

Nonlinear Optical Characterization of New Thiophene-Based Conjugated Polymers for Photonic Switching Applications

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ABSTRACT: This research article describes a technique to synthesize new donor–acceptor-type conjugated polymers carrying 1,3,4-oxadiazolyl-naphthalene and 3,4-(ethylenedioxy/diphenyl)-thiophene moieties (**P1** and **P2**) starting from 2,2'-sulfanediyl diacetic acid and diethyl ethanedioate through multistep reactions. The newly synthesized intermediates and the final polymers have been characterized by different spectroscopic techniques followed by elemental analysis. Their optical and electrochemical properties have been investigated by UV–visible, fluorescence spectroscopy, and cyclic voltammetric studies, respectively. Furthermore, the nonlinear optical transmission properties of these polymers have been investigated by the open

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aperture z-scan technique. The new polymers **P1** and **P2** have well-defined structures, good thermal stability, and band gaps of 1.98 and 1.88 eV, respectively. They emit bluish-green fluorescence both in solution and in film state. Interestingly, these polymers show saturable absorption behavior. The results of nonlinear optical studies reveal that they are potential candidates for photonic switching device applications. © 2011 Wiley Periodicals, Inc. *Adv Polym Techn* 30: 312–321, 2011; View this article online at wileyonlinelibrary.com. DOI 10.1002/adv.20227

KEY WORDS: NLO, Optical properties, Poly(thiophene)s, Saturable absorption, Synthesis

Introduction

Currently, investigation of new materials possessing significant nonlinear optical (NLO) properties is one of the most important subjects of research interest. Among the various properties, saturable absorption, which is characterized by an increase in transmission with increasing incident intensity, has been extensively applied in laser physics, such as mode locking, picosecond pulse shaping, and optical bistability.^{1,2} Particularly, two-photon absorption and reverse saturable absorption, characterized by a reduction in transmission with respect to intensity, are being studied for numerous optical device applications such as optical switches, optical rectification, and optical limiters.^{3,4}

A thorough literature survey reveals that thiophene-based conjugated polymers are currently under active investigation for third-order NLO properties. Among the various types of conjugated polymers, they are in the forefront of research efforts mainly because of their easy processability, chemical stability, and readiness of functionalities. Furthermore, NLO properties can be synthetically tuned in polythiophenes by introducing electron-releasing and electron-accepting segments in the polymer chain, which would result in improved delocalization in the molecule. Also, the flexibility of introduction of required side chains to the monomer unit and consequently to the polymer chain is possible in its synthetic design. This enables to improve the processability of polymers.^{5,6} Their properties such as good film forming characteristics, solubility, optical transparency, and adequate mechanical strength have made them more attractive for device fabrication in comparison with their inorganic counterparts.^{7–9}

Based on these observations, several polymers derived from thiophenes were synthesized and studied^{10–12} for their NLO properties. According to these reports, donor and acceptor groups along the polymer backbone would be an encouraging molecular design for enhancing the NLO properties. Motivated by this, it has been thought of designing new conjugated thiophene-based polymers with the hope that the new design would yield enhanced NLO properties.

In this context, it has been planned to incorporate naphthalene moiety as additional conjugative spacer between 3,4-disubstituted thiophenyl oxadiazole systems in our molecular design of new polymers to enhance the extent of effective delocalization along the polymer chain. Furthermore, in the new polymers, there is a scope for modification of molecular structure through functionalization of the naphthalene ring for improving their physical properties. It is expected that the resulting molecules would show large NLO properties, which make them potential candidates for optical device applications. In this report, we describe the synthesis and characterization of two new donor-acceptor-type of polymers containing 3,4-disubstituted thiophene as electron-rich segment and 1,3,4-oxadiazole moiety as electron-deficient unit. Furthermore, their nonlinear optical transmission has been determined using the open aperture z-scan technique, employing nanosecond laser pulses at 532 nm from an Nd:YAG laser.

Experimental

MATERIALS AND INSTRUMENTATION

3,4-Ethylenedioxythiophene-2,5-dicarboxylic acid (c) and 3,4-diphenyl-2,5-dicarboxylic acids (d) were synthesized from corresponding diethyl 3,

4-didodecyloxythiophene-2,5-dicarboxylates according to the reported procedure.^{13–16} *N,N*-Dimethylformamide (DMF), *N*-methyl pyrrolidone (NMP), and acetonitrile (ACN) were dried over CaH₂ and used. Thiodiglycolic acid, diethyl oxalate, and tetrabutylammoniumperchlorate (TBAPC) were purchased from Lanchaster (London, UK). Naphthalene-2,6-dicarboxylate (**a**) and dibromoethane were purchased from Aldrich (St. Louis, MO) and used as received. All the solvents and reagents were of analytical grade, purchased commercially and used without further purification.

Infrared spectra of intermediate compounds and the polymers were recorded on a Nicolet Avatar 5700 FTIR (Thermo Electron Corporation). The UV-visible and fluorescence spectra were taken in GBC Cintra 101 UV-visible and Perkin Elmer LS55 fluorescence spectrophotometers, respectively. ¹H NMR spectra were obtained with AMX-400 MHz FT-NMR spectrometer using TMS per solvent signal as an internal reference. Elemental analyses were performed on a Flash EA1112 CHNS analyzer (Thermo Electron Corporation). The electrochemical studies of the polymers were carried out using an Autolab PGSTAT30 electrochemical analyzer. Cyclic voltammograms were recorded using a three-electrode cell system, with glassy carbon button as a working electrode, a platinum wire as a counterelectrode, and an Ag/AgCl electrode as the reference electrode. Molecular weights of the polymers were determined with a WATERS make gel permeation chromatograph (GPC) against polystyrene standards with tetrahydrofuran (THF) as an eluent. The thermal stability of the polymer was studied by a SII-EXSTAR6000-TG/DTA6300 thermogravimetric analyzer.

