Picosecond Photoinduced Dichroism in *Trans*-$(CH)_x$: Direct Measurement of Soliton Diffusion

Z. Vardeny[(a)] and J. Strait
Division of Engineering and Department of Physics, Brown University, Providence, Rhode Island 02912

and

D. Moses, T.-C. Chung, and A.J. Heeger
Institute for Polymers and Organic Solids, University of California at Santa Barbara,
Santa Barbara, California 93106

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Photoinduced dichroism caused by bleaching of the interband transition in *trans*-$(CH)_x$ was observed in the picosecond time domain. The bleaching is induced instantaneously and decays with time as $t^{-1/2}$, changing to a lower power after ~50 psec. Although the photoinduced bleaching persists to long times, polarization memory is lost after ~10^{-9} sec. The results provide a measurement of the diffusion constant of the charged excitations; $D \simeq 2\times10^{-2}$ cm^2 sec^{-1} at 300 and 80 K.

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Soliton-antisoliton (S-$\bar{S}$) pairs can be generated in *trans*-$(CH)_x$ either by charge-transfer doping or by photoexcitation. Dynamical calculations which follow the time evolution of a $(CH)_x$ chain after injection of an electron-hole (e-h) pair have been carried out by Su and Schrieffer.[1] They found that the photoinjected e-h pair evolves to S-$\bar{S}$ in a time of the order of ~10^{-13} sec. Because of e-h symmetry, the formation of a soliton causes the formation of a localized electronic state at midgap.[2] The resulting soliton can be neutral with spin $\frac{1}{2}$ or charged + or − with spin 0.

Initial confirmation of these ideas came from photoexcitation experiments.[3,4] The photoproduction of S-$\bar{S}$ pairs implies the photogeneration of states in the gap, as observed experimentally.[5,6] The reversed spin-charge relation is consistent with the results of ESR experiments[7] which demonstrated that the quantum efficiency (QE) for photoproduction of spins is below the QE for photoproduction of charge carriers. Therefore, the photogenerated charge carriers are spinless and are identified as charged S-$\bar{S}$ pairs.

In this study, we investigate the time evolution of the photoexcited carriers in the picosecond time domain by using the pump and probe technique (both polarized) with subpicosecond resolution. We find photoinduced bleaching ($\Delta\alpha < 0$) in the interband transition region at 2 eV. The bleaching is generated instantaneously and decays with time as $t^{-1/2}$ followed by a slower decay. We observe photoinduced dichroism for the first time in a macroscopically isotropic solid, $\Delta\alpha_\parallel \neq \Delta\alpha_\perp$, where $\parallel$ and $\perp$ refer to the polarization of the probe being parallel or perpendicular, respectively, to that of the pump. This photoinduced anisotropy is lost in the nanosecond time range. The polarization memory results from the photogeneration of localized states in regions of the polymer where the $(CH)_x$ chains are parallel to the pumping polarization. The eventual loss of photoinduced anisotropy at later times results from diffusion of the solitons over sufficiently large distances (~10^3 Å) that the excited $(CH)_x$ chains are random with respect to the pump polarization. This effect directly measures the diffusion coefficient; $D \simeq 2\times10^{-2}$ cm^2 sec^{-1} at 300 and 80 K.

The picosecond pump and probe measurements were done in the time domain 0.2 psec $< t <$ 1.5 nsec. For $t > 1$ psec, we used a cavity-dumped passively mode-locked dye laser[8] delivering 0.7-psec-duration pulses, linearly polarized, at $\hbar\omega = 2$ eV, 2 nJ per pulse, and repetition rate of 5×10^5 sec^{-1}. For $t < 1$ psec, we used a different configuration (a ring laser) that delivers 0.2-psec-duration pulses (0.3 nJ) with 80 mHz repetition rate.[9] The probe beam was delayed mechanically and then passed through a polarization rotator which set its polarization at 45° with respect to that of the pump. A polarizer was used on the transmitted probe beam to analyze $\Delta\alpha$ both for parallel and perpendicular polarization.[10] The pump and probe beams (beam diameter ~40 μm) were carefully adjusted to maintain complete spatial overlap on the sample.[11] The samples were semitransparent films (~0.1 μm thick) on glass or sapphire, initially polymerized as *cis*-$(CH)_x$ and subsequently isomerized to *trans*-$(CH)_x$. Taking into account losses in the light path and reflection losses at the sample, the photogenerated carrier density per 2-nJ pulse (assuming a QE of unity) is 3×10^{18} cm^{-3}.

