chopped excitation at 457.9 nm.

80 to 17 K the 1.35-eV feature increases strongly while that at 1.80 eV increases very little. The procedure of numerically adjusting the phase to separate the two overlapping photoinduced absorption components works best when the states responsible have well-defined and different decay times such that each signal has a clearly defined phase. The latter requirement is met for the 1.35-eV feature which as we discuss below shows an excitation chop-frequency dependence characteristic of monomolecular decay. For the 1.80-eV feature, however, there is a much less clearly defined phase, a fact that is reflected in the difficulty of removing fully this component to reveal the undistorted spectral shape of the 1.35-eV feature. While this is not an ideal situation it is one that cannot be readily avoided without introducing extra experimental parameters: Photoinduced absorption-detected magnetic-resonance experiments can be used to distinguish the different features[18] and thus to provide spectra free from "cross talk" between the two components but we are not set up to undertake such measurements.

As discussed more fully below, the feature peaking at 1.80 eV is assigned to the higher of the two optical transitions involving the intragap energy levels of a doubly charged bipolaron. The lower bipolaron transition is detected, as expected, in the lower half of the π-π^* gap ($0 \leq E \leq \Delta$) and peaks at 0.68 eV. The two bipolaron peaks are shown together in Fig. 7 at temperatures of 80 and 300 K. The association of these two features with a single excited state is confirmed by their identical temperature dependences as shown in Figs. 8(a) and 8(b). In both cases, the photoinduced absorption signal changes little from the lowest temperatures up to 200 K but then drops off more rapidly above this.

The 1.35-eV feature has a markedly different temperature dependence (shown in Fig. 9) to that of the bipolaron peaks. The signal falls much more rapidly with increasing temperature and follows a nearly exponential decrease for temperatures above *circa* 50 K. Note that the residual signal at 250 K is expected to be largely due to the contribution from the overlapping bipolaron peak at 1.80 eV, which it is difficult to fully remove via the numerical phase adjustment procedure. The observed temperature dependence and the relative position of the transition within the π-π^* energy gap are very similar to those of the feature seen in PPV at 1.45 eV, which has been assigned to a triplet-triplet transition of a triplet exciton.[7] We believe that the feature observed at 1.35 eV here has the same origin and discuss this further below.

Information on the characteristic decay times of the bi-

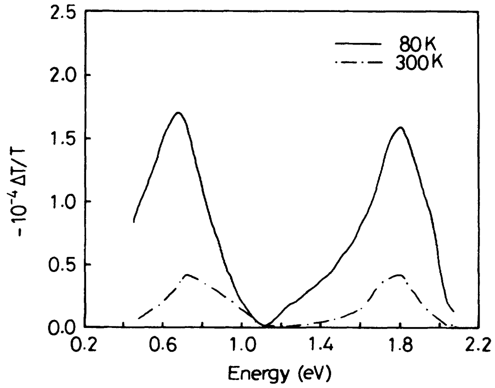

FIG. 7. Correlated photoinduced absorption features at 0.68 and 1.8 eV recorded at 80 K (solid line) and room temperature (dashed-dotted line) for 317-Hz mechanically chopped excitation at 457.9 nm.

