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Measurement of Optical Nonlinearities in Poly (1- Naphthyle acrylate) Dissolved in Cyclohexane Using TTL Modulated Laser Beam

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Abstract
Polymer poly (1-naphthyle acrylate) (PNA) dissolved in cyclohexane optical nonlinear properties are determined by the employment of thermal lens, diffraction rings and Z-scan techniques using visible 532 nm TTL modulated laser beam. Nonlinear refractive index, n_2, and the thermo-optic coefficients, dn/dT, are obtained. The three techniques led to the values of $10^{-7} cm^2/W$ and $10^{-5} k^{-1}$ respectively. It appears to us that nonlinear optical properties of PNA are governed by the solvent.

Keywords: Nonlinear refractive index, Thermal effect, TTL modulated laser.

1. Introduction
It is well recognized that the measurements of the thermophysical properties is important for the researchers interested in the optical materials area. The interaction between lasers and matter can results in thermal loading causing degradation and / or reduction of the thermal performance . The changes in properties such as thermal conductivity, thermal diffusivity, and temperature coefficient of optical length with the sample temperature rise define the figure of merit of a given material. The measurements of these properties as a function of temperature with traditional methods is always a challenging goal since it required the construction of high cost devices and appropriate excitation regime to obtain the data, especially when performed in the temperature interval where the material is submitted to phase modification.

The thermal lens (TL) spectroscopy is one of the most sensitive absorbance methods used on the measurement of the temperature rise following the conversion of the absorbed optical radiation into heat through non-radiative relaxation process [1]. Absorption of a laser beam generates thermal energy in the medium through non-radiative de-excitation resulting in the increase of the temperature of the irradiated region. The temperature distribution of the irradiated region will be the same as the intensity distribution across the beam cross section which is usually Gaussian. Since most liquids have a positive coefficient of thermal expansion, thermo-optic coefficient, dn/dT , is negative and consequently thermal lens generated is divergent one.

Changes in refractive index induced by optical field can give rise to various nonlinear phenomena in optical material. In the spatial dimension, the interplay between divergence of the propagating beam and nonlinear optical response of the medium can give rise to wide range of self-action ranging from optical-self trapping and spontaneous formation of ring patterns due to modulations instability [2]. A related phenomenon is the spatial self-modulation of a coherent beam which generates concentric intensity rings in the far field.

The Z-scan technique [3] is based on the self-focusing or defocusing of a converging beam of known spatial structure induced by moving a nonlinear sample along the light propagation direction (z-axis).The technique permits a rapid evaluation of the magnitude and sign both for the real (nonlinear refraction, NLR) and imaginary (nonlinear absorption, NLA) parts of the nonlinearity of transparent solid and liquids.

In this paper we report the observation of thermal lens effect and diffraction ring patterns of polymer poly (1- naphthyle acrylate) (PNA) dissolved in cyclohexane using modulated cw laser beam with 532 nm wavelength together with the calculation of the total change of refractive index , Δn, the nonlinear refractive index , n_2, and thermo-optic coefficient , dn/dT , by the two techniques. Obtained results by TL and diffraction techniques are confirmed by the Z-scan technique measurements.

2. Theory

Consider the transmission of optical radiation through an absorbing medium and let $I_\circ$ be the incident intensity. In TL technique thermal gradient established after absorption and thermal relaxation of the sample results in a change in intensity at the beam center owing to the incident beam divergence. The thermal lens signal is expressed as the relative change in power [4]

$$\theta = \frac{I_\circ - I}{I} \tag{1}$$

$$\theta = \frac{\Delta I}{I} = \frac{\alpha L_{eff} P}{\lambda k}\left(-\frac{dn}{dT}\right) \tag{2}$$

where $I_\circ$ and I are the transmitted power before and after the formation of the thermal lens respectively. α is the linear absorption coefficient, L_{eff} is the effective thickness of the sample, P is the laser input power , λ is the pump laser wavelength, k is the thermal conductivity and dn/dT is the thermo-optic coefficient. The characteristic thermal time of the medium, t_c , can be written as:

$$t_c = \frac{\omega_\circ^2}{4D} \tag{3}$$

$\omega_\circ$ is the beam radius at the sample and D is the thermal diffusivity which can be written as:

$$D = \frac{k}{\rho C} \tag{4}$$

k is the thermal conductivity, ρ is the sample density and C is the specific heat of the sample.

For the thermal nonlinearity and steady state case, the change in nonlinear index, Δn, can be expressed as [5]:

$$\Delta n = \frac{dn}{dT}.\frac{I\alpha\omega_\circ^2}{4k} \tag{5}$$

I , α, k and dn/dT have their usual definition given above.