The photoinduced $\Delta\alpha(\tau)$ produced with the ring laser for parallel and perpendicular polarizations at 300 K is shown up to 4 psec in Fig. 1 ($\Delta\alpha\sim\Delta T/T$, where T is the transmission and ΔT is the photoinduced change). At 300 K and at 80 K, $\Delta T/T\simeq4\times10^{-4}$. The bleaching is induced instantaneously; i.e., $<2\times10^{-13}$ sec. Moreover, the initial decay in $\Delta\alpha$ is extremely fast; by 2×10^{-13} sec, decay is evident. Since the films are macroscopically isotropic, the most unusual feature is that $\Delta\alpha_{\parallel}\neq\Delta\alpha_{\perp}$. The ratio, $\rho=\Delta\alpha_{\perp}/\Delta\alpha_{\parallel}$, at $t\simeq t_p$ is $\rho\simeq0.5$, with little change in the picosecond time range.

Electron microscopy studies[12] of thin $(\mathrm{CH})_x$ films indicate that the fibrils lie predominantly in the plane. For such a polycrystalline *uniaxial* material, the initial polarization ratio, $\rho(0)$, should be $\frac{1}{3}$.[10,11] With *trans*-$(\mathrm{CH})_x$ we observed $\rho(0)\simeq0.5$ even for times shorter than 1 psec. The higher value arises from a combination of incomplete crystallinity (amorphous regions) and deviations from completely uniaxial behavior even in the crystalline regions. With neglect of the latter, an amorphous fraction $f=0.33$ would raise $\rho(0)$ to 0.5. Although analysis of x-ray scattering data from stretch-oriented free-standing films yields[13] $f\simeq0.2$, the short polymerization time (~ 1 sec) for the thin semitransparent films may lead to a somewhat higher value for f.

In a traditional semiconductor, the photoexcited carriers are delocalized and consequently lose polarization memory in times[14] as short as 10^{-14} sec. Even in amorphous silicon,[10] where the band-edge states are localized, photoinduced anisotropy is not observed. Our observations in *trans*-$(\mathrm{CH})_x$ therefore imply that the electronic structure is quasi-one-dimensional and that localization of the photoexcited carriers takes place extremely rapidly. This is consistent with S-$\bar{S}$ pair production.[1] Moreover, since these localized photoexcitations are spinless,[7] we identify them as S-$\bar{S}$ pairs.

In Fig. 2 we plot $\Delta\alpha_{\parallel}(\tau)$, $\Delta\alpha_{\perp}(\tau)$, and $\Delta\alpha=\Delta\alpha_{\parallel}+\Delta\alpha_{\perp}$ from 1 psec to 1.5 nsec. The data indicate the existence of a slow depolarization process; $\Delta\alpha_{\parallel}$ gradually approaches $\Delta\alpha_{\perp}$ (at 1.5 nsec, $\rho\simeq1$). The curve $\Delta\alpha(t)$ shows the true decay, not influenced by polarization-memory relaxation. At 300 K, $\Delta\alpha(t)$ decays as $t^{-1/2}$ up to about 50 psec and then slows to $t^{-0.37}$. At 80 K, the $t^{-1/2}$ behavior extends only to 12 psec and then slows to $t^{-0.25}$. The relative response, $\Delta\alpha(1500\text{ psec})/\Delta\alpha(1\text{ psec})$, is 5.7×10^{-2} (80 K) and 3.8×10^{-2} (300 K).

The initial, more rapid decay of $\Delta\alpha$ may be due to geminate recombination of S-$\bar{S}$ (or e-h) pairs. However, attempts to influence the decay with electric fields up to 5×10^{4} V cm^{-1} were unsuccessful (at 300 and at 80 K). Moreover, the slower decay at 80 K (which results in a higher steady-state QE at lower temperatures) is in disagreement with geminate recombination.[15]

Mele[16] has extended the dynamical calculations to include e-h pair injection well away from the band edges. He finds that simultaneous relaxation of the injected carriers toward the band edge plus the onset of distortions which lead to soliton

