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## Brief Reports

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# Femtosecond transient absorption saturation in poly(alkyl-thiophene-vinylene)s

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We report on ultrafast transient absorption measurements on solutions of poly(3-decyl-thiophene-2,5-diyl-vinylene), poly(3,4-dibutyl-thiophene-2,5-diyl-vinylene), and poly(3,3′-dibutyl-2,2′-dithiophene-5,5′-diyl-vinylene). In these polymers, a stiffening of the thiophenic backbone has been accomplished by inserting intrachain double bonds (vinyl groups). The transient absorption data seem to be consistent with the formation and decay of self-trapped excitons. The bleaching decays are independent of the size and location of the side groups, while they are sensitive to the backbone rigidity. A random-walk process on a finite polymer chain with recombination centers at the end is proposed to contribute to the relaxation mechanism of self-trapped excitons.

## I. INTRODUCTION

Among conjugated polymers, poly(alkyl-thiophene)s are gaining considerable interest as materials for nonlinear optics since they are soluble, chemically stable, and easily processable. Pump-and-probe and four-wave-mixing techniques can be used to determine the amount and time response of optical nonlinearities in these materials. Picosecond and femtosecond pump-and-probe experiments have been performed on poly(alkyl-thiophene)s with different alkyl substituents. Photoinduced bleaching of the interband transition accompanied by photoinduced absorption in the band gap were observed with picosecond resolution in poly(3-hexyl-thiophene) and poly(3-octyl-thiophene).[1] In femtosecond pump-and-probe experiments transient absorption followed by transient bleaching was observed in poly(3-hexyl-thiophene) and poly(3-dodecyl-thiophene).[2] A detailed study of the ultrafast relaxation processes of poly(3-dodecyl-thiophene) was performed by using as a probe white light continuum.[3]

The aim of this work is to investigate the effects of the insertion of an intrachain vinyl group on the ultrafast excited-state kinetics of the polythiophenic backbone. The band gap in these polymers is redshifted with respect to poly(alkyl-thiophene)s, since the vinyl group increases both the conjugation length and the backbone rigidity. Femtosecond pump-and-probe experiments have been performed on newly synthesized polymers with different alkyl substituents and vinyl group sequences, namely, poly(3-decyl-2,5-thiophene-vinylene) (PTV3$C_{10}$) and poly(3,4-dibutyl-thiophene-2,5-diyl-vinylene) (PTV3,4$C_4$) and poly(3,3′-dibutyl-2,2′-dithiophene-5,5′-diyl-vinylene) (PDTV3$C_4$). The polymers PTV3$C_{10}$ and PTV3,4$C_4$, which differ only by location and size of the side groups, are characterized by a backbone of alternating vinyl and thiophene units, while the polymer PDTV3$C_4$ is characterized by the presence of a vinyl group every two thiophene rings.

## II. EXPERIMENT

The chemical structures of monomeric units of polymers are shown in the insets of Fig. 1. The polymers PTV3$C_{10}$ and PTV3,4$C_4$ were synthesized according to the procedure described in Ref. 4. PDTV3$C_4$ was prepared by oxidizing poly(3,3′-dybutyl-2,2′-dithienyl ethylen) with $FeCl_3$ in chloroform.[5] All the polymers were studied in a chloroform solution. The excitation source was a cavity-dumped hybrydly mode-locked Rhodamine 6G dye laser with 3,3′-diethyloxadicarbocyanine iodide (DODCI) as saturable absorber synchronously

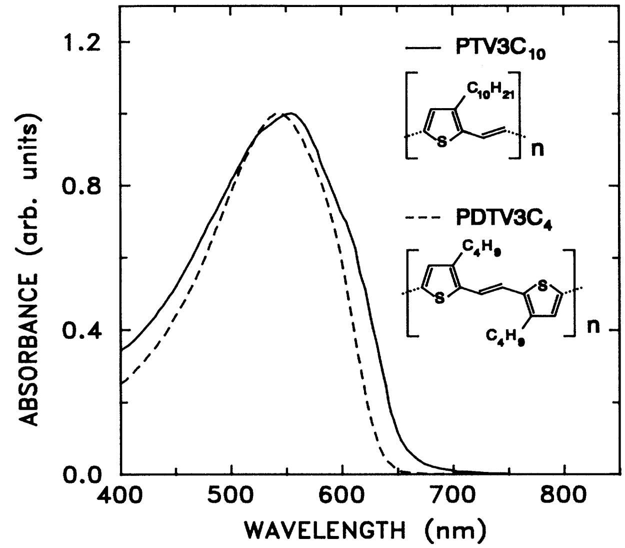

FIG. 1. Electronic absorption spectra of PTV3C$_{10}$ and PDTV3C$_4$ in a chloroform solution. The chemical structure of the corresponding monomeric units is shown in the insets.

