# *Z*-Scan Measurements of the Third-Order Optical Nonlinearity of a $C_{60}$ Doped Poly(dimethylacetylendicarboxylate)

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The third-order nonlinear optical properties of $C_{60}$/poly(dimethylacetylendicarboxylate) have been studied using *Z*-scan technique. Experiments are performed using a CW diode laser at 635 nm wavelength and 26 mW power. The nonlinear absorption coefficient $\beta$, nonlinear refractive index $n_2$, $\mathrm{Re}\chi^3$, and $\mathrm{Im}\chi^3$ in $C_{60}$ doped poly(dimethylacetylendicarboxylate) are measured using *Z*-scan data. Our results show that the values of the nonlinear optical parameters ($\beta$, $n_2$, $\mathrm{Re}\chi^3$, and $\mathrm{Im}\chi^3$) of $C_{60}$ doped poly(dimethylacetylendicarboxylate) are smaller than the polymer itself.

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## 1. Introduction

With the extensive use of high-power laser in many different applications, much interest is currently being directed towards the search for new nonlinear optical materials as passive optical limiters used to protect human eyes and solid-state optical sensors from intense laser beams [1–3]. Over the past decades, extensive studies on optical limiting materials have been focused on nonlinear organic molecules [4, 5], organic dyes [6], conjugated compounds [7], and fullerenes molecules and their derivatives [8, 9] with respect to nanosecond optical limiting behavior.

Fullerene ($C_{60}$) is a good material to be used as optical limiting materials. But, its poor solubility makes it difficult to be processed into parts. In contrast, mixing $C_{60}$ with polymers is one of the easiest ways to resolve the problem. Since early work of doping $C_{60}$ into PMMA polymer [10], numerous investigators have demonstrated the optical limiting behavior of fullerenes doped polymer matrices using a pulse laser at 532 nm [11–14].

*Z*-scan technique proposed by Sheik-Bahae et al. [15, 16] based on the spatial distortion of a laser beam, passed through a nonlinear optical material, is widely used in material characterization because of its simplicity and high sensitivity. Early work reporting on open-aperture *Z*-scan on $C_{60}$ in toluene solution are performed over the visible region (440–660 nm) using optical parametric oscillator [17], and $C_{60}$ in toluene [18]. The nonlinear absorption coefficients of $C_{60}$:toluene solution were measured at 532 and 1064 nm [19], also the open aperture *Z*-scan of $C_{60}$, $C_{60}$/polymer ($C_{60}$/PSVPY32 and $C_{60}$/PS) was measured [20].

Following our previous optical limiting investigations on $C_{60}$ doped EPDM polymer [5], poly(dimethylacetylendicarboxylate) [21], and $C_{60}$ doped poly(dimethylacetylendicarboxylate) [22], this paper reports the *Z*-scan measurements of $C_{60}$ doped poly(dimethylacetylendicarboxylate) using a CW diode laser at 635 nm wavelength and at power of 26 mW. To our knowledge, there is no report on the investigation of *Z*-scan measurements of $C_{60}$ doped poly(dimethylacetylendicarboxylate) polymer.

## 2. Experimental techniques

The $C_{60}$ was purchased from Fluka and used without any purification.

Poly(dimethylacetylendicarboxylate) material has been prepared and identified [21]. The method of preparing the sample of $C_{60}$/poly(dimethylacetylendicarboxylate) was mentioned in detail in previous publication [22]. The concentrations samples of $C_{60}$ dissolved in toluene, $C_{60}$/poly(dimethylacetylendicarboxylate) and poly(dimethylacetylendicarboxylate) were at $5\times10^{-4}$, $4.4\times10^{-4}$ and $10^{-3}$ M/l and dissolved in toluene solvent, too, respectively.

