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$\chi^{(3)}$ and optical power limiting measurements of Polyaniline and its derivative Poly (o-toluidine) under CW regime

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ABSTRACT

We present the synthesis and results on the third-order optical nonlinearity and optical limiting properties of Polyaniline and Poly (o-toluidine) studied in N,N-Dimethyl Formamide solution using a single-beam z-scan technique. Experiments were performed using continuous wave He–Ne laser operating at 633 nm wavelength as an excitation source. The samples exhibit absorption and refraction nonlinearities. The negative sign of the nonlinear refractive index n_2 indicates that both materials exhibit self-defocusing optical nonlinearity. The nonlinear refractive index n_2, the nonlinear absorption coefficient β_{eff} and the third-order optical susceptibility $\chi^{(3)}$ were determined and found to be of the order of 10^{-7} cm^2/W, 10^{-2} cm/W and 10^{-7} esu respectively. The FTIR and UV–visible characterization spectra confirm the expected molecular structure of the polymers. Multiple diffraction rings were observed when the samples were exposed to laser beam. The appearance of rings is due to the refractive index change and thermal lensing. The polymer samples with different concentrations exhibits strong optical power limiting under continuous wave laser at the experimental wavelength. Reverse saturable absorption is the dominating mechanism for the observed absorption nonlinearities.

1. Introduction

Nonlinear optical materials have been explored greatly for their various applications in all-optical switches, opto-electronic devices, 3-D optical memory devices, optical modulation, telecommunications, human eyes and optical sensors protection, etc., and future applications in biological and medical sciences [1–6]. Continuous wave (CW) lasers ranging from μW to kW are widely used in many applications [7]. Wide range of materials including liquid crystals, porphyrins, dyes, semiconductor nanoparticles, thin films, phthalocyanines and crystals are known to be optically nonlinear under CW laser illumination [8–16].

Organic materials are of great importance for optical limiting, as they possess high nonlinearity and ultra-fast response time. Among organic materials, π-conjugated polymers have received significant interest as third-order nonlinear optical materials for photonic switching devices, optoelectronic materials for light emitting diodes, solar cells, and xerographic photoreceptors [17–20]. Π-conjugated polymers include polypyrrole, polyaniline, polythiophene, and other conjugated polymers. Electroactive polymers (EAPs) belong to the class of smart materials, as they experience a change in shape or size in response to the applied electric field. EAPs are divided into electric EAPs and ionic EAPs. Ionic EAPs are of importance due to their practical applications such as their use in sensors, actuators and micro electro-mechanical systems. The smart materials under investigation are Polyaniline and Poly (o-toluidine); they are conductive polymers which belong to the class of ionic EAPs. The conductive polymers conductivity is directly associated with the presence of a conjugated backbone which enables electron delocalization. A conjugated backbone signifies a primary axis of carbon atoms interconnected by alternating single and double bonds.

Polyaniline (PANI) is an intrinsically conductive polymer located in the subgroup of ionic EAPs. It is a flexible polymer with characteristics that are similar to semiconductors. PANI is considered as one of the promising conducting polymer due to its (i) easy synthesis, (ii) comparatively stable in environment, (iii) good conductivity, (iv) variety of applications such as light emitting diodes, sensors, electro chromic devices, rechargeable batteries, corrosion resistant paints, etc. [21]. Disadvantages include low electrochemical strain, insolubility in most solvents and infusibility which makes it unsuitable for melting processes. Poly (o-toluidine) (POT) on the other hand, is a PANI derivative which contains the –CH_3 group in the ortho position of the aromatic ring of the aniline monomer. Like the parent material, electroactive POT are readily prepared and are stable in aqueous acid media. Among the ring-substituted PANI derivatives, POT has been probably the most widely studied one because of its interesting electro-optical properties [22].

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We report for the first time, the experimental measurements of third-order nonlinear susceptibility $\chi^{(3)}$ and strong optical limiting properties of PANI and POT polymer samples in solutions using z-scan technique with continuous wave He–Ne laser (35 mW) irradiation at 633 nm wavelength. Self-diffraction ring patterns were observed for different concentrations and with varying intensity. Further with change in sample position, variation in the beam spot size was also observed.

2. Experimental

2.1. Materials and methods

The compounds under investigation were synthesized as per the following procedure. Aniline and o-toluidine were purchased from Merck Company. Monomer solutions were prepared by dissolving 0.46 ml of aniline (molecular weight 93.13 g mol^{-1}, chemical formula is $C_6H_5NH_2$) and 0.43 ml of o-toluidine (molecular weight 107.15 g mol^{-1}, chemical formula is 2-$(CH_3)C_6H_4NH_2$) in 0.1 N Sulphuric acid (H_2SO_4) separately. By using the magnetic stirrer the monomer solutions was stirred for 1 h at the temperature range between 0 °C and 5 °C. 2 M ammonium persulfate is added drop by drop to the monomer solutions and this led to the formation of green coloured and slightly dark brown coloured precipitates respectively. The precipitates were filtered and then dried in an oven at 70 °C for 3 h. The obtained PANI and POT samples were then used for z-scan and optical limiting measurements. For determining the absorptive and refractive nonlinearities, 5 mg of PANI and POT samples were weighed and dissolved in 5 ml research grade N,N-Dimethyl Formamide (DMF) separately. For optical limiting studies we prepared additional samples along with above specified one with 10, 20 and 40 mg of polymer samples dissolved in 5 ml research grade DMF separately.

