Non-Resonant *z*-Scan Characterization of the Third-Order Nonlinear Optical Properties of Conjugated Poly(thiophene azines)

Alessandro Faccinetto,[a] Simone Mazzucato,[a] Danilo Pedron,[a] Renato Bozio,*[a] Silvia Destri,*[b] and William Porzio[b]

The nonlinear optical properties of a functionalized poly(thiophene azine), namely, poly(3,4-didodecylthiophene azine), PAZ, at the optical telecommunication wavelength of 1550 nm are investigated by means of the closed-aperture z-scan technique in both thin films and solutions. Values of $\chi^{(3)} = (2.4 \pm 0.4) \times 10^{-13}$ esu, $n_2 = (4.0 \pm 0.7) \times 10^{-15}$ cm^{2}W^{-1}, and $\gamma = (4.5 \pm 0.7) \times 10^{-34}$ esu are estimated for the third-order (Kerr) susceptibility, the intensity-dependent refractive index, and the molecular second hyperpolarizability of solution samples, respectively. A very small dependence on the polymer chain length is found. Markedly higher values of $(4.4 \pm 1.1) \times 10^{-11}$ esu, $(6.6 \pm 1.0) \times 10^{-13}$ cm^{2}W^{-1}, and $(5.0 \pm 0.8) \times 10^{-33}$ esu are measured for the corresponding quantities in thick (up to 20 μm) polymer films cast on quartz plates. The enhancement of the NLO responses on going from solution to solid samples is attributed to a partially ordered structure and to the presence of interchain interactions leading to greater π-electron delocalization in the cast polymer films. The results are compared with those previously obtained by using third-harmonic generation (THG), taking into account that those data were measured under conditions of three-photon resonance, whereas our z-scan measurements are fully off-resonance.

1. Introduction

Because of their possible use in many optoelectronic applications, organic polymers, and in particular conjugated polymers, have been widely investigated in recent years.[1,2] They can be designed to display properties similar to those of conventional semiconducting materials, which makes it possible to fabricate organic light sources, such as organic light-emitting diodes (OLEDs) and laser diodes,[3] photovoltaic cells,[4,5] and thin-film transistors.[6,7] In the field of nonlinear optics, conjugated polymers are of interest for potential applications in all-optical devices such as optical switches, modulators, and active waveguides[8] due to their very large molecular hyperpolarizabilities and ultrafast responses. In turn, these properties originate from the strong delocalization of the π-electronic system that is a distinctive feature of conjugated organic polymers.

Conjugated organic polymers have alternating single and double bonds. Specifically, in the class of polymers considered here, the polyazines, HC=N linkages are followed by N–N bonds,[9] and they are characterized by strong electron delocalization, spread virtually over the entire molecule through the π bonds. It is this property that allows them to respond almost instantaneously to ultrafast optical stimuli. Moreover, the high values of molecular polarizability and hyperpolarizability lead to nonresonant nonlinear third-order susceptibility values of up to 10^{-11} esu or even higher.[10] This requirement is essential in order to develop compact optical waveguides in the telecommunication wavelength regions of 1300 and 1550 nm.

Finally, a further advantage is the possibility to deposit these polymers on flexible substrates by using inexpensive and environmentally friendly techniques such as casting and spin coating.[11] The fabrication of cost-competitive, high-technology, integrated nonlinear optical (NLO) devices relies on the development of new polymer materials.

Here, we describe the characterization of the third-order NLO properties of a poly(thiophene azine) displaying rapid film-forming capability[9] and envisage its potential use in all-optical devices.

Relatively compact devices can be obtained using materials with high NLO responses. This property must be present in solid-state devices to fulfill technological application requirements, for example, thin films for optical waveguides. However, the first step in characterizing such materials is to investigate them in solution. Working with solutions is easier, as the sample is isotropic and the system can dissipate heat more efficiently. In the solid state, samples of very good optical quality are required to avoid position-dependent results.

Since the NLO properties of a material may result from different contributions (depending, in particular, on whether the experiment is carried out under resonant or nonresonant conditions[12]), the obtained $\chi^{(3)}$ value is expected to depend on the employed measurement technique. In this context, we car-

[a] Dr. A. Faccinetto, Dr. S. Mazzucato, Prof. D. Pedron, Prof. R. Bozio
Dipartimento di Scienze Chimiche e Unità di Ricerca INSTM di Padova
Università di Padova, via Marzolo 1, 35131 Padova (Italy)
Fax: (+39) 049 827 5681
E-mail: renato.bozio@unipd.it

[b] Dr. S. Destri, Dr. W. Porzio
Istituto per lo Studio delle Macromolecole del C.N.R.
via E. Bassini 15, 20133 Milano (Italy)
Fax: (+39) 02 70636400
E-mail: s.destri@ismac.cnr.it

ried out closed-aperture *z*-scan measurements and compared the results with those previously obtained by using third-harmonic generation (THG).[13]

The $\chi^{(3)}$ values measured by means of THG may turn out to be markedly higher in the presence of three-photon resonance between an electronic transition of the material and the experimental exciting wavelength. This happened in our case, in which the excitation wavelength at 1550 nm (0.80 eV) corresponds to a three-photon resonance with the material absorption peak at 512 nm (2.42 eV). In contrast, the $\chi^{(3)}$ contribution to the measured *z*-scan data is only influenced by one- or two-photon resonances. Contributions from three-photon resonances occur only at the fifth order and would result in an intensity dependence of nonlinear refraction and nonlinear absorption parameters estimated under the assumption that they stem from an effective $\chi^{(3)}$ response.

