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Magnetic field effects on triplet exciton fission and fusion in a polydiacetylene

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We have studied the origin and decay dynamics of triplet excitons in the conjugated polymer poly(4BCMU) in its sol (yellow) and gel (red) phases. Wavelength and intensity dependencies of the triplet yield show that the triplet exciton cannot be produced by excitation into the singlet exciton edge but only from higher lying states. The observed lifetime of the triplet state, coupled with the magnetic field dependence of the triplet state production and decay, indicate that the triplet state is created by a fission process from the excited singlet. The time and magnetic field dependence of the triplet exciton decay indicate that the triplet exciton decay in the red phase occurs by diffusive bimolecular fusion, but in the yellow phase the triplet exciton decay is nondiffusive. We postulate that the unimolecular decay of the triplet exciton in the yellow phase results from exciton pinning by conformational disorder.

The growth and properties of materials with reduced dimensionality are important current problems in condensed matter science. Especially interesting are experiments that detail the changes in electronic properties that accompany the transition from the bulk phase to one of lower dimensionality. For example, recent studies of the diffusion of triplet excitons in low dimensional "wires" of naphthalene¹ showed a transition from two-dimensional to one-dimensional behavior when the radius of the wire approached 40 nm. While the diffusion of the excitons was truly one dimensional at long times, the finite cross section of the wire led to three-dimensional behavior at short times. To observe one-dimensional effects at short times the radius of the wire needs to be decreased even further, with the ultimate reduction in dimensionality corresponding to the confinement of excitations to isolated linear chains of atoms such as a soluble conjugated polymer.

In principle, the soluble polydiacetylenes offer a unique opportunity for studying the electronic properties of materials that are truly one dimensional.² For example, while inter-chain effects can greatly perturb or even dominate the physics of photoexcitations in polyacetylene,³ soluble polydiacetylenes can be separated in solution to make inter-chain effects improbable. Thus, the photoexcitations and their decay in such materials can be used to address the problem of one-dimensional diffusion.

Several soluble polydiacetylenes have been widely studied, especially the closely related poly(4BCMU) and poly(3BCMU).⁴ These materials are true high polymers with molecular weights exceeding 2×10^5 Daltons, and consist of a conjugated backbone with a repeat sequence of single, double, single, and triple bonds. Large substituents attached to the carbon atoms of the double bond confer room temperature solubility in organic solvents such as chloroform, and high temperature ($>60^\circ\text{C}$) solubility in less polar solvents such as toluene.

Chloroform solutions of poly(4BCMU) are yellow, but

the addition of a nonsolvent induces a color change to red and eventually the formation of a red gel.⁵ The polymers in yellow solution have been interpreted as either randomly coiled⁶ chains with no inherent stiffness or worm-like chains⁷ with a finite persistence length, while the red phase has been viewed as either a solution⁶ or aggregate⁸ of rod-like chains. There is disagreement over whether the conversion to the rod-like state occurs via a unimolecular process, or by the cooperative effects of several chains. Unfortunately this uncertainty impacts upon the dimensionality of the condensed phase, since a highly condensed chain would be expected to show strong interchain effects, while a dilute gel made of stiff chains would be expected to remain predominantly one dimensional.

It is our belief that the strong evidence for worm-like (stiff) chains in the gel phase⁹ and the large volume of the gel phase of 4BCMU support the analysis of our data from a 1D perspective. Thus, in our view, the two states of 4BCMU present a rare opportunity to study the formation and decay of excitations in 1D. In this communication, we describe our studies on the formation and diffusion of triplet excitations in poly(4BCMU), and show that the diffusional behavior of such excitations is grossly altered as the polymer changes its molecular conformation, and that a 1D diffusional model can be used to interpret the data.

