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Photochromism and photoinduced bond-structure change in the conjugated polymer polydiacetylene

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The photoinduced change in absorption spectra has been measured on PDA-(12,8) (polydiacetylene) films for various photon energies and light intensities. The observed photochromic behaviors indicate that photoexcited electron-hole pairs in polymer backbone chains relax into a metastable state which develops into clusters with a local change in bond structure via a temperature-independent and self-activated multiple excitation process produced by light irradiation.

In the presence of a strong electron-lattice interaction, photoexcitation in solids often leads to a temporary or permanent change in local structures. Such a defect formation by light in conjugated organic polymers has been attracting considerable interest in relation to lower-lying excitations, such as solitons, polarons, or bipolarons, in a quasi-one-dimensional Peierls-Hubbard system. In this Rapid Communication, we report on the photoinduced structure change in polydiacetylene as studied by characteristic photochromic properties.

Polydiacetylenes (PDA's) are conjugated polymers obtained from solid-state polymerization of various diacetylene monomers $R_1C\equiv C-C\equiv CR_2$, $R_{1,2}$ being substitutional side groups.[1] In these PDA's, a characteristic phase transition is often observed between two spectroscopically different forms.[2,3] In our previous studies,[4-8] these two forms have been designated as the *A* and *B* forms, so we shall refer to this transition as the *A*-*B* transition in this paper. This transition is characterized by a prominent color change, between the blue *A* form and the red *B* form when viewed by absorption in films or solutions, or between the golden *A* form and the greenish *B* form by reflection in single crystals. From a remarkable change in Raman spectra due to polymer backbone vibrations at the *A*-*B* transition,[1,7] it is evident that this phase transition is associated with a structure change in conjugated backbone chains. It has been suggested that the *A*-*B* transition takes place between two isomeric forms of PDA, i.e., the acetylenic $[\!\!+\! RC-C\equiv C-CR \!+\!\!]$ and butatrienic $[\!\!+\! RC=C=C=CR \!+\!\!]$ bond structures, from an x-ray study on PDA single crystals.[9] However, a recent x-ray study[10] has cast a doubt on this interpretation. In any case, this unique phenomenon is believed to be directly related to the dynamics of photoexcited states in the electron-lattice system in PDA's. The present study provides some new experimental findings on this challenging subject.

Samples used in measurements are vacuum-deposited films of PDA-(12,8) with $R_1=(CH_2)_{11}CH_3$ and $R_2=(CH_2)_8\,COOH$. Polycrystalline powders of the monomer were vacuum deposited on glass substrates to a thickness of about 0.2 μm by a procedure described before.[5] Colorless monomer films were polymerized in vacuum by uv light from a high-pressure Hg lamp. Polymerized films are composed of randomly oriented microcrystalline grains of about 0.1-μm diameter. Thermo- and photochromic changes of absorption spectra were measured on the initially blue *A*-form films. Thermochromic spectra were measured by annealing these blue films in vacuum at various temperatures as reported before.[5] In the measurements of photochromism, a light pulse of about 10-ns duration from an excimer-laser-driven dye laser was focused upon a spot of about 1-mm diameter on films. The intensity of the laser pulse was varied by a suitable combination of filters. After an irradiation by a single shot pulse, absorption spectra were measured on a fine spot of about 0.3-mm diameter carefully located at the center of irradiated spot.

A comparison of thermo- and photochromic spectra of PDA-(12,8) film is shown in Fig. 1. Photochromic spectra shown in Fig. 1(b) were obtained for the 440-nm light irradiation, for an example. Absorption spectra in the original blue *A*-form films consist of the main peak A and its vibrational side peak A′. This blue *A* phase is eventually converted to the red *B* phase which is characterized by absorption peaks B and *B*′ as shown in Fig. 1. The spectral changes in the *A*-to-*B* conversion are very similar in the thermochromic and photochromic processes. In the thermal process, the *A*-*B* transition is promoted when the annealing temperature exceeds about 340 K. After the conversion, the red *B*-form films remain quite stable against temperature change, being unable to be converted back to the blue *A* form by cooling. Likewise, an irreversible *A*-*B* transition is caused by light irradiation. The conversion efficiency for a single shot pulse irradiation is dependent on both photon energy and light intensity. The *A*-to-*B* conversion ratio is considered to be nearly unity in both thermo- and photochromic processes, from the presence of an isosbestic point.[5] The photochromic change is almost independent of temperature in a range from 300 K down to 77 K, indicating that the observed photochromism is predominantly due to a photon mode, that is, a process via a certain electronic excited state without much influence of local heating by irradiation.