2. Optical Properties

Recent experimental measurements on conjugated polymers confirmed the presence of interesting third-order NLO properties. In contrast to second-order materials, few design principles and guidelines are available to optimize the optical response of third-order materials. There are no symmetry restrictions, and the instantaneous motion of the π electrons inside the molecule determines the strength of this response. For conjugated systems, as a general rule, the larger the conjugation length along the main polymer chain, the more intense the third-order nonlinear response, and the nonlinear refractive index exhibits a power-law dependence.[14,15] Of course, this implies, as a necessary (but not sufficient) condition, that the polymer have long, regioregular chains.

Conjugated poly(thiophene azines) recently gained importance for their promising features related to high NLO coefficients, absence of absorbance in the near-IR region, high threshold for optical damage, ultrafast optical response, and relatively easy synthesis.[16] In particular, C. Amari et al.[17] reported the synthesis and characterization of poly(3,4-didodecylthiophene azine), PAZ, having the structure shown in Figure 1, where *m* varies from 20 to 300.

Figure 2 shows the UV/Vis/NIR (NIR = near infrared) absorbance spectra of PAZ in solution in a film—about 0.88 µm thick—deposited by means of spin coating from a chloroform solution and another film of comparable thickness deposited by casting from chlorobenzene. An amorphous quartz slab was used as substrate for both films. The main π–π* transition band peaks at around 500–530 nm (depending on the
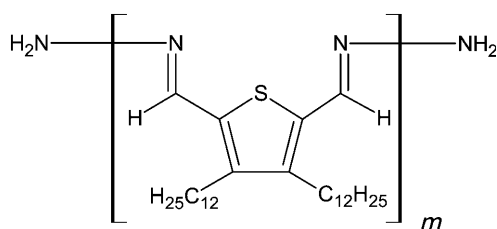
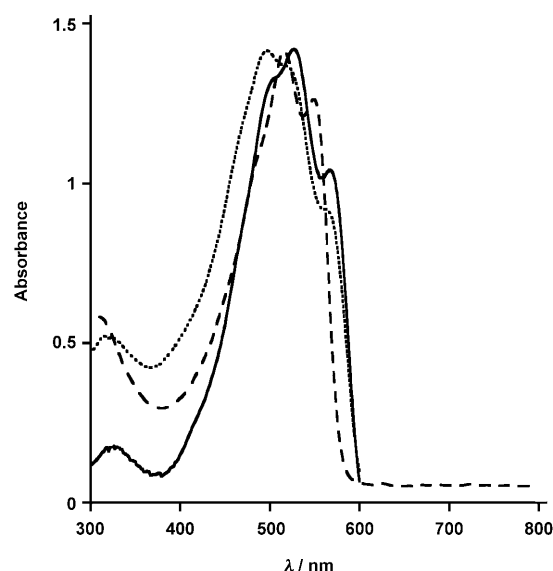**Figure 1.** Chemical structure of poly(3,4-didodecylthiophene azine), PAZ.

Figure 2. Normalized UV/Vis/NIR absorbance spectra of PAZ in solution (‑‑‑‑), in a spin-coated film from chloroform (•••••), and in a cast film from chlorobenzene (——).

sample), and the absorbance falls rapidly to zero above 600 nm in all the spectra, so that the samples are completely transparent in the near-IR region, that is, the spectral range of interest for telecommunications.

There are noteworthy differences between the spectra of the solution and those of the solid-film samples. The solution spectrum exhibits two peaks, with the strongest one at 510 nm and a secondary maximum at 550 nm. The absorption spectra of the films are shifted to longer wavelengths by about 20 nm and exhibit three peaks. In the spin-coated film the absorption band is broader and the strongest peak is at 495 nm with secondary maxima at 525 and 570 nm. In the cast film the peak at intermediate wavelength is the strongest and the drop to negligible absorbance above 600 nm is markedly sharper than in the spin-coated film. As a result, the centroid of the absorption band of the cast film is at longer wavelength than that of the spin-coated film.

Herein, closed-aperture *z*-scan experiments were performed by using an optical parametric amplifier pumped by a Ti:sapphire regenerative amplifier, emitting approximately 160 fs long laser pulses at the excitation wavelength of 1548 nm with 1 kHz repetition rate. The laser beam was focused with a lens of 20 cm focal length onto the sample, which was either contained in a 1 mm-thick quartz cell (solution) or deposited onto a quartz slab (film). Neutral-density filters permitted the input irradiance to be varied from 5 to 50 GW cm^{-2}. The transmitted intensity was recorded in the near field through a 0.21 aperture transmittance with sample translated along the beam axis *z* by using a 20 cm-long translational stage, according to our *z*-scan setup.[18]

The use of femtosecond laser pulses guarantees that there is not enough time for the molecule to orientate according to the input field, and hence no orientational effects contribute to the final value measured for solution samples. Furthermore,

such a short pulse width, combined with the low repetition rate, limits thermal effects in the sample. In this way it is possible to determine just the electronic contribution to the nonlinear refractive index, which is related to $\chi^{(3)}(\omega;\omega,\omega,-\omega)$.[19]

Initial characterization of the NLO properties of PAZ by using the THG technique[13] on thin films (30–70 nm thick) deposited on amorphous quartz substrate gave a value of $\chi^{(3)}(3\omega;\omega,\omega,\omega) = 5\times10^{-11}$ esu[8] at an excitation wavelength of 1550 nm. Since $1550/3 \approx 517$ nm, that is, very close to the maximum absorbance of the sample (512 nm in $CHCl_3$ solution and 530 nm in ordered solid state), this measurement was certainly affected by three-photon resonance. This contribution was considered in the data analysis.

