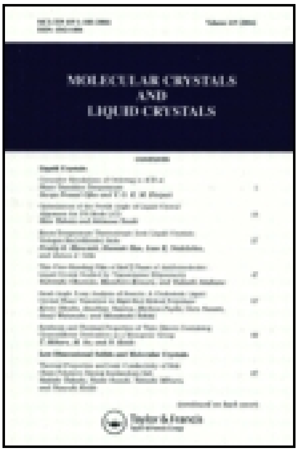

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PICOSECOND TRANSIENT PHOTOMODULATION IN POLY(2,5-THIENYLENE VINYLENE)

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Abstract Using the picosecond pump-probe spectroscopy technique we measured the photomodulation temporal (with 5 ps resolution) and spectral response from 610 to 750 nm, in a thin film of poly (2,5 thienylene-vinylene) (PTV). We found a fast electronic response which decays within 4 ps, and two non-electronic responses, which are due to the photoproduced strain in the film. One response is due to the static strain, and the other is from the strain waves launched in the film following the fast exciton recombination.

The study of ultrafast nonlinear optical properties and photoexcitation relaxation mechanism in π-conjugated polymers is important for potential applications and theoretical understanding of the excited electronic energies in these quasi-one dimensional systems. Considerable interest in the poly(arylene-vinylene) family has been recently generated following the discovery[1] of light emitting diodes (LED) with up to 2% efficiency produced with various derivatives of poly(p-phenylene-vinylene) (PPV)[2]. This has been possible since PPV shows high efficiency photoluminescence (PL) emission of up to few percents[3]. However, when the phenylene moiety is replaced by a thienylene moiety to form poly (2,5-thienylene-vinylene) (PTV), the PL efficiency decreases by more than six orders of magnitude (to $\approx 10^{-5}$) compared to PPV[4]. Within the theoretical picture of excitonic energy levels in π-conjugated polymers[5], the extremely weak PL in PTV may indicate that a forbidden exciton ($2A_g$) lies below the allowed exciton ($1B_u$), which in PTV is at about 1.85 eV[4].

In this work, picosecond time-resolved spectroscopy in the small signal limit has been used to measure the photomodulation (PM) spectral and temporal response in a thin film of PTV. The emphasis of previous femtosecond spectroscopic studies of PTV[6,7] was on the ultrafast femtosecond response. A biexponential decay of the PM signal with time constants of ~1 and ~15 ps, respectively, was interpreted[6] as due to recombination of hot and thermalized excitons, respectively.

EXPERIMENTAL

The picosecond transient PM spectra were measured using the pump and probe technique. Two dye lasers (Coherent, Inc.) synchronously pumped by a mode-locked Nd:YAG laser produced a pump beam at 570 nm and a probe beam with wavelength ranging from 610 nm to 750 nm, using different dyes. The pulses were typically 5 ps duration with a repetition rate of 76 MHz. The pump beam was modulated at 10 MHz by an acousto-optic modulator and delivered about 13 pJ of energy per pulse to the sample. Both beams were focused onto the same spot of about 30 μm in diameter and the PM measurements were done with pump-probe polarization either parallel ($\|$) or perpendicular $\perp$ to each other. We then measured the transient polarization memory P(t), where $P=(\Delta\alpha_{\|} - \Delta\alpha_{\perp})/(\Delta\alpha_{\|} + \Delta\alpha_{\perp})$. The subpicosecond measurements were done using a CPM laser, which produced 100 fs pulses at 625 nm. The PTV sample was a thin film spun from solution on a sapphire substrate. The PTV polymer was prepared via the precursor route outlined in ref. 8.

RESULTS

The observed PM signal is composed of three ΔT components: a very fast component, ΔT_a, decaying within several picoseconds, a slow component, ΔT_b, with a time constant of order 10 ns and an oscillatory component, ΔT_c, with a decay time of several hundred picoseconds. Typical decay of the fast component ΔT_a measured with 200 fs time resolution at 625 nm is shown in Fig. 1. $\Delta T_a > 0$ and it decays within 4 ps into a persistent plateau. However, within about 150 ps ΔT changes sign into PA and shows an oscillatory response (ΔT_c) riding on top of a slow PA signal (ΔT_b), as shown in Fig. 2. Actually we can observe in Fig. 2 about 10 periods of oscillation in ΔT_c, with period τ_{os} of about 200 ps. A Fourier analysis of $\Delta T_c(t)$ showed that the oscillation amplitude decays exponentially with a time constant $\tau_c \approx 700$ ps (Fig .2). We found that both τ_{os} and τ_c depended linearly on the sample thickness d. Also all ΔT components depended linearly on the laser fluence I and their transient decay response did not change with I.

