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Dynamics of a photoinduced phase transition in polydiacetylene crystals

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The dynamical process of the photoinduced phase transition in polydiacetylene (PDA) single crystals has been investigated by time-resolved spectroscopy with varying temperature, excitation photon energy, and intensity. The photoinduced phase transition can be driven bidirectionally between the two (A and B) phases by dichromatic irradiation of a laser pulse, when the temperature of the PDA crystal is kept around the phase transition temperature (T_c). It was found that primary process of the photoinduced phase transition is mostly completed within 50 ns. In addition, occurrence of a transient domain injection has been confirmed at temperatures far below and above T_c. Together with the time-resolved measurement of photocurrent, we have found a close correlation between the photocurrent intensity and the phase conversion efficiency. This suggests that the domain walls separating the A and B phases can carry the charge.

I. INTRODUCTION

Polydiacetylenes (PDA's), $(=RC—C\equiv C—CR=)_x$, are a family of representative π-conjugated polymers with various side groups (R,R'), and available in various forms such as cast films, vacuum deposited films, and single crystals. One of unique properties in PDA's is a chromic phase transition which can be caused by various internal and external stimulations.[1-14] Most of the PDA's show two spectroscopically distinct phases: the gold colored phase and greenish one which are called the A and B phases, respectively. Change of temperature, stress, photoexcitation, and carrier injection can trigger the phase transition between the A and B phases (A-B transition). Among various PDA's, we have confirmed that single crystals of the alkyl-urethane substituted families [$R=R'=(CH_2)_4OCONH(CH_2)_{n-1}CH_3$, $n=1-8$; hereafter abbreviated as poly-4*Un*] undergo the first-order reversible A-B transition with change of temperature.[13] In Fig. 1, we show a schematic structure of poly-4*Un*. The backbone planarity in the both (A and B) phases is maintained by the hydrogen bonds among urethane groups which are separated from the carbon backbone by the inner alkyl chains. Upon the A-B transition, the excitonic absorption spectra as well as the Raman spectra for the backbone vibrational modes show a drastic change as shown in previous reports,[2,9,13] indicating the change in the bond structure of the backbone. NMR (Ref. 15) and calorimetric studies[13] revealed that the A-to-B transition is accompanied with conformation-

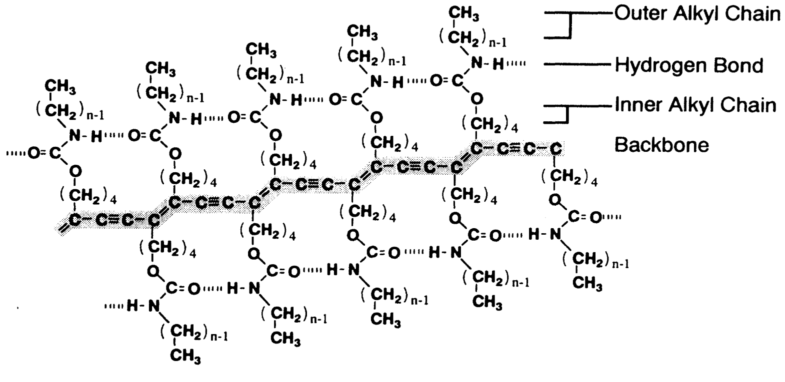

FIG. 1. Structure of polydiacetylene poly-4*Un*.

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al (gauche-to-trans) changes in two kinds of (inner and outer) alkyl chains in side groups. The thermally induced *A*-*B* transition is reversible if the crystal is not heated up beyond the melting temperature at which the hydrogen bonds among side groups are irreversibly interrupted.[11,13,16]

Lately, we have discovered the reversibly (bidirectionally) photoinduced *A*-*B* transition in poly-4*U*3 single crystals.[14] The obtained results showed that the photocarrier generation plays an important role in the driving process of the photoinduced phase transition. In this paper, we report on new dynamical aspects of this unique photoinduced phenomenon in poly-4*U*3 single crystals.

The format of the present paper is as follows: First, we give a brief review on the characteristics of the thermally and photoinduced phase transition in poly-4*U*3 crystals (Sec. III). Second, we report on the success of the bidirectional photoswitching between the two phases using dichromatic laser pulses without changing temperature (Sec. IV). Namely, the direction of the photoinduced transition can be controlled by tuning the photon energy of the excitation laser pulse. Third, we investigate the dynamical process of the photoinduced phase transition and transient domain injection at various temperatures, to obtain information about how the local excited species evolve into the macroscopic domain or otherwise how the photoinjected domain of the unstable phase goes back to the stable one (Secs. V and VI). In the final part of this paper (Sec. VII), we report on dynamics of the photocurrent with varying the excitation photon energy and intensity, and correlate the characteristics with those of the photoinduced phase conversion.

