ULTRAFAST ELECTRONIC AND ACOUSTIC EFFECTS IN CONDUCTING POLYMERS

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The polarized picosecond pump and probe technique with 50 fsec resolution has been used to generate and detect electronic excitations and propagation of ultrasonic phonons in thin films of oriented and unoriented polyacetylene and polythiophene. We found that the photoexcitations are instantaneously generated followed by a power law decay, which is interpreted as fast geminate recombination; only up to about 2% of the intrachain carriers are able to escape fast recombination.

The photoinduced ultrasonic vibrations are generated by the photoinduced thermal stress associated with the heating of the thin abosrption layer by the pump pulse. We have used this phenomenon to measure the sound velocity and ultrasonic attenuation for phonons in the frequency range of 5 to 200 GHz in trans and cis-rich polyacetylene and polythiophene.

INTRODUCTION

It has been proposed by Su and Schrieffer (1) and consequently by Ball, Su and Schrieffer (2) that a photogenerated electron-hole pair in tran-$(CH)_x$ is unstable towards the formation of charged soliton-antisoliton (s^+-s^-) pair and that the evolution into s^+s^- takes less than 0.1 second. The topological soliton is unique to trans-$(CH)_x$ in that it separates the two degenerate ground-state structures of the trans isomer (3). However, it is but one of a family of self-localized carriers which play a central role in the photophysis of quasi 1D semiconductors (4). Of particular interest is the lower ground state symmetry cis-$(CH)_x$ isomer, in which photoexcitation is thought to give rise to a confined s-$\bar{s}$ pair (5,6). The ultrafast response in cis-$(CH)_x$ is complicated however, because the existence of segments of trans isomer in the sample (7). A better candidate therefore for investigating the ultrafast carriers response in a non-degenerate ground state polymer is polythiophene (PTO):$(C_8H_4S_2)_x$. It is highly crystalline with a simple backbone geometry (8) similar to that of cis-$(CH)_x$ but stabilized in that structure by the sulfur atoms.

EXPERIMENTAL

The experimental method we have used is the polarized picosecond pump and probe technique. The laser beam is divided into pump (95%) and probe (5%) beams. The pump pulse induced changes ΔT in the transmission T which are monitored by the probe pulse as a function of the mechanically adjusted delay time between pump and probe. We have used a passively modelocked colliding-pulse ring dye laser with a photon energy of 2 eV, and a sync pump laser with varying wave length. The repetition rates of the lasers were 110 MHz and 80 MHz and the pump beam was chopped at 4 MHz using an acousto-optical modulator. We have measured ΔT for probe beam polarization parallel to the polarization of the pump beam ($||$) or perpendicular to it ($\perp$). The samples were semi transparent films (~1000Å thick) of oriented and unoriented $(CH)_x$ and unoriented PTO electrochemically polymerized on conducting glas substrates. The samples were mounted in an optical exchange gas type dewar and the temperature could be varied from 80 to 300 K.

RESULTS AND DISCUSSION

(i) Electronic Response. In Fig. 1 we show the response $\Delta T(t)$ of PTO at 300 K up to 3 psec; $\Delta T > 0$ and therefore the response is photoinduced bleaching. ΔT is induced in times less than 50 femtosec indicating that carriers localization occurs instantaneously. We have also measured a photoinduced dichroism ($\Delta T_{||} > \Delta T_{\perp}$) which is also induced instantaneously implying that the photoexcitations are preferentially polarized along the chains direction. The depolarization ratio $\rho = \Delta T_{\perp}/\Delta T_{||}$ is 1/3 at $t = 0$ and increases thereafter. At $t > 0$ ΔT decays. The decay is faster for $t < 0.5$ psec and has a time constant of about 1 psec if the response is approximated by an exponential. At $t \simeq 0.5$ psec we notice a change in the slope and ΔT decays much slower up to 45 psec as is evident in Fig. 2. We have checked that this decay is not exponential but can be approximated by a power law $t^{-\alpha}$ for $1 < t < 30$ psec similar to trans-$(CH)_x$ in Fig. 3 (9); at room temperature α in PTO is 0.9 compared to 0.5 for trans-$(CH)_x$. We note (Fig. 3) that $\Delta T(t)$ in trans-CH_x decays faster than in PTO (Fig.2), but it changes into a slower decay at 10 psec resulting in a larger ΔT at longer times. This is in agreement with the theory (5) which predicts lower photocarrier surviving probability in polymers without degeneracy in their ground state (like PTO).

We interpret the fast exponential decays with about 1 psec times constant in both $(CH)_x$ and PTO as geminate recombination of hot photocarriers (probably in the form of bound charge solitons) and the change in decays at approximately 0.5 psec as a cross-over to a second state, probably a bound state of neutral solitons pair. The power law decay is due to the recombination of the latter state into the ground state. This neutral state was not as yet observed in steady-state

photomodulation experiments of PTO (8) implying a much shorter lifetime compared to trans-$(CH)_x$ whose neutral state has been observed by many groups.

We have also measured photoluminescence (PL) transient using a Hamamatsu synchroscan streak-camera with 2 psec resolution. We found in PTO a very fast PL decay which was only limited by the resolution of the camera, and a slow decay component which is not correlated with the power law decay of ΔT in Fig. 2. This indicates that a fast cross-over to a dipole-forbidden state occurs in PTO for time shorter than 2 psec, in agreement with the interpretation of $\Delta T(t)$ response. Similar conclusions were reached for a trans and cis-$(CH)_x$ (10). The rapid cross-over into a neutral state is allowed probably by a charge conjugation symmetry breaking interaction which most likely exists in $(CH)_x$ and PTO (11).

