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# Confinement Effect of Photogenerated Soliton–Antisoliton Pair on the Ultrafast Relaxation in a Substituted Polyacetylene

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**Abstract**—Femtosecond pump-probe experiments have been performed on poly[o-(trimethylsilyl)phenylacetylene] thin films to investigate the effect of confinement of a photogenerated soliton–antisoliton pair on its ultrafast relaxation dynamics. The decay kinetics of transient photoinduced absorption due to the photoexcitations of the polymer were found to behave as  $\text{erf}(t^{-n})$  with  $n = 0.65 \pm 0.05$ , implying a geminate recombination process of the soliton–antisoliton pair on a quasi-one-dimensional chain. The distance between the soliton and antisoliton could be estimated as about six repeat unit lengths, suggesting a fairly strong confinement of the pair. It is consistent with the size of a certain regular structure indicated to exist in this material by X-ray diffraction measurements. Creation of confined pairs of likely charged solitons due to interchain photoexcitation is also discussed in terms of the following energetically favored reaction between likely charged polarons on the same chain:  $P^{\pm} + P^{\pm} \rightarrow S^{\pm} + S^{\pm}$ .

## I. INTRODUCTION

DURING the last decade, one-dimensional (1-D) conjugated polymers have attracted much attention [1], [2], partly because they provide interesting systems for experimental and theoretical investigations in that the electronic motion is anisotropically restricted along the main chain and partly because they are potentially useful as optical devices due to their fast response and large optical nonlinearities.

Among the conjugated polymers,  $\text{trans}(\text{CH})_x$  has the simplest chemical structure and is a prototypical conjugated polymer. Since Su, Schrieffer, and Heeger (SSH) [3], [4] predicted the existence of a soliton excitation, i.e., a domain wall separating the two dimerization phases corresponding to the doubly degenerate ground states, and Su and Schrieffer [5] demonstrated the evolution of an electron-hole pair photoexcited into the main chain of  $\text{trans}(\text{CH})_x$ , a great deal of attention has been paid to the

excited state dynamics of  $\text{trans}(\text{CH})_x$ . Due to its strong electron–phonon coupling and one dimensionality, the photogenerated electron and hole induce a local distortion of lattice spontaneously and rapidly separate to relax, forming a spinless charged soliton–antisoliton pair. The soliton has a localized electronic state deep in midgap [6] and associated infrared active vibrations (IRAV) [7], which are both spectroscopically accessible. Photoinduced absorption (PA) and photoinduced bleaching (PB) of  $\text{trans}(\text{CH})_x$  under quasi-static conditions [8] have experimentally confirmed the existence of the solitons, and their relaxation dynamics have been also investigated so far with picosecond [9]–[12] and femtosecond [13]–[15] time resolution.

Vardeny *et al.* [9] observed the PB of interband transition in  $\text{trans}(\text{CH})_x$  with picosecond time resolution and that the bleaching decayed with time as  $t^{-1/2}$  up to 50 ps. They also estimated the diffusion constant of charged excitations as  $2 \times 10^{-2} \text{ cm}^2\text{s}^{-1}$  from the decay of the polarization memory. Shank *et al.* [13] investigated the femtosecond dynamics of the PA in  $\text{trans}(\text{CH})_x$  and  $\text{cis}(\text{CH})_x$ . They observed that in  $\text{trans}(\text{CH})_x$  the PA appeared at 1.45 eV within less than 150 fs after photoexcitation, and that its recovery dynamics could be modeled by geminate recombination controlled by 1-D diffusion, though the identification of the PA peak was remained unclear. Direct measurement of the lower energy (LE) in-gap absorption in the subpicosecond time regime was recently demonstrated by Rothberg *et al.* [15], who observed direct generation of charged solitons within 500 fs after photoexcitation. They found that over 95% of those recombined geminately in about 2 ps.

However, there still remain difficulties in identifying the observed PA peak near 1.4 eV especially on the ultra-short time scale. Isolated charged solitons are somewhat doubtful because the feature appears at different energy from that expected by the SSH model. Although the PA associated with neutral solitons is known to appear above the midgap by taking into account the Coulomb interaction between soliton sites [16], it does not seem to be the case here because the branching ratio of neutral to charged solitons is less than  $10^{-2}$  in the photogeneration process

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[17]. It is also unlikely from the fast rise of the PA that isolated neutral solitons are created by a reaction between photogenerated charged species.

In this paper, to clarify the complicated feature and also to elucidate the ultrafast relaxation dynamics, the stress is placed on the importance of *confinement* of charge carriers photogenerated into the main chain of 1-D conjugated polymers, and the possibility for an elementary excitation to take the form of a *confined soliton-antisoliton pair* is discussed. Since conjugated polymers inevitably have some chemical impurities and structural defects which will limit the motion of solitons, the ultrafast relaxation dynamics in such a confined system is considered to be different from the picture predicted by the SSH model which is based on an independent electron picture in *infinite* 1-D chain.

