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Nonlinear Optical Properties of Polyaniline Liquid Solutions

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Nonlinear optical properties of polyaniline solutions were measured for different concentrations with the single beam Z-scan technique. Results obtained with pulse trains consisting of several 70-ps-duration pulses at 532 nm indicate that the nonlinearity initially presents a fast electronic contribution, followed by a cumulative thermal lensing associated to the pulses' arrival.

Keywords: polyaniline; nonlinear index; thermal lens

INTRODUCTION

Nonlinear optical properties of polyaniline (PANI) have attracted considerable attention. Z-scan measurements recently carried out with both the time-averaged pulse train of a Q-switched and modelocked laser [1] and with single pulses [2] presented a marked discrepancy in both magnitude and sign of the nonlinearity. This is probably due to an accumulative thermal process that arises because the non-radiative decay to the ground state produces a refractive index change due to the local heating. The present work employs the Z-scan technique with pulse trains [3] to investigate the origin of the nonlinear refractive index of polyaniline liquid solutions. We verified that the nonlinearity initially presents an electronic contribution, followed by the build up of

a cumulative thermal lens as consequence of the pulses' arrival. In this way, the nonlinearity changes both sign and magnitude along the pulse train, elucidating the contradiction between References [1] and [2].

EXPERIMENTAL

Polyaniline (PANI) samples were prepared in the protonated state according to conventional methods [4] and dissolved in DMSO to concentrations ranging from 0.008 to 0.061 wt%. All optical measurements were carried out with the sample placed in a 2-mm quartz cuvette. The absorption spectra for different concentrations show no significant shift, indicating that aggregation processes are unlikely.

The dynamic behavior of the optical nonlinearity was investigated with the Z-scan technique with pulse trains described in Reference [3]. The pump source is a frequency-doubled, Q-switched and mode-locked Nd:YAG laser, delivering 70-ps-duration pulses at 532 nm, in pulse trains containing about 20 pulses (separated by 13.2 ns) at 5 Hz. We use a Pockels cell sandwiched between two crossed polarizers to truncate the first half of the Q-switch envelope, as shown in the inset of Figure 1. We use the expression $\Delta T_{pv} = 0.406\ (1\text{-}S)^{0.25}\ \Delta\phi_{NL}$ to obtain the induced nonlinear phase, $\Delta\phi_{NL} = (2\pi/\lambda)\Delta n L_{eff}$, where λ is the wavelength, $L_{eff} = (1\text{-}e^{-\alpha L})/\alpha$, α is absorption coefficient, L is the sample thickness and Δn is the light-induced refractive index change.

RESULTS AND DISCUSSION

Figure 1(a) presents ΔT_{pv} measured along the pulse train for the sample with the lower PANI concentration investigated. For the first pulse the nonlinearity is positive and can be attributed to a fast

electronic contribution. However, as the energy of the arriving pulses is accumulated in the sample, the thermal effect plays the major role and the nonlinearity becomes negative. Measurements carried out at higher concentrations present marked differences with the one at low concentration, as shown in Figure 1(b) for the solution with 0.061 wt% of PANI. The main difference is that the nonlinear effect occurring at the first peak decreases in magnitude as the concentration increases, as shown in Figure 2. We attribute this behavior to the formation of a thermal lens. After the light is absorbed by PANI molecules, the energy must be transferred to adjacent solvent molecules in order to

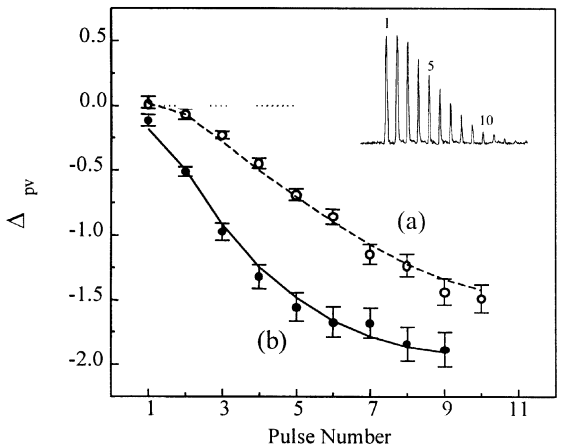

FIGURE 1. ΔT_{pv} measured along the pulse train for a sample with PANI concentrations of (a) 0.019 and (b) 0.061 wt%. Solid lines are theoretical fittings as described in the text.

arrive to the local thermal equilibrium [5]. We estimate this time simply by multiplying the time for energy transfer between two adjacent solvent molecules, τ, by half the number of solvent molecules between two neighboring solute molecules. τ depends on the specific

solvent and the amount of excess energy converted into heat and typically ranges from 5 to 50 ps [6]. In our model it enters as a fitting parameter. The characteristic time for the thermal lens to build up depends on the fraction $\eta=(N_{PANI}/N_{DMSO})$ of PANI molecules relative to DMSO molecules according to $\frac{1}{2}\ \eta^{-1/3}\ \tau$. Considering the PANI dispersivity, average molecular weight and density we estimate that η ranges from 7×10^{-5} to 5.5×10^{-4} for the concentrations used. This means that there are, in average, from 15 to 25 DMSO molecules between two adjacent PANI molecules. Taking into account that the build up time for the thermal lens can be shorter the 70-ps pulse duration, the time averaged index change for the first pulse is given by:

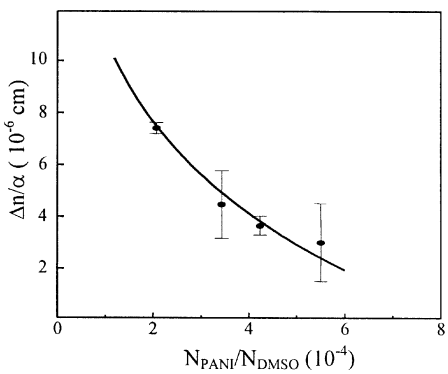

FIGURE 2. Light-induced refractive index change observed for the first pulse in the pulse train as a function of the concentration.

$$\langle \Delta n \rangle_1 = \frac{n_2 I_1}{\sqrt{2}} + \frac{n_2^{th}}{F_1} \int_{-\infty}^{+\infty} I_1(t) \int_{-\infty}^{t} I_1(t') \left[1 - \exp\left\{ -\frac{2(t-t')\eta^{1/3}}{\tau} \right\} \right] dt'dt \qquad (1)$$

where the first term accounts for instantaneous electronic nonlinearity and the second refers to the buildup of the thermal lens, whose

subsequent relaxation, in the millisecond range, is neglected. I_1 and F_1 are respectively the intensity and fluence of the first pulse. Besides τ, n_2 and n_2^{th} were also used as fitting parameters, and the result shown as the solid line in Figure 2 yielded $\tau = (10\pm3)$ ps, $n_2/\alpha = 3.7\text{x}10^{-15}$ cm^3/W and $n_2^{th}/\alpha = -2 \text{ x } 10^{-4}$ cm^3/J.

The nonlinearity evolution as a function of the pulse number, shown in Figure 1, can be explained by adding the fast contribution due to the j^{th} pulse (expression (1), with j replacing 1) to the thermal index variation originating from previous pulses. The later can be calculated by considering both the diffusive and acoustic parts to the thermal contribution according to [7, 8]:

$$\left\langle \Delta n^{diff} \right\rangle = \frac{n^{diff}}{2} \sum_{i<j} F_i \, \text{erfc}[-u] \tag{2}$$

$$\left\langle \Delta n^{ac} \right\rangle = \frac{n^{ac}}{2} \sum_{i<j} F_i \left[\frac{m^2}{\sqrt{2\pi(2+m^2)}} * \int_0^{\infty} \frac{\exp[-(2s^2+u^2]}{s} \left(\frac{u - sm}{2+m^2} X - \frac{u+sm}{2+m^2} Y \right) ds \right] \tag{3}$$

with $\text{erfc}[z] = 1 - \frac{2}{\sqrt{\pi}} \int_0^z e^{-t^2} dt$, and the functions X and Y given as [7]:

$$X = \exp\left[\frac{(2s+mu)^2}{2+m^2} \right] \text{erfc}\left(- \frac{2s+mu}{\sqrt{2+m^2}} \right) \tag{4}$$

$$Y = \exp\left[\frac{(2s-mu)^2}{2+m^2} \right] \text{erfc}\left(\frac{2s-mu}{\sqrt{2+m^2}} \right) \tag{5}$$

where $m = \tau_{ac}/T_p$ is the ratio between the acoustic time ($\tau_{ac} = w/v_s$, w being the laser beam radius and v_s the speed of sound) and the pulse

duration (70 ps in our case), and $u = (j-i)\Delta t/T_p$, where $\Delta t \approx 13$ ns is the time interval between consecutive pulses. The dot line in Figure 1(a) is a theoretical fitting using equations (2) to (5), and the parameters: $n_2/\alpha = 4.3 \times 10^{-15}$ cm^3/W, $n_{2c}^{th}/\alpha = -1 \times 10^{-4}$ cm^3/J, $n^{diff}/\alpha = -0.9 \times 10^{-4}$ cm^3/J, $n^{ac}/\alpha = -0.6 \times 10^{-4}$ cm^3/J. In Figure 2(b) we used $n_2/\alpha = 4 \times 10^{-15}$ cm^3/W, $n_{2c}^{th}/\alpha = -2 \times 10^{-4}$ cm^3/J, $n^{diff}/\alpha = -0.5 \times 10^{-4}$ cm^3/J, $n^{ac}/\alpha = -1.2 \times 10^{-4}$ cm^3/J.

CONCLUSIONS

We verified the occurrence of a fast electronic contribution to the nonlinearity, followed by the build up of a cumulative thermal lens as the pulses arrive. The theoretical model fits well the experimental data, with parameters in ranges that should be expected. We have therefore made clearer the contradiction between already existing results.

References

[1] D. V. Petrov, A. S. L. Gomes, C. B. de Araújo, J. M. de Souza, W. M. de Azevedo, J. V. de Melo, F. B. Diniz, *Opt. Lett.* **20**, 554 (1995).
[2] M. Samoc, A. Samoc, B. Luther-Davies, J. Swiatkiewicz, C. Q. Jin, J. W. White, *Opt. Lett.* **20,** 2478 (1995).
[3] L. Misoguti, C. R. Mendonça, S. C. Zilio, *Appl. Phys. Lett.* **74**, 1531 (1999).
[4] G. E. Asturias, A. G. MacDiarmid, R. P. MacCall, A. J. Epstein, *Synth. Metals* **29**, E157 (1989).
[5] T. H. Wei, T. H. Huang, M. S. Lin, *Appl. Phys. Lett.* **72** 2505 (1998).
[6] A. Seilmeier, W. Kaiser, *Ultrashort Laser Pulses*, 2nd edition, edited by W. Kaiser (Springer, Berlin, 1993), pp.305-306.
[7] P. Brochard, V. Grolier-Mazza, R. Cabanel, *J. Opt. Soc. Am.* B **14**, 405 (1997).
[8] S. R. J. Brueck, H. Kildal, L. J. Belanger, *Opt. Commun.* **34**, 199 (1980).