International Journal of Current Engineering and Technology
E-ISSN 2277 – 4106, P-ISSN 2347 – 5161

Available at http://inpressco.com/category/ijcet

Research Article

Nonlinear Optical Properties of Polyaniline Iodine Doped Thin Films prepared by Aerosol Assisted Plasma Jet Polymerization at Atmospheric Pressure

Hammad R.Humud*, **Manal Midhat Abdullah and Dawood Majed Khudhair**

Department of Physics, College of Science, University of Baghdad

Accepted 30 Sept 2015, Available online Oct 2015, **Vol.5, No.5 (Oct 2015)**

Abstract

In this work, the nonlinear optical properties of pure polyaniline and in situ iodine doping polyaniline thin films on glass substrate, prepared by aerosol assisted plasma jet polymerization at atmospheric pressure, thin films were studied through open and closed Z-scan technique under laser excitation at 532 nm, CW solid state laser with an output power of 100 mW. The nonlinear optical properties of pure polyaniline thin films prepped at different gas flow rate and polyaniline thin films iodine doped at constant gas flow rate 1lm^{-1} and different iodine weight concentration 1, 3, 5, and 7%were studied. the closed aperture Z-scan data indicates that the sign of the refraction nonlinearity is negative for thin films prepared at gas flow rate 1lm^{-1}, n_2 1.965×10^{-5} cm^2/mw and positive nonlinearity for thin films prepared at other gas flow rate,n_2 1.207×10^{-5}, 1.076×10^{-5} and 1.214×10^{-5} cm^2/mw for gas flow rate 2,3 and 5 lm^{-1} respectively. And the open Z-scan measurements show two photon absorption β cm/mW, 1.40, 1.16, 1.12 and 1.37cm/mW for gas flow rate1, 2, 3 and 5 lm^{-1}respectively. For polyaniline thin films iodine doped at constant gas flow rate the closed aperture Z-scan measurements shows positive nonlinearity for thin films prepared at iodine concentration 3 and 5% n_2 1.606×10^{-5}, 0.830×10^{-5} cm^2/mw respectively. While thin films prepared with iodine concentration 1 and 7% shows negative nonlinearity n_2 0.857×10^{-5}, 0.801×10^{-5} cm^2/mW respectively. The open aperture Z-scan measurements for polyaniline thin films doped with iodine by different concentration 1, 3, 5, and 7% and constant gas flow rate show saturated absorption for all gas flow rate. It can be concluding that, the possibility of obtaining direct and inexpensive method to prepare saturated absorption thin films material, by aerosol assisted plasma jet polymerization at atmospheric pressure.

***Keywords**: polyaniline iodine doping, thin films, nonlinear optical properties.*

1. Introduction

Nonlinear optical properties have been the subject of numerous investigations by both theoreticians and experimentalists during recent years. The nonlinear optical properties of materials have been developed for wide ranging applications such as optical limiting (Xiao-Liang *et al*, 2011) multi-photon absorption (Daniel *et al*, 2007) as well as photo electronics devices (Manjunatha *et al*, 2013). Polyaniline is one of the most investigated conducting polymers. Due to its high chemical and thermal stability and the ease of polymerization, together with the relative low cost of production and it also has the potential of many technological applications .The effect of the in situ iodine doping on the nonlinear optical properties of polyaniline thin films prepared by aerosol assisted plasma jet polymerization at atmospheric pressure has not been reported. The technique of plasma polymerization is an inexpensive method and often requires very less infra-.structure. This method includes by the employment of ac, rf, dc, microwave and pulsed sources. They produce pinhole free homogeneous films on appropriate substrates under controlled conditions. In conventional plasma polymerization set up, the monomer is fed into an evacuated chamber and an ac, rf, dc, pulsed discharge is created which enables the monomer species to dissociate, leading to the formation of polymer thin films. In this work polymer thin films produced under atmospheric pressure. Plasma polymerization can be used to produce polymer films of organic compounds that do not polymerize under normal chemical polymerization conditions. The plasma coating at atmospheric pressure is viable and low cost technique due to no need of expensive vacuum equipment and higher deposition rates. Different precursor systems can be used: gasses, liquid vapors, aerosols. This work deals with the atmospheric plasma jet deposition technic using aerosols. Only elements and compounds

