

## Third-order nonlinear optical studies of newly synthesized polyoxadiazoles containing 3,4-dialkoxythiophenes

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### Abstract

The third-order nonlinear optical properties of newly synthesized soluble polyoxadiazoles containing 3,4-dialkoxythiophenes were investigated by 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 the experiments. Z-scan results indicate a negative nonlinear refractive index,  $n_2$ , whose magnitude is of the order of  $10^{-10}$  esu for all the copolymers. The variation of nonlinear response among the copolymers clearly indicates the dependence of  $\chi^{(3)}$  on donor and acceptor type of units present in these copolymers. The copolymers exhibit strong reverse saturable absorption and good optical limiting properties at 532 nm.

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**Keywords:** Nonlinear optics; Z-scan; DFWM; Conjugated polymers; Optical limiting

### 1. Introduction

Organic materials exhibiting strong nonlinear optical (NLO) properties have attracted considerable interest in recent years because of their possible applications in opto-electronic and all-optical devices such as optical limiters, optical switches and optical modulators [1,2]. Conjugated polymers are a promising class of third-order nonlinear materials because of their potentially large third-order susceptibilities associated with fast response time in addition to their variety and processability. The strong delocalization of  $\pi$ -electrons in the polymeric backbone determines a very high molecular polarizability and thus remarkable third-order optical nonlinearities [3]. Among various  $\pi$ -conjugated materials, thiophene based polymers are currently under intensive investigation as

materials for nonlinear optics because of their large third-order response, chemical stability, and their readiness of functionalization [4,5]. A necessary step in improving the NLO properties of conjugated polymers is to understand the fundamental relationship that exists between the molecular structure and hyperpolarizabilities. A deeper understanding in this subject should improve the design of organic conjugated molecules by the judicious choice of functional substituents, and thus to tune their optical properties for applications in opto-electronic and photonic devices. Cassano et al. have reported a new strategy for tuning the linear and nonlinear optical properties of soluble paraphenylenevinylene derivatives based on the effect of simultaneous presence of electron-acceptor and electron-donor units in the conjugated backbone [6]. Using the similar strategy, we have synthesized a new series of copolymers with alternating donor–acceptor arrangement along the polymer backbone, so as to enhance the  $\pi$ -electron delocalization in the polymers' chain. We have used 3,4-dialkoxythiophene and 1,4-divinylbenzene units as

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electron donors and 1,3,4-oxadiazole as electron acceptor unit. The alkoxy pendant at 3- and 4-positions of the thiophene ring serves as both solubilizing group as well as strong electron donating group. The function of vinylene linkages is to planarize the polymer backbone by overcoming torsional interactions between the rings that could serve to increase the  $\pi$ -electron delocalization along the polymer chain. The NLO measurements have been performed using single beam Z-scan and DFWM techniques in the nanosecond domain. The effect of length of alkoxy pendants at 3- and 4-positions on the thiophene ring on NLO properties of the polymers has been discussed. We demonstrate the strong optical limiting of visible, nanosecond pulses with these copolymers. The concentration dependence of NLO properties of these copolymers has been reported.

## 2. Experimental

The synthesis and linear optical characterization of the copolymers (P1, P2 and P3) have been reported elsewhere [7]. The general structure of synthesized copolymers is shown in Fig. 1. The UV–Vis absorption spectra of copolymers, shown in Fig. 2, were recorded at room temperature in dilute dimethylformamide (DMF) solutions [ $1 \times 10^{-5}$  mol/L] using a Varian CARY 500 spectrophotometer. The linear refractive indices of copolymers were recorded with an Abbe refractometer.

### 2.1. Z-scan measurements

Z-scan [8] is a well-known technique that allows the simultaneous measurement of both nonlinear refractive index and nonlinear absorption coefficient. The basic idea behind Z-scan technique is self-focusing or self-defocusing. A Gaussian beam is focused by a lens onto the sample and the variation in the beam profile is observed at the far field as the sample is taken through the focus of the lens. The beam propagation direction is taken as  $z$ -direction and hence this technique is known as Z-scan technique. By properly monitoring the transmittance change through a small aperture placed at the far-field position (closed aperture), one is able to determine the amplitude of the phase shift. By moving the sample through the focus and without placing an aperture at the detector (open aperture), one can measure the intensity dependent absorption as a change of transmittance through the sample.