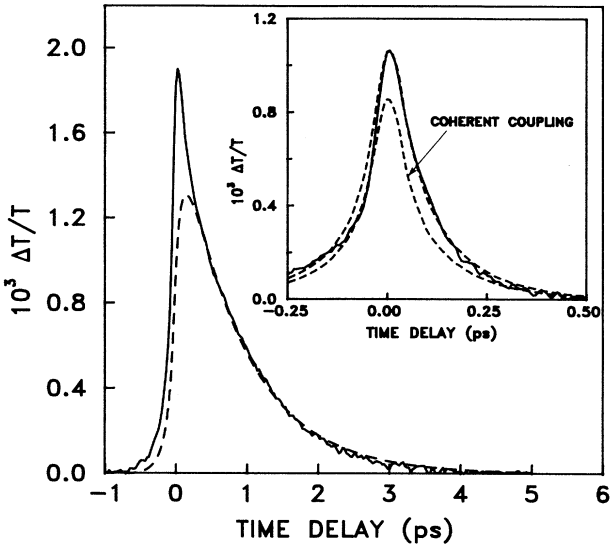

FIG. 2. Fractional changes $\Delta T/T$ in the probe transmission measured as a function of probe delay for PTV3C$_{10}$; the dashed line represents the fitting of the slow exponential component. In the inset an enlarged view of the decay curve with the slow decay component subtracted is shown; the fitting (dashed line) includes the coherent coupling contribution, which is also reported.

pumped by the second harmonic of a 76-MHz cw mode-locked Nd:YLiF$_4$ laser. The double-pass cavity dumper operated at a repetition rate of 1.9 MHz. Highly stable 60-fs pulses at 627 nm were generated using an innovative resonator design combined to an active cavity length stabilization of the dye laser.[6] The polymer solutions were held in thin 500-$\mu$m cells with absorption occurring in the range 20–40%. The time separation between the pump-and-probe pulses was changed by a translation stage of 1-$\mu$m step. The pump beam was mechanically chopped at a repetition rate of 1 kHz and differential detection was used to increase the signal-to-noise ratio. All the measurements have been performed using cross polarizations of the pump-and-probe beams to avoid the formation of cumulative thermal gratings, which provide asymmetric contributions to the coherent artifact when the excitation wavelength is off resonance.[7]

## III. RESULTS AND DISCUSSION

The electronic absorption spectra of PTV3C$_{10}$ and PDTV3C$_4$ in a chloroform solution are shown in Fig. 1. The absorption spectrum of PTV3,4C$_4$ is very similar to that of PTV3C$_{10}$. The transient transmission change for PTV3C$_{10}$ as a function of probe time delay (see Fig. 2) can be fitted by a two-exponential curve. The slower part of the decay is characterized by a time constant of 880($\pm$60) fs. For the initial fast component, the best fit to the data taking into account the coherent coupling term (see inset of Fig. 2) provides a time constant of 40($\pm$20) fs. The large uncertainty in the fast time constant is due to the limit in time resolution. The pump-and-probe data for PTV3,4C$_4$ present a behavior very similar to that of PTV3C$_{10}$. These results indicate that the relaxation dynamics is quite independent of the size and location of the side groups. The pump-and-probe data for PDTV3C$_4$, shown in Fig. 3, can be fit by a two-exponential function with time constants, respectively, of 80($\pm$10) and 1010($\pm$90) fs.

Since in our experiments the wavelengths of the pump-and-probe pulses are the same, the probe transient absorption is sensitive both to the excited-state relaxation and ground-state recovery. To interpret our experimental results we consider the relaxation scheme shown in Fig. 4, based on self-trapped exciton formation and decay.[3] Free excitons (FE), created by the pump pulse, transform into hot self-trapped excitons (HSE) upon lattice deformation; HSE can relax directly to the ground state ($G$) with a time constant $\tau_D$ or can relax by phonon emission to form thermalized self-trapped excitons (TSE) with a time constant $\tau_S$. The time constant $\tau_G$ of the thermalized self-trapped excitons which decay to the ground state can be related both to a tunneling process in the configurational space and to an exciton diffusion process towards recombination centers along the polymer chain,[8,9] as will be discussed later on. Assuming an instantaneous formation of HSE, the excited-state relaxation kinetics can be obtained by solving the following rate equations:

$$\frac{dN_{\mathrm{HSE}}}{dt} = -N_{\mathrm{HSE}}\left[\frac{1}{\tau_D}+\frac{1}{\tau_S}\right], \tag{1}$$

$$\frac{dN_{\mathrm{TSE}}}{dt} = \frac{N_{\mathrm{HSE}}}{\tau_S}-\frac{N_{\mathrm{TSE}}}{\tau_G}, \tag{2}$$

$$N_G(t)=N_0-[N_{\mathrm{HSE}}(t)+N_{\mathrm{TSE}}(t)], \tag{3}$$

where $N_G$, $N_{\mathrm{TSE}}$, and $N_{\mathrm{HSE}}$ are the densities of ground-state, thermalized self-trapped excitons, and hot self-trapped excitons, and $N_0$ is the saturation density of the

