Femtosecond Study of Exciton Transport Dynamics in (Phthalocyaninato)polysiloxane

Jan Ern,[†] Alexander Bock,[†] Lionel Oddos-Marcel,[†,‡] Heiko Rengel,[§] Gerhard Wegner,[§] H. Peter Trommsdorff,[‡] and Carola Kryschi*,[†]

Lehrstuhl für Festkörperspektroskopie (IPkM), Universität Düsseldorf, D-40225 Düsseldorf, Germany, Laboratoire de Spectrométrie Physique, Université Joseph-Fourier Grenoble I, B.P. 87, F-38402 St. Martin d'Hères, France, and Max-Planck-Institut für Polymerforschung Mainz, Ackermannstrasse 10, D-55128 Mainz, Germany

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The transport and relaxation dynamics of singlet excitons of rodlike [tetramethoxytetrakis(octyloxy)-phthalocyaninato]polysiloxane (PcPSi) in tetrahydrofuran solution were investigated on the femtosecond scale by transient absorption spectroscopy. Singlet excitons are generated upon excitation into the ground-state absorption at 555 nm using laser pulses of 120 fs duration with different intensities. Transient absorption spectra were recorded at variable delays using a white-light continuum probe pulse. Both photoinduced bleaching and transient absorption show nonexponential decay dynamics with a pronounced dependence on the excitation energy density. The analysis of the decay dynamics of the photoinduced bleaching and transient absorption at lower excitation densities is made by including, in addition to the monomolecular, exponential decay with lifetime τ, a time-dependent bimolecular exciton−exciton annihilation rate constant $\gamma t^{-1/2}$, characteristic of one-dimensional diffusive exciton transport. At high excitation densities, the observed decay strongly deviates from this behavior, as a new relaxation channel is opened, which is attributed to short-lived, charge-separated states.

Introduction

(Phthalocyaninato)polysiloxane (PcPSi) composed of siloxane-polymerized, cofacially stacked phthalocyanines (Pc), staggered at an angle of 36°, is a one-dimensional molecular conductor.[1] The linear stacking and the rather small ring−ring interplanar spacing of about 0.33 nm[1−3] favor efficient intermacrocycle $\pi-\pi$ interactions, so that optical excitation is expected to lead to extensive excitonic coupling between the extended π-conjugated electron systems of the phthalocyanine cycles.[2,4,5] In particular, Langmuir−Blodgett multilayer structures of PcPSi exhibit high photoconductivity and strong light absorption in the visible, properties that are the basis for the successful development of photoactive devices such as photodiodes and sensors.[6,7] The photogeneration of charges in PcPSi films has been the subject of intense research for many years.[2,4−8] There are several issues of central importance in studying the photogeneration of charge carriers as well as the transport dynamics of excited states and charge carriers. The proper characterization of the relaxation dynamics of the initially excited electronic states and, in particular, of the exciton transport dynamics is of great interest in this regard.

In films of metallophthalocyanine stacks, the Pc rings are spaced by van der Waals distances and exciton coupling of neutral−electronic transitions between neighboring macrocycles becomes very efficient. The characterization of the dynamics of the exciton motion together with the related exciton−exciton annihilation at high excitation densities has been an area of active theoretical and experimental research.[3,9−12] For large exciton densities, nonexponential bimolecular exciton−exciton annihilation has been observed by femtosecond spectroscopy studies in H_2Pc thin films,[9] FAlPc thin films,[10] VOPc films,[11,12] and Langmuir−Blodgett films of SiPc polymers.[8] The analyses of these data are based on the assumption of unidimensional exciton transport, a condition not well fulfilled in films because of the interactions between the Pc stacks. In addition, local heating of thin films may affect the exciton dynamics. These factors impede considerably the elucidation of exciton transport dynamics in metallophthalocyanine films. On the other hand, linear polymers of (phthalocyaninato)siloxane in solution strictly limit the exciton transport to one dimension and heating effects can be avoided in flowing solutions.

