Photoexcited states in poly(*p*-phenylene vinylene): Comparison with *trans, trans*-distyrylbenzene, a model oligomer

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We present measurements of the photoexcited states of poly(*p*-phenylene vinylene), PPV, and a model oligomer, *trans, trans*-distyrylbenzene, probed by detection of photoluminescence and photoinduced absorption. Photoluminescence is strong in both materials and due to radiative recombination of the singlet exciton. Triplet excitons are also photogenerated, and in the case of the oligomer are seen directly in light-induced ESR measurements. We find a signal with a peak-to-peak width of 12 G at 1580 G for a probe frequency of 9.14 GHz. We assign this to the "forbidden" $\Delta m_s = 2$ transition between the triplet sublevels. From the position of the minimum field $H_{\min}$ for this microwave transition, we determine the zero-field splitting of the triplet sublevels to be 0.07 cm^{-1}. We find an associated photoinduced absorption at 1.95 eV in the oligomer which we attribute to a triplet-triplet transition of the excited state. For the polymer we find a photoinduced absorption response at 1.45 eV, very similar to that of the oligomer, and we consider that this is similarly due to a triplet exciton, although we have not been able yet to find direct ESR evidence. In the case of the polymer, charged photoexcitations are also seen in photoinduced absorption measurements, characteristic of bipolarons, with induced absorption at 0.6 and 1.6 eV. We do not find similar excitations in the oligomer, and we consider that intermolecular charge transport is necessary for the generation of the long-lived charged excitations probed in our experiments.

I. INTRODUCTION

The electronic excitations of conjugated polymers are modeled through the electron-lattice interaction to exhibit self-localization to form polaronlike states.[1,2] Though much of the interest in this field has been directed to the charged excitations of the polymer (polarons and bipolarons), these materials also support the metastable neutral excitations typically observed in organic molecular solids.[3] The experimental investigation of these neutral excited states has been commonly ignored because many of the conjugated polymers that have been synthesized are prepared in an oxidized (and, therefore, conducting) form, and show very low quantum yields for photoluminescence which provide the standard measure of the properties of singlet excitons. An important exception is the family of poly(arylene vinylenes), which can be prepared via a sulphonium polyelectrolyte precursor polymer. For the case of poly(*p*-phenylene vinylene) (PPV), thin films of good optical quality can be conveniently prepared with very low concentrations of charge and spin defects.[4–9] The scheme for synthesis of this polymer is shown in Fig. 1. We have carried out several investigations of the optical excitations of this polymer,[10–14] and we have suggested that, in addition to charged states, both singlet and triplet excitons are generated by photoexcitation. We distinguish between intrachain photoexcitation, for which we expect to see the formation of neutral excited states, or excitons, and photoexcitation, which results in the separation of charge between chains and leads to the creation of metastable charged photoexcitations.

In this paper we present further measurements of PPV (principally, of photoinduced absorption) that give information about the long-lived charged photoexcitations, which we consider to be bipolarons, and that also show a quite different feature, at 1.45 eV, which we consider to be due to a triple-triplet transition of a triplet exciton. In addition, we present similar measurements on a model oligomer of PPV, *trans, trans*-1,4-distyrylbenzene (*t,t*-DSB), the structure of which is shown in Fig. 2. We find that triplet excitons can also be generated in this model oligomer, though we find no evidence for formation of charged photoexcitations in the oligomer, reflecting, we consider, the difficulty in producing intermolecular charge separation in the smaller molecule. Comparison of the results for the oligomer and the polymer does provide a useful insight into the properties of the polymer, and single-photon absorption experiments on oligomers of poly(*p*-phenylene vinylene) have already been used to interpret the optical-absorption spectrum of the polymer.[15]

The excitation energy of triplet states in conjugated molecules provides information about the strength of

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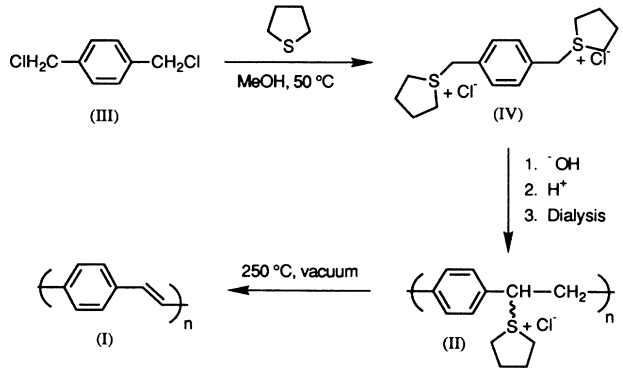

FIG. 1. Synthesis of PPV (I) via a sulphonium polyelectrolyte precursor (II). The starting material (III) is reacted with a suitable alkyl sulphide to form the precursor monomer (IV). The latter is polymerized in the presence of base (typically NaOH) to produce the precursor polymer (the reaction being quenched by addition of acid), which is purified by dialysis prior to sample fabrication. Conversion to the conjugated PPV is effected by thermal treatment *in vacuo*. The synthesis shown is with tetrahydrothiophene (THT) as the alkyl sulphide; dimethyl sulfide (DMS) is also used. Tetrahydrothiophene is the preferred choice, giving easier elimination and conversion from precursor polymer to PPV.

electron-electron interactions, as it is this interaction which breaks the degeneracy between the lowest triplet (T_1) and lowest singlet (S_1) excited states. There remains considerable theoretical uncertainty about the role that these interactions play in the electronic structure of the ground and excited states of conjugated polymers.[16,17] In the particular case of the polyenes, however, it is clear that electron-electron interactions strongly influence the ordering of electronic levels.[18] Hence the identification and characterization of the triplet excited states in conjugated polymers and their oligomers are of fundamental interest. Since triplet excitons are usually long lived, the triplet excited states of small conjugated molecules are readily studied by pump-probe spectroscopic techniques. For example, both flash photolysis and pulse radiolysis have been used to investigate triplet excited states in polyenes,[19] although no analogous state has yet been identified in polyacetylene. By contrast, a long-lived (milliseconds) transient species, which may be a triplet state, has been observed in photoinduced absorption experiments on PPV.[13] In addition, the lowest triplet state of its shortest oligomeric analog, *trans*-stilbene, has been identified and characterized through its transient absorption[20] and associated electron spin-resonance (ESR) signal.[21] Both the ESR and spectroscopic measurements indicate that the nonradiative lifetime of the triplet is of the order of milliseconds at 77 K. Our measurements here are of *t,t*-DSB, a slightly longer oligomeric analog of PPV, and we have carried out both optical and ESR measurements which give information about the triplet exciton. Fluorescence and optical absorption in solution of this oligomer, in both the *cis-trans* and *trans-trans* isomers, have previously been studied by several groups.[22–24]

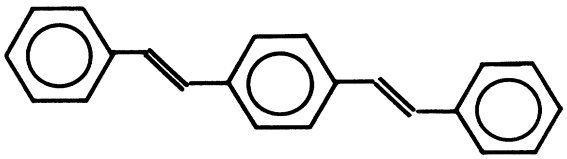

FIG. 2. Chemical structure of *trans,trans*-1,4-distyrylbenzene.

