

Nonlinear optical studies of a newly synthesized copolymer containing oxadiazole and substituted thiophenes

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Abstract

We investigated the third-order nonlinear optical properties of a newly synthesized soluble copolymer containing oxadiazole and thiophene units using Z-scan and Degenerate Four Wave Mixing (DFWM) techniques. The measurements were performed at 532 nm with 7 ns pulses from a Nd:YAG laser. We found a good agreement between the values of $\chi^{(3)}$ determined from both experiments. Z-scan results indicate a negative nonlinear refractive index, n_2 , whose magnitude is of the order of 10^{-10} esu. The copolymer exhibits strong nonlinear absorption and good optical limiting properties at 532 nm, and hence may be a potential material for optical limiting applications.

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1. Introduction

The prospect of using organics as third-order nonlinear optical (NLO) materials for photonic switching and optical limiting applications has been the subject of many investigators during the past decade [1]. Especially, conjugated polymers with alternate single and multiple bonds in their backbone structure have emerged as the most widely studied group of $\chi^{(3)}$ organic materials [2,3]. A strong delocalization of π -electrons has been found to be responsible for high third-order nonlinearities of these conjugated polymers. Among conjugated polymers, polythiophenes are gaining interest as materials for nonlinear optical (NLO) applications since they are soluble, chemically stable, and easily processible [4]. Various authors have

reported measurement of $\chi^{(3)}$ effects in thiophene oligomers and polymers far from the resonant region with different methods like third harmonic generation, Z-scan and DFWM [5–7]. Here we report on our experimental investigation of third-order nonlinear optical properties of a newly synthesized copolymer containing alternating substituted thiophenes and 1,3,4-oxadiazole units. Recently, Casano et al. have reported that the nonlinear optical properties of soluble poly(*p*-phenylenevinylene) derivatives were improved due to the effect of the simultaneous presence of electron-acceptor and electron-donor substituted aromatic rings in the conjugated backbone [8]. A similar strategy was used to synthesize the copolymer under present study, which contains both electron donor (thiophene) and electron acceptor (oxadiazole) units. In order to increase the donating ability, the thiophenes were substituted with alkoxy (OC₂H₅) groups. The alkoxy pendant at 3- and 4-positions of the thiophene ring serves as both solubilizing group as well as strong electron donating

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group. We used single beam *Z*-scan technique to determine n_2 , and the real and the imaginary parts of $\chi^{(3)}$. The copolymer exhibits strong reverse saturable absorption at 532 nm. It shows a very strong optical limiting of nanosecond laser pulses. We also report on the dependence of NLO properties on the concentration of copolymer in dimethylformamide (DMF) solution. The DFM experiment was performed on the sample solution in order to compare the value of $\chi^{(3)}$ with that obtained through *Z*-scan technique.

2. Experiment

The synthesis and linear optical characterization of this copolymer containing oxadiazole and thiophene units is reported elsewhere [9]. Sample solution of concentration 1×10^{-5} mol/L was prepared in DMF. The linear absorption spectrum and the structure of the copolymer are shown in Figs. 1 and 2 respectively. The linear absorption spectrum was recorded with a Varian CARY 500 Spectrophotometer. The linear refractive index (n_0) of the sample was recorded with an Abbe refractometer.

The single beam *Z*-scan [10] and the DFM techniques were used to measure the nonlinear susceptibility of the copolymer. Both *Z*-scan and DFM experiments were performed on the copolymer in order to compare $\chi^{(3)}$ values obtained from two methods. *Z*-scan is a simple experimental technique to evaluate both real and imaginary parts of $\chi^{(3)}$ simultaneously. It is based on self-focusing or self-defocusing of an optical beam by a thin medium. It consists of focusing an optical beam by a single lens to a narrow waist; the sample is positioned near the beam waist, and the transmittance is measured with a detector kept behind an aperture. The sample is moved by using a computer-controlled translation stage, along the direction of beam propagation (*z*-direction), and the transmittance versus sample position with respect to the focal plane is recorded. A plot of this normalized transmittance versus sample position gives the information about the nonlinearities. *Z*-scan allows the simultaneous measurement of nonlinear absorption (NLA) and nonlinear refraction (NLR). However, it does not give information on the temporal evolution of nonresonant nonlinearity. The Q-switched Nd:YAG laser with a pulse width of 7 ns at 532 nm was used as a source of light in the *Z*-scan experiment. The experiment was performed using a Gaussian beam. A lens of focal length 26 cm was used to focus the laser pulses onto a 1 mm quartz cuvette, which contained the sample solution. The resulting beam waist radius at the focused spot was 19.6 μm . This corresponds to a Rayleigh length

