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Multiphoton absorption of solutions of polydiacetylene polyDCHD-HS measured using ps Z-scan at 1064 and 1500 nm

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Abstract

The nonlinear absorption of benzene and toluene solutions of polydiacetylene polyDCHD-HS was measured at $\lambda = 1064$ and 1500 nm by using Z-scan and picosecond pulses with a trimmed Airy beam configuration. In the data analysis, we took into account both the saturation of the open aperture Z-scan traces occurring for high values of nonlinear absorption and the possible occurrence of cross-talk effects between nonlinear refraction and multiphoton absorption. The polymer exhibits three-photon absorption at both 1064 and 1500 nm. The molecular three-photon absorption coefficient at 1064 nm was $\sigma_3 = 1.8 \times 10^{-38}$ cm⁶/W² and $\sigma_3 = 2.3 \times 10^{-38}$ cm⁶/W² in toluene and benzene, respectively, while at 1500 nm it was $\sigma_3 = 1.5 \times 10^{-39}$ cm⁶/W² in toluene. On this basis, the optical limiting behavior of polyDCHD-HS in the near infrared range is also shown.

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1. Introduction

The challenging requirements of future all-optical signal processors have stimulated the investigation and characterization of nonlinear materials, such as polydiacetylenes (PDAs) [1]. These polymers are unidimensional semiconductors that, since the pioneering work of Sauteret et

alii on PTS [poly bis(*p*-toluene sulfonate) of 2,4-hexadiene-1,6diol], have been studied extensively because of their unique π -electronic properties, which produce large off-resonant third-order optical nonlinearities in the telecommunications windows [2]. The value of the refractive nonlinearity n_2 of PDAs and other conjugated compounds has been measured using different techniques and in different regions of the electromagnetic spectrum [3]. The n_2 value reported for PTS is still the largest nonresonant nonlinearity known for any materials [2], although the poor processability prevents application of PTS in

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operating devices. In addition to n_2 , a knowledge of the nonlinear absorption (NLA) mechanisms is also mandatory, because it can severely limit the performance of all-optical switching devices. In contrast, NLA can also be exploited advantageously for the development of optical limiters [4], particularly when related to high-order multiphoton absorption mechanisms. Two-photon absorption spectra of conjugated polymers have been reported over the past ten years [5,6]. Three-photon absorption was observed in a solution of 2,5-benzothiazole 3,4-didecyloxy thiophene at 1064 nm [7] and in PTS [5]. Experiments of phase conjugation performed at 1064 nm on red PDA poly4BCMU revealed seventh-order processes that were related to a NLA induced by two-photon absorption [8], while four-photon absorption was more recently detected by Z-scan in PTS single crystals at 1600 nm [9].

In this paper we report on the multiphoton absorption of solutions of polyDCHD-HS [1,6-bis-(3,6-dihexadecyl-*N*-carbazolyl)-2,4-hexadiyne], a π -conjugated compound of recent synthesis [10] belonging to the family of polycarbazolyldiacetylenes. Polycarbazolyldiacetylenes are characterized by the highly polarizable carbazolyl rings attached to the backbone through one methylene group. Among these, polyDCHD-HS exhibits solubility in common organic solvents, due to hexadecyl substituents at the carbazolyl rings, and enables the fabrication of optical waveguides by spin coating [11]. These properties stimulated an in-depth investigation of the nonlinearity of the material both in solution and in the solid state, by using complementary methods, such as Third Harmonic Generation [12], two-photon fluorescence excitation [13] and nonlinear transmission [14]. Moreover, a giant value of the intensity-dependent refractive index of ultra-thin films (10–150 nm) of polyDCHD-HS ($|n_2| \approx 10^{-15} \text{ m}^2/\text{W}$) was also measured at 1064 nm by using Surface Plasmon Spectroscopy (SPS) and ps pulses [15] and was related to a local field enhancement of the nonlinear effect due to a nanostructuring of the metal/polymer interface. Here, we describe the results of picosecond Z-scan measurements of solutions of polyDCHD-HS in toluene and benzene, performed at 1064 nm and at 1500 nm. In fact,

while 1064 nm is still the most commonly adopted wavelength for nonlinear characterization and permits useful comparisons with other materials, a measurement at around 1500 nm is mandatory with a view to applications for operating telecommunications devices. We observed three-photon absorption at both wavelengths.