As mentioned before, the two optical susceptibilities $\chi^{(3)}(3\omega;\omega,\omega,\omega)$ and $\chi^{(3)}(\omega;\omega,\omega,-\omega)$ obtained by THG and z-scan are not necessarily expected to be the same, due to the presence of various resonance contributions in the relation between the elements of the third-order susceptibility tensor and the optical field frequency. In particular, the definition of $\chi^{(3)}(\omega;\omega,\omega,-\omega)$[19] includes only one- and two-photon resonances, but these do not make any contributions for our sample, which absorbs neither at 1550 nm nor at $1550/2 = 775$ nm.

3. Experimental Techniques: A Comparison

Starting from simple transmittance measurements, the z-scan technique[20,21] allows the magnitude of any odd-order NLO effect to be determined independent of the underlying microscopic mechanism. By assuming a pure electronic nonlinearity of the refractive index, a closed-aperture z-scan measurement can provide the value of $\chi^{(3)}(\omega;\omega,\omega,-\omega)$. Possible contributions arising for higher order susceptibilities can be singled out by investigating the power dependence of the z-scan data.

z-Scan measurements performed in the two possible configurations, closed-aperture and open-aperture, have the advantage of providing the real and imaginary parts of the third-order susceptibility, respectively. They can also be used to find both the amplitude and the sign of n_2 and, ultimately, it is an easy-setup technique which presents no particular alignment difficulty.

As a counterpart to these advantages, this technique has a stringent need to operate with high-quality Gaussian beams[1] and requires high input power densities and often long interaction lengths. This leads to some experimental restrictions for thin polymer films, because of possible sample damage resulting in burnt spots on its surface. Narrow pulse width and low repetition rate, combined with sufficiently low input peak irradiance, are ideal parameters for avoiding such risks.[22]

In THG, once the sample is irradiated with a monochromatic optical beam at frequency ω, a beam at frequency 3ω and one at frequency ω, both dependent on the third-order polarization, are generated. These two signals interfere inside the material to produce the so-called Maker fringes when the sample is rotated.[23] From this figure the value of $\chi^{(3)}(3\omega;\omega,\omega,\omega)$ can be

obtained. Since THG is not based on perturbation of the optical-beam propagation, it is not influenced by all physical mechanisms that can modify the refractive index, such as molecular orientational and/or thermal effects. Therefore, it accounts only for the instantaneous electronic contributions.[24] Finally, this technique requires low input beam intensities and thus avoids optical damage.

Unfortunately, THG has the enormous disadvantage of being an experimentally difficult technique to set up, as all media present in the beam path between the light source and the sample (air included) contribute to the resulting NLO effect.[25,26] Contributions of five media for solutions (two air media, the two optical windows of the cell, and the liquid), and of four media for polymer films (two air media, the substrate supporting the film, and the film itself) must be taken into account. Predicting and then removing these additional spurious signals is not easy, and different methods have been proposed to handle this situation.[13,27]

Additional problems in THG arise when working with films. For a thin film deposited on a substrate, the acquired signal depends on which side is nearest the detector. Variations in the value of $\chi^{(3)}$ are possible by choosing one side or the other, often due to inaccurate positioning of the sample due to its not being parallel to the direction of the optical polarization or its rotation axis not being centered at the focus of the incident beam.[28] A full study on both sides is therefore essential.[29] In common with the z-scan method, nonuniformities in the sample thickness create further problems in determining an unambiguous value of $\chi^{(3)}$.

4. Investigated Samples

Here, we investigate two different samples of poly(3,4-didodecylthiophene azine), differing in the average number of monomer units m in the main chain (see Figure 1). The repeat unit has formula mass $M = 4.728\times10^2$ g mol^{-1}. The first sample, denoted PAZ1, is composed of 45 units and has number-average molecular weight M_n of 2.14×10^4 g mol^{-1} and a polydispersity of 1.86, while the second, hereafter PAZ2, has a longer chain ($m = 253$) and $M_n = 1.196\times10^5$ g mol^{-1} with a polydispersity of 1.41.

5. Experimental Results

We analyzed solutions of PAZ1 (0.22 M) and PAZ2 (0.18 M) in chlorobenzene, and various films of PAZ1 deposited on an amorphous quartz slab by casting or spin coating, with thicknesses varying from 3 to 20 μm. The film thickness is an important parameter to be considered when performing z-scan measurements, as it affects the quality and magnitude of the z-scan signal. Considering our experimental setup, we estimated a minimum thickness of 0.9 μm to obtain a reckonable signal. All investigated films satisfied this condition.