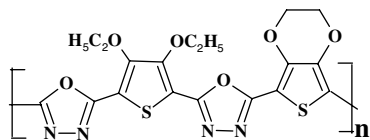


Fig. 1. Structure of the copolymer.

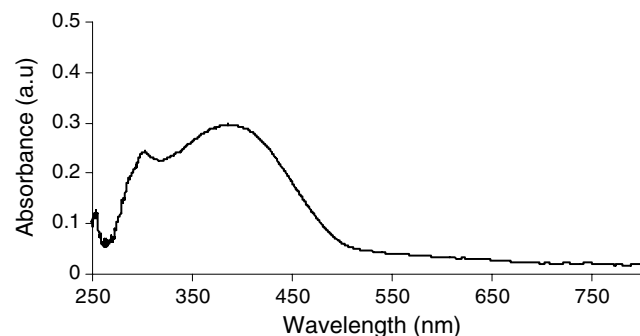


Fig. 2. The linear absorption spectrum of the copolymer solution in DMF (1×10^{-5} mol/L).

of 2.27 mm. Thus the sample thickness of 1 mm was less than the Rayleigh length, and it could be treated as a thin medium. The scan was obtained with a 50% ($S = 0.5$) aperture. The laser outputs were adjusted to give a typical power of 4.44×10^8 W/cm². Both the incident and the transmitted pulse energies were measured simultaneously by two pyroelectric detectors (Laser Probe Rj-7620 Energy Radiometer with two pyroelectric detectors). In order to avoid cumulative thermal effects, data were collected in the single shot mode [11]. The optical limiting measurements were carried out when the sample was at the focal point.

DFWM measurements may include contributions from orientational as well as dynamic resonant nonlinearities (excited state populations, thermal effects, etc.) depending on the experimental conditions. In DFM, three waves (two pump beams and one probe, all of same frequency) are mixed in the sample and the sample generates the fourth beam due to third-order interaction along the direction opposite to that of the probe beam [12]. The DFM experiment used 7 ns pulses at 532 nm from the second harmonic output of a Q-switched Nd:YAG laser. The laser energy at the sample was varied by the combinations of neutral density filters. Sample was taken in a 1-mm thick glass cuvette, with a concentration of 10^{-5} mol/L. We used the standard backward geometry for $\chi^{(3)}$ measurement, consisting of two strong, equal energy counter-propagating pump beams and a weak probe beam incident at a small angle ($\sim 4^\circ$) to one of the pumps [12]. A small portion of the pump beam was picked off and measured by a photodiode to monitor the input energy. The DFM signal generated in the sample solution was separated by a second photodiode. The photodiode signals were averaged over a number of laser shots and displayed by a Tektronix TDS2002 digital storage oscilloscope.

3. Results and discussion

3.1. *Z*-scan

The linear absorption spectrum of the copolymer shows that the excitation wavelength of 532 nm is close to one of

the absorption edges. A small absorption tail at 532 nm gives the linear absorption coefficient (α) of 0.045 cm^{-1} , which is very small compared to that at absorption peak ($\lambda_{\text{max}} = 385 \text{ nm}$, $\alpha = 0.29 \text{ cm}^{-1}$). Fig. 3 shows the normalized transmission without aperture at 532 nm (open aperture) as a function of distance along the lens axis. Since the transmission is symmetric about the focus ($z = 0$) where it is a minimum, an intensity dependent absorption effect is obvious. The model described by Sheik Bahae et al. [9] was used to analyze the curve. The normalized transmission for the open aperture condition is given by [13]

$$T(z) = 1 - \frac{q_0}{2\sqrt{2}} \quad \text{for } q_0 < 1, \quad (1)$$

$$\text{where } q_0(z) = \frac{\beta I_0 (1 - \exp - \alpha L)}{(1 + z^2/z_0^2)^\alpha}.$$