Δn can be related too to the total refractive index of the medium , n , and the background refractive index, $n_\circ$, as [6]

$$n = n_\circ + \Delta n \tag{6}$$

and

$$\Delta n = n_2 I \tag{7}$$

where n_2 is the nonlinear refractive index.

Due to the average change refractive index change, Δn, the beam traversing the medium acquire nonlinear phase-shift , $\Delta\Phi$, given by [5]

$$\Delta\Phi = \Delta n k_\circ d \tag{8}$$

Where $k_\circ (= \frac{2\pi}{\lambda})$ is the beam wave-vector in vacuum and d is the sample thickness.

The on-axis nonlinear phase-shift, $\Delta\Phi$, can be related to the number of rings , N , observed as [7]:

$$\Delta\Phi = 2\pi N \tag{9}$$

By the combination of equations (6-9) one can calculate, $\Delta n, n_2$, and dn/dT .

From the open aperture (OA) z-scan technique, the nonlinear absorption coefficient, β , can be calculated using the following formula[3]

$$\beta = \frac{2\sqrt{2}\Delta T}{I_\circ L_{eff}} \tag{10}$$

ΔT is the one valley transmittance at the open aperture z-scan curve. L_{eff} is the effective thickness of the sample which is given by

$$L_{eff} = \frac{1-e^{-\alpha\ell}}{\alpha} \tag{11}$$

ℓ is the sample thickness and α is the linear absorption coefficient. $I_\circ$ is the laser input intensity $(= 2p/\pi\omega_\circ^2)$. p is the laser input power and $\omega_\circ$ is the beam radius at the sample. The difference between the normalized peak and valley transmittances , ΔT_{p-v} , can be written as [3]:

$$\Delta T_{p-v} = 0.406(1-S)^{0.25}|\Delta\Phi_\circ| \tag{12}$$

and

$$S = 1-\exp(-2r_a^2/\omega_a^2) \tag{13}$$

$\Delta\Phi_\circ$ is the on-axis phase shift at the focus, S is the linear transmittance of the aperture, r_a is aperture radius and ω_a is the radius of the beam at the aperture .The nonlinear refractive index, n_2, can be approximated using the following equation

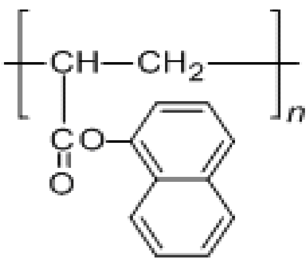
$$n_2 = \Delta\Phi_\circ\lambda/2\pi I_\circ L_{eff} \tag{14}$$

3. Experiment

3.1 Sample preparation and absorption spectra

Poly (1- naphthyle acrylate) (PNA) was synthesized and condensation polymerization adopting method previously reported [8, 9].

Acrylyl chloride was distilled before use. Isobutyryl chloride was prepared from isobutyric acid and thionyl chloride and was purified by distillation. Esters (monomers and their small molecule models) were prepared by a standard Schotten-Baumann reaction between sodium 1-naphtholate and the corresponding acid chloride. The esters were extracted with ether, washed with dilute NaOH and water, dried, and vacuum distilled: 1-naphthyl acrylate (NA), mp 28-31^{0}C, bp 100^{0}C (1 torr). Poly (1-naphthyl acrylate) (PNA) was prepared by free-radical polymerization in benzene solution degassed to $\leq$0.005 torr residual pressure. Decanoyl peroxide was used as initiator. The choice of solvent and initiator was based on their low tendency to add fluorescing and quenching impurities to the polymer chain, compared to other common solvents and initiators. PNA was polymerized to ca. 100% yield for 70h at 70^{0}C. The polymers were purified by multiple precipitations from benzene into methanol and were freeze dried from benzene. Further precipitation had no effect on the emission spectra PNA, (M_m = 16000). Figure (1) shows the structure and chemical formula of the polymer under the present study.



$C_{13}H_{10}O_2$

Figure 1: The structure and chemical formula of (PNA).

The ultraviolet–visible (UV–vis) absorption spectrum of PNA was recorded using an UV–vis spectrophotometer (CECIL-CE 3055). The optical absorption of the polymer dissolved in cyclohexane solvent with 0.05 mM concentration shows an absorption value at 532 nm equal to 0.378, as shown in Fig. 2.