2. Experimental procedure

The Z-scan technique is based on an analysis of the perturbation induced by a nonlinear sample on the propagation of an optical beam of known structure, for different positions of the sample along the beam axis (*Z*-axis). It permits evaluation of the magnitude and sign of both the real (NLR) and imaginary (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 from a closed aperture Z-scan or, more accurately, from an independent measurement of the overall sample transmission versus its position along the *Z*-axis (open aperture Z-scan) [16]. In the latter arrangement, when using adequately thin samples, the measurement of NLA can be made almost independent (at least as a first approximation) from the effect of NLR, as has been shown by Polyakov et al. [17]. We will discuss this issue in more detail later.

The laser that we employed for the non linear measurements at 1064 nm was a 10 Hz oscillator/amplifier, mode-locked Nd:YAG laser (EKSPLA mod. 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 was 8–10%, and the linewidth was 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 [18,19]. The beam waist radius w_0 was estimated as 28 and 35 μm at 1064 and 1500 nm, respectively.

The intensity at the pulse peak in the focal plane ranged between 0.1 and 40 GW/cm² at 1500 nm, and between 0.1 and 13 GW/cm² at 1064 nm. After the focus, the beam was split into two beams: the first one passed through a 5% transmitting aperture placed in the far field and on the beam axis, and reached a photodiode PH_C (closed aperture Z-scan); the second one was sent directly onto another photodiode PH_O for open aperture Z-scan. A beam splitter placed between the iris and the lens sent part of the pulse energy to a reference photodiode PH_R. The signals were stored in a PC which evaluated the pulse energy transmission for each laser pulse. For every sample position, these values were averaged over several laser pulses (typically, 30). The samples under test were mounted on a motorized stage and controlled by the same PC.

PolyDCHD-HS is soluble in many organic solvents: in particular, toluene is the best solvent as far as the fabrication of guiding films is concerned [11], while benzene solutions are the most stable [20]. Solutions of polyDCHD-HS and DCHD-HS monomer in toluene and benzene were prepared using standard procedures; concentrations ranged from 0.5 up to 50 g/l in the case of toluene, while we limited ourselves to the 0.5–3 g/l range for benzene. Fig. 1 reports the room tem-

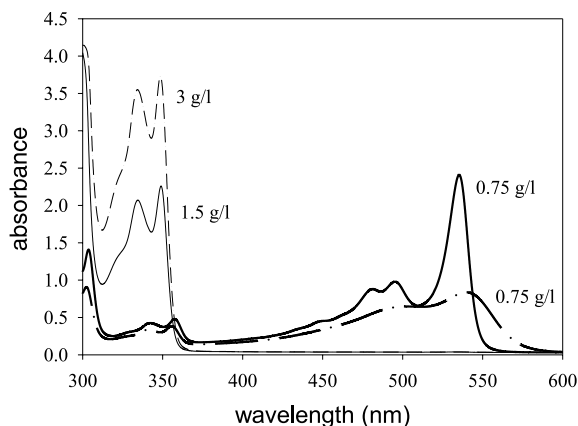


Fig. 1. Electronic absorption spectra of solutions of DCHD-HS (thin lines) and polyDCHD-HS (thick lines) in toluene (dot-dashed lines) and benzene (continuous lines). 1- and 2-mm-thick cuvettes were used for polymer and monomer solutions, respectively.

perature electronic spectra of fresh solutions of polyDCHD-HS and DCHD-HS monomer in toluene (dot-dashed lines) and in benzene (continuous lines). Both polymer solutions exhibit excitonic absorption peaks around 540 nm, corresponding to the red form of PDAs, and a low absorption band around 350 nm, due to the carbazolyl side groups. The same UV band is present in the monomer spectra, although blue-shifted by about 5 nm. It is worth noting that benzene solutions exhibit an efficient fluorescence, that is almost absent in toluene solutions [20]. Moreover, in the case of benzene, the resolution of the spectral bands in the visible is much higher than in toluene, and the excitonic peak has an intensity and a sharpness which has never been observed before in solutions of PDAs and is typical of the blue form of PDA single crystals. However, by increasing the temperature, these features are gradually lost and the spectrum of polyDCHD-HS in benzene becomes very similar to that in toluene at room temperature. This suggests that, in general, the polymer chain is maintained in the extended rod form typical of red PDAs by the interaction with these aromatic media, and that the temperature

