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Nonlinear optical and optical power limiting studies on a new thiophene-based conjugated polymer in solution and solid PMMA matrix

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ABSTRACT

An experimental investigation of the third-order nonlinear optical properties of new poly[2-*{5-[3,4-ditetradecyloxy-5-(1,3,4-oxadiazol-2-yl)thiophen-2-yl]-1,3,4-oxadiazol-2-yl}pyridine*] (**P**) in tetrahydrofuran (THF) solution and in solid poly(methylmethacrylate) (PMMA) matrix, by Z-scan technique is reported. The Z-scan traces reveal that the composite films exhibit large negative nonlinear refractive index of the order 10^{-10} esu. The excited-state absorption cross-section was found to be larger than the ground-state absorption indicating that the operating nonlinear process is reverse saturable absorption (RSA). The new polymer **P** exhibits good optical power limiting properties in the nanosecond regime in solution and as well in solid PMMA matrix.

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1. Introduction

In recent years, the search for novel nonlinear optical materials with large nonlinear optical properties has increased because of their applications in integrated optics such as optical modulation, optical information, optical data storage, optical power limiting, fluorescence excitation microscopy and imaging [1,2]. In this regard, organic materials are potential candidates because they can be tailored chemically to fit wide range of photonics and optoelectronics applications [2]. Among the organics, conjugated polymers are emerging as most widely studied materials for nonlinear optics. The presence of the delocalized π -electron system in them leads to large values of third-order nonlinear optical parameters and fast response times [3,4]. Polythiophenes are very versatile class of conjugated polymers, which is gaining significant scientific interest because of the possibility of making systematic structural modification at molecular level.

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Recently, Cassano et al. [5] 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 of tuning the linear and nonlinear optical coefficients in polymers based on the effect of the simultaneous presence of electron-acceptor and electron-donor substituted aromatic rings in the conjugated polymer backbone [6]. In this approach, we have designed a new molecule with electron donor and acceptor groups, arranged alternatively along the polymer backbone. From the photonics and opto-electronics applications point of view, the basic requirement for a good nonlinear optical material is that it should exhibit high optical quality with large and stable optical nonlinearity in the solid state. It has been observed that the difficulty in the processing of organic conjugated polymers such as polythiophenes, poly(*p*-phenylenevinylene) has made intricacy in fabricating the solid-state optical devices and assembling them into a system [7–9]. In this context, one can dope the superior nonlinear optical materials into suitable host forming composites with good optical transparency [7–11]. In the present work, the newly synthesized polymer **P** was blended with poly(methylmethacrylate) (PMMA) as matrix to prepare the composite film.

In this paper, we report experimental studies on third-order nonlinear optical properties of new polymer **P** in tetrahydrofuran

(THF) solution and in PMMA matrix, using Z-scan technique at 532 nm. Further, we present the strong optical power limiting of nanosecond laser pulses of the composite films, based on reverse saturable absorption (RSA).

2. Experiments

To prepare the composite films, PMMA was selected as the host material because PMMA is hard, rigid and has a glass transition temperature of 125 °C. It also exhibits good linear optical transmittance, optical stability, thermal stability and moreover better compatibility with organics [12,13]. PMMA and polymer **P** were dissolved in THF separately and stirred well to form uniform solution later both the solution were mixed together and stirred for 8–10 h using a magnetic stirrer. The mixed solution was poured into a petridish and kept for drying at room temperature for overnight. Then the sample was kept in an oven at ~70 °C for 24 h. The composite film of thickness ~0.36 mm was obtained which was used for Z-scan and optical power limiting measurements. We also prepared the composite films with different weight % of polymer **P** in PMMA for the concentration dependence studies. The synthesis and characterization of the polymer used in this study has been reported elsewhere [14]. Fig. 1 shows the structure of PMMA and structure of the polymer investigated. The linear absorption spectrum of the polymer is shown in the Fig. 2, was obtained at room temperature by using the UV–visible fiber optic spectrometer (Model SD2000, Ocean Optics Inc.).

The single beam Z-scan technique [15–17] was used to evaluate the third-order nonlinear optical susceptibility of the polymer in both solution and solid medium. This technique enables simultaneous measurement of nonlinear refraction (NLR) and nonlinear absorption (NLA). Basically, in this technique the nonlinear sample is scanned through the focal plane of a tightly focused Gaussian beam and the changes in the far-field intensity pattern with and without aperture is monitored. Experiments were performed using a Q-switched, frequency doubled Nd:YAG laser (Spectra—Physics USA, Model-GCR170) producing 7 ns laser