Here, L is the length of the sample, I_0 is the intensity of the laser beam at the focus, z is the position of the sample, and z_0 is the Rayleigh range of the lens. A fit of Eq. (1) to the open aperture data yields a value of $\beta = 3.0 \times 10^{-10} \text{ m/W}$ for the nonlinear absorption.

The excited state cross section σ_{ex} can be measured from the normalized open aperture Z-scan data [13]. We assume that the molecular energy levels can be reduced to a three level system in order to calculate σ_{ex} . Molecules are optically excited from the ground state to the singlet-excited state. The molecules from this state relax either to the ground state or the triplet state, when excited state absorption can occur from the triplet to the higher triplet excited state.

The change in the intensity of the beam as it passes through the material is given by $\frac{dI}{dz} = -\alpha I - \sigma_{\text{ex}} N(t) I$, where I is the intensity, and N is the number of molecules in the excited state. The excited state density of molecules appears as a result of a nonlinear absorption process whose intensity dependence can be obtained from $\frac{dN}{dt} = \frac{\sigma_{\text{ex}} I}{h\nu}$, where ν is the frequency of the laser. Combining the above two equations and solving for the fluence of the laser and over the spatial extent of the beam gives the normalized transmission for open aperture as

$$T = \ln \left(1 + \frac{q_0}{1 + x^2} \right) / \frac{q_0}{1 + x^2}, \quad (2)$$

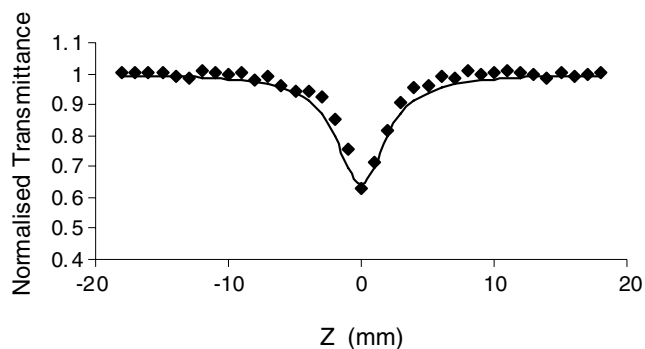


Fig. 3. Open aperture curve for copolymer solution in DMF at $1 \times 10^{-5} \text{ mol/L}$. Solid line is fitted with $\beta = 3 \times 10^{-10} \text{ m/W}$ to Eq. (1).

where $q_0 = \frac{\sigma_{\text{ex}} F_0 L_{\text{eff}}}{2h\nu}$, F_0 is the fluence of the laser at the focus and $L_{\text{eff}} = \frac{(1 - \exp - \alpha L)}{\alpha}$.

A fit of Eq. (2) to the open aperture data at 532 nm with q_0 , yields a value of $\sigma_{\text{ex}} = 4.197 \times 10^{-17} \text{ cm}^2$ for the copolymer. The ground state absorption cross section calculated from $\alpha = \sigma_{\text{g}} N_a C$, where N_a is Avogadro's number and C is the concentration in moles/cm³, is $\sigma_{\text{g}} = 7.473 \times 10^{-18} \text{ cm}^2$. The value of σ_{ex} is larger than the value of σ_{g} , which is in agreement with the condition for observing reverse saturable absorption [13]. Fig. 4 shows a plot of β versus I_0 for two different concentrations of the copolymer in DMF. Generally, NLA can be caused by free carrier absorption, saturated absorption, direct multiphoton absorption, or excited state absorption. If the mechanism belongs to simple two-photon absorption, β should be a constant that is independent of the on-axis irradiance I_0 . If the mechanism is direct three-photon absorption, β should be a linear increasing function of I_0 and the intercepts on the vertical axis should be nonzero [14]. But the graph (Fig. 4) shows that β is decreasing with increasing I_0 . The fall-off of β with increasing I_0 is a consequence of the reverse saturable absorption [15]. A small linear absorption at 532 nm and the measured σ_{ex} value indicate that there is a little contribution from excited state absorption to the observed NLA. Therefore, we attribute this observed nonlinear absorption to a reverse saturable absorption followed by a small excited state absorption. However, we can note that a decrease of β with increasing I_0 has also been reported for the optical limiting action of thiophene oligomers by Hein et al. [7], where it is attributed to saturation of instantaneous two-photon absorption.