For purposes of investigating the confinement effects of a photogenerated soliton-antisoliton pair on its ultrafast relaxation dynamics, we have performed femtosecond time-resolved absorption measurements with a pump-probe technique on poly[o-(trimethylsilyl)phenylacetylene] (referred as PMSPA hereafter), which has the same backbone geometry as that of trans-(CH)<sub>x</sub>, but an ortho-substituted phenyl ring is attached to every two carbon sites. This introduces a reduction of an electronic conjugation length because of a distortion of the main chain due to steric hindrance, resulting in the confinement of the soliton and antisoliton. The experimental results that the spectrum and decay kinetics of the observed PA can be well accounted for by a picture of a confirmed soliton-antisoliton pair are presented. Although the use of the term solitons for incomplete degenerate systems such as PMSPA seems to be somewhat misleading, we think that PMSPA has basically the same electronic excitations as trans-(CH)<sub>x</sub> even with a small perturbation introduced by side groups. The confined soliton-antisoliton pair is referred to in this paper as an overall neutral pair of charged excitations with changes of dimerization pattern.

The classification is also made for various polymers in terms of a degree of confinement, and a picture of a "confined excitation," which takes a form of an isolated soliton, a confined soliton-antisoliton pair, or an exciton according to the degree of confinement is proposed. Due to the similarity of the main chain geometry, the results obtained here will give hints to elucidate the relaxation mechanism in trans-(CH)<sub>x</sub> by comparing the photoinduced features and their temporal behaviors of both materials.

An interchain photoexcitation process is also discussed. There are two proposed mechanisms so far for polarons generated by the interchain photoexcitations to relax to form solitons. First, as has been proposed by Orenstein *et al.* [18], the neutral defects  $S^0$  which exist inherently in trans-(CH)<sub>x</sub> and also in PMSPA, act as trapping sites, and the polarons encountering the  $S^0$  sites are converted to charged soliton states according to the following reaction:  $P^\pm + S^0 \rightarrow S^\pm$ . Rothberg *et al.* [11] ascribed the increase of the LE in-gap absorption ob-

served after 20 ps following the photoexcitation to charged solitons converted from polarons by this mechanism. The mechanism is expected to be dominant in the sample with larger number of neutral defects. This is supported by the fact that the LE in-gap absorption observed by Rothberg *et al.* [11] was greatly suppressed in trans-(CH)<sub>x</sub> where fewer neutral defects were observed in ESR measurement. Secondly, when more than two polarons are generated on the same chain by interchain photoexcitations, two likely charged polarons on the same chain are expected to be converted to a likely charged soliton pair by the energetically favored reaction:  $P^\pm + P^\pm \rightarrow S^\pm + S^\pm$  [19]. This time, it has been found that the observed component due to long-life species in PA and PB results from the interchain photoexcitation, and that the amplitude of the long-lived component has the quadratic dependence on the pump intensity, implying that the latter mechanism is the case in PMSPA.

After describing our experimental apparatus in Section II, we present experimental results in Section III-A, and discuss on the confinement of the soliton and antisoliton by comparing PMSPA and trans-(CH)<sub>x</sub> in Section III-B. In Section III-C, the distance between the confined soliton and antisoliton is estimated, and the comparison with other polymers in terms of confinement parameter is presented in Section III-D. Interchain photoexcitation is also discussed in Section III-E.

## II. EXPERIMENTAL

Our experimental apparatus [20], [21] is shown in Fig. 1. Pulses of 70 fs duration were generated by a colliding pulse mode-locked (CPM) ring dye laser pumped by a CW argon ion laser (Spectra Physics, Model 2030). Rhodamine 6G and DODCI dye solutions in ethylene glycol were used as a gain medium and a saturable absorber, respectively. Pulse duration was measured using the background-free autocorrelation scheme with a KDP crystal of 0.2 mm thick, which serves a real-time monitor of the duration. The femtosecond pulses were amplified by a factor of  $10^6$  with a four-stage dye amplifier pumped by the second harmonic of a Q-switched Nd:YAG laser (Quanta Ray, DCR-1) operated at 10 Hz. After compensation for a group-velocity dispersion by a grating pair, pulse duration, pulse energy, and center wavelength were typically 100 fs, 0.2 mJ, and 625 nm (1.98 eV), respectively. The beams of the femtosecond pulses were split into two beams. One was used as pump pulses after passing the mechanically variable delay-line, and the other was focused into a glass cell (3 mm thick) containing CCl<sub>4</sub>, generating the femtosecond white continuum pulses by self phase modulation (SPM). They served probe and reference pulses, which extended from 400 to 1000 nm. The pump and probe pulses were both focused and overlapped on the sample, and the spot size of pump pulses was adjusted to be two or three times larger than that of probe pulses. Transmitted probe pulses and reference ones were spectrally dispersed with a pair of two 20 cm focal length