In the solution phase, the choice of solvent is determined by the need for a high sample concentration, on the order of 10^{-2}–10^{-3} M, to give a detectable z-scan signal. The NLO response of the solvent, which must not influence that of the

---

1 *R. Bridged et al. were able to remove this limitation: R. Bridged, G. Fisher, B. Boyd, Opt. Lett.* **1995**, *20, 1821.*

material under study, was primarily considered. Our scans were limited to the irradiance range in which the background NLO response (quartz cell and solvent) was negligible. Furthermore, the use of femtosecond laser pulses at low repetition rate guarantees that thermal effects are absent and the results account just for the electronic contribution to $\chi^{(3)}$.[19] Note that pure thermal effect would in fact account for negative values of n_2, contrary to what we found (see below).

Figure 3 shows some z-scan traces for the PAZ1 solution. The peak-to-valley amplitude increases on increasing the input irradiance, but the fact that the peak and valley z positions do not change confirms the goodness of the interpolation model, according to which the z-scan traces should depend only on the beam diffraction length.[20]
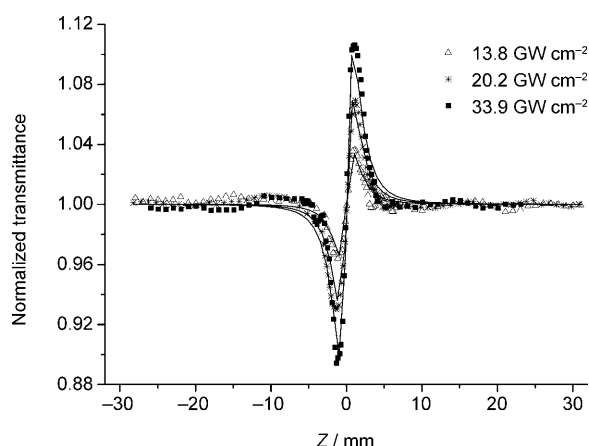

Figure 3. z-Scan closed aperture traces for a PAZ1 solution (0.220 ± 0.004 M) in chlorobenzene at various irradiances. Symbols and continuous lines represent experimental data and fitting curves, respectively.

Data interpolation allows the nonlinear refractive index to be determined for the two solutions and therefrom the third-order susceptibility. The z-scan traces are fitted to Equation (1):[20]

$$T(Z, \Delta\varphi_0) = 1 - \frac{4\Delta\varphi_0 x}{(x^2 + 9)(x^2 + 1)} \tag{1}$$

in which $x = Z/Z_0$, where Z_0 is the beam diffraction length, and $\Delta\varphi_0$ is the nonlinear phase change, which is related to n_2 by Equation (2):[20]

$$\Delta\varphi_0 = k n_2 I_0 L_{\text{eff}} \tag{2}$$

where k, n_2, I_0, and L_{eff} are the wave-vector modulus, the nonlinear refractive index, the peak irradiance, and the optical path in the nonlinear medium, respectively.

As shown in Figure 4, no clear dependence of the nonlinear refractive index on irradiance is observed. In view of the comparison with the THG results, this is an important finding that confirms that the z-scan data for solution samples are not affected by a possible contribution of three-photon resonances; in fact, that contribution would predictably bring about a dependence of the n_2 value on the input irradiance.
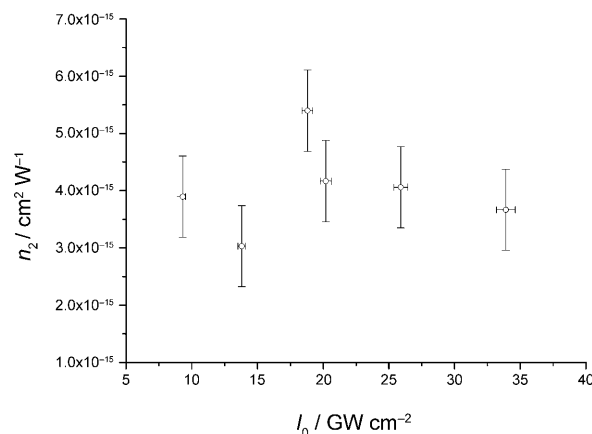

Figure 4. Nonlinear refractive index versus input beam irradiance trend for a 0.22 M PAZ1 solution in chlorobenzene.

The value of the nonlinear susceptibility is derived from the nonlinear refractive index by using the standard relation of Equation (3):[19]

$$\chi^{(3)}(\text{esu}) = \frac{n_0^2 c}{12\pi^2} 10^{-7} n_2 \left(\frac{cm^2}{W}\right) = 25.313 \times n_0^2 \times n_2 \left(\frac{cm^2}{W}\right) \tag{3}$$

where n_0 is the linear refractive index. For solution samples we use the refractive index value of the pure solvent. The resulting off-resonance values of n_2 and $\chi^{(3)}$ obtained for PAZ1 and PAZ2 solutions are listed in Table 1.

Table 1. NLO coefficients measured out of resonance for PAZ1 and PAZ2 solutions.

Sample	c [M][a]	n_2 [cm²W⁻¹]	$\chi^{(3)}$ [esu]
PAZ1	0.220 ± 0.004	$(4.0 \pm 0.7) \times 10^{-15}$	$(2.4 \pm 0.4) \times 10^{-13}$
PAZ2	0.18 ± 0.01	$(3.2 \pm 0.7) \times 10^{-15}$	$(1.9 \pm 0.4) \times 10^{-13}$
[a] Molar concentration.			

