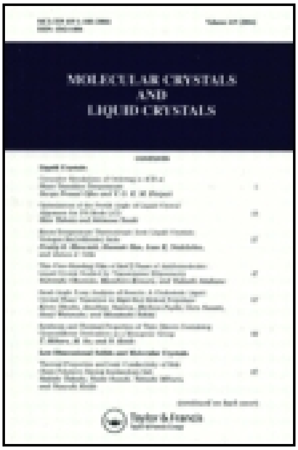

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Ultrafast Response of Polymers with Large Optical Nonlinearity

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ULTRAFAST RESPONSE OF POLYMERS WITH LARGE OPTICAL NONLINEARITY

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Abstract Ultrafast optical response in polydiacetylenes and polythiophense was investigated by femtosecond time–resolved absorption spectroscopy. Several nonlinear optical processes, i.e. hole burning, Raman gain, and induced–frequency shift, were observed and the third–order nonlinear susceptibilities were determined. The ultrafast relaxation dynamics following after the photoexcitation was investigated and the formation and relaxation of self–trapped exciton was observed. A model of the relaxation processes of excitons in conjugated polymers is proposed. The short life of STE and difference between fluorescent and nonfluorescent polymers are explained.

INTRODUCTION

The large and ultrafast optical nonlinearities of conjugated polymers and their role as model compounds for quasi–one dimensional semiconductors have attracted great interest. Polydiacetylenes (PDAs) and polythiophenes (PTs) belong to the rather well studied conjugated polymers. Their properties can be modified by changing the side–groups. Several PDA films and crystals have blue–phase and red–phase according to the color [1]. Blue–phase PDAs have an absorption peak due to excitons near 2.0 eV and emit no fluorescence. The absorption peak in red–phase PDAs and PTs appears around 2.4 eV. Red–phase PDAs and PTs emit weak fluorescence. Both blue– and red–phase PDAs have ultrafast relaxation processes with time constant of a few picoseconds [2–5].

In the present study time evolutions in blue– and red–phases PDAs and PTs were investigated by femtosecond absorption spectros–

copy. The relaxation kinetics and fluorescent properties are well explained by using the potential curve of the ground state, free exciton, and self-trapped exciton in configuration space.

EXPERIMENTAL RESULTS

Blue-Phase PDA-4BCMU

Figure 1 shows the transient absorbance change (ΔA) of a blue-phase oriented film of PDA-4BCMU (butoxycarbonylmethylurethane) prepared by vacuum deposition. Both the polarizations of the pump and probe pulsed light are parallel to the oriented polymer chain. At 0 ps delay a bleaching peak appears at the pump photon energy of 1.98 eV. Then the bleaching peak shifts to 1.96 eV. The bleaching peaks at 1.98 eV and 1.96 eV are due to coherent interaction between the pump and probe pulses and saturation of the excitonic absorption, respectively. When the pump and probe pulses overlap in time at the sample, two small minima are observed at 1.80 and 1.72 eV. They are assigned to Raman gain of stretching vibrations of the C=C bond and C≡C bond, respectively. The imaginary parts of

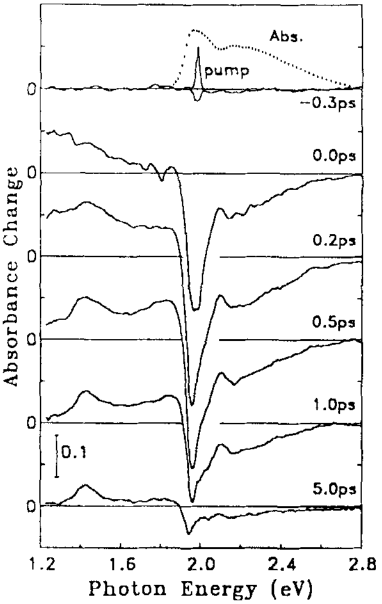

FIGURE 1 Transient absorption spectra of blue-phase PDA-4BCMU film at 290 K.

the third-order susceptibilities are estimated as $\mathrm{Im}[\chi^{(3)}_{1111}(-\omega_1;\omega_1,\omega_1,-\omega_1)]=-3.2\times10^{-9}$ esu for $\hbar\omega_1=1.98$ eV and $\mathrm{Im}[\chi^{(3)}_{1111}(-\omega_2;\omega_2,\omega_1,-\omega_1)]=-4.8\times10^{-10}$ esu for Raman gain at $\hbar\omega_1=1.98$ eV and $\hbar\omega_2=1.80$ eV [5].

After the photoexcitation the bleaching due to the absorption saturation and broad absorption below 1.9 eV are observed. At 0.0 ps a peak of ΔA is lower than 1.4 eV, while ΔA peak at 0.5 ps appears at 1.8 eV. The absorption below 1.9 eV is assigned to the transitions from the lowest singlet excitons to the conduction band and/or other higher excited states. The spectral change is explained by the geometrical relaxation of free excitons to self-trapped excitons (STEs). The formation time of the STEs is obtained as 140±40 fs. The ΔA due to STEs decays exponentially with time constant of 1.6± 0.1 ps at 290 K. The ΔA peak at 1.4 eV observed after 1.0 ps is due to triplet excitons and the lifetime is much longer than 100 ps.