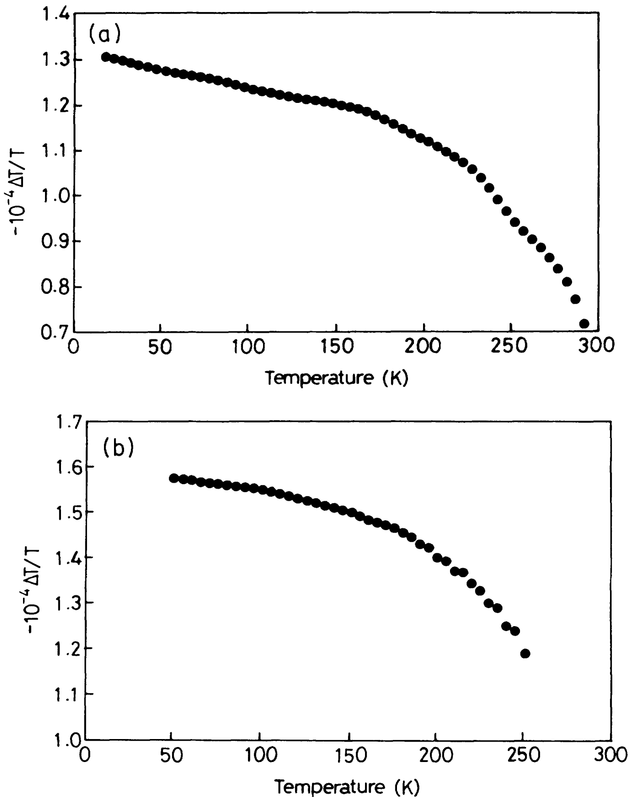

FIG. 8. Temperature dependence of photoinduced absorption at (a) 0.68 eV and (b) 1.8 eV for 317-Hz mechanically chopped excitation at 457.9 nm.

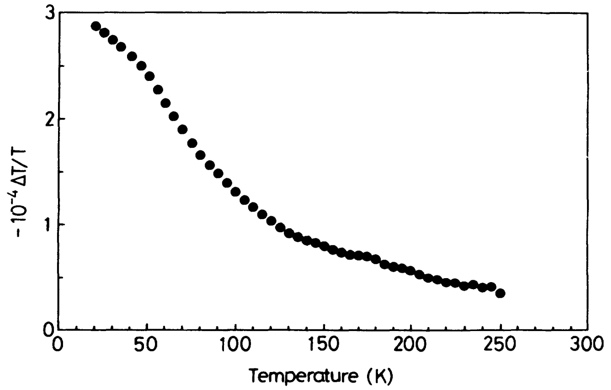

FIG. 9. Temperature dependence of photoinduced absorption at 1.35 eV for 317-Hz mechanically chopped excitation at 457.9 nm.

polaron and triplet exciton states responsible for the above features can be obtained from the dependence of the corresponding photoinduced absorption signals upon the frequency at which the excitation source is modulated by mechanical chopping. The modulation frequency was varied over the range from 10 Hz to 3 kHz, and the consequent variations in photoinduced absorption measured at 80 K at 0.68 eV (bipolarons) and at 1.35 eV (triplet excitons) are shown in Figs. 10(a) and 10(b), respectively.

For the 0.68-eV data in Fig. 10(a), absence of a plateau region, even down to the lowest measured frequencies, indicates that a substantial proportion of the photoexcited bipolaron states have lifetimes in excess of 100 ms at 80 K. Furthermore, the fall off in signal with increasing frequency is too gentle to be described in terms of a well-characterized monomolecular decay. The signal decreases approximately as $\omega^{-0.4}$ over a large part of the frequency range while an ω^{-1} dependence is expected for monomolecular decay kinetics. We consider that the weakened frequency dependence results from a spread in recombination rates for the bipolarons, and that this must arise from a distribution of excitation state energies and environments within the sample. The lack of a well-defined decay time supports the idea that extrinsic effects may play a role in stabilizing the bipolaron excitation. This is discussed further below.

In contrast to the behavior seen for the bipolaron transition at 0.68 eV, the transition at 1.35 eV shows the essential features of a monomolecular decay. The signal in Fig. 10(b) has a clear ω^{-1} dependence for frequencies above ≈400 Hz. Below this there is a much weaker dependence with the signal approaching a constant value for the lowest frequencies. The crossover at 400 Hz corresponds to an excited-state lifetime of $\tau \approx 2.5$ ms for the triplet exciton at 80 K.

