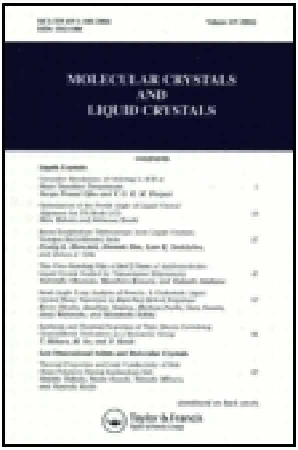

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Reversibly Photo-Induced Phase Transition in Single Crystals of Polydiacititlenes

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REVERSIBLY PHOTO-INDUCED PHASE TRANSITION IN SINGLE CRYSTALS OF POLYDIACETYLENES

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Abstract We have observed novel photo-induced phenomena in conjugated polymers; the reversibly photo-induced phase transitions in single crystals of poly-diacetylene(PDA). Dependence of the phase conversion efficiency on excitation photon energy shows that the photo-generation of charge-carriers (polarons), not excitons, is responsible for the macroscopic phase change.

INTRODUCTION

Polydiacetylenes (PDAs) are the π-electron conjugated polymers obtained from diacetylene monomers $R-C{\equiv}C-C{\equiv}C-R'$ (R,R'; substitutional side-groups) by solid state polymerization[1]. The one-dimensional conjugated backbones coupled with side groups are responsible for their unique characters such as a drastic color change by various stimulations and their large nonlinear optical susceptibilities. The PDAs invesitigated here possess alkyl-urethane side groups ($R=R'=(CH_2)_4OCONH(CH_2)_{n-1}CH_3$), and hydrogen bonds between side groups maintain the planarity of carbon backbone as shown in Fig. 1. (Hereafter the family of the alkyl-urethane substituted PDA is abbreviated as poly-4Un.) The thermally-induced first order phase transition between the A-phase (low temperature phase) and the B-phase (high temperature phase) occurs in poly-4Un single crystal[2]. This phase transition is accompanied with a conspicuous color change. In the followings, we focus on the case of poly-4U3 as a typical example.

In the A-phase, the poly-4U3 crystal shows a strong optical transition due to the ^1B_u exciton at 1.95 eV (peak A in Fig. 2) which is strongly polarized along the polymer chain axis. This exciton absorption band shifts to ca. 2.4 eV abruptly upon the A-to-B transition at 408K (see Fig. 2). The crystal in the B-phase goes back to the A-phase accompanying a shift of the exciton band back to 1.95 eV when it is cooled down to 300K as shown in Fig. 2. The phase transition is thus reversible, as far as the crystal is not over-heated beyond 500 K.

The observed change in the π-electronic structure upon the A-B transition seems to originate from a change of the polymer backbone structures. This bond structural change is reflected in the temperature dependence of Raman spectra (see the right part of Fig.2). The Raman bands of C=C and C≡C stretching modes position at considerably higher frequencies in the B-phase than in the A-phase. Therefore, both electronic and Raman spectra can be used as sensitive probes for the A-B transition. Here, we present experimental evidences for the occurence of the bidirectional (both A-to-B and B-to-A) photo-induced phase transitions in poly-4U3 single crystals using the above-mentioned two kinds of spectroscopic probes.

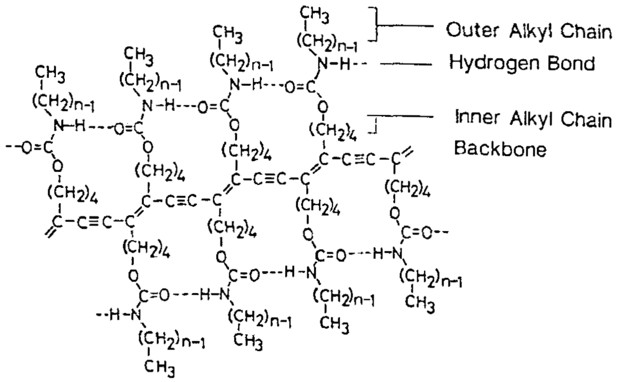

Figure 1: Structure of poly-4Un. Dashed lines show hydrogen bonds between side groups.

