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# Femtosecond probing of exciton relaxation and transport dynamics in polybithiophene

Alexander M. Bock, Dankward Schmid, and Carola Krysch<sup>a)</sup>

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The relaxation and transport dynamics of singlet excitons in 100 nm thick, electrochemically prepared polybithiophene films were investigated by monitoring the time evolution of photoinduced bleaching of the  $S_0$ – $S_1$  absorption and photoinduced absorption ( $S_1$ – $S_n$ ) with femtosecond resolved transient absorption spectroscopy. The decay dynamics of both photoinduced bleaching and photoinduced absorption in the spectral range from 500 to 800 nm are observed to be independent of the pump pulse wavelength and can be fitted by a double exponential, the time constants of which are  $\tau_1 = 120 \pm 20$  fs and  $\tau_2 = 2 \pm 0.3$  ps. The fast decay process with  $\sim \tau_1 = 120$  fs was ascribed to the transport dynamics of the initially generated free excitons migrating over parallel aligned polymer segments to structural defects acting as traps. The competing process, occurring predominantly in structurally disordered regions, is structural relaxation of the initially generated free excitons to self-trapped excitons decaying with a lifetime of about 2 ps. © 1999 American Institute of Physics. [S0021-9606(99)70727-0]

## I. INTRODUCTION

Polythiophene and its derivatives, representatives of the class of  $\pi$ -conjugated polymers, have attracted great interest because of their ultrafast relaxation dynamics of photoexcitation,<sup>1–4</sup> high electric conductivity,<sup>5</sup> large optical nonlinearities,<sup>6</sup> and excellent photochemical stability.<sup>1–5</sup> Despite intense theoretical and spectroscopic research work on the electrical and optical properties of  $\pi$ -conjugated polymers there is still controversy about the nature of the photo-generated excitations and their transport properties and of the relaxation dynamics in these systems.<sup>7–12</sup> There are three conflicting concepts for the theoretical approach of photoexcitations: first, the semiconductor band model of Heeger and co-workers,<sup>1,7</sup> second, the molecular exciton model of Bässler and co-workers,<sup>9,10</sup> and, third, the free/self-trapped exciton model of Kobayashi *et al.*<sup>2,11</sup> The semiconductor band model postulates infinite one-dimensional  $\pi$ -electron systems delocalized along the linear polymer backbone. The electron system is described by the Hamiltonian which neglects Coulomb and electron correlation effects.<sup>1,7</sup> Photoexcitations are considered to be uncorrelated electron-hole pairs forming polaron excitons or bipolarons due to self-consistently generated local structural distortions (e.g., strong electron–phonon coupling).<sup>7</sup> On the other hand, the Kobayashi model, also based on the assumption of one-dimensional conjugated electron systems on linear polymer chains, proposes the relaxation scheme of photoexcitations as follows: free singlet excitons, initially generated by ultrashort laser pulses ( $\tau_p = 70$ –120 fs), decay by nonthermal self-trapping within 10–20 fs, which is followed by quasithermalization (70–150 fs for P3MT) to thermalized self-trapped excitons and subsequent relaxation to the ground

state within 1–5 ps.<sup>2,11</sup> Contrary to this, in the molecular approach optical excitation generates Frenkel excitons. As Bässler *et al.*<sup>9</sup> and Teresaki *et al.*<sup>11</sup> showed by low-temperature site-selective fluorescence spectroscopy on, e.g., poly(*p*-phenylenevinylene)s (PPV), the optical properties of this type of conjugated polymers is determined by both conformational disorder and structural defects (e.g., linkage defects, kinks, and geometrical distortions). This has very recently been confirmed by Kersting *et al.*,<sup>12</sup> who studied exciton motion in the same material with fluorescence up-conversion and picosecond single-photon timing techniques. The time evolution of the fluorescence spectra of PPV derivatives is understood in terms of the random walk of Frenkel excitons within the density of states associated with the polydispersity of effective conjugation lengths of polymer segments. Recently, Mukamel *et al.*<sup>13</sup> performed a comprehensive theoretical study of the electronic excitations of PPV approximated by a linear chain of 10 and 30 monomer units. Successfully utilizing the collective electronic oscillator (CEO) approach these authors analyzed the linear optical absorption spectrum in terms of five (dominant) electronic normal modes, which allows one to elucidate the motion of charges and delocalization of  $\pi$ -electron excitations (e.g. the exciton coherence size) for the associated excited singlet states. They were able to show that the exciton coherence size is about five monomer units, which corresponds to the effective conjugation length of the polymer segments.