*Corresponding author: **Hammad R.Humud**

with a low molecular weight can be utilized as gas precursor in plasma depositing applications. As there are much more liquid than gaseous precursors available, the number of possible material is clearly higher when working with aerosol precursors. Working with aerosol precursors offers more flexibility and more treatment possibilities. Different techniques can be used for aerosol production: ultrasonic piezoelectric technology special nozzles. In this work special nozzle was used to generate the aerosol. Z-scan technique is a simple and effective tool to determine the nonlinear properties (Sheik-Bahae *et al*, 1990). It has been widely used in material characterization because it provides the magnitudes of the real and imaginary part of the nonlinear susceptibility and the sign of the real part. The nonlinear refraction (closed aperture Z-scan) and nonlinear absorption (open aperture Z-scan) of samples can be measured easily by Z-scan technique, which use the change of transmittance of nonlinear materials (Xia *et al*, 1994). In this work, the nonlinear optical properties of pure polyaniline and in situ iodine doping polyaniline thin films on glass substrate prepared by aerosol assisted plasma jet polymerization at atmospheric pressure were studied through Z-scan technique under laser excitation at 532 nm CW solid state laser with an output power of 100 mW.

Experimental

Thin films deposition

The films were deposited via a plasma jet. The plasma was generated downstream to the substrate which was positioned at fixed distance from the plasma torch end. The jet was generated via Argon gas flow (flow rate of 1-7 L/min) through a nebulizer which contained aniline. The aniline was converted into aerosol; the aerosol was guided by the Ar gas through tephlon tube to the plasma jet. The plasma was ignited by using an electric source at fixed frequency 28.0 kHz and 10k volt peak to peak (Hammad *et al*, 2014). The films deposition was carried out for 5min under various conditions of carrier gas flow rate for each. In order to obtain homogeneous films thickness along the substrate area, the substrates were mounted on a movable x - y stage.

Iodine doping Polyaniline

Iodine doping Polyaniline is carried out by in situ doping of iodine using aerosol assisted plasma jet polymerization techniques. The iodine powder is mixed with aniline by different wight mixing ratio1, 3, 5 and 7%. Iodine and the monomer were put into the nebulizer then Argon gas with constant flow rate1lm^{-1} passes through the nebulizer which contains the mixture of iodine and the monomer. The mixture convert to aerosol, this aerosol was guided by the Ar gas to the plasma jet and convert to solid thin films as shown in Figure 1.

The Z-scan experiments were performed using a 532 nm CW second harmonic Nd- YAG laser beam, which was focused by 120 mm focal length lens. The beam radius ω_0 at the focus is measured to be 0. 42 mm. The schematic of the experimental set up used is shown in Figure 2. The sample (thin films) holder is translated across the focal region along the axial direction. The transmission of the beam through an aperture 1.5 mm placed in the far field was measured using a photodetector. For an open aperture Z-scan, a lens was used to collect the entire laser beam transmitted through the sample and replaced the aperture.

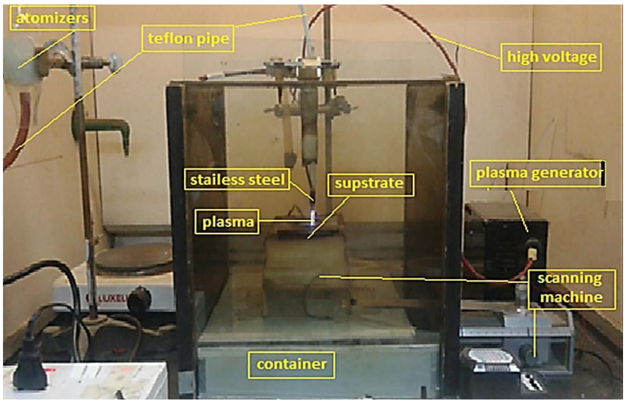

Figure 1: Schematic diagram for the non-equilibrium atmospheric pressure plasma jet Iodine-doped polyaniline thin films