3.2 Experimental setup

The Poly (1- naphthyle acrylate) (PNA) was prepared in a glass cell of 1mm thickness as the nonlinear material in the experiment. The apparatus consists of a diode laser of 5 mW output power and beam radius 1.5 mm at $1/e^2$, 532 nm wavelength, a positive glass lens of +50mm focal length, a glass cell 1mm thickness filled with PNA dissolved in cyclohexane solution , a transparent screen of 30cmx30cm, a digital camera, two power meters to measure input and output transmitted beams through the cell, a frequency generator model (EM1634) and an oscilloscope model (lodestar -MOS-620CH). For the ring pattern the output power meter is replaced by the screen. Output of the laser is TTL modulated at 20Hz for the TL measurements. Fig.3 shows the experimental setup.

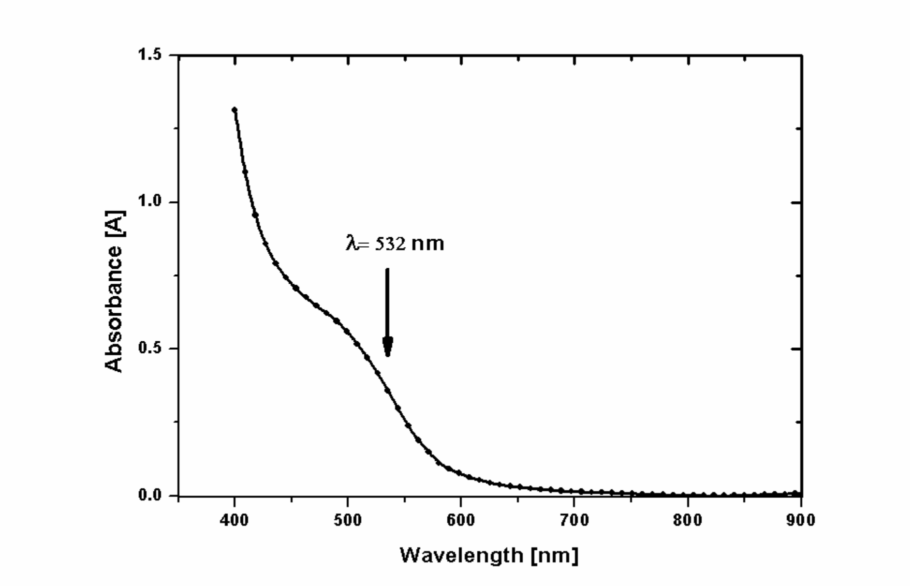


Figure 2: Linear absorption spectra of PNA.

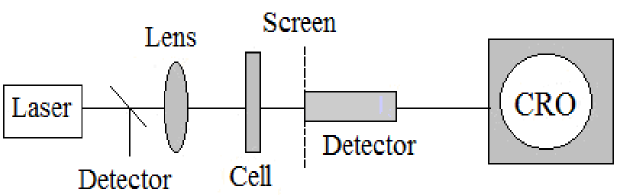


Figure 3: Experimental setup

4. Results and discussion

The transient signal of PNA dissolved in cyclohexane is shown in Fig.4. It supplies the characteristic thermal time, t_c, and the relative change in power, θ.With the aid of input power (TTL input signal) of 4mWatt, 532nm in wavelength, cell length 1mm ,frequency 20 Hz, sample at z= +5mm , T = 25 $^{\circ}C$ and the data given in table1, t_c the thermally induced phase shift, θ (rad), and thermal diffusivity, $D(m^2/\sec)$, are calculated, the results of which are given in Table 2.

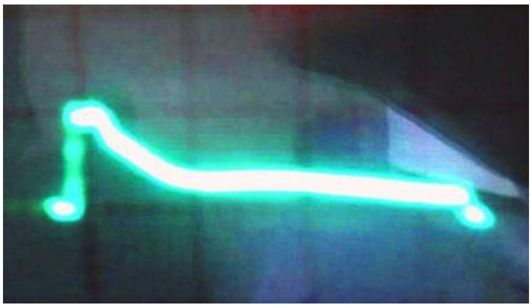


Figure 4: The signal transmitted through PNA dissolved in cyclohexane solution.

Table 1: Thermal conductivity and absorption coefficient of PNA dissolved in cyclohexane.

Solvent	k (W m^{-1} K^{-1})	α (cm^{-1})=(2.303log (P_{in}/P_{out}))/L
Cyclohexane	0.123	8.8

Table 2: The measurement details and the results of TL technique obtained for PNA dissolved in cyclohexane.

Solvent	t_c (ms) characteristic TL time constant	θ (rad) thermally induced phase shift	D (cm^2/s) thermal diffusivity
Cyclohexane	4.537	5.226	0.25×10^{-4}

Based on these calculations, we obtained the nonlinear refractive index , n_2 , and the thermo-optic coefficient, dn/dT as given in Table 3 for the PNA dissolved in cyclohexane solution.