In contrast to PPV derivatives, polythiophene and its derivatives are nonfluorescent polymers and may easily form films with high crystallinity.<sup>14</sup> Recently Kobayashi has reported femtosecond resolved transient absorption spectroscopy studies on the decay dynamics of photoexcitations in electrochemically prepared poly-3-methylthiophene (P3MT) and poly-3-dimethylthiophene (P3DT) films. The experimental data were analyzed in terms of a one-dimensional poten-

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tial model describing the relaxation scheme from initially photogenerated free excitons via the subsequent formation of self-trapped (ST) excitons to their radiationless decay. The formation time  $\tau_f$  and the decay time  $\tau_d$  of the ST excitons in these polymers are  $\tau_f = 70 \pm 50$  fs and  $\tau_d = 620 \pm 70$  fs for P3MT and  $\tau_f = 100 \pm 50$  fs and  $\tau_d = 450 \pm 60$  fs for P3DT.<sup>2</sup> However, since these results are based on a one-dimensional potential model that completely ignores the strong dipole-dipole interactions between closely spaced neighboring polymer segments in a partially crystalline polythiophene film, interpretation of the nature of the observed photoexcitations as well as rationalization of the exciton relaxation scheme with the assignments of the time constants are quite ambiguous.

In this article we present a detailed study of the relaxation and transport dynamics of singlet excitons in polybithiophene films on the time scale from 120 to 20 ps using transient absorption spectroscopy. Electrochemically prepared, 100 nm thick polybithiophene films were excited at room temperature into the  $S_0$ – $S_1$  absorption band with a 120 fs pump pulse tuned to the center and into the red edge of the absorption spectrum. The decay dynamics of the singlet excitons were measured via transient absorption of the white-light probe pulse between 600 and 800 nm, while the time evolution of photoinduced bleaching probes the recovery dynamics of the ground-state ( $S_0$ ) population between 500 and 600 nm. Any influence of the polydispersity of the effective conjugation lengths on the static absorption spectrum of polybithiophene films could be excluded by comparing the time evolutions of the transient absorption spectra, which were measured with pump pulses at different central wavelengths, 578, 614, and 636 nm. The short time dynamics ( $\tau < 1$  ps) of the transient absorption spectra were systematically investigated as to their dependence on the pump pulse intensity. Nonlinear effects, in particular those due to bimolecular exciton–exciton annihilation, were not observed and thus need not be accounted for in the analyses of the experimental data. The dynamics of photoinduced bleaching and absorption were observed to be independent of the polarization of the pump and probe pulse. By achieving a significantly higher signal to noise (S/N) ratio, the experimental data obtained from measurements with a parallel polarization geometry are presented here.

## II. EXPERIMENT

### A. Sample preparation

Polybithiophene films with a thickness of about 100 nm were prepared on ITO glass substrates (Merck,  $R_\perp = 16.8 \Omega$ ) by electrochemical anodic oxidation of dithiophene in acetonitrile/0.1 mol/l  $\text{LiClO}_4$  at a current density of 200  $\mu\text{A}/\text{cm}^2$  and by subsequent cathodic reduction at  $-0.2$  V (SHE).<sup>15</sup>

### B. Transient absorption spectroscopy

Transient absorption spectra with a time resolution of about 180 fs were measured using the pump–probe technique. Pump and probe pulses are generated by a femtosecond laser system that consists of a passively mode-locked