II. EXPERIMENTAL DETAILS

We prepared PPV (I) via a solution processible precursor polymer, in the form of a sulphonium polyelectrolyte (II), according to the scheme shown in Fig. 1. We have used materials prepared with both dimethyl sulphonium[4–9] and tetrahydrothiophenium[25] sulphonium groups, and have found, as reported elsewhere,[26] that the tetrahydrothiophenium material produces PPV with a better degree of conjugation. This is considered to be due to unwanted side reactions, such as the formation of methyl mercaptan groups in place of the dimethyl sulphonium group with the dimethyl sulphonium precursor. Results discussed here are for samples prepared via both routes.

The soluble precursor polymer was used to prepare the thin films necessary for optical work. Films up to a few hundred nanometers thick were deposited onto wide-field spectrosil or potassium bromide substrates from methanol solution by spin coating. These films were then converted to fully dense PPV by heating them (above 300 °C for the sulphonium salt, or above 200 °C for the tetrahydrothiophenium salt) under dynamic vacuum ($\sim 10^{-6}$ torr) for several hours. The conversion was confirmed by checking for the loss of the characteristic vibrations of the saturated precursor groups in the infrared-absorption spectra of the films.

We prepared *t,t*-DSB by the standard Wittig condensation of tributylphosphonium bromide and terephthalaldehyde in dimethyl formamide or ethanol, using sodium ethoxide as the base.[27] The reaction product was purified by recrystallization. For ESR measurements, the resulting yellow polycrystalline flakes were used as-prepared in quartz ESR tubes. For the preparation of samples for optical measurements, a dilute solution ($\sim 10^{-6}$ M) of *t,t*-DSB in dichloromethane was mixed with dry potassium bromide. The solvent was then removed by evaporation, and the resulting mixture of KBr and *t,t*-DSB was pressed into a pellet of suitable optical density.

For the optical measurements, samples were mounted in an Oxford Instruments CF 204 optical access helium-flow cryostat. Sample temperature was monitored with a silicon-diode sensor mounted next to the sample in the cryostat. To probe spectrally resolved optical absorption,

light from a tungsten halogen lamp was passed through the sample, subsequently dispersed with a Spex Minimate monochromator, and detected with a photomultiplier tube or appropriate solid-state detector. Standard light-chopping and phase-sensitive detection methods were used.

For both the photoluminescence and transient absorption measurements, photoexcitation was provided in the uv by two lasers. The first was a cw argon-ion laser, lasing all lines in the ultraviolet, with emission at 363.8 nm, 351.1 nm, and a trio of lines centered near 335 nm. For measurement of the photoinduced change in sample absorption, the laser light was chopped at frequencies between 10 and 3500 Hz, and the detector signal passed to an EG&G 5208 lock-in amplifier referenced to the chopper frequency. The second uv source was provided by the tripled output of a Q-switched neodymium-doped yttrium aluminum garnet (Nd:YAG) laser, at 355 nm, with a repetition rate of 10 Hz, and signal detection was either performed by integration over the repetition rate of the laser with the lock-in amplifier or by direct measurement of the output of a photomultiplier tube with a digital oscilloscope.

Electron spin-resonance measurements were performed with a Varian E109-E ESR spectrometer, operating at a frequency of 9.14 GHz. For low-temperature measurements, the spectrometer was fitted with a system for flowing cold nitrogen gas through the microwave cavity. In this case, photoexcitation was provided by a 150-W xenon arc lamp, which illuminated the sample through an optical access in the cavity. Quartz focusing optics were used, and the entire apparatus was checked with an empty sample tube for spurious signals.

III. RESULTS

A. Absorption and photoluminescence

The absorption and photoluminescence of a fully converted sample of PPV (prepared via the tetrahydrothiophenium salt precursor route) are shown in Fig. 3. The onset of π-π^* interband transitions is seen at about 2.4 eV, with the peak a little below 3 eV. There is clear evidence for vibronic structure in the absorption edge, and this has been seen more clearly at low temperatures.[26] Photoluminescence is quite strong, with a quantum yield of several percent,[11] and there is again clear evidence of vibronic structure, with the zero-phonon transition at 2.37 eV. For PPV prepared via the dimethyl sulphonium salt precursor route, the absorption and photoluminescence are slightly blue shifted relative to those in Fig. 3, but are otherwise qualitatively the same.[25]

The optical absorption of a suspension of t,t-DSB in KBr is shown in Fig. 4. The principal absorption edge is at about 3 eV, some 0.2 eV lower than reported for t,t-DSB in solution.[23,28] This absorption red shift may indicate that the molecular conformation in the solid is more planar than that in solution. A more planar conformation allows greater π-electron delocalization in individual molecules, and a corresponding decrease in the π-π^* transition energy. Figure 4 also shows the sample photoluminescence at room temperature, with ultraviolet laser irradiation. Apart from a red shift corresponding to that of the absorption edge, these data are the same as the photoluminescence reported for t,t-DSB in solution.[23,28] We also note that the uv-visible absorption spectrum of t,t-DSB resembles that of a partially converted sample of

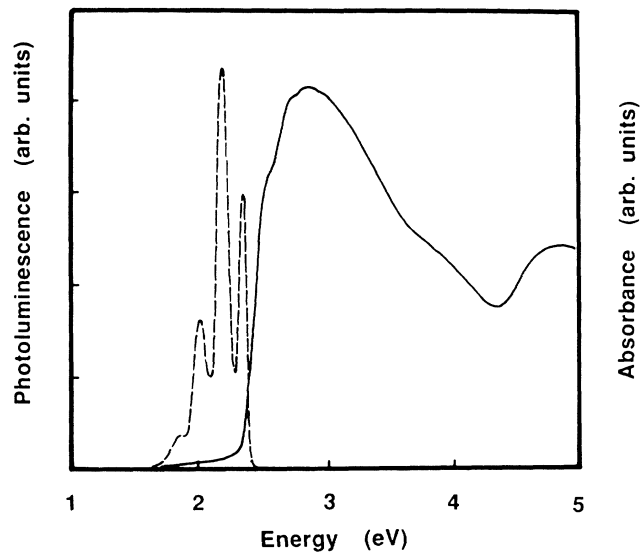

FIG. 3. Room-temperature optical-absorption and low-temperature (80 K) photoluminescence spectrum of a thin film of PPV on a spectrosil substrate. The PPV for these measurements was prepared with the THT precursor.