II. EXPERIMENT

Single crystals of PDA poly-4*U*3 were prepared by the procedures which were previously reported in detail.[13] The crystals show well-developed (1 0 0) surfaces and the polymer backbones run parallel along the [0 1 0] axis. Time-resolved spectroscopic studies have been made by a conventional nanosecond pump-probe system composed of an excimer laser pumped dye laser (20-ns pulse width) and a halogen incandescent lamp as a probe. Reflected light from the (1 0 0) surface of single crystals in the condition of nearly normal incidence was used as a probe for the chromatic change. Time dependence of the reflectance change has been measured with a digital oscilloscope and time-resolved reflectance spectra have been obtained by a polychromator equipped with a gated image intensifier. A resolution time for the time-resolved spectroscopic measurement was 50 ns. For the measurement of the transient photocurrent, the gold electrode was evaporated on to the (1 0 0) surface of the poly-4*U*3 single crystals. An electric field (800 V/cm) was applied parallel to the polymer backbone direction [0 1 0]. The photocurrent induced by an irradiation of laser pulse was detected using a current-voltage converter and digital oscilloscope with the resolution time of 80 μs.

III. CHARACTERISTICS OF THERMALLY AND PHOTOINDUCED PHASE TRANSITIONS IN POLY-4*U*3 CRYSTALS

Single crystals and polycrystalline thin films of poly-4*U*3 show the first-order phase transition (*A*-*B* transition).[13] We can probe this transition by reflection (or absorption) and Raman spectroscopies. The reflection band due to the ^1B_u exciton (*A* band) accompanied by its phonon (backbone vibrational mode) sideband (*A*′ band) was observed at 1.95 eV in the *A* phase (low-temperature phase). This excitonic reflection (or absorption) band shifted to ~2.35 eV (*B* band) showing a similar phonon sideband (*B*′ band) in the *B* phase (high-temperature phase). Reflectance changes at 1.95 and 2.35 eV on the *A*-*B* transition are so large that the *A*-*B* transition is easily traceable by monitoring the reflectivity around these two photon energies. As an example, temperature dependence of the reflectivity at 1.95 eV is plotted in Fig. 2. Temperature was changed in a sequence of the numbers in this figure (1→2→3→4→5→6→7). In the heating process (1→2→3→4), the system was kept in the *A* phase below 400 K, but showed an abrupt decrease of the reflectivity at 1.95 eV around 400 K in coincidence with the *A*-to-*B* transition. The *A*-*B* transition in poly-4*U*3 showed a wide hysteresis and the crystal was kept in the *B* phase down to 360 K in the cooling process (4→5→6→7) as shown in Fig. 2.

The change in the π-electronic structure as observed upon the *A*-*B* transition is obviously due to the structural change of the carbon backbone, though the overall

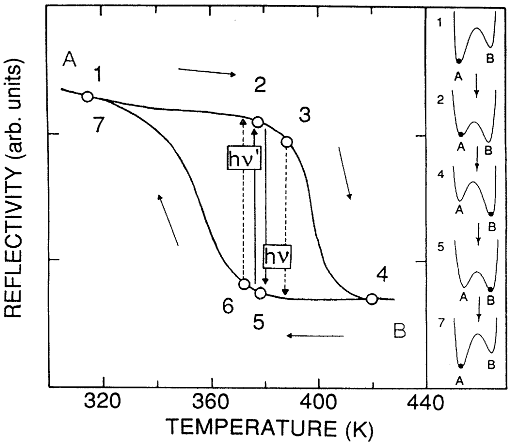

FIG. 2. Temperature dependence of reflectivity of a poly-4*U*3 single crystal observed at 1.95 eV (left-hand side) and the schematic diagrams for free energy (right-hand side). The two minima of the free energy correspond to the *A* and *B* phases. The crystal was heated up (1→2→3→4) and cooled down (4→5→6→7) in the order of the number. $h\nu$ and $h\nu'$ represent photon energies for excitation; $h\nu = 2.81$ or 2.58 eV and $h\nu' = 3.18$ eV.

acetylene-type conformation seems to be maintained in the both phases.[17–20] The change of the bond structure can be sensitively probed by Raman spectroscopy.[13,21] The C$=$C stretching mode in the B phase is located at ~ 50 cm^{-1} higher frequency than in the A phase.