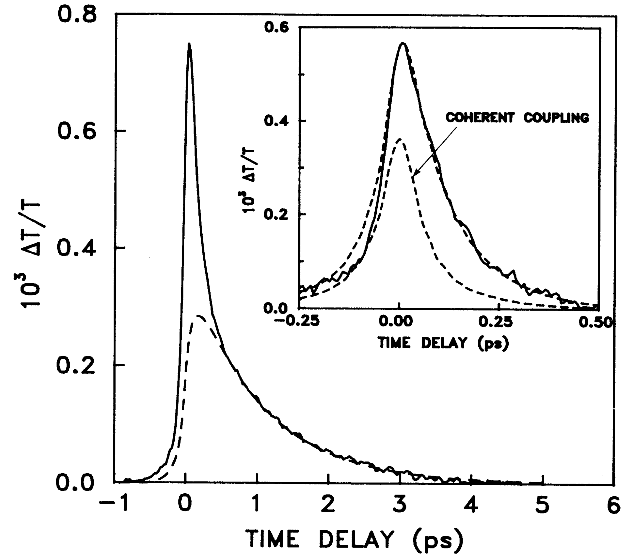

FIG. 3. Fractional changes $\Delta T/T$ in the probe transmission measured as a function of probe delay for PDTV3C$_4$; the dashed line represents the fitting of the slow exponential component. In the inset an enlarged view of the decay curve with the slow decay component subtracted is shown; the fitting (dashed line) includes the coherent coupling contribution, which is also reported.

excitons. The time response of the probe transmission change $\Delta T$ for the transition between the ground-state level and HSE level to a delta-function pump pulse is obtained by solving Eqs. (1)–(3) and assumes the following expression in the limit of small absorption variations:

$$\Delta T \propto [N_0 - N_G(t) + N_{\mathrm{HSE}}(t)]$$

$$\propto A \exp[-t/T_1] + B \exp(-t/\tau_G) \, , \tag{4}$$

where

$$\frac{1}{T_1} = \frac{1}{\tau_S} + \frac{1}{\tau_D} \, , \tag{5}$$

$$B = \frac{1}{2\tau_S \left[ \dfrac{1}{T_1} - \dfrac{1}{\tau_G} \right]} \, , \tag{6}$$

$$A + B = 1 \, . \tag{7}$$

According to Eqs. (5) and (6), the initial amplitude $B$ must fulfill the condition $B < \frac{1}{2}(1 - T_1/\tau_G)$, where the upper limit corresponds to the absence of the tunneling process from HSE to the ground state ($1/\tau_D$ negligible compared to $1/\tau_S$). Since in our experiments $T_1 \ll \tau_G$, we expect $B < 0.5$. The initial amplitude $B$ and time constants $T_1$ and $\tau_G$ can be obtained from the fittings to the pump-and-probe data for PTV3C$_{10}$ and PDTV3C$_4$. For PDTV3C$_4$ a value of $B = 0.31$ has been found; this implies that both a direct recombination process of HSE and thermalization of HSE are taking place, even though other ultrafast nonlinear effects such as the Stark shift cannot be ruled out. From Eqs. (5) and (6), one can obtain $\tau_D = 186$ fs and $\tau_S = 140$ fs. In the case of PTV3C$_{10}$ it is rather difficult to estimate $B$ since the fast initial decay is below our time resolution. However, from the data fitting, in order to have $B < 0.5$, $T_1$ should be less than 30 fs; this implies that either one or both of the relaxation processes of HSE are faster in PTV3C$_{10}$ than in PDTV3C$_4$. It is worthwhile to note that upon progressive stiffening of the backbone, the fast initial time constant decreases from 300 fs as observed for poly(3,4 dodecyl-thiophene) (Ref. 3) to 80 fs for PDTV3C$_4$ and to less than 30 fs for PTV3C$_{10}$. This is consistent with a more efficient phonon relaxation process that could take place in PTV3C$_{10}$ since the presence of a vinyl group every thiophene ring making the backbone structure more rigid should speed up the excess energy dissipation process. In the case of PDTV3C$_4$ and poly(3-dodecyl-thiophene), the backbone structure is less rigid due to presence of adjacent thiophene rings, which can rotate one with respect to the other, and therefore the thermalization of the free exciton may occur on a much longer time scale.