Poly(4BCMU) was synthesized by the ultraviolet-induced polymerization of a slurry of finely ground monomer crystals in water. Polymer free of low molecular weight contaminants was obtained by fractional precipitation resulting in a molecular weight of 200 000 Daltons, as determined by size exclusion chromatography. Red phase samples were prepared in an oxygen-free dry box by adding a portion of the dried red gel to dry, deoxygenated toluene in a glass cuvette, which was then sealed under vacuum. Upon heating the gel dissolved to form a yellow solution, which changed to a uniform red gel when cooled. No changes in the sample were noted after optical experiments, or after repeated cy-

cling between red and yellow phases.

Transient absorption measurements were made using a pulsed Nd:YAG laser (Quanta Ray DCR-2) as the excitation source operating either at the second (532 nm) or third (355 nm) harmonic. Additional wavelengths were obtained by passing the output of a DCM dye laser through a pressurized hydrogen cell and tuning the dye to obtain the appropriate Raman-shifted output. The probe beam was provided by a 200 W tungsten-halogen light source focused with off-axis ellipsoidal mirrors onto the sample and wavelength selected by a grating monochromator. A photomultiplier served as the detector, and a transient recorder averaged the signal. Although the laser excitation pulse width is approximately 5 ns, the time resolution of the apparatus was 1 μ s, determined by fluorescence scattering from the sample. A small iron-core electromagnet with a 2 cm gap was used for the experiments on the magnetic field dependence of the signal.

The size of the induced signal was quite small. The fractional transmission change $\delta I/I_0$ was on the order of 1×10^{-3} at the maximum wavelength for the triplet state. Triplet-triplet absorption manifolds typically have roughly the same oscillator strength as singlet-singlet manifolds.¹³ Since the samples had an absorption coefficient of about 1 optical density units at the excitation wavelength, we can infer from this and the known energy density that the quantum yield for triplet state production is quite low in these samples, on the order of 10^{-3} . In Fig. 1 we show the transient absorption spectra observed for the red and yellow phases of poly(4BCMU) 10 μ s following photoexcitation. Photoinduced absorption (PA) is observed at 1.5 and 1.7 eV for the red and yellow phases, respectively, the magnitude of the absorption at 1.7 eV has been corrected for the smaller red phase absorption at the excitation wavelength (355 nm). Of particular interest is the shape of the two transients. Both are narrow absorption spectra, with a full width at half-maximum of 0.2 eV, while the absorption edge of the yellow phase is considerably broader than that of the red phase. The PA spectra and its slow (approximately 100 μ s) decay rates for both forms are similar to the PA signal discovered in the

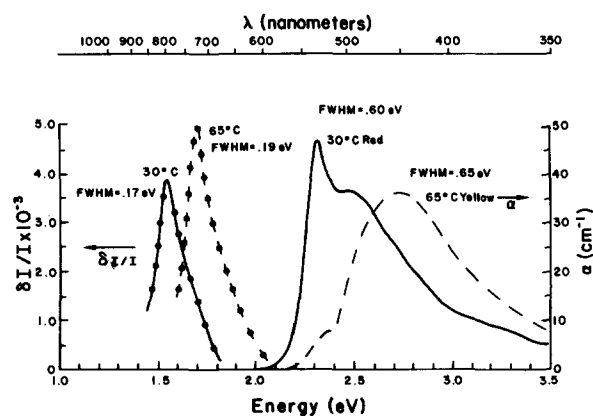


FIG. 1. Triplet absorbance spectra: The right-hand side of this figure and associated axis shows the optical absorbance of the poly(4BCMU) sample in the red (30 °C, solid line) and yellow (65 °C, dashed line) phase. The left-hand side shows the transient absorbance induced 10 μ s after laser excitation at 355 nm for the red phase (30 °C, solid line) and the yellow phase (65 °C, dashed line).

crystalline polydiacetylene PTS,¹⁰ whose origin was identified as a triplet exciton.¹¹ In order to confirm the triplet nature of these excitations in 4BCMU we have taken advantage of the polymer's solubility and performed oxygen quenching experiments. We find that in the presence of a small amount of dissolved oxygen the PA signals are rapidly quenched.