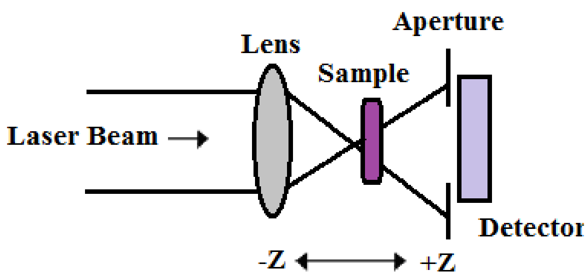

Figure (2): Schematic diagram of experimental arrangement for the Z-scan measurement

In the case of close aperture Z-scan, the measured transmittance remains constant Z-independent at far distance from the lens focal plane. As the sample was approaches the beam focus, irradiance increases, leading to self-lensing in the sample. A negative self-lens before the focal plane will tend to collimate the beam on the aperture in the far field, increasing the transmittance measured at the aperture position. After the focal plane, the same self-defocusing was increases the beam divergence, leading to a widening of the beam at the aperture and thus reducing the measured transmittance. Far from focus (Z >0), again the nonlinear refraction is low resulting in a transmittance Z-independent. A pre-focal transmittance maximum (peak), followed by a post-focal transmittance minimum (valley) is a Z-scan signature of a negative nonlinearity. An inverse Z-scan curve a valley followed by a peak characterize is a positive nonlinearity. Figure (3) shows these two situations (Winter *et al*, 1992).

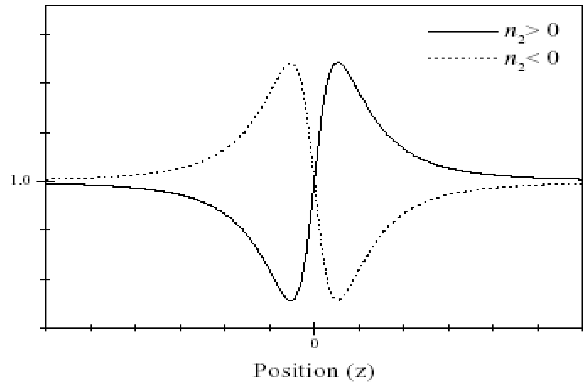

Figure (3): Calculated Z-scan transmittance curves for a cubic Nonlinearity

The relative on-axis transmittance of the sample measured at the small aperture of the far-field detector is given by (Sheik-Bahae *et al*, 1990).

$$T_{(z,\Delta\Phi_\circ)} = 1 - \frac{4\Delta\Phi_\circ \frac{Z}{Z_\circ}}{\left\{\left(\frac{Z^2}{Z_\circ^2}\right)+9\right\} \times \left\{\left(\frac{Z^2}{Z_\circ^2}\right)+1\right\}} \quad (1)$$

where T is the transmittance through the aperture, which is a function of the sample position Z, the nonlinear refractive index, is calculated from the peak to valley difference of the normalized transmittance by the following formula Sheik-Bahae.

$$n_2 = \Delta\Phi_\circ / I_\circ L_{eff} k \quad (2)$$

$$\Delta T_{P-V} \approx 0.406|\Delta\Phi_0|$$

where, ΔT_{P-V} the deference between peaks and valley, ΔΦo is nonlinear phase shift, k = 2π /λ, λ, is the wavelength of the beam $z_o = kw_0^2/2$ the diffraction length of the beam. Leff: - the effective length of the sample can be determined from the following formula Sheik-Bahae (Sheik-Bahae *et al*, 1990).

$$L_{eff} = \left(1 - e^{-\alpha_\circ l}\right) / \alpha_\circ \quad (3)$$

where, L: - the sample length (thin film thickness), α_o: - linear absorption coefficient, in equation (4), I_o is the intensity at the focal spot given by (Ready, 1978).

$$I_\circ = 2p_{peak} / \pi w_\circ \quad (4)$$

where, ω_o: the beam radius at the focal point, P_{peak}: the peak power.

The open-aperture z-scan measures the change in intensity of a beam, focused by lens in the far field at the detector *D*, which captures the entire beam. In open aperture Z-scan the transmittance is no longer sensitive to the beam distortion and Z-scan data is a function of nonlinear absorption (Sheik-Bahae *et al*, 2007). In the focal plane where the intensity is greatest, the largest nonlinear absorption is observed. At the "tails" of the Z-scan signature, where $|z| > z_o$, the beam intensity is too weak to gating nonlinear effects. Figure (4) shows the relative transmittance change recorded by the open-aperture detector for a sample exhibiting two-photon or high absorption. A symmetric valley is the feature of a positive nonlinear absorption coefficient *β*.

