Molecular Crystals and Liquid Crystals Incorporating Nonlinear Optics

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl17

Femtosecond Spectroscopy of Polydiacetylene

Takayoshi Kobayashi [a] , Masayuki Yoshizawa [a] & Makoto Taiji [a]

[a] Department of Physics, Faculty of Science, University of Tokyo, Hongo 7-3-1, Bunkyo-ku, Tokyo, 113, Japan

Version of record first published: 04 Oct 2006.

To cite this article: Takayoshi Kobayashi , Masayuki Yoshizawa & Makoto Taiji (1990): Femtosecond Spectroscopy of Polydiacetylene, Molecular Crystals and Liquid Crystals Incorporating Nonlinear Optics, 183:1, 153-156

To link to this article: http://dx.doi.org/10.1080/15421409008047450

Mol. Cryst. Liq. Cryst., 1990, vol. 183, pp. 153–156
Reprints available directly from the publisher
Photocopying permitted by license only

Printed in the United States of America

FEMTOSECOND SPECTROSCOPY OF POLYDIACETYLENE

TAKAYOSHI KOBAYASHI, MASAYUKI YOSHIZAWA, and MAKOTO TAIJI
Department of Physics, Faculty of Science, University of Tokyo,
Hongo 7-3-1, Bunkyo-ku, Tokyo 113, Japan

Abstract Time evolution in polydiacetylene (PDA-3BCMU) was investigated by femtosecond spectroscopy. The relaxation of photoexcited free excitons to self-trapped excitons was observed. The broad-band absorption due to self-trapped excitons was observed below 1.86 eV. The formation and decay times of self-trapped excitons at 10 K were 150±50 fs and 2.0±0.1 ps, respectively. At short delay times several nonlinear optical processes, i.e. hole burning, Raman gain, and dynamic Stark shift, were observed.

INTRODUCTION

Polydiacetylenes (PDAs) belong to one of the most extensively studied conjugated polymers because of their large and fast optical nonlinearities, the phase transition with dramatic color change and their properties which can be modified by changing the side-groups[1]. The elementary excitations in PDA are excitons, polarons and bipolarons. Singlet and triplet excitons were observed by time-resolved reflection spectroscopy in PDA-pTS[2,3] and bipolaron was observed by infrared spectroscopy. The results of photoluminescence measurements have been reported that the decay time constants are several picoseconds in red-phase PDA[4], while no fluorescence has been observed in blue-phase PDAs.

In the present study, we investigated the relaxation dynamics of photoexcitations in a blue phase PDA film (PDA-3BCMU) by femtosecond time-resolved absorption spectroscopy.

EXPERIMENTAL

The output of a colliding-pulse mode-locked dye laser was amplified by a four-stage dye amplifier pumped by the second harmonic pulses of a Q-switched Nd:YAG laser. The amplified pulses were used as pump and probe

pulses of absorption spectroscopy[5]. The center wavelength and duration of the amplified pulses were 628 nm (1.97 eV) and 100 fs, respectively. The PDA-3BCMU (3-butoxycarbonylmethylurethane) film was prepared by casting condensed solution in chloroform on a glass substrate.

RESULTS AND DISCUSSION

The transient photoinduced absorption spectra of the PDA-3BCMU film observed at 10 K are shown in Fig. 1. The polarizations of the pump and probe pulses are parallel to each other. At the delay times between -0.1 ps and 0.1 ps, i.e. the pump and probe pulses temporally overlap each other at the sample, the sharp bleaching peak at 1.97 eV and the two small minima at 1.79 and 1.71 eV are observed.

The sharp bleaching peak at 1.97 eV is considered to be mainly due to a hole burning, but it has an asymmetric shape. The asymmetry can be explained in terms of the optical Stark effect. Since the pump photon energy in the present study is slightly higher than the absorption peak of the excitons, the transition energy shifts to lower energy and the absorbance change has a maximum at 1.95 eV just below the pump photon energy. The small two minima at 1.79 and 1.71 eV can be explained in terms of Raman gain. The corresponding Raman shifts are 1450 and 2100 cm^{-1}, which are assigned to the stretching vibrations of C=C bond

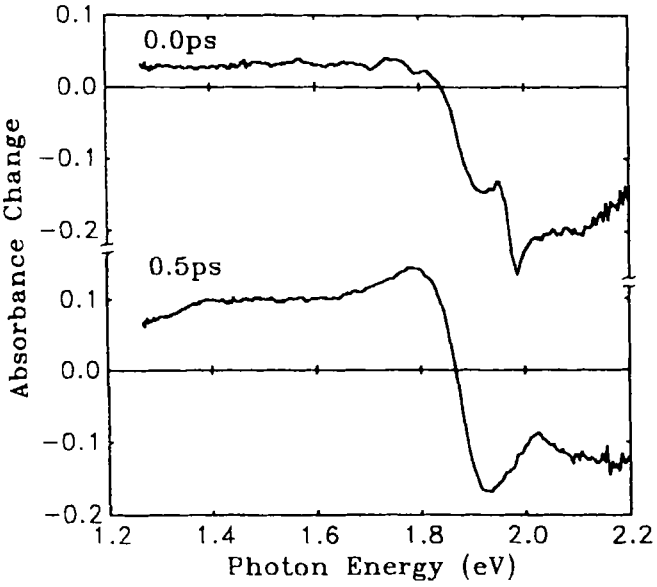

FIGURE 1. Transient absorption spectra of PDA-3BCMU at 10 K at delay times of 0.0 and 0.5 ps.

and C≡C bond, respectively. The optical Stark effect mediated by same phonon modes was also observed in PDA-pTS[6].