Ti:sapphire laser oscillator (Clark-MXR, NJA-4), a regenerative Ti:sapphire amplifier (Clark-MXR, TRA-1), and an optical parametric amplifier (OPA) (Clark-MXR, V-GOR). The OPA produces, at a repetition rate of 1 kHz, 120 fs pulses that are used as pump pulses, and which are tunable between 470 and 670 nm and have energies from 10 to 20  $\mu\text{J}$  per pulse. White-light continuum probe pulses (300–1000 nm), with a time dispersion of 0.5 ps,<sup>16</sup> are generated by focusing the unconverted remainder of the amplified fundamental laser pulses (0.2 mJ per pulse) in the OPA into a 10 mm thick  $\text{D}_2\text{O}$  flow cuvette. A variable delay stage provides temporal delay for the pump pulses up to 20 ps with a resolution of 9.7 fs. The pump and probe pulses are parallel polarized in all pump–probe experiments. The pump pulse energy was kept below 0.5  $\mu\text{J}$ . The intensity of the transmitted probe beam with and without pump pulse excitation,  $I(p)$  and  $I(0)$ , respectively, was measured by chopping the pump beam at a frequency of 6 Hz. For each data point, 13 000 pulses were averaged. The ratio,  $I(p)/I(0)$ , corresponding to the pump pulse induced change of the transmission,  $\Delta T = T(p)/T(0)$ , is determined with a precision of  $10^{-3}$ . The time dispersion of 0.5 ps over the spectral range of the white-light continuum probe pulses has been corrected for by determining the  $\tau = 0$  point from the rise of the bleaching or transient absorption signals at spectral intervals of about 0.7 nm.<sup>16</sup> The transmission spectra of the white-light probe pulses behind the sample were analyzed using a home-built polychromator containing a 400 lines/mm grating and a charge coupled device (CCD) camera (LOT, Instaspec). Analyses of the temporal evolution of transient absorption and bleaching were carried out using biexponential rise and decay functions, respectively, and were exemplary in combination with a deconvolution procedure.

## III. RESULTS AND DISCUSSION

The static absorption spectrum of a 100 nm thick polybithiophene film, consisting of a structureless broad band ranging from 380 to 620 nm with its maximum at 480 nm, is assigned to the excitonic  $\pi$ – $\pi^*$  transition (see Fig. 1). The full width at half maximum (FWHM) of this absorption band, with  $\sim 10\,000 \text{ cm}^{-1}$ , lies in the range of the typical bandwidths of polarized absorption spectra of oligothiophene films (e.g., sexithiophene, hepta-, and octathiophene).<sup>17</sup> This suggests that conformational disorder in polybithiophene plays a major role in the inhomogeneous broadening of the absorption band. In contrast, structural disorder, purported to exist in PPV films due to linkage defects, chain distortions, and/or chemical defects, gives rise to a statistical variation of the effective conjugation lengths of the polymer segments and thereupon causes a dispersion of the segment energy states.<sup>9,10,12</sup> In Bässler's molecular exciton picture the absorption spectra of polymers are rationalized as arising from the superposition of the individual spectra of distinctly long polymer segments.<sup>9,10</sup> Thus, the absorption spectra of polymer segments, characterized by their effective conjugation length, resemble those of the respective, equally long oligomers. This implies that the polymer spectrum, consisting of energetically shifted oligomer spectra, should exhibit a bandwidth considerably larger than that of the individual oligo-

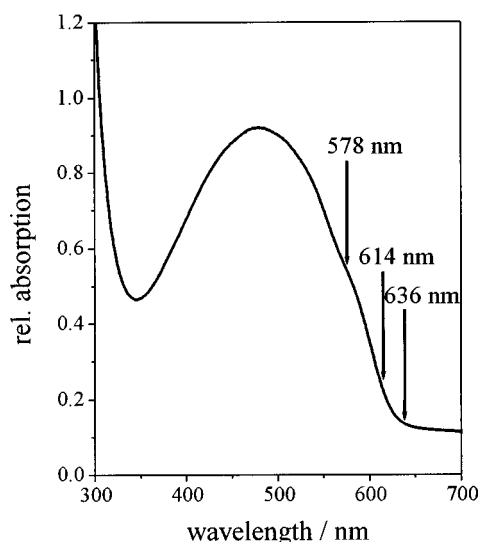


FIG. 1. Static absorption spectrum of a 100 nm thick polybithiophene film recorded at room temperature; the three arrows indicate the central wavelengths of the respective distinctly tuned pump pulse.

