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# Studies on third-order nonlinear optical properties and reverse saturable absorption in polythiophene/poly (methylmethacrylate) composites

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**Abstract** We report here the studies on third-order nonlinear optical properties of two novel polythiophene composite films investigated using the Z-scan technique. The measurements were carried out using a Q-switched, frequency doubled Nd:YAG laser producing 7 nanosecond laser pulses at 532 nm. Z-scan results reveal that the composite films exhibit self-defocusing nonlinearity. The real and imaginary parts of the third-order nonlinear optical susceptibility were of the order $10^{-12}$ esu. The effective excited-state absorption cross section was found to be larger than the ground state absorption cross section, indicating that the operating nonlinear mechanism is reverse saturable absorption (RSA). The polythiophene composite films also exhibit good optical power limiting of the nanosecond laser pulses. The nonlinear optical parameters are found to increase on increasing the strength of the electron-donor group, indicating the dependence of $\chi^{(3)}$ on the electron-donor/acceptor units of polythiophenes.

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## 1 Introduction

Novel nonlinear optical materials exhibiting a large third-order optical nonlinearity with ultra fast response time are in great demand because of their potential applications in three-dimensional optical data storage, two-photon fluorescence imaging, optical power limiting, optical modulation, optical switching, optical signal reshaping, stabilizing fast fluctuations of laser power, telecommunications, human eye protection etc. [1–4]. In this regard, organic materials are promising candidates because of the flexibility in tailoring and making systematic structural modifications at the molecular level. Among the organics, conjugated polymers have received significant attention, due to the presence of a high density of polarizable $\pi$-electrons along the polymer chain, which results in large optical nonlinearities [5, 6]. Polythiophenes, a very versatile class of conjugated polymers, are currently of interest [7–9], due to the combination of the intrinsically conducting properties and an asymmetric charge distribution produced by the donor and acceptor substituents. It made them particularly useful in the fabrication of ultrafast and highly efficient devices for optical communication and information processing [9].

In order to utilize these optically active organic compounds for photonics based device applications, it is necessary that they exhibit high optical quality with large and stable optical nonlinearity in the solid state form. The major concern with the organic conjugated polymers such as polythiophenes, poly(p-phenylenevinylene) is with the fabrication of solid state optical devices and assembling the devices into a system because of their poor processability [10–12].

In this context, researchers have combined the materials exhibiting large nonlinear optical coefficients into suitable host forming composite materials possessing good optical quality [10–14].

Recently Cassano et al. [15] have shown that, by a proper choice of the side chains in a series of dialkoxy substituted poly(P-pheneylenevinylene), it is possible to enhance the third-order nonlinear optical coefficients, and they also reported on a new strategy of tuning the linear and nonlinear optical coefficients 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 [16]. Following the strategy reported by Cassano et al. [16], here we report our efforts in tuning the nonlinear optical properties of newly synthesized polythiophenes. We have designed the polythiophenes with an alternating electron-donor-acceptor group arrangement along the polymer backbone. These newly synthesized polythiophenes were then utilized to prepare the composite films by blending with poly (methylmethacrylate).

In this article, we present the results of third-order nonlinear optical properties of poythiophene/PMMA composite films investigated by the Z-scan technique at 532 nm. Optical power limiting measurements were also conducted on the composite films, and measurements indicate that the composite films exhibit a good optical power limiting of nanosecond laser pulses based on reverse saturable absorption at the input wavelength used. We have also studied the dependence of $\chi^{(3)}$ on the electron-donor/acceptor units of polythiophenes.