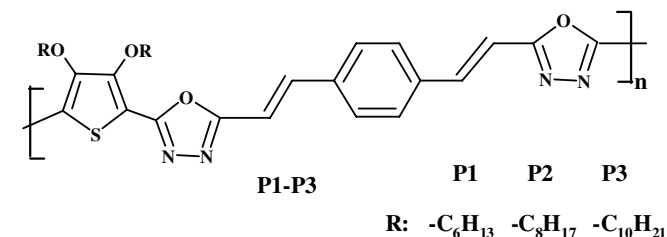


Fig. 1. General structure of the copolymers.

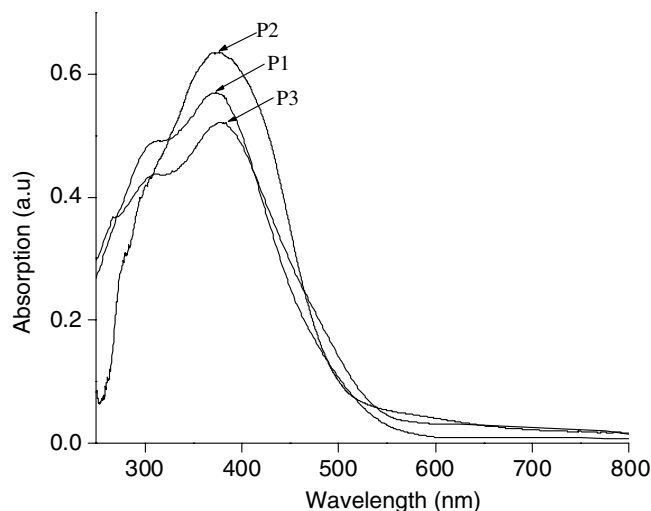


Fig. 2. UV–Vis absorption spectra of the copolymers in DMF solution ( $1 \times 10^{-5}$  mol/L).

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 output of the laser had a nearly Gaussian intensity profile. A lens of focal length 26 cm was used to focus the laser pulses into a 1 mm quartz cuvette containing the sample solution. The resulting beam waist radius at the focused spot, calculated using the formula  $w_0 = \frac{1.22\lambda f}{d}$ , where  $f$  is focal length of the lens and  $d$  is the diameter of the aperture, was found to be  $19.6 \mu\text{m}$ . The corresponding Rayleigh length, calculated using the formula  $z_0 = \frac{\pi w_0^2}{\lambda}$ , was found to be 2.3 mm. Thus the sample thickness of 1 mm was less than the Rayleigh length and hence it could be treated as a thin medium. The scan was obtained with a 50% ( $S = 0.5$ ) aperture and at pulse energy of  $10 \mu\text{J}$ , which corresponds to a peak irradiance of  $0.22 \text{ GW}/\text{cm}^2$ . In order to avoid cumulative thermal effects, data were collected in single shot mode [9]. The experiments were performed at room temperature. The optical limiting measurements were carried out when the sample was at focal point by varying the input energy and recording the output energy. Both the incident and the transmitted energies were measured simultaneously by two pyroelectric detectors with Laser Probe Rj-7620 Energy Ratio meter.

### 2.2. DFWM studies

Four-wave mixing refers to the interaction of four waves in a nonlinear medium via the third-order polarization. When all the waves have same frequency, it is called as degenerate four-wave mixing. There are several geometries used in studying this phenomenon. One of such geometries used in our experiment is the backward geometry or the phase conjugate geometry. Here, two counter propagating strong beams are called forward pump beam and the backward pump beam. A third wave called the probe beam is incident at small angle  $\theta$  ( $\sim 4^\circ$ ) to the direction of the for-

ward pump. A fourth beam, called the conjugate beam, is generated in the process and propagates counter to the probe beam [10].