We have measured the intensity dependence of the triplet exciton yield at several selected wavelengths and found that log-log plots of the initial triplet yield vs excitation intensity yielded straight lines with a slope of 1 at 355 nm for both the yellow and red phase, and a slope of 2 at either 532 (red phase) or 500 nm (yellow phase). See Fig. 2. Direct excitation of triplet exciton(s) from the lowest energy sing-

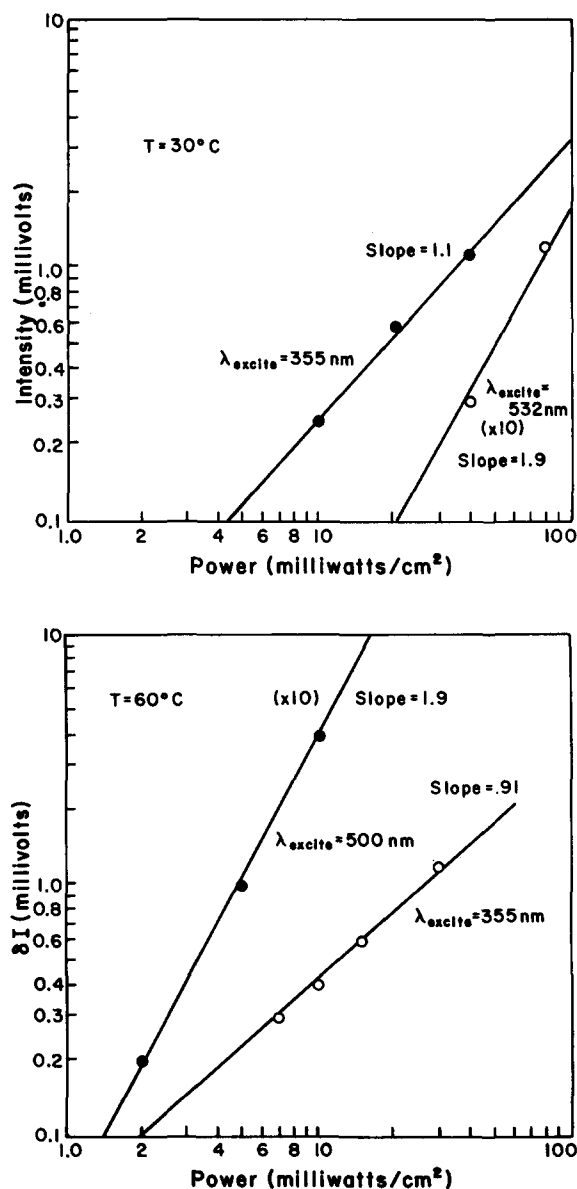


FIG. 2. Triplet yield vs laser intensity: The log of the prompt transmission change at the maximum of the triplet absorbance plotted vs the log of the time-averaged laser intensity at 532 and 355 nm. Power measurements were made by a Scientech 362 power meter. Straight lines are least-squares fits. Note that the 532 nm triplet yield values have been multiplied by 10. (a) Measurements of the red (gel) phase at 30 °C. (b) Measurements of the yellow (sol) phase at 60 °C.

let transition can be ruled out from these observations. If one or more triplets could be created directly by excitation into the singlet exciton edge then the yield would be linear with excitation energy. However, since the yield varied closely with the square of the excitation energy (or intensity, since the pulse width is constant) this means that a higher excited state reachable by a two-photon process was responsible for triplet production. Confirmation of this is evident from the linear energy (intensity) dependence with the tripled Nd:YAG beam at 355 nm. Similar intensity dependent yields of long-lived states have been seen by Greene *et al.* in the polydiacetylene PDA-pTS.¹²

We can immediately rule out simple intersystem crossing from the lowest excited state singlet manifold as the pathway for the triplet formation¹³ because of the two-photon intensity dependence at the singlet edge, and we need only consider models of triplet exciton production which are non-linear at the singlet exciton absorption edge. Such processes include electron-hole (or, radical ion pair) recombination¹⁴ or triplet exciton creation occur via fission of a singlet exciton into two triplet excitons.^{15,16} Unfortunately both models are compatible with the experimental intensity dependence of the triplet yield.