In a previous study,[14] we confirmed that genuine photoexcitation can also trigger a macroscopic phase change at temperatures within the hysteresis region (e.g., at the temperature points 3 and 6 in Fig. 2) by the measurement of the photoinduced changes in absorption and Raman spectra (refer to Fig. 1 in Ref. 14). At temperature point 3, the system is kept in the A phase perhaps due to the large potential barrier although the B phase is expected to be more stable. At this temperature (point 3) we observed that the A-to-B phase conversion of 100% efficiency can be induced by irradiation of a single shot of 2.81 eV ($=h\nu$) light pulse (20 ns width) with excitation intensity of 7×10^{18} photons/cm^3. Hereafter, excitation intensity, i.e., a density of absorbed photons on the crystal surface, is simply denoted in units of cm^{-3}.

At temperature point 6, large photoinduced changes in the reflectance and Raman spectra were similarly observed. From the obtained results, we could estimate that 50% of the B phase was converted to the A phase by a single shot irradiation with 3.18-eV ($=h\nu'$) light pulse (20 ns width) at the excitation intensity of 7×10^{18} cm^{-3}.

The photoinduced phase conversion efficiencies (Φ) for the A-to-B (observed at 390 K) and B-to-A (at 370 K) directions showed a nonlinear (thresholdlike) dependence on the excitation intensity: The photoexcitation with an intensity weaker than 2×10^{18} cm^{-3} induced no permanent change in Raman nor absorption spectra. Φ abruptly increased for each A-to-B or B-to-A case when the excitation intensity exceeded 2×10^{18} cm^{-3}. The threshold intensity ($I_{\rm th}=2\times10^{18}$ cm^{-3}) corresponds to the absorption of one photon in the fraction of about 480 repeated [$=R$C—C$\equiv$C—C$R=$] units of the polymer. Φ reached the maximum (~ 1.0 for A-to-B) and 0.5 for B-to-A) with the excitation intensity of $\sim 6\times10^{18}$ cm^{-3} for the respective transitions and kept these optimum values as long as the excitation intensity did not exceed 8×10^{18} cm^{-3}.

In the region beyond 8×10^{18} cm^{-3}, the Φ for the B-to-A direction rather decreased as the excitation intensity increased (see Fig. 3 in Ref. 14), though that for A-to-B still kept its optimum value (about 100%). This was attributed to the photoinduced interruption of the hydrogen bonds among the side groups, which permanently stabilizes the B-phase-like bond structure of the polymer backbone.[13]

Φ also strongly depends on the excitation photon energy (see Fig. 4 in Ref. 14). The excitation spectra for the converted fraction showed a threshold which is located 0.3–0.5 eV higher than the ^1B_u exciton absorption peak for both the A-to-B and B-to-A phase changes. The efficiencies were very low near the exciton absorption peaks where the excitation light is strongly absorbed. This is in contradiction to the situation expected for the thermal phase changes induced by the laser-heating effect. An excitation light pulse with the photon energy between 2.3 and 2.9 eV could induce the A-to-B conversion with 100% efficiency. However, the photoconversion in the reverse direction (B-to-A) was not efficient in the above photon energy range and the optimum efficiency ($\sim 50\%$) could be attained only when the photon energy is above 3.0 eV. These characteristics are utilized for the bidirectional photoswitching, as demonstrated in Sec. IV.

Another point to be noted in Fig. 4 of Ref. 14 is a close similarity between the excitation photon energy dependences of Φ (solid circles) and the photoconductivity (open circles). This shows that the photoexcitation with the energy exceeding the gap energy (E_g) is necessary for triggering the photoinduced phase transition.[14] Detailed discussion will be given on this point in Sec. VII.

IV. BIDIRECTIONAL PHASE SWITCHING BY DICHROMATIC EXCITATION

The free energy for poly-4U3 crystal is expected to be represented by a curve with double potential minima, which correspond to the A and B phases, separated by a potential barrier (see schematics shown in the right part of Fig. 2). At temperature point 2 or 5 in Fig. 2, levels of the free-energy minima which correspond to the A and B phases are considered to be nearly degenerate, though the phase change is thermally inhibited due to the presence of the potential barrier. Our expectation was that near the middle point of the hysteresis (temperature 2 or 5),

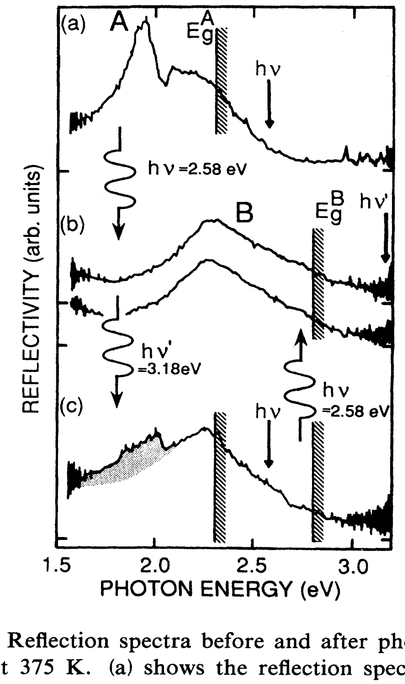

FIG. 3. Reflection spectra before and after photoexcitation observed at 375 K. (a) shows the reflection spectrum (the A phase) before photoexcitation. After the irradiation by the first excitation pulse ($h\nu=2.58$ eV and 20 ns width), the spectrum changes to the upper curve of (b). (c) and the lower curve of (b) are the spectra observed after the second and third photoexcitations by $h\nu'=3.18$ and $h\nu=2.58$ eV, respectively. $E_g^{(A)}$ ($\simeq 2.3$ eV) and $E_g^{(B)}$ ($\simeq 2.8$ eV) represent the band gap energies in the A and B phases, respectively.

