

Nonlinear Optical Studies of Newly Synthesized Polythiophenes Containing Pyridine and 1,3,4-Oxadiazole Units

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We report measurements of the third-order nonlinear optical properties of a newly synthesized thiophene-based copolymer. The nonlinear transmission measurements were performed on the copolymer dissolved in tetrahydrofuran by employing the single beam Z-scan technique. Q-switched laser output at 532-nm wavelength was used for this purpose. The nonlinear absorption coefficient, β , nonlinear refractive index, n_2 , and the real and imaginary parts of third-order susceptibility, $\chi^{(3)}$, were, 18.93 cm/GW, 3.037×10^{-17} m²/W (-1.022×10^{-10} esu), 1.512×10^{-20} m²/V² (-1.080×10^{-12} esu) and 0.399×10^{-20} m²/V² (0.285×10^{-12} esu), respectively. The excited state absorption crosssection σ_{exc} , was found to be larger than the ground state absorption crosssection σ_g , indicating reverse saturable absorption (RSA) in the copolymer sample. The copolymer exhibits an optical power limiting threshold of about 120 μ J and saturated output of less than 80 μ J. Hence, the copolymer seems to be a promising material for photonic device applications. POLYM. ENG. SCI., 49:875–880, 2009. © 2008 Society of Plastics Engineers

INTRODUCTION

Nonlinear optics has drawn increasing attention from researchers because of its potential applications in optical switching, optical data storage, optical communications, and eye and sensor protection [1–3]. The emphasis has been on identifying new materials those possess large third-order nonlinear optical properties with ultra fast response times. In recent times, there has been an enormous interest in organic materials possessing strong π -electron delocalization which determines the strength of third-order nonlinearity. An important advantage of using organic materials is the fact that their molecular structure

can be modified, there by altering optical properties. Among the organic materials, conjugated polymers possess a unique combination of electronic and optical properties. In recent years, variations in molecular structure have yielded conjugated polymers with excellent solubility, adequate thermal stability, and desirable optical properties. The possibility of making systematic structural modification at the molecular level has made these materials attractive candidates for photonic device applications [4, 5].

Conjugated polymers such as polyacetylenes, polydiacetylenes, polyphenylenevinyls, etc. were extensively studied for their third-order nonlinear optical properties [2, 6]. In recent times, polythiophenes, a very versatile class of conjugated polymer, have been widely investigated because of their good optical stability, easy processability and large third-order nonlinear optical properties [7, 8]. In Polythiophenes, nonlinear optical properties can be tuned by attaching an alkyl chain to the thiophene ring, which enhances the delocalization of π -electrons in the polymer.

Recently Cassano et al. [9] have showed that, by a proper choice of the side chains in a series of dialkoxy substituted poly(*p*-phenylenevinylene), it is possible to enhance the third-order nonlinear optical coefficients. They also reported a new strategy for tuning the linear and nonlinear optical properties of soluble derivatives of fluorinated poly(*p*-phenylenevinylene) copolymers based on the effect of the simultaneous presence of electron-acceptor and electron-donor substituted aromatic rings in the conjugated backbone [10]. Using similar design concepts, we have synthesized a polythiophene containing 1,3,4-oxadiazole and pyridine as electron-accepting units and 3,4-didecyloxythiophene as electron-donating units along the polymer chain. In this article, we present the experimental measurements of third-order nonlinear optical properties of the newly synthesized polythiophene carried out using the single beam Z-scan Technique.