Red-Phase PDA-4BCMU

Figure 2 shows the ΔA spectra in a red-phase cast film of PDA-4BCMU excited by 3.94-eV pump pulse. The saturation of the excitonic absorption and the broad absorption below 2.2 eV due to STEs are observed. The ΔA spectra excited by 1.97-eV pulse have an asymmetric oscillatory structure near 1.97 eV [5]. The oscillatory structure was observed in semiconductors and was explained in terms of perturbed free induction decay [6]. However, it is not the case in the red-pahse PDA-4BCMU, because the frequency change of the oscillation predicted by the perturbe free induction decay [7] is not observed. The structure can be explained in terms of pump induced-frequency shift of probe light or in another word cross-phase modulation. The probe light has a peak at 1.97 eV. When the probe light shifts to higher energy induced by the pump pulse, the observed ΔA above 1.97 eV becomes negative and the ΔA below 1.97 eV becomes positive. The real part of the third-order susceptibility is estimated from the ΔA as $\mathrm{Re}[\chi^{(3)}_{1111}]=-1.9\times10^{-12}$ esu.

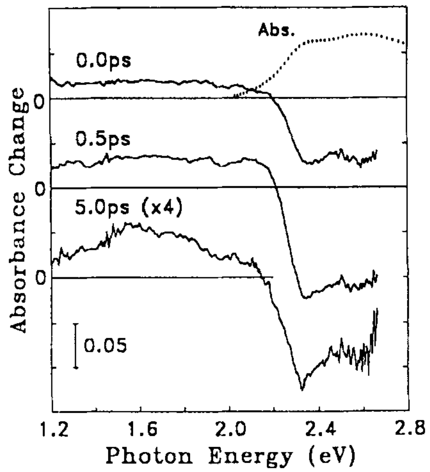

FIGURE 2 Transient absorption spectra of red-phase PDA-4BCMU film at 290 K excited by 3.94 eV pump pulse.

The formation time of STEs in the red-phase PDA-4BCMU is estimated from the spectral change around 2 eV as 120±60 fs. After this initial spectral change the ΔA in the red-phase PDA continues to change the spectra until about 5 ps. The time constant of the slow spectral change is obtained as 1.1±0.1 ps. The decay kinetics of STEs in the red-phase PDA-4BCMU cannot be fitted to a single-exponential function and the decay becomes slower at longer delay time. When the decay curve at 2.34 eV is empirically fitted to a biexponential function, the time constants of the short and long components are obtained as 660±70 fs and 4.4±0.4 ps.

Poly(3-dodecylthiophene)

The ΔA in poly(3-dodecylthiophene) has similar properties to the red-phase PDA-4BCMU. The bleaching due to absorption saturation and the broad absorption below 2 eV were observed. The decay kinetics of the ΔA can be fitted to the biexponential function and the time constants are obtained as 0.3±0.1 ps and 4.7±1.6 ps at 2.2 eV.

Relaxation Kinetics

The decay kinetics and fluorescence properties of red-phase PDAs are close to those of PTs and they are in good contrast to blue-phase PDAs. The formers are fluorescent and exciton decay is nonexponential, while the latters are nonfluorescent and show exponential decay of exciton.

The relaxation kinetics of the excitons in PDAs can be explained using a model shown in Fig. 3 [5]. The model corresponds to the relaxation in red-phase PDAs. Since the formation process of STE has no barrier in one-dimensional system, the photoexcited free excitons (FE (1)) are coupled with the C–C stretching modes within the phonon periods of 10–20 fs. However, the STEs have not relaxed to the bottom of the potential curve and the binding energy remains as the kinetic energy of the lattice vibration (unrelaxed STE (2)). The unrelaxed STEs emit the phonons which are strongly coupled to the excitonic transition and relax to unthermalized STEs (3). The observed spectral change with time constant of 100–150 fs is due to this phonon emission process. Then the energy of the vibrational modes of the unthermalized STEs are distributed among phonon modes of lower frequency and thermalize (thermalized STE (4)). The slow spectral change with time constant of 1.1 ps in the red-phase PDA-4BCMU corresponds to the thermalization process.

During the emission of the phonon which strongly coupled to the exciton transition and thermalization processes STEs relax to the ground state (G) by passing over the crossing point and/or tunneling through the barrier between the STE and ground-state potentials. The unrelaxed STEs can relax to the ground state

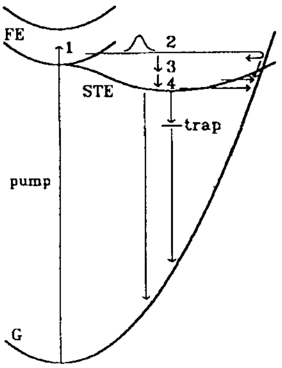

FIGURE 3 Models of the relaxation kinetics shown in adiabatic potential surfaces of excitons in red-phase PDA. FE(1): free exciton, STE: self-trapped exciton, 2: unrelaxed STE, 3: unthermalized STE, 4: thermalized STE, and G: ground state.

rapidly with time constant shorter than 1 ps. After the phonon emission and thermalization the STEs come down to the bottom of the potential and the loss rate due to the tunneling becomes smaller.

Since the exciton energy in blue–phase PDAs is smaller than that in red–phase PDAs, the crossing point between STEs and the ground state is expected to be lower than that in red–phase PDAs [8]. The decay time constant of STEs in blue–phase PDAs is 1.6 ps at 290 K. Therefore, the major part of the STEs relax to the ground state before thermalization and the decay kinetics can be fitted to a single–exponential function.

The difference of the decay kinetics between nonfluorescent blue–phase PDAs and fluorescent red–phase PDAs and PTs can be explained by the height of the crossing points between the ground state and STE in adiabatic potential. Red–phase PDAs and PTs have higher crossing point than blue–phase PDAs. The decay rate by tunneling is slower and the number of remaining STE is larger in red–phase PDAs. Therefore red–phase PDAs have weak fluorescence and blue–phase PDAs have no fluorescence. The decay kinetics observed in other PDAs and poly(3–alkylthiophenes) can be explained by the same relaxation model [2–5].

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