the bidirectional (A-to-B and B-to-A) phase switching can be caused by the dichromatic excitation making use of the different photon energy dependences of the conversion efficiency (Φ) for the $A \rightarrow B$ and $B \rightarrow A$ directions.

Figure 3 shows the change in the reflectance spectrum of poly-4U3 single crystals induced by dichromatic excitation at 375 K. In this figure the band gap energies are indicated by hatched stripes in the respective phases ($E_g^{(A)}$) for the A phase and $E_g^{(B)}$ for the B phase) which were determined by taking the threshold energies for the action spectra of the photocurrent.[14] At temperature point 2 (Fig. 2), the crystal was kept in the A phase as shown in Fig. 3(a). After the excitation by a single shot of 2.58-eV ($=h\nu$) light pulse, the reflectance spectrum turned into the upper one of Fig. 3(b). The observed shift of the reflectance maximum energy from 1.95 to 2.35 eV signals the occurrence of the phase transition from A to B. After the photoinduced change from the A to B phase, the same crystal was excited by a single shot of 3.18-eV ($=h\nu'$) pulse (the second excitation). Then the reflectivity between 1.5 and 2.0 eV increased and the new reflection band (hatched region) reminiscent of the A-phase region was formed around 1.9 eV as shown in Fig. 3(c). This reflectance peak arising from the A-phase region could be completely extinguished by irradiation of the third excitation light pulse ($h\nu=2.58$ eV) [see the lower spectrum of Fig. 3(b)]. As denoted before, the photoexcitation with a 2.58-eV light pulse, that is above $E_g^{(A)}$ but below $E_g^{(B)}$, can induce the A-to-B conversion, but not the B-to-A transition. This is the reason why the A phase disappeared selectively after the third photoexcitation. In the experiments for Fig. 3, the excitation intensity was always kept at $\sim 6.5 \times 10^{18}$ cm^{-3}. It was also confirmed that the photoexcitation with the same intensity but below E_g^A causes no change in the spectra at any stage of the phase cycle.

V. TIME-RESOLVED REFLECTION SPECTRA IN CASE OF THE PERMANENT PHASE TRANSITION

The time-resolved study was carried out to measure the speed of the phase conversion and possibly detect the evolution process from the microscopic excited species into the macroscopic phase in the course of the photoinduced phase transition. Figures 4 and 5 are the time-resolved reflection spectra at various delay times (Δt) after photoexcitation for the A-to-B and B-to-A transition, respectively. Crystals were kept at the temperature in the hysteresis region (375 K), i.e., points 2 and 5 in Fig. 2. Photon energies of laser pulses were tuned to 2.81 and 3.18 eV, and excitation intensities were set at 6.5×10^{18} cm^{-3} and 6×10^{18} cm^{-3} for the excitation of the A and B phases, respectively. The time dependences of the reflectivity change ($\Delta R/R$) at photon energies 2.4 and 1.9 eV are shown in the upper panels of Figs. 4 and 5. These photon energies, 1.9 and 2.4 eV, approximately correspond to the positions of the excitonic reflectance maxima in the A and B phases, respectively, and hence are suitable for probing the A-B transition.

Figures 4(b) and 4(c) show the reflection spectra at $\Delta t = 150$ ns and $\Delta t = 2$ ms after photoexcitation with the 2.81-eV pulse, respectively, in the case of the A-to-B transition. The reflectance maximum due to the A phase seen in the original spectrum [Fig. 4(a)] was extinguished immediately after excitation and a broadband characteristic of the B phase was formed around 2.4 eV as shown in these figures. The change in the reflection spectrum appears to be mostly completed within the period less than the resolution time (50 ns) of our experimental apparatus (see the upper panel of Fig. 4), apart from a further slight red shift (about 0.04 eV) of the reflectance maximum position observed over a long period ($\Delta t = 2$ ms). Thus, the photoinduced A-to-B phase transition occurs faster than 50 ns.