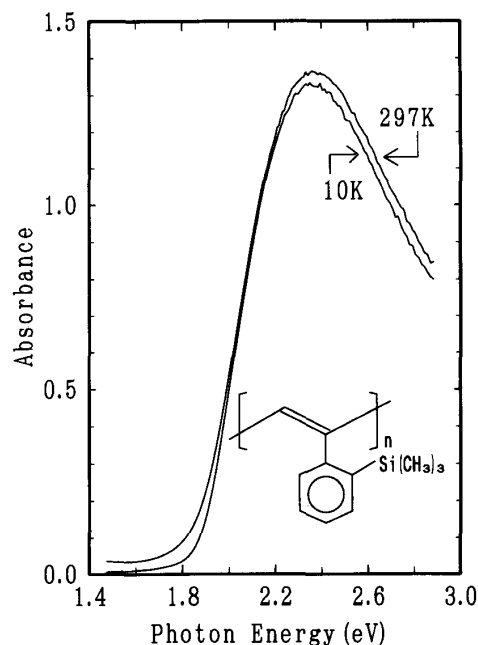


Fig. 2. Absorption spectra of PMSPA measured at 297 and 10 K. Inset: chemical structure of PMSPA.

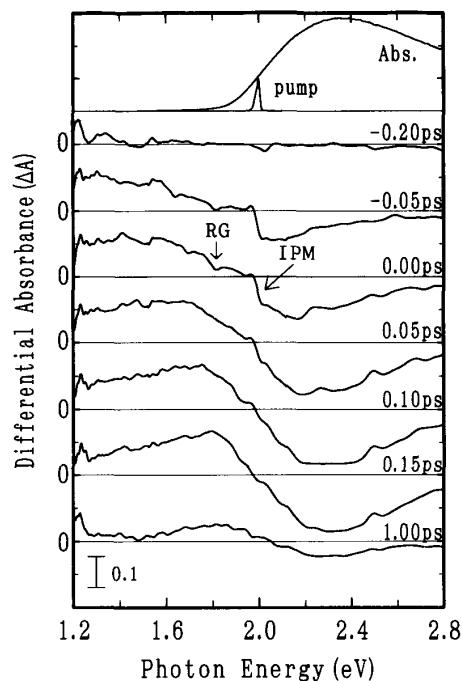


Fig. 3. Differential absorbance spectra of PMSPA measured at 10 K up to 1 ps after photoexcitation at 1.98 eV. Pump duration and excitation density are 100 fs,  $2 \times 10^{16}$  photons/cm<sup>2</sup>, respectively. The positive change means photoinduced absorption, while the negative one means photoinduced bleaching. The absorption spectrum (Abs.) of PMSPA and pump laser spectrum (pump) are also shown for comparison at the top. RG: peak minimum due to the Raman gain, IPM: sharp dispersion-type feature due to induced phase modulation.

gain, appearing at Stokes side from the pump frequency at  $1410 \text{ cm}^{-1}$ , corresponding to the  $C = C$  stretching mode of the ground state configuration. Finally, a sharp dispersion-type feature can be seen at small positive delay time as indicated with IPM in the same figure. It is due to the induced phase modulation [28]. It was also observed for other polymers by our group for the first time [29]. The origin of this feature is that at this delay time a probe pulse experiences the frequency blue shift due to a modulation of the refractive index of the sample caused by a trailing tail of a strong pump pulse. Since the probe spectrum has a peak at the fundamental frequency of the laser (1.98 eV), the shift of the probe spectrum results in the dispersion-type feature. It should be noted that such an effect (change of refractive index) will be always superimposed more or less on the population-induced absorbance change (change of extinction coefficient) in this time scale.

Although the femtosecond time regime is too short for the heat given by the pump flux to be transferred to the lattice, it is important to evaluate the magnitude of the thermal effect on the absorbance change. The estimation of the effect is done below, though it is only the rough estimation because detailed values for weight density  $\rho$ , specific heat capacity  $C_p$ , and film thickness  $d$  of the sample have not been obtained. From the pump photon density  $N = 2 \times 10^{16}$  photons/cm<sup>2</sup> and optical density at the pump frequency  $A = 0.5$ , the actually absorbed energy per one pulse is calculated as  $Q = 4.4 \times 10^{-3} \text{ J/cm}^2$ . Using the relation  $Q = C_p \rho d \Delta T$ , the temperature increase  $\Delta T$  of the sample is estimated as  $\Delta T = 24 \text{ K}$ . Here, the parameters for polymethylmethacrylate,  $\rho = 1.2 \text{ g/cm}^3$ ,  $C_p = 1.5 \text{ J/gK}$  are used, and  $d = 1 \mu\text{m}$  is estimated. By combining  $\Delta T$  and the temperature variation of the absorbance  $dA/dT = 1.7 \times 10^{-4}$  (at 1.8 eV), the absorbance change due to the thermal effect is evaluated to be about  $4 \times 10^{-3}$  at the largest, which is still two orders of magnitude smaller than the obtained signal, and hence is to be neglected.