mer spectra. This does not apply to the absorption spectrum of polybithiophene. Nevertheless, we have to examine effects by structural disorder in polybithiophene films, since disorder with respect to the effective conjugation lengths is known to play an essential role in the transport topology and dynamics of singlet excitons in PPV and its derivatives.<sup>9,10,12</sup> This has been successfully shown by femtosecond site-selective fluorescence spectroscopy: excitation of the so-called high-energy sites (i.e., short polymer segments) results in energy-dispersive, incoherent exciton migration from the initially excited short segments via longer conjugated segments to those with the largest conjugation length and the lowest energy, which act as exciton traps.<sup>9,10,12</sup> As a consequence, exciton transport and relaxation dynamics become faster with increasing excitation energy.<sup>12</sup> This type of exciton relaxation scheme is reported to be responsible for the spectral diffusion observed on the femtosecond scale as a transient redshift and narrowing of fluorescence spectra.<sup>12</sup>

To obtain information about the dispersion of effective conjugation lengths and to gain, thereby, insight into the microscopic morphology of our polybithiophene samples we have investigated the influence of the excitation energy on the temporal and spectral evolution of photoinduced bleaching as well as of photoinduced absorption. Therefore, transient absorption spectra were excited with pump pulses tuned to wavelengths of 578, 614, and 636 nm, respectively, as indicated by the arrows in Fig. 1. The rise dynamics of the structural features in the transient absorption spectra were observed to be independent of the excitation wavelength. Figure 2 illustrates the time evolution of transient absorption spectra of a 100 nm thick polybithiophene film between  $\tau = -250$  (base line) and  $+150$  fs (the maximum of transmission changes), which were excited at 614 nm and are representative also of those excited at 578 nm and 636 nm. The time dependence of the photoinduced transmission changes  $\Delta T(\tau, \lambda)$  is given by the delay time  $\tau$  of the pump pulse relative to the arrival time of the probe pulse in the sample.

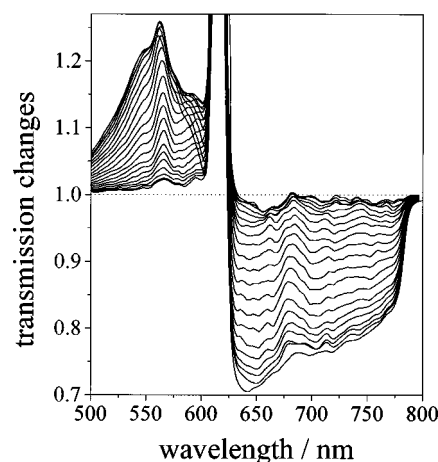


FIG. 2. Time evolution of transient absorption spectra of a 100 nm thick polybithiophene film recorded between  $\tau = -250$  and  $+150$  fs; the central wavelength of the pump pulse is 614 nm.