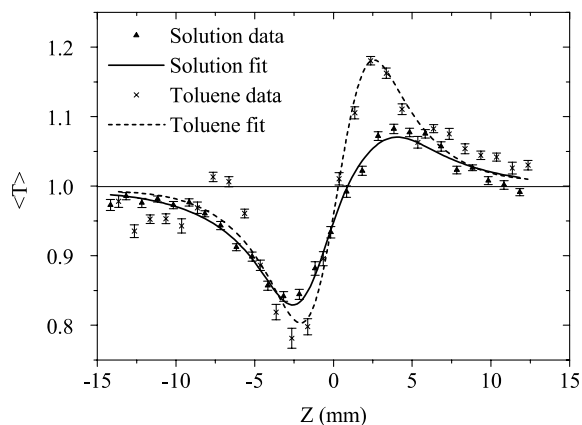


Fig. 2. Closed aperture Z-scan traces obtained at 1500 nm from pure toluene (crosses and dashed line) with $11.3 \pm 0.6 \mu\text{J}$ incident pulse energy, and from a 7 g/l polyDCHD-HS solution in toluene (solid triangles and continuous line) with $10.6 \pm 0.5 \mu\text{J}$ incident pulse energy. Sample length was 1 mm. Dashed and solid lines are theoretical best fits obtained with classical Z-scan equations. The peak-valley asymmetry of the trace of the polymer solution was due to strong NLA.

activates torsional intramolecular motions that are responsible for the broadening of the excitonic peak and that, at room temperature, are normally frozen in benzene solutions [20].

We used 1- and 4-mm-thick quartz cuvettes, in order to explore the high and low intensity regimes, respectively. Open and closed aperture Z-scan traces were simultaneously registered for pure solvents and, subsequently, for polymer solutions. No multiphoton absorption from the solvents was detected in the intensity range explored. Fig. 2 shows typical closed-aperture experimental traces obtained at 1500 nm from pure toluene (crosses) and from a 7 g/l polyDCHD-HS solution in toluene (triangles). The Z-scan traces indicated a positive value for the refractive nonlinearity. Indeed, at both wavelengths, it was purely third order ($\chi^{(3)} \approx 10^{-21} \text{ m}^2/\text{V}^2$) in the case of solvents, while it exhibited a more complex behavior, possibly due to higher order terms, in the case of polymer solutions.

3. Theoretical approach

The change in intensity I experienced by a beam propagating along z through a medium exhibiting n -photon absorption can be written as $dI = -\alpha_n I^n(z) dz$ [7], where α_n is the n -photon absorption coefficient. For $n = 1$ (namely, linear absorption), integration of Eq. (1) gives Lambert–Beer’s law; but for $n > 1$ the transmission T after a path length L is given by

$$T_{\text{nph}} = \frac{1}{[1 + (n-1)\alpha_n I_0^{n-1}]^{1/(n-1)}}, \quad (1)$$

where I_0 is the input intensity. Let us define the incident intensity level at a distance r from the beam axis, at a position z along the beam path and at a time t as $I(r, z, t) = I_0 F(r, z) p(t)$. The spatial distribution $F(z, r)$ and the pulse temporal shape $p(t)$ are renormalized so that I_0 is the intensity on the beam axis at the focal plane and at the pulse peak. In the thin sample approximation, and by assuming an instantaneous nonlinearity, the open aperture transmission for a given position z of the sample, averaged along the pulse duration, is

$$\langle T_{\text{open}}(z) \rangle = \frac{\int_{-\infty}^{\infty} dt \int_0^{\infty} r p(t) F(r, t) T(I_0 F(r, z) p(t)) dr}{\int_{-\infty}^{\infty} dt \int_0^{\infty} r p(t) F(r, t) dr}, \quad (2)$$

where the nonlinear transmission T is given by Eq. (1). The spatial intensity distribution resulting from the focusing of a trimmed Airy beam can be calculated by using the integral expression provided by Eq. (1) of [18]. As in the case of an open aperture Z-scan trace acquired with a focused Gaussian beam, the variation in the transmission saturates rapidly for increasing values of the NLA [16,21]; therefore an approach based on a simple first-order approximation as proposed in [18] can be inadequate in the case of high-order nonlinear processes and/or of large absorptions. In particular, it can lead to a significant underestimation of α_n . Furthermore, it is worth noting that the time-averaged transmission of Eq. (2) depends on the pulse shape, and the time integral with the correct shape of the laser pulse has to be evaluated. We assumed $p(t) = \text{sech}^2(t/\tau)$ in this analysis.

