Reversible Photoinduced Phase Transitions in Single Crystals of Polydiacetylenes

S. Koshihara[a] and Y. Tokura
Department of Physics, The University of Tokyo, Tokyo 113, Japan

K. Takeda
Tsukuba Research Laboratory, Japan Synthetic Rubber Co., Ltd., Tsukuba 305, Japan

T. Koda
Department of Applied Physics, The University of Tokyo, Tokyo 113, Japan

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It was observed that bi-directional phase changes can be triggered by genuine photoexcitation between two phases with different bond structures in polydiacetylenes. The observed photoinduced phase transition was found to be mediated by photogeneration of charge carriers (and not of excitons). The extremely high efficiency is perhaps due to cooperative interaction between the locally photoconverted domains.

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Bi-directional photoswitching of molecular structures has been observed in a number of photochromic dye molecules, which are of renewed interest because of their potential for application to memory storage [1]. In solid state aggregates of these photochromic units, however, the efficiency of the photochromism is, in general, much reduced due to the steric hindrance effect. Here we report the finding of a new photochromic phenomenon in the solid state phase, that is, a photoinduced phase transition in conjugated polymers, polydiacetylenes [2]. We have observed that reversible changes between two phases with different bond structures can be induced by genuine photoexcitation in single crystals of polydiacetylenes. Photoexcitation across the band gap with an intensity above a threshold value is necessary to cause the photoinduced phase transition. Because of some cooperative process in the phase change, however, the threshold excitation intensity is fairly low, corresponding to only one absorbed photon per 500 repeat units of the polymer. Therefore, the presently observed phenomenon can be viewed as a sort of extremely efficient photochromism, which may also have some significance in possible applications.

In this study we investigated single crystals of polydiacetylenes (PDAs), $[\!+\!RC-C\equiv C-CR\!+\!_x]$, with alkyl urethanes, $(CH_2)_4OCONH(CH_2)_{n-1}CH_3$, as the side-group R. Hereafter, we will abbreviate them as poly-4U*n*. In poly-4U*n*, the adjacent urethane groups are connected by hydrogen bonds to form a linear linkage of −OCONH− running parallel to the polymer backbones [3]. As is common in many other PDAs [4–8], there are two spectroscopically distinct phases in the poly-4U*n* series, namely, the so-called blue (or *A*) and red (or *B*) phases. In Fig. 1 are shown the ϵ_2 (the imaginary part of the complex dielectric constant) and Raman spectra for a poly-4U3 crystal. The latter spectra detect the backbone C=C stretching modes. The different spectral sets, numbered 1–5, were measured at various steps of a thermal cycle starting from 315 K (1), warming up to 420 K (3), and again cooling down to 315 K (5), as shown in Fig. 2. The ϵ_2 spectra were obtained by Kramers-Kronig analysis of polarized reflectance spectra for the crystal. The ϵ_2

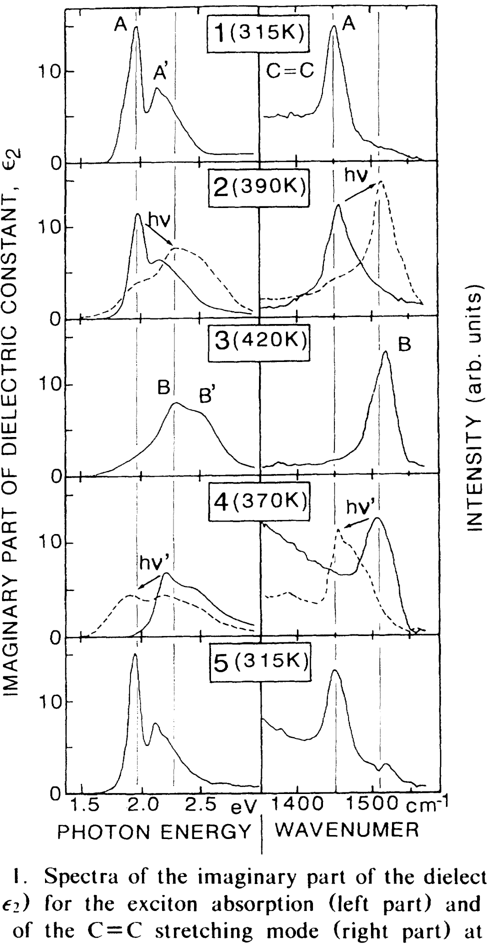

FIG. 1. Spectra of the imaginary part of the dielectric constant (ϵ_2) for the exciton absorption (left part) and Raman spectra of the C=C stretching mode (right part) at various temperatures. The temperature points labeled 1–5 are indicated on the hysteresis loop shown in Fig. 2. Dashed lines in the spectra at temperature points 2 and 4 show those observed after photoexcitation by a single shot of a pulsed dye laser (see text). The excitation photon energies, $h\nu$ and $h\nu'$, are 2.81 and 3.18 eV, respectively.