The dynamics of the transition in the backward direction (B-to-A) is quite similar to that of the A-to-B conversion. Figure 5(a) is the reflectance spectrum of the same crystal which was first photoconverted from the A to B phase by 2.81-eV excitation; i.e., from point 2 to 5 in Fig. 2. This crystal was excited by a single shot of a 3.18-eV laser pulse. The rapid (faster than 50 ns) increase of the reflectivity around 1.9 eV after excitation indicates that the B-to-A photoconversion (from point 5 to 2 in Fig. 2) is mostly completed within 50 ns as in the case of the A-to-B conversion.

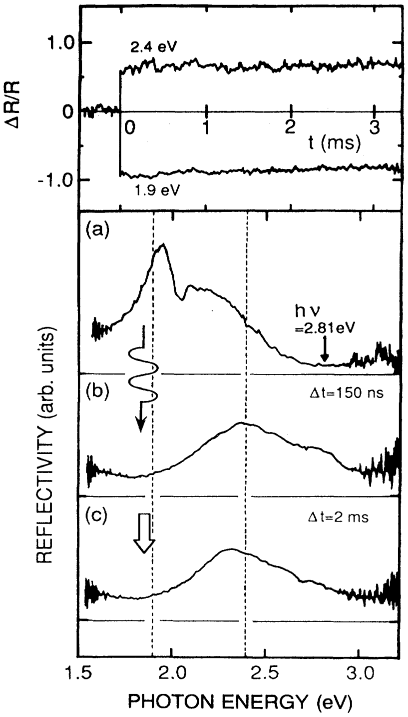

FIG. 4. Time-resolved reflection spectra at 375 K observed (a) before (the A phase) and at (b) 150 ns and (c) 2 ms after photoexcitation by a 2.81-eV light pulse. The upper panel shows the time dependence of the reflectance change ($\Delta R/R$) observed at 1.9 and 2.4 eV. The photon energies of 1.9 and 2.4 eV, which are suitable for probing the A- and B-phase components, are indicated by vertical dashed lines.

In addition to the fast primary process within 50 ns, a slow "shape-up" process was observed in the temporal changes of the spectra for both photoinduced transitions. The feature is particularly conspicuous for the *B*-to-*A* conversion: *A* broad reflection band spreading from1.6 to 2.7 eV is observed at $\Delta t = 150$ ns, but after a long interval (e.g., 2 ms) it splits into two bands whose maxima are located around 1.9 and 2.3 eV [Figs. 5(b) and 5(c)]. In other words, the component around 2.1 eV formed immediately after photoexcitation slowly shifts to 1.9 eV, being reminiscent of the formation of the partly photoconverted *A* phase.

In previous studies,[11,13,15] it was reported that the thermally induced *A*-*B* transition in poly-4*U*3 crystals is accompanied not only by the structural changes in the carbon backbone but also with the configurational changes in sidegroups. According to the ^{13}C NMR study by Tanaka *et al.*[15] and our previous calorimetric study,[13] a conformational change in the alkyl groups, especially a trans-gauche change in the inner-alkyl chains (see Fig. 1), occurs upon the *A*-*B* transition. Therefore, the structural changes in both the backbone and side groups are necessary for the whole process of the photoinduced *A*-*B* transition. The conformational change in the alkyl chains is likely to take a much longer interval than the change in the backbone structure. On the basis of this speculation, we tentatively attribute the broadened profile of the photoconverted band at a short delay time to the stressed backbones accompanied with the incommensurate configuration of the sidegroup. To obtain a more conclusive interpretation, the time-resolved spectroscopic study in the IR region is necessary.

VI. TIME-RESOLVED REFLECTION SPECTRA IN CASE OF THE TRANSIENT PHASE CHANGE

By the time-resolved reflectance spectroscopy at the temperature points outside the hysteresis region [points 1(7), 300 K and 4, 420 K], we have confirmed the occurrence of the transient domain injection of the unstable phase. At 300 K (low-temperature side out of the hysteresis loop), only the *A* phase is stable and the crystal was kept in this phase before excitation as shown in Fig. 6(a). Within 50 ns after photoexcitation by a 2.81-eV light pulse, the reflection band around 1.9 eV in the *A* phase almost disappears and a new band around 2.5 eV, whose spectral shape is characteristic of the *B* phase, ap-