Measurements with films present various problematic aspects when compared to the solution case. Two issues, in particular, must be carefully addressed: the first is related to the need for films with high optical quality, as any imperfection and/or inhomogeneity in the sample surface can lead to ambiguous and irreproducible results. Therefore, the first step when acquiring z-scan traces consists of finding an homogeneous area on the sample large enough to contain the entire beam spot, the size of which increases on moving away from the focal plane during the z-scan. To this end, a preliminary analysis of the film surface was made with an optical microscope to identify the target areas for our investigations.

Although the z-scan measurements in the solid state were carried out on eight films of PAZ1, all of different thicknesses, the traces of only three films proved to be reproducible and were used in the subsequent calculations. Films 1 (2.9 ± 0.1 μm thick) and 2 (3.04 ± 0.5 μm thick) were obtained by means of

spin coating and casting, respectively, from chlorobenzene solution (8 mg mL^{-1}). Optimum spin-coated films were obtained by using a spinning rate of 500 rpm and slightly heated substrate. Film 3 was instead obtained by means of casting and had a thickness of 22 ± 1 µm. The thicknesses of films 1 and 2 were determined by using a surface profiler (Stylus Profiler Dektak 8, Veeco), while that of film 3 was estimated from the absorbance spectrum in a region where there was no signal saturation.

Figure 5 shows some z-scan traces for film 1. Again, the normalized signal increases with increasing irradiance, and there is no change in the z position for the peak and the valley.
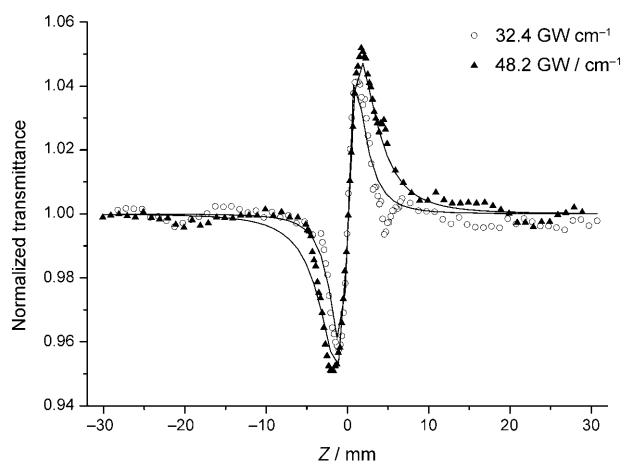

Figure 5. Closed-aperture z-scan traces for PAZ1 film 1 (with a thickness of 2.9 µm) at various irradiances. Symbols and continuous lines represent experimental data and fitting curves, respectively.

The second important issue when measuring reliable z-scan data from polymer films is to choose a suitable window of input pulse energies. The lower limit of this window is set by the need to get acceptable signal-to-noise ratio to allow sufficiently accurate data analysis. The upper pulse-energy limit is set in order to avoid contributions to the signal from the substrate and, even more importantly, to avoid laser damage to the polymer sam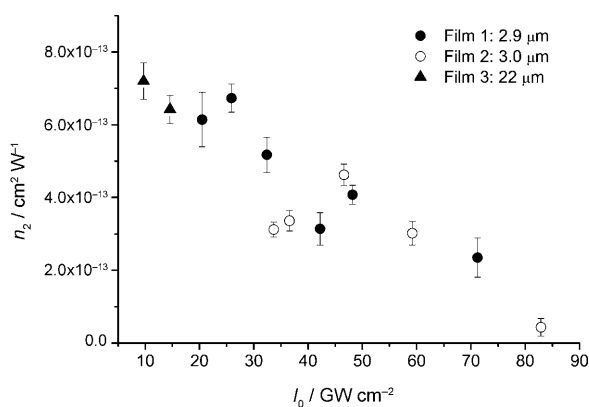ple. As shown by the data in Figure 6, this is a critical issue; the n_2 values estimated from analysis of z-scan data recorded with varying pulse energies exhibit a clear tendency to decrease dramatically as the pulse energy increases. Although an intensity-dependent n_2 could arise from fifth-order contributions to the NLO response, we attribute this behavior to optical damage to the sample. At the end of the z-scan measurements performed at high input pulse energy, films 1 and 2 were investigated by FTIR and UV/Vis spectroscopy. The spectra recorded on the recovered samples showed new bands which were not present before z-scan irradiation, while the maximum of the electronic absorption peak was shifted towards lower wavelengths. Then the samples were washed with methanol. In the worst case, we estimate that around 50% of the sample dissolved, and thin layer chromatography (TLC) analysis showed the appearance of low molecular weight compounds for both samples. The methanol solutions showed dramatically reduced intensity of bands of imine linkages in the FTIR spectra. All these findings indicate significant sample degradation. In view of this, many z-scan traces were discarded since it is reasonable to suppose that they corresponded to the more heavily damaged regions.

However, if the input pulse energy is kept below 26 GW cm^{-2}, reproducible data can be obtained on repeated measurements. Indeed, the n_2 values estimated from analyses of the data for films 1 and 3 in this range of moderate laser energies turned out to be stable (within the estimated experimental error) and substantially independent of the pulse energy. The weighted average value was $n_2 = (6.6 \pm 1.0) \times 10^{-13}$ cm^2 W^{-1}.