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EXPERIMENT

Single beam Z-scan technique [11], was employed to measure the third-order optical nonlinearities of the copolymer samples prepared. This technique enables simultaneous measurement of nonlinear refraction (NLR) and nonlinear absorption (NLA). Basically, in this technique a Gaussian laser beam is focused, using a lens, on the cuvette containing the liquid sample. The cuvette is translated across the focal region and changes in the far-field intensity pattern are monitored. The experiments were performed using a Q-switched, frequency doubled Nd: YAG laser (Spectra-Physics GCR170) which produces 7ns pulses at 532 nm and at a pulse repetition rate of 10 Hz. The laser beam was focused by using a lens of 25 cm focal length. The laser beam waist at the focused spot was estimated to be $18.9 \mu\text{m}$ and the corresponding Rayleigh length is 2.11 mm. The Z-scan measurements were carried out using a cuvette of 1 mm thickness, which is less than the Rayleigh length. Hence, the thin sample approximation is valid. The Z-scan experiment was performed at an input peak-intensity of 0.478 GW/cm^2 . The nonlinear transmission of the copolymer, with and without the aperture in front of the detector was measured in the far-field using Laser Probe Rj-7620 Energy Meter with Pyroelectric detectors. The optical power limiting experiments were performed by keeping the cuvette containing copolymer solution, at the focus of the laser beam and measuring the transmitted laser energy at various input laser energies.

The synthesis and characterization of the conjugated copolymer used in this study have been reported elsewhere [12]. Figure 1 shows the general structure of the copolymer. The UV-Visible absorption spectrum of the copolymer dissolved in tetrahydrofuran (THF), was recorded using a Fiber Optic Spectrometer (Ocean Optics) and is shown in Fig. 2. For the Z-scan experiments polymer solution of concentration $5 \times 10^{-4} \text{ mol/L}$ was used.

Z-SCAN RESULTS AND DISCUSSION

The Open aperture Z-scan (i.e. without aperture in front of the detector) was performed to measure the nonlinear absorption in the copolymer sample, which is related to imaginary part of third-order optical susceptibility $\chi^{(3)}$. Figure 3 shows the open aperture Z-scan curve of the copolymer sample which is symmetric with respect to the focus indicating intensity dependent absorption. The

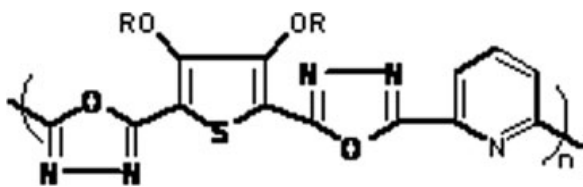


FIG. 1. Structure of the copolymer with $R = \text{C}_{10}\text{H}_{21}$.

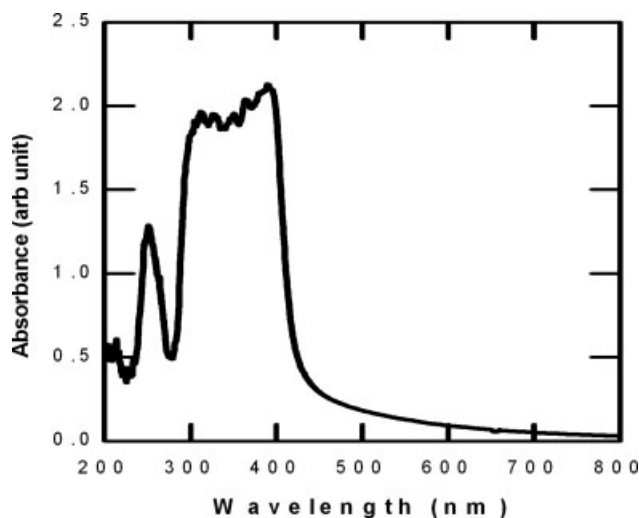


FIG. 2. UV-Visible absorption Spectrum of the copolymer in THF.