Fig. 4 shows the temporal decay profiles at three different photon energies. In the lower probe photon energy region near 1.43 eV, and PA almost disappears by 1 ps and the ground state is recovered to some extent. Assuming an exponential decay, the time constant of the decay is ca. 135 fs. Since it seems to follow the pump pulse profile, it is possible that the actual decay rate at this energy is still faster. In contrast, the temporal behavior around the PA peak at 1.88 eV has some finite rising component, which corresponds to the initial blue shift of the PA peak mentioned above. The following decay rate is observed to become much slower than that at the lower energy region, which clearly can be seen by comparing (a) and (b) of Fig. 4. Furthermore, the existence of a long-lived component is also confirmed because no significant reduction of the signal can be observed at a delay time of more than 20 ps. At PB peak [2.3 eV, (c)] again, a long-lived component is observed after the initial fast decay.

Since we failed in the fitting of the decay profile (b) in

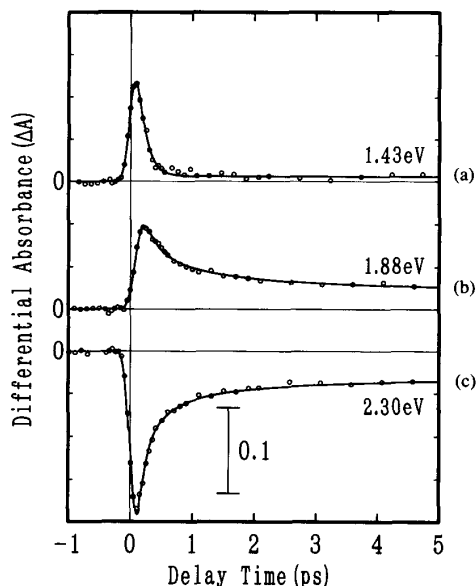


Fig. 4. Decay profiles at three different probe photon energies. Open circles represent the experimental data, and solid lines show the fitting curves with an exponential function for (a) and a power-law function for (b) and (c).

Fig. 4 to the exponential function, and in turn, obtained linear behavior versus delay time over almost three orders of magnitude in the log-log plot, the PA signal can be considered to follow a power-law decay. So, the fitting of the decay profile (b) with the following function was made:

$$\Delta A(t) = A \cdot \text{erf}[(\sigma t)^{-n}] + C \quad (2)$$

where  $\text{erf}()$  is an error function. The first term represents the component showing the power-law decay, while the second term  $C$  represents the long-lived component (baseline signal) mentioned above. The fitting was performed by convoluting (2) with the pump-pulse profile which was assumed as a Gaussian type. The least-squares method was used to determine all parameters at the same time, so that an ambiguity of subtracting the baseline was avoided.

As a result of this fitting, the power (exponent) and the value of the baseline signal for PA peak at 1.88 eV were obtained as  $n = 0.65 \pm 0.05$  and  $C = (1.5 \pm 0.18) \times 10^{-2}$ , respectively. The variation of  $n$  is less than 0.05 around the PA peak. The fitted curves are also shown with solid lines in Fig. 4.

### B. Confinement of the Soliton-Antisoliton Pair

Since, from a theoretical point of view, the power-law behavior corresponds to a geminate recombination process between two excitations after their random walks in a 1-D chain [30], it is implied that the observed PA is associated with photogenerated soliton-antisoliton pairs and that its decay results from the geminate recombination of the soliton and antisoliton after encountering each other. Such a power-law behavior was also observed in

the experiments on  $\text{trans}(\text{CH})_x$  demonstrated by Shank *et al.* in the same time scale [13], [14]. They found that the decay profile of PA can be fitted with  $n = 0.5$  which is expected for an ideal 1-D system. However, the power  $n$  obtained in our present work is slightly larger than 0.5 for the PA peak. One of reasons which yield such a discrepancy of  $n$  even with the same backbone geometry between PMSPA and  $\text{trans}(\text{CH})_x$  is considered to be the difference in initial distance between the soliton and antisoliton photogenerated. That is, in the case of  $\text{trans}(\text{CH})_x$ , a photogenerated electron-hole pair can induce a distortion of the surrounding lattice due to a strong electron-phonon coupling and relaxes to form a soliton-antisoliton pair within an order of  $10^{-13}$  s according to the SSH mechanism. Since  $\text{trans}(\text{CH})_x$  has doubly degenerate ground states, the total energy with a soliton-antisoliton pair is independent of the distance between them and therefore they are free to dissociate. So, after separation by using the excess energy of photoexcitation, the soliton and antisoliton can exist being isolated from each other, and therefore their decay is considered to follow the power-law with power  $n$  being near to 0.5.