(ii) Strain Related Response. In Fig. 4 we show $\Delta T(t)$ in PTO up to 450 psec measured at 600 nm. Two damped oscillations can be clearly seen with a period $\tau \simeq 200$ psec. Similar effects were also observed in thin films of cis rich-$(CH)_x$ (12). This oscillatory response is unpolarized: We measured $\rho = 3/4$ at $t \simeq 100$ psec (peak of ΔT). At a later time we measured $\rho \simeq 1/2$ from the background signal (measured at a delaly in which the probe pulses precede the pump pulses). This shows that some photo- excitations survive the fast geminate recombination; eventually the neutral state dissociates and carriers are trapped in the form of bipolarons at much longer time (8).

We attribute the oscillations in ΔT to strain related effects. The pump pulse is absorbed in a thin layer of order 300 Å and most of the energy absorbed is released very quickly to phonons due to hot carriers thermalization and fat geminate recombination. This energy raises the layer temperature and sets up a stress due to thermal expansion. The stress in turn produces a strain pulse propagating into the film and consequently bouncing back and forth in the film due to reflection at the interfaces (12). The strain wave dynamics produces the oscillations in $\Delta T(t)$ since the strain changes sign at the free surface. This occurs every round trip so that the period τ of oscillations in ΔT is $\tau = 4d/v$, where v is the longitudinal sound velocity and d is the film thickness. From the estimated film thickness $d \simeq 1000$ Å and $\tau = 200$ psec we calculate for PTO $v = 20 \pm 3$ Å/psec (2000 m/sec); this value agrees favorably with v extracted for cis-$(CH)_x$ (12). The strain-wave diminishing amplitude is due to the ultrasound attenuation in the film and to the strain loss into the substrate at the film-substrate interface.

To detect the strain related ΔT, it is necessary that the optical constants at the measured laser wavelength is sensitive to

strain $\frac{d\alpha}{d\mu} \neq 0$. The later depends on the energy derivative of α and on the electron phonon coupling (12); $\frac{d}{d\mu}\frac{\alpha}{} = \frac{d}{dE}\frac{\alpha}{} \frac{dE}{d\mu}$. We have verified this relation by changing the laser wavelength. We have found in trans-$(CH)_x$ (9) that the strain related effects were unobserved at 620 nm since $d\alpha/dE = 0$ at this wavelength. We have also found in PTO that the strain related effects are at their maximum observance at 580 nm where $d\alpha/dE$ reaches its maximum and slowly diminish at long wavelength ($\lambda > 630$ nm).

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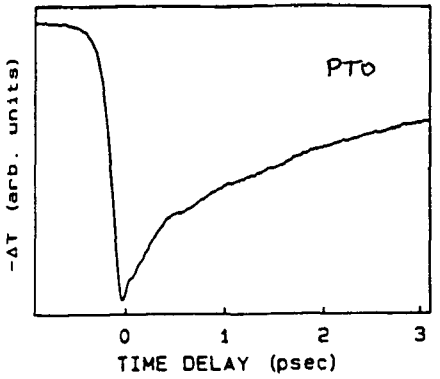


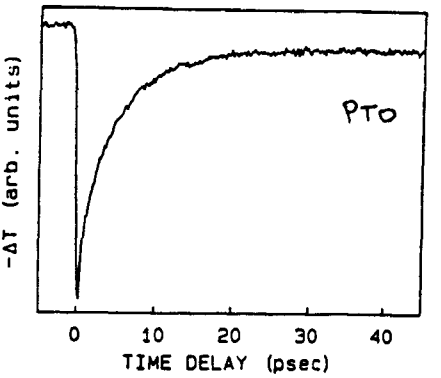
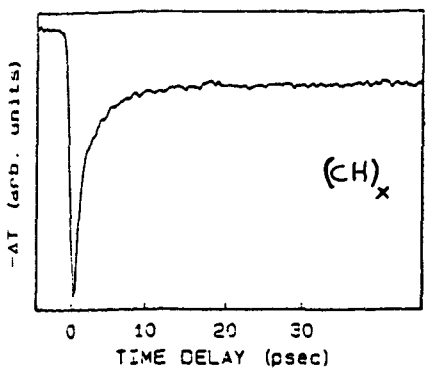


FIG. 1 - Transient photoinduced changes in transmission $\Delta T(t)$ at 620 nm for cross pump-probe polarizations in a film of polythiophene at room temperature.

FIG. 2 - Same as Fig. 1 up to 45 psec.



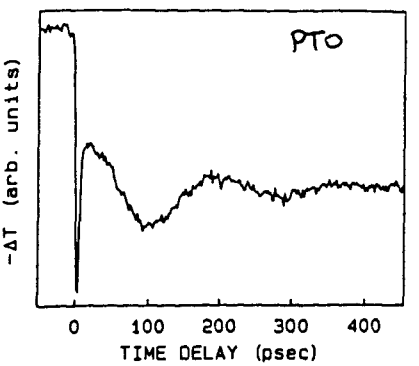


FIG. 3 - Same as Fig. 2 for a film of unoriented trans-$(CH)_x$.

FIG. 4 - $\Delta T(t)$ in polythiophene up to 450 psec measured at 600 nm.