

FEMTOSECOND DEPHASING IN A POLYDIACETYLENE FILM MEASURED BY DEGENERATE FOUR-WAVE MIXING WITH AN INCOHERENT NANOSECOND LASER

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Dephasing times in a polydiacetylene (poly-3BCMU) film were resolved for the first time at two wavelengths by degenerate four-wave mixing using incoherent light. The dephasing times, 30 fs at 648 nm and 130 fs at 582 nm, correspond to excitons in chains of the polymer with different conjugation lengths.

1. Introduction

There has been much interest in the dynamical properties of the excited states of polydiacetylenes (PDAs). They have been studied experimentally by time-resolved absorption, reflection and emission spectroscopy [1–6], and excited-state lifetimes of 9 ± 3 ps in aqueous solution [1] and 1 ps in the crystalline phase [2] were obtained.

Knowledge of the dephasing dynamics of PDAs is of great importance not only for elucidating the properties of excited states and the mechanism of the optical non-linearity but also for various applications such as optical switching and optical signal processing. Degenerate four-wave mixing (DFWM) was applied to dephasing time measurements [7–9], but dephasing times have not been resolved so far. Dennis et al. [7] observed DFWM from two PDA (2*d* and 2*j*) solutions with 180 ps pulses, but they found that the response times were faster than their resolution time. Carter et al. [8] observed DFWM from a PDA (PTS) crystal with 6 ps pulses, and they concluded that the response time was faster than 6 ps. Rao et al. [9] performed similar measurements on a PDA (poly-4BCMU) film with 500 fs pulses, but they could not resolve the dephasing time either.

It has been shown that one can obtain very short resolution times by using broad-band (incoherent) light in dephasing measurements by degenerate four-

wave mixing (DFWM) [10–12], and by coherent anti-Stokes Raman scattering (CARS) or Stokes scattering (CSRS) [13]. The delay-time dependence of the DFWM signal intensity is expressed entirely in terms of the field autocorrelation and the response function of the matter [14], and therefore, the time resolution is limited only by the correlation time of the incoherent light.

In this study, we applied DFWM with incoherent light to the measurement of the dephasing times in a film of a PDA, poly(4,6-decadiyne-1,10-diol-bis((*n*-butoxycarbonyl)-methyl)urethane), abbreviated hereafter as poly-3BCMU. By detecting signals diffracted in two directions simultaneously, we could resolve a dephasing time as short as 30 fs. We measured dephasing times of the sample at two wavelengths, 648 and 582 nm, and found that the dephasing of an exciton in a chain of the polymer with a longer conjugation length (at 648 nm) is four times faster than that in a chain with a shorter conjugation length (at 582 nm). This result explains the difference in the fluorescence efficiencies between the rod-like and coil-like forms of the acetylene-type phase.

2. Experimental

The experimental apparatus used for the dephasing time measurement is shown in fig. 1. The inco-

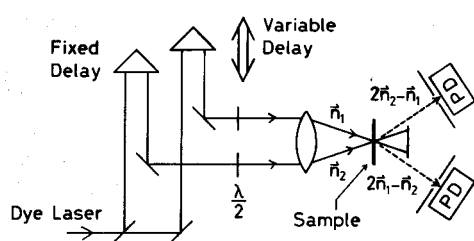


Fig. 1. Experimental apparatus for degenerate four-wave mixing measurements. PD and $\frac{1}{2}\lambda$ stand for a photodiode and a half-wave plate (Fresnel rhomb), respectively. The vectors, n_1 and n_2 , are the unit vectors representing the directions of the two exciting beams.

herent light source was a broad-band dye laser pumped by a N_2 laser. The output of the oscillator was amplified by a dye cell pumped by the same N_2 laser. In order to obtain very broad-band laser light, the oscillator cavity of the dye laser was constructed with a highly reflecting aluminum mirror and a glass plate as an output mirror, and no tuning element was placed in the cavity. Rhodamine 6G and rhodamine 640 were used as laser dyes. The center wavelengths and the band widths (fwhm) of the power spectra were 582 and 7.7 nm for rhodamine 6G, and 648 and 8.7 nm for rhodamine 640, respectively.

