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Electrochemical and Nonlinear Optical Studies of New D–A Type π-Conjugated Polymers Carrying 3,4-Benzyloxythiophene, Oxadiazole, and 3,4-Alkoxythiophene Systems

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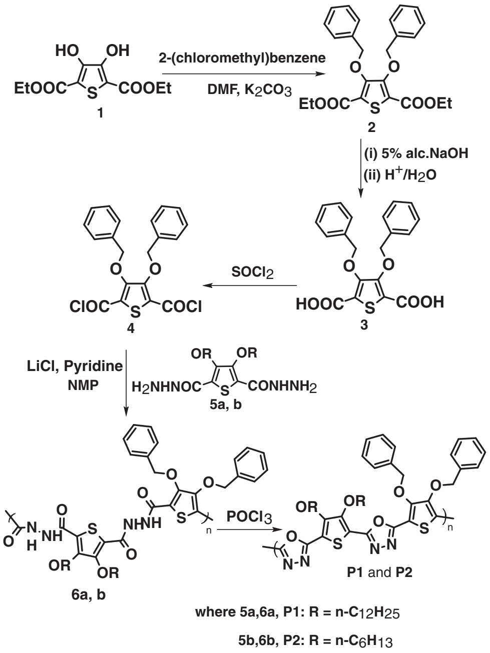
We investigated the nonlinear optical (NLO) properties of two newly synthesized conjugated polymers **P1** and **P2** carrying 1,3,4-oxadiazole, 3,4-dibenzyloxythiophene, and 3,4-dialkoxythiophene moieties along the main chain, as potential NLO active materials. Their structures have been well characterized. The nonlinear measurements were performed by Z-scan using 532 nm, 7 ns laser pulses. Calculated values of figure of merit and β follow the criteria for good NLO materials. These results suggest that polymers are promising materials for applications in photonics.

In recent times, NLO materials are gaining attention of many researchers because of their potential applications in optical communications, optical storage, optical computing, optical switching, optical limiting, etc.[1,2] Polymeric systems with delocalized π-electrons have been shown to possess a very high molecular polarizability and third-order optical nonlinearities. Recently, D–A type conjugated polymers gathered much importance as they carry enhanced polarizability and dipole moment, due to which they are widely used in high speed nonlinear susceptibility studies.[3–5] Among various D–A type conjugated polymers, thiophene-based polymers and oligomers are of special interest mainly due to their high thermal stability, readiness to accommodate functional groups, and solubility in common organic solvents. It is observed that enhancement in their optical nonlinearity can be achieved by introducing proper electron-donating and electron-withdrawing groups as well as by optimizing steric repulsion between these groups through structural modification. This generates a highly polarizable charge-transfer system with an asymmetric electron distribution.[6–8]

Though several reports are available on NLO properties of conjugated polymers, the quest to design and synthesize new organic D–A type polymers possessing high molecular hyperpolarizability and dipole moment (μ) is still on.[9] One way to achieve this is to fine tune the optoelectronic properties of these polymers depending on the choice of the functional substituents.[10–13]

Keeping this in view, we have designed new polymers with 3,4-aryloxy-/3,4-alkoxy-substituted thiophene as electron donor moieties and 1,3,4-oxadiazole as electron-withdrawing segment along the polymer chain with the hope of improved NLO activity. Besides, the NLO properties of these new polymers have been studied by Z-scan technique and their results are discussed. These polymers are believed to possess high molecular hyperpolarizability due to effective delocalization of π-electron cloud along the polymer main chain. Moreover, charge transfer would take place over nonconjugated bonds between benzyl and thiophene units owing to the presence of $-OCH_2$ linkage. Further, this may also decrease the torsional angle between the benzyl groups in the polymeric chain.



Scheme 1. Synthetic route for the preparation of polymers **P1** and **P2**.

The synthetic route toward the preparation of new intermediates, monomers and polymers is outlined in Scheme 1. The required intermediate 3,4-bis(benzyloxy)thiophene-2,5-dicarboxylic acid (**3**) was synthesized by alkali hydrolysis of the diethyl 3,4-bis(benzyloxy)thiophene-2,5-dicarboxylate (**2**), which was obtained by condensation of diethyl 3,4-dihydroxythiophene-2,5-dicarboxylate (**1**) with benzyl chloride in presence of potassium carbonate and DMF. The diacid **3** was refluxed with excess thionyl chloride to obtain 3,4-bis(benzyloxy)thiophene-2,5-dicarbonyl dichloride (**4**), which on treatment with the dihydrazides **5a** and **5b** in presence of lithium chloride and pyridine underwent smooth polycondensation to give required polyhydrazides **6a** and **6b**. The compounds **6a** and **6b** obtained were converted into corresponding target polymers **P1** and **P2** through cyclo-dehydration reaction using phosphorus oxychloride as dehydrating agent. The molecular structures of newly synthesized intermediates, monomers, precursors, and the final polymers were confirmed by their FTIR, ^1H NMR, and ele-