The time distance between the individual spectra is about 19.4 fs. The transient absorption spectrum is defined as the wavelength dependency of the photoinduced transmission changes at a given delay time  $\tau = \tau_0$  [i.e.,  $\Delta T(\lambda)$ ]. While transmission changes with  $\Delta T(\lambda) > 1$  characterize photoinduced bleaching of the  $S_0-S_1$  absorption, photoinduced ( $S_1-S_n$ ) absorption is ascribed to transmission changes with  $\Delta T(\lambda) < 1$ . The transient absorption spectra in Fig. 2 consist of photoinduced bleaching and photoinduced absorption in the ranges of 400–600 and 625–800 nm, respectively. Scattering light of the pump pulse at the central wavelength of 614 nm is superimposed on the border area between the photoinduced bleaching and the absorption. The structural features in the bleaching spectra, consisting of a prominent peak at 561 nm, a shoulder at 577 nm, and a bump at 545 nm, decay within 200 fs and are ascribed to transient photoinduced resonance Raman scattering (TPRRS).<sup>18</sup> These anti-Stokes lines with Raman shifts of 1540, 1030, and 2063  $\text{cm}^{-1}$  are assigned to the C=C and C—C stretching vibration and its overtone, respectively.<sup>19</sup> The photoinduced absorption spectra also contain TPRRS peaks, occurring at 658 and 678 nm, with Stokes shifts of  $\sim 1090$  and  $1540 \text{ cm}^{-1}$ , which resemble the vibrational structure of the photoinduced bleaching. Since TPRRS decays within the apparatus time resolution of about 250 fs, these peaks are ideal time markers for  $\tau = 0$ . They have been utilized to correct for the chirp of the white-light continuum pulse. Apart from the TPRRS signals the time evolution of the transient absorption spectrum does not show any structural changes, which is characteristic of spectral diffusion due to energy-dispersive exciton migration and predicted in Bässler's model.<sup>9,10,12</sup> The time dependence of photoinduced transmission changes recorded at a constant wavelength  $\lambda = \lambda_0$  [i.e.,  $\Delta T(\tau)$ ] is termed a transient or decay curve of photoinduced bleaching with  $\Delta T(\tau) > 1$  or absorption  $\Delta T(\tau) < 1$ . We have investigated the influence of the pump pulse energy on the transients between 0.5 and 5  $\mu\text{J}$  and could not observe any change in the transients for pump pulse energies below 2  $\mu\text{J}$ .<sup>16</sup> To avoid exciton–exciton annihilation effects and coherence

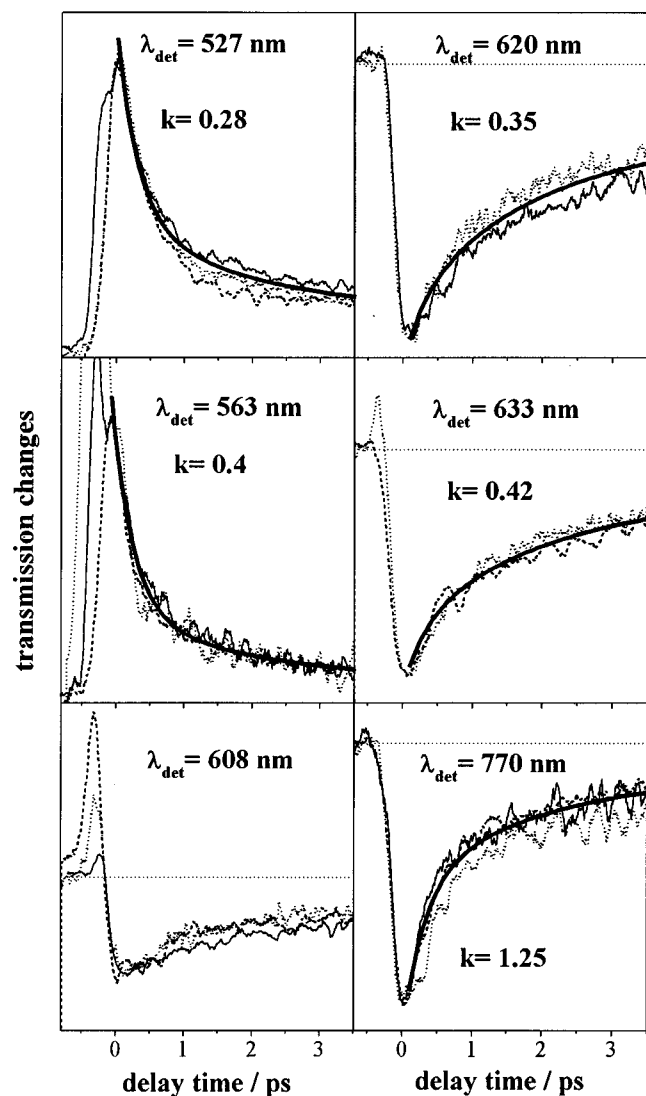


FIG. 3. Transients of photoinduced bleaching detected at 527 and 563 nm and transients of the photoinduced absorption detected at 608, 620, 633, and 770 nm; the transients were excited at 578 nm (dotted line), 614 nm (dashed thick line) and 636 nm (thin solid line); the biexponential fit functions (thick solid line) differ in their amplitudes ratio  $k$  (see the text).