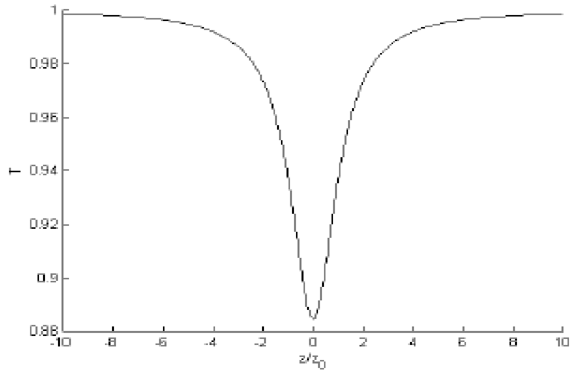

Figure (4): Open-aperture Z-scan signature for a sample with positive nonlinear absorption coefficient

The nonlinear absorption coefficient for pure two-photon absorption is calculated as in eq. (6)

$$T(Z) = \sum_{m=0}^{\infty} \frac{\left[\frac{\beta I_\circ L_{eff}}{1+(Z/Z_\circ)^2}\right]^m}{(m+1)^{3/2}} \quad (6)$$

where *Z:* - is the sample position at the minimum transmittance, *m*: - integer, *(z₀)*:-position of the minimum transmittance. The two terms in the summation are generally sufficient to determine *β*.

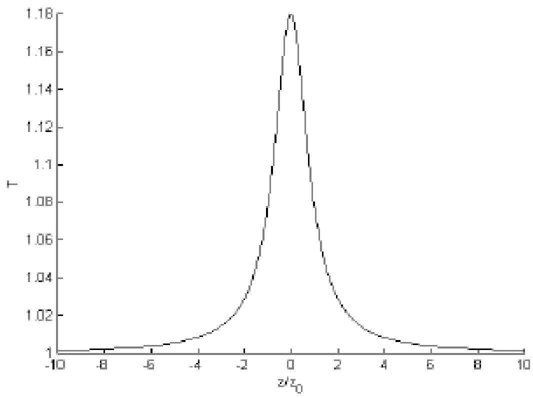

Figure (5): Open-aperture z-scan signature for a sample with saturation absorption

Figure (5) shows the relative transmittance change recorded by the open-aperture detector, for a sample exhibiting absorption saturation. A symmetric peak is the hallmark of a negative nonlinear absorption coefficient β, indicating absorption saturation.

Results and discussion

The nonlinear refractive index of two cases pure polyaniline at different gas flow rate and polyaniline controlled iodine doped at constant gas flow rate were studied. All these two cases were measured by the Z-scan technique. Figure (6) shows a closed-aperture Z-scan for the pure polyaniline at different gas flow rate. In Figure (6), the nonlinear effect region is extended from -1.5 cm to1.5 cm. The peak followed by a valley transmittance curve obtained from the closed aperture Z-scan data indicates that the sign of the refraction nonlinearity is negative,(i.e. self-defocusing) for thin films prepared at gas flow rate 1 lm^{-1}.and positive nonlinearity for thin films prepared at other gas flow rate .

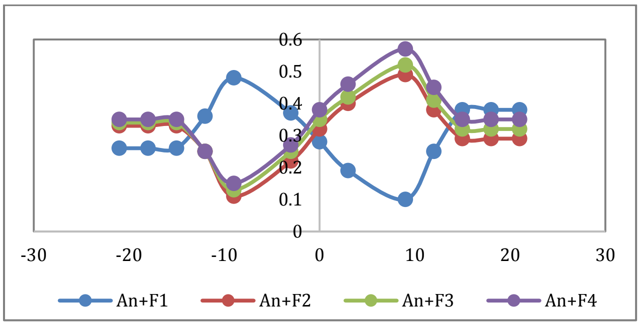

Figure (6): Closed aperture Z-scan measurement for pure polyaniline at different gas flow rate for CW laser at 532 nm