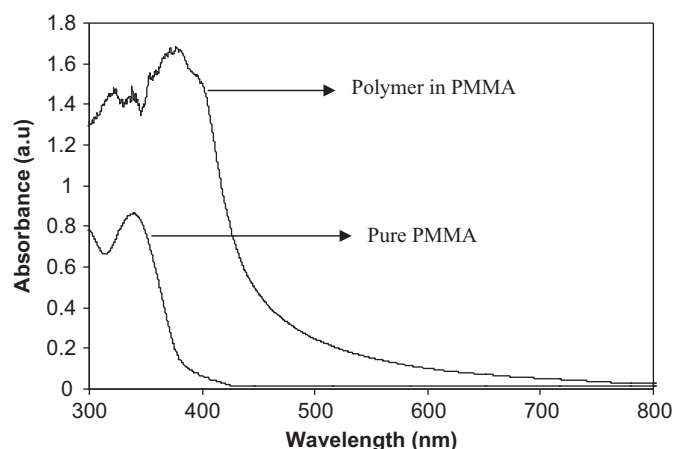


Fig. 2. UV–visible absorption Spectrum of polymer composite and pure PMMA films.

pulses (FWHM) at 532 nm and at a pulse repetition rate of 10 Hz. The output of the laser beam had a nearly Gaussian intensity profile. The Gaussian laser beam was focused by using a lens of 25 cm focal length. The resulting beam waist radius at the focused spot, calculated using the formula $\omega_0 = 1.22\lambda f/d$, where f is focal length of the lens and d the diameter of the aperture, was found to be 18.9 μm . The corresponding Rayleigh length, calculated using the formula $Z_R = \pi\omega_0^2/\lambda$, was found to be 2.11 mm. For solution Z-scan measurements, cuvette of 1 mm thickness was used. Thus, the sample thickness is less than the Rayleigh length for both the systems i.e. solution and solid medium; hence the thin sample approximation is valid [15]. The Z-scan experiments were performed at an input intensity of 1.195 GW/cm^2 . For the optical power limiting study, the samples were kept at the focus of the laser beam. By varying the input laser energy, the change in the output laser energy was noted using Laser Probe Rj-7620 Energy ratio meter with two pyroelectric detectors.

3. Results and discussion

In this section, we present the results of nonlinear optical measurements obtained for polymer in solution and in PMMA matrix. In presence of high-intensity laser irradiation, the nonlinear absorption and refraction are expressed by the equations

$$\alpha(I) = \alpha + \beta I \quad (1)$$

$$n(I) = n + n_2 I \quad (2)$$

where α is the linear absorption coefficient, n the linear refractive index, β the nonlinear absorption coefficient and n_2 the nonlinear refractive index, and I the intensity of the laser beam.

3.1. Nonlinear absorption

The magnitude of nonlinear absorption coefficient β , of polymer in solution n and in PMMA matrix was estimated by performing the open aperture Z-scan (i.e. without keeping aperture in front of the detector) which is related to the imaginary part of third-order optical susceptibility $\chi^{(3)}$. Fig. 3 shows the open aperture Z-scan trace of the polythiophene in solution and in solid PMMA matrix (0.25 wt%), which is found to be symmetric with respect to the focus indicating intensity-dependent absorption. This may include nonlinear optical processes like two-photon absorption (TPA), excited-state absorption (ESA), free carrier absorption and reverse saturable absorption. Nonlinear absorption under nanosecond

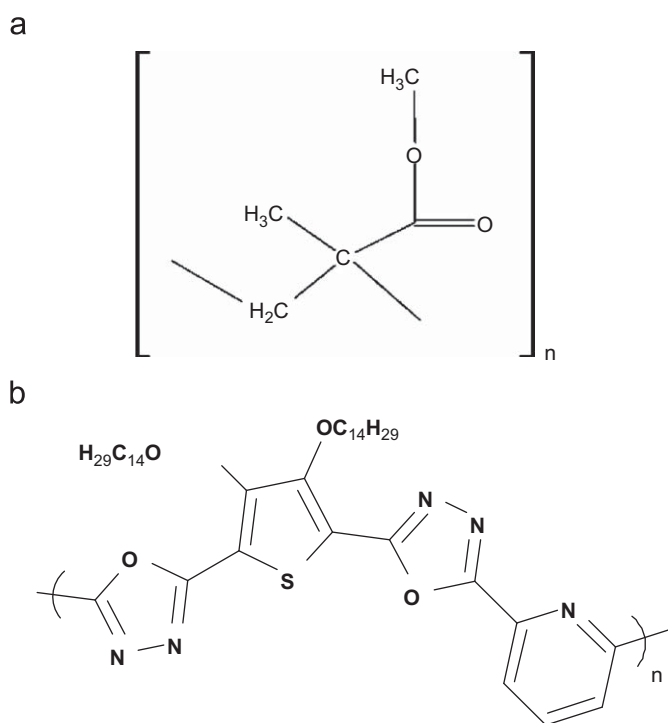


Fig. 1. (a) Structure of PMMA. (b) Structure of the polymer **P** with $R = C_{14}H_{29}$.

