Evolution of Excitons and Polarons in Polythiophene from Femtoseconds to Milliseconds

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We have studied the photoexcitation dynamics in electrochemically polymerized polythiophene thin films using transient photomodulation spectroscopy measured from 100 fs to 20 ms in the spectral range from 0.25 to 2.2 eV, and by the novel technique of absorption-detected magnetic resonance (ADMR). Our results show that photogenerated exciton polarons are formed within 300 fs; they subsequently decay in the nanosecond time domain by 1D diffusion toward recombination centers. The dominant excitations after about 250 ns are charged polarons and bipolarons, which are identified by optical transitions correlated with a spin-$\frac{1}{2}$ ADMR signal at $g \simeq 2.003$.

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The recently developed theoretical picture of electronic excitations in conducting polymers has created a great deal of interest both experimentally and theoretically [1]. In this elegant picture, electronic photoexcitations across the Peierls-Hubbard gap are entirely different from the photoinduced electron-hole (*e-h*) pairs of conventional semiconductors. Instead, the proper description of the intrachain photogenerated quasiparticles in *trans*-$(\mathrm{CH})_x$ is given in terms of separated charged soliton ($S^{\mp}$) pairs [2], whereas in most polymers with nondegenerate ground states (NDGS), polaron excitons are formed due to the intrinsic confinement of the polymer backbone structure [3]. Interchain photoexcitations, however, may form separated charged polarons in both types of polymers [1,2].

The experimental studies of photoexcited polymers, however, have revealed several unexpected phenomena that were not predicted by the conventional theoretical models. First, neutral soliton ($S^0\bar{S}^0$) pairs as well as $S^+\bar{S}^-$ pairs are generated in *trans*-$(\mathrm{CH})_x$, both with high quantum efficiency [4]. Second, electroluminescence (EL) with quite high quantum yield has been observed in poly(phenylene vinylene), a member of NDGS-type polymers, when polarons are injected at the opposite electrodes [5]; surprisingly, it was found that the EL and the photoluminescence (PL) spectra are the same. Third, a fast photoconductive (PC) response has been measured in polythiophene [6], a second member of the NDGS-type polymers, with a PC magnitude comparable to that in *t*-$(\mathrm{CH})_x$. In addition, several magneto-optics measurements have shown [7,8] that triplet as well as singlet excitons play important roles as photoexcitations in NDGS polymers. These studies have therefore shown that the photophysics of conducting polymers is far richer than what was originally thought [1-3].

In this paper we present quite a complete study of the photoexcitation evolution in polythiophene, one of the simplest members of the class of NDGS polymers. This has been achieved by transient photomodulation (PM) spectroscopy spanning the time interval from 100 fs to 20 ms in the spectral range from 0.25 to 2.2 eV, by transient PL, and also by the novel technique [8] of absorption-detected magnetic resonance (ADMR).

The spectral evolution of the excited states in the picosecond time domain was studied by the pump-and-probe correlation technique using two dye lasers synchronously pumped by a frequency-doubled mode-locked Nd:YAG laser at a repetition rate of 76 MHz, and by a streak camera with 10-ps resolution for the PL transient. The dye laser system had a pump-probe cross correlation of about 5 ps. Transient spectra of photoinduced changes ΔT in transmission T were obtained by fixing the pump wavelength at 580 nm (2.14 eV) and varying the probe wavelength between 1.2 and 2.1 eV with a sensitivity in $\Delta T/T$ of 3×10^{-6}. For the PM measurements in the femtosecond time domain we used a colliding-pulse mode-locked (CPM) dye laser with 60-fs pulse duration at 620 nm (2 eV). In the time interval between 250 ns and 20 ms the pump beam was a frequency-doubled Q-switched Nd:YAG laser with 20 pulses/s, 10 ns pulse duration, and 100 μJ energy per pulse. The probe beam was derived from an incandescent lamp that was spectrally resolved by a set of interference filters in the spectral range between 0.2 and 1.9 eV. In this case $\Delta T(t)$ was measured by a set of fast detectors with matched preamplifiers and a signal averager; $\Delta T/T$ of 10^{-6} could be easily measured. The initial photoexcitation density $N(0)$ in the transient experiments was about 10^{18} cm^{-3}.