As we will show below, the effect of external magnetic fields on the exciton lifetime allows us to differentiate between these two models. Figure 3 shows that magnetic fields lowered the prompt yield for both the yellow and the red phase, although a significantly smaller effect of the magnetic field was seen in the yellow phase compared to the red phase. Similarly, magnetic fields increased the lifetime of the red phase triplet exciton (Fig. 4), but had a much smaller effect on the yellow phase. Further, the lifetime of the yellow phase triplet has an exponential decay at all field strengths used, while the red phase had a highly nonexponential decay at all fields.

These observations allow us to choose between the electron-hole recombination and the exciton fission models for triplet exciton formation. Both models predict a general decrease in the quantum yield for triplet formation in the high field limit, but the models predict significantly different rates

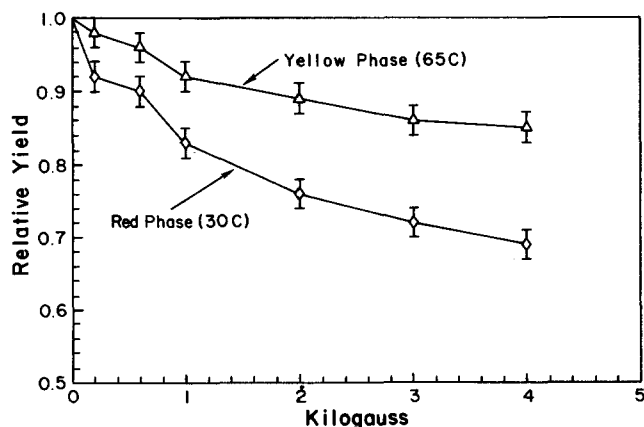


FIG. 3. Triplet yield vs magnetic field: The prompt triplet yield at 10 μ s after excitation for the red and yellow phase as a function of magnetic field strength. The solid lines are drawn to guide the eye and are not theoretical fits.

of triplet production. In the electron-hole recombination model, the field dependent yield results from the spin precession of geminate charge carriers followed by recombination. This requires that electrons and holes separate and recombine, a process that takes place on the nanosecond time scale in solution. Schulten¹⁴ has done an exhaustive analysis of this process.

In the exciton fission model, the field dependence of the quantum yield results from the perturbation of crossing levels caused by the Zeeman splitting. Exciton fission processes occur promptly at some rate k_{1-3} , and the ratio between the fission rate and the fusion rate k_{3-1} is roughly¹⁷

$$k_{1-3}/k_{3-1} = 9 \exp\{(E_s^* - 2E_t)/k_b T\}, \quad (1)$$

where E_t is the energy of the triplet state and E_s^* is the energy of the excited singlet state, as required from our observation that only UV excitation results in linear triplet yield. Equation (1) assumes the population of the excited singlet is in thermal equilibrium, which is somewhat unlikely since the singlet lifetimes are on the order of picoseconds¹² while vibrational cooling times are on the order of tens to hundreds of picoseconds.¹⁸ However, we must for the sake of simplicity assume that the effect of hot molecules will only