Table 3: Nonlinear refractive index and thermo-optic coefficient for PNA dissolved in cyclohexane.

Solvent	n_2 (W/cm^2)	dn/dT (k^{-1})
Cyclohexane	6.25×10^{-7}	7.33×10^{-5}

The experimental setup for the diffraction ring patterns is the same as previously mentioned, except that the power meter detector is replaced by the transparent screen .The on-axis change refractive index Δn can be calculated using the relation :

$$\Delta n = \frac{\Delta\Phi}{k.L_{eff}} \tag{15}$$

Based on the number of rings, incident intensity $I_\circ = 0.554\, Kw/cm^2$,$\Delta\Phi, \Delta n, n_2$ and dn/dT are calculated as given in table 4. The diffraction ring pattern for the PNA dissolved in cyclohexane solution is shown in Fig.5.

Table 4: The measurement details and the results of diffraction ring patterns for PNA dissolved in cyclohexane.

Solvent	N	ΔΦ	Δn	n_2 (W/cm^2)	dn/dT (k^{-1})
Cyclohexane	2	0.21	0.28×10^{-4}	0.51×10^{-7}	0.60×10^{-5}

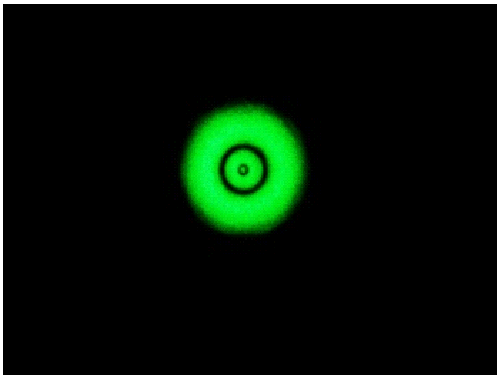
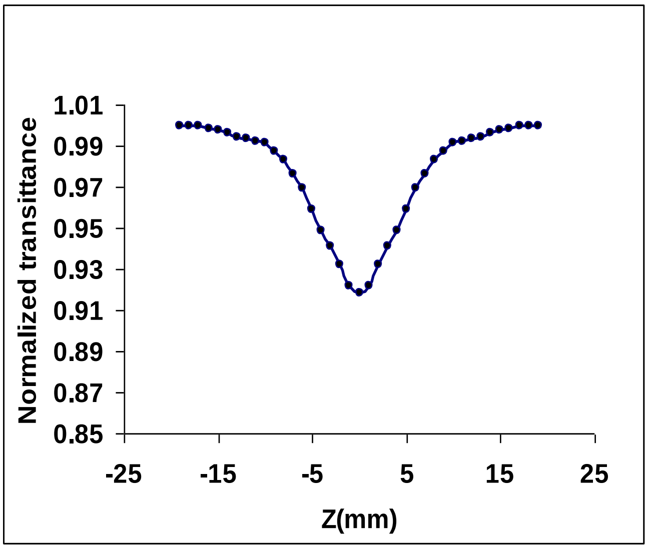
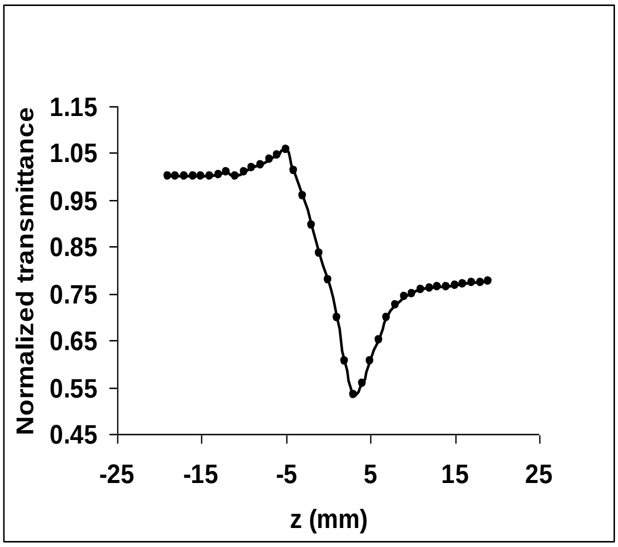


Figure 5: Diffraction ring pattern for the PNA dissolved in cyclohexane.