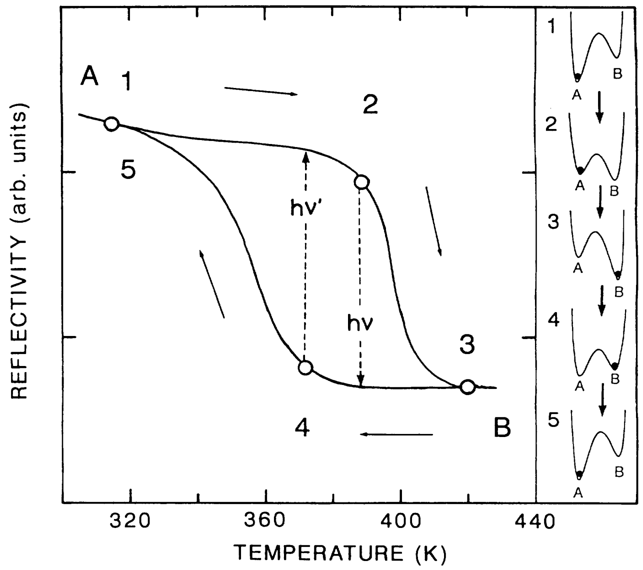

FIG. 2. Temperature dependence of reflectivity in a poly-4U3 crystal at 1.95 eV (left-hand side), and schematic diagrams of free energy with the minima corresponding to the *A* and *B* phases (right-hand side). The temperature points at which the reflectance and Raman spectra were measured are denoted by open circles and are numbered in the order of the heating and cooling process. At points 2 and 4, the crystal surface was irradiated with a single shot of a pulsed laser as denoted by dashed lines, and the photoinduced effect on the electronic absorption and Raman spectra were measured (see the spectra at points 2 and 4 in Fig. 1).

peaks labeled *A* and *A'* in Fig. 1 are due to the 0-0 exciton (an electron-hole bound composite) and its vibronic sideband for the *A* phase. Likewise, *B* and *B'* are those for the *B* phase. In accord with the change of these electronic spectra for the thermal cycle from the *A* phase (1) to the *B* phase (3), the Raman frequency of the C=C stretching mode shifts from 1450 to 1500 cm^{-1}, as shown on the right-hand side of Fig. 1. This clearly indicates that the *A* and *B* phases correspond to two different minima of free energy for the conjugated π-electron system coupled with the conformation of the backbone. The microscopic nature of these states remains to be clarified.

We have previously shown that single crystals of the entire poly-4U*n* series ($n=1$-10) exhibit a similar temperature-induced reversible phase transition between the *A* and *B* phases, accompanied by a thermal hysteresis [3]. In this study, we deal mainly with results for poly-4U*n* ($n=3$), as fairly high-quality single crystals can be obtained for this polymer. We plot in Fig. 2 the reflectivity of a poly-4U3 single crystal monitored at peak *A* (1.95 eV) during the thermal cycle, 1 to 5. The trace shows a hysteresis loop in the temperature range of ca. 60 K. From a thermodynamical point of view, the free energy for this crystal is represented by a curve with double local potential minima corresponding to the *A* and *B* phases, which are separated by an energy barrier. The relative stability for the two minima is interchanged at a certain temperature somewhere in the temperature region showing the hysteresis. Schematic free energy curves at the respective temperatures are shown on the right-hand side of Fig. 2.

In the course of the thermal cycle shown in Fig. 2, the temperature was kept at point 2, and the sample was irradiated with a *single shot* (2.81 eV) from a pulsed dye laser (20 nsec width) which was pumped by an XeCl excimer laser. The electronic absorption (ϵ_2) and Raman spectra after the photoexcitation are shown by dashed curves in panel 2 of Fig. 1. The results clearly show almost full conversion of the *A* phase into the *B* phase. Similarly, the sample kept at point 4 in the cooling cycle was excited by a single pulse (3.18 eV). The ϵ_2 and Raman spectra after the photoexcitation are shown by dashed curves in panel 4 of Fig. 1. The results show that ca. 50% of the *B* phase is converted into *A*. To cause such conspicuous changes as shown in the figure, the photon energy of the exciting laser pulse need not be unique, as long as it exceeds a threshold value; ca. 2.4 eV for the *A*-to-*B* and ca. 2.7 eV for the *B*-to-*A* change (cf. Fig. 4). The excitation photon density also must be higher than some threshold value and was set at 5×10^{18} cm^{-3} (*vide infra*) in the present case. These photoinduced changes could be observed visually; the irradiated surface region was distinguished from the unirradiated one by differently colored lusters.