To extract a value of the third-order susceptibility from the measured n_2, we need to know the linear refractive index n_0 of the solid polymer in the film samples [see Eq. (3)]. A value of $n_0 = 1.63$ at 1.55 µm was measured for poly(3,4-didodecylthiophene azine) films obtained by spin coating from chloroform solutions.[8] The polymer had a number of repeat units ($m = 32$) and a polydispersity (1.8) quite similar to those of our PAZ1 sample. Using the literature value of $n_0 = 1.63$, we calculated a susceptibility value of $\chi^{(3)} = (4.4 \pm 1.1) \times 10^{-11}$ esu.

6. Discussion and Conclusions

The first aspect to consider in the discussion of our results is the comparison between the values of n_2 and $\chi^{(3)}$ obtained in solution and in the films. These values must not necessarily be the same, as these quantities depend on the material density, N, expressed as the number of molecules per unit volume. Therefore, we compared the data after normalization to the molecular second hyperpolarizability, γ, which is independent from the sample concentration and is defined by Equation (4):

$$\chi^{(3)} = \mathcal{L}^{(3)} N \gamma \tag{4}$$

where $\mathcal{L}^{(3)}$ is the local field correction.[19] In this way, we found a similar value for γ within the same phase, as summarized in Table 2.

Solutions of PAZ1 and PAZ2 show γ values of 4.5×10^{-34} esu, which coincide within the experimental error, independently of

Figure 6. Nonlinear refractive index versus input beam irradiance trend for the three PAZ1 films with different thicknesses.

Table 2. Summary of measured and calculated values of the nonlinear coefficients n_2, $\chi^{(3)}$, and γ for PAZ1 and PAZ2 solutions and films.

Sample	Technique	C [mol cm^{-3}]	n_2 [cm^{2}W^{-1}]	$\chi^{(3)}$ [esu]	γ [esu][a]
PAZ1 (solution)	*z*-scan	$(2.2\pm0.04)\times10^{-4}$	$(4.0\pm0.7)\times10^{-15}$	$(2.4\pm0.4)\times10^{-13}$	$(4.5\pm0.7)\times10^{-34}$
PAZ2 (solution)	*z*-scan	$(1.8\pm0.1)\times10^{-4}$	$(3.2\pm0.7)\times10^{-15}$	$(1.9\pm0.4)\times10^{-13}$	$(4.4\pm0.9)\times10^{-34}$
PAZ1 (film)	*z*-scan	$(2.52\pm0.02)\times10^{-3}$[b]	$(6.6\pm1.0)\times10^{-13}$	$(4.4\pm1.1)\times10^{-11}$	$(5.0\pm0.8)\times10^{-33}$
PAZ1 (film)	THG[8]	–	–	$(5.4\pm0.05)\times10^{-11}$	$(5.5\pm0.05)\times10^{-33}$[c]

[a] To calculate γ, it was necessary to know the material linear refractive indices at frequencies of ω and 3ω. The refractive index of chlorobenzene was used for the solutions, whereas for the films we used the values of 1.63 and 1.78 measured at 1.55 and 0.53 µm, respectively.[8] [b] Molar concentration based on a polymer film density of 1.2 g cm^{-3}. This value is common to most polymer materials with fluctuations of typically $\pm3\%$, well within the overall experimental error in the values of the nonlinear responses. [c] Calculated by assuming the same material density for our sample and for that investigated in ref. [8].

the chain length. This finding provides further evidence of the expected saturation of the material's optical properties when the polymer length exceeds an effective electronic conjugation length. The polymer length of our samples (45 monomer units) is well above the conjugation length generally accepted for conjugated polymers.[30]

On the other hand, the value obtained for the film (5.0×10^{-33} esu) is markedly higher than those of the solution samples. It is comparable to that of 5.5×10^{-33} esu deduced from the measured THG susceptibility, despite the fact that the latter is enhanced by three-photon resonance.

One plausible explanation for the fact that $\gamma(\omega;\omega,-\omega,\omega)$ obtained in solution is markedly smaller than $\gamma(3\omega;\omega,\omega,\omega)$ might be that the former parameter is measured by *z*-scan under off-resonance conditions, whereas the latter one is derived from THG data measured in full three-photon resonance. A one-order-of-magnitude difference between resonant and nonresonant values of $\chi^{(3)}$ was also observed for polythiophenes structurally similar to poly(3,4-didodecylthiophene azine).[12] However, the values of γ and $\chi^{(3)}$ obtained by *z*-scan for the film samples are comparable to those obtained by means of THG. This is in apparent contradiction with what is expected because of the presence of resonances.

Note that the molecular nonlinear response, γ, of PAZ1 in the film is strikingly larger than that in solution, despite the fact that both values were obtained by using the same *z*-scan technique and care was taken to avoid laser damage or any other modification of the samples. The significance of this comparison depends on the accuracy of our knowledge of the number density of the active species and of the linear refractive index of the materials. For the latter data, we rely on measurements[8] performed by variable-angle spectroscopic el-

lipsometry on spin-coated films of poly(3,4-didodecylthiophene azine) with properties quite similar to those of our PAZ1 samples.