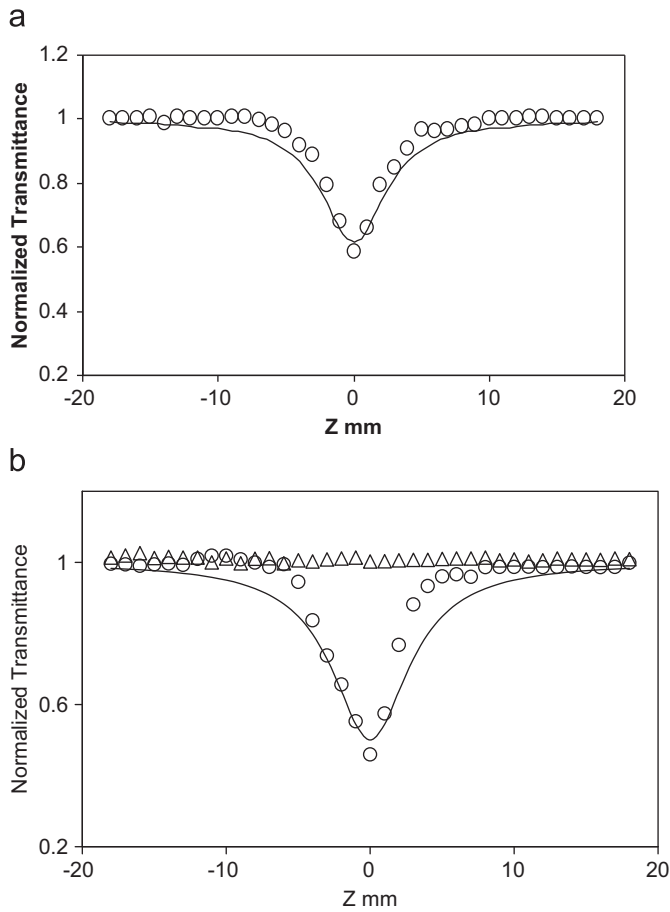


Fig. 3. Open aperture Z-scan traces of polymer P: (a) in solution and (b) in PMMA matrix (i) pure PMMA and (ii) polymer P composite film (0.25 wt%). Solid line depicts theoretical fit.

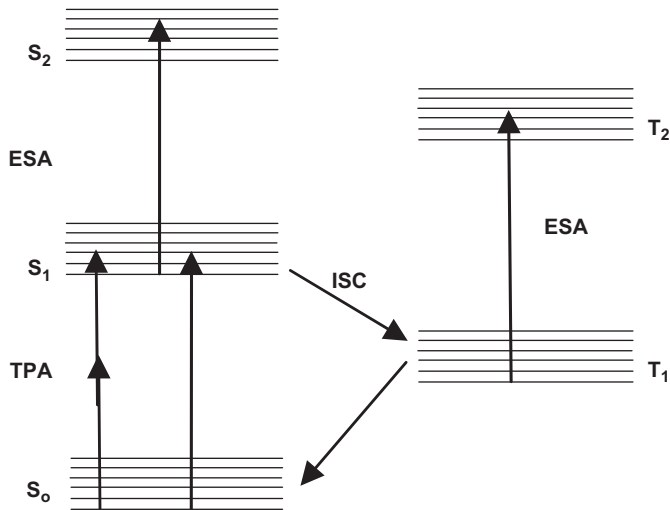


Fig. 4. Energy level diagram showing both two-photon absorption (TPA) and excited-state absorption (ESA) (five-level model).

excitation can be explained using the five level energy diagram [8,18–20] as shown in Fig. 4. This includes ground state S_0 , the first singlet state S_1 , the next higher excited singlet state S_2 , lower triplet state T_1 and next higher triplet state T_2 . Each of these states contains number of vibrational levels. When two photons, of the same or different energy are simultaneously absorbed from the ground state to a higher excited state ($S_1 \leftarrow S_0$), it is denoted as two-photon

absorption. When excited-state absorption occurs molecules are excited from an already excited state to a higher excited state (e.g. $S_2 \leftarrow S_1$ and/or $T_2 \leftarrow T_1$). 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. 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 occurs. If more absorption occurs from the excited state than from the ground state it is usually called reversed saturable absorption. 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 is true in our case, triplet–triplet transitions are expected make significant contribution to nonlinear absorption. Under open aperture Z-scan condition, normalized transmission is given by [21]

$$T(z) = 1 - \frac{q_0}{2\sqrt{2}} \quad \text{for } |q_0| < 1 \quad (3)$$

where q_0 is a free factor defined as

$$q_0 = \frac{\beta I_0 (1 - \exp^{-\alpha L})}{(1 + Z^2/Z_0^2)\alpha}$$

where L is the length of the sample, I_0 the intensity of the laser beam at the focus and Z_0 the Rayleigh range of the lens. A fit to the Eq. (1) to the open aperture data yielded a value of nonlinear absorption coefficient β_{eff} for the polythiophene. The excited-state absorption cross-section (σ_{ex}) was measured from the normalized open aperture Z-scan data [21–24]. It was assumed that the molecular energy levels could be reduced to a three level to calculate σ_{ex} . Molecules are optically excited from the ground state to the singlet excited state, and from this state, they relax either to ground state or to 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 laser beam as it propagates through the sample is given by

