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Picosecond photoinduced exciton bleaching in emeraldine base: Crossover in decay mechanisms

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We report picosecond photoinduced bleaching (PB) of the exciton absorption of the emeraldine base form of polyaniline. The temperature- (T-) independent dispersive decay, $\sim t^{-0.11}$, observed in this study differs markedly from the dynamics of earlier studied semiconductors. It also contrasts with long-time PB, which varies as $t^{-\beta}$ with $\beta \sim 0.5$, and is weakly T dependent. These results point to the likely role of rotations in ring-containing polymers.

The electronic relaxation response of semiconducting polymers such as undoped *trans*-polyacetylene[1–8] and amorphous semiconductors such as hydrogenated amorphous silicon (a-Si:H) (Refs. 5 and 9) undergoes profound changes on picosecond or shorter time scales,[1–8] reflecting the dynamic processes in these systems. For example, picosecond time-resolved studies of the midgap photoinduced absorption (PA) associated with photogenerated charged solitons in polyacetylene have revealed both direct photogeneration of charged soliton pairs on a subpicosecond time scale and neutral-to-charged soliton conversion at times of order 20 ps,[8] while picosecond studies of the interband photoinduced bleaching (PB) are explained by the geminate recombination of the photoexcited diffusing solitons.[3] In contrast, the picosecond PA of a-Si:H monitors the dispersive (due to multiple trapping) diffusion-limited transport of electrons in the conduction-band tail to neutral traps dominated by light-induced electronic defects.[9] These rapid transformations of electronic structure have a central role in the development of an understanding of these systems as well as applications in nonlinear-optical and photovoltaic devices.

We report here the picosecond PB of the semiconducting emeraldine base (EB) form of the polyaniline family of polymers. The phenomena observed are characteristically different than those reported earlier either for polyacetylene or a-Si:H. Different dispersive decays of the PB are observed for short times ($t < 4$ ns, T independent) and long times ($t > 1$ ms, weakly T dependent). The variation of PB as $t^{-\beta}$ with $\beta \simeq 0.115$ for 40 ps $< t <$ 4 ns rules out the usual geminate recombination process [$\beta = 0.5$ (Ref. 10)] on this time scale, in contrast to PB in polyacetylene.[4] The T independence of β rules out the role of thermalization of photoinduced carriers via multiple trapping[11] as, for example, in a-Si:H.[9] These results for EB support the central role of exciton formation with subsequent lattice relaxation, pointing to the importance of rotations in ring-containing polymer systems.

The electronic properties of the polyaniline family of polymers can be modified through variation of the number of protons, the number of electrons, or both.[12,13] The insulating EB form of polyaniline (inset of Fig. 1) differs from other earlier studied polymers in the absence of charge-conjugation symmetry and the presence of alternating carbon rings and nitrogen atoms (yielding an "A-B" polymer[14]). The optical absorption at 2 eV in EB, Fig. 1, has been attributed[12,13] to the transition from a primarily benzenoid-ring-based energy level to a quinoid-based energy level. This transition has been suggested to correspond to exciton formation[13] because of the localized nature of the molecular orbital associated

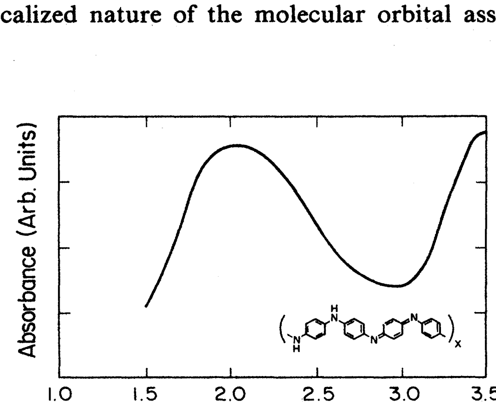

FIG. 1. Optical-absorption spectrum of emeraldine base, showing the large exciton absorption at 2 eV. Inset: The repeat unit of the idealized structure of emeraldine-base polymer.

with the quinoid-based level. The excitonic nature of the 2-eV absorption peak is supported by the unimolecular decay kinetics (the magnitude of the photoinduced bleaching is linearly proportional to the pump-laser intensity) reported in near-steady-state photoinduced-absorption studies.[15,16] Several calculations of the electronic structure of the EB system and its excitations support this picture,[17–19] although it was predicted[17,19] that substantial ring rotations of the quinoid ring with respect to adjacent benzenoid rings distinguish the lowest-energy exciton configuration from the ground-state structure of EB.