In contrast, in the case of our material, PMSPA, it is supposed that the photogenerated soliton and antisoliton pair are confined and cannot separate at a long enough distance compared to the width of the soliton wave function. The possible reasons for this are described below. First, since the conjugation length of PMSPA is rather short as mentioned above and also discussed later again, a soliton and its antisoliton cannot separate without a loss of electronic coherence, and therefore they are confined in a conjugation-length-limited segment of the main chain. Second, unlike the  $\text{trans}(\text{CH})_x$ , an ortho-substituted phenyl group attached to the main chain of PMSPA still has a rotational freedom against the plane of the main chain, which leads to a small lifting of ground state degeneracy. Though this effect may become obscured as the size of the system under consideration increases, if the separation of the soliton and antisoliton is restricted within the above mentioned segment, the ground state does not necessarily become degenerate. If we assume that nearly degenerate ground states consist of  $A$  phase with energy  $E_0$  and  $B$  phase with  $E_0 + \delta E$  ( $\delta E > 0$ ), then the energetically lowest state of this system consists of purely  $A$  phase, and photogeneration of a soliton-antisoliton pair is accompanied by the appearance of the energetically disfavored  $B$  phase. The existence of the  $B$  phase will raise the total energy of this system by [23],

$$\Delta E = \left( \frac{\delta E}{a} \right) L \quad (3)$$

where  $a$  is a unit length,  $\delta E/a$  represents an energy difference per site, and  $L$  is the length of the  $B$  segment. An energy loss proportional to the soliton-antisoliton distance prevents further separation. Last, the existence of soliton-antisoliton pairs may obstruct the other pairs on the same chain.

### C. Estimation of the Distance Between the Soliton and Antisoliton

From the reasons discussed in the previous section, the photogenerated soliton and antisoliton are considered to exist not as separated solitons in the distance but as confined soliton-antisoliton pairs in PMSPA. Estimation of the distance between them has been done below according to the results of Fesser *et al.* [23]. In the continuum model proposed by Takayama *et al.* [31], the SSH Hamiltonian is transformed as

$$H = \sum_s \int \frac{dy}{a} \left[ \frac{\omega_Q^2}{2g^2} \Delta^2(y) + \psi_s(y) \cdot \left[ -iv_F \sigma_3 \frac{d}{dy} + \Delta(y) \sigma_1 \right] \psi_s(y) \right]. \quad (4)$$

Here,  $\omega_Q^2/2g^2 = K/4\alpha^2$ ,  $V_F = 2at_0$ , where  $K$ ,  $\alpha$ ,  $a$  are a spring constant of a  $\sigma$ -bond, an electron-phonon coupling constant, a lattice constant, respectively, and  $t_0$  is a hopping matrix element of a  $\pi$ -electron. The lattice displacement pattern is described by  $\Delta(y)$  and electronic field by spinor  $\psi_s(y)$ . In our nearly degenerate case,  $\Delta(y)$  can be assumed to consist of the following two components [32]:

$$\Delta(y) = \Delta_i(y) + \Delta_e. \quad (5)$$

Here,  $\Delta_i(y)$  denotes the intrinsic component sensitive to an electron-phonon coupling, while  $\Delta_e$  represents the constant displacement due to extrinsic origin. Now let the case be specified where the intrinsic gap parameter of a soliton-antisoliton pair with the distance  $2d$  is given by

$$\Delta_i(y) = \Delta_0 - K_0 v_F \{ \tanh [K_0(y + d)] - \tanh [K_0(y - d)] \} \quad (6)$$

with

$$\tanh (2K_0 d) = K_0 \xi. \quad (7)$$

The parameter  $K_0$  exhibiting the extension of a soliton is related to  $d$  by (7), and  $\Delta_0$  is the gap parameter corresponding to the ground state configuration of trans-(CH)<sub>x</sub>. When the Coulomb interaction between a soliton and its antisoliton is negligible, (4) yields two bound states for this dimerization pattern as the lowest excited state with energy separation from the gap center at  $+\omega_0$  and  $-\omega_0$  as drawn in the inset of Fig. 5, where,

$$\omega_0 = (\Delta^2 - K_0^2 V_F^2)^{1/2} \quad (8)$$

is a half-confinement energy.

The ratio  $\omega_0/\Delta$  as a function of  $d$  can be calculated with (7) and (8), the result being shown in Fig. 5. Its behavior is qualitatively interpreted as follows. When the soliton and antisoliton are far apart, the confinement energy becomes zero and the associated gap states appear in the middle of band gap with twofold degeneracy. On the other hand, when the soliton and antisoliton get closer, the confinement energy suddenly increases due to an overlapping of wave functions of two solitons, and upper gap state

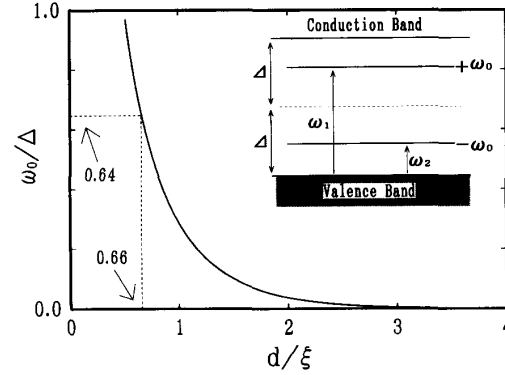


Fig. 5. Plot of the half confinement energy ( $\omega_0$ ) as a function of the distance between the soliton and antisoliton ( $d$ ). Inset: Energy diagram associated with a soliton-antisoliton pair.

comes near to the conduction band. The latter extreme case corresponds to an exciton picture, where photogenerated electron and hole cannot separate from each other due to a strong confinement and Coulomb binding. This is followed by the formation of a self-trapped exciton [20] with a geometrical relaxation due to an electron-phonon coupling, just as the soliton-antisoliton pair formation in the system with the degenerate ground states.