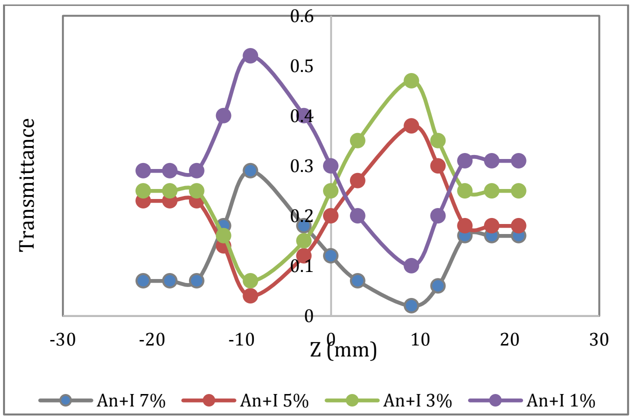

Figure (7): Closed aperture Z-scan measurement for iodine doping polyaniline by different iodine weight concentration (1, 3, 5, 7%) at constant gas flow rate using CW laser at 532 nm

The closed aperture measurements for polyaniline thin films doped with iodine by different concentration (1, 3,5 and 7%) at constant gas flow rate, shown in Figure (7). Figure (7) shows positive nonlinearity for thin films prepared at iodine weight concentration 3 and 5%. While thin films prepared with iodine weight concentration 1 and 7% shows negative nonlinearity. From the figure can be seen that the iodine doping and the gas flow rate change the nonlinear behavior of the thin films, where the gas flow rate alters the thin films Composition and the iodine atoms linked into the polymer and become part of its composition and the results new material.

The nonlinear absorption coefficients β for the two cases, pure polyaniline at different gas flow rate and polyaniline controlled iodine doped at constant gas flow rate were studied. They were measured by performing the open aperture Z-scan technique. Figure (8), represent the open Z-scan aperture measurement for pure polyaniline thin films at different gas flow rate. The behavior of the transmitted intensity for thin films prepared at gas flow rate 1, and 2 lm^{-1} is caused by two photon absorption. And for thin films prepared at gas flow rate 3, and 5 lm^{-1} the behavior of transmittance is demonstrated by saturated absorption.

For polyaniline thin films doped with iodine by different concentration (1, 3, 5, and 7%) and constant gas flow rate the open aperture Z-scan measurements were shown in Figure (9).from the figure the nonlinear optical absorption response for these thin films are demonstrated by saturated absorption.

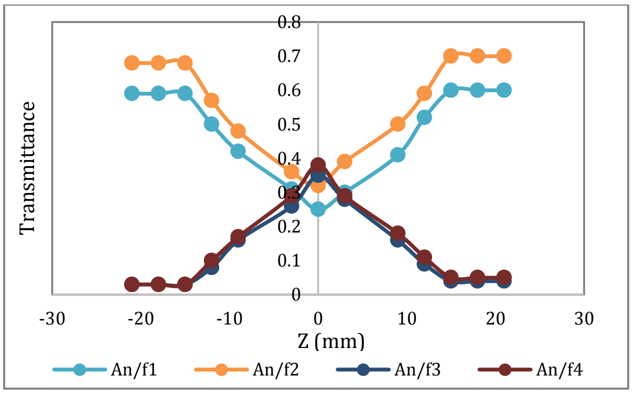

Figure (8): Open Aperture Z-Scan measurement for pure polyaniline thin films at different gas flow rate using CW laser at 532 nm

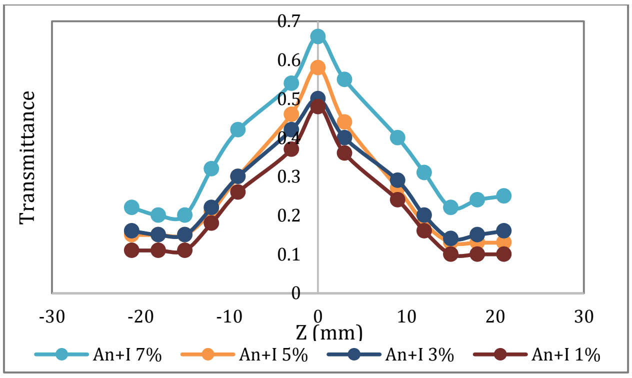

Figure (9): Open Aperture Z-Scan measurement for iodine doping polyaniline by different iodine weight concentration (1, 3, 5 and7%) at constant gas flow rate using CW laser at 532 nm