absorption may be due to two photon absorption (TPA), excited state absorption (ESA), reverse saturable absorption (RSA), etc. Nonlinear absorption of nanosecond pulses can be understood using the five level model [13, 14] shown in Fig. 4. The relevant energy levels are the singlet levels S_0 , S_1 , and S_2 and the triplet levels are T_1 and T_2 . Each of these states contains number of vibrational levels. When the molecule is excited by the laser pulse, electrons are initially excited from lowest vibrational level of S_0 to upper vibrational levels of S_1 , where they relax in picoseconds by nonradiative decay. In nanosecond time scale, singlet transition does not deplete the population of S_1 level appreciably, since atoms excited to S_2 decay to S_1 itself within picoseconds. From S_1 , electrons are transferred to T_1 via intersystem crossing (ISC), from where transitions to T_2 occur. The process ($S_1 \leftarrow S_0$) is known as ground state absorption. The two process ($S_2 \leftarrow S_1$) and ($T_2 \leftarrow T_1$) are known as ESA (Excited

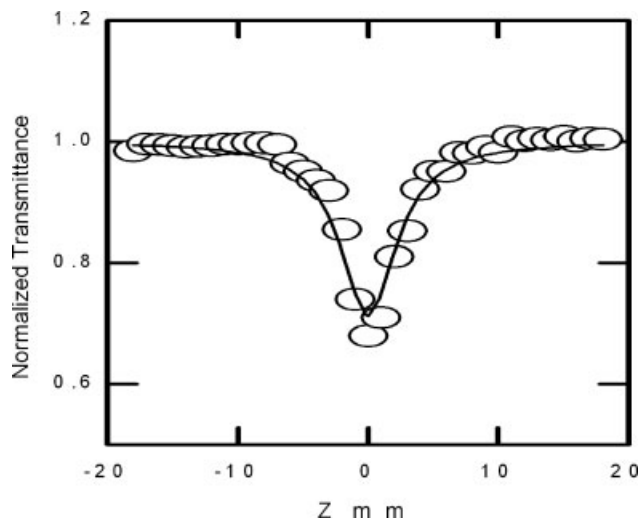


FIG. 3. Open aperture Z-scan trace. Solid line depicts theoretical fit.

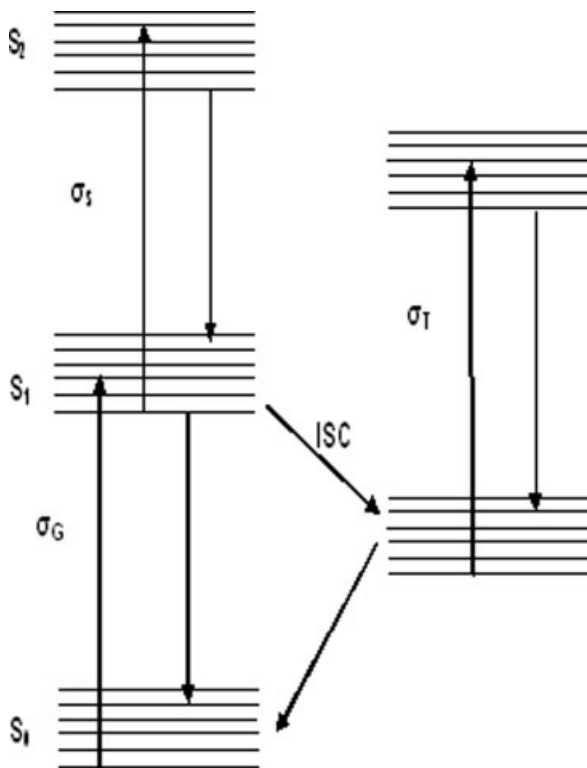


FIG. 4. Energy level diagram (Five level model) adopted from W. Feng et al. Ref [13].

state absorption), and if the absorption cross-sections are larger than that of the ground state the process is called RSA (reverse saturable absorption). With excitation of laser pulses on the nanosecond scale, which is true in our case, triplet-triplet transitions are expected to make significant contribution to nonlinear absorption.

