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Dynamics of photoexcitations in *cis*-polyacetylene

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The photoinduced absorption of *cis*-(CH)_x has been investigated by nanosecond time-resolved spectroscopy. Photoinduced absorption at 1.55 eV and bleaching of the interband transition at 2.05 eV are observed. The photoinduced absorbance change decays as $\exp[-(t/\tau)^{1/2}]$ with $\tau=2.3\pm 0.2 \mu\text{s}$ at 80 K. The photoinduced absorption is considered to be due to exciton bipolarons or polarons. The decay kinetics is interpreted by the trapping model, i.e., an excited species disappears at traps after a one-dimensional random walk.

Recently, there has been a great deal of interest in the generation and relaxation of photoexcitations in polyacetylene. *Trans*-polyacetylene especially has attracted much interest and has been extensively studied because of its degeneracy, which allows the existence of solitons.¹⁻⁸ The properties of the photoexcitations in *cis*-polyacetylene are much different from those in *trans*-polyacetylene. *Trans*-polyacetylene is photoconductive, while *cis*-polyacetylene does not show this property.⁹ The photoluminescence from *trans*-(CH)_x is much weaker than from *cis*-(CH)_x.¹⁰⁻¹² These differences between *trans* and *cis* forms have been interpreted in terms of the soliton, which can migrate in *trans* chains but not in *cis* chains because of nondegenerate molecular structures of two *cis* forms, *cis-transoid* and *trans-cisoid*.

The photoinduced absorption of *trans*-polyacetylene has been investigated by several groups in ranges from subpicosecond to millisecond.²⁻⁸ In the picosecond range, charged solitons are generated by the intrachain photoexcitation and disappear by pair recombination.^{2,3} The photoinduced absorption in the nanosecond range is due to polarons formed in different chains by the interchain photoexcitation. The photoinduced polarons disappear by interchain recombination.^{4,5} The photoexcitations in the millisecond range are charged solitons which are generated by the reactions of photoinduced polarons with neutral solitons.⁶⁻⁸ The charge carriers in the photoconductivity are the charged solitons generated from polarons. The photoinduced excitations in *trans*-polyacetylene are charged solitons and polarons.

Shank *et al.* and Vardeny studied the photoinduced absorbance change in *cis*-(CH)_x with the use of subpicosecond and picosecond dye lasers, respectively.^{2,13} The photoinduced absorption peak appears at 1.55 eV and the absorbance change decays in the same way as in *trans*-polyacetylene up to 10 ps, but at about 15 ps after excitation it stops decaying and the absorbance change remains constant at the level of one-seventh of the peak absorbance change just after excitation. The photoinduced absorption at 1.55 eV is also observed at delay times of 10

μs and in the millisecond range, but no intense peak is observed in the infrared region.^{6,13} The photoinduced absorption at 1.55 eV in *cis*-(CH)_x has been considered to be due to photoinduced kinks in *cis* chains,² or soliton-antisoliton pairs, which are bound within the limits of isolated short *trans* segments in *cis*-rich polyacetylene.¹³

The decay kinetics of the photoinduced absorbance change is of key importance to investigate the detailed mechanism of the photoexcitations, but the dynamics of the photoexcitations in *cis*-polyacetylene in the nanosecond range has not so far been investigated. In the present study, the photoinduced absorption of *cis*-(CH)_x between 10 ns and 10 μs has been studied for the first time. The photoexcitations in the nanosecond range and the relaxation mechanisms are discussed.