In this work, we present a study of the femtosecond excited-state dynamics of [tetramethoxytetrakis(octyloxy)phthalocyaninato]-polysiloxane (PcPSi) in tetrahydrofuran solution. This linear polymer consists of an average of 32 cofacially stacked oxo-bridged silicon phthalocyanine rings with stacking distances of $d_{\mathrm{Si-O-Si}} = 0.33$ nm (see Figure 1) and constitutes fairly rigid rods of ca. 11 nm length.[2,3] The temporal evolution of the singlet exciton states created at different excitation energy densities between ca. 0.5 and 2.5 mJ/cm^2 was studied by femtosecond transient absorption spectroscopy. Both photoinduced bleaching and transient absorption were observed, and decay dynamics, which strongly depend on the excitation energy density, are nonexponential. At higher excitation densities, the observed relaxation dynamics in PcPSi are dominated by exciton−exciton annihilation. The excited state lifetime of singly excited chains is ca. 4.5 ps, drops to about 0.5 ps for doubly excited chains and becomes less than the instrumental resolution of 150 fs at higher excitation densities. An analysis of the decay dynamics was made in terms of a model, which has been successfully utilized to rationalize the exciton transport dynamics in VOPc films[1,12] and PbPc films,[12] and in which the exciton−exciton

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[†] Universität Düsseldorf.

[‡] Université Joseph-Fourier Grenoble I.

[§] Max-Planck-Institut für Polymerforschung Mainz.

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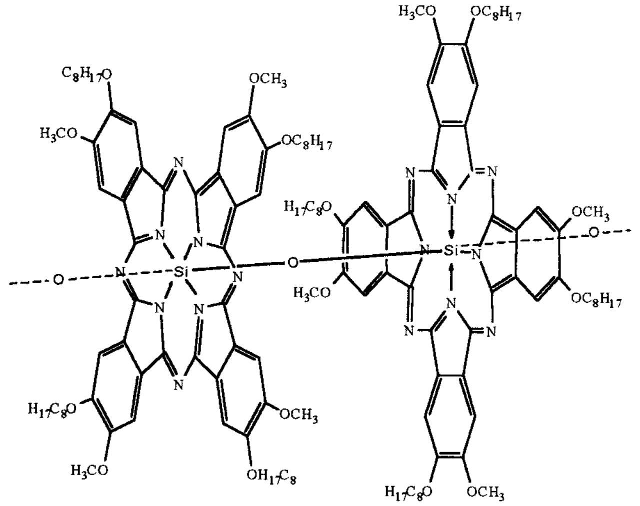

Figure 1. Structure formula of [tetramethoxytetrakis(octyloxy)-phthalocyaninato]polysiloxane.

annihilation rate is time-dependent ($t^{-1/2}$). For low excitation densities the decay behavior can be well reproduced, while at higher densities the recovery of the ground state is faster than predicted. We suggest that this fast recovery is due to creation of charge-separated states, which efficiently quench all excited states of a polymer chain.

Experimental Section

Steady-state absorption spectra were recorded using a UV/vis absorption spectrophotometer (Beckman UV 35). Transient absorption spectra with femtosecond time resolution were measured using the pump−probe technique. Pump and probe pulses are generated by a femtosecond laser system consisting 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 (Clark-MXR, V-GOR). The optical parametric amplifier (OPA) produces, at a repetition rate of 1 kHz, 120 fs duration pulses with a central wavelength of 555 nm (18 020 cm^{-1}) and with energies of 0.5−10 μJ per pulse, which are used as pump pulses. The pump pulse intensity was measured with a calibrated power meter (Coherent, LaserMate Q). White-light continuum probe pulses over the spectral range of interest (12 500−24 000 cm^{-1}) are generated by focusing the amplified fundamental laser pulses (0.2 mJ per pulse), left over after frequency doubling in the OPA, into a 10 mm D_2O flow cuvette. A variable delay line provides a time delay, τ_D, for the pump pulses of up to 60 ps with a resolution of 2.4 fs.

The pump and probe beams are parallel polarized in all pump−probe experiments. The spot size in the sample is about 10^{-3} cm^2. Transmission spectra of the sample were obtained by dispersing the probe pulses with a polychromator containing a 400 lines/mm grating in combination with a CCD detector system (LOT, InstaSpec IV). 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, $I(p)/I(0)$, which equals 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 4 ps over the spectral range of the white-light continuum probe pulses has been corrected for by determining the $\tau_D = 0$ point from the rise of the bleaching or transient absorption signals at spectral intervals of about 80 cm^{-1}.