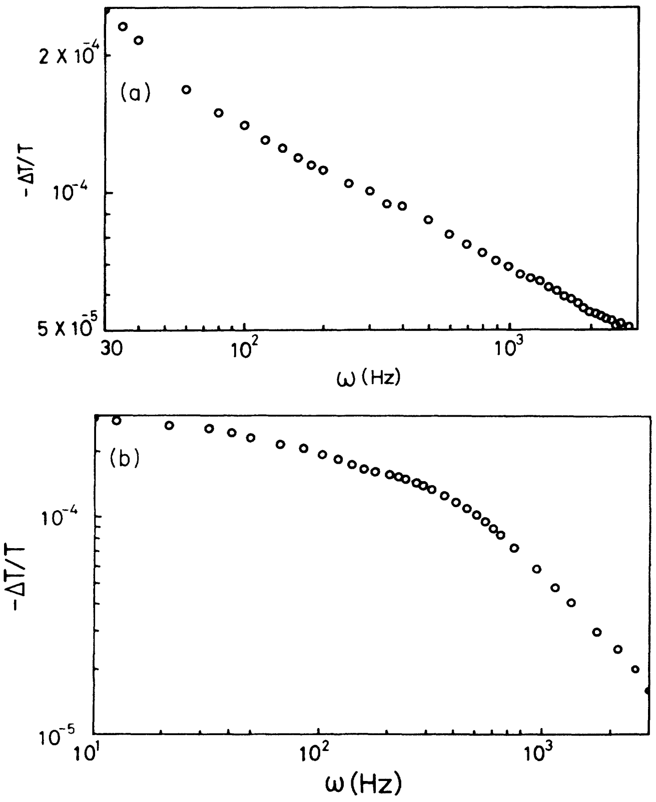

FIG. 10. Chop-frequency dependence of photoinduced absorption features at (a) 0.68 eV and (b) 1.35 eV for 457.9-nm excitation at 80 K.

IV. DISCUSSION

A. Singlet excitons

In conjugated polymers it is useful to distinguish between those excited states that result from excitation on a single chain, and those that result from separation of charge between chains.[6] In the case of intrachain excitation the generation of singlet excitons is likely to be the predominant result, and if these decay radiatively, they are responsible for the photoluminescence seen in Fig. 3. The probability of intrachain charge separation in the absence of external perturbations (applied electric fields, defects, etc.) is expected to be low since both the Coulomb interaction and any electron-lattice coupling will act to bind the electron-hole pair; indeed, the equilibrium configuration for the electron-hole pair is described by the polaron exciton.[19]

Experimentally, photoluminescence from singlet exciton radiative decay is commonly found to be very weak in conjugated polymers, and perhaps for that reason, has tended to be widely disregarded. However, a low quantum yield for photoluminescence can be due to rapid nonradiative decay channels which run faster than the radiative decay (which from the strength of the π-π^* absorption band is expected to have a lifetime of about 1 nsec) rather than due to an excited-state branching ratio that inhibits exciton formation. We have previously suggested[6,20,21] that nonradiative decay mechanisms of several types can be effective in conjugated polymers, including:

(i) Multiphonon emission: this is predicted to have an inverse exponential dependence upon the π-π^* energy gap and has been proposed as an explanation of the general trend in the conjugated polymers of a decreasing luminescence yield with decreasing energy gap. There are, however, difficulties with this simple picture in that polymers such as blue-phase polydiacetylenes [e.g., poly(5,7-dodecadiyn-1,12-diol-bis(3-butoxycarboxyl methylurethane) (PDA-3BCMU)] can show essentially no luminescence despite the large energy gaps (3.1 eV for PDA-3BCMU) and the presence of clear exciton signatures in their absorption spectra. This has recently been explained in terms of efficient nonradiative decay through rapid tunneling from a configurationally relaxed excited state (in this case a self-trapped exciton) potential-energy surface to the ground-state potential surface.[22] We emphasise that other factors, such as quenching through interaction with charge carriers (see below), are also important in this regard.

(ii) Bimolecular fusion: there is good evidence from studies on PPV that at high excitation densities[20] singlet-singlet collisions lead to a rapid decay of the luminescence emission. Such collisional annihilation is expected to be facilitated by extended conjugation since it requires that excitons have a high chance of meeting during their lifetime (already shortened by other nonradiative decay processes), and this is borne out by experiment.