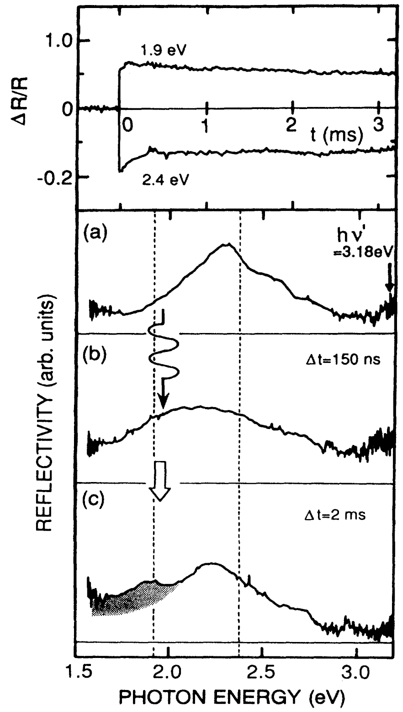

FIG. 5. Time-resolved reflection spectra observed (a) before (the *B* phase) and at (b) 150 ns and (c) 2 ms after the photoexcitation by a 3.18-eV light pulse. The sample temperature was kept at 375 K during the experiment. The upper panel shows the time dependence of the reflectance change ($\Delta R/R$) observed at 1.9 and 2.4 eV. (These photon energies are denoted by vertical dashed lines.)

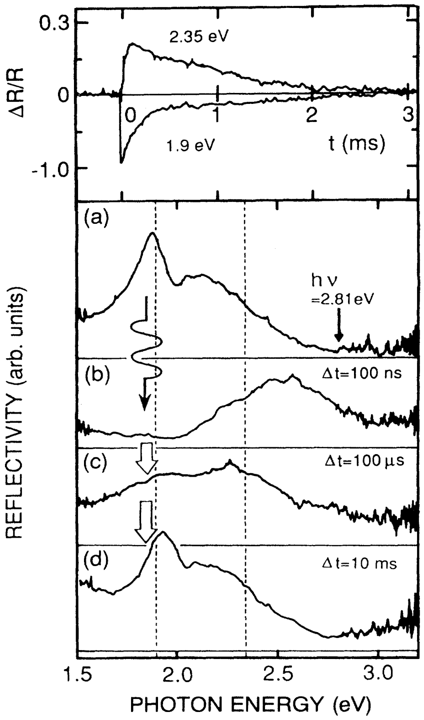

FIG. 6. Photoinduced reflectance change at a temperature point (300 K) below the transition temperature (T_c). (a) shows the spectrum of the *A* phase before photoexcitation. The time-resolved reflectance spectra (b), (c), and (d) were observed at 100 ns, 100 μs, and 10 ms after photoexcitation by a 2.81-eV ($= h\nu$) pulse, respectively. Time dependence of the reflectance change observed at 1.9 and 2.35 eV is plotted in the upper panel. Vertical dashed lines denote the photon energies at which the temporal behavior of the reflectance change is monitored.

pears [see Fig. 6(b), $\Delta t = 100$ ns]. At $\Delta t = 100$ μs, the reflectance maximum shifts to 2.3 eV and the 1.9-eV band (A band) begins to reappear. At $\Delta t = 10$ ms, the spectrum comes back to the same one as before photoexcitation. The temporal shift of the photoinjected B-phase band from 2.5 to 2.3 eV may reflect the slower relaxation process of the side-group configuration than the change in the polymer backbone structure as discussed before. A similar transient domain injection into the B-phase ground state has been observed at 420 K (high-temperature side out of the hysteresis) by the irradiation of the 3.18-eV light pulse (see Fig. 7). For the unstable phase domain to be injected, additional energy is considered to be necessary. The lattice relaxation energy of the photoexcited species perhaps serves as an effective fuel for the initial evolution of the local excited species into the macroscopic domain.

In the above experiments, the excitation photon density was set at 6×10^{18} cm^{-3} to avoid the permanent damage as previously noted. The excitation light with the same intensity can trigger the phase transition at a temperature within the hysteresis loop, e.g., 375 K. When the crystal was photoexcited with the same intensity but below E_g, essentially no change (at most 2 orders of magnitude smaller signal in comparison with the case of above E_g photoexcitation) was observed in the reflection spectra. This indicates that the photocarrier generation is also playing an important role in the driving process of the transient photoinjection of the unstable domain as in the photoinduced permanent phase transition.

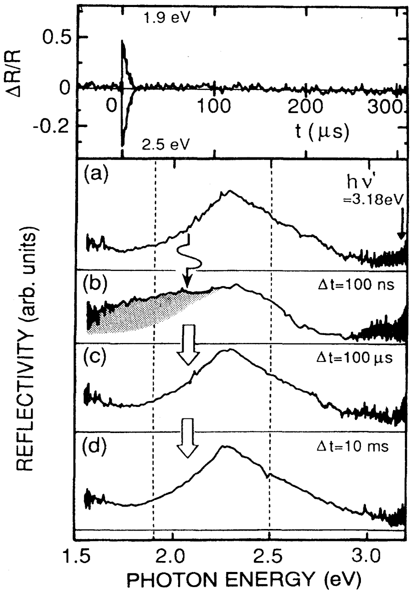

FIG. 7. The photoinduced reflectance change at a temperature point (420 K) above the transition temperature (T_c). (a) shows the spectrum of the B phase before photoexcitation. Reflectance spectra (b), (c), and (d) were observed at 100 ns, 100 μs, and 10 ms after photoexcitation by a 3.18-eV ($=h\nu'$) light pulse, respectively. Time dependence of the reflectance change observed at 1.9 and 2.35 eV (denoted by vertical dashed lines in lower panel) is plotted in the upper panel.