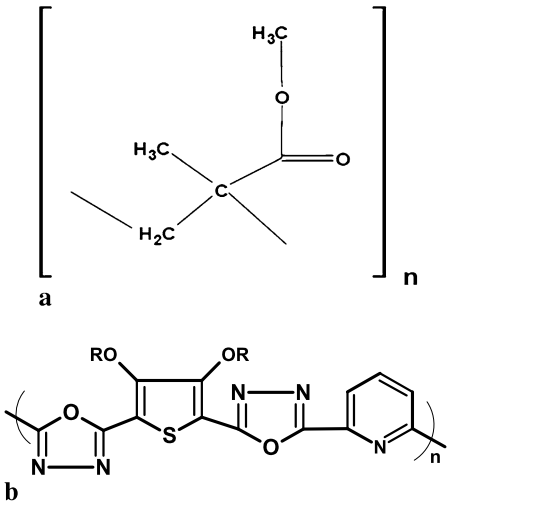


**Fig. 1** (**a**) Structure of PMMA. (**b**) Structure of the polythiophene with $R = C_{10}H_{21}$ (PTH1), $R = C_{12}H_{25}$ (PTH2)

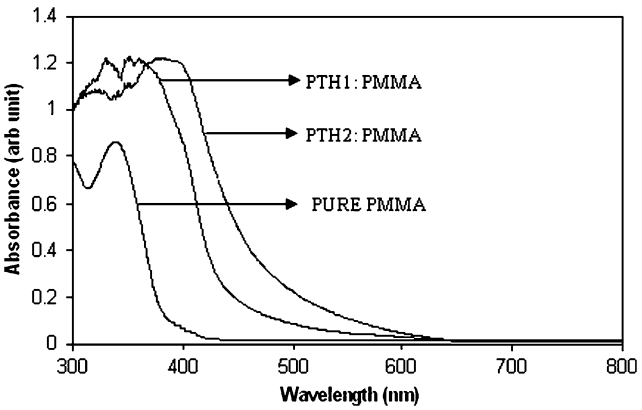


**Fig. 2** UV-Visible absorption spectrum of the polythiophene PTH1, PTH2 and pure PMMA film

## 2 Experiments

To prepare the composite films, we have selected PMMA has host material, because PMMA is hard, rigid and has a glass transition temperature of 125°C [17]. It also exhibits good linear optical transmittance, optical stability, thermal stability and, moreover, better compatibility with organics [18, 19]. PMMA and polythiophene were dissolved in THF separately and stirred well to form a uniform solution; next, both solutions were mixed together and stirred for 8–10 hrs using a magnetic stirrer. The mixed solution was poured into a petridish and kept for drying at room temperature overnight. Then the sample was kept in an oven at ∼70°C for 24 hours. 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 polythiophenes in PMMA for the concentration dependence studies. The synthesis and characterization of the polythiophenes used in this study have been reported elsewhere [20]. Figure 1 shows the structure of PMMA and structure of the polythiophenes investigated. The linear absorption spectra of the polythiophenes shown in Fig. 2 were obtained at room temperature by using the UV-Visible fiber optic spectrometer (Model SD2000, Ocean Optics Inc.).

The single beam Z-scan technique [21–24] was used to obtain the third-order nonlinear optical susceptibility of the composite films. This technique allows for simultaneous measurement of nonlinear refraction (NLR) and nonlinear absorption (NLA). Basically, the technique relies on the fact that the Gaussian beam is tightly focused, using a lens, on the sample, and by translating the sample through the focus, the change 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 nanosecond laser 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 laser beam waist at the focused spot was estimated to be 18.9 μm and the corresponding Rayleigh length is 2.11 mm. Thus the sample thickness of 0.36 mm is less than the Rayleigh length, hence the thin sample approximation is valid [21]. The Z-scan experiments were performed at an input intensity of 1.195 GW/cm$^2$. For the optical power limiting study, the solid samples were kept at the focus of the laser beam. By varying the input laser energy the change in the output laser energy was observed using a Laser Probe Rj-7620 Energy meter with two Pyroelectric detectors.