The pulsed excitation light source was either the second-harmonic pulse (2.33 eV, 532 nm, 5 ns) of a Q-switched Nd:YAG (YAG stands for yttrium aluminum garnet) laser (Quanta Ray, DCR-1A) or a 10-ns pulse (1.97 eV, 630 nm) of a dye laser (Quantel, TDL-III). The probe light wavelength of a pulsed xenon lamp (Varian, VIX300F, 500 μs) was selected with a monochromator (Shimadzu Bausch&Lomb, with either a grating of focal length $f=17$ cm, 1350 grooves/mm, and blaze wavelength at 500 nm, or of $f=17$ cm, 675 grooves/mm, and blaze wavelength at 1.0 μm) and was detected by a photomultiplier (Hamamatsu, R666S or R1767). The output signal of the photomultiplier was digitized with a high-speed digital memory (Iwatsu, DM901) and analyzed by a microcomputer (NEC, PC-9801VM2). The resolution time of the total system was 10 ns.⁴

The polyacetylene films were synthesized on glass plates at -78°C by Shirakawa's method.¹⁴ The various *cis-trans* contents of the polyacetylene films were prepared by thermal *cis-trans* isomerization. The content ratio of the isomers were determined by the Raman intensity ratio. The excitation light of Raman spectroscopy was a 514.5-nm light of a cw Ar laser (spectra physics, model 171).

Figure 1 shows the photoinduced absorption spectra of

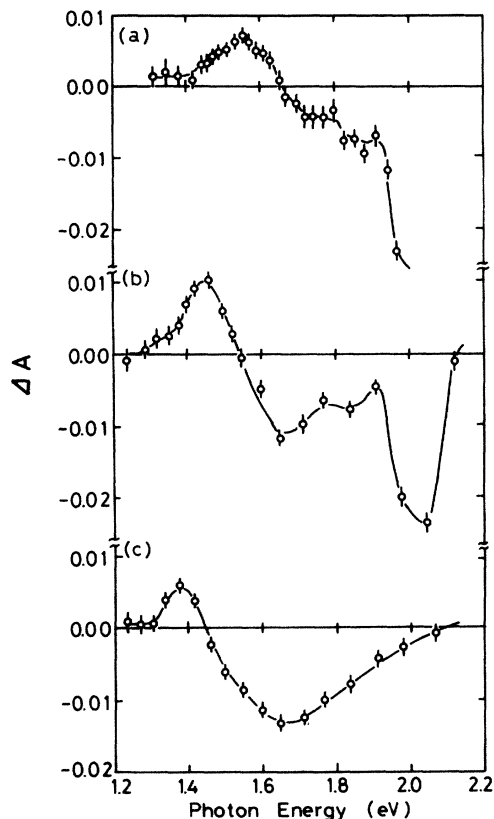


FIG. 1. The photoinduced absorption spectra of $(\text{CH})_x$ at 80 K. (a) 90% *cis*- $(\text{CH})_x$, (b) 70% *cis*- $(\text{CH})_x$, and (c) 100% *trans*- $(\text{CH})_x$. The excitation photon density is 1.2×10^{15} photons/cm².

several $(\text{CH})_x$ samples with different *cis-trans* ratios at 80 K. The figure shows the absorbance change averaged between 10 and 30 ns after photoexcitation. A bleaching peak at 2.05 eV and an absorption peak at 1.55 eV are observed in *cis-rich* $(\text{CH})_x$. The absorbance of the 90% *cis*- $(\text{CH})_x$ film above the photon energy of 1.98 eV is so large that the absorbance change could not be measured. When the *cis* content increases, both the bleaching intensity at 1.70 eV and the absorbance change at 1.40 eV decrease, but on the other hand the bleaching at 2.05 eV and the absorption peak at 1.55 eV increase. Moreover, the photoinduced absorbance change at 2.05 and 1.55 eV are induced more efficiently by the 2.33-eV excitation light than the 1.97-eV excitation light. The photon energies of the absorption peaks in *trans*- and *cis*- $(\text{CH})_x$ are about 2.0 and 2.4 eV, respectively. Therefore, the bleaching at 2.05 eV and the absorption at 1.55 eV are attributed to the change induced in *cis*-form in the samples.