(iii) Singlet-to-triplet conversion: in the presence of electron-electron correlations the first triplet excited state is expected to lie at lower energy than the first singlet state, such that singlet-to-triplet conversion should be favored. Crossing from the singlet to the triplet configuration can arise in several ways, with direct intersystem crossing the simplest. Higher-lying singlet fission is also possible, as is charge separation (exciton ionization), followed by loss of spin memory and subsequent recombination in the triplet configuration. The formation of triplet excited states is well documented in many molecular systems and is clearly seen for polydiacetylenes.[23,24] We argue below, as we have previously done for PPV,[7] that triplet states are readily formed in PDMeOPV.

(iv) Quenching at nonradiative recombination sites: migration of the excitons to quenching sites is another important mechanism. These sites could in principle take several forms but there is strong evidence that, in particular, charged polarons and bipolarons can strongly enhance nonradiative decay. Thus doping,[25] photoexcitation,[11] and carrier injection[3] have all been shown to lead to strong photoluminescence quenching. Our proposed mechanism is that the self-localized states act as local regions of reduced potential giving a large cross section for exciton capture. The annihilation then occurs because the interaction between the exciton and polaronic state splits their energy levels and allows more efficient nonradiative decay by multiphonon emission. Bipolarons are expected to be especially effective in this respect due to their deep-lying energy levels. Note that neither bipolarons nor polarons will be consumed in the annihilation process (see Fig. 11); they only act as a "catalyst" for the nonradiative decay. The presence of such polaronic states is expected as a consequence of unintentional doping which can occur for many conjugated polymers due to residual catalyst, oxidative coupling agents, electrochemical counterions, etc., left over from the synthesis procedure. These are often very difficult to remove fully and can cause significant levels of doping. For poly(arylene vinylene) polymers the precursor route synthesis greatly reduces the number of sources for unintentional doping. Nevertheless, doping by atmospheric oxygen during handling of the conjugated product is still possible and is proposed to be largely responsible for the conductivities of $\approx 10^{-10}$ Scm^{-1} and $\approx 10^{-9}$ Scm^{-1} found for as-prepared PDMeOPV (Ref. 26) and PTV,[27] respectively. Thermal annealing in vacuo reduces these values to $\approx 10^{-15}$ Scm^{-1} and $\approx 10^{-11}$ Scm^{-1}, respectively,[26,27] and upon compensation with ammonia a further reduction to $\approx 10^{-15}$ Scm^{-1} is achieved for PTV.[27] The conductivity of as-prepared PDMeOPV is lower than that of PTV, but that of PPV,[28] at 10^{-12} Scm^{-1}, is smaller than both. This variation is in agreement with the expectation that unintentional doping becomes more serious as the π-π^* gap (and ionization potential) decreases. Unintentional doping would thus provide a strong extrinsic contribution to the decrease in photoluminescence yield with decreasing π-π^* gap, complimentary to the (intrinsic) multiphonon emission process discussed in (i) above. This process, just like bimolecular annihilation [see (ii) above], is expected to be facilitated by extended conjugation since it also requires that excitons are sufficiently mobile that they have a high chance of meeting a polaron or bipolaron before radiative decay can occur.

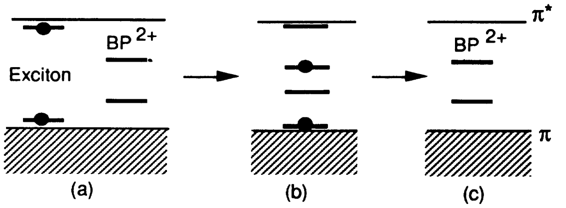

FIG. 11. Schematic representation of the annihilation of an exciton by interaction with a bipolaron (shown for the case of a positive bipolaron). The interaction (a) leads to a splitting of the levels (b) which facilitates rapid nonradiative decay. Following loss of excess energy of the lattice, the bipolaron is regenerated (c). The filled circles represent single electrons in the corresponding energy levels.