## 3 Results and discussions

The open-aperture Z-scan (i.e. without aperture in front of the detector) was performed to measure the magnitude of the nonlinear absorption coefficient $\beta_{\text{eff}}$, of the composite films, which is related to the imaginary part of third-order optical susceptibility $\chi^{(3)}$. Figures 3(a) and 4(a) show the open-aperture Z-scan curve of the composites PTH1 and PTH2, which is 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 (RSA). Nonlinear absorption of nanosecond pulses can be explained using the five level model [12, 24–26] shown in Fig. 5. This includes ground state $S_o$ the first singlet state $S_1$, the next higher excited singlet state $S_2$, the lower triplet state $T_1$ and the next higher triplet state $T_2$. Each of these states contains a number of vibrational levels. When two photons, of the same energy or different energies, are simultaneously absorbed from the ground state to a higher excited state ($S_1 \leftarrow S_0$), 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. $S_2 \leftarrow S_1$ 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

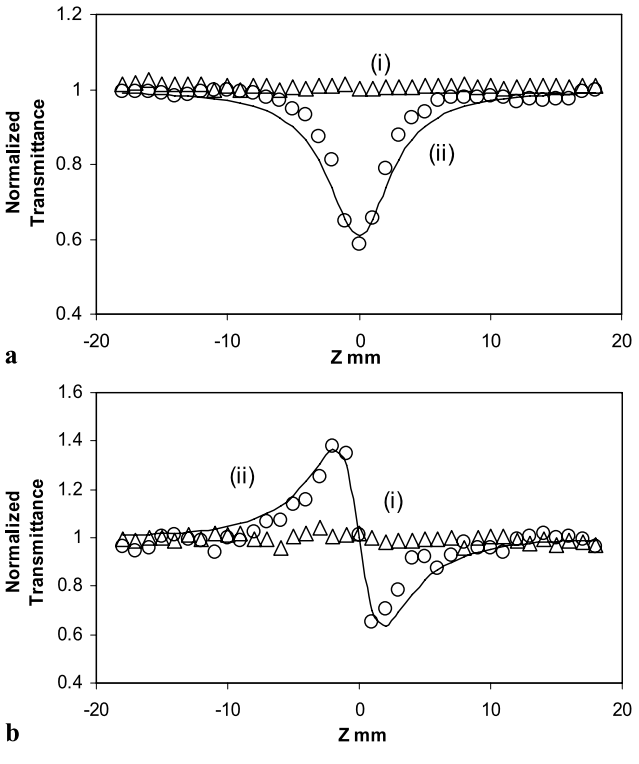


**Fig. 3** Z-scan traces of (i) pure PMMA and (ii) PTH1 composite film (0.25 wt%). (**a**) Open aperture. (**b**) Pure nonlinear refraction. The *solid line* depicts a theoretical fit

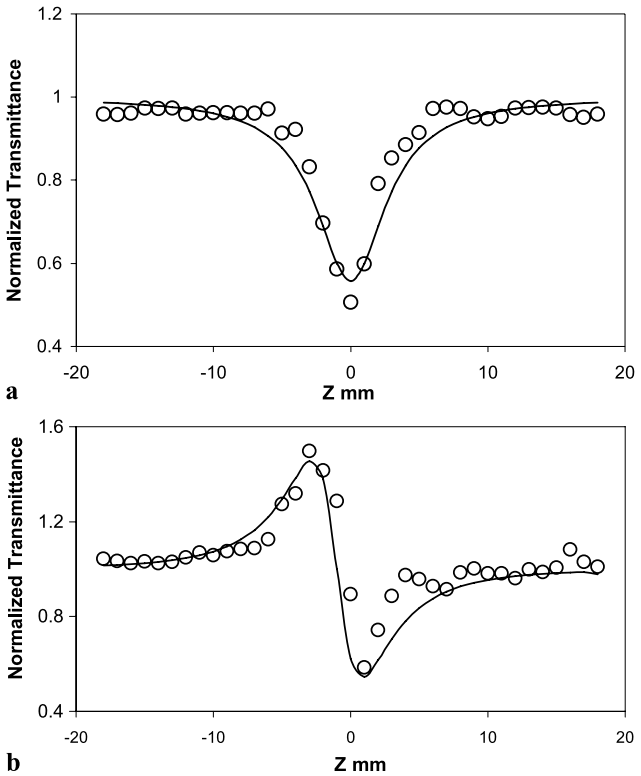


**Fig. 4** Z-scan traces of PTH2 composite film (0.25 wt%). (**a**) Open aperture. (**b**) Pure nonlinear refraction. The *solid line* depicts a theoretical fit