$$\frac{dI}{dZ} = -\alpha I - \sigma_{\text{exc}} N(t), \quad (4)$$

$$\frac{dN}{dt} = \frac{\alpha I}{\hbar \omega}, \quad (5)$$

where I is the intensity, Z the sample position, N the density of charges in the excited state, ω the angular frequency of the laser and α linear absorption. By combining Eqs. (3) and (4) yield

$$\frac{dI}{dZ} = -\alpha I - \frac{\sigma_{\text{exc}} \alpha I}{\hbar \omega} \int_{-\infty}^t I(t') dt', \quad (6)$$

Solving the above equation for the fluence and integrating over spatial extent of the beam, gives the normalized energy transmission for open aperture and is given by [23]

$$T = \ln \left(1 + \frac{q_0}{1 + \chi^2} \right) / \left(\frac{q_0}{1 + \chi^2} \right), \quad (7)$$

where $\chi = z/z_0$, z is the distance of the sample from the focus, z_0 the Rayleigh length given by the formula $Z_0 = 2\pi w_0^2/\lambda$ (k is the wavelength and w_0 the beam waist at the focus) and q_0 is given by the equation [21–24]

$$q_0 = \frac{\sigma_{\text{exc}} \alpha F_0(r=0) L_{\text{eff}}}{2\hbar \omega}, \quad (8)$$

where α is the linear absorption coefficient, $L_{\text{eff}} = [1 - \exp(-\alpha L)]/\alpha$, ω the angular frequency of the laser and F_0 the on-axis fluence at the focus which is related to the incident energy E_{total} .

Table 1Third-order nonlinear optical coefficients of polymer **P** in THF solutions at concentration of 5×10^{-4} mol/L.

Sample	n_2 ($\times 10^{-10}$ esu)	β_{eff} (cm/GW)	σ_g ($\times 10^{-19}$ cm ²)	σ_{exc} ($\times 10^{-18}$ cm ²)	Re χ^3 ($\times 10^{-12}$ esu)	Im χ^3 ($\times 10^{-12}$ esu)
In solution	-1.723	28.10	10.72	8.93	-1.821	0.423

Table 2Third-order nonlinear optical coefficients of polymer (**P**) composite films and second-order hyperpolarizability of the polymer.

Sample	Dopant concentration (wt%)	n_2 ($\times 10^{-10}$ esu)	β_{eff} (cm/GW)	σ_g ($\times 10^{-17}$ cm ²)	σ_{exc} ($\times 10^{-16}$ cm ²)	Re χ^3 ($\times 10^{-12}$ esu)	Im χ^3 ($\times 10^{-12}$ esu)	γ_h ($\times 10^{-28}$ esu)
In PMMA	0.25	-1.678	34.55	7.738	2.297	-1.992	0.619	4.835
	0.50	-1.913	43.39	4.330	2.666	-2.271	0.778	
	0.75	-2.024	47.80	2.970	2.754	-2.458	0.884	
	1.00	-2.177	50.25	2.236	2.835	-2.655	0.930	

The values of effective excited-state absorption cross-section σ_{exc} , of the polymer were obtained by fitting the open aperture data using the Eq. (6). The ground-state absorption cross-section, σ_g , was calculated using the relation

$$\sigma_g = \frac{\alpha}{N_a C}, \quad (9)$$

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

The measured values of ground-state and effective excited-state absorption cross-sections of the polymer in solution and in PMMA matrix are given in Tables 1 and 2, respectively. The larger values of σ_{exc} , as compared to σ_g , indicates that the operating nonlinear process is reverse saturable absorption [21–24]. Further, if the nonlinear mechanism belongs to the simple two-photon absorption, β_{eff} should be a constant independent of on-axis input intensity I_o [25,26]. But the plot in Fig. 5(a) and (b) shows the value of β_{eff} decreases on raising the on-axis input intensity I_o for both the systems, which is the consequence of sequential two-photon absorption [27,28]. With increasing intensity, the total absorption of the polythiophene approaches asymptotically the absorbance of the triplet state. Therefore, the β_{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 polymer. Similar trends were observed by Couris et al. [27] and Bindhu et al. [28] for C_{60} and C_{70} in toluene solutions, where they have attribute to sequential two-photon absorption via excited-state absorption (reverse saturable absorption). For instance, Chen et al. [29] have also observed similar decrease in the effective intensity-dependent nonlinear absorption coefficient β_{eff} on increasing input intensities in case of $t\text{Bu}4\text{PcTiO}$ /polymer composites, where they ascribe it to the possibility of high-order triple-state transitions of the excited-state population. This indicates the presence of higher-order effects to the observed nonlinearity [30]. However, Hein et al. [31] have also reported decrease of β_{eff} with increasing I_o for the thiophene oligomers, where they attributed to saturation of instantaneous two-photon absorption. The obtained values of excited-state and ground-state absorption cross-section of the polymer is comparable with the values obtained by Henari et al. [24] for organometallic phthalocyanine.