Fig. 5 shows the normalized transmission for the closed aperture Z-scan. The pure nonlinear refraction curve was obtained by the division of the closed aperture data by the open aperture data. The Z-scan signature shows a negative nonlinearity of the sample. The experimental data was fitted with equation as described in [10]. For closed aperture condition, the normalized transmission is given by [16]

$$T(x) = 1 + \frac{4x\Delta\phi_0}{[(x^2 + 9)(x^2 + 1)]} - \frac{2\Delta\psi_0(x^2 + 3)}{[(x^2 + 9)(x^2 + 1)]}, \quad (3)$$

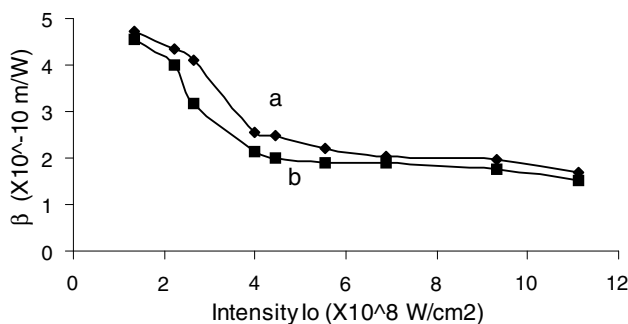


Fig. 4. β versus I_0 at two concentrations of the sample in DMF solution: (a) $1 \times 10^{-5} \text{ mol/L}$; (b) $5 \times 10^{-6} \text{ mol/L}$.

where $\Delta\phi_0$ is the phase change given by $\Delta\phi_0 = \frac{\Delta T_{p-v}}{0.406(1-S)^{0.25}}$ for $|\Delta\phi_0| \leq \pi$, and $\Delta\Psi_0$ is the on axis phase shift due to nonlinear absorption, given by $\Delta\Psi_0 = \frac{1}{2}\beta I_0 L_{\text{eff}}$. Now, the real part of the third-order nonlinear susceptibility is related to γ through $\text{Re}\chi^{(3)} = 2n_0^2 c \epsilon_0 \gamma$ and the imaginary part is related to the nonlinear absorption through $\text{Im}\chi^{(3)} = n_0^2 c \epsilon_0 \lambda \beta / 2\pi$ where ϵ_0 is the permittivity of free space. The nonlinear refractive index n_2 is related to γ by $n_2 \text{ (esu)} = \frac{cn_0}{40\pi} \gamma \text{ (m}^2/\text{W)}$. The values of n_2 , β and $\chi^{(3)}$ are given in Table 1. The determined values were consistent in all repeated scans with a maximum error of $\pm 12\%$. The n_2 and β values are comparable with those values obtained for fluorinated poly(*p*-phenylenevinylene) copolymers by Casano et al. [8]. The obtained $\chi^{(3)}$ values are comparable with that obtained for poly(3-dodecyloxymethylthiophene) (PDTh), which is 5×10^{-12} esu, by Sasabe et al. [17].

