

Picosecond acoustics in polythiophene thin films

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(Received 21 May 1990)

The picosecond correlation technique has been used to study the generation and detection of ultrasonic strain waves in polythiophene thin films, in the range of 0.3–19 GHz. We show that the strain generation is mainly due to thermal expansion following energy relaxation associated with exciton formation and that the spectral dependence of the strain response is proportional to $\partial\alpha(\omega)/\partial\omega$, the first partial derivative of $\alpha(\omega)$. We found a linear dispersion relation for the LA-phonon branch in the measured frequency range, with a room-temperature sound velocity of 28 Å/ps; it stiffens by 10% at 80 K.

Recently, it has been demonstrated^{1–5} that longitudinal acoustic (LA) phonons in thin films of amorphous and crystalline semiconductors can be generated and detected with use of the picosecond pump-and-probe correlation technique. The method was consequently applied to thin films of conducting polymers,^{6,7} where it was treated as an artifact superimposed on the transient electronic response. In essence, when an ultrashort optical pulse is absorbed in a thin solid film, a propagating strain pulse is photoinduced, which then modulates the optical absorption of a time-delayed probe beam. The resulting transient photoinduced change in transmission of the probe exhibits an oscillatory response with a period corresponding to one or two round trips of the acoustical pulse in the film, depending on whether the film has one or two free surfaces.³

In this work we focused our studies on the transient oscillatory response in the ultrashort optical response of polythiophene (PT) thin films. We show that the spectral dependence of the strain response is proportional to $\partial\alpha(\omega)/\partial\omega$, the first partial derivative of $\alpha(\omega)$. We also show that the LA-phonon dispersion relation in the frequency range of 0.3–19 GHz is linear, with a room-temperature sound velocity V_s of 28 Å/ps. We report the dependence of V_s on temperature from 80 to 300 K; it decreases linearly with a 10% maximum change.

The pump-and-probe experiments were performed⁷ with a mode-locked neodymium-doped yttrium aluminum garnet (Nd:YAG) laser (Quantronix), which pumps a (Coherent, Inc.) dye laser producing light pulses typically of 2-ps duration at a repetition rate of 76 MHz in the spectral range λ_L of 570–670 nm. The pump beam was modulated at 4 MHz by an acousto-optic modulator and delivered about 0.1 nJ of energy per pulse to the illuminated spot on the sample; the probe pulse was a delayed small replica of the pump pulse. Both beams were focused onto the same spot, about 30 μm in diameter (D). $\Delta T(t)$, the transient modulated change in transmission T , was measured with the polarization of the probe beam orthogonal to that of the pump. The PT sample was a thin ($d \sim 1400$ Å) electrochemically polymerized film deposited on a glass substrate. The film was thermally anchored to a coldfinger and the temperature was varied between 80 and 300 K.

In Fig. 1 we show $\Delta T(t)$ of PT at 300 K on a 500-ps

scale for $\lambda_L = 608$ and $\lambda_L = 585$ nm. $\Delta T(t)$ exhibits fast photobleaching at $t = 0$ which quickly begins to decay. At $\lambda_L = 608$ nm, superimposed on this decay is an oscillatory response with a period $\tau = 200 \pm 10$ ps. The sharp peak at $t = 0$ has been observed in many conducting polymers including *cis*- and *trans*-(CH)_x,^{8,9} polydiacetylene^{10,11} and other forms of PT,¹² and is attributed to fast geminate recombination of the photoexcited carriers. This response exhibits a dichroism such that $\rho = \Delta T_{\parallel}/\Delta T_{\perp} = 2$, where ΔT_{\parallel} and ΔT_{\perp} are the photoinduced ΔT for pump and probe polarizations in parallel and perpendicular configurations, respectively. For the oscillatory response, however, $\rho = 1$;⁷ this response is unpolarized and therefore it cannot be of electronic origin. Moreover, we found that the oscillatory period τ depends on the film's thickness (see below), and thus we conclude that the oscillations are due to propagating waves in the film, as observed by others before^{1–5} in various crystalline and amorphous thin films. These are longitudinal strain waves due to the geometry used in our experiments: $D \gg d$.