The excited state absorption cross section σ_{exc} , can be measured using the normalized energy transmission of open aperture Z-scan (i.e. without aperture.) [15–18]. The change in the intensity of the laser beam as it propagates through the sample is given by

$$\frac{dI}{dZ} = -\alpha I - \sigma_{exc} N(t), \quad (1)$$

$$\frac{dN}{dt} = \frac{\alpha I}{\hbar\omega}, \quad (2)$$

where I is the intensity, Z is the sample position, N is the density of charges populated in the excited state, ω is the angular frequency of the laser and α is linear absorption. By combining Eqs. 1 and 2 yield

$$\frac{dI}{dZ} = -\alpha I - \frac{\sigma_{exc}\alpha I}{\hbar\omega} \int_{-\infty}^t I(t') dt', \quad (3)$$

Solving the above equation for the fluence and integrating over spatial extent of the beam, gives the normal-

ized energy transmission for open aperture and is given by [17],

$$T = \ln\left(1 + \frac{q_0}{1+x^2}\right) / \left(\frac{q_0}{1+x^2}\right), \quad (4)$$

where $x = z/z_0$, z is the distance of the sample from the focus, z_0 is the Rayleigh length given by the formula $z_0 = 2\pi w_0^2/\lambda$ (k is the wavelength and w_0 is the beam waist at the focus) and q_0 is given by the equation [15–17],

$$q_0 = \frac{\sigma_{exc}\alpha F_o(r=0)L_{eff}}{2\hbar\omega}, \quad (5)$$

where α is the linear absorption coefficient, $L_{eff} = [1 - \exp(-\alpha L)]/\alpha$, ω is the angular frequency of the laser and F_o is the on-axis fluence at the focus which is related to the incident energy E_{total} by,

$$F_o = \frac{2E_{total}}{\pi\omega_0^2}, \quad (6)$$

The value of excited state absorption cross section σ_{exc} , of the copolymer was obtained by fitting the open aperture data to the Eq. 4. The linear absorption spectra of the copolymer in the Fig. 2 show that the absorption edge is close to experimental wavelength 532 nm. The small absorption tail at 532 nm gives the linear absorption coefficient $\alpha = 0.2943 \text{ cm}^{-1}$, for the copolymer. The ground state absorption cross section, σ_g , was calculated using the relation,

$$\alpha = \sigma_g N_a C, \quad (7)$$

where N_a is the Avogadro's number and C is the concentration in mol/L.

The measured values of ground state and excited state absorption cross sections of the copolymer were $9.77 \times 10^{-19} \text{ cm}^2$ and $6.42 \times 10^{-18} \text{ cm}^2$ respectively. The larger value of σ_{exc} , as compared to σ_g , of the copolymer indicates that the operating nonlinear mechanism is reverse saturable absorption (RSA) [15]. To confirm this we have measured β_{eff} as a function of the on-axis input laser intensity I_o . As seen from Fig. 5, β_{eff} decreases on increasing I_o which is a signature of RSA [19]. In contrast, for two photon absorption β_{eff} is known to be independent of I_o [20]. However, Hein et al. [21] have reported decrease of β_{eff} , with increasing I_o for the thiophene oligomers, where they attributed to saturation of instantaneous two-photon absorption.

To determine the sign and magnitude of nonlinear refraction, closed aperture Z-scan was performed by placing an aperture in front of the detector. Figure 6 shows the closed aperture Z-scan curve of the copolymer. The peak-valley shape of the curve indicates negative nonlinear refraction. The nonlinear refractive index $\gamma(m^2/w)$ is given by the formula [11],

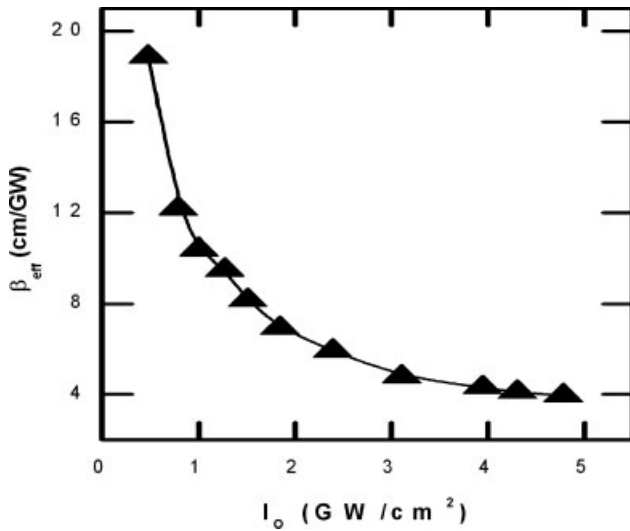


FIG. 5. Nonlinear absorption coefficient (β_{eff}) Vs on-axis input intensity I_0 of the copolymer.