Dye-laser light was linearly polarized by a Glan-Thompson prism. It was then divided into two beams, n_1 and n_2 , by a beam splitter, and n_2 was delayed with respect to n_1 by a delay time τ . The delay time was varied by a translation stage driven by a stepping motor. The polarization planes of the two beams could be rotated independently by the use of half-wave plates. The pulse energies of the 10 ns dye laser were about 3 μ J at the sample position, and the beam diameters of the focused areas on the sample were 40 μ m.

Degenerate four-wave mixing signals diffracted in two directions, $2n_2 - n_1$ and $2n_1 - n_2$, were detected simultaneously by photodiodes, as shown in fig. 1, to obtain resolution times shorter than the correlation time of the incoherent light [12]. Output signals of the photodiodes were processed with sample-and-hold circuits and an A/D converter, and stored in a microcomputer.

The sample used in the experiment was a film of poly-3BCMU, which was cast on a glass plate from a chloroform solution. The absorption spectrum of the

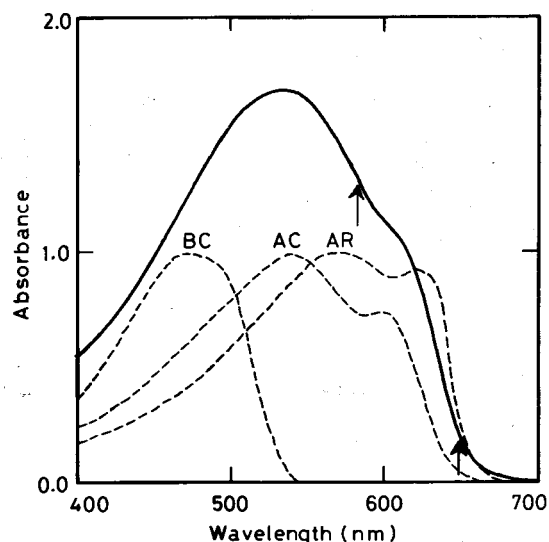


Fig. 2. Absorption spectrum of the film of poly-3BCMU (solid line) with those of three forms in solution from ref. [15] (broken lines). AR, AC, and BC denote acetylenic type in rod-like conformation, acetylenic type in coil-like conformation, and butatrienic type in coil-like conformation, respectively. The two exciting wavelengths utilized in the present study, 648 and 582 nm, are indicated by arrows.

film is shown in fig. 2. The transmittances of the film were 5% at 582 nm and 60% at 648 nm. All measurements were performed at $26 \pm 3^\circ\text{C}$.

3. Results and discussion

Fig. 3 shows the data which were obtained with the two exciting beams under parallel polarization conditions. Background signal due to scattering of the exciting beams was subtracted from the data. No peak shift or tail was observed. The peak intensity of the signal was about thirty times higher than those obtained with perpendicular polarization. From these experimental results, the signal obtained with parallel polarization can be attributed almost exclusively to diffraction from a thermal grating, which is generated only when mutual coherence between the two exciting beams exists [14].

The contribution of the thermal grating to the DFWM signals is eliminated when the polarizations of the two exciting beams are perpendicular to each other, and we can obtain DFWM signals which are

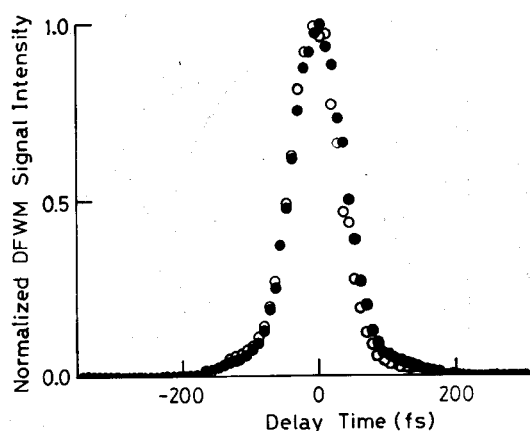


Fig. 3. DFWM signals obtained with the two exciting beams of polarizations parallel to each other. The wavelength of the excitation light was 648 nm. Open circles show the signal intensity diffracted in the direction $2\mathbf{n}_1 - \mathbf{n}_2$, and closed circles show that in the direction $2\mathbf{n}_2 - \mathbf{n}_1$.