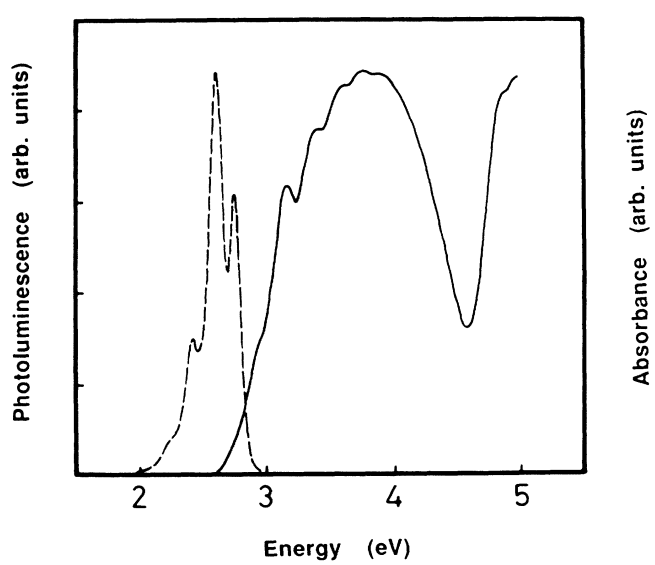

FIG. 4. Room-temperature optical-absorption and photoluminescence spectra of a solid suspension of t,t-DSB in KBr.

PPV when prepared by thermal conversion from the dimethyl sulphonium polyelectrolyte precursor polymer.[5] This is to be expected, as the partially converted polymer is a copolymer of short conjugated oligomers with nonconjugated precursor sequences.

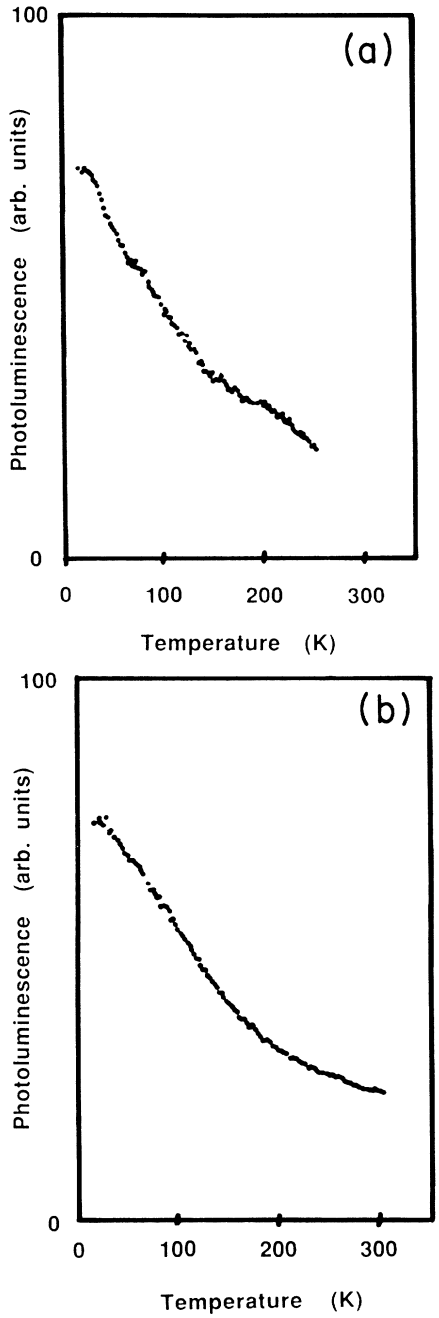

FIG. 5. Temperature dependence of the photoluminescence of (a) t,t-DSB and (b) PPV. Excitation for the data in (a) was provided by 100 mW/cm^2 of ultraviolet laser radiation, chopped at 87 Hz. The data in (b) were collected during photoexcitation with 5-mJ pulses from a Q-switched Nd:YAG laser, repeating at 10 Hz. The two sets of data have been suitably scaled to facilitate ready comparison of their temperature dependences. The PPV for these measurements was prepared from the DMS precursor.

Relative to the absorption edge in t,t-DSB, that of PPV is red shifted to $\sim$2.4 eV as a result of the greater π-electron delocalization in the longer conjugated segments of the polymer. Similarly, a shift is observed in the photoluminescence of the polymer, for which the zero-phonon transition is at 2.37 eV, as compared with 2.70 eV for the analogous transition in the oligomer. The photoluminescence behavior for the two materials also shows very similar temperature dependences, as is seen in Figs. 5(a) and 5(b). Both show a steady fall in luminescence output as temperature is raised, particularly on the range up to about 120 K.

B. Photoinduced absorption

Photoinduced absorption provides a very sensitive means for the detection of transient excited states, particularly those that have excitations that lie within the semiconductor gap. The measured response is sensitive to the concentration of the excited states averaged over the integration time of the experiment. For the experiments that we have carried out here, with chopping of the pump beam in the frequency range of 10–3500 Hz, we are only able to detect metastable states that have lifetimes of between a few tens of microseconds and a few tens of milliseconds; lifetimes longer or shorter than these limits do not give measurable signals. Within the context of conjugated polymers, we expect to be able to detect, therefore, the relatively long-lived charged excitations, which are generally found to be bipolarons,[10,29,30] and the low-lying triplet-triplet transitions for triplet excitons, as have been found in the case of the polydiacetylenes.[31]

The photogeneration of charged excitations has been extensively studied for a number of polymers, including PPV,[10,12,13] and the related poly(2,5-thienylene vinylene).[29] We have argued previously that the formation of long-lived excitations requires a two-step mechanism. The first step is that of the photogeneration of electron and hole pairs, separated between chains, which are expected to relax to form singly charged polarons, but which will still be able to move three-dimensionally through the lattice. The second step is the self-trapping of these charged excitations by coalescence of pairs of like charges to form bipolarons (oppositely charged excitations will, of course, annihilate); it is the much stronger degree of self-localization of the bipolarons[1] that results in strong confinement to the polymer chain and very slow interchain motion with eventual decay to the ground state. [An alternative proposal for the stabilization of long-lived excitations in polyacetylene involves ionization of neutral spin-$\frac{1}{2}$ defects, which are known to be present in *trans*-polyacetylene at a suitable concentration;[32] this model is not consistent with experimental measurements for all samples of polyacetylene,[33] and is not appropriate for polymers such as PPV, for which the excitations are polarons (not solitons) and which can be prepared with very low concentrations of spin and charge defects.]

There is rather less known about the photoexcitation of triplet excitons. However, we can expect that this is a

relatively frequent process, with the spin-orbit interaction changing the spin multiplicity of the excited state, effecting a nonradiative crossover to the triplet manifold. Although the resulting triplet excited state can radiatively decay to any lower-lying triplet levels, subsequent radiative relaxation to the singlet ground state is dipole forbidden. Consequently, the generation of triplet states usually leads to long-lived phosphorescence. However, if the dominant mechanism of triplet relaxation is nonradiative, as in the case of *trans*-stilbene,[34] the phosphorescence will be very weak. The presence of photoexcited triplet states in a molecule should also lead to new optical transitions, corresponding to the dipole-allowed excitation of the lowest-lying triplet to higher triplet states. The observation of this triplet-triplet absorption at 77 K provided the first direct evidence of the photoexcited triplet in *trans*-stilbene.[20]

1. PPV

The experimental complication in measurements of photoinduced absorption in PPV is that there are, at least, three contributions to the measured signal: two associated with photoinduced absorption, and the third from photoluminescence, which is also detected at the chop frequency of the excitation source.[13,14] The photoluminescence response is fast [decay times are considerably less than 1 ns (Ref. 11)], and one of the schemes used here to remove the photoluminescence from the measured response is to chop the excitation beam at a sufficiently high frequency, so that the true photoinduced absorption response (which is very much slower) is phase shifted with respect to the excitation, and to measure the response in quadrature to the photoluminescence signal. This is very satisfactory, though it does make it more difficult to make quantitative measurements of the photoinduced absorption changes. It was found to be very useful to simultaneously record both in-phase and quadrature responses with the lock-in, so that the adjustment of the chosen phase angle could be made numerically after the data were collected.