In the ADMR technique [8] a cw pump beam (from an Ar$^+$ laser) and a probe beam (from a tungsten lamp) constantly illuminate the sample, which is mounted in a high-Q microwave cavity (at 3 GHz) equipped with optical windows and a superconducting magnet producing a field H. Microwave resonant absorption, modulated at 500 Hz, leads to small changes δT in the probe transmission T proportional to δn, the change in the photoexcitation density n produced by the pump. δn is induced by transitions in the microwave range that change spin-dependent recombination rates. Two types of ADMR spectra were obtained [8]: the P-ADMR spectrum in which δT is measured at a fixed probe wavelength λ while sweeping H, and the H-ADMR spectrum, in which δT is measured at a constant H, in resonance, while λ(probe) is changed. With suitable signal averaging, the system $\delta T/T$ sensitivity was 3×10^{-8} in the visible to near-ir range and 3×10^{-7} in the mid-ir spectral range.

The polythiophene (PT) samples were thin films (thickness of about 1500 Å) electrochemically polymerized on sapphire substrates.

The transient PM spectrum obtained with the synchronously pumped system at $t=0$ is shown in Fig. 1. We observe a broad photoinduced absorption (PA) band that changes into photobleaching (PB) at 2.05 eV. The PA band is generated with high quantum efficiency according to our estimate of the density of absorbed photons. Using the CPM laser we found (Fig. 1, lower inset) that the PA band is formed within 300 fs following the initial PB. This was determined by fitting the data shown by a convolution of the pulse autocorrelation function with a response function of the form $1-e^{-t/\tau}$, where τ ($=310$ fs) is the formation time. The value of τ is consistent with the characteristic relaxation time of the lattice for a polaron, $\tau_r \simeq \xi/v_s$, where ξ is the spatial extent of a polaron in PT ($\xi \approx 20$ Å [9]) and v_s is the sound velocity along the chain ($v_s \simeq 100$ Å/ps as inferred from measurements on unoriented films [10]). Therefore, we interpret this initial decay process as self-trapping of the photoexcited free carriers [11].

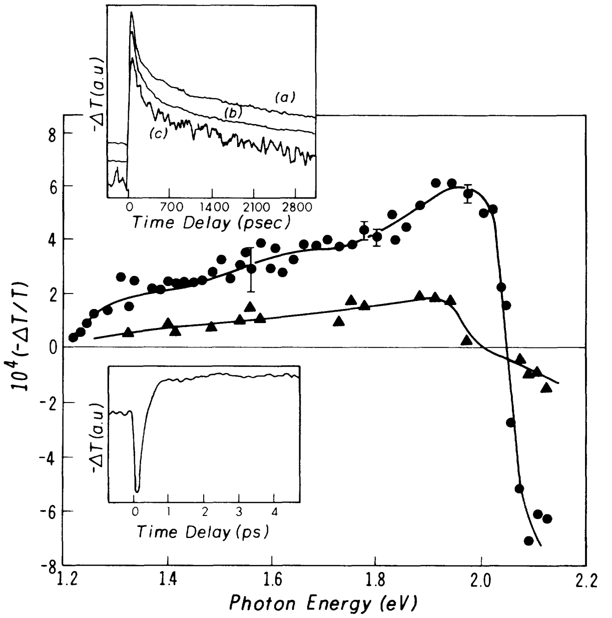

FIG. 1. Room-temperature picosecond PM spectrum of electrochemically polymerized polythiophene film at $t=0$ (circles) and $t=400$ ps (triangles), measured with two synchronously pumped dye lasers with 5-ps resolution, with the pump excitation fixed at 2.14 eV. The lower inset shows the PA signal of the PT film obtained with a CPM laser with 60-fs pulse duration, where the pump and probe are at 2 eV. The upper inset compares the decay dynamics at 1.7 eV excited with full power at (a) 300 K and (b) 80 K, and (c) at a power reduced by a factor of 50 at 80 K.

The PA spectrum of the self-trapped species remains essentially unchanged up to 3 ns. For example, the spectrum at 400 ps is compared to that at $t=0$ in Fig. 1. The small redshift of the peak at longer times is an artifact due to a strain-induced oscillation in $\Delta T(t)$ that tends to add a bleaching component to the main electronic response, particularly where $\partial\alpha/\partial\omega$ (α is the absorption coefficient and ω is the probe frequency) is large [10]. We infer from the overall intransigence of the spectrum that the dominant photoexcitations at 3 ns are the same as those generated at 300 fs.