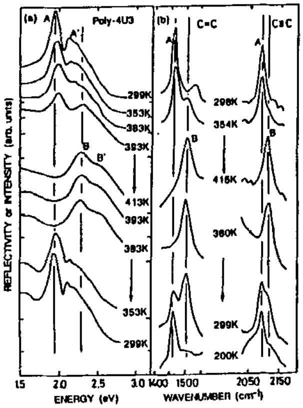

Figure 2: Temperature dependences of (a) reflectance and (b) Raman spectra of poly-4U3 single crystal for the light polarized parallel to the polymer backbone.

PHOTO-INDUCED CHANGES IN REFLECTANCE AND RAMAN SPECTRA

We have previously shown[2] that single crystals of all poly-4Un series (n=1-10) exhibit the temperature-induced reversible phase transition between the A- and B-phases. This transition is accompanied by a thermal hysteresis (∼ca.60K). We plotted in Fig. 3 a change in the reflectivity of a poly-4U3 single crystal monitored at the peak A (1.95eV) during the thermal cycle, 1→2→3→4→5. From a thermodynamical point of view, the free energy for this crystal is represented by a curve with double potential minima corresponding to the A- and B-phases, which are separated by a potential barrier. The relative stability for the two minima is interchanged at a certain temperature somewhere in the temperature region showing the hysteresis. A schematic free energy curves at respective temperatures (1,2,3,4 and 5) are also shown in Fig. 3.

The ε_2 (imaginary part of complex dielectric constant) and Raman spectra observed at various steps (1→2→3→4→5) in the thermal cycle along the hysteresis loop are plotted in Fig.4. The ε_2 spectra were obtained by Kramers-Kronig analysis of polarized reflectance spectra for the crystal. In the course of this thermal cycle, the temperature was kept at the point 2 and the sample was irradiated with a single shot of pulse from a dye-laser (20 ns duration) which was pumped by a XeCl excimer laser. The excitation photon energy was chosen at 2.81 eV for the reason as mentioned later. The electronic absorption (ε_2)

and Raman spectra after the photo-excitation are shown by dashed curves in the second top (labeled 2) in Fig.4. The results clearly show almost full conversion of the A-phase into the B-phase. Similarly, the sample kept at the point 4 in the cooling cycle was excited by a single shot pulse, whose photon energy was set at 3.18 eV in this case. The ε_2 and Raman spectra after the photo-excitation are shown by dashed curves in the second bottom, labeled 4, in Fig.4. The results show that more than 50% of the B-phase is converted into the A-phase. The excitation photon density in the both cases was $7\mathrm{x}10^{18}\mathrm{cm}^{-3}$.

It is worth noting that the fraction of the phase change is considerably high even for the 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 $7\mathrm{x}10^{18}$ cm^{-3}, a value corresponding to the absorption of one photon in a fraction of the polymer crystal composed of about 140 repeated $[+RC-C\equiv C-CR+]$ units (one repeated unit occupies a volume of about 1100 $\mathrm{\mathring{A}}^3$ in crystal).

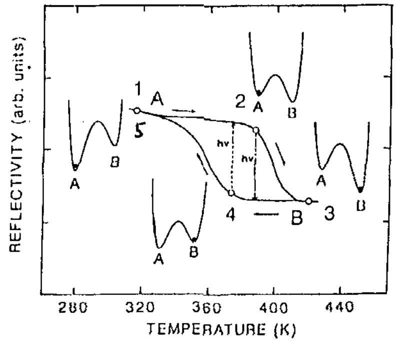

Figure 3: Temperature dependence of reflectivity in poly-4U3 crystal at 1.95 eV (left hand side), and schematic diagrams of free energy with the minima corresponding to the A- and B-phases. The temperature points at which the reflectance and Raman spectra were measured are denoted by open-circles and numbered in the order of heating and cooling process. At the points 2 and 4, the crystal surface was irradiated with a single shot of laser pulse, and the photo-induced effect on the electronic absorption and Raman spectra were measured (see the spectra at the points 2 and 4 in Fig.4).