The bandwidth of the valence band arising from the benzenoid-ring-based highest occupied energy level[18,19] (the initial state) accounts for the width of the exciton absorption. The relative isolation of the quinoid repeat units results in a localized final state for the 2-eV transition. Occupancy of the final state bleaches the broad 2-eV transition, as expected from a phase-space-filling model.[20]

Samples were prepared using a solution of chemically synthesized EB dissolved in dimethylsulfoxide to cast 0.2- to 0.5-μm-thick films onto either glass or quartz substrates. Samples were studied by optical absorption spectroscopy and by steady-state photoinduced-absorption spectroscopy. Picosecond photoinduced-absorption measurements were made using a dual synchronously pumped, cavity-dumped dye laser system that has been described previously.[21] A pump-probe experiment was performed using time modulation[21] of the probe-beam delay to extract the change in transmission of the probe beam produced by the pump beam. Since neither beam was modulated in intensity, no artifacts due to heating of the sample by the laser beams are introduced by this technique. In addition, measurements of the temperature-dependent transmittance of EB show only very weak thermally induced absorption changes near the 2-eV absorption maximum, ruling out pulsed heating as the origin of the observed $\Delta T/T$. For our experiments, the pump laser was operated at a photon energy of 2.11 eV with an average power of 1.7 mW and was focused to a 100-μm-diam spot on the sample. The probe laser was operated at 2.01 eV with an average power of 0.5 mW and was focused to a 50-μm-diam spot completely contained within the larger pump spot. Both lasers produced ~8 ps long pulses at a repetition rate of 500 KHz. The 10-ps cross correlation of the pump and probe pulses was the limiting factor for the time resolution of the experiment.

A typical decay curve, taken at a substrate temperature of 210 K, is shown in Fig. 2. Data acquired at temperatures between 40 and 300 K were essentially identical. The initial sharp rise of $\Delta T/T$ observed at $t=0$ is resolution limited and is linearly proportional to the pump intensity for the range of pulse energies utilized (1 to 4 nJ). This initial rise is followed by a rapid decay for the first 40 ps and then by a much slower decay for longer times. After 4 ns, roughly half of the exciton population present at 10 ps remain.

During the measurement process, a steady increase in the sample transmittance at ~2 eV was also observed. This effect persisted over tens of minutes without saturation. Simultaneous measurement of the transmittance and the picosecond photoinduced-transmittance change at each time delay allowed the observed decay curve to be corrected for this effect. The change in transmittance grew in time as $t^{0.5}$ when the pump beam was allowed to strike the sample and decayed in time as $t^{-0.5}$ when the pump beam was blocked. The same time dependence was measured for the excitation decay in near-steady-state (~ms) photoinduced bleaching at 1.8 eV.[15,16] This observation suggests that, rather than being an effect due to heating, the slow rise in transmittance results from a buildup of very long-lived excitations in the sample, bleaching the 2-eV transition. Assuming this to be the case, it is possible to calculate the probability for the formation of the long-lived excitons.

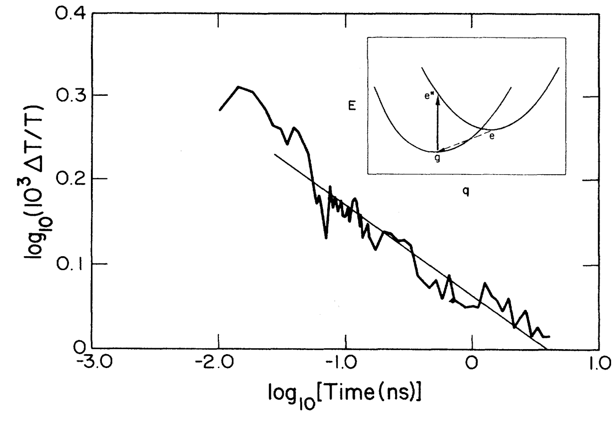

FIG. 2. Log-log plot of the photoinduced bleaching decay at 210 K. Line shown is a fit to $t^{-0.11}$. Inset: Schematic "configuration diagram" for low-lying excitations in emeraldine base. The bold line represents excitations from the ground state g to the excited state e^*. Relaxation of e^* to excited state e likely involves ring rotations. The solid lines represent fast relaxations, while the dashed line indicates a slower relaxation. Not shown are the P^+ and P^- states formed from e^* (see text).

During a typical data run, the value of the transmission was observed to rise by 4% over about ten minutes. Given that the pulse repetition rate was 500 KHz, this implies that each pulse must give rise to long-lived excitations which cause a $\Delta T/T$ of approximately 10^{-10}. This contrasts with the $\Delta T/T \sim 10^{-3}$ observed 10 ps after the pump pulse is absorbed by the sample. Thus, only one excitation in 10^7 present at 10 ps after photoexcitation gives rise to a very long-lived (~minutes) exciton. The buildup of this long-lived component of ΔT does not affect the measurement of the ps time scale decay, as both ΔT and T are measured at each time delay used.