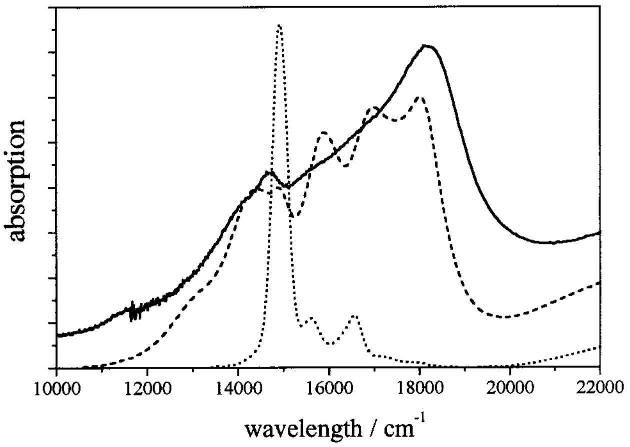

Figure 2. Absorption spectra of the (phthalocyaninato)siloxane monomers (PcMSi, dotted line), dimers (PcDSi, broken line), and polymers (PcPSi, thick solid line) in tetrahydrofuran.

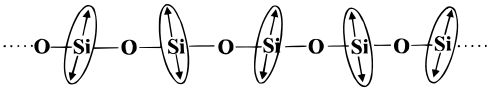

Figure 3. Tilted stacking of the phthalocyanine macrocycles with respect to the siloxane chain.

PcPSi, synthesized as described in refs 13 and 14 and consisting of an average of 32 monomer units, was dissolved in spectrograde tetrahydrofuran (THF) at a concentration of 2.8 × 10^{-5} mol/L. The solutions were pumped at 5 mL/s through a 400 μm flow cell ensuring a complete replacement of the sample volume between laser pulses.

Results and Discussion

Absorption Spectra. Figure 2 shows the absorption spectra of the (phthalocyaninato)siloxane monomers (PcMSi, dotted line), dimers (PcDSi, broken line), and polymers (PcPSi, thick solid line) in tetrahydrofuran solution. The absorption spectrum of PcMSi shows the Q-band at 14 900 cm^{-1}, assigned to the electronic transition from the ground state ($a_{1u}{}^2$) to the first excited singlet state ($a_{1u}{}^1e_g{}^1$), and to the associated vibronic sidebands involving totally symmetric vibrations of Pc (at 700 cm^{-1}, 1630 cm^{-1}), respectively.[1,15,16] Excitonic coupling between the π electron systems of the phthalocyanine macrocycles and vibronic coupling and the admixture of ring-to-ring charge-transfer configurations cause the blue shift and the quite dramatic broadening of the dimer and polymer absorption spectrum.[15,16] The absorption spectrum of PcPSi in tetrahydrofuran solution (see thick solid line in Figure 2) exhibits two maxima at 18 180 cm^{-1} and 14 685 cm^{-1} superimposed on a ca. 8000 cm^{-1} broad, weakly structured band. The two maxima, separated by ca. $\Delta = 3500$ cm^{-1}, are assigned to the electronic transitions into the lower and upper exciton states of the Q-band. The observation of the upper exciton component (forbidden in C_4 symmetry) indicates a slightly tilted (e.g., oblique or alternate translational) stacking of the phthalocyanine macrocycles with respect to the siloxane chain (see Figure 3).[17,18] The exciton band splitting of the polymer is very similar to the splitting of 3540 cm^{-1} determined for the dimer (PcDSi) in the strong coupling limit.[16] The absorption spectrum of the dimer (PcDSi) in tetrahydrofuran (see broken line in Figure 2) shows a weakly structured band between 12 000 and 19 000 cm^{-1} and resembles coarsely the intensity distribution of the polymer spectrum.