Table 1. Electrochemical potentials, energy levels, and electrochemical band gap of **P1** and **P2**

	E_{oxd} (onset)	E_{red} (onset)	E_{HOMO} /eV	E_{LUMO} /eV	$E_g{}^a$ /eV	$E_g{}^b$ /eV
P1	1.37	−1.05	−5.77	−3.35	2.42	2.45
P2	1.01	−1.19	−5.41	−3.21	2.20	2.38

[a]Electrochemical band gap. [b]Optical band gap.

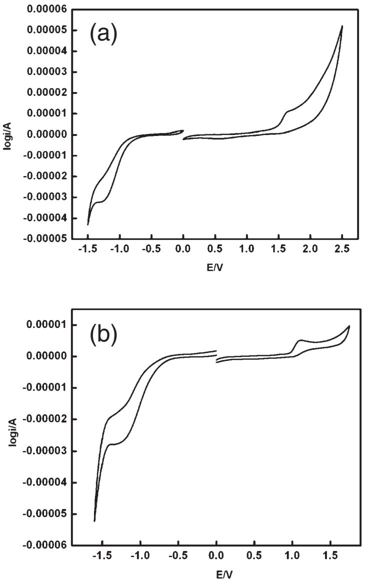


Figure 1. Cyclic voltammetric waves of **P1** (a) and **P2** (b).

mental analyses. Thermogravimetric analysis showed that polymer is thermally stable up to 300 °C. The detailed characterization data are given in Supporting Information.[21]

Cyclic voltammetry (CV) was employed to determine redox potentials of new polymers and then to estimate the HOMO, LUMO energy and band gap of the polymers using a reported equation.[14] Electrochemical data of **P1** and **P2** are summarized in Table 1 and CV waves are as shown in Figure 1. These reduction potentials are lower than that of 2-(4-*tert*-butylphenyl)-1,3,4-oxadiazole (PBD), one of the most widely used electron-transporting materials.[14–16] It has been observed that **P1** exhibited lower band gap compared to **P2**. The variation in band gap of **P1** and **P2** may be attributed to difference in the alkyl chain length of alkoxy substituents at positions 3 and 4 of thiophene ring. The length of alkyl substituent affects the electronic energy levels significantly. In general, the introduction of sterically hindered bulkier alkoxy side chain twists the monomer units out of plane leading to loss of planarity. Hence, increase in band gap has been observed in **P1**.

The absorption measurements were taken for dilute solutions (10^{-5} M) and for film state having thickness of 1.83 µm for **P1** and 1.64 µm for **P2**. The optical absorption maxima for polymers **P1** appeared at 388 and 395 nm (Figure 2) and for **P2** appeared at 372 and 379 nm (Figure 3) for solution and film state, respectively. The absorption maxima of the polymers in film state showed bathochromic shift of ca. 7 nm compared to that obtained in solution state, indicates the presence of interchain interactions in the solid state of polymers.

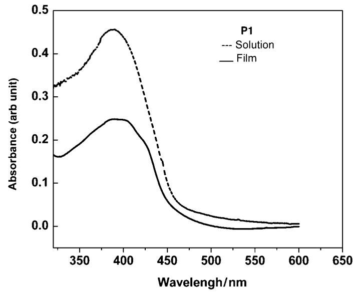


Figure 2. UV–visible absorption spectra of **P1** in solution and film states.

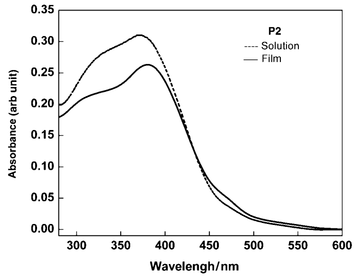


Figure 3. UV–visible absorption spectra of **P2** in solution and film states.

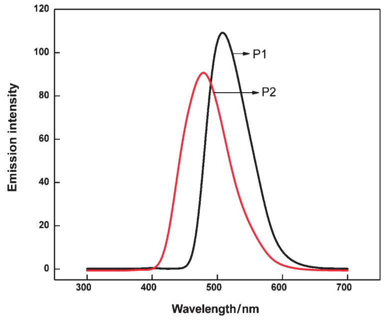


Figure 4. Photoluminescence spectra of **P1** and **P2**.