The mechanism for producing these waves is as follows:³ The pump pulse is absorbed in a thin layer ζ of

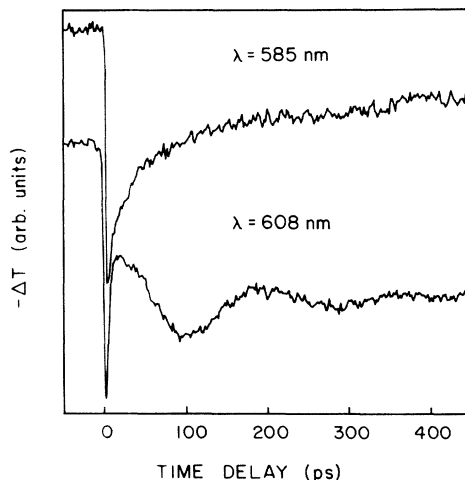


FIG. 1. Transient $\Delta T/T$ in a thin film of polythiophene at $\lambda_L = 585$ and 608 nm. The oscillatory response is due to propagating strain waves in the film.

about 500 Å, and within about a fraction of a ps, much of the energy is released to phonons due to thermalization and nonradiative recombination of hot photogenerated carriers. The temperature of the layer ζ increases, and its thermal expansion creates a stress, which then causes a strain pulse to propagate into the film. The strain pulse bounces back and forth in the film upon reflection off the interfaces. At the free surface the strain changes sign, leading to the oscillation in $\Delta T(t)$. The sign change occurs once every round trip so that $\tau = 4d/V_s$, where V_s is the longitudinal sound velocity. A computer simulation of the strain propagating in a PT film indicates¹³ that the diminishing amplitude of the oscillations is due mostly to partial transmission of the strain into the substrate. The thickness of the PT film corresponding to the data in Fig. 1 is not known, but by comparing our optical density data on the sample with a previously published absorption spectrum of PT,¹⁴ we infer $d \approx 1400$ Å. For $\tau = 200$ ps we thus find $V_s \approx 28$ Å/ps ($= 2800$ m/s) at a phonon frequency of roughly 12 GHz.

The wavelength λ of the LA phonons which contribute the most to the strain pulse³ is roughly 2ζ , where $\zeta = \alpha_L^{-1}$ (the laser excitation penetration length) if $\alpha_L^{-1} < d$, or $\zeta = d$ if $\alpha_L^{-1} > d$. We can therefore measure the LA dispersion relation $\omega = V_s(q)q$ where $q = 2\pi/\lambda$, if we change λ in our measurements. This can be achieved by changing α_L using different laser wavelengths λ_L , or by changing d as shown in Fig. 2. In this case the sample was a poly-(3-hexylthiophene) film (P3HT) evaporated from solution onto a sapphire substrate. The film's inhomogeneity in thickness allowed us to obtain many data sets (at $\lambda_L = 598$ nm) with different τ . The data in parts A through D show how the period of oscillation increases for correspondingly thicker portions of the film. The summary of our results is shown in the inset, where we plot transmission T as a function of τ . A relative measure of the thickness associated with the illuminated spot on the sample is $-\ln T$ since $T \approx \exp(-ad)$. A linear dependence of τ on $\ln T$ shows, therefore, that V_s is constant in the frequency range of these measurements (0.3–1.3 GHz). A constant V_s was also obtained¹³ when changing λ_L , but for a much broader frequency range (10–19 GHz). We conclude therefore that the LA-phonon branch in PT has a linear dispersion relation in our frequency range (0.3–19 GHz).

Figure 1 shows that the strain waves cannot be detected at $\lambda_L = 585$ nm. We have measured the complete spectral dependence of the strain-related response $(\Delta T/T)_s$ for $570 \text{ nm} \leq \lambda_L \leq 680$ nm. For each λ_L we normalized $(\Delta T/T)_s$ by the absorbed laser power and the measured illuminated spot area on the sample. The results are shown in Fig. 3. $(\Delta T/T)_s$ was calculated by Thomsen and co-workers.^{1,3}

$$\left[\frac{\Delta T}{T} \right]_s = \frac{d}{\hbar} \frac{\partial \alpha(\omega)}{\partial \omega} \frac{\partial E_g}{\partial \eta} \langle \eta(t) \rangle, \quad (1)$$

where $\partial \alpha(\omega)/\partial \omega$ is the first partial derivative of the absorption coefficient $\alpha(\omega)$ and we have used the relation $\partial \alpha(\omega)/\partial \omega = -\hbar \partial \alpha/\partial E_g$. $\partial E_g/\partial \eta$ is the deformation potential and $\langle \eta(t) \rangle$ is the average strain in the film at time t . We measured both α and $\partial \alpha(\omega)/\partial \omega$ of the PT film us-