Note also that strong intermolecular interactions and the onset of intermolecular coherence of the electronic excited states may dramatically modify the nonlinear responses[18] and, strictly speaking, void altogether the concept of molecular hyperpolarizability. In the solid state, the interactions related to intermolecular excitons and/or charge transfer can lead to a higher electronic delocalization, with a consequent increase of linear and nonlinear polarizabilities. Indeed, the second hyperpolarizability in films is higher than in solution, which represents the case of randomly disordered noninteracting molecules. It is well known that polymer chains organize to different degrees in the solid state, depending on the technique used to prepare samples suitable for different types of measurements. For THG, very thin films (thickness in the range 70–100 nm)[8] are employed, while *z*-scan measurements require thicker samples (on the order of several micrometers), which must be prepared from a high-boiling solvent. In the film spun from dilute chloroform solution, as used in the THG technique, macromolecules stay on the substrate plane with poor organization and orientation, while in thicker *z*-scan films they can self-organize into crystallites during chlorobenzene evaporation, irrespective of the deposition technique. Such organization, is proved by XRD measurements (Figure 7a) on films of PAZ1 cast from chlorobenzene solution (thickness ca. 2 µm) carried out in the Bragg–Brentano geometry (specular diffraction), in contrast to thin films obtained by spin coating
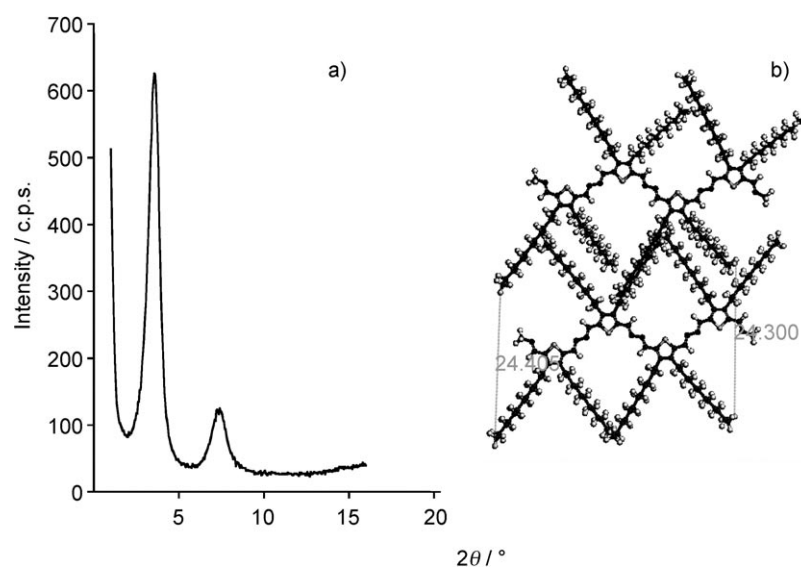

Figure 7. a) XRD spectrum of a cast film of PAZ1 on silica, deposited from a chlorobenzene solution (thickness: ca. 2 µm). b) Structural model consistent with the XRD spectrum.

(<100 nm thick), which appeared completely amorphous by XRD analysis.

XRD spectra indicate the presence of a long spacing (>2.4 nm) due to interchain periodicity. Molecular model calculations with the MATSTUDIO package reveal that this spacing is compatible with an all-*anti* configuration of the main chain and an extended chain conformation of dodecyl side chains (see Figure 7b). Thus, the macromolecules are predominantly edge-on with respect to the substrate and probably closely packed, consistent with the observation of a second-order peak.

Such packing would have a positive effect on the magnitude of the third-order susceptibility for two reasons. First, in the films the long polymer chains lie parallel to the substrate plane. Therefore, averaging of the strongest component of $\chi^{(3)}$ parallel to the chains must be performed in two dimensions only. When compared with solution samples, which are isotropic in all three dimensions, this accounts for the higher value of $\chi^{(3)}$ observed for the film, by a factor of up to (3/8): (1/5) = 1.875. Second, the close-packed arrangement of the polymer chains lying edge-on with respect to the substrate implies that the thiophene rings are parallel to each other, and thus interchain interaction of the π-electron systems is favored. In turn, the stronger electron delocalization enhances the NLO response beyond the value that can be attained by isolated polymer chains in solution. In fact, the centroids of the UV/Vis spectra of spin-coated and cast films are significantly different; the latter is red-shifted by about 20 nm (see Figure 2), in agreement with improved film ordering.

The fact that the $\chi^{(3)}$ and γ values measured by the z-scan and THG techniques are comparable, although three-photon resonance occurs only in the latter case, remains rather intriguing. Focusing on structural and electronic factors, one might be tempted to ascribe this observation to greater intermolecular organization and stronger interchain interactions in the thick films used for the z-scan measurements compared to the thin ones used for THG experiments.

We recently demonstrated that intermolecular (excitonic) interactions can contribute to marked enhancement of NLO responses of J-aggregates of porphyrins.[18,31] On the other hand, recent work on conjugated polymer films experimentally confirmed that different values can be obtained by using z-scan or THG.[32]

In summary, we have studied the third-order NLO properties of poly(3,4-didodecylthiophene azine). Samples in solution, containing polymer chains with different lengths and films with different thicknesses, were analyzed by using the closed-aperture z-scan technique. Upon comparing the $\chi^{(3)}$ and γ values determined using this experimental approach with those previously obtained from THG measurements, we observed an increasing trend in $\chi^{(3)}$ which we have tentatively ascribed to a progressively greater degree of aggregation and orientation and, consequently, of interaction among adjacent polymeric chains.