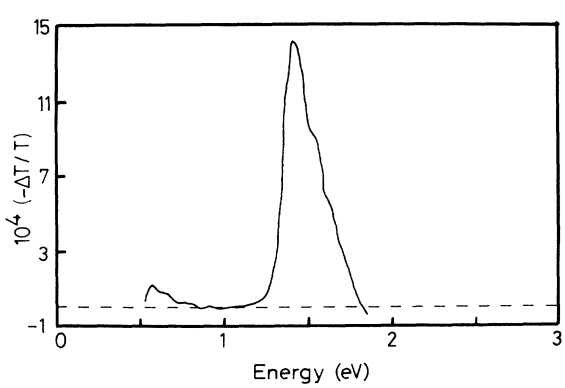

FIG. 6. Photoinduced absorption in PPV at 80 K. Excitation was provided by the uv lines from an argon-ion laser, chopped at 67 Hz, and detected with the lock-in at a phase angle of 15° lag with respect to the excitation. The PPV for these measurements was prepared from the DMS precursor.

Figure 6 shows the photoinduced absorption spectrum for a sample of PPV [prepared via the dimethyl sulphonium salt (DMS) precursor] at a temperature of 80 K with cw uv excitation chopped at 67 Hz, and detected with a phase angle of 15° with respect to the pump beam. This phase angle was chosen to maximize the strong photoinduced absorption signal seen near 1.45 eV, which (as discussed further below and also in Refs. 13 and 14) we suggest arises from a triplet-triplet transition of a triplet exciton. The signal falls below zero above 1.7 eV, and this is due to the contribution from photoluminescence, which is not rejected at this phase angle. At lower photon energies, a smaller photoinduced absorption feature is seen, peaking at 0.6 eV. We have previously associated a feature at this energy with a charged photoexcitation, and specifically identified it as the lower of the two transitions between the band edges and the two gap states of the bipolaron.[10–14] The higher-energy transition was seen at 1.6 eV and, as discussed below, is in fact also present here, but does not appear in Fig. 6 since it lies beneath the much stronger 1.45-eV feature. The assignment to a charged excitation[10,11] is on the basis of the close correlation of this and the related 1.6-eV feature, in terms of their intensity, temperature, and frequency dependence with the infrared modes that are simultaneously photoinduced. The latter are known to arise due to infrared activation of normally Raman-active vibrations in the presence of charges added to the polymer chain (Refs. 2 and 10, and references therein).

It is readily shown, through its very different recombination kinetics (see below) and temperature dependence [compare Figs. 8(a) and 8(b)], that the 1.45-eV feature arises from a different excited state to that responsible for the 0.6 and 1.6 eV peaks. Moreover, since the 1.45-eV feature shows no correlation with the photoinduced infrared modes, we assign it to result from a neutral state.

The 1.6-eV peak due to the higher-energy band- to gap-state transition of the bipolaron is, as already noted, fully covered by the much stronger 1.45-eV feature in Fig. 6. It can, however, be seen using the same data used to obtain the plot in Fig. 6, if the phase angle for detection of the photoinduced absorption is adjusted to be 90° out of phase with the excitation beam. This removes the photoluminescence and substantially, though not completely, removes the 1.45-eV feature, which has a much faster time response than the bipolaron features. The result of this procedure is shown in Fig. 7. The data above 1.2 eV have been scaled (by 20%) and shifted to correct for the residual signal due to the 1.45-eV feature. Both bipolaron transitions are clearly resolved, with the upper peaking at 1.6 eV, as noted earlier. These have previously been shown with poorer resolution for excitation with the tripled output from the *Q*-switched Nd:YAG laser.[10,12] (Note that, in these earlier measurements, the signal was gated for about 100 μs after each excitation pulse before being passed to the lock-in amplifier, and that the faster response of the 1.45-eV features was, therefore, not readily detected.) We observe here that there appears to be structure in the photoinduced absorption bands, with well-defined shoulders separated by energies in the range 70–220 meV. We consider that these

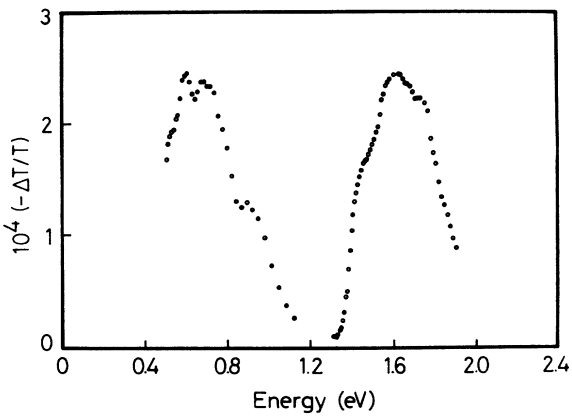

FIG. 7. Photoinduced absorption in PPV at 80 K, showing the features associated with photoinduced bipolarons. Conditions are as in Fig. 6, but with detection at a phase angle of 90° with respect to the pump beam. Some corrections for the data above 1.2 eV have been made, as discussed in the text.

may be due to vibronic excitations of the bipolaron, analogous to the vibronic structure associated with the ground state of the polymer, which are seen in the photoluminescence measurements (Fig. 3).

The frequency dependence of the photoinduced absorption due to the charged photoexcitations is shown in Fig. 8. The response here was measured at 0.52 eV, in the region of the lower of the two bipolaron bands, which is free of other contributions to the measured signal. In the case where a single monomolecular decay time τ governs the relaxation of the photoexcited states, the time-dependent density of excitations, $n(t)$ satisfies a rate equation of the form

$$\frac{dn}{dt} = -\frac{1}{\tau} n(t) + g(t) , \tag{1}$$

where the driving term $g(t)$ represents the rate at which the photoexcitations are generated. For $g(t) \propto 1 + \sin(\omega t)$, the frequency dependence of the steady-state solution of Eq. (1) is given by

$$n(t) \propto \frac{\tau[1+\sin(\omega t)]}{[1+(\omega\tau)^2]^{1/2}} . \tag{2}$$

In the low-frequency limit ($\omega\tau \ll 1$), Eq. (2) leads to an absorption signal that is independent of frequency, while, in the high-frequency limit ($\omega\tau \gg 1$), it yields a signal that decreases with increasing frequency as ω^{-1}. The measured data show clearly that the metastable excitations are rather long lived at 80 K, but that the decay kinetics do not obey a simple monomolecular decay law. Even at the lowest frequencies measured here (18 Hz), the response is still rising as the frequency is lowered, and the absence of a cutoff down to 18 Hz implies that there are states with lifetimes in excess of 60 ms. The falloff with increasing frequency is much too gentle for monomolecular behavior; the solid line shown in Fig. 8 has a gradient of $-\frac{1}{2}$ (i.e., response proportional to $\omega^{-1/2}$). We consider that this is due to a spread in recombination rates for the excitations, and that this must arise from a distribution of excitation site energies and environments.