only due to electronic non-linear susceptibilities [12]. The data obtained with perpendicular polarization are shown in fig. 4, after subtraction of the background scattering intensity. There are shifts of delay times between the peaks of the signal intensities of the two directions, as shown in fig. 4. The peak shifts were 30 and 90 fs at 648 and 582 nm, respectively. Here we define the peak shift as the distance in the delay time between the two peaks of the signal intensities of the two directions. The widths (fwhm) of the signals were 100 fs for 648 nm and 130 fs for 582 nm, which give the correlation time of the exciting incoherent light at each wavelength with a certain factor according to the signal shape and the definition of correlation time. There are no pronounced asymmetric tails which indicate dephasing times much longer than the correlation time. The tails seen in the data at 648 nm are due to the spectral shape of the light deviated far from Gaussian, since the field autocorrelation is a Fourier transform of the power spectrum.

When only one-photon resonant DFWM is responsible for the signal, the delay-time (τ) dependence of the signal intensities is expressed by the following equation [11]:

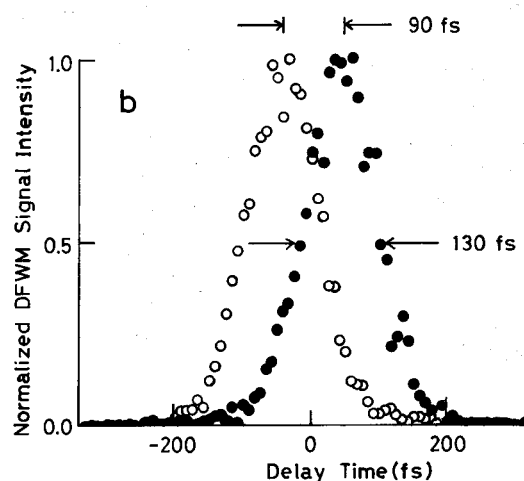
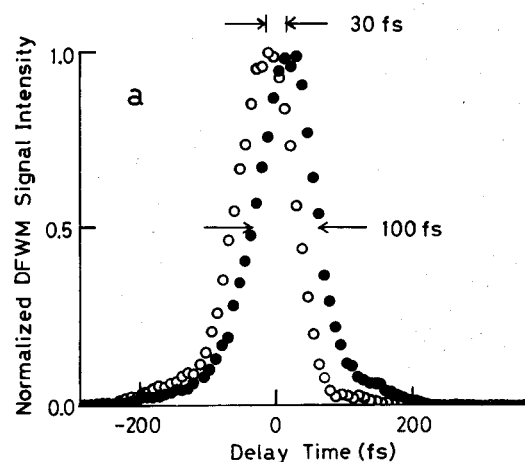


Fig. 4. DFWM signals with the two exciting beams of polarizations perpendicular to each other. Open circles show the signal intensity diffracted in the direction $2\mathbf{n}_1 - \mathbf{n}_2$, and closed circles show that in the direction $2\mathbf{n}_2 - \mathbf{n}_1$. The wavelengths of the excitation light are (a) 648 nm and (b) 582 nm.

$$I(\tau) \propto \int_0^\infty dt \int_0^\infty dt' G(t' - t) G(t - \tau) G^*(t' - \tau) \times \exp[-2(t + t')/T_2]. \quad (1)$$

Here $G(\tau)$ is the autocorrelation function of the incoherent light field,

$$G(\tau) = \langle E(t + \tau) E^*(t) \rangle, \quad (2)$$

where $E(t)$ is the envelope of the electric field of the light. For eq. (1) to be applicable, the condition that

the population lifetime is much longer than the dephasing time must be satisfied. Our preliminary data by a picosecond absorption experiment with the second harmonic of a mode-locked Nd:YAG laser (532 nm, 30 ps) show that the population lifetime of excitons in a poly-3BCMU film is of the order of the laser pulse width [16]. When the dephasing time is much longer than the correlation time of the light field, the signal decays exponentially at the rate of $4/T_2$. On the other hand, when the dephasing time is comparable with or slightly shorter than the correlation time, which is the case in the present study, the dephasing time of the matter can also be obtained from the peak separation of the two signals diffracted in two directions even though the signal shapes have no prominent tails [12,14].