The two gap states ( $\pm\omega_0$ ) will give the PA peaks in the transparent region. One state will appear just below the conduction band and the other just above the valence band in the case of strong confinement. Since the observed PA peak near 1.8 eV appears only 0.4 eV below the optical gap and its decay profile shows the power-law behavior, the transition associated with the confined soliton-antisoliton pairs is the most relevant to this peak. Furthermore, its rather broad feature suggests that it involves a transition from (to) the continuum states. Therefore, the observed PA peak near 1.8 eV can be assigned to  $\omega_1$  transition from the valence band to the upper gap state as schematically drawn in the inset of Fig. 5. From our experimental results,  $E_g = 2\Delta = 2.2$  eV and  $\omega_0 = \omega_1 - \Delta = 0.7$  eV have been obtained. This leads to the ratio  $\omega_0/\Delta = 0.64$ , corresponding to  $d/\xi = 0.66$ , as shown in Fig. 5. Since, if the substituents give only a little effect on  $a$  and  $t_0$ , an extension of a soliton is nearly proportional to  $\Delta^{-1}$ , the soliton width in PMSPA turns out to be

$$\xi = \xi_0 \times \frac{\Delta_0}{\Delta} = 4.5 a. \quad (9)$$

Here,  $\xi_0 = 7a$  and  $\Delta_0 = 0.7$  eV are used, which are both appropriate for trans-(CH)<sub>x</sub>. Thus the distance between the soliton and antisoliton can be estimated as

$$L = 2d = 5.9a. \quad (10)$$

This is a fairly small separation, implying the strong confinement of the photogenerated soliton-antisoliton pair, as expected from the large steric hindrance. It is consistent with the fact that the power  $n$  obtained above is slightly larger than 0.5, because the probability for the soliton and

antisoliton to encounter each other becomes larger as the initial distance gets smaller. Another estimation of the separation was also done according to the theory presented in [33]. When the soliton wave function is overlapped, the degenerate soliton states at the gap center will be lifted by

$$\Delta E = 4\Delta e^{-L/\xi} \quad (11)$$

where  $L$  is the distance between the soliton and antisoliton. Substitution with  $\Delta E = 2\omega_0 = 1.4$  eV and  $\Delta = 1.1$  eV leads to  $L = 5.1a$ , which is consistent with our former estimation [(10)]. If the length of  $C - C$  and  $C = C$  bonding is assumed to be 1.463 and 1.368 Å, respectively, and the zig-zag structure of the main chain is taken into account,  $L = 5.9a$  corresponds to the size of 14.4 Å. This size should be compared with 11.6 Å which is the size of a certain regular structure indicated to exist in PMSPA by X-ray diffraction measurements [22]. It may be possible that the main chain of PMSPA is divided into segments with the size of ca. 14.4 Å by some structural distortions and that the photogenerated soliton and antisoliton are locked in the segments.

Since the above separation experimentally determined is not larger than the size of lattice deformation, one may suspect the diffusion picture in PMSPA. On this point, we should, at first, note that our estimation does not include the effect of Coulomb interaction. It might shift the energy spectra associated with soliton-antisoliton pairs and lead to a different separation. Therefore the obtained results are not quantitatively correct, but give a measure for the degree of confinement. Second, the spectral shift observed in  $\Delta A$  spectra may have some relations with the diffusional motion of the solitons. As stated in [14], in the formation process of the two in-gap states associated with two interacting excitations, they are expected to move through the bandgap, resulting in the spectral shift of the in-gap absorption as well. Since the formation process occurs in the same time scale as our experimental time resolution, we believe that the observed shift is associated with the formation process accompanied by the diffusion of two interacting solitons and that the shift may indicate the translational freedom of solitons.

Another feature we should note is that the PB recovers faster than the PA as shown in Fig. 4. Concerning this point, we think it possible that the bleaching may recover faster than the absorption signal due to species like intrachain polaron pairs and polaron excitons which can not escape from the initial fast recombination. They should also give absorption signals below the optical gap. Although we have not yet succeeded in extracting their spectra because of rather broad  $\Delta A$  spectra, it is conceivable that a fast decay observed at lower photon energy region below 1.6 eV [Fig. 4(a)] may correspond to that of the polaron pairs or polaron excitons. That is, the initial absorption at lower photon energy region is associated mainly with species like polaron excitons which can be regarded as single quasi-particle. This is followed by a separation of those charged particles which can escape

from the initial recombination to form soliton-antisoliton pairs with the observed spectral shift. Therefore we think that the fast exponential decay seen in Fig. 4(a) may be included in the recovery of the bleaching signal and that this makes the bleaching signal decay faster. The bleaching signal is probably composed of both the fast exponential decay seen in Fig. 4(a) and the power law decay with  $n = 0.65$ .