Optical limiters have been utilized in a variety of circumstances where a decreasing transmission with increasing excitation is desirable. However, one of the most important applications is eye and sensor protection in optical systems

[18]. Based on the strong reverse saturable absorption, a good optical limiting of nanosecond laser pulses in the copolymer can be expected. Fig. 6 shows the optical limiting behavior of the sample at three different concentrations. In the case of sample solution of concentration 1×10^{-5} mol/L, for incident energies less than 20 $\mu\text{J/pulse}$, the output was linearly increasing with the input. But for energies more than 20 $\mu\text{J/pulse}$, optical limiting of pulses was observed. Limiting threshold was found to be increasing with decreasing concentration of the sample in DMF solution.

Fig. 7 shows a plot of β versus concentration of the sample. It shows a linear increase in β with concentration, confirming the dependency of nonlinear properties on the concentration of the solute in the DMF solution.

3.2. DFWM

Variation of the DFWM signal as a function of the pump intensity is shown in Fig. 8. The signal is

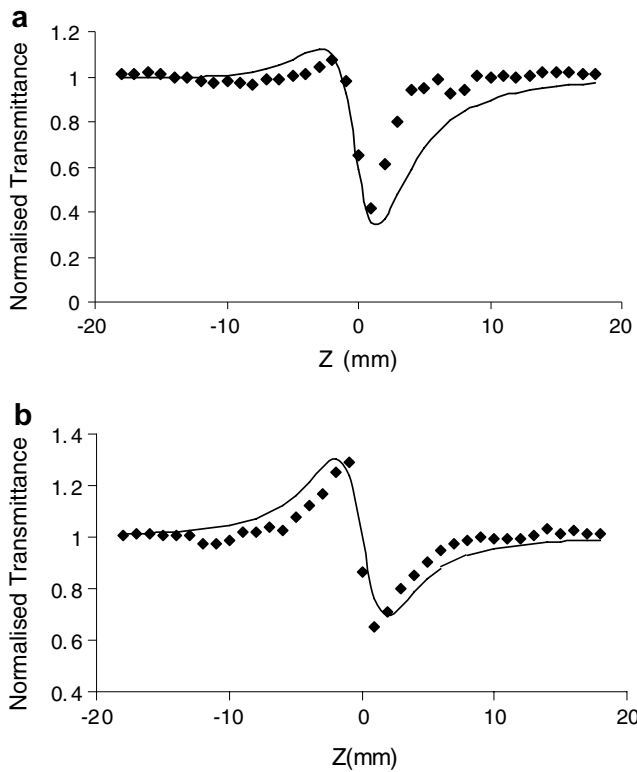


Fig. 5. (a) Closed aperture Z-scan curve. Solid line is fitted to Eq. (3) with $\Delta\phi_0 = 1.6$ and $\beta = 3 \times 10^{-10}$ m/W; (b) pure nonlinear refraction curve obtained through dividing the closed aperture data by open aperture data. Solid line is fitted with $\Delta\phi_0 = 1.6$.

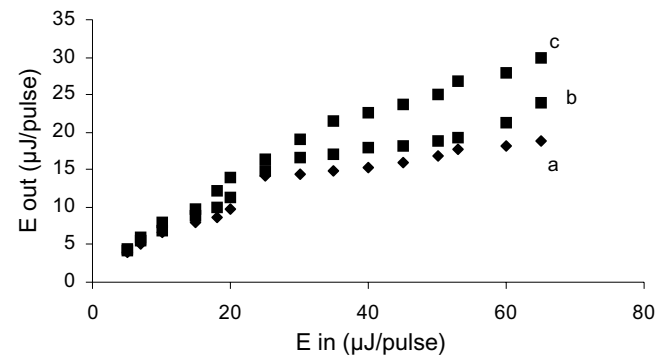


Fig. 6. Optical limiting behavior of copolymer at three different concentrations. (a) 1×10^{-5} mol/L, (b) 5×10^{-6} mol/L and (c) 2.5×10^{-6} mol/L.