The shape of the measured picosecond decays was found to fit well to a power law of the form $t^{-\beta}$, Fig. 2. The data points beyond $t=40$ ps define a line of slope -0.115. Data for $t<40$ ps show a more rapid decay ($\beta \sim 0.2$). Attempts were also made to fit the decay curves to other functional forms including stretched exponentials,[22] dispersive transport,[11,23] and error functions (one-dimensional diffusion). The only other functional form providing a good fit to the data was $A\exp(-t/\tau_1)+B\exp(-t/\tau_2)+C$, with $\tau_1=30$ ps, $\tau_2=600$ ps, $B/A=0.5$, and $C/A=1.14$. This fit, however, involved four free parameters, while the power-law fit has only one. The presence of a power-law decay for $t>1$ ms suggests a power-law description at short times as well.

Fits on 15 separate exciton time decays, taken at a variety of substrate temperatures, gave a T-independent value for β of 0.113 ± 0.011 for $t>40$ ps. This contrasts greatly with the long-time behavior ($t>1$ ms) (Ref. 15) with chopping frequencies from 4 to 400 Hz, in which β was found to be ~0.5 at 300 K, and ~0.4 at 15 K. This demonstrates that two different exciton recombination processes exist for the two time scales studied, $t<4$ ns and $t>1$ ms.

The origins of the short-time recombination process and long-time decays are of fundamental interest. The absence of $t^{-0.5}$ kinetics for $t>40$ ps demonstrates that the recombination process is substantially different than that predicted[10] for geminate recombination and observed[3] for polymers such as polyacetylene. Separation of all the excited electrons (e) and holes (h) with promotion of the electrons to the π^* conduction band[24] is ruled out by the linear intensity dependence of the near-steady-state and picosecond PB of the 2-eV transition, as well as by the absence of a T dependence of β expected[11] for charge motion of the photoexcited electrons in a disordered conduction band as observed, for example, in a-Si:H.[9] This T independence of the short-time β is in accord with the absence of significant transient photoconductivity in EB.[25] It is noted that some fraction of the initially excited e-h pairs results in formation of separated positive and negative polarons (P^+, P^-); however, the laser intensity, temperature, and temporal dependences of the near-infrared through ultraviolet[15,16] and far-infrared[25,26] features associated with the P^+ and P^- are dramatically different than the corresponding behavior of the 2-eV bleaching. For $t>1$ ms, the P^+ and P^- that were formed have little effect on the observed dynamics of the bleaching of the 2-eV absorption.[15,25,26]

During the excitation process, the Franck-Condon principle is expected to hold, so that the excited state of the system is not initially in its energetically preferred configuration, as shown schematically in the inset of Fig. 2. Relaxation directly from the excited state e^* to the ground state g does not involve lattice relaxation, hence may be rapid and not thermally activated. On the other hand, relaxation from the higher-energy state e^* to the more favored state e is likely to involve coordinated ring rotations that require the presence of free volume sufficient to allow rotation. Decay from the state e back to the ground state g will require thermal activation of free volume for rotation. The reported temperature dependence of long-time photoinduced polaron decays[25,26] and nuclear magnetic resonance studies of the temperature dependence of ring-flipping processes[27] in emeraldine support this view. Hence, the long-lived excitations which bleach the 2-eV transition are likely to be exciton states stabilized by ring rotations.[17]

The EB form of polyaniline has substantial amorphous content, with no more than 50% crystallinity (and x-ray coherence lengths less than, or of order, 100 Å within the "crystalline" regions).[28] The disorder present in the polymer is expected to lead to variations in free volume activation energies (i.e., a distribution of waiting times for recombination) and in overlap integrals and site energies (i.e., a distribution of spatial properties) that is the likely origin of the difference in the recombination rates at short and long times. The direct e^* to g relaxation likely corresponds to the more rapid decays that occur for $t<40$ ps. Relaxation from sites within EB where the local chain configuration leads to a very low energy barrier between e and the g manifold of states are suggested to correspond to the nearly T independent $\beta\simeq0.11$ relaxation observed for 40 ps $<t<4$ ns. In contrast, weak-T behavior with $\beta\simeq0.5$ for $10^{-3}<t<1$ s (Ref. 15) may correspond to states e with a larger barrier to the g manifold, while the strongly T dependent, very long time recovery ($t>10$ s) (Refs. 25 and 26) may be due to much larger barriers for recovery from the excited state. The latter relaxation then requires coordinated molecular motion[27] for ring rotations to occur. These ring-rotation processes are also expected to play an important role in the dynamics of the polarons formed in polyaniline.[25,26,29] It is noted that charge recombination within the exciton without concomitant ring relaxation to the ground-state configuration may lead to the formation of neutral defects or "conformons" that can contribute to the very-long-time bleaching of the exciton transition. In addition, proton T_1 studies of polycarbonate[30] provide evidence for a broad range of relaxation rates in other amorphous, ring-containing systems.

In summary, measurements of the photoinduced bleaching in EB contrast with results for earlier studied systems. These data indicate the existence of two distinct decay mechanisms for the recombination of photoexcited excitons in emeraldine base. It is suggested that the long-lived excitations are stabilized by ring rotations and constraints that prevent ring relaxation to the initial conformation.

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