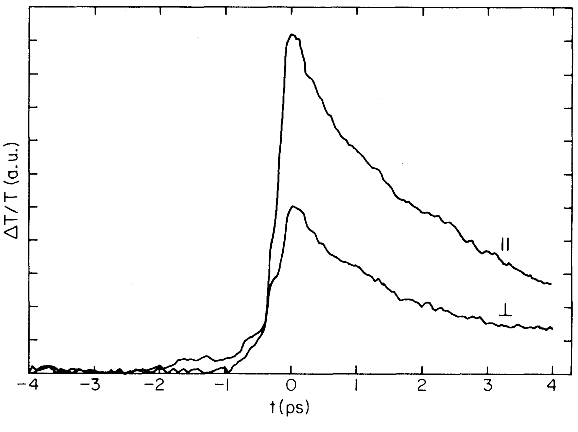

FIG. 1. Time dependence of the photoinduced bleaching in *trans*-$(\mathrm{CH})_x$ for parallel and perpendicular polarization at 300 K.

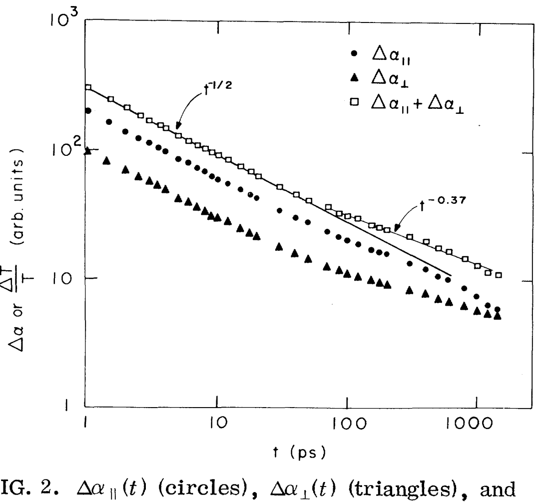

FIG. 2. $\Delta\alpha_{\parallel}(t)$ (circles), $\Delta\alpha_{\perp}(t)$ (triangles), and $\Delta\alpha(t)=\Delta\alpha_{\parallel}+\Delta\alpha_{\perp}$ (squares) at 300 K.

formation expands the time scale beyond the 10^{-13} sec obtained for band-edge injection.[1] Thus, the initial $t^{-1/2}$ decay may be providing direct information on the short-time evolution of the photoexcited carriers into S-$\bar{S}$ pairs.

Defining the degree of polarization as $P(t) = (\Delta\alpha_{\parallel} - \Delta\alpha_{\perp})/(\Delta\alpha_{\parallel} + \Delta\alpha_{\perp})$, we eliminate the natural decay of both $\Delta\alpha_{\parallel}$ and $\Delta\alpha_{\perp}$. A semilog plot of $P(t)$ is shown in the inset to Fig. 3. The induced polarization decays with a time constant of about 1200 psec. Note, however, that as demonstrated in Fig. 3, the photoinduced bleaching signal persists out to longer times,[5] implying a relatively long lifetime for the photoexcitations.

The recovery of induced dichroism after picosecond laser pulses has been studied in liquids and gases.[17] In a fluid, the anisotropic orientational distribution created by an intense linearly polarized picosecond pulse transforms to an isotropic one via the rotational motion of the molecules. At high concentrations the anisotropy can decay also by intermolecular energy transfer between molecules of differing orientations.

In *trans*-$(\mathrm{CH})_x$ the optical absorption is anisotropic as a result of the quasi-one-dimensional electronic structure.[18] After photoexcitation of a soliton on a $(\mathrm{CH})_x$ chain, the interband absorption remains uniaxial; thus we expect that only the component of the optical electric field parallel to the local chain direction will be effective in pumping. Consequently, initially after the pump $|\Delta\alpha_{\parallel}| > |\Delta\alpha_{\perp}|$. Since the $(\mathrm{CH})_x$ chains are parallel to one another within a given fibril[20] and oriented parallel to the fibril axis,[20] interchain excitation transfer within a fibril will not lead to polarization decay. The loss of polarization memory occurs, therefore, by diffusion of the photogenerated solitons along the fibrils over distances sufficiently great that the fibril direction has rotated by $\pi/4$. Since electron microscopy has characterized such distances as typically $\sim 10^3$ Å, the corresponding diffusion constants must be relatively large.