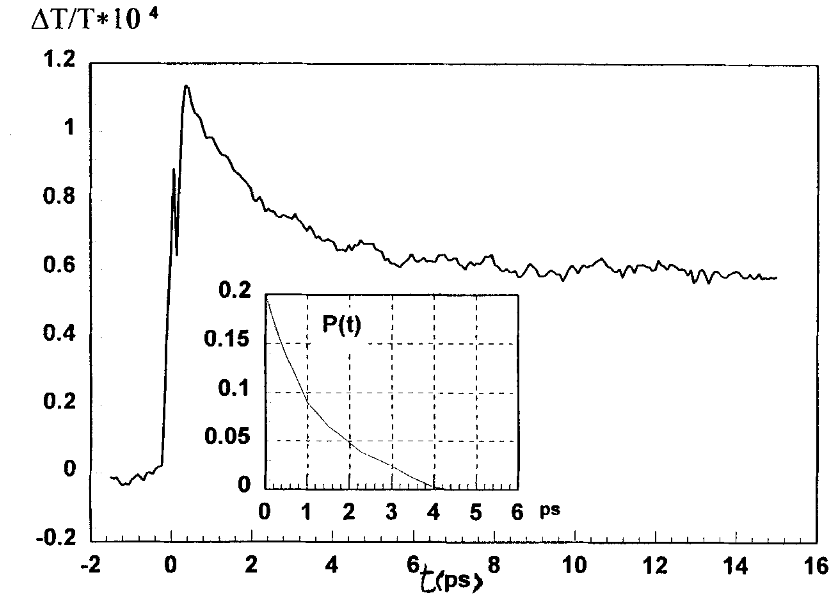

FIGURE 1 ΔT(t) response of PTV measured at 625 nm with 100 fs time resolution. The inset shows the polarization memory decay P(t).

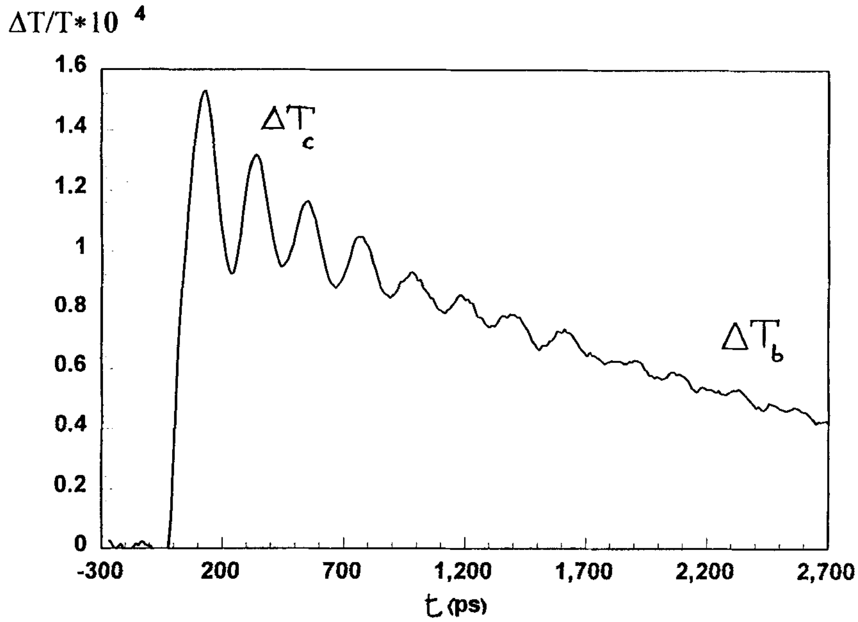

FIGURE 2 ΔT(t) response up to 2700 ps showing the oscillatory (ΔT_c) and the long-lived response (ΔT_b) in PTV.

The polarization memory P was measured at 625 nm (Fig. 1 inset). For the fast component (ΔT_a) we found $P>0.2$ at $t=0$. At $t>0$ P decays to zero in the same way as ΔT_a (Fig. 1). In contrast, we measured $P=0$ for both ΔT_b and ΔT_c components.