We 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 concentration of  $10^{-5}$  mol/L. A small portion of the pump beams was picked off and measured by a photodiode to monitor the input energy. The DFWM 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 measurements

The linear absorption spectra of the copolymers show that 532 nm is close to one of the absorption edges. Small absorption tails at 532 nm give the linear absorption coefficients ( $\alpha$ ) for copolymers, which are tabulated in Table 1. Fig. 3 shows the normalized transmission without aperture at 532 nm (open aperture) as a function of distance along the lens axis for P3. The transmission is symmetric about the focus ( $z = 0$ ) where it has a minimum transmission, thus an intensity dependent absorption effect is observed. A number of nonlinear absorption (NLA) mechanisms can be represented in an energy diagram as shown in Fig. 4. The diagram shows the different energy levels of a molecule, the singlet ground state  $S_0$ , the excited singlet states  $S_1$  and  $S_2$ , as well as the triplet excited states  $T_1$  and  $T_2$ . It also dis-

Table 1  
The values of  $\alpha$ ,  $\sigma_g$  and  $\sigma_{ex}$  for the copolymers

Polymer	$\alpha$ (cm <sup>-1</sup> )	$\sigma_g$ ( $\times 10^{-18}$ cm <sup>2</sup> )	$\sigma_{ex}$ ( $\times 10^{-17}$ cm <sup>2</sup> )
P1	0.0487	8.092	9.66
P2	0.0622	10.32	5.44
P3	0.068	11.26	5.93

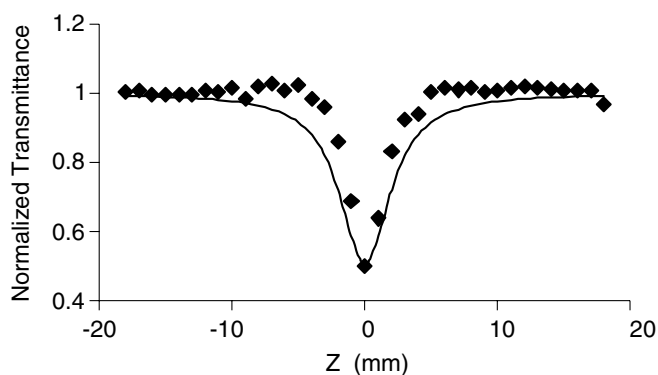


Fig. 3. Open aperture curve for P3. Solid line is fitted to Eq. (1), with  $\beta_{eff} = 63.6$  cm/GW.

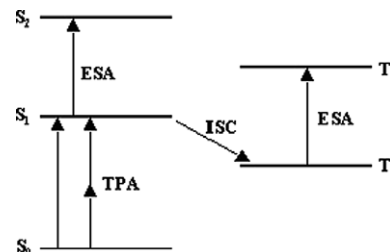


Fig. 4. Energy level diagram showing both two-photon absorption (TPA) and excited state absorption (ESA).

plays the different transitions between the energy levels. When two photons, of the same or different energy are simultaneously absorbed from the ground state to a higher excited state ( $S_0 \rightarrow S_1$ ), it is denoted as two-photon absorption (TPA). When excited state absorption (ESA) occurs molecules are excited from an already excited state to a higher excited state (e.g.  $S_1 \rightarrow S_2$  and/or  $T_1 \rightarrow T_2$ ). For this to happen the population of the excited states ( $S_1$  and/or  $T_1$ ) needs to be high so that the probability of photon absorption from that state is high. The ESA could be enhanced if the molecules could undergo intersystem crossing (ISC) to the triplet state. If more absorption occurs from the excited state than from the ground state it is usually called reversed saturable absorption (RSA). The triplet excited state absorption may result in RSA if the absorption cross-section of triplet excited state is greater than that of singlet excited state. With excitation of laser pulses on the nanosecond scale, which in our case, triplet–triplet transitions may make significant contribution.