In the case of a trimmed Airy beam structure, the time-averaged transmission given by Eq. (2) must be evaluated numerically. The behavior of $\langle T_{\text{open}}(z/z_d) \rangle$ (z_d is the beam diffraction length [18]) for a trimmed Airy beam is shown in Fig. 3 in the case of three-photon absorption, and for several values of the product $\alpha_3 I_0^2 L$. When the incident

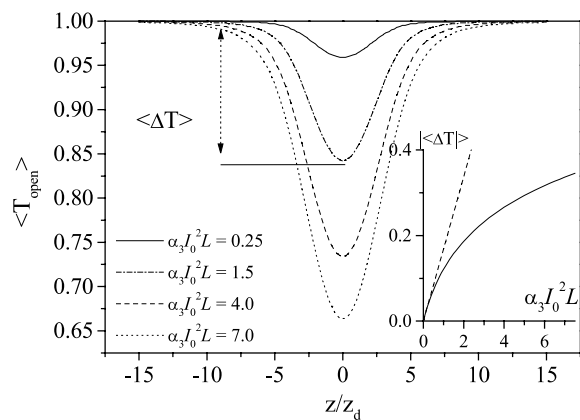


Fig. 3. Time-averaged transmission $\langle T_{\text{open}}(z/z_d) \rangle$ in the case of three-photon absorption for several values of the product $\alpha_3 I_0^2 L$. The inset shows the deviation of the transmission minimum $\langle \Delta T \rangle$ from the level $\langle T_{\text{open}} \rangle = 1$ for increasing values of $\alpha_3 I_0^2 L$.

intensity increases, the minimum in the transmission profile becomes broader and tends to saturate. This behavior is exemplified in the inset of Fig. 3, showing the deviation of the transmission minimum $\langle \Delta T \rangle$ from the level $\langle T_{\text{open}} \rangle = 1$ for increasing values of $\alpha_3 I_0^2 L$. We notice that, even for relatively small values of $\langle \Delta T \rangle$, there is a significant deviation from the linear dependence on $\alpha_3 I_0^2 L$ predicted by substituting the first-order approximation of Eq. (1) (namely, $T_{3\text{ph}}(I_0) \approx 1 - \alpha_3 L I_0^2$) in the expression for the Z-scan transmission. It can be shown that the deviation becomes even more pronounced when the order of the nonlinearity increases and confirms that, in general, to obtain an accurate determination of the value of α_n from the fitting of transmission traces featuring high values of $\langle \Delta T \rangle$, the exact expression for T_{nph} has to be inserted in Eq. (2).

4. Experimental results and discussion

Fig. 4 shows the measured absorption coefficient of a 50 g/l polymer solution in toluene versus the intensity, obtained at 1064 nm. The dependence of the experimental data on I is quadratic

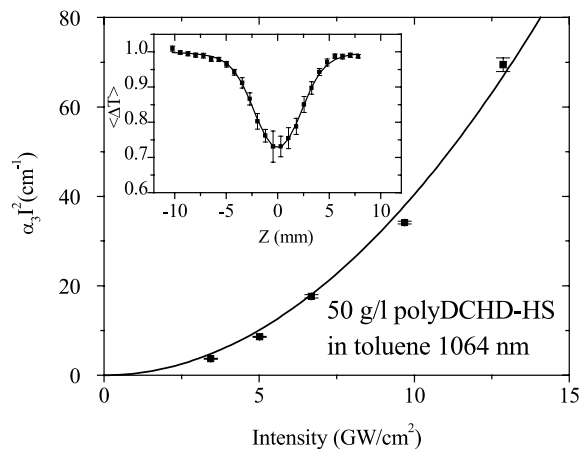


Fig. 4. Absorption coefficient versus incident intensity for a 50 g/l solution of polyDCHD-HS in toluene at 1064 nm. Inset: open aperture Z-scan trace (solid squares) and best fit (solid line) obtained at 1064 nm from a 18.5 g/l polyDCHD-HS solution in toluene with $9.3 \pm 0.4 \mu\text{J}$ incident pulse energy. Sample length was 1 mm.

