Nonlinear Optical Studies of a D-A Type Conjugated Polymer Containing Heterocyclic Moieties

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Abstract—In the present work we aim to synthesize new conjugated polymers possessing a good nonlinear optical property (NLO) for applications in photonics. Herein we report the synthesis of a new donor-acceptor (D-A) type conjugated polymer consisting of 3, 4-propylenedioxythiophene, 1,3,4-oxadiazole and 3,4-diphenylthiophene units by following multistep reactions. The new polymer was characterized by using FTIR, ^{1}H NMR, UV-vis, fluorescence spectroscopy, GPC followed by elemental analysis. The band gap of the polymer was calculated by cyclic voltammetric technique. Further, its NLO properties in THF solution were investigated by Z-scan technique using 532 nm, 7 ns laser pulses. The results indicate that polymer exhibit good optical limiting behavior due to effective two-photon absorption (TPA). The optical and electrochemical properties reveal that the polymer is a promising candidate for photonic applications.

Index Terms—Two-photon absorption, NLO, conjugated polymer, optical properties

I. INTRODUCTION

NLO materials have been widely studied because of their potential applications in the domain of photoelectronics and photonics [1], [2]. Conjugated organic polymers possessing NLO properties occupy a prominent position owing to their versatility, high thermal and chemical stability along with the ease of synthesis. Among various conjugated polymers, thiophene based conjugated polymers have gained increased consideration [3]-[5]. Thiophene, not only behaves as one of the most effective heterocyclic rings in enhancing NLO properties, but also promotes the desirable targets of high solubilty and easy processability of the materials. Presently, D-A type conjugated polymers are of great interest due to their high molecular hyperpolarisability (β) and dipole moment (μ), which are essential requisites for large third order nonlinear susceptibility [6]. Keeping this in view, we designed a new D-A type conjugated polymer carrying 3,4-propylenedioxy thiophene as a donor unit and 1,3,4-oxadiazole as an acceptor moiety with 3,4-diphenylthiophene as a conjugation extending system. Here we report the synthesis and characterization of polymer, poly{2-(5-(1,3,4-oxadiazol-2-yl)-3,4-diphenylthiophen-2-yl)-5-(3,4-dihydro-2H-thieno[3,4-b][1,4]dioxepin-6-yl)-1,3,4-oxadiazole}. Its electrochemical and optical properties were investigated. Further, its NLO property was studied using Z-scan technique at 532 nm, 7 ns laser pulses.

II. EXPERIMENTAL PROCEDURE

As outlined in Fig. 1, 3,4-diphenylthiophene-2,5-dicarboxylic acid (3) was synthesized by condensing diethyl thiodiacetate (1) with benzil (2) in presence of sodium methoxide solution at room temperature. Further, dimethyl 3,4-diphenylthiophene-2,5-dicarboxylate (4) was obtained by esterification of 3, which was then treated with hydrazine hydrate in methanol: chloroform (5:2) to give 3,4-diphenylthiophene-2,5-dicarbohydrazide (5) in good yield. The monomer 5 was then reacted with 3,4-propylenedioxythiohene-2,5-dicarboxylic acid chloride (6) to give precursor polyhydrazide 7. Finally, the polyhydrazide 7 was cyclized to yield required polyoxadiazole *P* using phosphorousoxychloride as dehydrating agent.
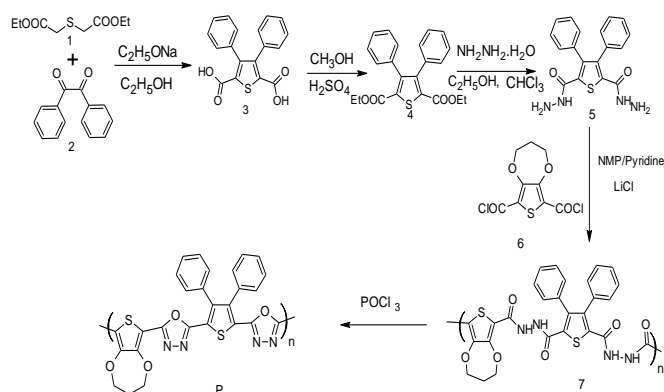

Fig. 1. Synthetic route for polymer (*P*) synthesis.