#### D. Comparison with Other Polymers

The confinement parameter  $\gamma$  [23], [34] defined as

$$\gamma = \frac{1}{2\lambda} \frac{\Delta_e}{\Delta_0 + \Delta_e} = \frac{\frac{\omega_0}{\Delta} \sin^{-1} \left( \frac{\omega_0}{\Delta} \right)}{\sqrt{1 - \left( \frac{\omega_0}{\Delta} \right)^2}} \quad (12)$$

indicates an extrinsic contribution to the displacement, where  $\lambda$  is an electron-phonon coupling constant, and  $\Delta$  and  $\omega_0$  are both experimentally accessible. For example, in ideal trans-(CH)<sub>x</sub> with no confinement, soliton states should appear in the center of the gap ( $\omega_0 = 0$ ) and  $\gamma$  should be zero. On the other hand, in our material, PMSPA,  $\gamma$  is calculated as 0.57, again showing that the strong confinement is the case.

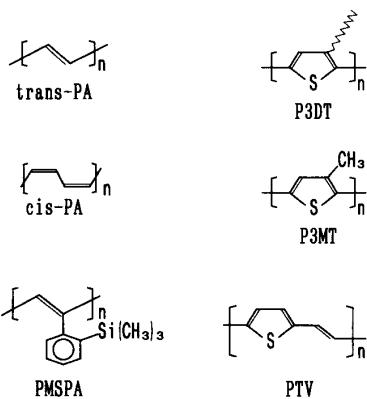
In general, the ultrafast relaxation dynamics after photoexcitation can be considered to depend on the initial distance between photogenerated charge carriers. In systems where soliton formation can take place, these electrons and holes will relax to isolated solitons (in the case of trans-(CH)<sub>x</sub>) or confined soliton-antisoliton pairs and subsequently separate more or less according to the degree of confinement. The following decay dynamics will be dominated by a geminate recombination process of these solitons, showing the power-law behavior. In the other extreme, for example in polydiacetylene, photoexcited electrons and holes cannot separate due to strong confinement caused by a highly nondegenerate ground state and Coulomb binding. Then the relaxation dynamics is dominated by that of excitons which decay monomolecularly with an exponential behavior, as has been already observed [20], [27].

The confinement parameters  $\gamma$  of several polymers are listed in Table I with their optical gaps and also with their chemical structures. All these data are calculated based on the results of femtosecond transient spectroscopy. The table clearly shows that the confinement of charge carriers is caused partly by a distortion of the main chain structure introduced by the steric hindrance between side groups as in the case of PMSPA and partly by the nondegeneracy of the ground state configuration. In other words, the energy difference between the ground state and the alternate dimerization phase,  $\delta E = E_B - E_A$ , determines the degree of confinement. Thus the 1-D  $\pi$ -electron conjugated polymers with carbon backbone structure can be classified using the confinement parameter  $\gamma$  as an index, and the relaxation of the photoexcited state including its func-



TABLE I  
CONFINEMENT PARAMETERS ( $\gamma$ ) OF SEVERAL POLYMERS DETERMINED FROM THE RESULTS OF FEMTOSECOND TRANSIENT SPECTROSCOPY. CHEMICAL STRUCTURE OF EACH POLYMER IS ALSO SHOWN. Eg: OPTICAL GAP,  $\omega_1$ : TRANSITION ENERGY FROM THE VALENCE BAND TO THE UPPER GAP STATE (SEE INSET OF FIG. 5),  $\omega_0$ : A HALF CONFINEMENT ENERGY. TRANS-[CIS]-PA: TRANS-[CIS]-POLYACETYLENE. P3DT: POLY(3-DODECYLTHIOPHENE). P3MT: POLY(3-METHYLTHIOPHENE). PTV: POLY(2,5-THIENYLENEVINYLENE).

| polymer  | $E_g=2\Delta$ (eV) | $\omega_1$ (eV) | $\omega_0$ (eV) | $\omega_0/\Delta$ | $\gamma$ |
|----------|--------------------|-----------------|-----------------|-------------------|----------|
| trans-PA | 1.4                | 0.70            | 0               | 0                 | 0        |
| cis-PA   | 2.1                | 1.55            | 0.50            | 0.48              | 0.27     |
| PMSPA    | 2.2                | 1.80            | 0.70            | 0.63              | 0.57     |
| P3DT     | 2.2                | 1.88            | 0.78            | 0.71              | 0.80     |
| P3MT     | 2.1                | 1.88            | 0.83            | 0.79              | 1.17     |
| PTV      | 1.9                | 1.80            | 0.85            | 0.89              | 2.14     |



tional type and characteristic decay time can be mapped along the “ $\gamma$ -axis” for every system from trans-(CH)<sub>x</sub> to polydiacetylene. The boundary between a power-law and exponential behavior is ill-defined and further investigations are required to discuss it in full detail.