The *Z*-scan experimental setup was analogous to that described in Ref. [23]. The measurements were done with linearly polarized TEM00 Gaussian beam of a CW diode laser at 26 mW ($\lambda = 635$ nm as shown in Fig. 1). The experimental parameters during the measurements of the samples were used as follows: the laser beam is focused by a 10 cm focal length lens to a waist radius $\omega_0$ of 34 $\mu$m at the focal point ($I_0 = 424$ W/cm$^2$). The diffraction length $z_0$ is 5.5 mm, the radius of the aperture $r_a$ is 0.5 mm and $\omega_a = 1$ mm is the radius beam waist on the aperture. The sample cell used in this work is a standard 2 mm thick quartz cell since the standard 1 mm thick quartz cell is not available and the cell was hold on an optical rail and translated across the focal region

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along the axial direction that is in the direction of the propagation of the laser beam (Fig. 1). The transmitted power through the sample is measured as a function of the sample distance $z$ from the waist plane of the Gaussian beam. The transmission of the beam through an aperture placed in the far field is measured with a power meter (Thorlabs PM300E).

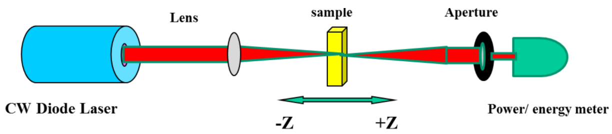


Fig. 1. $Z$-Scan experimental setup.

## 3. Results and discussions

$Z$-scan measurements, in the cases of open and closed aperture, allow us for the determination of the nonlinear absorption coefficient $\beta$ and the nonlinear refractive index $n_2$, respectively.

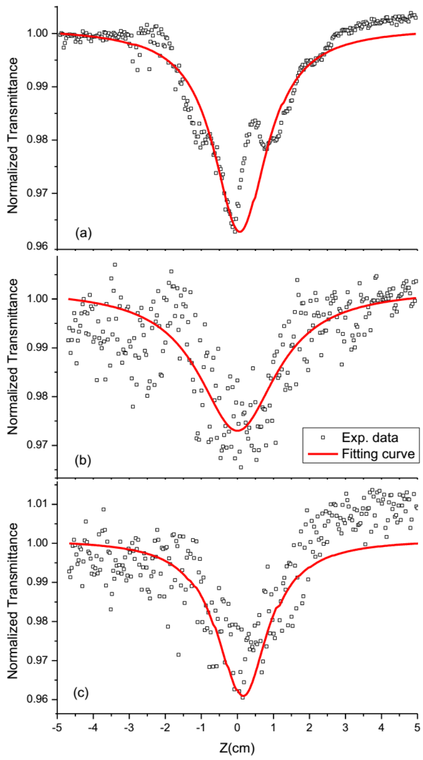


Fig. 2. Open-aperture $Z$-scan data (a) $C_{60}$ in toluene, (b) poly(dimethylacetylendicarboxylate) and (c) $C_{60}$/poly(dimethylacetylendicarboxylate).

Figure 2 displays the open aperture $Z$-scan results of $C_{60}$, poly(dimethylacetylendicarboxylate), and $C_{60}$/poly(dimethylacetylendicarboxylate) in toluene. The nonlinear absorption coefficient $\beta$ can be calculated from the open aperture $Z$-scan data. In this case, the linear transmittance of the aperture $S$ is equal to 1, and in general $S$ is given by

$$S = 1 - \exp(-2r_a^2/\omega_a^2), \tag{1}$$

where $r_a$ is the radius of the aperture and $\omega_a$ is the radius beam waist on the aperture

$$\omega_a^2 = \omega^2\left[1 + (z_a/z_0)^2\right], \tag{2}$$

where $\omega$ is the beam waist radius at the focus, $z_a$ is the distance between the aperture and the focal point, and $z_0$ is the diffraction length of the beam with wave vector $k$. The normalized transmittance for $q_0 < 1$, for the open aperture condition is given by [15, 16]:

$$T(z) = \sum_{m=0}^{\infty} \frac{(-q_0)^m}{(m+1)^{\frac{3}{2}}}, \tag{3}$$

where $q_0(z) = I_0 L_{\text{eff}} \beta/(1 + z^2/z_0^2)$ is a parameter function of $I_0$, $L_{\text{eff}}$ and $\beta$, $z_0 = \pi\omega_0^2/\lambda$ is the diffraction length of the beam, $\lambda$ is the laser wavelength, and $I_0$ is the intensity of the laser beam at focus $z = 0$, $L_{\text{eff}} = (1 - \exp(-\alpha_0 L))/\alpha_0$ is the effective thickness of the sample ($L$ is the thickness of the sample and $\alpha_0$ is the linear absorption coefficient). Solving the summation (3) for $\alpha \ll 1$ gives

$$T(z) = 1 - (I_0 L\beta)/[2^{3/2}(1 + z^2/z_0^2)], \tag{4}$$

The solid line in Fig. 2 is the fitting curve while the symbols are the experimental data. The values of nonlinear absorption coefficient $\beta$ for the studied samples at $I_0 = 424$ W/cm$^2$ can be estimated from the open aperture $Z$-scan experimental data as

$$\beta = 2\sqrt{2}\Delta T/I_0 L_{\text{eff}}, \tag{5}$$

where $\Delta T$ is the one-valley value at the open aperture $Z$-scan curve in Fig. 2.

Figure 3 shows the dependence of reverse saturable absorption (RSA) nonlinear absorption coefficient $\beta$ as a function of incident laser intensity $I_0$ for both the $C_{60}$ and polymer in toluene. It has been noted that the values of the nonlinear absorption coefficient $\beta$ decrease with increase in on-axis input intensity $I_0$. This means that the observed nonlinear absorption behavior is due to the results of two photon absorption (TPA) and excited state absorption (ESA) assisted RSA process [24]. It should be mentioned here that if the observed nonlinearity is due to TPA alone, the nonlinear absorption coefficient $\beta$ should be a constant independent of on-axis input intensity $I_0$ [24].

Since the closed aperture transmittance is affected by the nonlinear refraction and nonlinear absorption, it is necessary to separate the effect of nonlinear refraction from that of the nonlinear absorption. A simple and approximate method to obtain purely effective $n_2$ is to divide the closed aperture transmittance by the corresponding open aperture scan. The data obtained in this way reflect purely the effect of nonlinear refraction of $C_{60}$, poly(dimethylacetylendicarboxylate), and $C_{60}$/poly(dimethylacetylendicarboxylate) in toluene as shown in Fig. 4. The studied samples exhibit strong self-defocus behavior and negative sign of $n_2$ as revealed in the peak-valley shaped curves.

To estimate $n_2$, the $Z$-scan theory proposed by Sheik-Bahae et al. [15, 16] is used

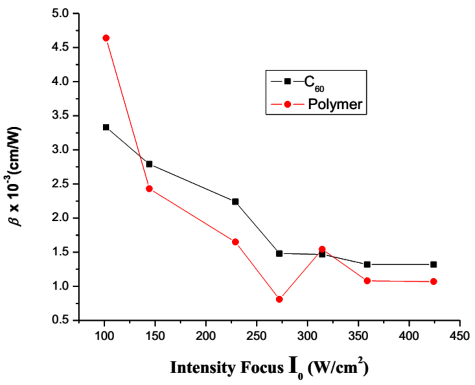


Fig. 3. Nonlinear absorption coefficient $\beta$ versus on-axis input intensity $I_0$ of $C_{60}$ and poly(dimethylacetylendicarboxylate) in toluene.