More quantitative measurements of the photoinduced phase conversion fraction were made under the same conditions as mentioned above, but using various photon densities. The excitation photon densities have been estimated assuming that the total photon flux of pump light is absorbed uniformly within a depth of ca. 1 μm from the surface, as estimated from absorption coefficients. The absorption coefficients were directly measured on highly oriented thin films [9], which are also in good agreement with those obtained by Kramers-Kronig analysis of reflectance spectra in single crystals. The converted fractions were estimated from the photoinduced changes in the integrated intensity of Raman peaks due to the C=C stretching mode. The results are shown in Fig. 3. As seen, the photoinduced changes are nonlinear in the excitation intensity with a threshold at ca. $(2\text{-}3)\times10^{18}$ cm^{-3}. This suggests that some cooperative interaction is necessary for individual local photoexcited species to evolve into the macroscopic phase conversion, as discussed by Nagaosa and co-workers [10,11].

It is worth noting that the fraction of the phase change is quite large even for single-shot irradiation by a laser pulse. The efficiency is nearly 100% for the *A*-to-*B* transition and about 50% for the *B*-to-*A* transition at the excitation photon density of 7×10^{18} cm^{-3}, as shown in Fig. 3, a value corresponding to the absorption of one photon in a fraction of the polymer crystal composed of about 140 repeat $[=RC-C\equiv C-CR=]$ units (one repeat unit occupies a volume of about 1100 Å^3 in the crystal [3]).

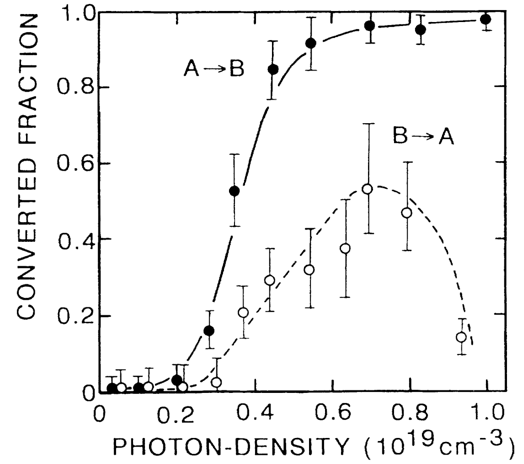

FIG. 3. Dependences of the photoconverted fractions on the absorbed photon density for the photoinduced A-to-B (closed circles) and B-to-A (open circles) transitions observed at temperature points 2 (390 K) and 4 (370 K), respectively (see Fig. 2). Excitation photon energies are 2.81 and 3.18 eV for the A-to-B and B-to-A conversions, respectively.

Such an extremely high efficiency of photoconversion indicates a collective nature of the phase transition occurring between the two phases when their free energies are nearly degenerate.

In the case of the B-to-A transition, the converted fraction does not exceed 50%, and seems to show a decrease at high excitation density beyond 9×10^{18} cm^{-3}. Furthermore, when a poly-4U3 crystal is kept at temperature point 4 (ca. 370 K) and is irradiated with a high photon density, say 1×10^{19} cm^{-3}, it does not return to the A phase when the crystal is cooled down to low temperatures, e.g., 77 K. By contrast, the residue of the B phase, after photoexcitation at temperature point 4, goes back fully to the A phase at low temperatures as long as the excitation photon density is kept below 7×10^{18} cm^{-3}. Previously, we have reported that an irreversible (permanent) A-to-B phase change occurs by photoexcitation with a density of ca. 1×10^{20} cm^{-3} in polycrystalline thin films of poly-4U2 (or so-called ETCD) [12]. In poly-4U2 films, such a strong excitation gives rise to a disorder in the hydrogen bonds running parallel to the polymer backbone and the photoinjected B phase cannot go back to the A phase even if the sample is cooled down to liquid-nitrogen temperature. The presently observed irreversible change caused by overirradiation is likely to arise from a similar photoinduced interruption of hydrogen bonds in the sidegroups.

The origin of the relatively low conversion efficiency (ca. 50%) for the B-to-A transition is not fully clear at present. It is probable, however, that upon photoexcitation above 3 eV (see also Fig. 4) the B-to-A and backward A-to-B phase conversions are in fast equilibrium during the photoexcitation process (ca. 20 nsec in duration). To test this hypothesis, pump and probe experiments with picosecond resolution are necessary.