In the discussion of the optical non-linearity of PDAs, however, contribution of the two-photon resonant state cannot be neglected [17,18]. The DFWM signal intensities by two-photon resonance can be expressed as

$$I(\tau) \propto \int_0^\infty dt' \int_0^\infty dt'' \langle E(t-\tau) E^*(t-\tau) \\ \times E(t-t') E^*(t-t') E(t-t'') E^*(t-t'') \rangle \\ \times \exp[-(t' + t'')/T_2^*]. \quad (3)$$

Here T_2^* is the inverse width of the relevant two-photon transition. In this case, the signal will have a tail on the other side of the peak than that of the signal by one-photon resonance [19], and the decay rate is $2/T_2^*$, since this process is a two-photon version of the free induction decay, and therefore, the dephasing by the inhomogeneous broadening is irreversible.

Note here, however, that the signal intensity given by eq. (3) does not vanish at a large τ . The ratio of the intensity at $\tau=0$ to the background depends on the statistical properties of the incoherent field and becomes three when a Gaussian random process [10] is assumed for the model of the incoherent field.

In the present experiments on poly-3BCMU, no background signal was detected other than scattering due to a linear process. Therefore, at the two wavelengths investigated in the present study, the contribution of the two-photon state to the DFWM signal is negligible, and the observed peak shifts are attributed to dephasing of one-photon resonant transi-

tions. Using eq. (1) and the observed peak shifts the dephasing times are calculated to be 30 fs at 648 nm and 130 fs at 582 nm by assuming Gaussian autocorrelation functions. The effect of spectral diffusion on these dephasing times can be excluded since spectral diffusion in polymeric systems such as PDA may take place on a subpicosecond time scale or slower.

This result that the dephasing time at a longer wavelength is shorter than that at a shorter wavelength is contrary to the results of previous studies [12,14]. The peak shift was reported to be larger at a longer wavelength than at a shorter wavelength with cresyl violet in cellulose, and the result was explained in terms of the difference between the rates of intramolecular relaxation processes at the two wavelengths [12]. Dephasing time measurements of three dyes, cresyl violet, Nile blue, and oxazine 720, in polymethylmethacrylate (PMMA) at 15 K at 620 nm were also reported [14]. The peak shift for cresyl violet was found to be 60 fs, whereas for the other two dyes shifts were shorter than 20 fs. The difference in the dephasing times was attributed to that in the excess energy of the exciting photon from the absorption edge of each sample.

The present sample has its own characteristics different from ordinary dyes [15,20]. It is known that poly-3BCMU in solution has two conformations, rod-like and coil-like, both of which can have two isomeric bond structures, the acetylenic and butatrienic types [15]. These four forms are realized depending on the temperature and the composition of the solvent. The shoulder of the absorbance of the sample in the present study at 620 nm (2.0 eV) corresponds to the AR (acetylenic type in rod-like conformation) band in fig. 3 of ref. [15], and the peak at 530 nm (2.3 eV) corresponds to the AC (acetylenic type in coil-like conformation) band. They are attributed to the $\pi-\pi^*$ exciton transition in each type of the polymer chain. Therefore, our sample is thought to be a mixture of a coil-like conformation (with shorter conjugation lengths of π electron) and a rod-like conformation (with longer conjugation lengths) in the acetylenic bond structure, or a mixture of the polymer chains with continuously distributed conjugation lengths between these two extreme forms realized in solution.