The dynamics of the PA and PL from 10 ps to 3 ns is shown in Fig. 2. The decays are nonexponential, and up to about 40 ps the PL signal is close to the derivative of PA [PL$\sim d$(PA)$/dt$]. This indicates that at short time the PA and PL share the same origin since PA$\sim N(t)$ and PL$\sim dN/dt$. From this and the similarity of the broad PA spectrum (Fig. 1) to that of polydiacetylene (PDA), in which self-trapped excitons were identified [11,12], we conjecture that the dominant photoexcitations in the ps to ns time ranges are self-trapped (polaronic) excitons. After 40 ps, when the separation between polarons increases, the recombination dynamics substantially changes and becomes predominantly nonradiative (Fig. 2).

The geminate nature of the exciton dynamics in the nanosecond time domain is illustrated in Fig. 1 (upper inset). The PA decay does not change when we decrease the photoexcitation density by a factor of 50. Moreover the PA signal at short time depends linearly on the exci-

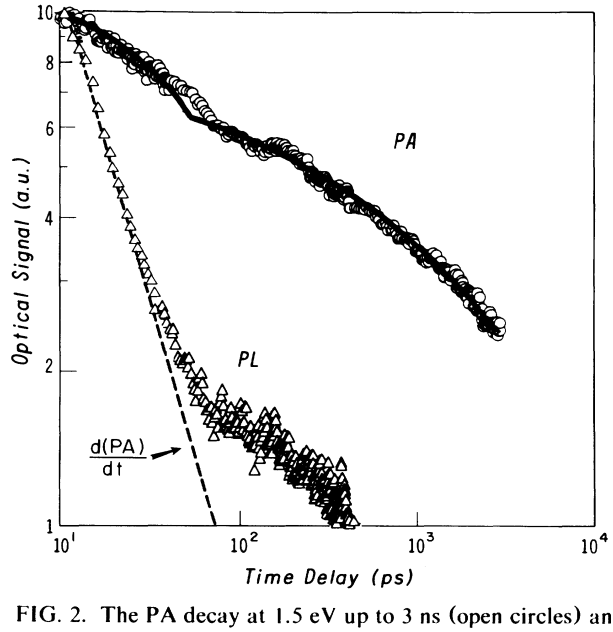

FIG. 2. The PA decay at 1.5 eV up to 3 ns (open circles) and PL decay at 1.9 eV up to 400 ps (open triangles). The full line is a theoretical fit to the PA data using Eq. (1); the broken line is the derivative d(PA)$/dt$ of a fit to the PA transient.

tation intensity (I_L) and its relaxation kinetics remains unchanged with I_L. Although the physical origin of the slow PA decay is not clear, the time independence of the PA spectrum up to 3 ns indicates that it is not due to a distribution of localized energy levels, such as traps, as may be the case for the PA in amorphous semiconductors [13]. Also the weak temperature dependence that we observed (Fig. 1, upper inset) does not fit a mechanism of multiple trapping [13]. Instead, we consider that the photogenerated excitons recombine upon diffusing to the boundaries of the conjugated chain segments. Such recombination centers might consist of 3D distortions [12] such as torsions between rings. The survival probability $S(t)$ of excitons diffusing in 1D among randomly distributed recombination centers is given asymptotically by [14]

$$S(t) \sim \begin{cases} 1-4c\left[\dfrac{Dt}{\pi}\right]^{1/2}, & t \ll \dfrac{1}{\pi^2 D c^2}, \\ \exp(-t/\tau)^{1/3}, & t \gg \dfrac{1}{\pi^2 D c^2}, \end{cases} \tag{1}$$