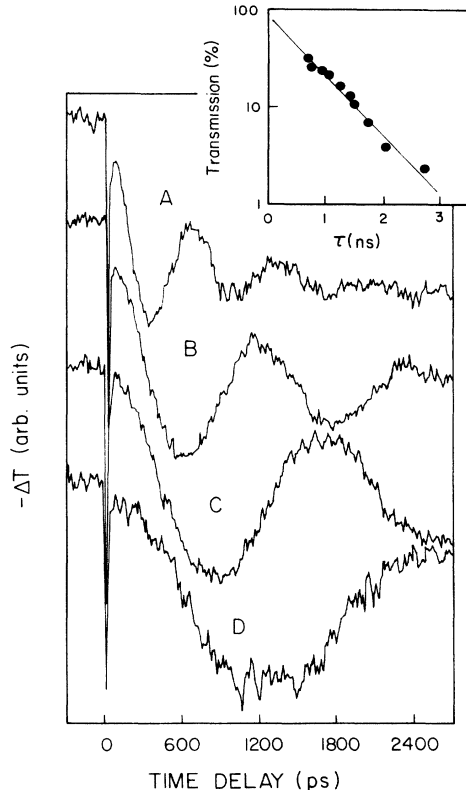


FIG. 2. Transient $\Delta T/T$ at $\lambda_L = 630$ nm in a P3HT film of inhomogeneous thickness (A to D) evaporated from solution. The inset summarizes the results of the oscillatory response in terms of the period of oscillations τ vs the film's transmission measured with the pump laser beam through the illuminated spot of the sample.

ing a Cary spectrometer; the optical density spectrum is shown in the inset of Fig. 3. Phonon sidebands are observed¹⁵ at 185-meV intervals with a local minimum in $\partial \alpha(\omega)/\partial \omega$ at $\lambda_L = 585$ nm, explaining the absence of an oscillation in $\Delta T(t)$ at this wavelength, as seen in Fig. 1. These data agree quite well with the measured spectrum of $\partial \alpha(\omega)/\partial \omega$ as predicted by Eq. (1). Figures 1 and 3 also show that to measure the electronic response at long times, a probe wavelength where $\partial \alpha(\omega)/\partial \omega \approx 0$ must be chosen to eliminate $(\Delta T/T)_s$ from the decay kinetics.

We can estimate the magnitude of $(\Delta T/T)_s$ from Eq. (1) by first calculating the amplitude of the average strain according to³

$$\langle \eta \rangle = [(1 + \nu)/(1 - \nu)] \beta (E_x/dAC_v), \quad (2)$$

where ν is Poisson's ratio and is about 0.35 for many polymers,¹⁶ β is the linear expansion coefficient ($\approx 10^{-4} \text{ K}^{-1}$ for polydiacetylene¹⁷), A is the illuminated area, C_v is the heat capacity ($\approx 0.5 \text{ J/cm}^3 \text{ K}$ for polydiacetylene¹⁸), and E_x is the fraction of the absorbed energy that is given to phonons. If we consider that the photogenerated carriers in PT form intrachain excitons at 1.95 eV,¹⁵ then only 0.19 eV of the 2.14-eV pump photon energy is available for strain production. Then from the 1.4 mW of absorbed pump power and the laser repetition rate, we obtain $E_x = 1.7$ pJ per pulse. Using Eq. (2) these give $\langle \eta \rangle$

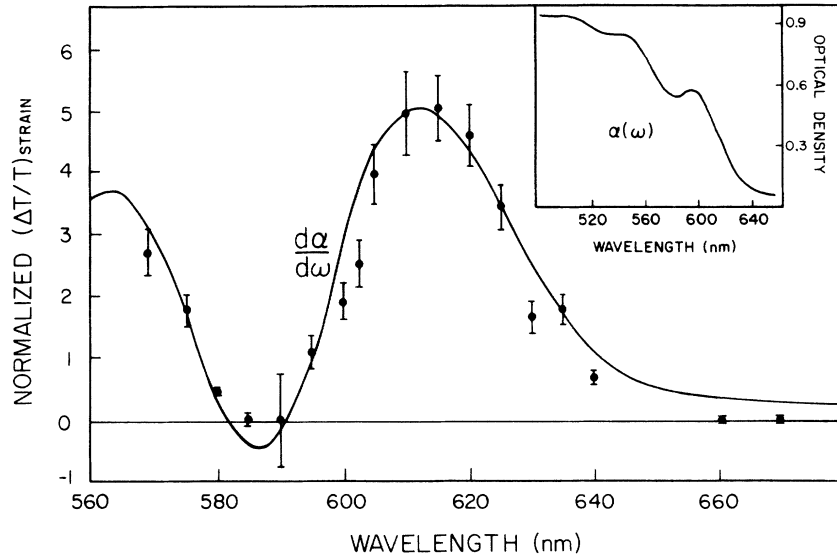


FIG. 3. The spectrum of the normalized strain-related response $(\Delta T/T)_s$ in PT measured at $t=100$ ps, compared with $\partial\alpha/\partial\omega$ (solid curve). The absorption spectrum $\alpha(\omega)$ of the PT film is also shown in the inset.