$$\gamma = \frac{\Delta\phi_0 \lambda}{2\pi L_{\text{eff}} I_0} (m^2/W), \quad (8)$$

where, $\Delta\phi_0$ is the on-axis phase change given by the equation,

$$\Delta\phi_0 = \frac{\Delta T_{p-v}}{0.406(1-S)^{0.25}} \quad \text{for } \Delta|\phi_0| \leq \pi, \quad (9)$$

where, ΔT_{p-v} is the peak to valley transmittance difference and S is the linear aperture transmittance, which is equal to 0.5 in our experiments.

The nonlinear refractive index n_2 (in esu) is related to $\gamma(m^2/w)$ by,

$$n_2(\text{esu}) = (cn_0/40\pi)\gamma(m^2/w), \quad (10)$$

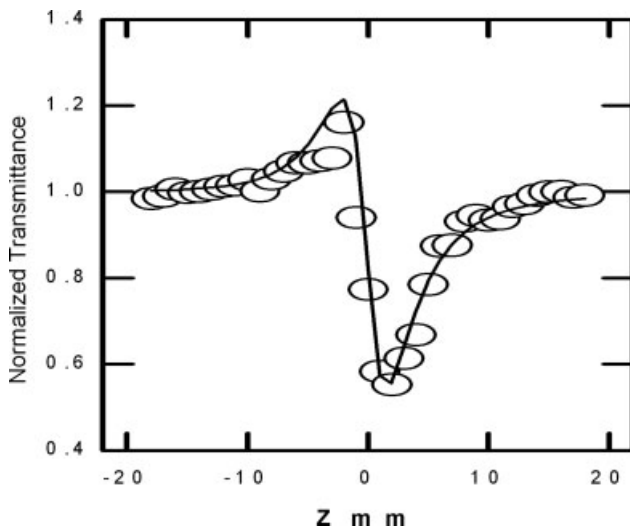


FIG. 6. Closed aperture Z-scan trace. Solid line depicts theoretical fit.

The normalized transmittance for the closed aperture Z-scan conditions is given by [11],

$$T(z) = 1 + \frac{4x\Delta\phi_0}{[(x^2+9)(x^2+1)]} - \frac{2\Delta\psi_0(x^2+3)}{[(x^2+9)(x^2+1)]}, \quad (11)$$

where $\Delta\psi_0$ is the on-axis phase shift due to nonlinear absorption and is given by

$$\Delta\psi_0 = \frac{1}{2}\beta_{\text{eff}}I_0L_{\text{eff}}.$$

The closed aperture Z-scan data also includes the contribution from nonlinear absorption. To extract the pure nonlinear refraction part, following Sheik-Bahae et al. [11], we have computed the value of the closed aperture data by the open aperture data. Figure 7 shows the resulting curve corresponding to pure nonlinear refraction. The normalized transmittance for pure nonlinear refraction is given by [11],

$$T(z) = 1 + \frac{4x\Delta\phi_0}{[(x^2+9)(x^2+1)]} \quad (12)$$

The nonlinear refractive index n_2 (esu), and nonlinear absorption coefficient β , are related to the real and imaginary part of third-order nonlinear optical susceptibility through the equations,

$$\text{Re}\chi^{(3)} = 2n_0^2 c \varepsilon_0 n_2(\text{esu}) \quad (13)$$

$$\text{Im}\chi^{(3)} = n_0^2 c \varepsilon_0 \lambda\beta/2\pi, \quad (14)$$

where n_0 is the linear refractive index, ε_0 is the permittivity of free space and c is velocity of light in vacuum.