Direct confirmation of the role of nonradiative recombination can be obtained from measurements of the photoluminescence decay. Measurements have been performed for PPV with high-intensity uv excitation and show decay rates consistent with a quantum yield of $\approx 8\%$ and with bimolecular kinetics at high excitation density.[20,21] More recent measurements with low-intensity pulses show decays consistent with a quantum yield of $\approx 25\%$ at room temperature. No measurements of decay kinetics have been reported yet for PDMeOPV, but we estimate that the photoluminescence yield is less than for PPV. This is still readily detectable, unlike the case of PTV where there is almost no photoluminescence.[8]

The spectra shown in Fig. 3 for the photoluminescence of PDMeOPV are similar in form to those of PPV and are characteristic of the spectra seen for many organic molecular materials. In particular, the structured emission with a series of peaks spaced by typical vibrational energies is a strong indication of the importance of electron-phonon coupling. The separations between the peaks should be characteristic of the energies of vibrational modes with which coupling occurs in the electronic ground state; the transitions observed in photoluminescence emission are those between the lowest vibrational level of the electronically excited state and the various possible vibrational levels of the electronic ground state. The observed separations of 0.15 eV at room temperature and 0.18 eV at 80 K do not, however, exactly match the directly measured energies of the Raman-active vibrational modes, the strongest three of which have energies of 0.196 (1582 cm^{-1}), 0.162 (1306 cm^{-1}), and 0.159 eV (1284 cm^{-1}). Moreover, the relatively large increase of 0.03 eV in peak separation seen in the emission spectra on cooling from room temperature to 80 K is not matched in the Raman spectra by any significant shifts of vibrational energies. This suggests that the peaks in the emission spectra do not arise from coupling to a single vibrational mode but contain contributions from several different modes; we note that photoluminescence spectra recently reported[29,30] for PPV at low temperature do show a splitting of the 0-n lines for $n \geq 1$, clearly indicating the involvement of more than one vibrational mode. The emission peaks are also likely to be further broadened by the presence of a distribution of electronic energy origins for the 0-n transitions, corresponding to the distribution of site energies arising from conformational disorder.

The observation of much better resolved structure in the emission spectrum than is seen in the absorption spectrum requires that spectral diffusion occurs following photoexcitation, but prior to emission. Spectral diffusion involves exciton migration through the polymer with the excitons descending the potential gradient associated with the inhomogeneous distribution of conjugated chain segment energies; low-energy sites are associated with chains that have high degrees of conjugation. Strong evidence for spectral diffusion in PPV comes from the invariance of the emission spectrum for all excitation energies above a threshold that lies close to the onset of the π-π^* absorption edge.[29] The threshold comes at the point where the density of sites to which migration is favored (i.e., those with lower energy) becomes sufficient that radiative decay no longer occurs predominantly from the same site as that at which the exciton was formed. Experimental determination of the degree of self-localization of the exciton in terms of a Stokes shift due to electron-lattice interaction is thus not entirely unambiguous, and we consider that it is important to carry out site-selective measurements with excitation in the vicinity of the onset of π-π^* absorption.

B. Triplet excitons

In addition to the formation of singlet excitons there is also the possibility for generation of triplet excitons. There is comparatively little known about the photoexcitation mechanisms for their generation in conjugated polymers. However, by analogy with molecular semiconductors we can expect that this is a relatively frequent process, arising from spin-orbit interactions which change the spin multiplicity of the excited state and effect a nonradiative intersystem crossing to the triplet manifold, or from fission of a higher-lying singlet excited state. Although the resulting triplet excited state can radiatively decay to any available lower-lying triplet level, subsequent radiative relaxation to the singlet ground state is dipole forbidden. Consequently, the generation of triplet states usually leads in molecular materials to long-lived phosphorescence rather than dipole-allowed fluorescence.