(continuous line): the same behavior was obtained with benzene solutions, at any concentrations and at both wavelengths and corresponds to a pure three-photon absorption process. This point is confirmed by the inset of Fig. 4, which reports a typical open aperture Z-scan experimental trace (squares) obtained at 1064 nm with a 18.5 g/l polymer solution in toluene. For a correct best fit (continuous line), a fifth-order absorptive nonlinearity had to be considered.

Since we did not observe any two-photon absorption within the explored intensity range and the linear absorption coefficient of polyDCHD-HS solutions was negligible at both wavelengths [12], we determined the three-photon absorption coefficient α_3 of each solution by using Eq. (1) with $n = 3$. In particular, the best fit of the experimental data shown in Fig. 4 gave $\alpha_3 = (4.0 \pm 0.35) \times 10^{-19} \text{ cm}^3/\text{W}^2$. Once α_3 of the solution is determined, the molecular three-photon absorption coefficient σ_3 of the solute can be inferred by using the relation $\alpha_3 = \sigma_3 N_A C \times 10^{-3}$, where N_A is Avogadro's number and C is the solute concentration (referred to the repeat unit) in mol/l [7]. An example of the concentration dependence of α_3 of polymer solutions at 1064 nm is reported in Fig. 5 for the cases of toluene and benzene (inset).

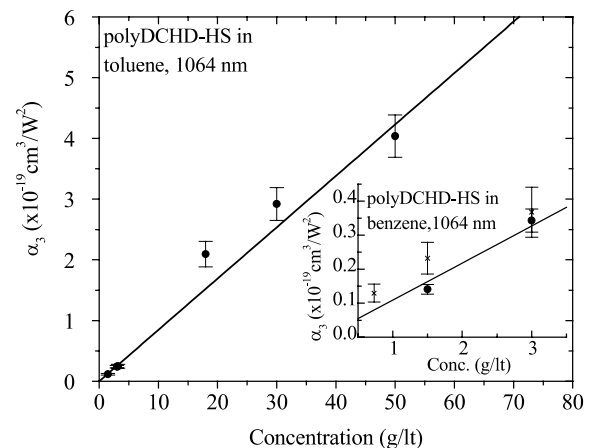


Fig. 5. Three photon absorption coefficient versus concentration for polyDCHD-HS solutions at 1064 nm in toluene and benzene (inset). Circles: 1-mm-long samples; crosses: 4-mm-long samples. The straight lines represent the theoretical best fits to the experimental points.

Continuous lines represent the linear best fits of the experimental data. The values of σ_3 resulting from the slopes of Fig. 5 are $\sigma_3 = (1.8 \pm 0.2) \times 10^{-38} \text{ cm}^6/\text{W}^2$ and $\sigma_3 = (2.3 \pm 0.3) \times 10^{-38} \text{ cm}^6/\text{W}^2$ for toluene and benzene solutions, respectively, while we obtained $\sigma_3 = (1.5 \pm 0.2) \times 10^{-39} \text{ cm}^6/\text{W}^2$ at 1500 nm. These results are summarized in Table 1.

As mentioned previously, the presence of a refractive nonlinearity (resulting either from the solvent or from the solute) can affect the determination of NLA in open-aperture Z-scan measurements [17]. This is due to the fact that, with a positive value of n_2 , self-focusing reduces the diffraction of the beam across the sample, increasing its intensity at the sample end, and possibly leading to an overestimation of NLA. Such a perturbation is not described by the theory outlined in the previous section, which disregards the propagation effects across the sample length. Indeed, the data reported in the inset of Fig. 5 show that the experimental points obtained with 4-mm-long samples (crosses) are systematically above the best fit line. To avoid this type of cross-talk effect, the sample length should be much smaller than the so-called *self-focusing length* $z_{SF} = \sqrt{(nw_0^2/4I_0n_2)}$ which, in the absence of other nonlinearities, is an estimate of the distance that the beam can travel before collapsing due to the Kerr effect [17]. In our experimental conditions, and at the highest incident intensities, $z_{SF} \approx 2 \text{ mm}$ at 1064 nm and $z_{SF} \approx 1.5 \text{ mm}$ at 1500 nm. A numerical simulation of our experiments, by means of the so-called Beam Propagation Method, based on split-step propagation using the Fourier transform [21,22] and adapted to describe the 3-photon absorption showed that, for the 1-mm long samples, the influence of NLR on the assessment of NLA is rather modest. For instance, in the least favorable experimental conditions, the interference from NLR increases the apparent value of α_3 retrieved from the transmission minimum by about 8% and

11% at 1064 and 1500 nm, respectively. The perturbation becomes more important when longer samples are used: for example, with a 4-mm-long sample having a concentration of 3 g/l in benzene, $\alpha_3 = 2.3 \times 10^{-20} \text{ cm}^3/\text{W}^2$ and an input intensity $I_0 = 9 \text{ GW}/\text{cm}^2$, the same simulation showed that NLR increased the apparent value of α_3 of about 28%. These overestimates were included in the error bars of Fig. 5.