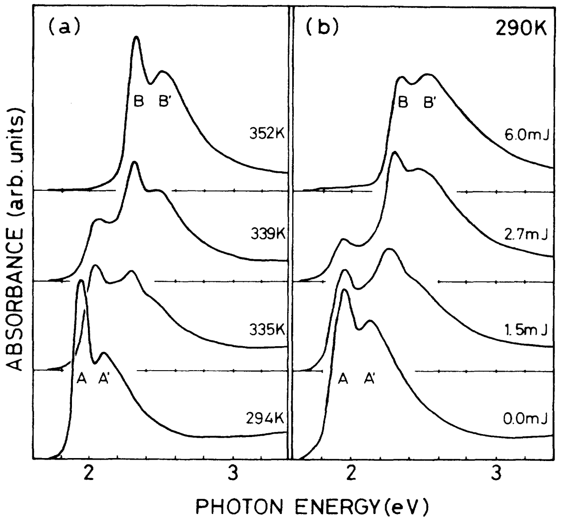

FIG. 1. (a) Thermochromic and (b) photochromic spectra of PDA-(12,8) films, both observed at room temperature. The light irradiation in (b) was made at 440 nm.

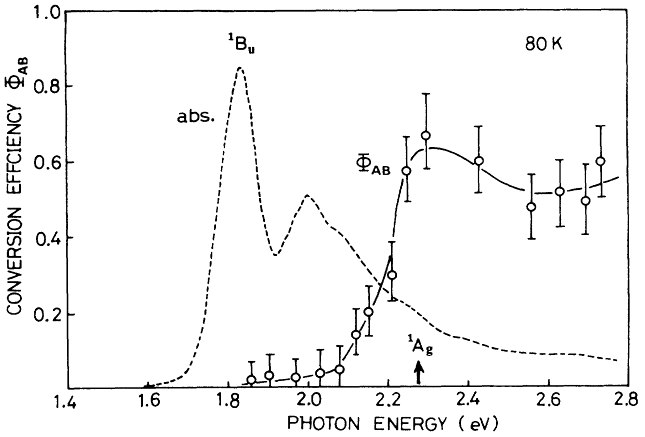

FIG. 2. Photochromic A-B conversion efficiency ϕ_{AB} of PDA-(12,8) film at 80 K plotted against photon energy. The absorption spectrum in the A form is also shown by dashed line for comparison. The arrow indicates the ^1A_g exciton energy (see text).

The A-B transition as studied in visible absorption spectra is also accompanied by a significant change in Raman bands associated with stretching vibrations in conjugated backbone chains.[1] In the present PDA-(12,8) film, the Raman bands observed around 1450 and 2070 cm^{-1} in the A form are shifted to about 1510 and 2120 cm^{-1}, respectively, after the A-to-B conversion. These results confirm an interpretation that the thermo- and photochromic behaviors in these PDA films are ascribed to a change in the bond structure in conjugated polymer backbone chains.

To get further detailed information on the underlying electronic process, we have measured the photoinduced A-to-B conversion efficiency ϕ_{AB} as a function of photon energy and light intensity. In order to avoid a local heating by irradiation, all measurements were made at about 80 K. Values for ϕ_{AB} have been estimated from relative decrements of absorption at the A peak, since the A-to-B conversion ratio is nearly unity over a wide range of photon energy and light intensity as described before.

An example of photon energy dependence of ϕ_{AB} is shown in Fig. 2 for the light intensity of about 60 $\mathrm{mJ/cm}^2$, together with the absorption spectrum in the A form (dashed line) for comparison. A notable feature in the ϕ_{AB} spectrum shown in Fig. 2 is that it is utterly different in shape from the absorption spectrum. The main peak A (or B in the B form) in the absorption spectrum is assigned to the lowest ^1B_u exciton, which is located at about 1.9 and 2.3 eV in the A and B form, respectively. Although absorption coefficients are very large, about $10^6 \mathrm{cm}^{-1}$ at the maximum, in this energy region the ϕ_{AB} values are considerably small there, and increase rather sharply at about 2.1 eV where the absorption coefficient decreases with photon energy. The ϕ_{AB} spectrum shows a broad maximum around 2.3 eV, which is followed by a plateau region above 2.5 eV. The conversion efficiency ranges between 0.6 to 0.5 above 2.3 eV for the light intensity of 60 $\mathrm{mJ/cm}^2$. The intensity dependence of ϕ_{AB} is described later.

It is worth noting that the maximum of ϕ_{AB} is located just at the energy where the second π-π^* exciton is observed in the A-form PDA's,[4,7] as indicated by an arrow in Fig. 2. This exciton has been assigned to the ^1A_g excited state which is forbidden in centrosymmetric conjugated polymers. It becomes observable in the electric-field-modulated reflection or absorption spectra through a mixing with the lowest ^1B_u exciton by the Stark effect. This particular excited state has a character of charge-transfer (CT) excitation in the conjugated π-electron system of backbone chains. In fact, an electron-hole (e-h) pair in this state is predicted to be separated from each other by several repeated units on a backbone chain. Hence, such a CT state is considered to play an important role in the photocarrier generation process in PDA's. In support of this prediction, photoconductivity action spectra in PDA's are known to start at around the ^1A_g exciton energy.[11,12] From these considerations, we argue that the coincidence between the maximum in the ϕ_{AB} spectrum and the ^1A_g exciton energy is not accidental but indicative of the fact that a photocarrier generation process via the ^1A_g exciton plays an essential role in the photochromism in PDA's. Although the ^1A_g exciton is forbidden in perfectly centrosymmetric polymers, it may be allowed, though weakly, by the effects of nonsymmetric substitutional side groups ($R_1 \neq R_2$) in PDA-(12,8), or possible disorder in films or a participation of symmetry-breaking vibrations.