In contrast to the behavior of the photoinduced ab-

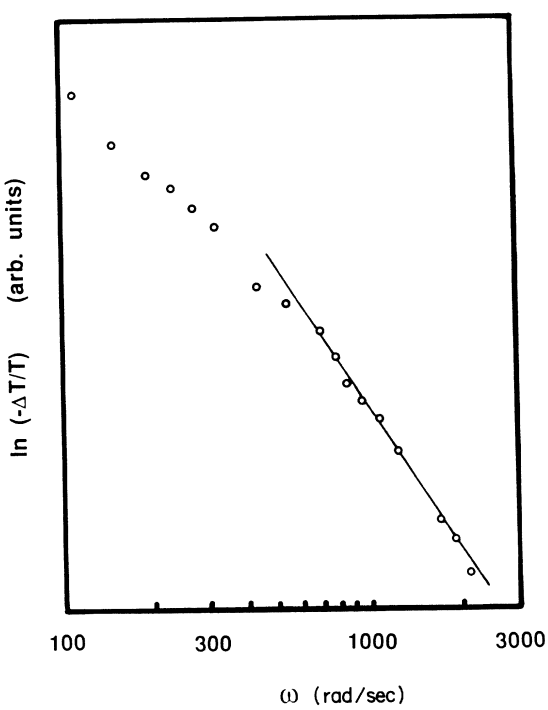

FIG. 8. Frequency dependence of the photoinduced absorption response in PPV, at 80 K, measured at 0.52 eV (note that the ordinate scale is in rad/s). The PPV for these measurements was prepared from the DMS precursor. The abscissa full scale corresponds to a factor of 4.5 in $-\Delta T/T$.

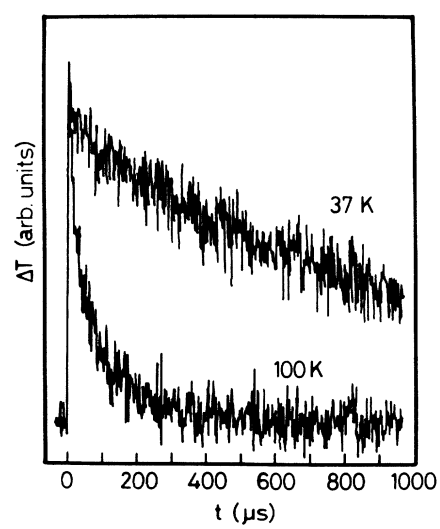

FIG. 9. Time-dependent change in the optical transmission of a PPV film for a probe-beam energy of 1.45 eV, following excitation by a 15-ns pulse from a tripled Nd:YAG laser. The data at the two temperatures shown have been normalized to the same initial value. The PPV for these measurements was prepared from the DMS precursor.

sorption due to charged photoexcitations, the behavior at 1.45 eV shows essentially monomolecular decay, strongly indicating its different origin. This is clearly shown by the direct temporal resolution of the photoinduced absorption response to excitation from the tripled output from the Q-switched Nd:YAG laser. Data as collected are shown in Fig. 9 and are plotted semilogarithmically in Fig. 10. The near-linear variation of log (response) versus time demonstrates the monomolecular behavior, and we find that the time constant varies between 70 μs at 100 K (the highest temperature at which the photoinduced absorption at 1.45 eV can be conveniently measured) and 1 ms at 37 K. The lifetime does not further increase at temperatures lower than this, down to 13 K—the experimental limit for our measurements.

The temperature dependence of the two photoinduced absorption responses is shown in Fig. 11, with the variation at 1.4 eV shown in Fig. 11(a) and that at 1.6 eV in Fig. 11(b). The response at 1.45 eV is fairly constant to about 50 K, and falls above this temperature. In contrast, and emphasizing its distinct origin, the response at 1.6 eV, due to the charged photoexcitations, decreases only very slightly up to 150 K before falling rapidly above this. At 1.45 eV, the tail of the 1.6-eV feature is probably responsible for the change in slope near 120 K, as seen in Fig. 11(a), and the persistence of a small signal until just above 150 K.

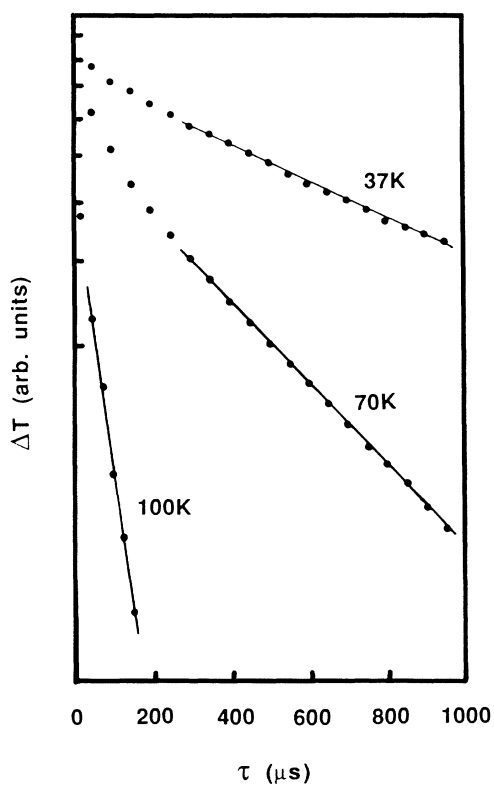

FIG. 10. Time-dependent change in the optical transmission of a PPV film for a probe-beam energy of 1.45 eV, following excitation by a 15-ns pulse from a tripled Nd:YAG laser. Data as shown in Fig. 9, but plotted semilogarithmically, to show the variation of lifetime with temperature. The abscissa full scale corresponds to a factor of 25 in ΔT.

The polarization dependence of the photoinduced absorption due to charged photoexcitations can be measured on free-standing samples that have been stretch oriented, as has been discussed previously.[10,12] We find that the preferential polarization of the excitation beam is perpendicular to the chain directions, and consider that this is due to the greater penetration of the excitation beam into the sample and a higher probability for interchain charge separation for the perpendicular polarization. The induced absorption is, however, very strongly polarized parallel to the chains, as expected for an excited state which is delocalized over several repeat units of the chain. We have carried out similar measurements here on the 1.45-eV photoinduced absorption feature, and find that the induced absorption is similarily polarized strongly parallel to the chain direction.