In Fig. 3 we show the PM spectra with 5 ps resolution, obtained with $\lambda_{pump} = 570$ nm, at $t=0$ (mainly the fast component, ΔT_a), at $t=3$ ns (the slow component, ΔT_b) as well as the spectrum of the oscillatory component ΔT_c, measured at the first oscillation peak. ΔT_a transforms from photobleaching (PB), ($\Delta T>0$) into PA ($\Delta T<0$) at about 650 nm. Its spectrum showing a PA peak at 690 nm ($\approx$1.8 eV), is very similar to the previous femtosecond PM spectra measured with large signals[6,7]. The spectra of ΔT_b and ΔT_c however, have not been measured before. ΔT_b (at 3 ns) shows a derivative like spectral feature with zero crossing at about 690 nm, which closely follows the spectrum of the second partial energy derivative of the absorption $\alpha(\omega)$ ($\Delta T_b \approx \partial^2\alpha/\partial^2\omega$). Actually, this is similar to the electro-absorption (EA) spectrum in PTV[9]. ΔT_c spectrum, on the other hand, is close to the first partial energy derivative of $\alpha(\omega)$ ($\Delta T_c \approx \partial\alpha/\partial\omega$), similar to the strain spectrum recently measured in polythiophene[10], using the same technique.

DISCUSSION

The fast PM component ΔT_a was attributed in previous studies[6,7] to self trapped excitons. In view of its spectrum and the associated polarization memory, which decays together with $\Delta T_a(t)$, we agree with this assignment. The electronic PA band at 1.8 eV may then be due to an excited optical transition into higher electronic levels[11]. We note that there might be another PA band in the transient electronic PM spectrum at much lower energies[7].

The spectrum of the slow component ΔT_b (Fig. 3(b)), on the other hand, resembles $\partial^2\alpha/\partial\omega^2$ and the EA spectra in PTV[9], but there are also pronounced deviations at wavelengths lower and higher, respectively, than the isosbestic point at 690 nm. ΔT_b is not due to thermal modulation (TM) of α, the spectrum of which in PTV follows $\partial\alpha/\partial\omega$[4]. This is different from the conclusions reached in previous transient PM studies[7] and we attribute the different spectrum to the much higher laser fluence (I) used in the previous measurements. We do not believe that ΔT_b is due to

