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Measurements of the third-order nonlinearity of a soluble polycarbazolyldiacetylene by picosecond Z-scan at 1064 and 1500 nm

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Abstract

The complex $\chi^{(3)}$ of toluene solutions of polydiacetylene, polyDCHD-HS, was measured by using Z-scan at $\lambda = 1064$ and 1500 nm and with picosecond pulses in order to estimate the potentials of this polymer for application to all-optical switching devices. The values of the real part of molecular hyperpolarizability γ were -2.3×10^{-47} and -3×10^{-47} m^5/V^2 at 1064 and 1500 nm, respectively. The nonlinear absorption could be better modeled with a three-photon process at both the wavelengths instead of the expected two-photon mechanism.
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1. Introduction

The challenging requirements of future all-optical signal processors based on guided-wave optics have stimulated the investigation and characterization of nonlinear materials, such as polycarbazolyldiacetylenes, that are expected to exhibit large off-resonance values of $\chi^{(3)}$ in the telecommunication windows. Among these, the polyDCHD-HS, a compound of recent synthesis exhibits high solubility in common organic solvents that made possible fabrication of high quality optical waveguides [1]; the easy polymer processing and the large value of $\chi^{(3)}$ observed at 1064 nm and with ultrathin films has stimulated a more in-depth investigation of material nonlinearity [2,3]. For this purpose, we started with the simplest system (a solution) and with the well-established Z-scan technique [4]. Results will be illustrated on Z-scan measurements performed with picosecond pulses at 1064 nm and, for the first time, at 1500 nm; indeed while 1064 nm is still the most commonly adopted wavelength for nonlinear characterizations and permits useful comparisons with other materials, a characterization around 1500 nm is mandatory with a view to applications for the operating devices. Furthermore, the strong absorption peak of polyDCHD-HS at 538 nm makes the measurements of the refractive part of $\chi^{(3)}$ not completely reliable at 1064 nm, due to the possible even if not detected, two-photon absorptions which, in principle, can hamper the correct evaluation of Re$\{\chi^{(3)}\}$ at this wavelength.

2. Nonlinear tests

The Z-scan technique, which is described in detail in Ref. [4], is based on the self-focusing or defocusing of a converging beam of known spatial structure induced by moving a nonlinear sample along the light-propagation direction (Z-axis). The above said technique permits a rapid evaluation of the magnitude and sign of both the real (nonlinear refraction, NLR) and imaginary (nonlinear absorption, NLA) parts of the nonlinearity of transparent solids and liquids. As far as NLR is concerned, the transmission across an aperture in the far field is registered as a function of the sample position along Z (closed aperture Z-scan), while NLA can be inferred either by closed aperture Z-scan or, more accurately, by independently measuring the overall sample transmission versus its position along the Z-axis (open aperture Z-scan).

The laser that we employed for the nonlinear measurements at 1064 nm was a 10 Hz oscillator/amplifier, mode-locked Nd:YAG laser (EKSPLA model PL2143A) with typical 2% pulse-to-pulse energy fluctuations and 30 ps pulse width. At 1500 nm, we used a BBO-based OPA/OPG pumped by the second harmonic of the Nd:YAG laser;
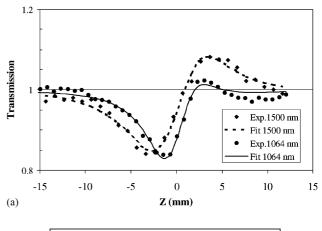
in this case, the pulse duration was 15 ps, the pulse-to-pulse energy fluctuation 8–10% and the linewidth 7 nm. We adopted the so-called trimmed Airy beam configuration because this beam structure is not only easier to obtain than the Gaussian one but also provides greater sensitivity. We obtained the trimmed Airy beam structure by first selecting the central part of the laser beam with a 600 μm diameter pinhole and then, after some free propagation, by selecting the central lobe of the Airy pattern with an iris. The beam was then focused on the sample using a lens placed next to the iris; the beam waist was estimated as 39 and 35 μm at 1064 and 1500 nm, respectively. The intensity in the focal plane could be varied between 0.1 and 40 GW/cm^2. After the focus, the beam was split into two beams: the first one passed through an aperture in the far field that had a transmission of about 5% and reached a photodiode PH$_C$ (closed aperture Z-scan); the second one was sent directly onto another photodiode PH$_O$ in order to register intensity-dependent absorptive effects (open aperture Z-scan). A beam splitter placed between the iris and the lens sent part of the pulse energy to a third photodiode, PH$_R$ (reference). The signals were stored in a PC which, for each laser pulse, evaluated the time-averaged aperture transmission with photodiode PH$_C$ and the whole beam transmission with photodiode PH$_O$. For every sample position, these values were averaged over several laser pulses (typically 30). The samples under test were mounted on a motorized stage (Microcontrole) with a 0.1 μm resolution and controlled by the same PC. The real part of the nonlinearity was obtained by means of relative measurements with respect to a 5 mm long Al$_2$O$_3$ crystal, whose Re$\{\chi^{(3)}\}$ has been accurately determined in the picosecond time regime by means of several methods including Z-scan [5,6]. In contrast, a calibrator for the imaginary part of the nonlinearity was not available; therefore, absolute measurements were performed. Solutions of polyDCHD-HS in toluene with concentrations ranging from 0.5 up to 10 g/l were prepared using standard procedures [1]. We used 1 and 4 mm thick quartz cuvettes. The experiments were performed as follows:

1. calibration of the setup with the Al$_2$O$_3$ sample;
2. simultaneous acquisition of closed and open aperture Z-scan traces using pure solvent;
3. simultaneous acquisition of closed and open aperture Z-scan traces using polymer solutions;
4. check of the quality of the solutions after irradiation by means of linear absorption spectra.

Fig. 1a and b reports typical experimental points and theoretical best-fit curves obtained with a 1.8 g/l solution at 1064 nm and with a 7 g/l solution at 1500 nm. For the best-fit curves, we assumed a dispersive $\chi^{(3)}$ effect and a three-photon absorption process ($\chi^{(5)}$).

Figs. 2 and 3 report the nonlinear phase shift (on the beam axis and in the focus) per unit length ϕ/L versus intensity I, in the case of a 3 g/l solution and pure solvent at 1064 nm
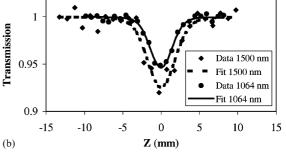

Fig. 1. Experimental points and theoretical best fits for Z-scan traces obtained with a 7 g/l solution in a 1 mm thick cuvette at 1500 nm (filled diamonds and dashed lines) and a 1.8 g/l solution in a 1 mm thick cuvette at 1064 nm (filled circles and continuous lines): (a) closed aperture configuration at 42 GW/cm^2 (1500 nm) and 11 GW/cm^2 (1064 nm); (b) open aperture configuration at 26 GW/cm^2 (1500 nm) and 8 GW/cm^2 (1064 nm).

(Fig. 2) and a 7 g/l solution and pure solvent at 1500 nm (Fig. 3).

The linear dependence of ϕ/L is a confirmation of a third-order nonlinear process although a higher-order component of the nonlinearity corresponding to a $\chi^{(5)}$ process of opposite sign was also observed at 1500 nm and above 20 GW/cm^2. The slopes of the straight lines in Figs. 2 and 3 are proportional to Re$\{\chi^{(3)}\}$ of the solution; once Re$\{\chi^{(3)}\}$ of the solvent (Re$\{\chi^{(3)}\}_{solv}$) is known from a comparison with the sapphire calibrator, Re$\{\chi^{(3)}\}$ of the dissolved polymer
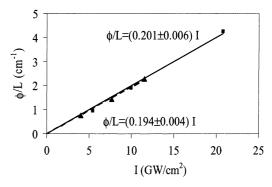

Fig. 2. Nonlinear phase shift versus intensity, in the case of a 3 g/l solution at 1064 nm: filled triangles and filled squares represent the experimental data for polymer solution and pure solvent, respectively, while dashed and continuous lines indicate the corresponding linear best fits.

Table 1

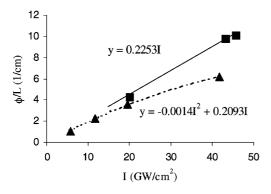| Concentration (g/l)	Wavelength (nm)	$\mathrm{Re}\{\gamma\}$ (m^5/V^2)	$\mathrm{Re}\{\chi^{(3)}\}_{\mathrm{film}}$ (m^2/V^2)	α_3 (cm^3/GW^2)	$\mathrm{Im}\{\chi^{(3)}\}_{\mathrm{film}}$ (m^2/V^2) ($I = 1$ GW/cm^2)
3	1064	-2.3×10^{-47}	-6×10^{-20}	0.0075	1.9×10^{-20}
7	1500	-3×10^{-47}	-7×10^{-20}	0.005	0.75×10^{-20}

Fig. 3. Nonlinear phase shift versus intensity, in the case of a 7 g/l solution at 1500 nm: filled triangles and filled squares represent the experimental data for polymer solution and pure solvent, respectively, while dashed and continuous lines indicate the corresponding best-fit curves.