phenomena, which would be manifested as nonexponential behavior or as coherence peaks in the transients, we have used pump pulses with energies of about  $0.3 \mu\text{J}$ . In addition, the transient absorption spectra of the polybithiophene films are obviously independent of the excitation energy. This is illustrated by the transients of photoinduced bleaching and absorption, excited at 578, 614, and 636 nm and detected at different wavelengths between 520 and 770 nm, which are depicted in Fig. 3. The transients, examples of the decay dynamics of the total transient absorption spectrum, can be described by the biexponential functions

$$\Delta T(\tau) \propto A_1 \times \exp(-t/\tau_1) + A_2 \times \exp(-t/\tau_2) \quad (\text{for bleaching}),$$

or

$$\Delta T(\tau) \propto A_1 \times [1 - \exp(-t/\tau_1)] + A_2 \times [1 - \exp(-t/\tau_2)]$$

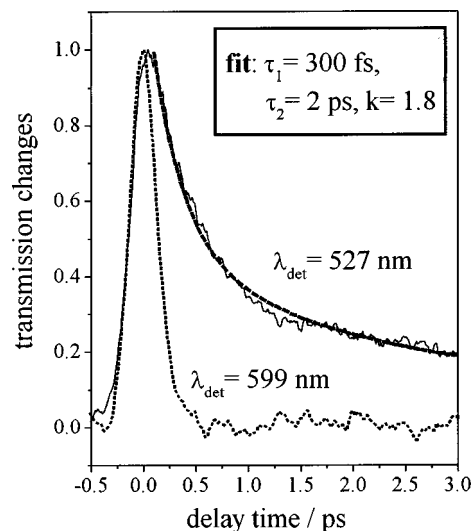


FIG. 4. Transients of photoinduced bleaching detected at 527 nm (thin solid line) and at 599 nm (dotted line); the central wavelength of the pump pulse is 578 nm; the transient at 527 nm was fitted by a biexponential function with the parameters  $\tau_1 = 300 \text{ fs}$ ,  $\tau_2 = 2 \text{ ps}$ , and  $k = 1.8$  (dashed thick line).

(for absorption). While the time constants are  $\tau_1 = 300 \pm 30 \text{ fs}$  and  $\tau_2 = 2 \pm 0.2 \text{ ps}$  for the total detection wavelength range of 500–800 nm, the ratio of amplitudes  $k = A_1/A_2$  shows a strong dependence of the detection wavelength. These results suggest the existence of two different types of excitonic states which are generated by the pump pulse within the apparatus time resolution. The photoinduced absorption spectra of both exciton species overlap one another. The increase of  $k$  with the detection wavelength implies that the absorption maximum of the shorter living excitonic states with  $\tau_1 = 300 \text{ fs}$  is shifted to longer wavelengths relative to that of the longer living states with  $\tau_2 = 2 \text{ ps}$ . Since the short-time dynamics of the transients are buried by the apparatus' time resolution, the biexponential fit cannot achieve a precise determination of the short-time constant  $\tau_1$ . To improve the precision we have performed a fast Fourier transformation (FFT) into the frequency domain of the transients of photoinduced bleaching (see Fig. 4). The transient detected at 599 nm, being an isobestic point of the transient absorption spectrum, can be fitted by a Gaussian function with the width  $t_w = 251 \text{ fs}$  that corresponds to the cross correlation between the pump and probe pulse (see Fig. 5). On the other hand, the transient detected at 527 nm displays the biexponential decay dynamics of photoinduced bleaching (see Fig. 6). While the Fourier transformation of the Gaussian-shaped cross correlation function is a Gaussian function with the width  $w_0 = 2.36 \times 10^{12} \text{ s}^{-1}$  again, the Fourier transformation of the bleaching transient is supposed to be a product of the Gaussian function with the sum of two Lorentzian functions describing homogeneous absorption lines of the two types of excitons. To extract the short-time constant from the FFT of the bleaching transient we have used the fit function