Table 1: Some of the linear and nonlinear optical properties for pure polyaniline and iodine doping polyaniline thin films using CW laser at 532 nm

pure polyaniline thin films	**α cm^{-1}**	**n_o**	**L_{eff} cm**	**$T_{pv}\Delta$**	**$\Phi_0\Delta$**	**n_2 cm^2/mW**	**T(z)**	**β cm/mW**
gas flow 1 lm^{-1}	5019	1.4	1.117×10^{-5}	0.38	0.9360	1.965×10^{-5}	0.2	1.403
gas flow 2 lm^{-1}	9613	1.6	1.819×10^{-5}	0.38	0.9360	1.207×10^{-5}	0.27	1.163
gas flow 3 lm^{-1}	9653	1.6	2.094×10^{-5}	0.39	0.9605	1.076×10^{-5}	0.3	1.123
gas flow 5 lm^{-1}	9598	1.6	1.999×10^{-5}	0.42	1.0344	1.214×10^{-5}	0.35	1.372
polyaniline thin films controlled iodine doping	**α cm^{-1}**	**n_o**	**L_{eff} cm**	**$T_{pv}\Delta$**	**$\Phi_0\Delta$**	**n_2 cm^2/mW**	**T(z)**	**β cm/mW**
PAN I 1%	5932	1.58	2.831×10^{-5}	0.42	1.0344	0.857×10^{-5}	0.48	1.329
PAN I 3%	5545	1.28	1.439×10^{-5}	0.4	0.9852	1.606×10^{-5}	0.5	2.723
PAN I 5%	13017	2.04	2.367×10^{-5}	0.34	0.8374	0.830×10^{-5}	0.58	1.921
PAN I 7%	15811	2.04	1.949×10^{-5}	0.27	0.6651	0.801×10^{-5}	0.66	2.654

Table 1 shows some of the linear and nonlinear optical properties for pure polyaniline, iodine doping polyaniline thin films using CW laser at 532 nm.

Conclusions

The polyaniline iodine doped thin films for all iodine doping concentration followed the behavior of saturated absorption material at the wavelength 532nm. From this it can be conclude the possibility of obtaining direct and inexpensive method to prepare saturated absorption thin films material.

Nonlinear optical studies of plasma polymerized thin films and iodine doped forms were carried out by employing the open and closed aperture Z-scan technique. These thin films are potential nonlinear optical materials. The Z-scan studies revealed that polyaniline exhibited a saturated absorption and two photons absorption when varying the preparation condition which candidates them for optical limiting and optical switching respectively. Incorporation of iodine in the polymer network of these films modifies the nonlinear optical properties of these thin films considerably.

References

Daniel S. Corre , Leonardo De Boni , Lino Misoguti , Ion Cohanoschi , Florencio E. Hernandez Cleber R. Mendonc (2007)¸ Optics Communications, 277, 440–44

Hammad R. Humud , Thikra Kh. Obayes and Qusay A. Abbas(2014), International Journal of Current Engineering and Technology, 4, 2580

Manjunatha K.B., Dileep R., Umesh G., and Bhat B.R. (2013), Opt. Laser Technol, 52 ,103-108.

Ready J.F., "Industrial Application of Lasers", 2nd, Academic Press, San Diego, (1978).

Sheik-Bahae, M., Said, A.A., Wei, T., Hagan, D.J., Van Stryland, E.W. (1990), IEEE., J. Quantum Electron., 26,760.

Sheik-Bahae M. Said Ali A., Tai-Huei Wei, David J. Hagan, E. W. Van Stryland, (2007), Special 30th Anniversary Feature IEEE, IEEE LEOS Newsletter 17-26

Winter C.S., Manning R.J., Oliver S.N. and Hill C.A.S (1992), Optics Communications, 90, 139

Xia, T., Sheik-Bahae, M., Said, A. A., Hagan, D.J., Van Stryland, E.W. (1994), Int. J. Nonlinear Opt.Phys., 3 489

Xiao-Liang Zhang, Xin Zhao, Zhi-Bo Liu, Shuo Shi, Wen-Yuan Zhou, Jian-Guo Tian, Yan-Fei Xu and Yong-Sheng Chen(2011), J. Opt. 13, 075202