3.2. Nonlinear refraction

To determine the sign and magnitude of nonlinear refraction, closed aperture Z-scan (i.e. by placing an aperture in front of the detector) was performed. A material with nonlinear refractive index depends on the sample position Z , and cause focusing

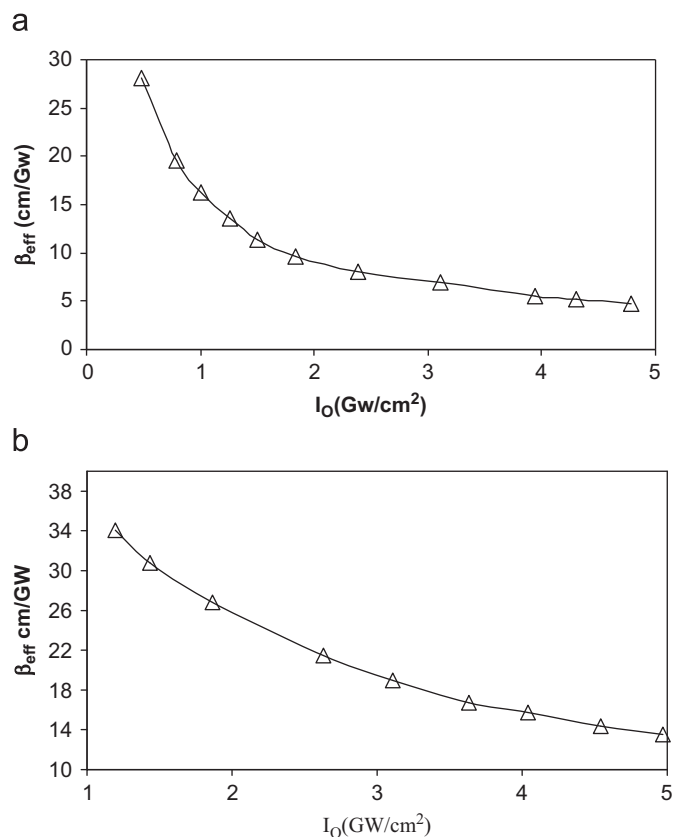


Fig. 5. Nonlinear absorption coefficient (β_{eff}) vs. on-axis input intensity I_o of polymer **P**. (a) In solution. (b) In PMMA.

or defocusing of light beam, hence there is change in the intensity of the beam in the far-field zone as the sample is traced along Z . The consequence of this results in a “peak-valley (negative n_2)” or “valley-peak (positive n_2)” type of Z-scan curve. Fig. 6 shows the closed aperture Z-scan trace of the polythiophene in solution and in solid PMMA matrix (0.25 wt%). It exhibits peak-valley characteristic for both the systems, indicating self-defocusing effect (negative nonlinear refraction, i.e. $n_2 < 0$). The nonlinear refractive index γ (m^2/w) is given by the formula [15]

$$\gamma = \frac{\Delta\phi_o \lambda}{2\pi L_{\text{eff}} I_o} (m^2/W), \quad (10)$$

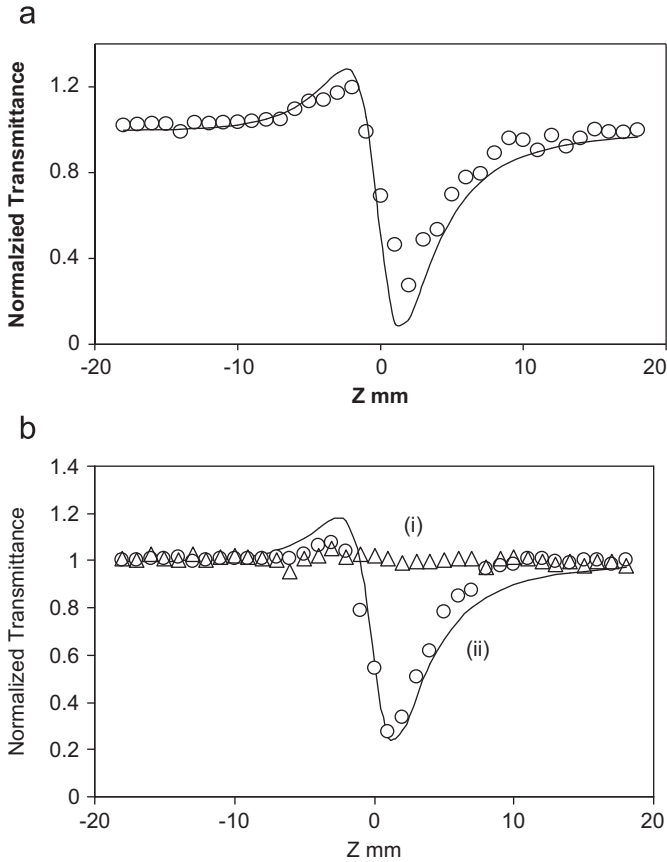


Fig. 6. Closed aperture Z-scan traces of polymer **P**: (a) In solution and (b) In PMMA matrix (i) Pure PMMA and (ii) polymer composite film (0.25 wt%). Solid line depicts theoretical fit.