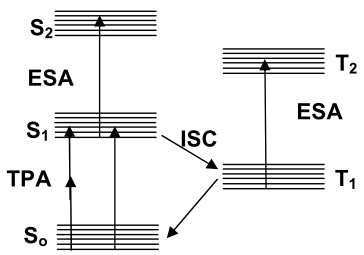


**Fig. 5** Energy level diagram showing both two-photon absorption (TPA) and excited-state absorption (ESA) (five level model)

the probability of photon absorption from that state is high. On the nanosecond time scale a 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. For our polymer composites, the magnitude of the effective excited-state absorption cross section was found to be of the order $10^{-16}$ cm$^2$, which is greater than the magnitude of the ground state absorption cross section of the order to $10^{-17}$ cm$^2$, indicating the nonlinear optical process is reversed saturable absorption (RSA). The triplet excited-state absorption may result in RSA if the absorption cross-section of the triplet excited state is greater than that of the singlet excited state. With the excitation of laser pulses on the nanosecond scale, which is true in our case, triplet-triplet transitions are expected to make a significant contribution to nonlinear absorption. Under the open-aperture Z-scan condition, normalized transmission is given by [27]

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

where $q_0$ is a free factor, defined as

$$q_0 = \frac{\beta_{\text{eff}} I_\text{o}(1 - \exp^{-\alpha L})}{(1 + Z^2/Z_\text{o}^2)\alpha}$$

where $L$ is the length of the sample, $I_\text{o}$ is the intensity of the laser beam at the focus, and $Z_\text{o}$ is the Rayleigh range of the lens. A fit of (1) to the open-aperture data yielded a value of the nonlinear absorption coefficient $\beta_{\text{eff}}$ for the polymer composite films. The effective excited-state absorption cross section ($\sigma_{\text{ex}}$) was measured from the normalized open-aperture Z-scan data [27–30]. It was assumed that the molecular energy levels could be reduced to a three level case to calculate $\sigma_{\text{ex}}$. Molecules are optically exited from the ground state to the singlet excited state, and from this state, they relax either to the ground state or to the triplet state, when exited-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

$$\frac{dI}{dZ} = -\alpha I - \sigma_{\text{exc}} N(t), \tag{2}$$

$$\frac{dN}{dt} = \frac{\alpha I}{\hbar\omega}, \tag{3}$$

where $I$ is the intensity, $Z$ is the sample position, $N$ is the density of charges in the excited state, $\omega$ is the angular frequency of the laser and $\alpha$ is linear absorption. By combining (2) and (3), we have

$$\frac{dI}{dZ} = -\alpha I - \frac{\sigma_{\text{exc}} \alpha I}{\hbar\omega} \int_{-\infty}^{t} I(t')\, dt', \tag{4}$$

Solving the above equation for the fluence and integrating over the spatial extent of the beam gives the normalized energy transmission for open aperture and is given by [29]

$$T = \ln\left(1 + \frac{q_0}{1 + x^2}\right) \Big/ \left(\frac{q_0}{1 + x^2}\right), \tag{5}$$

where $x = z/z_\text{o}$, $z$ is the distance of the sample from the focus, $z_\text{o}$ is the Rayleigh length given by the formula $Z_\text{o} = 2\pi w_\text{o}^2/\lambda$ ($k$ is the wavelength and $w_\text{o}$ is the beam waist at the focus) and $q_0$ is given by the equation [30, 31]

$$q_0 = \frac{\sigma_{\text{exc}} \alpha F_\text{o}(r = 0) L_{\text{eff}}}{2\hbar\omega}, \tag{6}$$

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

$$F_\text{o} = \frac{2E_{\text{total}}}{\pi\omega_\text{o}^2}. \tag{7}$$

The values of the effective excited-state absorption cross section $\sigma_{\text{exc}}$, of the composite films were obtained by fitting the open-aperture data using (4). The ground state absorption cross section $\sigma_\text{g}$ was calculated using the relation

$$\alpha = \sigma_\text{g} N_\text{a} C, \tag{8}$$

where $N_\text{a}$ is Avogadro's number and $C$ is the concentration in mol/L.