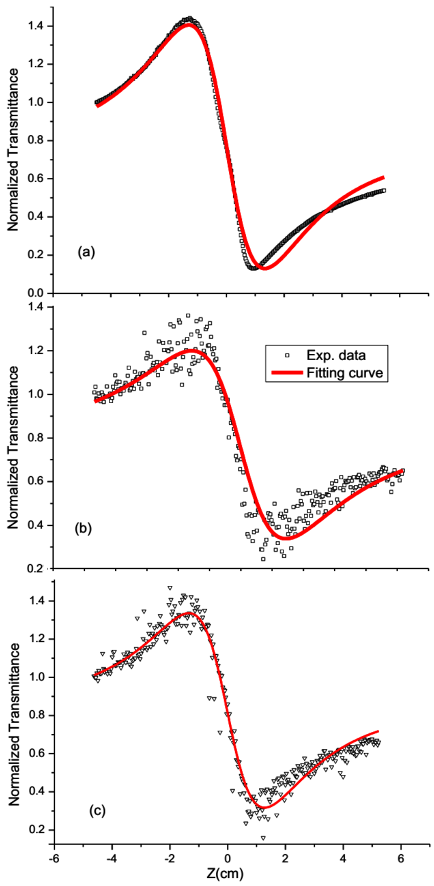


Fig. 4. Pure nonlinear refraction curves, (a) $C_{60}$ in toluene, (b) poly(dimethylacetylendicarboxylate) and (c) $C_{60}$/poly(dimethylacetylendicarboxylate).

$$T(z,\Delta\varphi_0) = 1 - \frac{4\Delta\varphi_0 X}{(X^2+9)(X^2+1)}, \tag{6}$$

where is $X = (Z/Z_0)$ and $\Delta\varphi_0$ is the induced phase distortion of radiation when passed through the sample, this produces a symmetry $\Delta T_{\mathrm{p-v}}$ (peak-valley) curve, where the nonlinear refractive index $n_2$ can be calculated by formula given

$$\Delta T_{\mathrm{p-v}} = 0.406(1-S)^{0.25}|\Delta\varphi|, \tag{7}$$

where $\Delta T_{\mathrm{p-v}}$ is the difference between normalized peak and valley transmittance of the divided data, $\Delta T_{\mathrm{p-v}}$ is measured from Fig. 4. $|\Delta\varphi_0|$ is the induced phase distortion of radiation when passed through the sample, and the linear transmittance of the aperture $S$ is estimated from Eqs. (1) and (2) ($S = 0.39$ for the present experiment).

The nonlinear refractive index $n_2$ can be estimated by the following relation:

$$n_2 = \lambda\Delta\varphi/2\pi I_0 L_{\mathrm{eff}}. \tag{8}$$

The solid line in Fig. 4 is the fitting curve, obtained by using Eq. (6). The nonlinear refraction ($n_2$) values of the studied samples can be obtained experimentally by measuring the distance between the normalized peak and normalized valley "$\Delta T_{\mathrm{p-v}}$" from Fig. 4 and Eqs. (7), (8).

The experimental measurements have been conducted for the far field range between $-50$ mm to $+50$ mm, in order to get the linear regime at the far field, this leads to get the initial and final values to be equal. It should be pointed out here that, in Figs. 2 and 4, due to the fluctuations in the recorded data, the fitting curves are applied to estimate the values of nonlinear refractive index ($n_2$) and nonlinear absorption coefficient ($\beta$).

The experimental measurements of the nonlinear refractive index ($n_2$) and nonlinear absorption coefficient ($\beta$) can be used to determine the real and imaginary parts of the third-order nonlinear optical susceptibility ($\chi^3$) according to the following relations [15, 16]:

$$\mathrm{Re}\chi^3(\mathrm{esu}) = (10^{-4}\varepsilon_0 c^2 n_0^2/\pi)n_2\ (\mathrm{cm}^2/\mathrm{W}), \tag{9}$$

$$\mathrm{Im}\chi^3(\mathrm{esu}) = (10^{-2}\varepsilon_0 c^2 n_0^2 \lambda/4\pi^2)\beta\ (\mathrm{cm/W}), \tag{10}$$

where $\varepsilon_0$ is the vacuum permittivity and $c$ is the speed of light in vacuum.