where $\tau = [(\frac{3}{2})^3 2\pi^2 c^2 D]^{-1}$, c is the density of the centers, and D is the diffusion coefficient. We have already shown that the stretched exponential correctly describes exciton recombination in another NDGS polymer, PDA-4BCMU, at high pressure [12]. In PT, diffusion apparently dominates the decay even at ambient pressure, giving rise to a much slower relaxation than that in PDA. For $t > 50$ ps, the stretched exponential of Eq. (1), with $\tau \approx 1.2$ ns, actually provides a good approximation to $\Delta T(t)$, as seen in Fig. 2. For $D \approx 10^{-2}$ cm^2/s, we find $1/c \approx 3000$ Å. For $t < 50$ ps, our fit to the short-time asymptote of Eq. (1) gives $1/c \simeq 350$ Å. The discrepancy between these two values may result either from a bimodal distribution of conjugation lengths, as has been conjectured for polyacetylene [15], in which case the PA would be probing primarily excitations on short chains at short times, and those on long chains at long times, or from a failure of the diffusion model, which treats the excitations as point particles, to accurately describe extended excitations on short segments.

In Fig. 3(a) we show the transient PM spectra from 0.25 to 1.9 eV at 1 μs, 100 μs, and 10 ms following the 10-ns pulsed excitation at 80 K. We see that within the spectral range of the ps measurements (1.2 to 2.2 eV, Fig. 1) there are now two PA bands observed, one at 1.35 eV (ω_2) and the other at 1.8 eV (HE); a third PA band (ω_1) is also seen at 0.5 eV. These PA bands appear as early as 250 ns. It is clear that the HE band decays much faster than the bands ω_1 and ω_2 which, however, decay together. The dynamics of HE [Fig. 3(b)] from less than 250 ns to 20 ms at 220 K follows $\exp(-t/\tau)^{0.2}$, where $\tau \approx 10$ μs, which is much slower than the dynamics of the ps PA. The small exponent and the large value of τ suggest that the PA dynamics after 250 ns cannot be due to a 1D trapping process. The narrowest of the HE band and its lower energy with respect to the PA band in Fig. 1 also indicate that the dominant photoexcited species in this time range are different from the majority of the initial excitations. From the similarity of our PM spectrum to that of voltage-modulated transmission due to charge injection in PT [5], we tentatively associate the HE with charged polarons $P^{\mp}$.

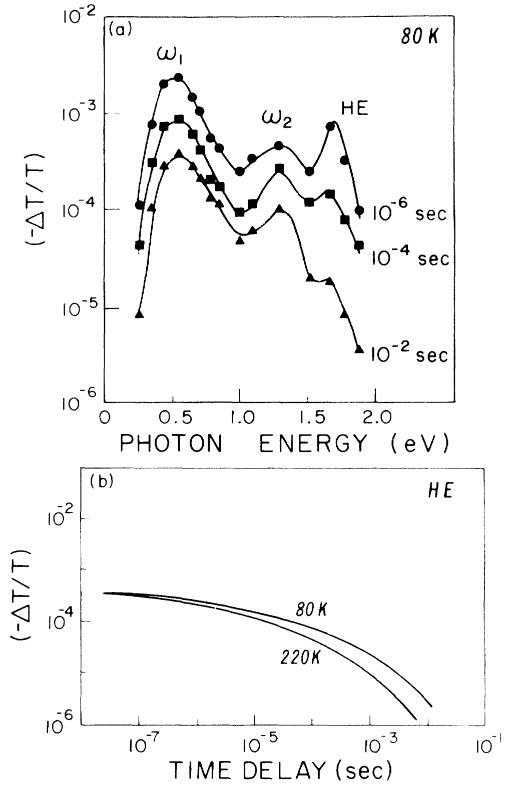

FIG. 3. (a) Transient PM spectra from 250 ns to 20 ms at 1 μs, 100 μs, and 10 ms at 80 K; the three PA bands at 0.5, 1.35, and 1.8 eV are identified in the text. (b) Time decay of the HE band at 80 and 220 K.

We have also measured the cw PM spectrum of the same PT films at 80 K and 500 Hz modulation, as shown in Fig. 4. The cw PM spectrum is quite similar to the transient PM spectra in Fig. 3(a) for times between 10^{-4} and 10^{-2}, showing the same three PA bands below the gap. Moreover, by measuring their dependencies on modulation frequency f we have found that the HE band decays slower with f than ω_1 and ω_2, consistent with its shorter lifetime in the transient spectra (Fig. 3). The bands ω_1 and ω_2, however, vary together identically with f, pump intensity, and pump wavelength. Additionally, in light of their similarity with the subgap absorption bands formed in PT films upon moderately high doping [16], we associate these PA bands with bipolarons ($BP^{2\mp}$) [1,3].