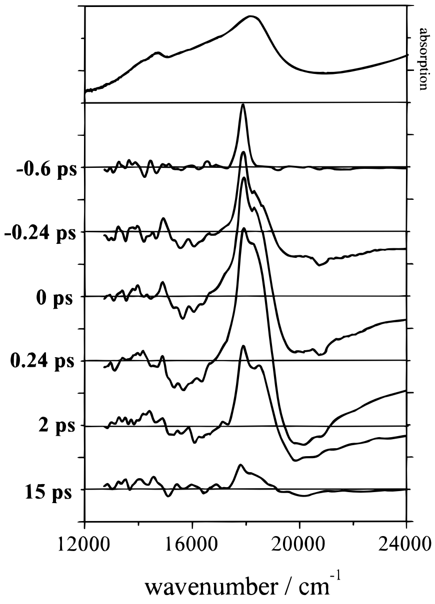

Figure 4. Time evolution of transient spectra of PcPSi in tetrahydrofuran excited with a 120 fs pump pulse at 555 nm (18 020 cm^{-1}) with an exitation density of ca. 0.5 mJ/cm^2. The spectrum at $\tau_D = -0.6$ ps constitutes the baseline with $\Delta T \approx 1$ except for the range of the scattering light of the pump pulse between 18 020 and 17 700 cm^{-1} where $\Delta T > 1$. Bleaching and absorption bands are recognized as increases and decreases with respect to the baseline, respectively.

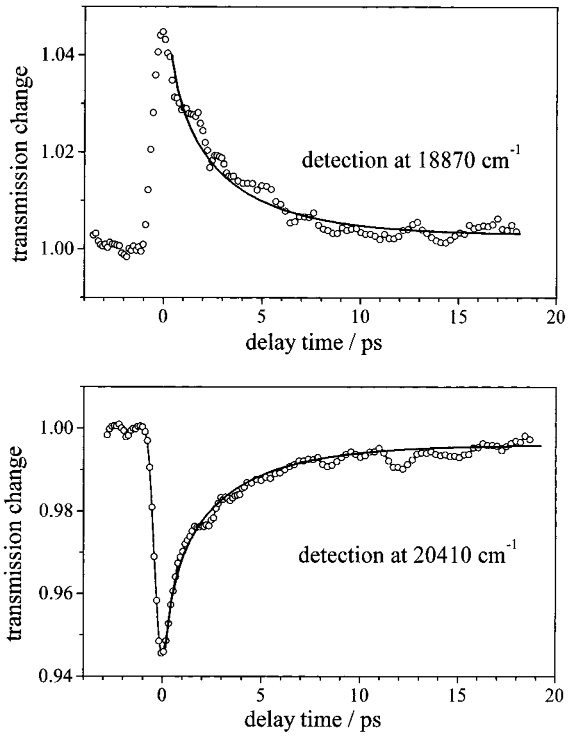

Figure 5. Experimental (open circles) and calculated (solid line) time dependencies of transient absorption and photoinduced bleaching of PcPSi in tetrahydrofuran detected at 20 410 and 18 870 cm^{-1}, respectively. The excitation energy density created by the 120 fs pump pulse was ca. 0.5 mJ/cm^2. The calculated curves use the functional form of eq 2 with the same parameters but do not include a convolution with the instrument response (see Figure 6).

Transient Absorption Spectra. Figure 4 displays the time evolution of the transient spectra of PcPSi in tetrahydrofuran solution recorded between −0.6 and +15 ps. The wavelength of the pump laser is 555 nm (18020 cm^{-1}) and the excitation density is ca. 0.5 mJ/cm^2. These measurements were made with a parallel polarized pump and probe pulses. Analogous transient absorption measurements on solutions of PcDSi had indeed demonstrated that the spectra were independent of the polarization conditions.[19]