The normalized transmission for the open aperture condition is given by [11]

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

where  $q_0(z) = \frac{\beta_{eff} I_0 (1 - \exp^{-2L})}{(1 + z^2/z_0^2)^2}$ . Here,  $\beta_{eff}$  is the effective value of two-photon absorption coefficient,  $L$  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  $\beta_{eff}$  for all the copolymers. The excited state cross-section  $\sigma_{ex}$  can be measured from the normalized open aperture Z-scan data [11]. The change in the intensity of the beam as it passes through the material is given by  $\frac{dI}{dz} = -\alpha I - \sigma_{ex} N(t) I$ , 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  $\frac{dN}{dz} = \frac{\sigma_{ex} I}{h\nu}$ , where  $\nu$  is the frequency of the laser. Combining the above two equations and solving for the fluence of the laser and integrating over the spatial extent of the beam gives the normalized transmission for open aperture as

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

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

The values of  $\sigma_{\text{ex}}$  of copolymers obtained through a fit of Eq. (2) to the corresponding open aperture data at 532 nm with  $q_0$ , are tabulated in Table 1. The ground state absorption cross-section of the copolymers calculated from  $\alpha = \sigma_{\text{g}} N_{\text{a}} C$ , where  $N_{\text{a}}$  is Avogadro's number and  $C$  is the concentration in moles/cm<sup>3</sup> is given in Table 1. It is clear that the value of  $\sigma_{\text{ex}}$  is larger than the value of  $\sigma_{\text{g}}$  in all the copolymers, which is in agreement with the condition for observing reverse saturable absorption [11,12]. Reverse saturable absorption generally arises in a molecular system when the excited state absorption cross-section is larger than the ground state cross-section. Fig. 5 shows a plot of  $\beta_{\text{eff}}$  versus  $I_0$  for P2 and P3 in DMF at a concentration of  $1 \times 10^{-5}$  mol/L. Generally, NLA can be caused by free carrier absorption, saturated absorption, direct multipho-

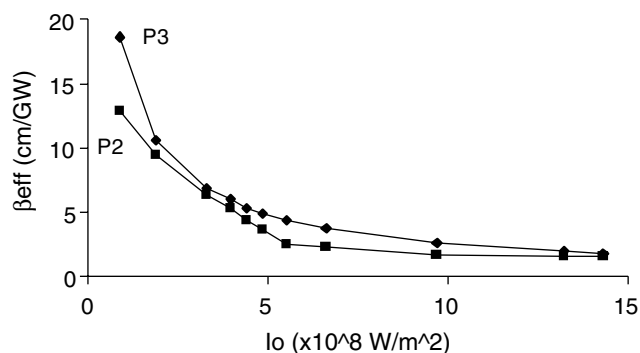


Fig. 5.  $\beta_{\text{eff}}$  versus intensity ( $I_0$ ) for P2 and P3 in DMF solution ( $1 \times 10^{-5}$  mol/L).  $\beta_{\text{eff}}$  decreases with increase in intensity.

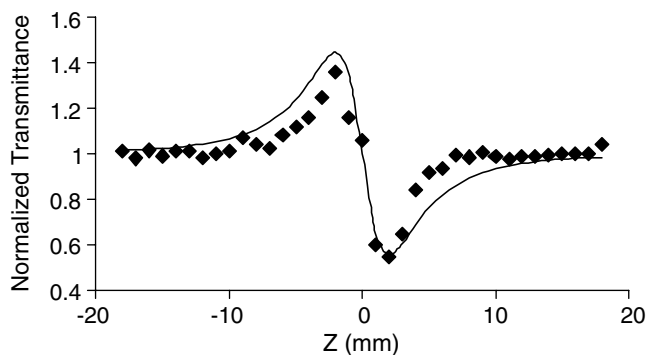


Fig. 6. Pure nonlinear refraction curve obtained through division method for P3. Solid line is a fit of data to Eq. (3) with  $\Delta\phi_0 = 2.2$ .