The fluorescence emission spectra of polymers **P1** and **P2** in THF showed emission peaks at 502 and 480 nm, respectively (excitation wavelength 380 nm) as shown in Figure 4. Their optical band gaps (E_g) calculated from the absorption edge of the spectrum were found to be 2.45 and 2.38 eV (Table 1) for **P1** and **P2**, respectively.

Figures 5 and 6 show the open aperture Z-scans and fluence curves of **P1** and **P2**, respectively. Numerically, a TPA type process was found to give the best fit to the measured Z-scan data. Both samples have a linear absorption of about 50% at the excitation wavelength when taken in a 1 mm cuvette. Therefore, strong two-step excited state absorption would 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 transmission equation for a two-photon absorption process.[17]

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

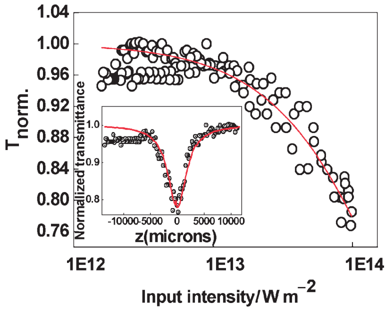


Figure 5. Input intensity versus the normalized transmittance for the polymer **P1**. Inset shows the Z-scan curve.

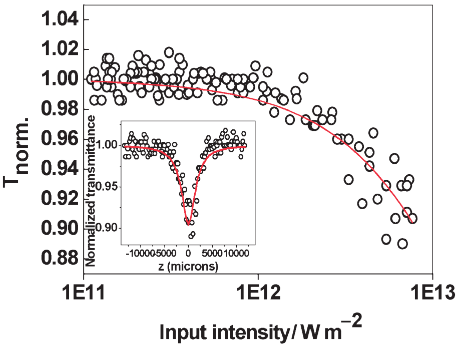


Figure 6. Input intensity versus the normalized transmittance for the polymer **P2**. Inset shows the Z-scan curve.

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 numerically calculated values of the effective TPA coefficient for polymers from the experiment are $5.3 \times 10^{-11}\,\mathrm{mW^{-1}}$ for **P1** and $1.4 \times 10^{-11}\,\mathrm{mW^{-1}}$ for **P2**. For comparison, under similar excitation conditions, NLO materials like Cu nanocomposite glasses had given effective TPA coefficient values of 10^{-10} to $10^{-12}\,\mathrm{mW^{-1}}$, bismuth nanorods and CdS quantum dots gave 5.3×10^{-11} and $1.9 \times 10^{-9}\,\mathrm{mW^{-1}}$, respectively.[18,19]

The figures of merit such as W and T were calculated using β, intensity of light and equation reported earlier,[20] which are important parameters to determine significant material properties required to achieve efficient optical switching. The values of $n_2(\lambda)$, W, and T have been calculated for polymers **P1** and **P2** and given in Table 2. The polymers follow the criteria ($W > 1$ and $T < 1$) and hence follow the optical requirements for better third order nonlinear optical materials. A detailed discussion on W and T is given in Supporting Information.[21]

The enhanced nonlinear behavior of the polymers can be explained based on their structure. In the polymers, alkoxy and benzyloxy pendants substituted at 3- and 4-positions of thiophene ring behave as donor moieties whereas 1,3,4-oxadiazole behaves as strong acceptor moiety. This alternate D–A arrangement gives rise to high π-electron density along the polymeric chain and are easily polarizable which in turn results in enhanced delocalization of the electrons in the polymer backbone. Moreover, the alkoxy and benzyloxy groups act as solubilising groups thereby facilitating the solubility of the polymers. All these factors collectively favored the nonlinear absorption of the polymers as a whole. The enhancement is well perceived as the resulting third-order nonlinear susceptibility has increased 10-fold when compared to the results of some of the D–A type polymers already reported.[12,13]

Table 2. Figures of merit calculated at 532 nm

	$n_2/\mathrm{cm\,W^{-1}}$	W	T	$I/\mathrm{J\,ms^{-1}}$
P1	1.142×10^{-10}	5.0	$\ll 1$	3.25×10^9
P2	7.31×10^{-11}	4.8	$\ll 1$	4.12×10^9

It can be concluded that two new conjugated polymers **P1** and **P2** were designed and synthesized successfully using the precursor polyhydrazide route. They exhibited good thermal stability up to 300 °C. Their UV–visible absorption spectra red shift of ca. 7 nm was observed in thin films. The electrochemical band gaps were determined to be 2.42 and 2.20 eV for **P1** and **P2**, respectively. The polymers showed strong absorptive nonlinearity due to an effective TPA process. The values of effective TPA absorption coefficients and figure of merits indicate a high optical nonlinearity in polymers. Hence they can find useful applications in photonics.

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