$$f(x) = \frac{A_0}{w_0 \sqrt{\pi/2}} e^{-(2x^2/w_0^2)} \times \left( \frac{2A_1}{\pi} \frac{w_1}{4x^2 + w_1^2} + \frac{2A_2}{\pi} \frac{w_2}{4x^2 + w_2^2} \right), \quad (1)$$

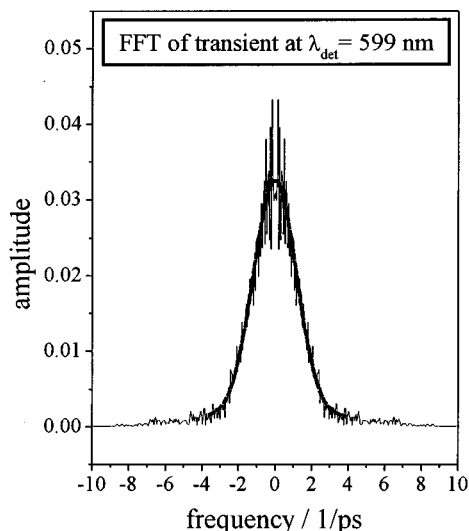


FIG. 5. Fast Fourier transformation of the transient at  $\lambda_{\text{det}}=599$  nm (thin solid line) fitted by a Gaussian function (dashed thick line); the frequency scale is in units of  $10^{12} \text{ s}^{-1}$ .

with the pre-set parameters  $w_0=2.36 \times 10^{12} \text{ s}^{-1}$  and  $w_2=0.5 \times 10^{12} \text{ s}^{-1}$  (with  $\tau_2=1/w_2=2$  ps). The best fit was obtained with the parameters  $A_1=10$ ,  $A_2=5$ , and  $w_1=8.33 \times 10^{12} \text{ s}^{-1}$ . The reciprocal value of  $w_1$  is the short-time constant  $\tau_1=1/w_1=120$  fs.

In this analysis we did not account for coherence effects initially generated by the overlap between the pump and probe pulse. The absence of typical coherent features in the transients, such as coherence peaks or quantum beats, as well as the imperfect coherence and the noise of the pump and probe pulse, do not justify any theoretical effort. We are aware that the short-time constant  $\tau_1=120 \pm 20$  fs might also arise from, or at least involve, decay by inhomogeneous

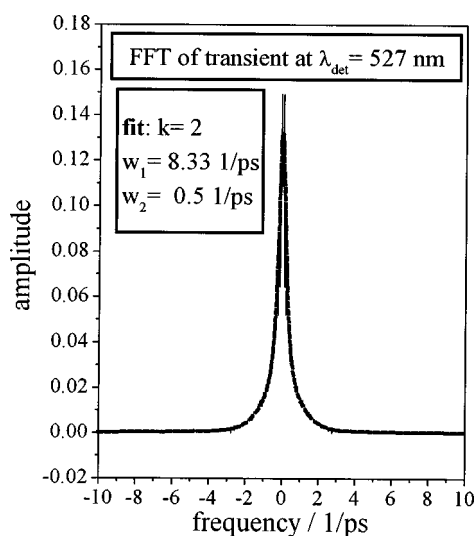


FIG. 6. Fast Fourier transformation of the transient at  $\lambda_{\text{det}}=527$  nm (thin solid line) with the fit function (dashed thick line); the fit consists of a product of the Gaussian fit function, depicted in Fig. 5, with a sum of two Lorentzian functions, the widths of which are  $w_1=8.33 \text{ s}^{-12}$  and  $w_2=0.5 \text{ s}^{-12}$  with an amplitude ratio of  $k=2$ ; the frequency scale is in units of  $10^{12} \text{ s}^{-1}$ .

dephasing.<sup>20</sup> Our argumentation against pure inhomogeneous dephasing within the first 200 fs is based on the significant dependence of the fast-decay amplitude on the detection wavelength that strongly indicates photoinduced absorption transitions of excited species.