The molecular structures of polymer samples are shown in Fig. 1. The optical characterization of the samples under investigation was studied by recording the electronic spectra in the wavelength range 300–800 nm using UV-1601PC Shimadzu spectrophotometer and are depicted in Fig. 2. To study FTIR measurements, pellets were prepared by mixing the synthesized samples with pure potassium bromide (KBr) in the ratio of 1:100 separately. The FTIR study spectrum was taken in the mid IR region of 400–4000 cm^{-1}using FTIR 8400S Shimadzu spectrophotometer with DLATGS detector with 16 scan speed and are depicted in Fig. 3.

2.2. z-Scan experimental technique

The sign and magnitude of third-order nonlinear susceptibility $\chi^{(3)}$ of PANI and POT samples in solution was evaluated by employing z-scan technique developed by Sheik Bahae et al. [23,24]. z-Scan is a single-beam technique which offers simplicity as well as high sensitivity for measuring the nonlinear absorption (NLA) and nonlinear refraction (NLR) simultaneously. The schematic experimental setup used for z-scan technique is shown in Fig. 4. In the present experiment, a polarized Gaussian laser beam is tightly focused to a narrow waist using a lens. The sample is mounted on the micro meter translation stage and by translating the sample between $+z$ and $-z$ positions along the z-direction, the transmitted intensity through the sample are measured, with and without ($s=1$) the presence of aperture at far field in front of the photo detector. As the sample moves through the beam focus ($z=0$), self-focusing or self-defocusing

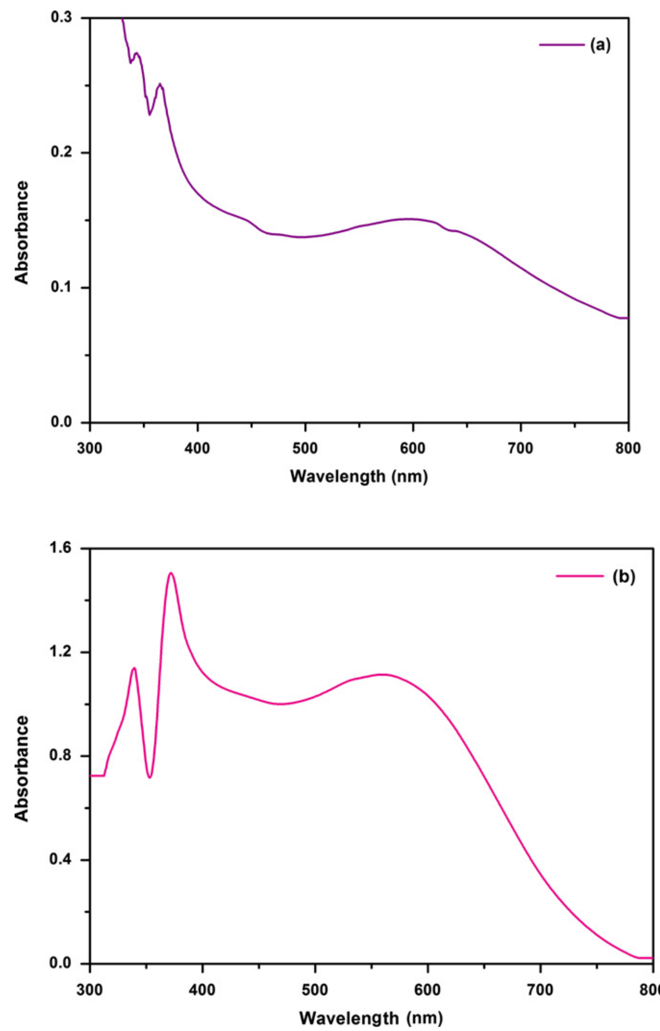

Fig. 2. Absorbance spectra of (a) Polyaniline and (b) Poly (o-toluidine) samples in DMF.

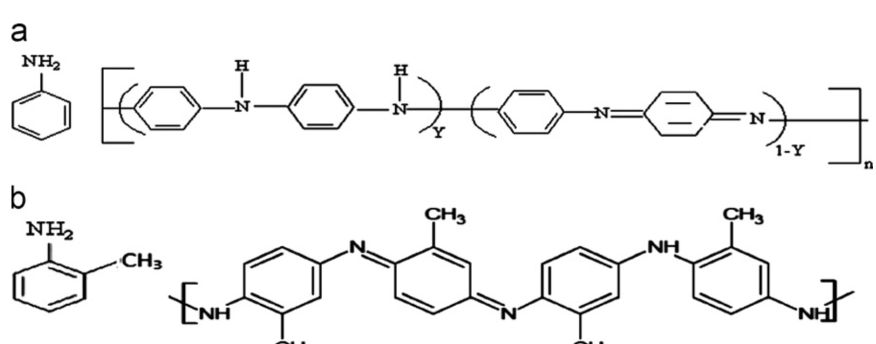

Fig. 1. Molecular structure of (a) Polyaniline and (b) Poly (o-toluidine) samples.