III. RESULTS AND DISCUSSION

A. Characterization of monomers and polymer

The structures of monomers, precursor and final polymer were investigated by ^{1}H NMR, FTIR spectral and elemental analyses. The ^{1}H NMR spectrum of the diacid (3) showed singlet peak at δ, 12.34 ppm and multiplet at 6.93-7.12 ppm corresponds to acid and aromatic protons. The compound 4 exhibited multiplet at 7.39-8.08 ppm corresponds to protons of phenyl ring and a singlet at 3.72 ppm for –OCH$_3$ of ester. The dihydrazide (5) showed broad peak at 4.52 ppm for –NH$_2$ protons, multiplets were observed around 7.36-7.40 ppm corresponds to aromatic protons and then at 8.85 ppm singlet appeared for –NH proton. The ^{1}H NMR spectrum of polyhydrazide 7 displayed two sharp peaks at δ values, 9.53 and 10.45 ppm, which are hydrazide protons (>NH). Aromatic protons were resonated at δ values 7.41- 7.12 ppm as multiplet. The peaks appeared 4.4 - 4.2 ppm corresponds

to –OCH$_2$–. Also, peaks at 2.12 ppm appeared corresponds to –CH$_2$–.The ^{1}H NMR spectrum of polymer *P* showed disappearance of amine (>NH) peaks at *δ* value, 9.53 andv10.45 ppm confirming the formation of 1,3,4-oxadiazole in the polymer backbone.

Further formation of precursor polyhydrazide 7 was evidenced by FTIR spectrum, wherein it exhibited sharp peaks at 3312 and 1627 cm^{-1} accounting for amine (>NH) and carbonyl (>C=O) groups, respectively. The successful conversion of polyhydrazide 7 to polyoxadiazole *P* was confirmed by FTIR spectrum. Disappearance of amine (>NH) and carbonyl (>C=O) stretching absorption bands and appearance of a sharp peak at around 1578 cm^{-1} due to imine (>C=N-) of the 1,3,4-oxadiazole ring clearly indicates the cyclization. The absorption band corresponding to >C–O–C< stretching of 1,3,4-oxadiazole ring was observed at 1058 cm^{-1}.The weight average molecular weight ($\overline{M}_w$) of the polymer *P* was determined to be 3335 g/mole and its polydispersity (PDI) was found to be 1.68. The thermogravimetric analysis showed polymer is thermally stable up to about 300 ℃.

B. Linear optical properties

The linear photophysics of the polymer solution in THF solution was investigated using UV-visible and fluorescence spectral studies. The absorption maxima of the polymer were at 402 nm and fluorescence emission peak at 481 nm as shown in Fig. 2 and Fig. 3 respectively.
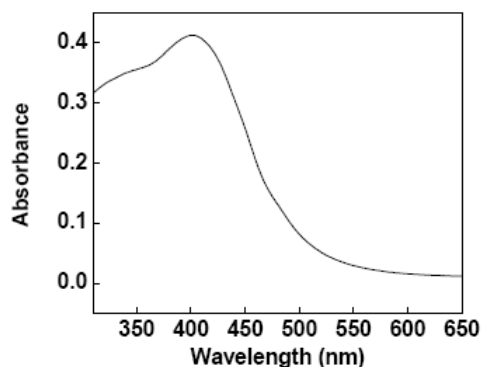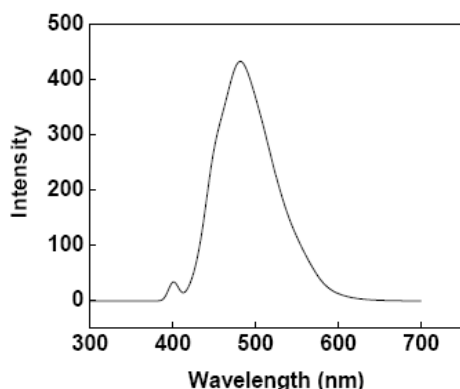