The ground-state depletion and excited-state absorption spectra are observed as bleaching between 18 200 and 19 000 cm^{-1} and photoinduced absorption in the ranges of 19 000−24 000 cm^{-1} and 15 000−17 000 cm^{-1}, respectively. These difference spectra can be decomposed into a sum of a bleaching spectrum, which equals the ground-state absorption spectrum, and of a broad, transient excited-state absorption spectrum centered at about 21 500 cm^{-1} and having a width of about 5000 cm^{-1}. The transient bleaching spectrum is in fact somewhat narrower than the steady-state absorption spectrum, indicating inhomogeneous broadening of the latter (see Figure 4). All spectral changes are generated within the duration of the pump pulse and decay homogeneously in time, as illustrated by the transmittance changes at 18 870 and 20 410 cm^{-1} as a function of delay time shown in Figure 5. The rise of both the bleaching and transient absorption signals is faster than the time resolution of our experiment (>220 fs). The decay is nonexponential, indicating the occurrence of exciton−exciton annihilation processes. This bimolecular process involves exciton motion and exciton−exciton annihilation. To ascertain this proposition, the influence of the excitation energy density on the decay dynamics was investigated. Figure 6 illustrates convincingly that the decay of the transient absorption at 19 610 cm^{-1} becomes drastically faster at excitation energy densities of 2.5 mJ/cm^2 and higher.

Two processes contribute therefore to the decay of the initially generated exciton population density, n: exciton−exciton annihilation and monomolecular decay. The evolution of this population is thus described by the following rate equation:[11]

$$\frac{\mathrm{d}n}{\mathrm{d}t} = -\Gamma(t)n^2 - \frac{n}{\tau} \qquad (1)$$

$\Gamma(t)$ describes the bimolecular exciton annihilation process and τ is the exciton lifetime without interaction between excitons (i.e., the lifetime observed in the limit of very low exciton density). For the sake of simplicity, population terms were omitted. The time dependence of the exciton−exciton annihilation arises from the fact that the initial, spatially randomly distributed exciton population changes as closest exciton pairs interact first, so that the distribution changes. The exciton transport in rodlike PcPSi is one-dimensional parallel to the siloxane backbone. The time dependence of annihilation constant for long-range dipole−dipole interaction between excitons is given by the expression: $\Gamma(t) = \gamma t^{-1/2}$.[20] Such a model was used successfully by Teresaki et al.[11] and Gulbinas et al.[12] to analyze the decay dynamics of transient absorption in VOPc.

Integration of rate eq 1, with $\Gamma(t) = \gamma t^{-1/2}$ leads to the expression:[11]

$$\frac{n}{n_0} = \frac{\exp(-t/\tau)}{1 + n_0\gamma\sqrt{\pi\tau}\,\mathrm{erf}(\sqrt{t/\tau})} \qquad (2)$$

The exciton density, n, with the initial value, n_0, will be given here as the number of excitations per polymer chain. Equation 2 is strictly valid only for infinite chains. For finite chains, this expression will be approximately valid for high excitation densities, when the finite chain length can be neglected, and/or if the range of exciton migration and interaction during the

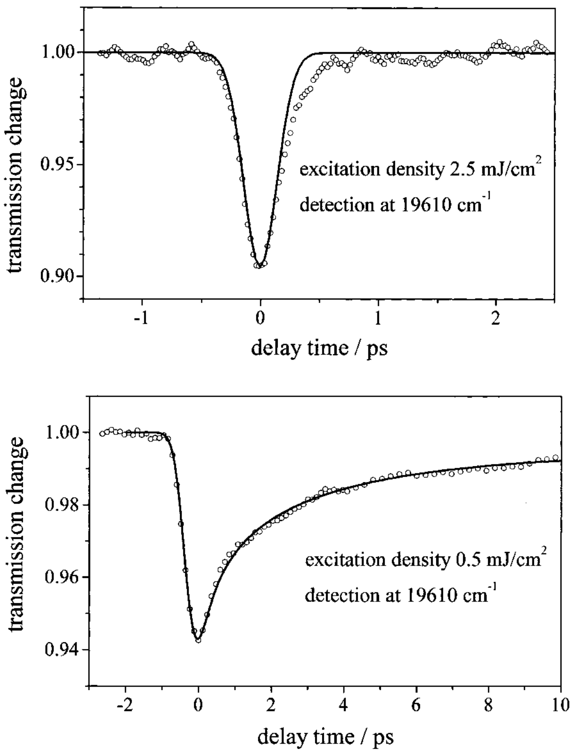

Figure 6. Decay dynamics of transient absorption of PcPSi in tetrahydrofuran measured for different excitation energy densities, as indicated (open circles). At high excitation density, the decay can hardly be resolved from the instrumental response (solid line), which is well represented by a Gaussian of fwhm = 280 fs. At low excitation density, eq 2 convoluted with a Gaussian (fwhm = 580 fs) instrument response function fits well the data with the parameters given in the text. Note the difference in time scale.