We assume that the TSE relaxation to the ground state is due both to an intrinsic tunneling process in the configurational space and to the migration of TSE along the polymer chain to reach recombination centers. If the exciton recombination centers correspond to chain defects, which interrupt the conjugation length, we can model the process as a one-dimensional random walk of a quasisingle particle diffusing within segments with absorbing ends. For a uniform initial distribution of single-particle locations (or sites), the survival probability $P(t)$ is given by[10]

$$P(t) = \frac{8}{\pi^2} \sum_{0}^{\infty}{}_{l} (2l+1)^{-2} \exp\left[ -\frac{(2l+1)^2 \pi^2 D t}{L^2} \right] \, , \tag{8}$$

where $D = c^2/t_d$ is the diffusion constant ($c$ is the intersite distance and $t_d$ is the intersite hopping time) and $L = rc$ is the length of the segment ($r$ is the number of sites). At longer times the decay is dominated by the $l = 0$ term and becomes exponential,

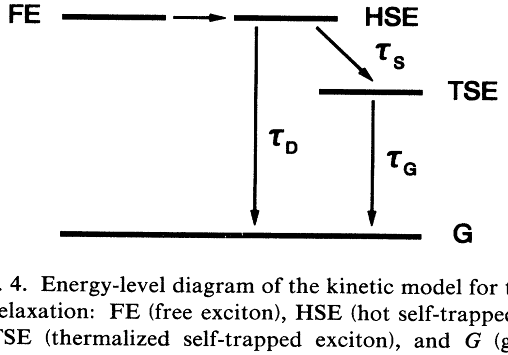

FIG. 4. Energy-level diagram of the kinetic model for the exciton relaxation: FE (free exciton), HSE (hot self-trapped exciton), TSE (thermalized self-trapped exciton), and $G$ (ground state). The time constants corresponding to the relaxation processes among the energy levels are also shown.

$$P(t)=\frac{8}{\pi^2}\exp\left[-\frac{\pi^2 t}{r^2 t_d}\right] . \tag{9}$$

Equation (9) shows that a random walk on a finite chain gives rise to an exponential decay with a recombination time constant $\tau_{\mathrm{RC}}$ given by

$$\tau_{\mathrm{RC}}=\frac{r^2 t_d}{\pi^2} . \tag{10}$$

Equation (9) can be modified in order to take into account the presence of an intrinsic exciton lifetime $\tau_{\mathrm{EX}}$ therefore,

$$P(t)=\frac{8}{\pi^2}\exp\left[-\frac{t}{\tau_{\mathrm{EX}}}\right]\exp\left[-\frac{t}{\tau_{\mathrm{RC}}}\right] . \tag{11}$$

According to Eq. (11), the longer time constant $\tau_G$ observed in our experiments is given by

$$\frac{1}{\tau_G}=\frac{1}{\tau_{\mathrm{EX}}}+\frac{1}{\tau_{\mathrm{RC}}} . \tag{12}$$

In the case where exciton relaxation only occurs at the recombination centers, from Eq. (9) a lower limit of $\tau_{\mathrm{RC}}$ can be obtained and therefore one can estimate the closest distance between two defects. Assuming $t_d=100$ fs as in polyacetylene,[11] the measured time constant $\tau_G$ for PTV3C$_{10}$ and PDTV3C$_4$ implies from Eq. (10) a random walk on a chain with a number of sites between two recombination centers of about 10. Since this value is in agreement with the limited effective conjugation length observed in poly(alkyl-thiophene)s,[12,13] we can argue that the recombination centers play a substantial role in the TSE relaxation process. Results recently reported on poly(2,5-thiophene-vinylene)[14] in film have shown an unresolved fast initial decay followed by an exponential decay. The time constant reported for the exponential decay (2.6 ps) is consistent with the above model, since the effective conjugation length in a solid state is probably higher than that in solution.

## IV. CONCLUSIONS

We have measured by femtosecond pump and probe the transient absorption saturation of poly(alkyl-thiophene-vinylene)s. The transient absorption data seem to be consistent with the formation and decay of self-trapped excitons. While changes in the location and size of the side groups seem to have little effect on the excited-state relaxation dynamics, the insertion of intrachain vinyl groups has the effect of stiffening the conjugated backbone thus resulting in a considerably faster decay of the photogenerated states compared to poly(alkyl-thiophene). The decay kinetics can be modeled with simple rate equations, which allow us to detect the presence of a fast relaxation process of hot self-trapped excitons towards the ground state. The recombination mechanism of thermalized self-trapped excitons can be interpreted in terms both of a tunneling process in the configurational space and of a diffusive motion of the exciton in a polymer segment with recombination centers at the ends.

## ACKNOWLEDGMENT

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