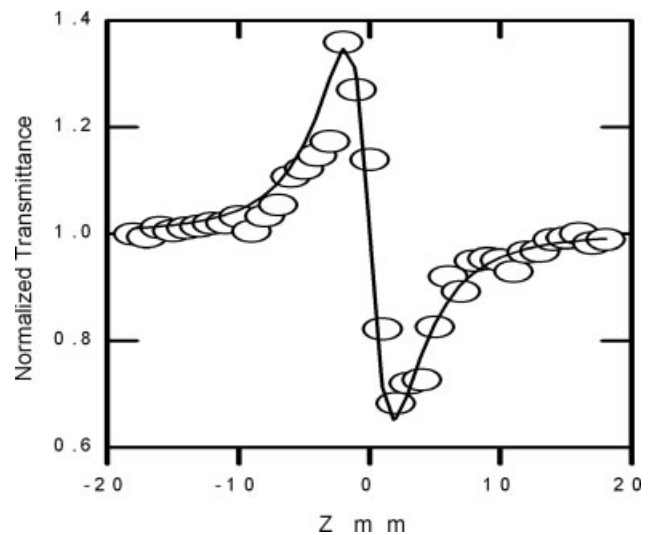


FIG. 7. Pure nonlinear refraction curve. Solid line depicts theoretical fit.

In π -conjugated polymers, electrons can move in large molecular orbitals, which result from the linear superposition of the carbon P_z atomic orbitals, leading to high $\chi^{(3)}$ [9]. The copolymer studied in our experiments consists of alternating electron donating (alkoxy pendant at 3,4 position) and electron withdrawing groups (1,3,4-oxadiazole and pyridine) in the chain. Thus the copolymer has the groups forming a donor-acceptor configuration which is essential to exhibit large third-order nonlinear optical properties. The substitution of the alkoxy group not only enhances the delocalization of π -electrons in the copolymer, but also acts as a solubilizing group. The third-order nonlinearity in the copolymer arises due to the high π -electron density along the polymer backbone which is delocalized. The coupling factor ρ is defined as the ratio of imaginary part to real part of the third-order nonlinear susceptibility,

$$\rho = \text{Im}\chi^{(3)}/\chi_R^{(3)} = \beta/2kn_{\text{esu}} \quad (15)$$

The coupling factor for the copolymer was found to be 0.264, which is less than 1/3, indicating that the nonlinearity is predominantly of electronic origin. The calculated values of nonlinear absorption coefficient, β_{eff} , nonlinear refractive index, γ in m^2/W (n_2 in esu), and the real and imaginary parts of third-order nonlinear optical susceptibility, $\chi^{(3)}$, were, 18.93 cm/GW, $3.037 \times 10^{-17} \text{ m}^2/\text{W}$ (-1.022×10^{-10} esu), $1.512 \times 10^{-20} \text{ m}^2/\text{V}^2$ (-1.080×10^{-12} esu), and $0.399 \times 10^{-20} \text{ m}^2/\text{V}^2$ (0.285×10^{-12} esu), respectively. The real and imaginary parts of $\chi^{(3)}$ were converted to SI units using the relation,

$$\chi^{(3)}(\text{SI}) = \frac{4\pi}{9} \times 10^{-8} \chi^{(3)}(\text{cgs}) \quad (16)$$

The value of n_2 is nearly three orders of magnitude larger than that of thiophene oligomers obtained by Hein et al. [21]. The value of β_{eff} is comparable with the value obtained by Cassano et al. [10]. The value of third-order nonlinear optical susceptibility $\chi^{(3)}$, is comparable with the value of poly(3-dodecyloxymethylthiophene) which is 5×10^{-12} esu obtained by Sasabe et al. [22].