2. *t,t-DSB*

Photoexcitation measurements on the oligomer show the appearance of a photoinduced absorption feature similar, in terms of its spectral shape, temperature and frequency dependence, and lifetime, to the 1.45-eV feature in PPV. Ultraviolet excitation with the argon-ion laser provides excitation across the π-π^* gap, and at low temperatures we see the photoinduced absorption, shown in Fig. 12 at 50 K. A strong transition at 1.95 eV is seen, with an additional weak feature near 1.75 eV, possibly vibrational in origin. We propose, both on the basis of the

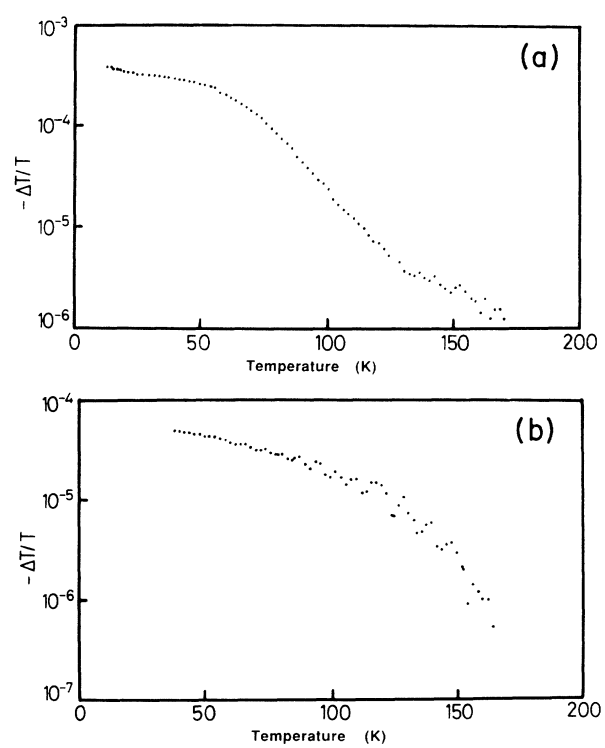

FIG. 11. Temperature dependence of the photoinduced absorption signal in PPV, with excitation at 355 nm from the tripled output of the Nd:YAG. (a) The response at 1.45 eV and (b) the response at 1.6 eV.

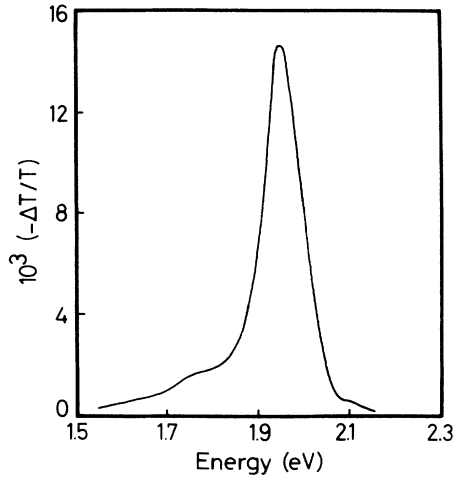

FIG. 12. Spectrum of the photoinduced triplet-triplet absorption in t,t-DSB at 50 K. Photoexcitation was provided by 100 mW/cm^2 of ultraviolet laser radiation, chopped at 87 Hz.

similarity of this feature to that seen in the shorter oligomer *trans*-stilbene, clearly identified there as a triplet-triplet transition,[20,21] and also, as discussed further below, on the basis of supporting photoinduced electron spin-resonance results, that this 1.95-eV feature arises from a triplet-triplet transition of a triplet exciton. We note that vibrational structure with an energy spacing of 0.2 eV is also seen in the triplet-triplet absorption in *trans*-stilbene.[20]

The lifetime of the proposed photoexcited triplet state in t,t-DSB can be inferred by measuring the dependence of the photoinduced absorption on the frequency of modulation of the exciting laser light. Figure 13 shows the dependence of the change in sample transmission at 1.95 eV on the frequency of modulation of the exciting laser at a temperature of 80 K. We observe a decrease as ω^{-1} for angular frequencies above ~ 500 s^{-1}, consistent with an interpretation in terms of a single well-defined decay time. This is also consistent with the observed linear dependence of the photoinduced absorption on the exciting laser intensity, up to intensities of the order of 50 mW/cm^2 (the highest intensity available with our excitation source).

The crossover from low- to high-frequency behavior in the data of Fig. 5 provides a measure of the lifetime of the proposed triplet exciton which we find to be of the order of 2 ms. This value is very similar to that reported for the photoexcited triplet in *trans*-stilbene at 77 K.[20,35] The experiments on *trans*-stilbene were, however, done on dilute solutions in glass-forming solvents, whereas our measurements were performed on solid suspensions in KBr. These suspensions almost certainly involve small aggregates of molecules, possibly making intermolecular transfer of excitations important in their decay kinetics.

As the sample temperature is lowered, the lifetime of the proposed triplet does not increase significantly. Data similar to those in Fig. 13 were collected at 15 K, and showed that the lifetime had only increased to about 5 ms. As the temperature is raised above about 90 K, however, the lifetime decreases dramatically. This is illustrated by the rapid disappearance of the photoinduced absorption, on the time scales probed by this technique, for temperatures above 90 K. The intensity of the photoinduced absorption at 1.95 eV as a function of temperature, measured for an excitation modulation frequency of 87 Hz, is shown in the semilogarithmic plot in Fig. 14. It is reasonable to assume that the rate of triplet photoexcitation $g(t)$ is independent of temperature, and Eq. (2) then implies that photoinduced triplet-triplet absorption data, plotted in the form of Fig. 14, should be proportional to the temperature-dependent triplet lifetime $\tau(T)$.

Note that the data shown in Fig. 14 are remarkably similar to the observed temperature dependence of the

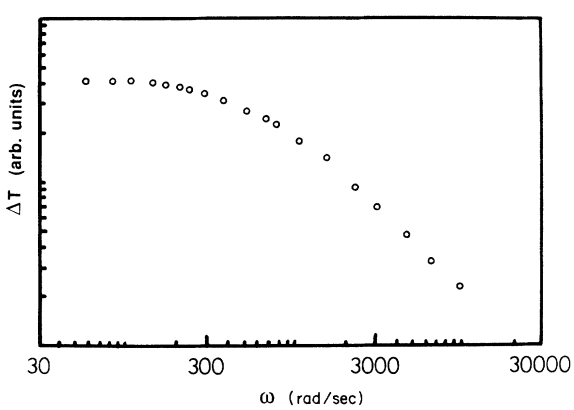

FIG. 13. Dependence of the strength of triplet-triplet absorption in t,t-DSB on the angular frequency of modulation of photoexcitation at 50 K. The crossover between low-frequency ($\omega\tau \ll 1$) and high-frequency ($\omega\tau \gg 1$) behavior near 500 Hz gives a triplet lifetime of the order of 2 ms.