We also performed Z-scan measurements with monomer solutions at 1064 nm, because this radiation is 3-photon resonant with the UV band around 350 nm exhibited by polymer and monomer solutions, as well (Fig. 1). This UV band is associated with carbazolyl side groups and has a structure and position that do not vary with solvent. For this purpose, 3 g/l DCHD-HS toluene and benzene solutions were measured at 1064 nm in 2-mm-thick quartz cuvettes. No NLA was observed up to an incident intensity of $26 \text{ GW}/\text{cm}^2$, at least within our experimental sensitivity, that corresponded to $\approx 1\%$ variations of sample transmission. This result put an upper limit to the 3-photon absorption coefficient of the monomer which, if anything, at 1064 nm is at least 15 times smaller than that of the polymer.

The occurrence of high-order NLA makes polyDCHD-HS interesting as an optical limiter in the near infrared range. In particular, the possibility of achieving an optical limiting action at 1064 nm from polyDCHD-HS in toluene solutions is exemplified in Fig. 6, which shows the experimentally observed amount of energy transmitted by a 1-mm-thick 50 g/l solution, for increasing incident laser pulse energy. The focusing conditions are those of the Z-scan measurements. The straight line corresponds to the linear transmission, whereas the dashed line is the actual transmitted energy with a 3-photon absorption coefficient $\alpha_3 = 4.0 \times 10^{-19} \text{ cm}^3/\text{W}^2$.

In all our experiments, the observed nonlinear response started around $2 \text{ GW}/\text{cm}^2$, no two-photon absorption was detected, the dependence of absorption on intensity was purely quadratic and the magnitude of σ_3 at 1064 nm was 10 times larger than at 1500 nm. However, our measurements performed with monomer solutions demonstrated that the large value of σ_3 at 1064 nm cannot be

Table 1
Molecular 3-photon absorption cross-sections

Wavelength (nm)	Solvent	σ_3 (cm^6/W^2)
1064	Toluene	$1.8 \pm 0.2 \times 10^{-38}$
1064	Benzene	$2.3 \pm 0.3 \times 10^{-38}$
1500	Toluene	$1.5 \pm 0.2 \times 10^{-39}$

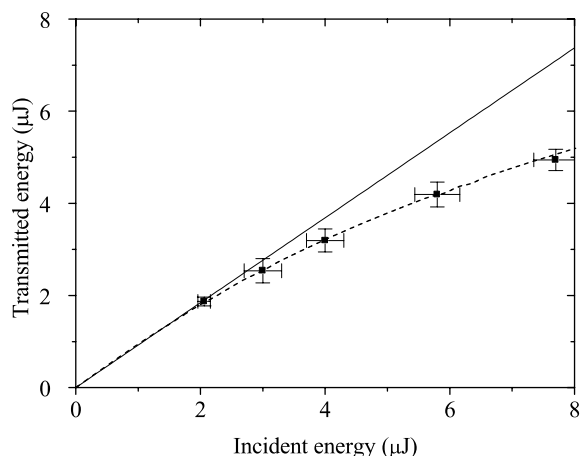


Fig. 6. Optical limiting in the energy transmission from a 1-mm-thick cuvette containing a 50 g/l solution of polyDCHD-HS in toluene (dashed line and solid squares). The continuous line represent the linear transmission. The focusing conditions are the same as those used in the Z-scan experiments.