($\mathrm{Re}\{\chi^{(3)}\}_{\mathrm{pol}}$) and the real part of its second-order molecular hyperpolarizability $\mathrm{Re}\{\gamma\}_{\mathrm{pol}}$ can be determined from the following equations:

$$\mathrm{Re}\{\chi^{(3)}\}_{\mathrm{pol}} = \mathrm{Re}\{\chi^{(3)}\}_{\mathrm{solv}} \left(\frac{\mathrm{Re}\{\chi^{(3)}\}}{\mathrm{Re}\{\chi^{(3)}\}_{\mathrm{solv}}} - 1 \right) \quad (1a)$$

$$\mathrm{Re}\{\gamma\}_{\mathrm{pol}} = \frac{\mathrm{Re}\{\chi^{(3)}\}_{\mathrm{pol}}}{N_A C L_F^4} \quad (1b)$$

where N_A is the Avogadro number, C the polymer concentration in moles/m^3 referring to repeat units and L_F is the local field factor which, in the hypothesis of spherical and non-interacting particles, is given by

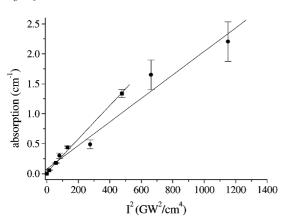$$L_F = \tfrac{1}{3}(n_0^2 + 2) \quad (2)$$

Fig. 4. NLA versus I^2 for a 3 g/l solution at 1064 nm (filled squares) and 7 g/l solution at 1500 nm (filled circles) with corresponding linear best fits (continuous lines).

Since toluene NLR was purely third order and positive within the irradiation regime adopted in all the experiments, the reduced slopes of the straight lines corresponding to polymer solutions indicate a negative contribution of polyDCHD-HS at both the wavelengths. These results are reported in Table 1.

Fig. 4 illustrates the intensity dependence of NLA; in this case, no solvent contribution was measured. NLA versus I^2 is reported for a 3 g/l solution at 1064 nm (filled squares) and 7 g/l solution at 1500 nm (filled circles) with corresponding linear best fits (continuous lines). This behavior, which is typical of a three-photon absorption process, was also observed for more dilute solutions. In contrast, within our intensity range, no two-photon absorption was observed. In this case, the absorption coefficient α of the solution can be expressed as:

$$\alpha = \alpha_0 + \alpha_3 I^2 \quad (3)$$

where α_0 represents linear absorption that is negligible for polyDCHD-HS at both the wavelengths and α_3 the three-photon absorption coefficient. This might be due to the high-intensity regime adopted in the experiments; however, also with thicker cuvettes and within our experimental sensitivity (1% at 1064 nm and 4% at 1500 nm), no evidence of a nonlinear contribution of the polymer could be measured for intensities lower than at least 3–4 GW/cm^2.

Table 1 also reports tentative extrapolations of the nonlinearity to the solid state in the rough hypothesis that molecular conformation and order are the same as those in solution; the only changes are in the refractive indices and the concentration (~770 moles/m^3 for the solid state). In particular for the imaginary part of the nonlinearity, an effective and intensity-dependent $\chi^{(3)}$ was considered that was calculated at 1 GW/cm^2. These results indicate that while at 1064 nm NLA is of the same order as NLR, at 1500 nm it is at least one order of magnitude smaller and decreases with intensity. This point makes polyDCHD-HS a promising material for applications in the third telecommunications window.

3. Conclusions

The nonlinearity of solutions of polyDCHD-HS in toluene was measured with picosecond pulses at 1064 nm and, for the first time at 1500 nm, by using the Z-scan method. The real part of the second-order molecular hyperpolarizability was negative and of the order of 10^{-47} m^5/V^2 at both the

wavelengths. Actually, at 1064 nm (as reported in Fig. 2), the difference between nonlinear phase shifts of solution and pure solvent is extremely small and very close to the experimental detection limit; such difference is sharper in the case of benzene solutions at the same wavelength and concentration as reported in Ref. [7]. In principle, larger concentrations could be used in order to enhance polymer contribution to the solution nonlinearity; however, due to the high three-photon absorption coefficient observed at 1064 nm, increased concentration would lead to distortion of closed aperture traces that cannot be simulated correctly with the theoretical tools presently available. In conclusion, closed aperture traces at 1064 nm give only an upper limit to the magnitude of the real part of second-order molecular hyperpolarizability of polyDCHD-HS toluene solutions at this wavelength.

As far as the imaginary part of the nonlinearity is concerned, three-photon absorption was observed at both the wavelengths. However, while at 1064 nm, NLA is of the same order as NLR, at 1500 nm, and in particular for operation intensities of the order of 1 GW/cm^2 or less, NLA is one order of magnitude lower than NLR making polyDCHD-HS very attractive for device development.

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