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

$$\Delta\phi_o = \frac{\Delta T_{p-v}}{0.406(1-S)^{0.25}} \text{ for } |\Delta\phi_o| \leq \pi, \quad (11)$$

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

The nonlinear refractive index n_2 (in esu) is related to γ (m^2/W) by

$$n_2(\text{esu}) = ((cn_o/40\pi)\gamma)(\text{m}^2/\text{W}), \quad (12)$$

Usually, the closed aperture Z-scan data also includes the contribution from nonlinear absorption. In order to extract the pure nonlinear refraction part, following Sheik-Bahae et al. [15], we have computed the value of the closed aperture data by the open aperture data. Fig. 7 shows the resulting curve corresponding to pure nonlinear refraction. It is observed that the peak-valley of closed aperture Z-scan satisfies the condition of $\Delta Z \sim 1.7\Delta Z_o$, thus confirming the third-order nonlinearity is due to electronic process [15]. The sign and magnitude of n_2 is determined from the relative position of the peak and valley with z [15]. The normalized transmittance for pure nonlinear refraction is given by [15]

$$T(z) = 1 + \frac{4x\Delta\phi_o}{[(x^2+9)(x^2+1)]}, \quad (13)$$

The nonlinear refractive index n_2 , and nonlinear absorption coefficient β , are related to the real and imaginary part of third-order nonlinear optical susceptibility $\chi^{(3)}$ through the

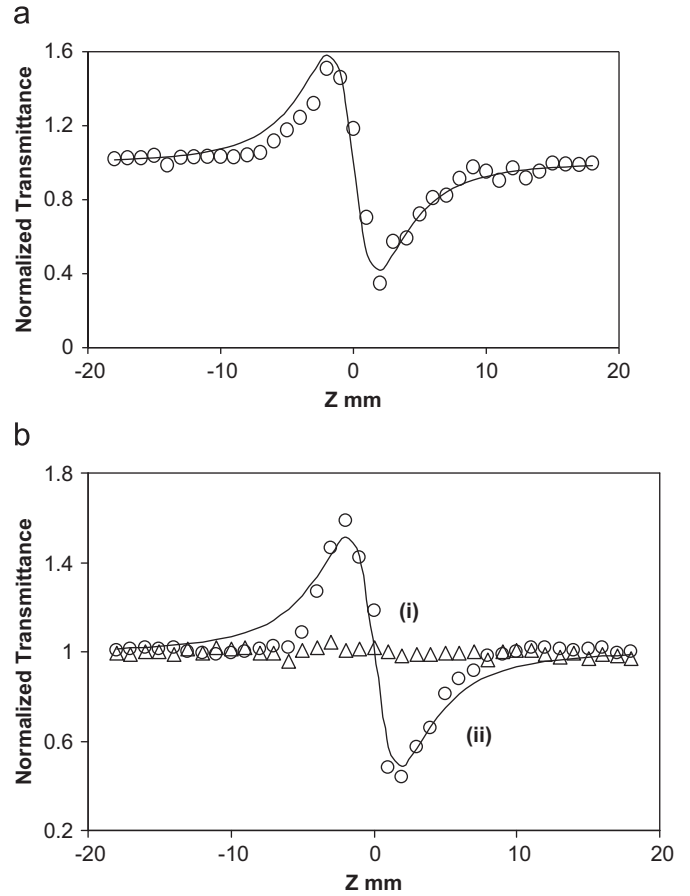


Fig. 7. Pure nonlinear refraction Z-scan traces of polymer **P**: (a) in solution and (b) in PMMA matrix (i) pure PMMA and (ii) polymer composite film (0.25 wt%). Solid line depicts theoretical fit.

equations

$$\text{Re}\chi^{(3)} = 2n_0^2 c \epsilon_0 n_2 (\text{esu}), \quad (14)$$

$$\text{Im}\chi^{(3)} = n_0^2 c \epsilon_0 \lambda \beta_{\text{eff}} / 2\pi, \quad (15)$$

Damage of the films was checked by using an optical microscope soon after performing the Z-scan measurements. We found there was no damage of the films at the region where Z-scan data was obtained at the input intensity used. While performing the Z-scan from $-Z$ to $+Z$, it was again repeated by translating the sample from $+Z$ to $-Z$ and calculated the values, we did not found significant differences. To determine any contributions from the solid PMMA matrix to the observed nonlinearity, we conducted Z-scan experiment on pure PMMA film (i.e. with 0 wt% dopant concentration) and found negligible contribution both for nonlinear refraction and nonlinear absorption at the input energy used. Therefore, any contribution from pure PMMA film to the observed nonlinearity is negligible at the input intensity used. It is evident that the total nonlinearity has significant contributions from both real and imaginary parts of third-order nonlinear optical susceptibility $\chi^{(3)}$. We expect the large nonlinearity in polymer arises due to the contributions from the population in the excited states and as well as due to the electronic response to the applied optical field.