In Figs. 6 and 7, the photoinjected domain of the unstable phase is observed to eventually disappear and the original phase to totally recover as increasing the delay time. However, there is a large difference in the time scale of the dynamics for the two cases (at 300 K and at 420 K): The photoinjected A-phase domain in the B-phase crystal (at 420 K) appears to extinguish within 50 μs whereas the injected B-phase into the A-phase crystal at 300 K remains over 1 ms (see the upper panels of Figs. 6 and 7). Such a difference in the lifetime of the photoinjected domain may arise from the temperature-dependent mobility of the domain walls (DW's) between the A and B phases. The DW's in PDA may show a thermally activated motion in the recovery process as in the case of DW motion in ionic donor-acceptor charge-transfer (CT) compounds.[22]

VII. A ROLE OF THE PHOTOCARRIER IN THE DRIVING PROCESS OF THE PHOTOINDUCED PHASE TRANSITION

As discussed before, the excitation photon energy dependence of Φ shows the thresholdlike behavior and close correlation with that of the photoconductivity.[14] It suggests an important role of charge carriers in the generation of the DW's which position between the photoinjected B- (or A-) phase domains and the host A- (B-) phase domains. Charge carriers in one-dimensional conjugated polymers such as PDA's are considered to be strongly coupled with lattice, forming polarons or bipolarons.[23] The situation in the PDA crystals at temperatures around the hysteresis-loop region seems to be analogous to the conjugated polymers with the nearly degenerate ground states, since the free energies of the A and B phases are nearly equal. It has been known for such polymers that a bipolaron state plays a main role in the charge transport phenomena.[23] In this context, we may speculate that a DW pair in PDA's is analogous to the bipolaron state.

In what follows, we report on the relaxation process of the photocarriers after an irradiation by a nanosecond laser pulse with varying the excitation intensity and argue a possible relation between the photocarrier transport and the DW dynamics. In Fig. 8 is plotted the temporal response of the photocurrent at 370 K for various excitation intensities. The crystal of poly-4U3 was of the A phase before photoexcitation. As mentioned before, the excitation with the photon energy higher than the band gap ($E_g^{(A)}$ 2.3 eV) is necessary to produce the photocarrier by a weak cw excitation light. This is also the case for the excitation by a nanosecond pulsed light source. The excitation was, therefore, done by 3.18 eV (above $E_g^{(A)}$) light pulse with varying photon density: Figs. 8(a) 1×10^{18} cm^{-3}, 8(b) 2×10^{18} cm^{-3}, and 8(c) 6×10^{18} cm^{-3}.

The photocurrent in the poly-4U3 single crystal contains two temporal (fast and slow) components as seen in transient behaviors of the photocurrent (Fig. 8). Hereafter, we denote the components with short lifetime (within the resolution time of the experimental apparatus $\simeq 80$ μs) as F. The integrated intensity of the F component

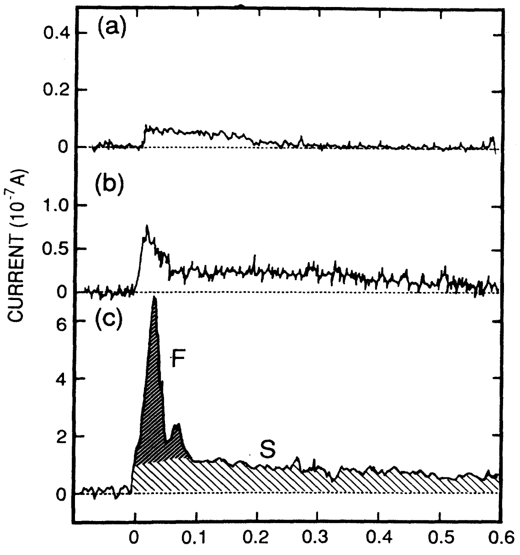

FIG. 8. Dependence of the dynamical behavior of the photocurrent on the excitation intensity observed at 370 K. Excitation photon densities are (a) 1×10^{18} cm^{-3}, (b) 2×10^{18} cm^{-3}, and (c) 6×10^{18} cm^{-3}. The two (fast, *F* and slow, *S*) components in the transient photocurrent are indicated.