ton absorption, or excited state absorption. If the mechanism belongs to the simple two-photon absorption,  $\beta_{\text{eff}}$  should be a constant that is independent of the on-axis irradiance  $I_0$ . If the mechanism is direct three-photon absorption,  $\beta_{\text{eff}}$  should be a linear increasing function of  $I_0$  and the intercepts on the vertical axis should be nonzero [13]. But the graph (Fig. 5) shows that  $\beta_{\text{eff}}$  is decreasing with increasing  $I_0$ . The fall-off of  $\beta_{\text{eff}}$  with increasing  $I_0$  is a consequence of the reverse saturable absorption [14]. With increasing intensity the total absorption of these copolymers approaches asymptotically the absorbance of the triplet state. Therefore, the  $\beta_{\text{eff}}$  will be reduced at least up to intensities where no other intensity dependence processes are involved which can further cause reduction of transmission of copolymer solution. A small linear absorption at 532 nm and the measured  $\sigma_{\text{ex}}$  values indicate that there is a contribution from excited state absorption to the observed NLA. Therefore, we attribute this observed nonlinear absorption to a reverse saturable absorption.

The pure nonlinear refraction curve of P3, shown in Fig. 6, was obtained by the division of the closed aperture data by the corresponding open aperture data. The Z-scan signature shows a large negative nonlinearity (self defocusing) for all the copolymers. The experimental data were fitted with the following equation [8]:

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

where  $\Delta\phi_0$  is the phase change given by  $\Delta\phi_0 = \frac{\Delta T_{p-e}}{0.406(1-S)^{0.25}}$  for  $|\Delta\phi_0| \leq \pi$ . Now, the real part of the third-order nonlinear susceptibility is related to nonlinear refractive index  $\gamma_{\text{eff}}$  ( $\text{m}^2/\text{W}$ ) through  $\text{Re}\chi^{(3)} = 2n_0^2 c \epsilon_0 \gamma_{\text{eff}}$  and the imaginary part is related to the nonlinear absorption through  $\text{Im}\chi^{(3)} = n_0^2 c \epsilon_0 \lambda \beta_{\text{eff}} / 2\pi$  where  $\epsilon_0$  is the permittivity of free space. The nonlinear refractive index  $n_2$  is related to  $\gamma_{\text{eff}}$  by  $n_2$  (esu) =  $\frac{cn_0}{40\pi} \gamma_{\text{eff}}$  ( $\text{m}^2/\text{W}$ ) [8].

The value of  $n_2$  is found to be of the order of  $10^{-10}$  esu for all the copolymers, which is nearly two order of magnitude larger than the  $n_2$  values reported for thiophene oligomers by Hein et al. [15]. The obtained  $\chi^{(3)}$  values are comparable with that obtained for poly(3-dodecyloxymethylthiophene) (PDTh), which is  $5 \times 10^{-12}$  esu, by Sasabe et al. [16]. The values of  $n_2$  and  $\chi^{(3)}$  for the copolymers are given in Table 2. The values were consistent in all the trials with maximum error of 12%. The observed variation of NLO responses of copolymers is related to their backbone structure. The copolymers contain alternating electron donating and electron withdrawing groups in their chain.

Table 2  
Determined values of linear and nonlinear optical parameters

Polymer	$n_0$	Z-scan				DFWM	
		$n_2$ ( $\times 10^{-10}$ esu)	$\beta_{\text{eff}}$ cm/GW	$\text{Re}\chi^{(3)}$ ( $\times 10^{-12}$ esu)	$\text{Im}\chi^{(3)}$ ( $\times 10^{-12}$ esu)	$\chi^{(3)}$ ( $\times 10^{-12}$ esu)	$F$ ( $\times 10^{-11}$ esu cm)
P1	1.422	-1.942	73.8	-2.086	1.139	2.055	4.21
P2	1.422	-2.20	53.0	-2.366	0.818	2.39	3.84
P3	1.415	-2.836	63.6	-3.01	0.968	2.895	4.26

‘OR’ refers to the alkoxy group. The lengths of the alkoxy groups at 3,4-positions of the thiophene rings play an important role in the third-order nonlinear response of the copolymers. The  $\chi^{(3)}$  values of the copolymers are found to be increasing from P1 to P3. This can be attributed to the increase in the electron donating abilities of the alkoxy groups with increase in chain length. Hence the copolymer P3, containing the longest alkoxy groups at 3,4-positions of the thiophene rings, shows the highest nonlinear response among the copolymers. Therefore, we attribute the enhancement in third-order nonlinear response to the increased  $\pi$ -electron delocalization in the copolymers. The study reveals that the nonlinear optical properties of the copolymers can be tuned by the structural design with simultaneous presence of alternating donor and acceptor groups along the polymer chain.