The measured values of ground state and effective excited-state absorption cross sections of the polymer composites are given in Table 1. The larger values of $\sigma_{\text{exc}}$, as compared to $\sigma_\text{g}$, indicate that the operating nonlinear process is reverse saturable absorption (RSA) [27–30]. Further, if the nonlinear mechanism belongs to simple two-photon absorption, $\beta_{\text{eff}}$ should be a constant independent of the on-axis input intensity $I_\text{o}$ [31, 32]. But the plot in

**Table 1** Ground state absorption cross-section and effective excited-state absorption cross-section of the polythiophene composite films

| Sample | Dopant conc. (wt%) | $\sigma_\text{g}$ ($\times 10^{-17}$ cm$^2$) | $\sigma_{\text{exc}}$ ($\times 10^{-16}$ cm$^2$) |
|---|---|---|---|
| PTH1 | 0.25% | 6.504 | 2.060 |
| | 0.50% | 3.791 | 2.375 |
| | 0.75% | 2.644 | 2.445 |
| | 1.00% | 2.029 | 2.511 |
| PTH2 | 0.25% | 7.968 | 2.273 |
| | 0.50% | 4.581 | 2.480 |
| | 0.75% | 3.369 | 2.506 |
| | 1.00% | 2.510 | 2.702 |

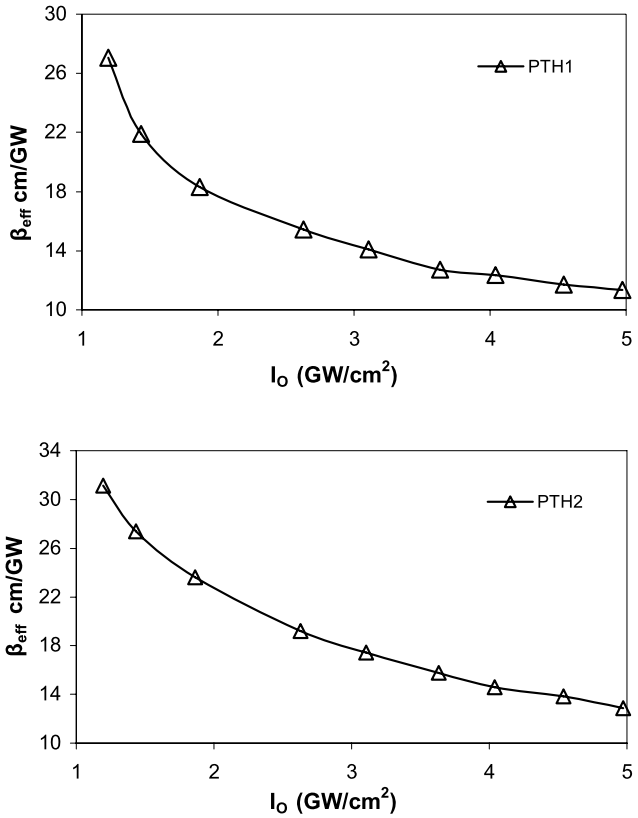


**Fig. 6** Nonlinear absorption coefficient ($\beta_{\text{eff}}$) versus on-axis input intensity $I_{\text{o}}$ of PTH1 and PTH2 composites films (0.25 wt%)