[1] *Advances in Synthetic Metals: Twenty Years of Progress in Science and Technology* (Eds.: P. Bernier, S. Lefrant; G. Bidab), Elsevier, Amsterdam, **1999**.

[2] T. W. Kelley, P. F. Baude, C. Gerlach, D. E. Ender, D. Muyres, M. A. Haase, D. E. Vogel, S. D. Theiss, *Chem. Mater.* **2004**, *16*, 4413.

[3] C. T. Chen, *Chem. Mater.* **2004**, *16*, 4389.

[4] M. M. Alam, S. A. Jenekhe, *Chem. Mater.* **2004**, *16*, 4647.

[5] K. M. Coakley, M. D. McGehee, *Chem. Mater.* **2004**, *16*, 4533.

[6] M. L. Chabinyc, A. Salleo, *Chem. Mater.* **2004**, *16*, 4509.

[7] M. C. Hamilton, S. Martin, J. Kanicki, *Chem. Mater.* **2004**, *16*, 4699.

[8] a) A. Zaopo, Y. Dubitsky, A. Zappettini, F. D'Amore, S. Destri, W. Porzio, M. Pasini, EP 1 340 793 A1, **2003**; b) S. Destri, M. Pasini, W. Porzio, A. Zappettini, F. D'Amore, *J. Opt. Soc. Am. B* **2007**, *24*, 1505.

[9] S. Destri, M. Pasini, C. Pelizzi, W. Porzio, G. Predieri, C. Vignali, *Macromolecules* **1999**, *32*, 353.

[10] F. D'Amore, A. Zappettini, G. Facchini, S. M. Pietralunga, M. Martinelli, C. Dell'Erba, C. Cuniberti, D. Comoretto, G. Dellepiane, *Synth. Met.* **2002**, *127*, 143.

[11] H. Ma, A. K. Y. Jen, L. R. Dalton, *Adv. Mater.* **2002**, *14*, 1339.

[12] H. S. Nalwa, S. Miyata in *Nonlinear Optics of Organic Molecules and Polymers*, CRC, Boca Raton, **1997**.

[13] G. R. Meredith, B. Buchalter, C. Hanzlik, *J. Chem. Phys.* **1983**, *78*, 1543.

[14] K. C. Rustagi, J. Ducuing, *Opt. Commun.* **1974**, *10*, 258.

[15] H. Kanbara, H. Kobayashi, T. Kaino, N. Ooba, T. Kurihara, *J. Phys. Chem.* **1994**, *98*, 12270.

[16] H. S. Nalwa, T. Hamada, A. Kakuta, A. Mukou, *Synth. Met.* **1993**, *57*, 301.

[17] C. Amari, C. Pelizzi, G. Predieri S. Destri, W. Porzio, *Synth. Met.* **1995**, *72*, 7.

[18] E. Collini, C. Ferrante, R. Bozio, *J. Phys. Chem. B* **2005**, *109*, 2.

[19] R. W. Boyd, *Nonlinear Optics*, Academic Press, Amsterdam, **2003**.

[20] M. Sheik-Bahae, A. A. Said, T. H. Wei, D. J. Hagan, E. W. Van Stryland, *IEEE J. Quantum Electron.* **1990**, *26*, 760.

[21] M. Sheik-Bahae, A. A. Said, E. W. Van Stryland, *Opt. Lett.* **1989**, *14*, 955.

[22] R. de Nalda, R. del Coso, J. Requejo-Isidro, J. Olivares, A. Suarez-Garcia, J. Solis, C. N. Alfonso, *J. Opt. Soc. Am. B* **2002**, *19*, 289.

[23] P. D. Maker; R. W. Terhune, M. Nisenoff, C. M. Savage, *Phys. Rev. Lett.* **1962**, *8*, 21.

[24] P. N. Prasad, D. J. Williams, *Introduction to Nonlinear Optical Effects in Molecules&Polymers*, Wiley, New York, **1991**.

[25] F. Kajzar, J. Messier, *Rev. Sci. Instrum.* **1987**, *58*, 2081.

[26] F. Kajzar, J. Messier, *Phys. Rev. A* **1985**, *32*, 2352.

[27] F. C. Blom, A. Driessen, H. J. W. M. Hoekstra, J. B. P. Van Schoot, Th. J. A. Popma, *Opt. Mater.* **1999**, *12*, 327.

[28] X. H. Wang, D. P. West, N. B. McKeown, T. A. King, *J. Opt. Soc. Am. B* **1998**, *15*, 1895.

[29] J. Jerphagnon, S. K. Kurtz, *J. Appl. Phys.* **1970**, *41*, 1667.

[30] J. Gierschner, J. Cornil, H.-J. Egelhaaf, *Adv. Mater.* **2007**, *19*, 173; H. Meier, U. Stalmach, H. Kolshorn, *Acta Polym.* **1997**, *48*, 379.

[31] E. Collini, C. Ferrante, R. Bozio, A. Lodi, G. Ponterini, *J. Mater. Chem.* **2006**, *16*, 1573.

[32] I. Rau, P. Armatys, P.-A. Chollet, F. Kajzar, R. Zamboni, *Mol. Cryst. Liq. Cryst.* **2006**, *446*, 23.