Fig. 2. UV-vis absorption spectrum of *P*

Fig. 3. Fluorescence spectrum of *P*

C. Electrochemical properties

The cyclic voltammogram of the *P* displayed distinct oxidation and reduction processes as shown in the Fig. 4. The onset oxidation and reduction potentials were found to be 1.15 and -1.24 eV respectively, which were used to estimate

band gap. The onset oxidation and reduction potentials are used to estimate highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO). The band gap was found to be 2.39 eV, as calculated using equations reported by de Leeuw et al. [7].
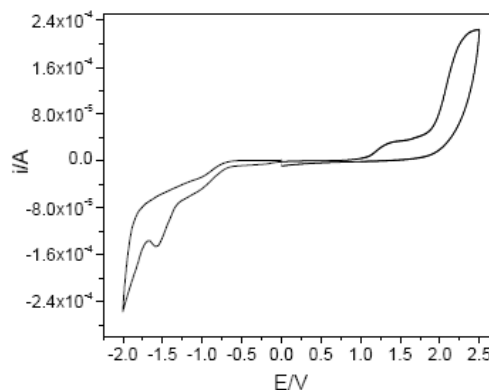

Fig. 4. Cyclic voltammetric waves of *P*

D. Nonlinear optical properties

The Z-scan is a widely used technique developed by Sheik Bahae et al. [8] to measure the nonlinear absorption coefficient and nonlinear refractive index of materials. The "open aperture" Z-scan gives information about the nonlinear absorption coefficient. Here a Gaussian laser beam is used for molecular excitation and its propagation direction is taken as the z-axis. The beam is focused using a convex lens, and the focal point is taken as $z = 0$. Obviously, the beam will have maximum energy density at the focus, which will symmetrically reduce towards either side of it, for the positive and negative values of z. The experiment is done by placing the sample in the beam at different positions with respect to the focus (different values of *z*), and measuring the corresponding transmission. For a focused Gaussian beam, each z position corresponds to an input laser energy density of $F(z) = 4\sqrt{\ln 2}E_{in}\big/ \pi^{3/2}\omega(z)^2$, and intensity of $I(z) = F(z)/\tau$, where E$_{in}$ is the input laser pulse energy, $\omega(z)$ is the beam radius, and τ is the laser pulse width. Thus the sample sees different laser intensity at each position, and hence, the measured position-dependent transmission gives information about its intensity-dependent transmission.
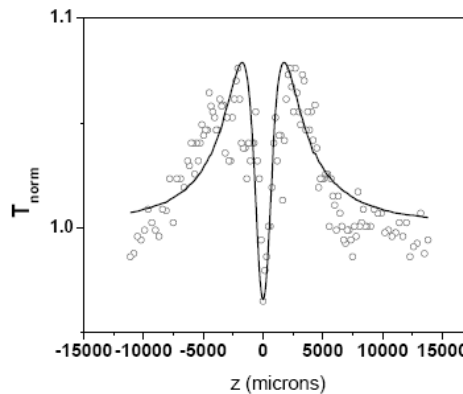

Fig. 5. Open aperture Z-scan curve for *P*

The open aperture Z-scan and optical limiting curve obtained from the sample is given in Fig. 5. From the open aperture z-scan data, the nonlinear absorption coefficient of the material can be calculated. The sample has linear

absorption of about 59% at the excitation wavelength in the 1 mm cuvette and hence strong two-step excited state absorption also will happen along with genuine TPA in the present case.

The net effect is then known as an "effective" TPA process. The data obtained are fitted to the nonlinear tra nsmission equation for a two-photon absorption process. The data obtained are fitted to the nonlinear transmission equation for a two-photon absorption process, given by (1).

$$T(z) = [1/\pi^{1/2}q(z)]\int_{-\infty}^{+\infty}\ln[1+q(z)\exp(-\tau^2)]d\tau \qquad (1)$$

where $T(z)$ is the sample transmission at position z. $q(z) = \beta I_0 L/[1+(z/z_0)^2]$, where I_0 is the peak intensity at the focal point, $L = [1 - \exp(-\alpha l)]/\alpha$, where l is the sample length and α is the linear absorption coefficient, and $z_0 = \pi\omega_0^2/\lambda$ is the Rayleigh range, where ω_0 is the beam waist radius at focus and λ is the light wavelength, β is the effective TPA coefficient. The absorption coefficient β was found to be 8×10^{-12} m/W. The NLO property of the polymer is due to the presence of D-A type arrangement in the polymer backbone. This arrangement will introduce more dipolar moment in the polymer, which is one of the criteria for the molecule to exhibit NLO property.

IV. CONCLUSION

The newly synthesized polymer showed band gap of 2.39 eV and green light emission. The polymer displayed strong absorptive nonlinearity due to an effective two-photon absorption process. The calculated nonlinear absorption coefficient value was comparable to reported compounds. Its nonlinear behavior indicates that it is a potential material for photonic applications.

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