$=4.7 \times 10^{-6}$. To estimate $(\Delta T/T)_s$ we need $\partial\alpha(\omega)/\partial\omega$ which we obtain from $\alpha(\omega)$; $(\hbar)^{-1}\partial\alpha(\omega)/\partial\omega=11.8$ eV^{-1} at $\lambda_L=608$ nm. For the deformation potential $\partial E/\partial\eta$ we used the relation $\partial E/\partial\eta = -B\partial E/\partial P$ (isotropic stress), where B is the bulk modulus [189 kbar (Ref. 19)]. We have measured the pressure dependence of $\alpha(\omega)$ in PT up to 60 kbar.²⁰ For small pressures we found $\partial E/\partial P = -10$ meV/kbar which gives $\partial E/\partial\eta = 1.9$ eV. Using these values in Eq. (1) we find $(\Delta T/T)_s = 1.4 \times 10^{-4}$. This is in agreement with the measured value of the strain amplitude of $(\Delta T/T)_s = 0.9 \times 10^{-4}$ at $\lambda_L = 608$ nm. Also the positive sign of $(\Delta T/T)_s$ shows that the strain waves are produced via thermal expansion rather than via a pure electronic effect.¹

In Fig. 4 we plot the relative change in the sound velocity $\Delta V_s/V_s$ versus temperature Θ , where V_s at room tem-

perature was chosen as a reference. It is seen that V_s decreases linearly with Θ (the solid line is a linear fit) by about 10% from 80 up to 300 K. For *cis*-(CH)_x V_s decreases by about 15% over the same region of Θ .⁶ Qualitatively, the behavior of V_s with temperature can be understood in terms of the temperature dependence of the elastic moduli. For an isotropic medium (our samples are unoriented) V_s can be expressed as¹⁶

$$V_s^2 = (4G/3 + B)/\rho, \quad (3)$$

where B and G are the bulk and shear moduli, respectively, and ρ is the density. Thus, we expect V_s to vary linearly with small changes in B , G , and ρ . However, since the density ρ would increase upon cooling of the film, ΔV_s must be dominated by the changes in B and G . Perepechko¹⁶ has discussed the temperature dependence

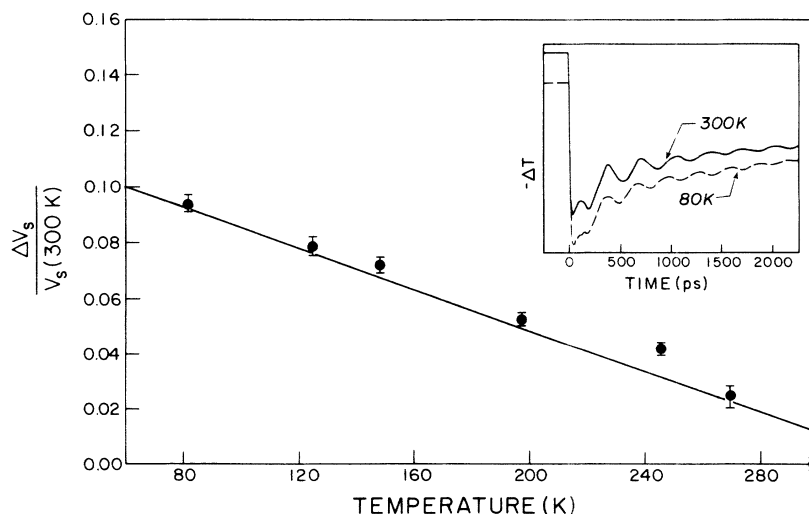


FIG. 4. The relative change in the sound velocity $\Delta V_s/V_s(300 \text{ K})$ of PT as a function of temperature. The inset shows typical oscillatory responses at 80 and 300 K.

of the sound velocity in terms of the relaxation time spectrum for the polymer, based on a model of wave propagation in a viscoelastic medium. According to his experimental results on V_s , the calculated B and G decrease monotonically with temperature, explaining the decrease in V_s with Θ .

In summary, we have shown that the oscillatory picosecond response in $\Delta T(t)$ is a genuinely acoustic response which appears in thin films of PT and other conducting polymers. We found for the LA branch a linear

dispersion relation in the 0.3–19-GHz frequency range with $V_s = 28 \text{ \AA/ps}$. The spectral dependence of the oscillatory strain response $(\Delta T/T)_s$ follows that of $\partial\alpha(\omega)/\partial\omega$. We also found that V_s falls linearly with temperature between 80 and 300 K.

This work was partially supported by U.S. Department of Energy (DOE) Grant No. DE-FG02-89ER45409, and by the Free Electron Laser (FEL) program at the University of Utah.

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