In the present experiment, the wavelength of 648 nm is on the absorption edge of the rod-like form

exciton, while that of 582 nm is on resonance with the exciton in polymer chains with shorter conjugation lengths. Therefore, from the present results on the dephasing times at the two wavelengths, it can be concluded that the exciton dephasing is about four times faster in the rod-like form than in a chain with a shorter conjugation length.

The present result may be explained in two ways. One explanation is that excitons are more mobile and the phases of them are changed more often in longer conjugated chains than shorter ones, where excitons do not move over long distances. The other explanation is that exciton levels lie more closely in longer conjugated chains than in shorter conjugated chains, and therefore, dephasing due to multilevel excitation is faster [14]. We cannot determine which is the case from the present data only. An extended study with other wavelengths and temperatures is in progress.

It has been reported that the fluorescence intensities are suppressed when the solution of poly-3BCMU is converted from a yellow (butatrienic, coil-like) form to a blue (acetylenic, rod-like) form, and when the solution of PDA (poly-4BCMU) is converted from the coil form to the rod form [15]. It has also been reported that only partially polymerized crystal of PDA (PTS) emits fluorescence [21]. Our results support the explanation [15,21] by which the changes in the fluorescence quantum efficiencies are attributed to the increase in the non-radiative decay rates with exciton delocalization.

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References

- [1] S. Koshihara, T. Kobayashi, H. Uchiki, T. Kotaka and H. Ohnuma, *Chem. Phys. Letters* 114 (1985) 446.
- [2] B.I. Greene, J. Orenstein and R.R. Millard, in: *Technical Digest of Topical Meeting on Ultrafast Phenomena* (1986).
- [3] T. Kobayashi, J. Iwai and M. Yoshizawa, *Chem. Phys. Letters* 112 (1984) 360.
- [4] T. Kobayashi, H. Ikeda and S. Tsuneyuki, *Chem. Phys. Letters* 116 (1985) 515.
- [5] J. Orenstein, S. Etemad and G.L. Baker, *J. Phys. C* 17 (1984) L297.
- [6] L. Robins, J. Orenstein and R. Superfine, *Phys. Rev. Letters* 56 (1986) 1850.
- [7] W.M. Dennis, W. Blau and D.J. Bradley, *Appl. Phys. Letters* 47 (1985) 200.
- [8] G.M. Carter, M.K. Thakur, Y.J. Chen and J.V. Hryniewicz, *Appl. Phys. Letters* 47 (1985) 457.
- [9] D.N. Rao, P. Chopra, S.K. Ghoshal, J. Swiatkiewicz and P.N. Prasad, *J. Chem. Phys.* 84 (1986) 7049.
- [10] N. Morita and T. Yajima, *Phys. Rev. A* 30 (1984) 2525.
- [11] H. Nakatsuka, M. Tomita, M. Fujiwara and S. Asaka, *Opt. Commun.* 52 (1984) 150.
- [12] M. Fujiwara, R. Kuroda and H. Nakatsuka, *J. Opt. Soc. Am. B* 2 (1985) 1634.
- [13] T. Hattori, A. Terasaki and T. Kobayashi, *Phys. Rev. A*, to be published.
- [14] A.M. Weiner, S. de Silvestri and E.P. Ippen, *J. Opt. Soc. Am. B* 2 (1985) 654.
- [15] T. Kanetake, Y. Tokura, T. Koda, T. Kotaka and H. Ohnuma, *J. Phys. Soc. Japan* 54 (1985) 4014.
- [16] K. Ichimura, T. Kobayashi and T. Kotaka, to be published.
- [17] Y. Tokura and T. Koda, *J. Chem. Phys.* 85 (1986) 99.
- [18] R.R. Chance, M.L. Shand, C. Hogg and R. Silbey, *Phys. Rev. B* 22 (1980) 3540.
- [19] J.-C. Diels and I.C. McMichael, *J. Opt. Soc. Am. B* 3 (1986) 535.
- [20] R.R. Chance, G.N. Patel and J.D. Witt, *J. Chem. Phys.* 71 (1979) 206.
- [21] H. Sixl and R. Warta, *Chem. Phys. Letters* 116 (1985) 307.