Fig. 6 shows that the value of $\beta_{\text{eff}}$ decreases on increasing the on-axis input intensity $I_{\text{o}}$, which is the consequence of sequential two-photon absorption [33, 34]. With increasing intensity, the total absorption of the polymer composites approaches asymptotically the absorbance of the triplet state. Therefore, $\beta_{\text{eff}}$ will be reduced at least up to intensities where no other intensity dependent processes are involved which can further cause a reduction of the transmission of the polymer. Similar trends were observed by Couris et al. [33] and Bindhu et al. [34] for $C_{60}$ and $C_{70}$ in toluene solutions, where they have been attributed to sequential two-photon absorption via excited-state absorption (reverse saturable absorption). For instance, Chen et al. [35] have also observed a similar decrease in the effective intensity dependent nonlinear absorption coefficient $\beta_{\text{eff}}$ on increasing input intensities in case of *t*Bu4PcTiO/polymer composites, where they ascribe it to the possibility of high-order triplet-state transitions of the excited-state population. This indicates the presence of higher-order effects to the observed nonlinearity as mentioned in [36]. However, Hein et al. [37] have also reported a decrease of $\beta_{\text{eff}}$ with increasing $I_{\text{o}}$ for the thiophene oligomers, where they attributed to the saturation of instantaneous two-photon absorption. The obtained values of the excited state and ground state absorption cross section of the polymer is comparable with the values obtained by Henari et al. [30] for organometallic pththalocyanine.

To determine the sign and magnitude of nonlinear refraction, a closed aperture Z-scan was performed by placing an aperture in front of the detector. Composite films exhibit peak-valley characteristics, indicating negative nonlinear refraction or a self-defocusing effect. The nonlinear refractive index $\gamma$ ($\text{m}^2/\text{W}$) is given by the formula [21]

$$\gamma = \frac{\Delta\phi_{\text{o}}\lambda}{2\pi L_{\text{eff}} I_{\text{o}}} \left(\text{m}^2/\text{W}\right), \tag{9}$$

where $\Delta\phi_{\text{o}}$ is the on-axis phase change given by the equation

$$\Delta\phi_{\text{o}} = \frac{\Delta T_{\text{p-v}}}{0.406(1-S)^{0.25}} \quad \text{for } |\Delta\phi_{\text{o}}| \leq \pi, \tag{10}$$

where $\Delta T_{\text{p-v}}$ 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 $\gamma$ ($\text{m}^2/\text{W}$) by

$$n_2\ (\text{esu}) = (cn_{\text{o}}/40\pi)\gamma \left(\text{m}^2/\text{W}\right). \tag{11}$$

Usually, the closed aperture Z-scan data also include the contribution from nonlinear absorption; in order to extract the pure nonlinear refraction part, we followed the division method given in Sheik-Bahae et al. [20]. Figure 3(b) and 4(b) show the pure nonlinear refraction curve obtained by the division method. The normalized transmittance for pure nonlinear refraction is given by [21]

$$T(z) = 1 + \frac{4x\Delta\phi_{\text{o}}}{[(x^2+9)(x^2+1)]}. \tag{12}$$

To determine the contributions from the solid PMMA matrix to the observed nonlinearity, we conducted a Z-scan experiment on pure PMMA film (i.e. with 0 wt% dopant concentration) and found a negligible contribution both for nonlinear refraction and nonlinear absorption at the input energy used. Therefore any contribution from a pure PMMA film to the observed nonlinearity is negligible at the input intensity used.

In $\pi$-conjugated polymers, electrons can move in large molecular orbitals, which results from the linear superposition of the carbon $P_z$ atomic orbitals, leading to a high $\chi^{(3)}$, which increases with the conjugation length [15]. The polythiophenes studied here consists of alternating electron donating and electron withdrawing groups in their chain. Here, the thiophene ring grafted with alkoxy pendant at the 3, 4 position is an electron donating group and the 1, 3, 4 oxadiazole and pyridine are the electron withdrawing groups, forming an donor-acceptor type of arrangement in the polymer backbone which is essential to exhibit large third-order