The photoinduced absorption peak at 1.55 eV can be attributed to polarons or exciton bipolarons in *cis*- $(\text{CH})_x$ from the following discussion. Polarons and bipolarons have two electronic levels in the band gap. A polaron has one or three electrons in the electronic levels and has two absorption peaks near the band edge and in the midgap level. An exciton bipolaron has two electrons in the electronic levels and its absorption has one intense peak near

the band edge.^{15,16} The bleaching at 2.05 eV is due to the reduction of the interband transition of *cis*- $(\text{CH})_x$.

The absorbance change at 1.55 eV in the nanosecond range shows saturation. The saturation photon density of the excitation laser pulse is about 2×10^{15} photons/cm². It corresponds to one photon per hundred carbon atoms and is equivalent to *trans*-polyacetylene.^{4,5} This means that the saturation occurs when some chains are photoexcited twice or three times by a single laser shot.

Figure 2 shows the decay curve of the absorbance change at 1.46 eV in 70% *cis*- $(\text{CH})_x$. All the decay curves of the absorbance change around 1.5 eV in *cis-rich* $(\text{CH})_x$ with different *cis-trans* content ratios can be fitted to the curve $\exp[-(t/\tau)^{1/2}]$. The time constants τ are 2.3 ± 0.2 μs for 90% *cis*- $(\text{CH})_x$, 2.7 ± 0.1 μs for 70% *cis*- $(\text{CH})_x$, and 2.7 ± 0.3 μs for 30% *cis*- $(\text{CH})_x$ at 80 K. The decay-time constant of *trans*- $(\text{CH})_x$ in the nanosecond range becomes shorter with increase of the *trans* content, because the decay kinetics in *trans*-polyacetylene in nanoseconds is determined by the interchain recombination of polarons and hence is dependent on the *trans* content.⁴ On the other hand, the decay-time constants of *cis*- $(\text{CH})_x$ with different *cis-trans* content ratios are nearly equal to one another. Therefore, the decay kinetics of the photoexcitations in *cis*- $(\text{CH})_x$ is considered to be determined by an intrachain process.

The decay curve of $\exp[-(t/\tau)^{1/2}]$ can be explained by a trapping model. An excited species executes a one-dimensional random walk and disappears at traps which exist on the polymer chain with a fraction z . The time dependence of the excitation density $N(t)$ is asymptotically represented by

$$N(t) \sim 16N_0(Wz^2t/3\pi)^{1/2} \exp[-3(\pi^2Wz^2t/4)^{1/3}] \quad (1)$$

for $t \gg 1/Wz^2$, where N_0 is the initial excitation density at time 0 and W is the jump rate of the excited species between the neighboring sites.^{4,17} Numerical calculation of the trapping model leads to the following description of $N(t)$:

$$N(t) \sim N_0 \exp[-(t/\tau)^{1/2}], \quad (2)$$

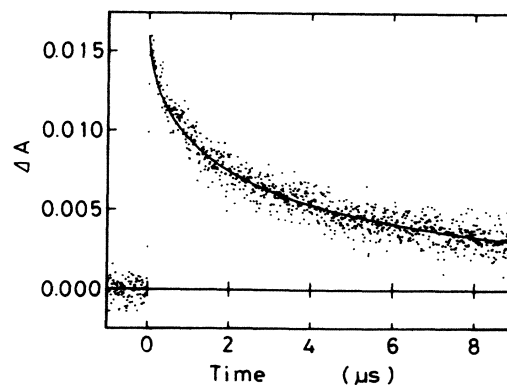


FIG. 2. The time dependence of the photoinduced absorbance change at 1.46 eV in 70% *cis*- $(\text{CH})_x$ at 80 K. The excitation photon energy is 1.7×10^{15} photons/cm². The solid curve is $\exp[-(t/\tau)^{1/2}]$ with $\tau = 2.7$ μs .

for $t \lesssim 1/Wz^2$, where $\tau = 1/4Wz^2$.