attributed simply to a contribution of side groups, but is somehow mediated and enhanced by the polymeric backbone. The observed behavior was not unexpected at 1500 nm, where the exciting wavelength is three-photon resonant with the excitonic transition around 540 nm (Fig. 1) and the two-photon resonance is quite far [13,14]. In contrast, at 1064 nm, we would have expected also a two-photon contribution to the NLA. Indeed, at this wavelength, red PDAs typically exhibit a large two-photon absorption [5,14,23] with subsequent onset of fifth- and seventh-order nonlinearities for pump intensities larger than 1 GW/cm^2 [8,23]. These higher-order processes are generally attributed to the population of excited states and the nonlinear polarization resulting from the generation of excited species. A fifth-order contribution to NLA was also observed at 1064 nm by Pender et al. [24] in channel waveguides of the blue PDA 3BCM.U. In that case, due to the negative sign of the α_3 coefficient, the effect was attributed to a bleaching of the 2-photon state at high intensities ($\geq 1 \text{ GW/cm}^2$). In our experiments, the large 3-photon absorption of polymer solutions observed at 1064 nm might be the result of a 2-step process due to a 1-photon absorption by 2-photon-excited states [25], or of a direct 3-photon absorption enhanced by a two photon resonance [26]. Lastly, we

observed only a slight difference in the NLA of polyDCHD-HS in toluene or benzene: the value of σ_3 at 1064 nm is smaller for toluene, but the difference from benzene is barely larger than the experimental errors. This was in contrast with the considerable differences in fluorescence and absorption spectra of polyDCHD-HS in different solvents [20], that might have suggested a larger difference in the NLA properties [14], as well.

5. Conclusions

We measured the NLA of polyDCHD-HS solutions at 1064 and 1500 nm, by using Z-scan and ps pulses. We used different solvents (toluene and benzene) and concentrations. Three-photon absorption was the dominant nonlinear mechanism at both wavelengths, with no evidence of two-photon absorption within the intensity range adopted in the experiments. The molecular three-photon absorption cross-section σ_3 of polyDCHD-HS at 1064 nm was the same as the one reported in [7] for solutions of 2,5-benzothiazole 3,4-didecyl-oxy thiophene – an organic compound with optical limiting characteristics in the near infrared and in [8] for poly4BCM.U. At 1500 nm, σ_3 was almost one order of magnitude smaller. At this latter wavelength, a rough extrapolation to the solid state (corresponding to a concentration of $\approx 0.7 \text{ mol/l}$ referred to the repeat unit) gave $\alpha_3 \approx 7 \times 10^{-18} \text{ cm}^3/\text{W}^2$, which is a value of the same order as the one measured for the reference polydiacetylene PTS at 1530 nm [5].

As a matter of fact, any extrapolation from solution to the solid state is not fully reliable. Direct measurements in bulk and, possibly, by using configurations as close as possible to those expected in real devices would be of interest [24]. However, in this respect, Z-scan could be more reliable than measurements in a waveguide configuration, because the technique is free from the uncertainties originating from the often poor knowledge of the coupling efficiency of light into the waveguide and of its intensity-dependence. For this purpose, we also performed some preliminary tests on polyDCHD-HS films having a thickness of 1–2 μm and obtained by spin coating on glass

substrates. However, the poor optical quality of the samples (i.e. thickness uniformity and scattering level) hampered the determination of the multiphoton absorption coefficient. This was not completely unexpected. Indeed, with a value of α_3 of the order of $10^{-17} \text{ cm}^3/\text{W}^2$ (as extrapolated for the solid at 1064 nm), the maximum thickness achievable with spin coating ($2 \mu\text{m}$) and an incident intensity of $13 \text{ GW}/\text{cm}^2$ (corresponding to the largest value used with solutions), $\alpha_3 I_0^2 L \approx 0.34$, that corresponds to a transmission variation $\langle \Delta T \rangle$ of about 5% (see Fig. 3). This is of the same order as the sensitivity limit obtained in the experiments with films. Consequently, a reliable determination of the multiphoton absorption coefficients in the solid state, with our experimental set-up, is bounded to the possibility of fabricating thick films having a better optical quality. Our activity is in progress on this subject.

We performed our experiments with a trimmed Airy beam configuration. We have shown theoretically and observed experimentally in the case of three-photon absorption that the first-order approximation of the sample transmission presented in [18] is not sufficient for a correct data analysis. It would lead to a significant underestimation of α_3 and would introduce an artificial saturating behavior with increasing $\alpha_3 I_0^2 L$. Moreover, our experiments showed that, in both cases of multiphoton absorption processes and/or co-existence of NLR and NLA, the interpretation of Z-scan data can be misleading if the experimental geometry and the incident intensity levels are not carefully tailored in advance. The latter point is particularly important when, as is the case of polyDCHD-HS, the NLA of a solute dispersed in a solvent having a rather large NLR, has to be determined.

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