**Table 2** Third-order nonlinear optical coefficients of polythiophene composite films

| Sample | Dopant conc. (wt%) | $n_2$ ($\times 10^{-10}$ esu) | $\beta$ (cm/GW) | Re$\chi^3$ ($\times 10^{-12}$ esu) | Im$\chi^3$ ($\times 10^{-12}$ esu) |
|---|---|---|---|---|---|
| PTH1 | 0.25% | −1.236 | 27.23 | −1.473 | 0.492 |
| | 0.50% | −1.459 | 36.80 | −1.740 | 0.661 |
| | 0.75% | −1.654 | 39.44 | −1.958 | 0.710 |
| | 1.00% | −1.716 | 42.07 | −2.046 | 0.759 |
| PTH2 | 0.25% | −1.516 | 31.42 | −1.803 | 0.564 |
| | 0.50% | −1.649 | 40.05 | −1.956 | 0.718 |
| | 0.75% | −1.789 | 44.05 | −2.130 | 0.823 |
| | 1.00% | −2.075 | 47.80 | −2.475 | 0.862 |

nonlinear optical properties. The substitution of the alkoxy pendant not only enhances the delocalization $\pi$-electrons in the polymer, but also acts as a solubilizing group. The third-order nonlinearity in the polythiophenes arises due the presence of a high $\pi$-electron density along the polymer backbone, which is easily polarizable. The values of the nonlinear absorption coefficient $\beta_{\text{eff}}$, the nonlinear refractive index $n_2$, and the real and the imaginary parts of the third-order nonlinear optical susceptibility $\chi^{(3)}$ of the polythiophene composites are given in Table 2. Among the two polythiophenes investigated, PTH2 exhibits large nonlinear optical properties compared to PTH1. This is because of the strong electron donating ability of $OC_{12}H_{25}$ as compared to $OC_{10}H_{21}$.

The value of $n_2$, is nearly three orders of magnitude larger than the $n_2$ values of thiophene oligomers obtained by Hein et al. [37]. The value of $\beta_{\text{eff}}$, is comparable with the value obtained by Cassano et al. [16]. The value of the third-order nonlinear optical susceptibility $\chi^{(3)}$ is comparable with the value of poly(3-dodecyloxymethylthiophene), which is $5 \times 10^{-12}$ esu, obtained by Sasabe et al. [38] and one order larger than the stilbazolium derivatives, a well-known class of optical materials for photonics and biophotonics applications [39, 40].

## 4 Optical power limiting studies

Optical power limiting has opened new opportunities for their application in laser switching systems for protection of eyes and optical sensitive devices from intense laser beams [3, 41]. 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 that cause optical limiting have different origins, such as two-photon absorption, free carrier absorption, reverse saturable absorption and nonlinear scattering. The molecules exhibiting RSA generally have an extremely fast response time, since it involves electronic transitions [24]. The best known reverse saturable absorbers are fullerene ($C_{60}$), porphyrin complexes and phthalocyanines [2, 13, 24, 26–29]. Optical power limiting experiments were performed by placing the composite polymer films at the focus of the laser beam and by measuring the transmitted energy for different input laser energies. Figure 7 shows the optical power limiting response of the composite films PTH1 and PTH2. The clamping levels of the composite film PTH1 were found to be ∼20 μJ, ∼16 μJ, ∼14 μJ and ∼12 μJ with a limiting threshold of ∼78 μJ, ∼60 μJ, ∼42 μJ, and ∼36 μJ, respectively at concentrations of 0.25%, 0.5%, 0.75% and 1.0%. The clamping levels of the composite film PTH2 were found to be ∼16 μJ, ∼12 μJ, ∼10 μJ and ∼8 μJ with a limiting threshold of ∼50 μJ, ∼42 μJ, ∼36 μJ, and ∼30 μJ, respectively at concentrations of 0.25%, 0.5%, 0.75% and 1.0%. The clamping levels and the limiting threshold of the composite films decreased on increasing the concentration; this is because the composite films with higher concentration possess more molecules per unit volume. Hence it will absorb the harsh laser pulses more efficiently. Among the two composite films, PTH2 exhibits good optical power limiting of nanosecond laser pulses compared to PTH1. The variation is due to the variation in conjugation length and the presence of acceptor/donor groups in the molecule. We ascribe the optical power limiting of the composite films to RSA. Therefore, the polythiophene composite films investigated here seem to be a promising material for making optical power limiting devices.