The relative energies of the phosphorescence and fluorescence emissions can provide a probe of the influence of electron-electron interactions in conjugated polymers. The amount by which the lowest triplet state is lowered relative to the lowest singlet excitation is a direct measure of the interaction strength. For both PPV and PDMeOPV, unfortunately, we do not see any evidence for phosphorescence and hence we are unable to address this important question. The absence of phosphorescence suggests strongly that the dominant mechanism of triplet relaxation is nonradiative, as for example, is also the case for trans-stilbene.[31]

We consider that the photoinduced absorption at 1.35 eV arises from the dipole-allowed excitation of the lowest lying triplet to a higher energy triplet state. Its assignment to a transition involving a neutral excitation is strongly suggested by the fact that there is no analogous feature observed as a result of charge-transfer doping (the other features are seen in both photoinduced and doping-induced spectra). The photoinduced absorption appearing at 1.35 eV in PDMeOPV also shows very similar characteristics in terms of relative position within the π-π^* gap, spectral profile, temperature dependence, and lifetime to the 1.45-eV feature in PPV, previously assigned[7] [on the basis of light-induced electron-spin resonance (ESR) measurements] to a triplet-triplet transition. Optically detected magnetic resonance (ODMR) measurements have not been undertaken on PDMeOPV to confirm this assignment but we note that ODMR measurements, with detection of photoluminescence, on very closely related poly(2,5-dialkoxy-*p*-phenylene vinylene)s with larger alkoxy substituents (hexoxy and octoxy) have been recently reported.[17,32] These clearly show that there is a triplet contribution to the photoluminescence emission, as also seen in poly(3-hexyl thienylene).[32] Measurements of ODMR with detection of photoinduced absorption have also been recently reported[18] for the same poly(2,5-dialkoxy-*p*-phenylene vinylene)s i.e., hexoxy and octoxy. These show a very clear distinction in terms of spin multiplicity between the two sets of photoinduced absorption signals that are detected. The single peak (analogous to the 1.35-eV peak reported here for PDMeOPV) seen at 1.36 eV in poly(2,5-dioctoxy-*p*-phenylene vinylene) appears on its own in the triplet ($S=1$) spin-dependent experiment whereas the pair of correlated peaks (analogous to the 0.68- and 1.8-eV peaks reported here for PDMeOPV) seen at 0.35 and 1.3 eV in poly(2,5-dioctoxy-*p*-phenylene vinylene) appear on their own in the doublet ($S=\frac{1}{2}$) experiment. These ODMR results[18] are in direct agreement with and support the assignments given here for the photoinduced absorption in PDMeOPV and confirm the assignments given previously for the photoinduced absorption in PPV.[7]

C. Charged photoexcitations

Assignment of photoinduced electronic absorption features to the presence of charged excitations is most directly supported by the simultaneous observation of photoinduced infrared-active vibrational modes that correlate in their dependence upon the experimental parameters (temperature, chop frequency, intensity, etc.) with the features in question. The latter arise from the activation of symmetric modes, normally only Raman active, in the presence of the added charge.[33] We are, however, not set up to undertake photoinduced absorption in this region of the infrared and hence do not have this direct confirmation of the generation of charged excitations. We note, however, that measurements undertaken elsewhere[34] do clearly show new infrared-active vibrational modes following optical excitation and that these are very similar to those previously observed for PPV.[34] Correlation with specific features in the electronic part of the photoinduced absorption spectrum has not yet been made for PDMeOPV, but in PPV the induced infrared vibrational modes were shown[35] to be associated with the two transitions at 0.6 and 1.6 eV that are assigned to bipolarons. Additional strong support for photogeneration of charged excitations in PDMeOPV comes from comparison of the photoinduced absorption with doping-induced absorption spectra for the same polymer.[36] There is a very close correspondence between the $FeCl_3^-$ or SbF_6^- doping-induced absorption peaks at ≈ 0.70 and ≈ 1.75 eV,[36] and the two peaks at 0.68 and 1.8 eV reported here for photoexcitation (see Fig. 7).