The two independent decay dynamics, characterized by  $\tau_1=120 \pm 20$  fs and  $\tau_2=2 \pm 0.3$  ps, respectively, are explained as originating from two independent exciton relaxation processes that occur in morphologically different regions of the polymer film. The fast decay dynamics with  $\tau_1=120$  fs is ascribed to the transport dynamics of the instantaneously generated (free) excitons over approximately parallel aligned polymer segments in crystalline regions to grain boundaries defects or structural defects. These defects may induce a thermally assisted dissociation of the excitons to electron-hole pairs followed by recombination to the ground state. The competing process of the transport dynamics in structurally disordered regions of polybithiophene is fast structural relaxation of the free excitons to the so-called self-trapped excitons<sup>2,4</sup> which decay without radiation with  $\tau_2=2$  ps to the ground state. The free and self-trapped excitons differ in their energies as well as in the spectral ranges and oscillatory strengths of their photoinduced absorption transitions. These differences are considered to be responsible for the significant detection wavelength dependence of amplitude ratio  $k$  in the biexponential fits of the transients. On the other hand, the biexponential decay dynamics of photoinduced bleaching and absorption are independent of the excitation wavelength. This observation suggests that the dispersion in the effective conjugation lengths of the polymer segments in polybithiophene films is small compared to that of the PPV class. This rationalization is consistent with the relatively small band width of  $S_0-S_1$  absorption band and supported by crystallographic data of polythiophene films.<sup>14</sup> Crystalline grains in polybithiophene films presumably consist of parallel aligned polymer segments, whereas structural disorder in the grain boundaries may be constituted by misaligned segments, linkage defects, and geometrical distortions [e.g., three-dimensional (3D) distortions]. The excitonic coupling between perfectly stacked polythiophene segments may become very strong, since the transition dipole momentum is aligned along the polymer chain and reaches high values (e.g., 10.4 debye for sexythiophene<sup>19</sup>). For instance, in H aggregates of sexythiophene the intermolecular distances range between 4.9 and 5.2 Å, resulting in excitonic bands with widths of about  $\Delta E \approx 10\,000 - 15\,000 \text{ cm}^{-1}$ .<sup>21</sup> This implies that the decay dynamics of free excitons, which are delocalized over crystalline grains, are determined by trapping and dissociation processes at defects in the grain boundaries. On the other hand, the structural relaxation dynamics of excitons, which are generated initially in the structurally disordered boundary regions, could not be temporally resolved by our experimental setup. The time constants of exciton self-trapping (or structural relaxation) in polythiophene derivatives were reported to range between 20 and 150 fs.<sup>2</sup>

#### IV. CONCLUSIONS

The time and spectral evolution of photoinduced bleaching of the  $S_0$ – $S_1$  absorption and photoinduced absorption ( $S_1$ – $S_n$ ) in 100 nm thick, electrochemically prepared polybithiophene films monitored by fs transient absorption spectroscopy are observed to be independent of the wavelength and intensity of the excitation (pump) pulse, while the respective biexponential transients exhibit a dependence on the detection wavelength with regard to the amplitude ratio  $k = A_1/A_2$ . The principal conclusion drawn from these femtosecond spectroscopic data is that the decay dynamics of the initially created singlet excitons reflect the microscopic morphology of the polybithiophene film: the fast dynamics ( $\tau_1 \approx 120$  fs) are ascribed to excitons photogenerated in crystalline grains of the polymer film. These excitons, which correspond to the free excitons in the Kobayashi model,<sup>2</sup> are delocalized over parallel aligned polymer segments and are trapped by 3D distortions at the boundaries, which act as recombination centers. On the other hand, structural disorder in amorphous regions localizes the photoexcitations to one polymer segment via fast structural relaxation. These so-called self-trapped excitons have a lifetime of about  $\tau_2 \approx 2$  ps.

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