Another important feature of photochromic properties in PDA-(12,8) film is a remarkable nonlinear dependence of ϕ_{AB} upon light intensity. A typical example is shown in Fig. 3 for irradiation at 2.5 eV which falls on the plateau region of ϕ_{AB} spectrum. The nonlinear rise of ϕ_{AB} with light intensity implies that the 1:1 A-to-B conversion is not promoted by independent photoexcitations but is promoted through a certain cooperative multiple excitation process. Experimental points (open circles) are well fitted to

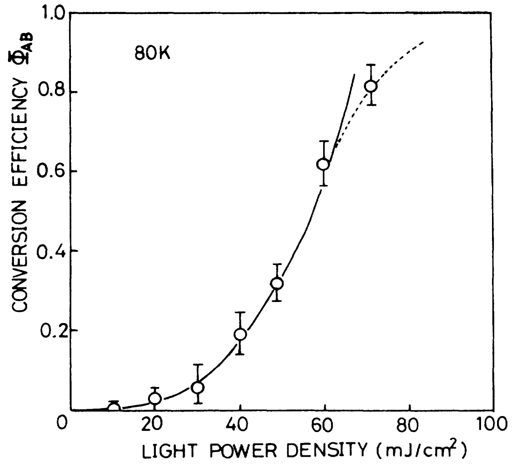

FIG. 3. Photochromic *A*-*B* conversion efficiency ϕ_{AB} of PDA-(12,8) film at 80 K plotted against light intensity I. The solid line represents a I^3 dependence of ϕ_{AB}.

a cubic dependence on light intensity I ($\phi_{AB} \propto I^3$) as shown by solid line in Fig. 3.

The nonlinearity observed in the photochromism cannot be attributed to an ordinary nonlinear optical absorption process. This conclusion is based on the following observations: The laser beam was divided by a beam splitter into two beams having nearly equal intensities. When the intensity of these beams is lower than, say, about 30 mJ/cm^2, the *A*-to-*B* conversion efficiency is rather small when irradiated by a single beam. But if irradiation is made by two simultaneous pulses with no delay time between them, a fairly large ϕ_{AB} value is attainable because of the strong nonlinearity. Then, the delay time Δt between two separated light pulses is varied. If an ordinary nonlinear optical absorption is predominant, the ϕ_{AB} value would drop sharply when Δt is made larger than the pulse width of about 10 ns. On the contrary, the observed ϕ_{AB} value for $\Delta t = 30$ ns was found to be almost equal to that for $\Delta t = 0$, excluding a possibility of nonlinear optical-absorption process. Thus, we have been led to a conclusion that the observed nonlinearity is predominantly due to a successive and cooperative multiple excitation process where some long-lived metastable excited state is involved. By means of similar double-beam-irradiation measurements with varying Δt over a wider range, the lifetime of this metastable state may be estimated. From a preliminary result of such measurements, it seems that the lifetime is not longer than 10 ms.

Now, based on experimental results presented above, we discuss a possible mechanism of the *A*-*B* transition in PDA's. From experimental results shown in Fig. 2, the formation of nearly free *e*-*h* pairs is supposed to be the first step in the photochromism. Because of a strong electron-lattice interaction, these *e*-*h* pairs will be promptly relaxed to a locally deformed state which is in favor of a bond-structure change into the *B* form. However, such a local state is not stable enough to develop by itself into a persistent *B*-converted region around it, when it is left isolated in the surrounding *A*-form region. For this initially excited species to develop into a stable *B*-form cluster, successive excitations must occur in the neighborhood of the deformed region within its finite lifetime. Otherwise, the metastable excited state returns back to the original *A*-form structure. This will explain small ϕ_{AB} values at low-light intensities and the nonlinear behavior as observed. The cubic dependence of ϕ_{AB} upon light intensity indicates that three *e*-*h* pairs are involved in an average to stabilize a *B*-converted cluster region. A recent theoretical study on photoinduced structural change in PDA's by Hanamura and Nagaosa[13] may be relevant to this interpretation. Once these stable cluster regions are formed, the optical *A*-to-*B* conversion process can proceed very fast, with a response time shorter than the resolution limit of about 30 ns in the present study. Furthermore, from a temperature-independent photochromic change as mentioned before, the photoinduced *A*-*B* transition is supposed to proceed without the help of a thermally activated process. These specific features in the photochromism of PDA's, namely, a very fast response supported by a self-activated lattice-relaxation process, are quite unique amongst a number of dynamical relaxation processes of photoexcited state in solids.

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