In the interpretation of the photoinduced change, heating effects by laser irradiation must be carefully checked in pump and probe spectroscopy like the present study. In the case of PDAs, the photoinduced heating effect, if any, induces the A-to-B transition. The observed photoinduced B-to-A transition, as shown in panel 4 of Fig. 1, is just opposite to this, indicating that it has nothing to do with a simple heating effect. From the following experimental results, both the A-to-B and B-to-A phase changes by photoexcitation can be attributed to genuine photoelectronic processes (i.e., the photon mode).

In Fig. 4, we show the phase conversion fraction as a function of the exciting photon energy for both the A-to-B (top) and B-to-A (bottom) phase changes. The photoexcitation was performed in similar experimental conditions as for the observation of the photoinduced spectra. In this experiment, a *single-shot* laser pulse with a duration of about 20 nsec was used, and the laser power was adjusted so that the absorbed photon density in the crystal remained constant at ca. 6.5×10^{18} cm^{-3}, which is most efficient for both transitions, as seen in Fig. 3. There are several notable features in this plot. First, the excitation spectra for the converted fraction show a threshold which is located 0.3–0.5 eV higher than the exciton absorption peak for both the A-to-B and B-to-A

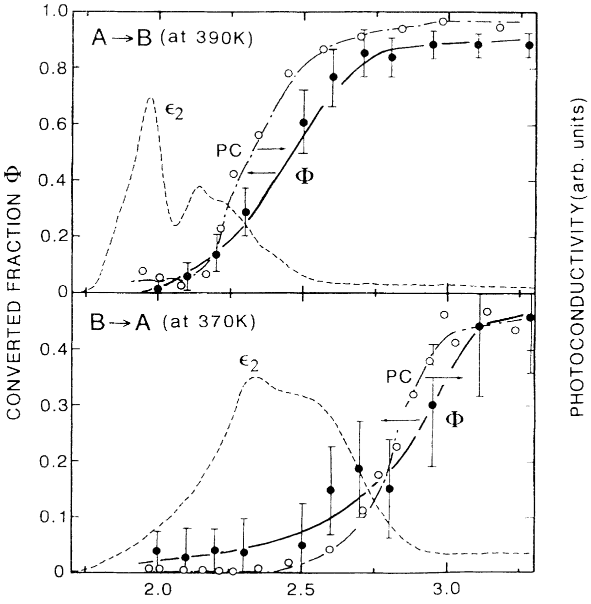

FIG. 4. Dependence of the converted fraction (Φ) (see the left ordinate) on the exciting photon energy (closed circles) for the photoinduced A-to-B (upper part) and B-to-A (lower part) phase transitions. Absorbed excitation photon density was kept constant at ca. 7×10^{18} cm^{-3}, for varying photon energy. Open circles and dashed lines show the action spectra of photoconductivity (PC) (see the right ordinate) and exciton absorption spectra (ϵ_2 spectra) in the respective phases.

phase changes. Note that the efficiences are very low near the exciton absorption peak where excitation light is strongly absorbed. Furthermore, the *A*-to-*B* conversion efficiency was observed to remain nearly zero in the case of 2.0-eV excitation (near the peak of ϵ_2 in the *A* phase), even when the intensity of photoexcitation was increased up to 20 times (i.e., ca. 1.3×10^{20} cm^{-3}). This is utterly in contradiction to the situation expected for the laser-heating effect (a thermal mode). In Fig. 4, we also plot the photocurrent action spectra which were measured on the single crystals of poly-4U3 at the same temperatures as for the measurements of the photoinduced phase changes. The thresholds of action spectra are supposed to correspond to the onset of the band-to-band transition. They are located at energies 0.4–0.5 eV higher than the exciton transition in both the *A* and *B* phases of poly-4U3. The similarity between the excitation spectra for photoconversion and the photoconductivity spectra obviously indicates that the photogenerated charge carriers, not excitons, are necessary for the photoinduced phase transitions to take place. Photocarriers in PDAs are supposed to form electron(hole)-phonon bound states, so-called polarons or bipolarons. Therefore, we speculate that photogenerated polaronic species play an important role in the transient formation of domain walls separating the *A* and *B* phase regions in the polymer backbones. The situation may be somewhat analogous to the bipolaron state in conjugated polymers with two nondegenerate ground states [13]. According to preliminary time-resolved measurements, the photoinduced phase transition is completed within the duration (20 nsec) of the exciting laser pulse. In the initial process of the transition, some cooperative interaction seems to take place between the photogenerated polaronic species, leading to an evolution of local distortions into a macroscopic phase change. It will be interesting to elucidate the details of the dynamics of the first-order phase transition after photoexcitation.

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[a] Present address: Photo-dynamics Research Center, RIKEN, 138-5 Minami-Yoshinari, Aoba-ku, Sendai 989-32, Japan.

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