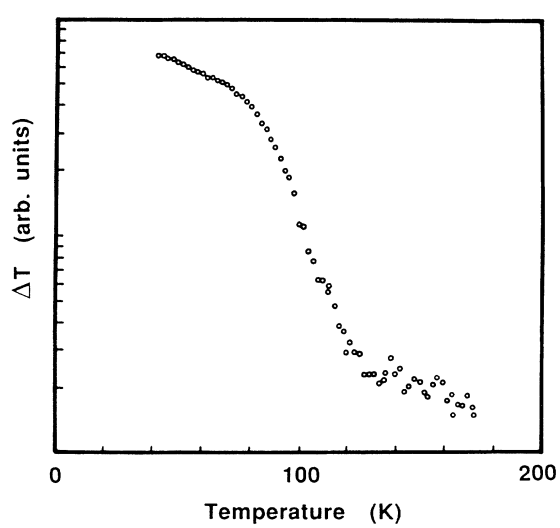

FIG. 14. Temperature dependence of the strength of photoinduced triplet-triplet absorption in t,t-DSB. The data show a rapid loss of oscillator strength above 90 K, indicating the activation of an efficient decay channel above that temperature.

1.45-eV photoinduced transition in PPV. The drop [seen in both Figs. 11(a) and 14] in the signal by nearly two orders of magnitude between 80 and 120 K indicates the activation of a strong decay channel near 90 K.

C. Light-induced electron spin resonance in *t,t*-DSB

The Zeeman splitting of the triplet sublevels in the presence of a moderate magnetic field should be observable by inducing transitions between the sublevels with microwaves. In a molecule with less than threefold rotational symmetry, such as *t,t*-DSB, the dipole-dipole interaction between the triplet spins leads to a strong anisotropy of the $\Delta m_s = 1$ transition, as a function of field orientation with respect to the molecular axis. Hence, in a randomly oriented noncrystalline sample, this transition is very broad and weak. We were, in fact, unable to observe this transition during photoexcitation of *t,t*-DSB. The dipole-dipole interaction also results in a mixing of the triplet states, which enhances the strength of the "forbidden" $\Delta m_s = 2$ transition. This transition is typically seen at roughly half the field strength at which the $\Delta m_s = 1$ transition occurs, and is an unambiguous signature of the presence of a triplet excitation. Because it is nearly isotropic with respect to field direction, it is also more easily observed. Figure 15 shows the ESR signal, which we associate with the photoexcited triplet state in *t,t*-DSB. For a microwave probe frequency of 9.14 GHz, a single weak asymmetric line of peak-to-peak width $\Delta H_{pp} \approx 12$ G is observed, centered near a field strength of 1580 G. The signal was only present while the sample was under ultraviolet illumination, and disappeared in consort with the 1.95-eV photoinduced absorption feature when the sample temperature was raised above 90 K. From the position of the low-field maximum in the ESR signal, the zero-field splitting of the triplet sublevels can be determined.[36] The appearance of this peak in Fig. 15 at 1575 G, for a probe microwave frequency of 9.14 GHz, corresponds to a zero-field splitting parameter $D^* = 0.07$ cm^{-1}. This value is significantly smaller than the value $D^* = 0.112$ cm^{-1} reported for the lowest triplet in *trans*-stilbene.[21,37]

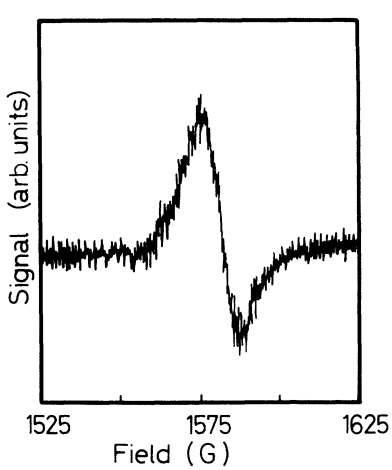

FIG. 15. Light-induced electron spin-resonance signal in solid as-prepared *t,t*-DSB at 80 K, for a microwave frequency of 9.14 GHz. The observed weak line corresponds to the "forbidden" $\Delta m_s = 2$ transition between triplet sublevels.

We consider that the photoinduced absorption feature in PPV at 1.45 eV is similar in origin to the photoinduced absorption at 1.95 eV in the model oligomer, for which the light-induced ESR response, shown in Fig. 15, gives strong support to our identification in terms of a triplet-triplet transition of a triplet exciton. We have thus attempted to find a light-induced ESR response in PPV, and to make, therefore, a direct identification of the triplet exciton in the polymer. We have not, however, been able to find a response; a limitation on the experiment was the temperature range set by the liquid-nitrogen cooling used for this experiment. We can make a comparison between the photoinduced absorption signals for polymer and oligomer at 80 K from the data in Figs. 6, 11, and 12, and find that the photoinduced absorption response for the polymer is a factor of 10 lower than in the oligomer. Presuming that the optical cross section for the polymer and oligomer are not too different, we expect the light-induced ESR signal for the polymer to be a factor of 10 lower than in the oligomer and, therefore, at the limit of the resolution of the experiment we were able to perform. In the absence of a more direct confirmation, our identification of the triplet origin of the 1.45-eV feature in PPV relies on the similarity of this response to that seen at 1.95 eV in the oligomer and on our knowledge of the neutrality of the excited state responsible.

IV. DISCUSSION

Photoexcitation in PPV produces a particularly rich range of excitations, both charged and neutral. We have previously considered that it is useful to distinguish between excitations that are associated with excitation on a single chain, and excitations that result in separation of charge between chains.[10,12] The former case, that of intrachain excitation, results predominantly in the generation of singlet excitons, which, if they decay radiatively, are responsible for the photoluminescence seen in Fig. 3. There is also the possibility of the generation of triplet excitons, with which, as discussed above, we associate the photoinduced absorption at 1.45 eV. Interchain separation of charge is expected initially to form singly charged polarons, but the evidence is that the long-lived excited states, which are seen spectroscopically, are doubly charge bipolarons. Here it is the "slow" photoinduced absorption response at 0.6 and 1.6 eV that we associate with bipolarons. As mentioned above and discussed in detail elsewhere,[10,11] the evidence that the excitations are charged comes from the observation of the infrared active vibrational modes associated with translation of the charged excitation along the chain. The model oligomer, which we have investigated here, *trans,trans*-distyrylbenzene, shows only the neutral excitations, both as singlet and as triplet excitons, and it is possible to make direct comparison for these excitons between oligo-

mer and polymer. We discuss, here in turn, the properties of the various excitations.