Accepting that charge carriers are indeed photogenerated, we must consider in what form they are present within the polymer. In PDMeOPV the lack of a degenerate ground state is expected to preclude the formation of charged solitons and instead, either singly charged polarons or doubly charged bipolarons should occur.[37,38] Light-induced electron-spin resonance (LESR) measurements can in principle differentiate between the spin-one-half polaron excitations and spin-zero bipolarons.[37,38] However, this is not a straightforward measurement and there are serious experimental difficulties in eliminating thermal modulation of the background spin signal through optical pumping. The evidence from the most thoroughly conducted experiments on polyactylene[39] and on polythienylene[16] is, however, that the charged photoexcitations are spinless. Measurements of ODMR with detection of photoinduced absorption can also be used and have the advantage of a direct association with the photoinduced absorption under consideration. Recently reported experiments[18] for poly(2,5-dihexoxy-*p*-phenylene vinylene) and poly(2,5-dioctoxy-*p*-phenylene vinylene) support the conclusion that bipolarons are the dominant long-lived charged photoexcitations in nondegenerate ground-state polymers.

An additional method to distinguish between polarons and bipolarons, namely through the number and relative energy (in comparison with the π-π^* gap energy $=2\Delta$) of the photoinduced absorption peaks.[19] For polarons, the two intragap levels are predicted by the Fesser, Bishop, and Campbell (FBC) (Ref. 19) model to lie close to the highest occupied π and lowest unoccupied π^* energies; a ratio $\omega/\Delta \geq 1/\sqrt{2}$ is expected where ω is half the energy separation between the two levels. In addition, three allowed optical transitions involving these levels should occur. For bipolarons, however, the expectation is that the two intragap levels will lie much deeper within the π-π^* gap. Moreover, due to the different occupancy of the intragap levels (i.e., both fully occupied or empty) there will be only two allowed optical transitions. In the case of PDMeOPV we observe three photoinduced features but only two of these, namely those at 0.68 and 1.8 eV, can be identified as arising from the same excited state, again in agreement with an assignment to bipolarons. A very similar situation occurs for PPV (Ref. 7) and bipolaron transitions have also been identified as a result of photoexcitation in PTV (Ref. 8) and for many other nondegenerate ground-state polymers.[10,24,40]

Analysis of the positions of the gap states within the framework of the FBC model then requires that these excitations are strongly self-localized,[8] and are thus likely to be prevented from moving between chains except by thermally activated processes, and in this way will be long lived. Singly charged polarons are expected to be less strongly localized, and may thus be able to move three dimensionaly through the lattice. The model for the formation of the doubly charged excitations by an intrinsic mechanism is thus a two-step process.[6] The first step is that of photogeneration of electron and hole pairs which separate to different chains, and which relax to form singly charged polarons, but which will still be able to move through the lattice. The second step is the self-trapping of these charged excitations by the coalescence of pairs of like charges to form bipolarons; it is the much stronger degree of self-localization of the bipolarons that results in strong confinement to the polymer chain and very slow interchain motion and eventual decay to the ground state.