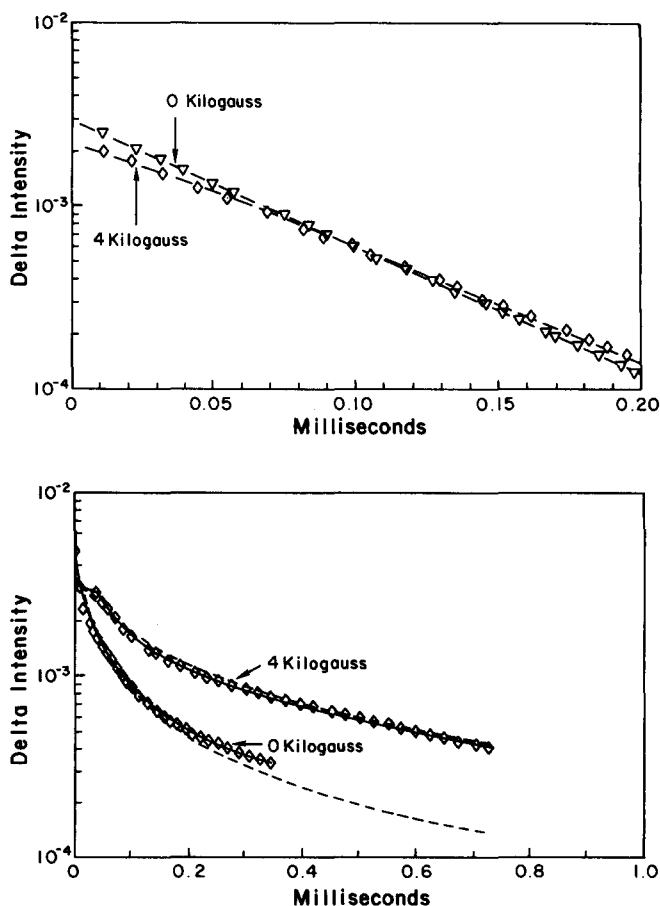


FIG. 4. Triplet lifetime vs magnetic field: The triplet decay as a function of magnetic field for the two extremum values of magnetic field used. (a) The triplet population vs time for the sol phase. Note that the decay is accurately a single exponential, and only shows a weak magnetic field dependence. (b) The triplet population vs time for the gel phase. The solid lines are fits to the bimolecular quenching model discussed in the text, and show both a decay law of the form t^{-1} and a strong magnetic field dependence.

have a quantitative and not qualitative effect on the analysis. A further approximation arises from our lack of knowledge of the triplet ground state energy. A rough estimate of red phase triplet exciton E_t can be obtained from the triplet-triplet transition energy of 1.55 eV, while the singlet excited exciton need have an energy no greater than the UV photon at 355 nm (3.5 eV). We calculate that the ratio of the fission to fusion rates should be on the order of 10^9 . Experimentally, it has been observed that triplet exciton creation is extremely fast (less than 10^{-13} s) with no appreciable lag between excitation and rise in the triplet population.¹⁹ Thus, a fast fission rate and a slow fusion rate (see below) of approximately 10^{-4} s are clearly consistent with this picture.

Further evidence that the same matrix elements involved in fusion process also occur in the fission process can be observed in the magnetic field dependence of the initial yield of the triplet state. The trend for both the yellow and the red phase is for the prompt yield to *decrease* with *increasing* magnetic field. Since the triplet recombination rate (see below) also seems to *decrease* with *increasing* magnetic field we can postulate that in the prompt fission process that an increased magnetic field lowers the fission rate and allows for alternate singlet quenching processes to compete more efficiently. Of course, none of these arguments prove that the actual act of triplet production is a fission process, but they indicate strong correlation with the model.

The basic picture of magnetic field effects in triplet fusion was developed by Merrifield,²⁰ and has been examined in great detail by Swenberg and Geacintov,²¹ who also have examined the dependence of the fission process on magnetic fields. The analysis reveals that when two triplet excitons collide there are nine possible spin states, which have close to equal occupation probabilities at high temperatures. Upon triplet exciton collision it is possible to either scatter without fusion (transition rate k_{-1}) or fuse with rate k_2 . The total fusion rate is the product of k_1 , the collisional frequency of the triplet excitons, and the product of k_2 times the density of singlet containing spin states. If the amplitude of singlet containing states is $S_i = \langle S | \psi_i \rangle$ then the bimolecular quenching rate k_b is

$$k_b = \frac{k_1}{9} \sum_{i=1}^9 \frac{k_2 S_i^2}{k_{-1} + k_2 S_i^2}. \quad (2)$$

Although the parameters of the above equation require detailed knowledge of the electronic energy levels, the ratio of the fusion rate at infinite field to that at zero field, $k_b(\infty)/k_b(0)$, can be calculated by assumed that the zero field dipolar splitting results in three states with singlet character and that optimal degeneracy of high field singlet states occurs. If the recombination rate is zero then the minimum value of $k_b(\infty)/k_b(0)$ is $1/3 = 0.333$. Our measured value is even lower, 0.22. The origin of the discrepancy may either lie with the singlet state composition of the triplet states at zero field or the effects of pairwise correlations in one dimension, as mentioned below. In any event, the sum of the above evidence supports the model of triplet fission/fusion as the primary production and decay mechanism for triplet excitations in poly(4BCMU).