The identification of the HE PA band with polarons is verified by ADMR, as shown in Fig. 4 by the H-ADMR spectrum at 1065 G and the P-ADMR spectrum at ω_2

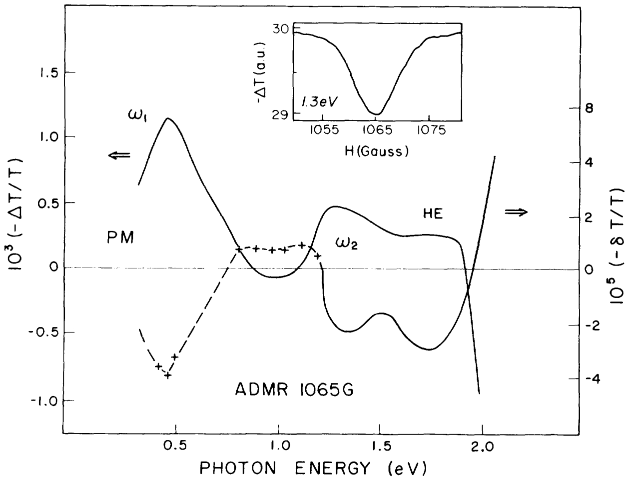

FIG. 4. PM (full line) and P-ADMR (full and dashed line) spectrum at 1065 G of PT at 4 K: The dashed-line part of the ADMR is a guide to the eye, whereas the full-line part was continuously measured. The inset shows the H-ADMR spectrum at 1.3 eV (ω_2 PA band).

(1.3 eV), shown in the inset. We note that the ADMR signal is negative, showing a decrease in the photoexcitation density induced by microwave absorption. We also measured the spin-dependent photoluminescence (ODMR) spectrum of the same PT films under identical experimental conditions. The ODMR signal is positive (more PL) showing enhanced microwave-induced recombination [7]. Both spin-dependent spectra show an asymmetric band at 1065 G ($g \simeq 2.003$). Since we were unable to find in ADMR another resonance at $g \simeq 4$ due to triplets [7,8], we conclude that the ADMR signal is due to spin-$\frac{1}{2}$ excitations.

The P-ADMR spectrum at 1065 G (Fig. 4) contains the same three bands as in the PM spectrum, but with different intensities. The relative microwave-induced changes in the photoexcitation density $\delta n/n$ is -3×10^{-2} for both BP bands ω_1 and ω_2, whereas $\delta n/n$ is -7×10^{-2} for the polaron band at HE. Recent careful light-induced ESR (LESR) studies of PT showed conclusively [17] that spin-$\frac{1}{2}$ charged species are photogenerated in the polymer chains. It was then speculated that the LESR signal is due to photogenerated polarons [16,17]; our ADMR results provide experimental proof and verify that the HE band is due to charged polarons. In fact the ADMR shows that this band is due to spin-$\frac{1}{2}$ photoexcitations that are correlated with BP, since the HE and the BP bands have the same H-SDPM spectrum and the same dependencies on the microwave modulation frequency and on the laser excitation intensity. We identify, therefore, the HE band with the optical transition between the localized polaron levels in the gap [3,5].

The polaron-enhanced recombination in ADMR can be explained by the distant-pair-recombination model [7]. In this process, for times shorter than the spin-lattice relaxation, there are more polaron pairs with parallel spins than those with antiparallel spins, due to the faster recombination rate of the latter. Saturated microwave absorption with $\Delta m_s = \pm 1$ leads to a randomization of the spins, thereby increasing the density of the pairs with antiparallel spins, which consequently enhances recombination. This leads to a reduction in the polaron density ($\delta n < 0$), causing a decrease in the BP density and an increase in PL (ODMR > 0). That $\delta n/n(P) \simeq 2\delta n/n(\mathrm{BP})$ shows that BP production ($P^{\mp} + P^{\mp} \rightarrow \mathrm{BP}^{2\mp}$) is only one of two channels of recombination of polaron pairs with antiparallel spins, the other channel being direct recombination to the ground state for polaron pairs with opposite charges ($P^{+} + P^{-} \rightarrow$ ground state).

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