Generally, in π -conjugated polymers, the charge cloud formed by conjugated π -electrons has the capability of being strongly deformed under the effect of an external optical field. The electrons move in large molecular orbitals, formed by the linear

superposition of the carbon p_z atomic orbitals, leading to high $\chi^{(3)}$, that increases with the conjugation length [5]. Further, nonlinear susceptibility depends on presence of hyperpolarizability in the molecules. The molecular hyperpolarizability can be enhanced by increasing dipole moment within the conjugated polymer chain. According to the literature [5], enhanced hyperpolarizability can be achieved by introduction of alternating electron donor and acceptor groups along the polymer backbone. Based on this observation, a new polymer carrying electron donor 3,4-ditetracycloxy thiophene ring and electron acceptor oxadiazolopyridine moiety has been synthesized. In the new molecule, existence of a strong delocalization of π -electrons along the polymer chain is the prime reason for its third-order nonlinearity. Further, the involvement of push-pull mechanism due to the presence of donor and acceptor type of arrangements leads to increase in molecular hyperpolarizability along the polymer backbone. Also, the presence of unsubstituted pyridine moiety is responsible for reduction in the steric repulsion between the bulky alkyl groups. This causes the enhanced planarity of the polymer chain and hence the greater delocalization. The values of nonlinear absorption coefficient β_{eff} , nonlinear refractive index n_2 , and the real and the imaginary parts of third-order nonlinear optical susceptibility $\chi^{(3)}$, of the polymer in solution and in PMMA matrix are given in Tables 1 and 2, respectively.

The second-order hyperpolarizability γ_h of a molecule is related to the third-order susceptibility $\chi^{(3)}$ as below [32]

$$\gamma_h = \chi^{(3)}/L^4 N \quad (16)$$

In the above equation, N is the density of molecules in the unit of molecules per cm^3 . The term L is the local field factor, which in the Lorentz approximation is given by $L = (n^2+2)/3$. The calculated value of molecular second hyperpolarizability γ_h , for the polymer is given in the Table 2, which is well comparable with the value reported for silicon naphthalocyanine, SiNc ($\gamma_h = 1.7 \times 10^{-31}$ esu), a widely known optical limiting material [22] and also the most interesting optical limiting organic material trans-4-[2-(pyrrl)vinyl]-1-methylpyridinium iodide[PVPI]—a stilbazolium like dye ($\gamma_h = 1.6 \times 10^{-31}$ esu) [33,34].

4. Optical power limiting studies

The necessity of protecting human eye and optically sensitive devices from intense optical beams calls for the development of potential optical power limiters. 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 [35]. The nonlinear optical mechanisms that cause optical limiting have different origins such as two-photon absorption, free carrier absorption, reverse saturable absorption, excited-state absorption and nonlinear scattering. The molecules exhibiting RSA generally have extremely fast response time, since it involves electronic transitions [18]. The best known reverse saturable absorbers are fullerene (C_{60}), porphyrin complexes, indocyanine green and phthalocyanines [11,18,20–23,36]. Due to the large value of excited-state absorption cross-section compared to the ground-state absorption cross-section of polymer, we expect major nonlinear optical process causing the limiting behavior is reverse saturable absorption. Optical power limiting experiments were performed by placing the sample at the focus of the laser beam and by measuring the transmitted energy for different input laser energies. Fig. 8(a) shows the optical power limiting response of the polymer in THF solutions. The polymer exhibits optical limiting threshold of ~ 120 , ~ 95 and $\sim 80 \mu\text{J}$ with the output energy clamped at ~ 50 , ~ 32 and $\sim 20 \mu\text{J}$, respectively, at concentrations of

1.25×10^{-4} mol/L, 2.5×10^{-4} mol/L and 5×10^{-4} mol/L. Fig. 8(b) shows the optical power limiting response of the polymer in solid PMMA matrix at various concentrations. The clamping levels of the polymer composite film P were found to be, ~ 13 , ~ 10 , ~ 8 and $\sim 6 \mu\text{J}$ with a limiting threshold of ~ 42 , ~ 36 , ~ 25 and $\sim 20 \mu\text{J}$, respectively, at concentrations of 0.25%, 0.5%, 0.75% and 1.0%. We found that the film was damaged when the input energy was increased beyond $400 \mu\text{J}/\text{Pulse}$. So we repeated the optical limiting experiment again by increasing the input energy up to $350 \mu\text{J}/\text{Pulse}$ and also we noted the energy while decreasing the input energy, the reverse path was found to be same as the initial which confirmed that the film was not damaged. We observed that the clamping levels of the polymer decreased on increasing the concentration. This is because at the higher concentration there