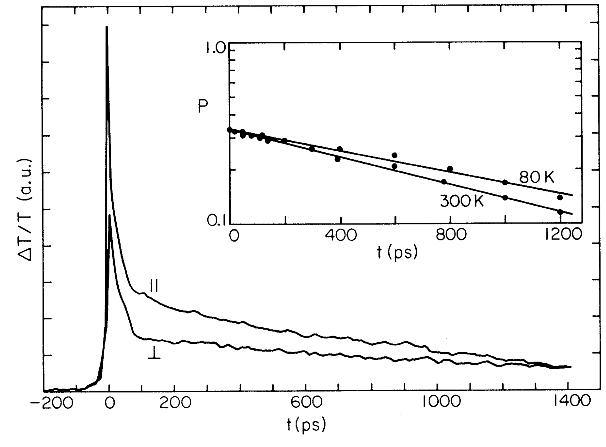

FIG. 3. $\Delta T/T$ at 300 K for $0 < t < 1400$ psec, showing the decay of polarization memory. The inset is a semilog plot of $P(t)$ at 300 and 80 K.

We assume that, at time t, the soliton arrives through diffusion to a position in the fibril forming an angle φ with respect to its initial position. Geometrically, $\varphi(t) = L(t)/R$, where $L(t)$ is the diffusion length, $L(t) = (2Dt)^{1/2}$, and R is the radius of curvature of the fibril. Averaging over all fibril orientations with respect to the pump polarization in a planar geometry, one obtains $P(\varphi) = \frac{1}{2}\cos(2\varphi)$. Averaging over the random diffusive motion yields $\langle P(\varphi)\rangle = \frac{1}{2}\langle\cos 2\varphi\rangle = \frac{1}{2}\exp(-2\langle\varphi^2\rangle)$. Thus,

$$P(t) = P(0)\exp(-4Dt/R^2). \qquad (1)$$

Best fits to the data (see Fig. 3) yield $D/R^2 = 2.2 \times 10^8$ sec^{-1} at 300 K and $D/R^2 = 1.7 \times 10^8$ sec^{-1} at 80 K. Taking $R \simeq 10^3$ Å, $D(300\ \mathrm{K}) = 2.2 \times 10^{-2}$ cm^2 sec^{-1} and $D(80\ \mathrm{K}) = 1.7 \times 10^{-2}$ cm^2 sec^{-1}.

Kivelson[21] described the diffusion of charged solitons in *trans*-$(\mathrm{CH})_x$ in terms of intersoliton electron hopping among the localized midgap states. The interchain diffusion of photogenerated solitons over large distances may be limited by a similar mechanism. In this case, however, since the charged solitons are not bound (to ions), phonon-assisted hopping would be less important implying a weaker temperature dependence, similar to that of neutral solitons. The values quoted above for D are, in fact, comparable to those obtained for neutral solitons from magnetic measurements.[22]

In conclusion, we found that the band-to-band transition in *trans*-$(\mathrm{CH})_x$ is bleached instantaneously within our resolution of 0.2 psec, in agreement with S-$\bar{S}$ pair production. Analysis of the decay of the photoinduced anisotropy indicates soliton diffusion over distances $\simeq 10^3$ Å with diffusion coefficient of about 0.02 cm^2 sec^{-1}.

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[a] Permanent address: Physics Department, Technion, Haifa, Israel.

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Picosecond Dynamics of Photoexcited Gap States in Polyacetylene

C. V. Shank, R. Yen, and R. L. Fork
Bell Telephone Laboratories, Holmdel, New Jersey 07733

and

J. Orenstein and G. L. Baker
Bell Telephone Laboratories, Murray Hill, New Jersey 07974

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The time dependence of photoinduced optical absorption in the prototype one-dimensional semiconductor, polyacetylene, is investigated with femtosecond resolution. It is found that the induced absorption appears in less than 150 fsec. The dynamics of the absorption decay are measured and compared with a model based on geminate recombination on a one-dimensional chain.

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The optical properties of photoexcited polyacetylene have revealed a wealth of important information about the electronic states of this prototype one-dimensional (1D) semiconductor.[1-4] Recently, Orenstein and Baker[4] have reported measurements of the photoinduced absorption spectrum of polyacetylene at delay times of 10 μsec or greater following excitation. In this paper we investigate the dynamics of the photoinduced absorption with 0.1 psec resolution.

Advances in short-pulse optical measurement techniques have pushed our ability to make optical measurements into the femtosecond (10^{-15} sec) time domain.[5] In our experiments we used the newly developed colliding-pulse mode-locked dye laser[6] to produce 70-fsec optical pulses at 2.0