A. Singlet excitons

The spectra shown in Fig. 3 for the polymer and in Fig. 4 for the oligomer of absorption and photoluminescence are characteristic of the spectra seen for many organic molecular materials, and we draw attention to the similarity between the spectra for the oligomer and polymer (apart from the obvious shift to lower energies for the polymer). Photoluminescence is generally expected for nondegenerate-ground-state polymers and is associated with the transition from the upper to lower gap state within the polaron-exciton description of Fesser, Bishop, and Campbell.[1]

Experimentally, photoluminescence is commonly found to be very weak in conjugated polymers and, perhaps for that reason, has tended to be disregarded. However, a low quantum yield for photoluminescence can be due to nonradiative decay channels, which run faster than the radiative decay (which is expected to have a lifetime of about 1 ns), and it seems that conjugated polymers are especially prone to effective nonradiative decay mechanisms. In particular, there is evidence that charged excitations can act as nonradiative decay centers,[38] and we do not expect to find high quantum yields, therefore, in polymers which are partially oxidized. The family of poly(arylene vinylenes) can be prepared with very low concentrations of charged and spin defects, and it is, therefore, to be expected that polymers of this type should be found to have high quantum yields for photoluminescence. What is somewhat surprising is that the quantum yield for photoluminescence among this family of polymers shows very considerable variation, with PPV as the strongest, and poly(2,5-thienylene vinylene) showing almost no photoluminescence.[29] We consider that there are several mechanisms for nonradiative decay: some of which may be extrinsic in origin, requiring motion of the exciton to a recombination center, and some of which may be intrinsic, due to coincidence of the potential surfaces for ground and excited states. Direct measurements of the photoluminescence decay in PPV have been reported[39–41] and show initial decay rates consistent with the quantum yield.

Experimental determination of the degree of self-localization of the exciton, due to the electron-lattice interaction, is not entirely unambiguous. It is expected that the exciton is mobile, and that it will be able to explore the local environment of the polymer, so as to trap on a region on a chain with the lowest potential energy, from which the radiative decay is made. It is well established that disorder in the polymer structure produces a distribution in energy of π and π^* states on the chains. However, if excitation is well into the π-π^* band, the measured photoluminescence is found to be independent of excitation energy, supporting this model for migration of the exciton.[42,43] However, as the excitation energy is taken down the low-energy side of the π-π^* absorption edge, the photoluminescence does shift to lower energies, indicating that there are further refinements to be made to the description of photoluminescence in PPV.[42,43]

B. Triplet excitons

For the case of the *trans,trans*-distyrylbenzene oligomer, we have direct evidence in the form of light-induced ESR for the photogeneration of triplet excitons. By comparison with the shorter oligomer *trans*-stilbene, we also would expect to see a triplet-triplet photoinduced absorption associated with the light-induced ESR. We do, indeed, find a photoinduced absorption feature, lying at 1.95 eV, which correlates with the light-induced ESR response, and we, therefore, attribute this to a triplet-triplet excitation of the excited state. For the case of the polymer, we were unable to measure directly the light-induced ESR expected for triplets, but did record a photoinduced absorption response at 1.45 eV which shows very similar characteristics to that of the 1.95-eV feature in the oligomer, and which we tentatively associated with the photogeneration of triplet excitons in the polymer.

Although the presence of the transient triplet-triplet absorption in the smallest oligomers of PPV suggests that the triplet exciton is also small, the results of our electron spin-resonance experiments indicate an increase in its extent between the two smallest oligomers. In *trans*-stilbene, it has been argued that the measured zero-field splitting of the triplet sublevels implies that the triplet excited state extends along the whole molecule.[21] The dependence of the zero-field splitting on the extent of the triplet can only be determined by a detailed quantum chemical calculation, although it does typically decrease monotonically with the separation between the spins.[44] Hence, a triplet more extended than that in *trans*-stilbene would explain the much smaller value we find for D^* in *t,t*-DSB. A similar decrease in D^* occurs between the poly(acene) oligomers naphthalene and anthracene.[45]

Triplet excited states provide an important probe of the influence of electron-electron interactions in conjugated polymers. Several recent calculations[46–48] indicate that these interactions act to stabilize the triplet as the lowest-lying excited state. The amount by which this state is lowered, relative to the lowest singlet excitation, is a direct measure of the interaction strength. For both *t,t*-DSB and PPV, the relative positions of the triplet-triplet transitions and the corresponding singlet-singlet transitions cannot be determined from our measurements. Hence, we cannot say anything about the singlet-triplet splitting. The most direct measure of this splitting, the delayed phosphorescence produced by the radiative decay of the lowest triplet to the ground state, is difficult to observe because of the low phosphorescent yield. As in the case of *trans*-stilbene,[34] this is due to the presence of an efficient nonradiative decay channel, even for temperatures below 90 K, which shortens the triplet lifetime to a few milliseconds.

For temperatures above 90 K, a new nonradiative decay channel further shortens the triplet exciton lifetime, rendering it unobservable under our experimental conditions. This nonradiative channel may also play a role in the decay of the singlet exciton, whose radiative decay produces the photoluminescence. The frequencies probed in our experiments ($\sim 10^2$ Hz) are much smaller than the inverse lifetime of the singlet exciton ($\tau_s < 10^{-9}$ s). Assuming that the decay is monomolecular, Eq. (2)

predicts a photoluminescent yield proportional to τ_s for this range of frequencies ($\omega\tau_s \ll 1$). As discussed above, the temperature dependence of τ_s is due to the nonradiative decay channels. Data showing the temperature dependence of the photoluminescence for *t,t*-DSB and PPV are presented in Fig. 5. Over the temperature range from 40 to 200 K, both sets of data in Fig. 5 can be fit to an exponential of the form $e^{-E_a/kT}$, with an activation energy E_a of the order of 10^{-2} eV. This corresponds to a temperature of the order of 100 K, which is quite similar to the temperature at which the strong decay channel for the triplet excitons is turned on. Although this correlation may be spurious, it may indicate the importance of a related process (such as singlet-triplet collisions, for example) for the nonradiative decay of both the singlet and the triplet excitons.

C. Charged photoexcitations

The results presented here on the photogeneration of charged excitations in PPV, obtained primarily with the cw ion laser as excitation source, provide further experimental detail that complements the earlier results obtained with excitation from the tripled output from the *Q*-switched Nd:YAG laser.[10–12] We note here that it is somewhat complicated to disentangle the photoinduced absorption response due to the photogenerated bipolarons, the 1.45-eV triplet-triplet feature, and the photoluminescence. The charged photoexcitations are significantly longer lived than those found, for example, in poly(2,5-thienylene vinylene) (Ref. 29) and the charged solitons in polyacetylene,[33] and the distribution in lifetimes extends beyond the low-frequency limit of the experiments performed here, as evident in Fig. 8.

Though the spectrum for the photoinduced absorption associated with charged bipolarons is well described within the model of Ref. 1, the two absorption bands at 0.6 and 1.6 eV require that the gap states associated with the bipolaron lie deep within the gap, with an energy separation of 1 eV between them. Within the formalism of the Fesser, Bishop, and Campbell model, this requires that the bipolaron is weakly confined and is spatially well extended along the chain. We have pointed out previously[10,49] that this finding is inconsistent with similar analysis of the photoluminescence for which the Stokes shift is small, with the separation of the gap states directly measured as the zero-phonon photoluminescence band at 2.37 eV. This larger separation of the gap states implies a much stronger degree of confinement, and the difficulty lies in the model of Fesser, Bishop, and Campbell, in that the bipolaron and the neutral polaron-exciton should show the same behavior. It is probably necessary to include Coulomb interactions for the charged excitation within the model, but this remains an important discrepancy between model and experiment.

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