The observed t^{-1} triplet decay kinetics in red phase in-

stead of the expected $t^{1/2}$ decay is related to an interesting effect of low dimensionality on the triplet fusion kinetics. As described above, two triplet excitons must recombine for fusion to occur, a reaction of the form $T + T \rightarrow S_{\text{inert}}$. In three dimensions, and assuming a random initial spatial distribution of triplet excitons, the rate equation for the triplet exciton lifetime would be

$$dN/dt = -k_0 N - k_b N^2, \quad (3)$$

where $N(t)$ is the triplet exciton concentration as a function of time, k_0 is the natural decay rate, and k_b is the biexcitonic decay rate due to fusion. We assume here that due to the very small triplet yield out of the excited singlet state that the excited singlet produced in the fusion process yield very few triplets by a refission and this term can be ignored. The solution to the above equation is

$$N(t) = N(0) \times \frac{k_0}{(k_b + k_0)e^{k_0 t} - k_b t}. \quad (4)$$

In the limit of $k_0 \ll k_b$ $N(t)$ decays as t^{-1} . The solid lines in Fig. 3 are fits of Eq. (4) to the experimental data. Computer fits demand that k_0 be much less than k_b , and thus the kinetics are closely hyperbolic in time and the intrinsic triplet lifetime in the red phase is much greater than 1 ms.

In low-dimensional systems, the expected exciton decay kinetics depends on the initial ensemble of excitations. For a *random* initial distribution of reactants, Toussaint and Wilczek²² concluded that the annihilation process in one dimension should decay as $t^{-1/2}$. Similarly, Shank *et al.*^{24,25} analyzed the relaxation of photoinduced solitons in *trans*-polyacetylene, and used the function $\text{erf}(\sqrt{\tau}/t)$ to fit the data, which for small arguments is the same as a $t^{-1/2}$ decay. Toussaint and Wilczek also point out that the bimolecular rate constant k_b cannot be interpreted in terms of a capture radius in $d \leq 2$ because of the reentrant nature of diffusion in lower dimensions.²³

From these results, one might also expect to observe a $t^{-1/2}$ decay in our data, instead of the observed t^{-1} decay for the red phase triplet exciton. We believe this apparent discrepancy is a simple consequence of the formation of triplet excitons by singlet fission; *the spatial correlation function is not random but is instead pairwise correlated*. Hence, there are no slowly decaying long wavelength statistical fluctuations and the analysis of Spitzer²³ can be used, which predicts a one-dimensional t^{-1} relaxation rate in the presence of pairwise correlations.

Note that the yellow phase has no significant bimolecular contribution to the decay under either low or high field conditions. The minimal effect of the magnetic field on the triplet exciton lifetime is due not only to the decreased size (length) of the excitation in the yellow phase but also must be due to some sort of pinning of the triplet exciton in the yellow phase, since the bimolecular rate constant for triplet exciton fusion is smaller in the sol phase. We believe that the increased conformational disorder in the yellow phase provides ample sites for localization of the exciton along the polydiacetylene chain.

In summary, we have studied the effect of conformational changes the dynamics of triplet excitons in a soluble polydiacetylene. We find that the magnetic field dependence

of the prompt triplet yield is consistent with the fission of singlet excitons into triplet excitons. The decay dynamics, however, is governed by the fusion of triplet excitons to form short lived singlet excitons. The rate limiting step of the fusion process is due to the pairwise correlated triplet exciton diffusion in one dimension.

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