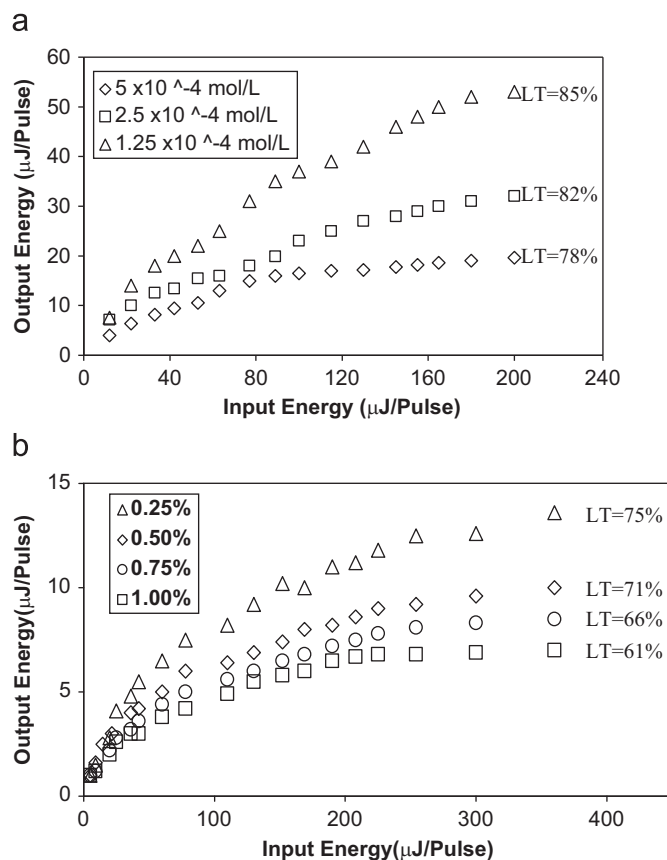


Fig. 8. Optical power limiting response of polymer P: (a) in solution and (b) in PMMA (LT = linear transmittance).

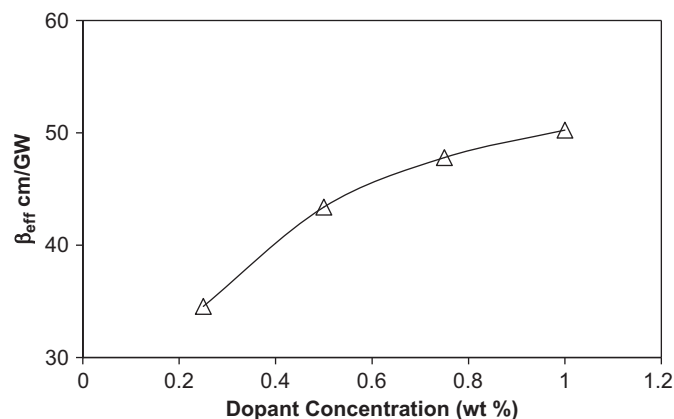


Fig. 9. Concentration dependence of nonlinear absorption coefficient β_{eff} .

exists more molecules per unit volume; hence it absorbs the harsh laser pulses more efficiently. Polymer investigated here exhibits good optical power limiting of nanosecond laser pulses both in solution and as well as in solid PMMA matrix. Therefore, the polymer investigated here seems to be a promising material for making optical power limiting devices.

Concentration dependence of nonlinear absorption coefficient, β_{eff} , was also studied. Fig. 9 shows the plot of nonlinear absorption β_{eff} vs. dopant concentration. The measured value of nonlinear absorption coefficient β_{eff} increases with the concentration of polymer in PMMA indicating that the contribution to nonlinear absorptions arises due to the presence of the polymer. The β_{eff} shows a saturating behavior to the guest concentration further indicating that the nonlinearity includes not only third-order but higher-order nonlinearity.

5. Conclusions

In summary, the third-order nonlinear optical properties of new poly{2-[5-[3,4-ditetradecyloxy-5-(1,3,4-oxadiazol-2-yl)thiophen-2-yl]-1,3,4-oxadiazol-2-yl]pyridine} (P) in THF solution and in PMMA matrix was estimated using the nanosecond Z-scan technique. The polymer possesses large negative nonlinear refractive index as high as 10^{-10} esu. The large third-order nonlinear optical property of the polymer arises due to the strong delocalization of π -electrons along the polymer chain and it is due to the contributions from the population in the excited states. Optical power limiting measurements indicated that the polymer exhibits good optical limiting of 7 ns laser pulses at 532 nm wavelength in both solution and as well as in solid-state form. The operating nonlinear optical process leading to optical power limiting was due to reverse saturable absorption. Hence, the polymer investigated here is a possible candidate for the development of photonic and optoelectronic devices.

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