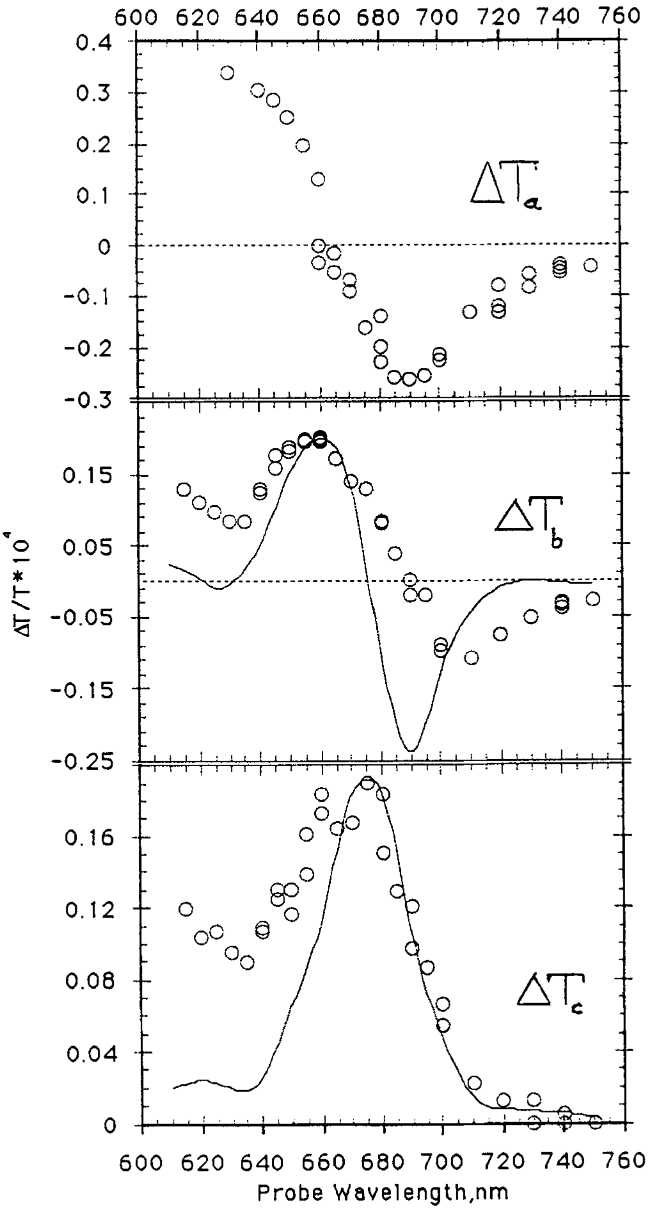

FIGURE 3 The spectra of the three ΔT components in the picosecond PM of PTV measured with 5 ps time resolution (a) ΔT_a at t=0, (b) ΔT_b measured at t=3 ns, (c) the oscillatory amplitude ΔT_c measured at t=170 ps.

EA induced by photogenerated carriers in PTV[7]. The reason for this is the linear increase of ΔT_b with I, whereas we expect a sublinear dependence with I if photocarriers were involved. Also ΔT_b does not have any polarization memory P, whereas P in the EA spectrum of PTV was measured to be ~ 2.3[9]. Since ΔT_b in PTV is neither due to TM nor due to EA, what is it?

We speculate that it is due to changes in $\alpha(\omega)$ induced by the photoinduced static strain in the film[12]. This strain is photoproduced as a result of the thermal expansion of the film's front surface due to the released heat following fast exciton recombination in PTV (t) (Fig. 1). Then the reason why ΔT_b does not follow $\partial\alpha/\partial\omega$ spectrum is that the static strain is not photogenerated homogeneously in the film, but its distribution follows the absorption profile of the pump beam $\sim \exp(-\alpha_p z)$, where z is the distance from the film's front surface and α_p is the absorption at the pump wavelength[12]. Since α_p in PTV[9] at 570 nm is of order 10^5 cm^{-1}, the strain distribution is highly anisotropic, and this in turn breaks the inversion symmetry of the electronic states in the PTV film. As a result A_g and B_u states may mix and consequently extra oscillation strength ΔS is given to A_g states at the expense of S from B_u states. Under these assumptions the PM spectrum contains regions of PA ($\Delta\alpha > 0$) at A_g states and regions of PB ($\Delta\alpha < 0$) at B_u states. Then from the PA and PB spectral features in the PM spectrum of ΔT_b (Fig. 3(b)), we conclude that an A_g exciton ($2A_g$) exists in PTV at 710 nm (=1.75 eV) whereas the $1B_u$ exciton is at 660 nm (= 1.88 eV). This means that the excitonic order in PTV is reversed, $E(2A_g) < E(1B_u)$, explaining the extremely weak PL efficiency in this material[4], in agreement with recent theory[5].

The PM spectrum of the oscillatory component, ΔT_c, agrees with previous results in other polymer thin films[10]. The mechanism for producing the oscillation is as follows[10,12]: the pump pulse is absorbed in a thin layer of order $(\alpha_p)^{-1}$ of about 500Å, and within a few ps much of the energy is released to phonons due to thermalization and nonradiative recombination of hot photogenerated excitons. The temperature of the layer 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[12] so that τ_{os}=4d/V_s, where V_s is the longitudinal sound velocity. Then the diminishing amplitude of the oscillations is due mostly to partial transmission of the strain into the substrate. The thickness of the PTV film corresponding to the data in Fig. 2 is not known, but by comparing our optical density data on the sample with a previously published absorption spectrum of PTV[9], we infer d≈500Å. Then from τ_{oc}=200 ps we find V_s=10Å/ps(=100 m/s) at a phonon frequency of roughly 12 GHz. The amplitude of the oscillation in ΔT_c induced by these strain waves was calculated by Thomsen and co-workers[12]:

$$\left(\frac{\Delta T}{T}\right)_s = \frac{d}{\hbar}\,\frac{\partial\alpha(\omega)}{\partial\omega}\,\frac{\partial E_g}{\partial\eta}\,<\eta(t)>, \qquad (1)$$

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 $<\eta(t)>$ is the average strain in the film at time t. This results in a PM spectrum which follows $\partial\alpha/\partial\omega$ spectrum[10], in agreement with ΔT_c spectrum shown in Fig. 3(c).

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