Values of $\alpha_0$ and $n_0$ were measured for each sample. Also, $n_2$, $\beta$, $|\mathrm{Re}\chi^3|$ and $|\mathrm{Im}\chi^3|$ were determined using fitting curves of the open/closed aperture measurements (Figs. 2 and 4) and Eqs. (1)–(10), and shown in Table. The reported values of the $\beta$ and $n_2$ of the studied samples in Table can be compared with recently reported values of the $\beta$ and $n_2$ of $C_{60}$ doped ADC polymer in different solvents with CW laser excitation [25]. Our present measurements of $n_2$ are at $4.51\times10^{-7}$ cm$^2$/W for $C_{60}$ in toluene, and the same order ($10^{-7}$ cm$^2$/W) for the polymer, and $C_{60}$/polymer; while $n_2$ values in Ref. [25] is at $2.82\times10^{-8}$ cm$^2$/W for $C_{60}$ in $CHCl_3$. Also, our present measurements of $\beta$ are in the same order of $10^{-3}$ cm/W with the reported values in Ref. [25]. The small difference is due to the nature of the used polymer and solvents. This means that our present measurements are reasonable in comparison with previous reported work.

Regarding the exhibited nonlinearities in studied samples, under CW laser irradiation, there is usually additional thermal induced nonlinearity in such material. This thermal effect arises from the predominantly nonradiative relaxation of the excited states, which causes a local temperature rise and thus a refractive index change through the thermo-optic coefficient [26].

The experiments were repeated for the pure solvent to account for its contribution, but no significant measurable signals were produced in either the opened or the closed $Z$-scan traces. Also, it was found that the time employed for recording the $Z$-scan data in each plot does not affect the results for evaluating the nonlinear coefficients.

The data show that the nonlinear absorption coefficient $\beta$ of $C_{60}$/poly(dimethylacetylendicarboxylate) have been found to be larger than poly(dimethylacetylendicarboxylate) and $C_{60}$ itself. For $\beta$, the following order is observed: $\beta(C_{60}/\text{polymer}) > \beta(C_{60}) > \beta(\text{polymer})$. Concerning the nonlinear refractive index, $n_2$ the following order is: $n_2(C_{60}) > n_2(C_{60}/\text{polymer}) > n_2(\text{polymer})$. Both values of $\beta$ and $n_2$ are mentioned in Table.

Many previous studies reported that the RSA and nonlinear refraction mechanisms were believed to play a dominant role in the optical limiting effect of $C_{60}$/polymer. A classical five-level model was proposed to explain the nonlinear optical limiting properties of $C_{60}$/polymer, as it was pointed out in references [22, 27, 28].

TABLE

The calculated nonlinear optical parameters of $C_{60}$ in toluene (A), poly(dimethylacetylendicarboxylate) (B) and $C_{60}$ doped poly(dimethylacetylendicarboxylate) polymer (C).

| Samples | $\alpha_0$ [mm$^{-1}$] | $n_0$ | $n_2 \times 10^{-7}$ [cm$^2$/W] | $\beta \times 10^{-3}$ [cm/W] | Re($\chi^3$) $\times 10^{-5}$ [esu] | Im($\chi^3$) $\times 10^{-5}$ [esu] |
|---|---|---|---|---|---|---|
| A | 0.063 | 1.50 | 4.51 | 1.32 | 2.57 | 3.80 |
| B | 0.07 | 1.55 | 3.07 | 0.973 | 1.87 | 3.00 |
| C | 0.068 | 1.53 | 3.62 | 1.40 | 2.18 | 4.24 |

## 4. Conclusion

We have presented the $Z$-scan measurements of $C_{60}$ doped polymer, using a CW diode laser at 635 nm wavelength. Depending on the experimental measurements, values of $\alpha_0$, $n_0$, $n_2$, $\beta$, Re$\chi^3$, and Im$\chi^3$ are estimated for the $C_{60}$/poly(dimethylacetylendicarboxylate). Our results show that the nonlinear absorption coefficient $\beta$ with the following order is observed: $\beta(C_{60}/\text{polymer}) > \beta(C_{60}) > \beta(\text{polymer})$, while the nonlinear refractive index ($n_2$) is observed: $n_2(C_{60}) > n_2(C_{60}/\text{polymer}) > n_2(\text{polymer})$, respectively.

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