Concentration dependencies of NLO properties can be analyzed to extract the information on the NLO properties of the solute. The concentration of solutes in solution was varied and the Z-scans were repeated on solutions at each concentration to study the variation of nonlinear response. Fig. 7 shows the dependence of nonlinear absorption ( $\beta_{\text{eff}}$ ) on the concentration of P1–P3 in solution. The  $\beta_{\text{eff}}$  increases with increase in the sample concentration. From  $0.25 \times 10^{-5}$  to  $1 \times 10^{-5}$  mol/L,  $\beta_{\text{eff}}$  increased linearly with the concentration. However, it was observed that  $\beta_{\text{eff}}$  decreased rapidly below  $0.25 \times 10^{-5}$  mol/L. The nonlinear absorption as well as the nonlinear refraction decreased as the concentration in solution decreased from  $1 \times 10^{-5}$  mol/L to  $1.25 \times 10^{-6}$  mol/L. Thus, the observed decrease in the nonlinear response has direct relation with the concentration of samples.

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 [12]. Based on the strong reverse saturation absorption, a good optical limiting property can be expected for P1, P2 and P3. Fig. 8 demonstrates optical limiting behavior of P1–P3. For incident energies less than 20  $\mu\text{J}/\text{pulse}$ , the output was linearly increasing with the input. But for energies more than 20  $\mu\text{J}/\text{pulse}$ , optical limiting of pulses was

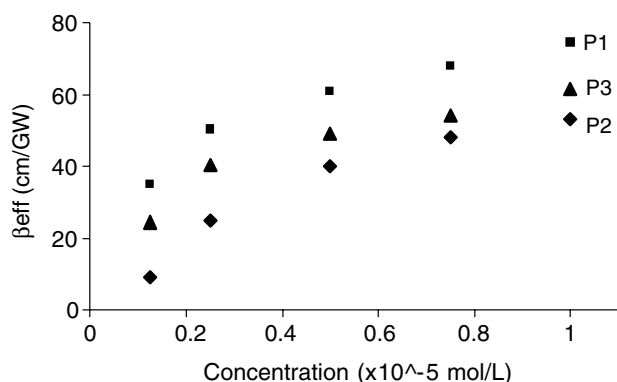


Fig. 7. Concentration dependence of  $\beta_{\text{eff}}$  of P1, P2, and P3.

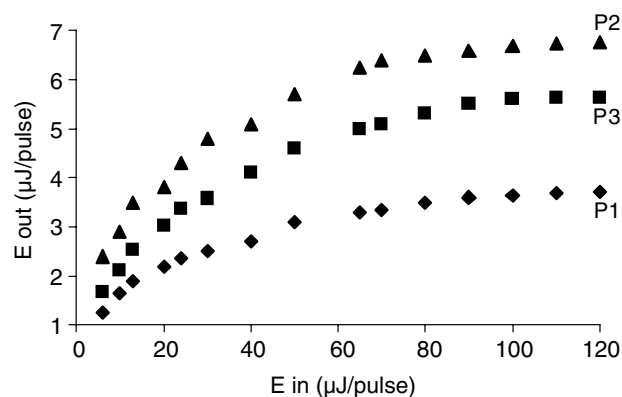


Fig. 8. Optical limiting behavior of the copolymers in DMF solution ( $1 \times 10^{-5}$  mol/L).