The decay curves cannot be used for the independent determination of the jump rate W and the trap fraction z , which appear only in the form of a product in the trap model. When the jump time W^{-1} in $cis-(CH)_x$ is assumed to be equal to the jump time of solitons in *trans*-polyacetylene, 1 ps, the trap fraction z becomes 3×10^{-4} for $\tau = 2.3 \mu s$ at 80 K. Impurities may be the traps in *cis*-polyacetylene, but there is a possibility that *trans* segments in *cis*-rich chains also work as the traps. Since a soliton is not mobile in a *cis*-chain, the photoexcited species which executes a random walk in a *cis*-polyacetylene chain is assumed to be a polaron or a bipolaron.

Figure 3 shows the temperature dependence of the decay time constant τ of 90% *cis*-(CH)_x at 80 K. The time constants can be fitted to $\exp(E/kT)$ at temperatures lower than 200 K. Assuming that the trap fraction z is independent of temperature, the activation energy E of the jump of the excited species between the neighboring sites is obtained to be 3.3 ± 1.4 meV. Above 200 K, the time constant decreases rapidly and photoisomerization from *cis* to *trans* form is observed. Therefore, the decay kinetics of the photoexcitations is expected to show the existence of another process such as photoisomerization at higher temperatures than 200 K.

Both polarons and exciton bipolarons are expected to have an absorption peak around 1.55 eV and can execute random walks in *cis*-polyacetylene chains. A polaron has a charge and has another absorption peak in the midgap level, while an exciton bipolaron is neutral and does not have intense absorption in the infrared region.^{15,16} Photoinduced absorption spectroscopy in the millisecond range shows the *cis*-(CH)_x has no intense absorption peak in the infrared region.¹³ Moreover, photoconductivity has not been observed in *cis*-(CH)_x.⁹ Therefore, the photoinduced absorption at 1.55 eV in *cis*-(CH)_x observed in the present study can be attributed to exciton bipolarons.

In the picosecond region, the photoinduced absorbance change in *cis*-(CH)_x decays rapidly up to 10 ps^{2,13} and the lifetime of the photoluminescence at 1.95 eV is shorter than 9 ps.¹⁰⁻¹² Therefore, the relaxation of photoexcitations in *cis*-polyacetylene is expected to have different decay kinetics, and it is assigned to electron-hole recombination.

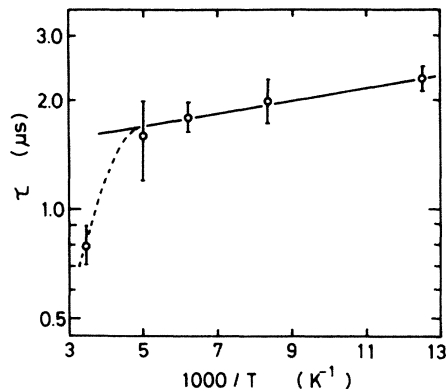


FIG. 3. The temperature dependence of the time constant τ in 90% *cis*-(CH)_x. The probe photon energy is 1.55 eV. The excitation photon density is 1.2×10^{15} photons/cm².

Taking into account all the experimental data above-mentioned and those in the literature, a model of the photoexcitation relaxation in *cis*-polyacetylene is proposed as follows. Electron-hole pairs are generated in *cis*-polyacetylene chains by the photoexcitation. In several picoseconds, some of the electron-hole pairs recombine and emit photoluminescence. The rest of the electron-hole pairs generate exciton bipolarons. The exciton bipolarons have an absorption peak at 1.55 eV and decay as $\exp[-(t/\tau)^{1/2}]$ with $\tau = 2.3 \pm 0.2 \mu s$ at 80 K. The decay kinetics is represented by the trapping model, i.e., an excited species disappears at traps after a random walk in a one-dimensional chain. However, the origin of the traps has not yet been definitely identified. Study of the decay kinetics in slightly doped samples and the polarization dependence in oriented samples will elucidate more clearly the dynamics of the photoexcitations in *cis*-polyacetylene.

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