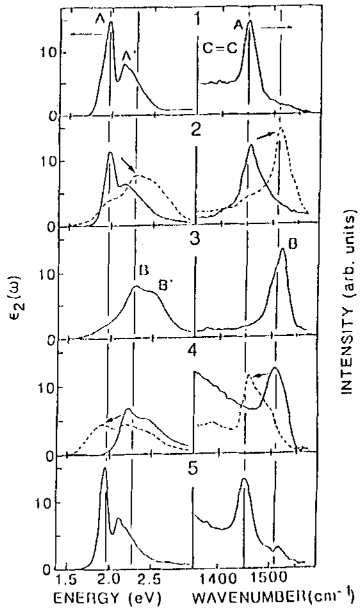

Figure 4: Spectra of imaginary part of dielectric constant (ϵ_2) for the exciton absorption (left part) and Raman spectra of the C=C stretching mode (right part) at various temperatures. The temperature points labeled 1-5, are indicated on the hysteresis loop shown in Fig.3. Dashed lines in the spectra at temperature points 2 and 4 show those observed after photo-excitation by a single shot of a pulsed dye-laser (see text).

Such an extremely high efficiency of photo-conversion is indicating a collective nature of the phase transition between the two phases when their free energies are nearly degenerate.

EXCITATION SPECTRUM OF PHOTO-CONVERSION EFFICIENCY

In Fig.5, we show the phase conversion fraction as a function of the exciting photon energy both for the A-to-B (a) and B-to-A (b) phase changes. In this experiment, a single shot laser pulse with the duration of about 20ns was used, and the laser power was adjusted so as the absorbed photon density in the crystal was kept constant, ca. $6.5x10^{18}cm^{-3}$.

There are two notable features seen in this plot. First, the excitation spectra for the converted fraction show a threshold which is located 0.3-0.5eV higher than the exciton absorption peak for both the A-to-B and B-to-A phase changes. The efficiencies are very low near the exciton absorption peak where excitation light is strongly absorbed. This is in contradiction to the situation expected for the phase change caused by the laser-heating effect. The second notable point is the similarity between the excitation spectra for photo-conversion and the photoconductivity (see Fig.5). The obtained results obviously indicate that the photo-generated charge carriers, not excitons, are necessary for the photo-induced phase transitions to take place. Photo-carriers in PDAs are supposed to form electron(hole)-phonon coupled states, i.e. so-called polarons or bi-polarons. We speculate that photo-generated polaronic species are playing an important role in the transient formation of microscopic domain-walls separating the A- and B-phase regions in the polymer backbones.

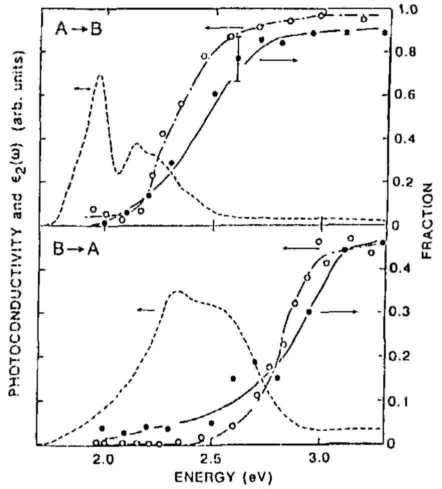

Figure 5: Dependence of the converted fraction (Φ) on the excitation photon energy (closed circles) for the photo-induced A-to-B (upper part) and B-to-A (down part) phase transitions. Absorbed excitation photon density was kept constant ($\sim$ca. 7x10^{18} cm^{-3}), in varying photon energy. Open circles and dashed lines show the action spectra of photoconductivity (PC) and electronic absorption spectra (ϵ_2 spectra), respectively, in the A-(upper) and B-phases(lower).

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