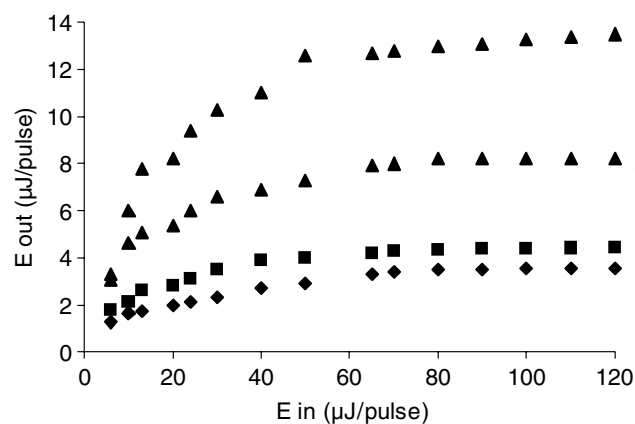


Fig. 9. Optical limiting behavior of P1 at different concentrations: (a)  $1 \times 10^{-5}$  mol/L; (b)  $0.5 \times 10^{-5}$  mol/L; (c)  $0.25 \times 10^{-5}$  mol/L; (d)  $0.125 \times 10^{-5}$  mol/L.

observed in all copolymers. The optical limiting behavior of P1 at different concentrations has been shown in Fig. 9. Both the limiting threshold as well as the clamping level change with lowering the concentration. The clamping level was found to be increasing with decreasing concentration of the sample in DMF solution, i.e. at high concentration ( $1 \times 10^{-5}$  mol/L) the clamping level was observed to be around 2–3  $\mu\text{J}/\text{pulse}$  whereas at lower concentration ( $0.125 \times 10^{-5}$  mol/L) it was observed to be around 13–14  $\mu\text{J}/\text{pulse}$ . Limiting threshold was found to be increasing with decreasing concentration. Although both nonlinear absorption and scattering can contribute to the optical limiting, we did not observe any significant scattering from the samples during our experiment within the energy limit used.

### 3.2. Degenerate four-wave mixing

Variation of the DFWM signal as a function of the pump intensity for P3 is shown in Fig. 10. The intensity dependence of the amplitude of the DFWM signal in other copolymers was found to follow a pattern similar to that



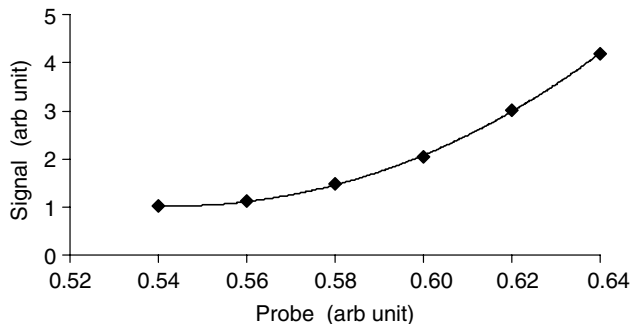


Fig. 10. Phase conjugate signal versus probe for P3.

presented in the figure. The signal is proportional to the cubic power of the input intensity as given by the following 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 optical pathlength, and  $n$  is the refractive index of the medium. The solid curves in Fig. 10 are cubic fit to the experimental data.  $\chi^{(3)}$  can be calculated from the following 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  $\text{CS}_2$  under identical conditions, and  $\chi_{\text{ref}}^{(3)}$  is taken to be  $4.0 \times 10^{-13}$  esu [17,18]. The figure of merit  $F$  is calculated by taking  $\alpha$  in to 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 2, which shows that the copolymers have very good  $F$  value. It can be noted that the largest  $\chi^{(3)}$  and  $F$  values have been measured for the copolymer attached with high electron donor among the copolymers. The value of  $\chi^{(3)}$  measured by DFWM technique very well matches with the value of  $\chi^{(3)}$  obtained by Z-scan technique.

#### 4. Conclusions

We investigated the third-order nonlinear optical properties of three newly synthesized copolymers containing oxadiazole and substituted thiophenes by Z-scan and DFWM techniques in the nanosecond excitation domain. The value of  $\chi^{(3)}$  is determined to be of the same order of magnitude from both the techniques. The nonlinear absorption is found to be originating from reverse satura-

ble absorption. The copolymers exhibit good optical limiting properties at 532 nm. The results show that the copolymer P3, containing the longest alkoxy group, exhibits highest nonlinearity among the three copolymers, and it may be a potential candidate for optical limiting, optical switching and other fast photonic applications. The study reveals that introduction of strong electron donor and acceptor groups along the polymer backbone can be a promising molecular design for enhancing the third-order NLO properties of conjugated polymers.

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