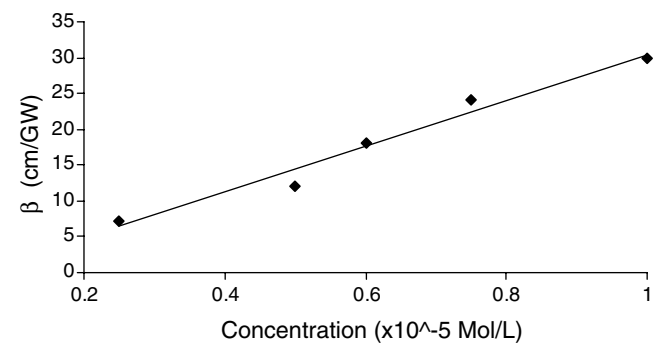


Fig. 7. β versus concentration of copolymer in DMF at $I_0 = 4.44 \times 10^8$ W/cm².

Table 1

Experimentally determined values of n_0 , n_2 , β and $\chi^{(3)}$

n_0	n_2 (esu)	Z-scan		$\text{Im}\chi^{(3)}$ (esu)	DFWM	
		β (cm/GW)	$\text{Re}\chi^{(3)}$ (esu)		$\chi^{(3)}$ (esu)	F (esu cm)
1.421	1.03×10^{-10}	30	1.106×10^{-12}	0.46×10^{-12}	1.26×10^{-12}	2.8×10^{-11}

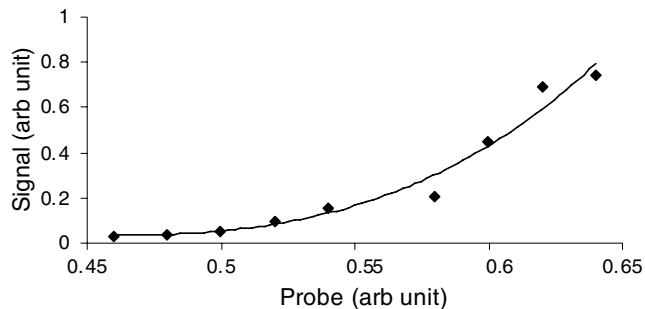


Fig. 8. Phase conjugate signal versus probe intensity for copolymer solution in DMF (1×10^{-5} mol/L).

proportional to the cubic power of the input intensity as given by the equation

$$I(\omega) \propto \left(\frac{\omega}{2\epsilon_0 c n^2} \right)^2 |\chi^{(3)}|^2 I_0^3(\omega), \quad (4)$$

where $I(\omega)$ is the DFWM signal intensity, $I_0(\omega)$ is the pump intensity, l is the length, and n is the refractive index of the medium. The solid curve in the figure is a cubic fit to the experimental data. $\chi^{(3)}$ can be calculated from the equation:

$$\chi^{(3)} = \chi_{\text{ref}}^{(3)} \left[\frac{I/I_0^3}{(I/I_0^3)_{\text{ref}}} \right]^{1/2} \left[\frac{n}{n_{\text{ref}}} \right]^2 \frac{l_{\text{ref}}}{l} \left(\frac{\alpha l}{(1 - e^{-\alpha l}) e^{-\frac{\alpha l}{2}}} \right), \quad (5)$$

where the subscript 'ref' refers to the standard reference CS_2 under identical conditions, and $\chi_{\text{ref}}^{(3)}$ is taken to be 4.0×10^{-13} esu [12,19]. The figure of merit F is calculated by taking α into account. F is given by $\chi^{(3)}/\alpha$. F is a measure of the nonlinear response that can be achieved for a given absorption loss, and is useful in comparing nonlinear materials in regions of absorption. The value of F is given in Table 1, which shows that the copolymer has a good F value. $\chi^{(3)}$ measured by the DFWM technique matches very well with that obtained by the Z -scan technique.

4. Conclusions

The third-order nonlinear optical properties of a newly synthesized copolymer containing oxadiazole and substituted thiophenes have been studied by Z -scan and DFWM techniques in the nanosecond excitation domain. The NLA is found to be originating from strong reverse saturable absorption. The value of $\chi^{(3)}$ is determined to be of the same order of magnitude from both the techniques. The copolymer exhibits good optical limiting properties at 532 nm. The results show that the copolymer, having high

third-order nonlinearity, may be a potential candidate for optical limiting, and other fast photonic applications.

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