### E. Interchain Photoexcitation

Although discussions have been made so far mainly on the results of *intra*chain photoexcitations, *inter*chain photoexcitation can also occur due to nonvanishing interchain transfer integral, generating a positive polaron ( $P^+$ ) on one chain and a negative polaron ( $P^-$ ) on the neighboring chain. Unlike a soliton which cannot hop to another chain because of its topological feature, these polarons can move separately on each chain or hop onto another chain, and therefore show 3-D diffusion [19]. They are considered to play an important role in transport phenomena such as photoconductivity [35] or quasi-static PA [8], [19], [36] as have been reported so far on trans-(CH)<sub>x</sub>.

Since the relaxation from the polaron states requires interchain hopping, the polarons are expected to have a long lifetime, probably an order of  $\mu$ s or longer. Therefore, it is natural to associate the long-lived component described by the second term of (2) with these polaron states. The amplitude of the long-lived baseline signal at both PA and PB peaks is plotted versus square pump intensity in Fig. 6. Since the data plotted in the figure are separate ones from those in Figs. 3 and 4, we cannot compare the am-

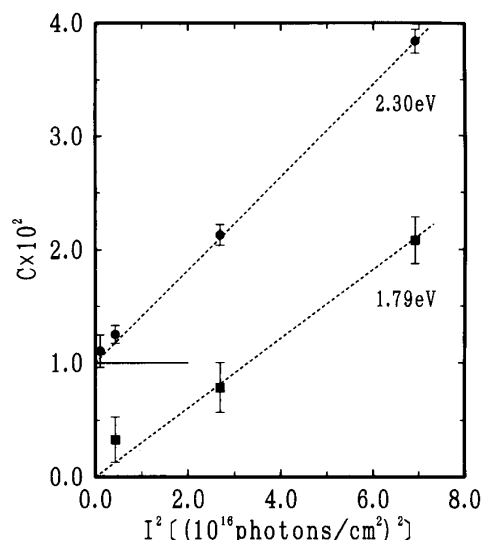
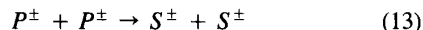


Fig. 6. Pump intensity dependence of the amplitude of the log-lived components at both PA and PB peaks. Data at 2.30 eV are shifted by 0.01.

plitude of the both data directly. A quadratic dependence of the baseline signal on the pump intensity is clearly seen from this figure, implying that it is caused by either a two-photon process or a reaction between two excitations, which themselves are generated by a one-photon process. Furthermore, for both PA and PB, these long-lived components have their peaks at the same energy as those of fast components which are due to intrachain soliton-antisoliton pairs. One of the possible ways to account for these two experimental facts is to associate the long-lived component with confined pairs of likely charged solitons. However here, these soliton pairs are considered to be generated by a different process. That is, at first, polarons are generated by interchain photoexcitations, and likely charged polarons on the same chain are converted to likely charged soliton pairs after encountering each other by the following reaction:



which is energetically favored. It should be noted that the confined pair of likely charged solitons is very similar to bipolarons from the viewpoint of lattice deformation and that the term soliton is used here in contrast with the intrachain soliton-antisoliton pair. The quadratic rather than linear dependence for both absorption and bleaching baseline seen in Fig. 6 may indicate the efficient conversion of polarons by the above mechanism or a relatively long lifetime of the soliton pairs compared to that of polarons probably due to higher mobility of polarons than that of soliton pairs.

However direct two-photon absorption as a mechanism for the baseline signal cannot be ruled out only from our experimental data. In this case, a creation of long-life species like triplet excitations is possible to occur.

## IV. CONCLUSION

We have performed the pump-probe experiments on poly[o-(trimethylsilyl)phenylacetylene] thin film with femtosecond time resolution. The photoinduced absorption peaked at 1.8 eV and interband bleaching centered at 2.3 eV were observed and the decay kinetics at the photoinduced absorption peak obeyed the power-law behavior with power  $n = 0.65 \pm 0.05$ . This implies that the geminate recombination process between the soliton and antisoliton generated by intrachain photoexcitation is most relevant. By taking into account of a significant reduction in a conjugation length of the polymer caused by a distortion of the main chain structure, we have concluded that these two features result from the intrachain soliton-antisoliton pairs which are confined in conjugation-length-limited segments of the main chain. The distance between the confined soliton and antisoliton was estimated as about six repeat unit lengths. This is consistent with the size of a certain regular structure indicated to exist in PMSPA by X-ray diffraction measurements.

A long-lived component was also observed at the same energy as that of intrachain feature. Since the amplitude of the signal had a quadratic dependence on the pump intensity, we have concluded that it is due to confined pairs of likely charged solitons, which are generated by a reaction between likely charged polarons created by interchain photoexcitations.

Various polymers can be classified by their confinement parameter  $\gamma$ . Small  $\gamma$  indicates that the photogenerated charge carriers can separate. The decay dynamics tend to obey a power-law behavior with a power nearly equal to 0.5. On the other hand, large  $\gamma$  corresponds to strong confinement in which the decay dynamics can be described by either a power-law function with a power larger than 0.5 or an exponential function.

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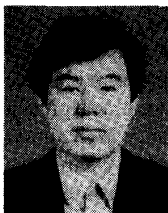
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