OPTICAL POWER LIMITING STUDIES

Optical power limiting is a very important nonlinear optical property in the context of eye and sensor protection against intense light [3]. An ideal optical limiter is perfectly transparent at light intensities below a threshold level, above which the transmitted intensity remains clamped at a constant value [2]. The nonlinear mechanisms leading to optical power limiting include two-photon absorption, free carrier absorption, reverse saturable absorption, nonlinear scattering, etc. The molecules exhibiting RSA generally have extremely fast response time, since it involves electronic transitions. The best known reverse saturable absorbers are fullerene (C_{60}), porphyrin

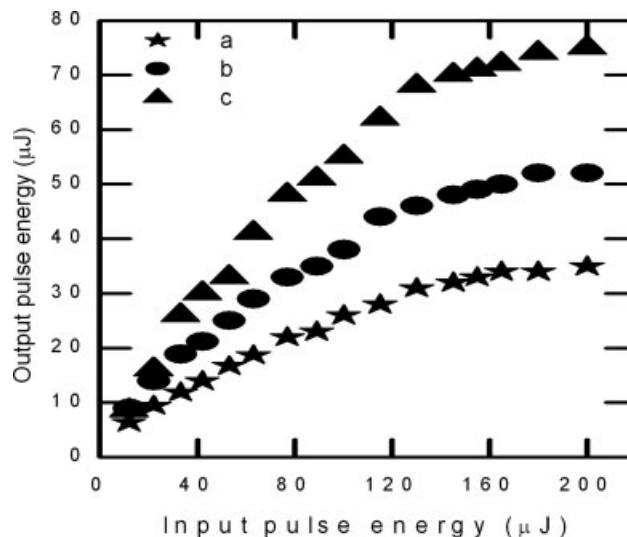


FIG. 8. Optical power limiting of copolymer at three different concentrations. (a) 5×10^{-4} , (b) 2.5×10^{-4} , (c) 1.25×10^{-4} mol/L.

complexes, phthalocyanines etc., [2, 8, 9]. Optical power limiting experiments were performed by keeping the cuvette, containing polymer solution at the focus of the laser beam and measuring the transmitted energy for different input laser energies. Figure 8 shows the optical power limiting of the copolymer. The copolymer was found to exhibit good optical power limiting property for the nanosecond laser pulses. The clamping levels of the copolymer were, ~ 34 , ~ 48 , and $\sim 72 \mu\text{J}$ respectively at concentrations of 5×10^{-4} , 2.5×10^{-4} , and 1.25×10^{-4} mol/L. The clamping levels of the copolymer decreased on increasing the concentration, this is because solutions with higher concentration possess more molecules per unit volume leading to more efficient absorption. We attribute the optical power limiting of the copolymer to reverse saturable absorption. Therefore, thiophene-based copolymer investigated by us is a promising candidate for making optical power limiting devices.

CONCLUSIONS

In summary, third-order nonlinear optical properties of a novel copolymer were investigated using the nanosecond single beam Z-scan technique. Z-scan results indicate that the copolymer exhibits self-defocusing effect or negative nonlinearity. The real and imaginary parts of third-order nonlinear optical susceptibility, $\chi^{(3)}$, were, $1.512 \times 10^{-20} \text{ m}^2/\text{V}^2$ (-1.080×10^{-12} esu) and $0.399 \times 10^{-20} \text{ m}^2/\text{V}^2$ (0.285×10^{-12} esu), respectively. The copolymer exhibits good optical power limiting of nanosecond laser pulses at 532 nm wavelength. The operating nonlinear mechanism leading to optical power limiting was found to be reverse saturable absorption. Large third-order nonlinear optical properties in the copolymer arise due to the strong delocalization of π -electrons along the polymer chain. Hence, the copolymer investigated here seems to be

promising material for making practical devices for photonics applications.