This model for the photogeneration of intrinsic metastable bipolarons is appealing, but it is not obvious that it is correct. These excitations are present at rather low concentrations (typically 10^{18} cm^{-3}) and it is hard to discount the role of extrinsic stabilization through the presence of chain defects of either chemical (present in concentrations below the detection limit for techniques such as infrared spectroscopy) or conformational nature. A difficulty with the intrinsic bipolaron model is that at the low concentration of charges present under the usual conditions for these experiments, we expect that even if there is a substantial binding energy for the formation of the bipolaran, the extra configurational entropy achieved by dissociation to form a pair of polarons will give a larger contribution to the free energy except at very low temperatures. The formation of a bipolaron from two polarons is calculated in single electron theories[41,42] to be energetically favored by ≈ 0.4 eV, but this stabilization energy will be lessened in practice by the Coulomb repulsion between the two charges bound in the same state and it is then not at all obvious that the bipolaron will be intrinsically stable. Optical spectroscopy of the charge accumulation layer in metal-insulator-semiconductor MIS device fabricated with poly(3-alkyl thienylene) shows clearly the presence of singly charged polarons in thermodynamic equilibrium at room temperature.[3] In the context of the transient photoexcitations, the system is of course not in thermal equilibrium, but the problem is to justify why the capture cross section for polaron-polaron interaction to form the bipolaron should be sufficiently large to account for the number of bipolarons created. A further difficulty is that both the polaron and also the singlet exciton (or polaron exciton) are found from analysis within the framework of the FBC model to the rather weakly self-localized, as indeed is expected from the strength of the electron-phonon coupling, and it is not then easy to reconcile the apparently much stronger electron-phonon coupling operating for the bipolaron.[7,8,10] As pointed out recently,[41] however, there are difficulties with the FBC model when generalized to nondegenerate ground-state polymers, and direct calculations at the one-electron level for PPV suggest that the electron-phonon coupling required to explain the observed displacement of the bipolaron levels into the π-π^* gap is in fact much smaller than that derived from the FBC model analysis. A problem still remains, however, in that all one-electron theories are unable to explain the experimentally observed[6,7] difference in the positions of the energy levels for the neutral exciton and doubly charged bipolaron. As we have previously pointed out,[6–8] this requires consideration of the interaction between the two charges present in these excited states.

In relation to the possible effect of extrinsic stabilization of bipolarons we note that the photoexcitations produced in PDMeOPV are found to be significantly longer lived than those found, for example, in both PPV (Ref. 7) and PTV.[8] The distribution in their lifetimes is seen to extend beyond the low frequency (≈ 10 Hz) limit of the experiments performed here, as is clearly evident in Fig. 9. The origin of this long-time stabilization and of the broad distribution in lifetimes is not yet confirmed, but we consider that a distribution of excitation site energies and environments is required and that it is the extensive disorder found in these PDMeOPV samples (already discussed above) that is responsible for the wide range of lifetimes detected. The enhanced stability may also be a manifestation of the mesomeric effect of the methoxy substituent oxygen lone pair which could act to stabilize positive charges on the polymer backbone. In this context we note that the addition of methoxy substituents to oligomeric analogues of PPV and PDMeOPV has been shown to stabilize their oxidative doping-induced charged excitations.[43]

V. SUMMARY AND CONCLUSION

In summary, in this paper we have presented results for photoinduced absorption and photoluminescence in the conjugated polymer PDMeOPV. At 80 K we find three photoinduced absorptions in the range 0.5–2 eV, of which two, at 0.68 and 1.8 eV, are correlated while the third, that at 1.35 eV, arises from a distinct excitation. The 0.68- and 1.8-eV absorptions are assigned to charged bipolarons and the 1.35 eV absorption to a triplet-triplet transition. Of particular interest is that the 0.68- and 1.8-eV features are very long lived and can survive even at room temperature, a fact that we believe is due in part to the strong conformational disorder in the PDMeOPV samples studied here. This disorder, even though sufficient to smear out the π-π^* absorption band, does not, however, prevent the observation of a structured photoluminescence emission. The latter behavior is a clear indication of the importance of exciton migration, with emission occurring only after the exciton has reached relatively well-ordered regions of the sample. Such spectral diffusion gives rise to an apparent Stokes shift of the emission relative to the absorption spectrum that is additional to any shift occurring through self-localization and makes detailed analysis of the latter difficult in the absence of site-selective studies.

Note added in proof. Recent calculations of the electronic structure of PDMeOPV [F. Meyers, J. L. Brédas, and A. J. Heeger (unpublished)] show that the reduction in the energy gap relative to PPV is predominantly due to destabilization of the highest occupied molecular orbital. This is consistent with methoxy substituent stabilization of positive charges as discussed above.

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