The z-scan experiments were performed using the same laser (532nm) which was focused by the same lens (+50mm).The laser beam waist , $\omega_{\circ}$, at the sample is measured to be 21.63 μm and the Rayleigh length, , $z_{\circ}$ is 2.76 mm, aperture radius, r_a , is 2mm, the radius of the beam spot at the aperture , ω_a , is 3.82mm, the distance from focal point to the detector , z_a , is 250mm and input power, p , is 4mWatt.
The linear transmittance at the aperture, S is 0.42. The z-scan measurements for PNA dissolved in cyclohexane solution for the open aperture (OA) ,closed aperture (CA) , and normalized (CA/OA) variations of output beam for the cell with out and with aperture are shown in Fig.6.

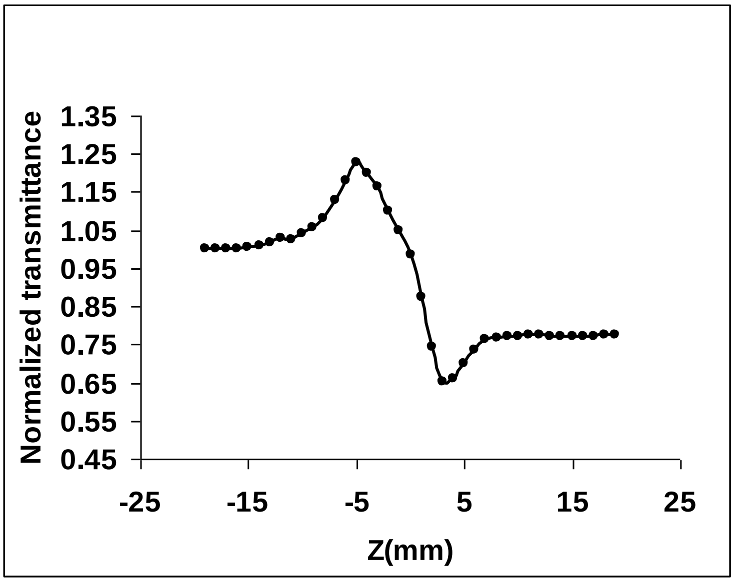


a



b

Figure 6: z-scan experimental data for PNA solution: (a) open aperture (OA) and (b) close aperture (CA)



c

Figure 6: z-scan experimental data for PNA solution: (c) CA/OA

These numerical leads to the parameter, ΔT_{p-v} ,the difference between normalized peak to valley transmittances, $\Delta\Phi_{\circ}$, the on-axis nonlinear phase shift at the focus, n_2 ,the change in refractive index, Δn ,the on-axis index change and, dn/dT , the thermo-optic coefficient, given in table 5 for PNA dissolved in cyclohexane solution.

Table 5: The measurement details and the results of the z-scan technique for PNA dissolved in cyclohexane.

Solvent	L_{eff} (mm)	ΔT_{p-v}	Δφ	n_2 (W/cm^2)	Δn	$dn/dT\ (k^{-1})$
Cyclohexane	0.066	0.416	1.17	3.18×10^{-7}	1.73×10^{-4}	3.73×10^{-5}

The physical and chemical properties of organic molecules used in different scientific and technological applications can strongly depend on the properties of the surrounding media [10, 11]. For liquid solutions, the solvent plays a fundamental role in photo-physical processes, leading to the modification of the ground and excited-state energies of the molecules. The interaction of solute with the surrounding solvent leads to solvation effect, which refers to the reorientation of the solvent molecules around a solute molecule .The result of interaction of solute with solvent molecules depends on the nature of arising forces (as hydrogen bonding in specific or universal interaction in general) which are determined by charge distribution and polarizability of the solvent and solute molecules. Considerable changes in the energy of the solvated solute molecules may occur with changes in the solvent, especially in polar media.

The diffraction ring pattern understood from the spatial self-modulation effect [12]. A pump beam with a Gaussian intensity profile should induce a phase shift, $\Delta\Phi$, with a bell-shaped transverse profile. For each point, y_1 on the Gaussian distribution of the beam there always exists another point, y_2, with the same slope. The radiation field from the regions around y_1 and y_2 have the same wave-vector and should interfere constructively or destructively when $\Delta\Phi(y_1)-\Delta\Phi(y_2)=m\pi$, if m is even or odd respectively.

Conclusion

Thermal lens, diffraction ring and z-scan techniques measurements have been carried out on polymer Poly (1-naphthyle acrylate) (PNA) dissolved in cyclohexane using 532nm (TTL) modulated laser beam. The nonlinear refractive index , n_2, and thermo-optic coefficients ,dn/dT, obtained were large and negative in nature and are strongly dependent on the properties of the solvent such as polarity, dipole moment, thermal conductivity, specific heat and absorption coefficient. The nonlinear refractive index and thermo-optic coefficient are found to be of the order of $10^{-7}\,cm^2/W$ and $10^{-5}\,k^{-1}$ respectively.

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