REFERENCES

1. P.N. Prasad and D.J. Williams, *Introduction to Nonlinear Optical Effects in Molecules and Polymers*, Wiley, New York (1991).
2. R.L. Sutherland, *Handbook of Nonlinear Optics*, Dekker, New York (1996).
3. J.W. Perry, K. Mansour, I.-Y.S. Lee, X.-L. Wu, P.V. Bedworth, C.-T. Chen, D. Ng, S.R. Marder, P. Miles, T. Wada, M. Tian, and H. Sasabe, *Science*, **273**, 1533 (1996).
4. A. Ronchi, T. Cassano, R. Tommasi, F. Babudri, A. Cardone, G.M. Farinola, and F. Naso, *Synth. Met.*, **39**, 831 (2003).
5. M. Falconieri, R. D'Amato, A. Furlani, and M.V. Russo, *Synth. Met.*, **124**, 217 (2003).
6. M. Samoc, A. Samoc, B. Luther-Davies, Z. Bao, L. Yu, B. Hsieh, and U. Scherf, *J. Opt. Soc. Am. B*, **15**, 817 (1998).
7. M. Nisoli, A. Cybo-Ottone, S. De Silvestri, V. Magni, R. Tubino, C. Botta, and A. Musco, *Phys. Rev. B*, **47**, 10881 (1993).
8. J. Roncali, *Chem. Rev.*, **92**, 711 (1992).
9. T. Cassano, R. Tommasi, M. Ferrara, F. Babudri, A. Cardone, G.M. Farinola, and F. Naso, *Chem. Phys.*, **272**, 111 (2001).
10. T. Cassano, R. Tommasi, F. Babudri, A. Cardone, G.M. Farinola, and F. Naso, *Opt. Lett.*, **27**, 2176 (2002).
11. M. Sheik-Bahae, A.A. Said, T.H. Wei, D.J. Hagan, and E.W. Van Stryland, *IEEE J. Quantum Electron.*, **26**, 760 (1990).
12. P.K. Hegede and A.V. Adhikari, Proceedings of International Conference on Advances in Polymer Science and Technology (POLY2008), CONP-PO-4 (2008).
13. W. Feng, W. Yi, H. Wu, M. Ozaki, and K. Yoshino, *J. Appl. Phys.*, **98**, 034301 (2005).
14. K.P. Unnikrishnan, J. Thomas, V.P.N. Nampoori, and C.P.G. Vallabhan, *Opt. Commun.*, **204**, 385 (2002).
15. F.Z. Henari, W.J. Blau, L.R. Milgrom, G. Yahioglu, D. Phillips, and J.A. Lacey, *Chem. Phys. Lett.*, **267**, 229 (1997).
16. W. Sun, C.C. Beyon, M.M. McKerns, C.M. Lawson, S. Dong, D. Wang, and G.M. Gray, *Proc. SPIE*, **16**, 3798 (1999).
17. G.L. Wood, M.J. Miller, and A.G. Mott, *Opt. Lett.*, **20**, 973 (1995).
18. L.W. Tutt and A. Kost, *Nature*, **356**, 225 (1992).
19. S. Couris, E. Koudoumas, A.A. Ruth, and S. Leach, *J. Phys. B: At. Mol. Opt. Phys.*, **28**, 4537 (1995).
20. S.L. Guo, L. Xu, H.T. Wang, X.Z. You, and N.B. Ming, *Opt. Int. J. Light Electron Opt.*, **114**, 58 (2003).
21. J. Hein, H. Bergner, M. Lenzner, and S. Rentsch, *Chem. Phys.*, **179**, 543 (1994).
22. H. Sasabe, T. Wada, T. Sugiyama, H. Ohkawa, A. Yamada, and A.F. Garito, "Third Harmonic Generation of Polythiophene Derivatives," in *Conjugated Polymeric Materials: Opportunities in Electronics, Optoelectronics, and Molecular Electronics, Series E: Applied Sciences, Vol. 182*, J.L. Bredas and R.R. Chance, Eds., Kluwer Academic Publishers, USA, 399 (1990).