The photoinduced bleaching around 1.92 eV is due to the absorption saturation of the ^1B_u excitons. The photoinduced absorption below 1.85 eV is not observed at -0.2 ps and appears more slowly than the bleaching. At 0.0 ps the absorbance is very broad and featureless in the whole spectral region between 1.3 and 1.8 eV except two small minima at 1.79 and 1.71 eV, while it has a maximum at 1.80 eV and drops below 1.35 eV at delay times longer than 0.5 ps. It suggests that the photoinduced absorption shifts to higher energy with time from 0.0 ps to 0.5 ps. The photoinduced absorption is assigned to the self-trapped excitons formed from the photoexcited free ^1B_u excitons. The free excitons relax to the self-trapped excitons and the transitions from the excitons to the conduction band shift to higher energy.

Figure 2 shows the time dependence of the absorbance change in PDA-3BCMU at 1.77 eV. The lifetime of the self-trapped excitons is estimated to be 2.0±0.1 ps. The formation time of the self-trapped excitons can be estimated by the convolution of the pump and probe pulses with several formation times comparing with the rise of the absorbance change at 1.77 eV. The calculated absorbance changes are plotted in Fig. 2. The formation time is estimated to be 150±50 fs. At 290 K, the formation and decay times of the self-trapped excitons are determined to be 150±50 fs and 1.5±0.1 ps, respectively.

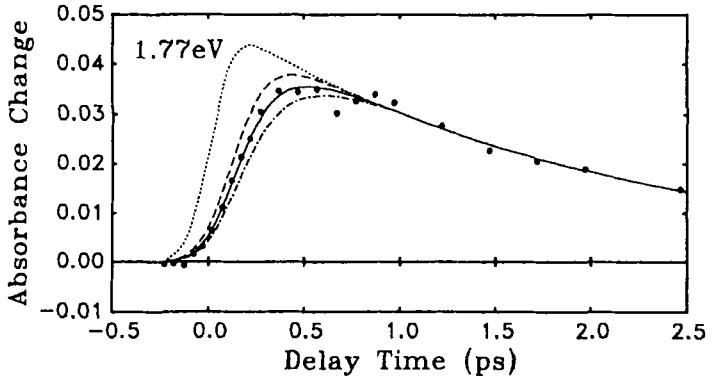

FIGURE 2. The time dependence of the absorbance change of PDA-3BCMU at 1.77 eV. Curves are the calculated absorbance changes with the formation times of 0 fs (dotted curve), 100 fs (dashed curve), 150 fs (solid curve), and 200 fs (dash-dotted curve). The decay time is set at 2.0 ps in the calculation, using the pulse shape of $sech^2$ with 150 fs half-width for both pump and probe pulses.

Since the formation process of self-trapped excitons has no barrier in the one-dimensional system, the formation process is expected to take place within the coupled phonon cycle. The excitons are strongly coupled with the C-C stretching modes and the frequencies are 1500-2100 cm^{-1} and correspond to the oscillation periods of 15-25 fs. While the trapping time constant of excitons is 150 fs and much longer than the phonon periods. It can be explained as follows. The binding energy remains as the kinetic energy of the lattice oscillation and the formation time of the self-trapped excitons is determined by the energy redistribution rate from the strongly coupled phonon to the other phonon modes.

When the second harmonic (3.94 eV) of the amplified femtosecond pulse is used as the pump pulse, the absorbance change around 1.5 eV has a long-life component. The long-life component is due to the triplet-excitons which was observed by the nanosecond spectroscopy by our group. The similar long-life component is induced by the 1.97-eV pump pulse with the photon density larger than $5x10^{15}$ photons/cm^2. It is due to the triplet excitons created by the two-photon absorption.

In conclusion, the time-resolved photoinduced absorption spectrum of PDA-3BCMU has been studied by the femtosecond absorption spectroscopy. The spectral change due to several nonlinear optical processes, i.e. hole burning, Raman gain, and optical Stark effect, were observed. The formation and decay times of the self-trapped excitons were determined. The spectral change due to triplet excitons excited by the second harmonic pulse and the two-photon absorption of the fundamental of the CPM laser was observed.

REFERENCES

1. See, e.g., Polydiacetylenes, edited by D. Bloor and R. R. Chance, (Martinus Nijhoff Publishers, Dordrecht, Netherlands, 1985).
2. B. I. Greene, J. Orenstein, R. R. Millard, and L. R. Williams, Chem. Phys. Lett., 139, 381 (1987).
3. T. Kobayashi and H. Ikeda, Chem. Phys. Lett., 133, 54 (1987).
4. D. Bloor, S. D. D. V. Rughooputhm, D. Phillips, W. Hays, and K. S. Wong, in Electronic properties of polymers and related compounds, edited by H. Kuzmany, M. Mehring, and S. Roth, (Springer-Verlag, Berlin, 1985) p.253.
5. M. Yoshizawa, M. Taiji, and T. Kobayashi, IEEE J. Quantum Electron, QE-25(12), (1989) in press.
6. G. J. Blanchard, J. P. Heritage, A. C. Von Lehman, M. K. Kelly, G. L. Baker, and S. Etemad, Phys. Rev. Lett., 63, 887 (1989).