seems to depend nonlinearly on the excitation light intensity. In Fig. 9, the excitation intensity dependence of the integrated intensity of the *F* component (i.e., electric charge transported by the *F* component; solid circles) and the photoinduced *A*-to-*B* phase conversion efficiency (Φ) are compared with each other. When scaled appropriately, both quantities show quite a parallel behavior as a function of the excitation intensity: In particular, the threshold intensities for Φ and the charge transported by the photocurrent component *F* are nearly the same ($\sim2\times10^{18}$ cm^{-3}). The present observation reinforces the idea that there is a close correlation between the photocarrier (considered to be polaron or bipolaron) and the DW (or DW pair). In addition, the lifetime of the *F* component is shorter than the resolution time ($\simeq80$ μs) which is compatible with the observation that the initial movement of the DW between the two (*A* and *B*) phases readily occurs within 50 ns just after photoexcitation (see Fig. 4). On the basis of these results, it is tempting to consider that component *F* is a direct consequence of the movement of the DW or DW pair as a charge-carrying polaron or bipolaron and that a weak perturbation by a small number of photo-carriers can trigger the macroscopic transition due to the cooperative interaction. Such a large and nonlinear amplification of the response to the external perturbation is often the case in the dynamical process of the first-order phase transition. Of course, this idea should not be pushed too much at the present stage. To confirm this speculation, measurements of the photocurrent with nanosecond resolution, photocarrier generation yield, photoinduced IR absorption, and ESR would be useful.[24]

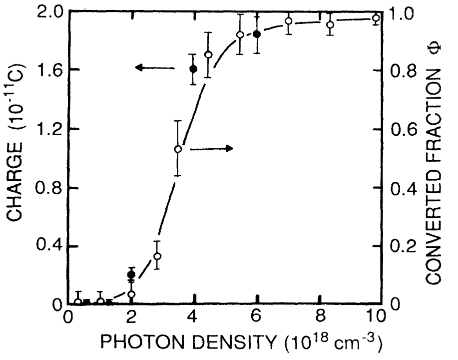

FIG. 9. The integrated intensity (i.e., carried charge) of the *F* (fast) component of the transient photocurrent observed at 370 K (solid circles) in comparison with the converted fraction (Φ) for the photoinduced *A*-to-*B* phase transition at 390 K (open circles) with various excitation photon densities (Ref. 14).

As for the *S* component, we have also confirmed the abrupt increase of the integrated intensity of this component at the threshold intensity for $\Phi(I_{\text{th}})$. It is likely that the *S* component is due to the polaronic species which have relaxed from the DW escaping geminate recombination. This *S* component may correspond to the ordinary photocurrent observed in PDA crystals.[25]

VIII. SUMMARY

We have reported on the dynamical process of the photoinduced phase transition in PDA single crystals with varying the sample temperature. We have found that the control of the direction of the phase transition is possible around the critical temperature (T_c) by changing the excitation photon energy, and that the primary process of the photoinduced phase transition is completed within 50 ns. In addition, the transient photoinjection of the unstable phase was also observed even at temperatures far below and above T_c. With the data by the time-resolved measurement of the photocurrent, we have demonstrated the close correlation between the photocarriers (polaron and/or bipolaron) and the domain-wall (DW) excitations. Thus, the change in the charge conjugation pattern is expected around the polaronic DW, details of which will be the subject of a future study. On the basis of the obtained results, we conclude that the photoinduced phase transition in poly-4*U*3 crystals is governed by early dynamics of the photoinjected carriers. Spectroscopic measurement with pico- and femtosecond time resolution would be necessary for making clear the dynamical process of the backbone structural changes induced by carrier generation.

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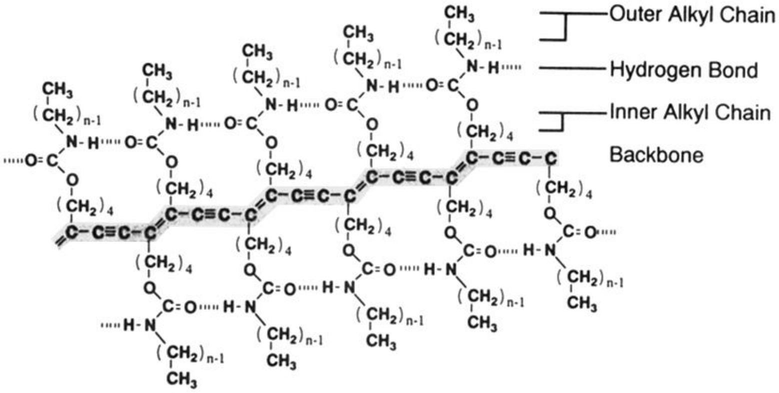

FIG. 1. Structure of polydiacetylene poly-4*Un*.