lifetime, τ, is smaller than the chain length. As illustrated in Figure 5, eq 2, fits well all decay curves recorded for low excitation densities (0.5 mJ/cm^2) with the following values of the parameters: $\tau = 4.5 \pm 0.3$ ps, $n_0\gamma = 1.8 \times 10^6 \pm 10^5$ s$^{-1/2}$ (see solid line). For this value of $n_0\gamma$, the time required for the exciton population to decay to half of the initial value by only exciton annihilation equals $(2n_0\gamma)^{-2} = 80 \pm 5$ fs. The decay at early times is thus dominated by exciton–exciton annihilation. This initial very fast decay is not resolved in the experiments.

Let us now consider the fact that the polymer consists of chains of finite length. Given the number density of polymer chains of 1.7×10^{16}/cm^3, the sample thickness of 0.04 cm, and the fact that about 50% of the 555 nm photons are absorbed, the value of n_0 is ca. 2, when the excitation density is 0.5 mJ/cm^2. At an average of two photons absorbed per polymer chain, 14% of the chains remain unexcited, 27% are singly excited, and the remaining 59% are doubly (27%) or higher excited. After about 1 ps, the decay of the signals in Figure 5 becomes exponential with a 4.5 ps decay constant. Indeed, the signals at times >0.3 ps, are equally well fitted by two exponentials of equal weights and decay constants of ca. 4.5 ps and ca. 0.5 ps, respectively. The 0.5 ps time constant must be associated with doubly excited chains, since higher excited chains decay even faster (see below).

At excitation densities of 2.5 mJ/cm^2 and higher, eq 2 is unable to fit the data, even allowing for some increase of the parameter γ, the value of which is underevaluated in the fit of the low excitation density data. Indeed, cutting an infinite chain in isolated segments will separate some pairs of excitations, which, in an uninterrupted chain, would be able to annihilate. Equation 2 predicts after the initial fast decay, a slow (4.5 ps) decay once the excitation density drops below about 0.5. In contrast to this prediction, all signals observed for high excitation densities decay completely (i.e., to less than the noise level of about 5%) on a very fast time scale (<200 fs). At excitation densities of higher than 2.5 mJ/cm^2, n_0 becomes larger than 5, and the number of unexcited or singly excited chains amounts to less than 5%. The observed fast and complete decay implies therefore that the exciton–exciton annihilation process opens a new relaxation channel for all excitations on a chain, which does not exist on a singly excited chain. We propose that the generation, via exciton–exciton annihilation, of short-lived, charge-separated states constitutes this relaxation mechanism.

Summary

The decay dynamics of singlet excitons of PcPSi in tetrahydrofuran solutions, studied on the femtosecond to picosecond scale at different excitation energy densities between ca. 0.5 and 2.5 mJ/cm^2, was shown to exhibit marked nonexponential characteristics. At excitation densities of about 0.5 mJ/cm^2, when a significant fraction of polymer chains carry one excitation, the decay at times larger than 1 ps becomes monoexponential with a lifetime of 4.5 ps, while the faster decay at shorter times can be attributed to exciton–exciton annihilation in doubly excited chains. Excitation densities of 2.5 mJ/cm^2 generate on average three to six excitations per chain. At these and higher excitation densities, the transient signals decay on a time scale of <300 fs, and the monomolecular decay is observed to be completely quenched. This ultrafast temporal evolution is attributed to the creation of charge-separated states, which open a very efficient relaxation channel for the singlet excitons.

On the finite chains, investigated here, the average separation of two completely localized excitations on a doubly excited chain is 10, while the exciton delocalization is greater than three, as can be estimated from the ratio of the line width to the exciton splitting. Since doubly excited chains of 32 monomer-unit length decay already on a ca. 0.5 ps time scale, the proper characterization of exciton migration requires chains of much greater length. In fact, concrete information of this ultrafast relaxation dynamics of two excitations on 32 monomer-unit chains may be achieved by saturation absorption spectroscopy with a time resolution higher than 200 fs.

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