The concentration dependence of the nonlinear absorption coefficient, $\beta_{\text{eff}}$, was also studied. Figure 8 shows the plot of the nonlinear absorption $\beta_{\text{eff}}$ versus dopant concentration. The measured values of the nonlinear absorption coefficient $\beta_{\text{eff}}$ increases with the concentration of PTH1 and PTH2 in PMMA indicating that the contribution to nonlinear absorption arises mainly from the nonlinear optical chromophores PTH1 and PTH2.

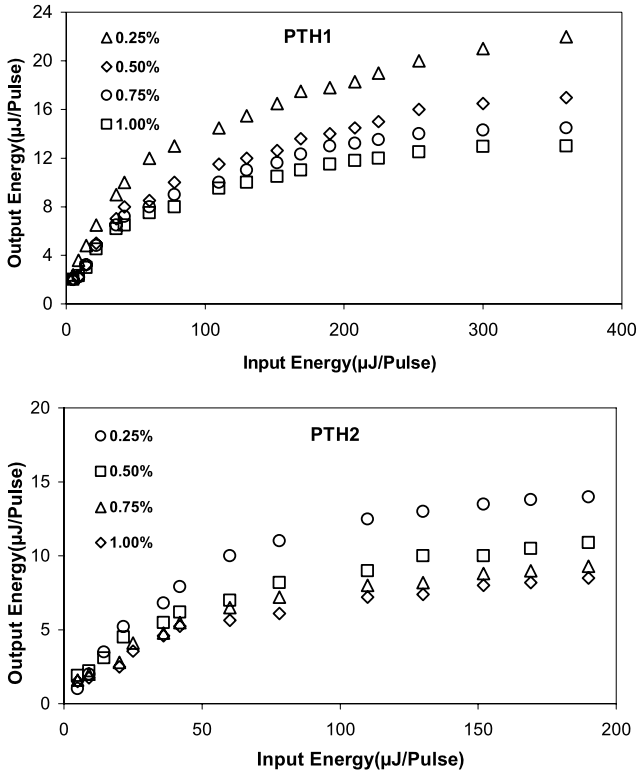


**Fig. 7** Optical power limiting response of PTH1 and PTH2 composite films with different wt% of polythiophene

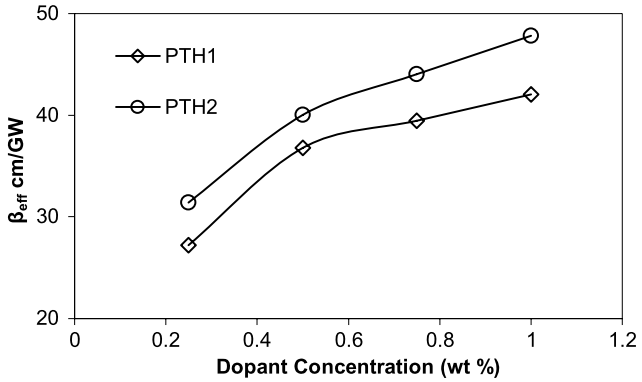


**Fig. 8** Concentration dependence of nonlinear absorption coefficient $\beta_{\text{eff}}$

## 5 Conclusions

In summary, polymer blends of polythiophene/PMMA were prepared and third-order nonlinear optical properties were investigated using the nanosecond Z-scan technique. Z-scan results indicate that the composites exhibit self-defocusing nonlinearity. The real and imaginary parts of the third-order nonlinear optical susceptibility were of the order $10^{-12}$ esu, respectively. Large third-order nonlinear optical properties in the polythiophenes arise due to the strong delocalization of $\pi$-electrons along the polymer chain and increased on increasing the strength of the electron-donor group, indicating the dependence of $\chi^{(3)}$ on the donor/acceptor units of polythiophenes. Optical power limiting measurements indicate that the polythiophene composites exhibit good optical 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. Hence, the polythiophene composites investigated here are a potential candidate for future photonics and optoelectronics applications.

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