Z-SCAN MEASUREMENT

The z-scan technique developed by Sheik Bahae et al.¹⁷ is ideal for measuring the nonlinear optical refraction and absorption coefficients of materials. The “open aperture” z-scan is normally used for measuring 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 $z = 0$. 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. The beam will have maximum energy density at the

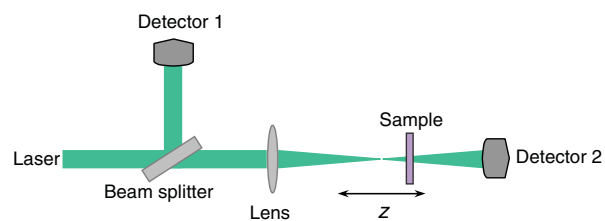


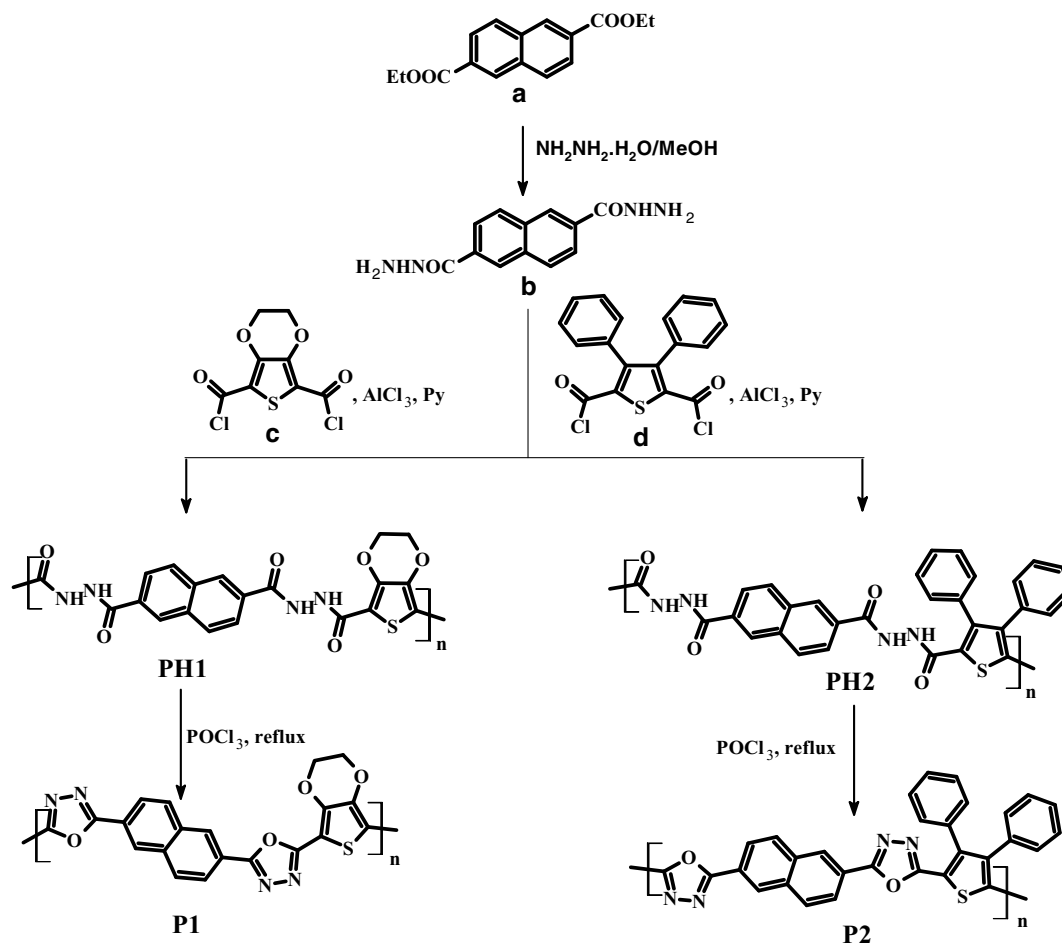
FIGURE 1. Schematic diagram of the open aperture z-scan experiment.

focus, which will symmetrically reduce toward either side of it, for the positive and negative values of z . Hence the sample sees different laser intensity at each z position. From the corresponding transmission values, the nonlinear absorption coefficient of the sample can be calculated.

The second harmonic output (532 nm) from a Q-switched Nd:YAG laser (Minilite, Continuum) was used for the measurements. The laser pulse width was 5 ns, and laser pulse energy of 50 μ J was used for the experiments. The sample was taken in a 1-mm path-length cuvette. The transmission of the sample at each point was measured by means of two pyroelectric energy probes (Rj7620, Laser Probe Inc.). One energy probe monitored the input energy, and the other recorded the transmitted energy through the sample. The pulses were fired in the “single shot” mode, allowing sufficient time between successive pulses to prevent accumulative thermal effects in the sample. Figure 1 shows the typical open aperture z-scan set up.

SYNTHESIS OF INTERMEDIATES AND POLYMERS

The target polymers were synthesized starting from naphthalene-2,6-carboxylate (**a**) following the reaction sequence as described in Scheme 1. The starting material **a** was converted into naphthalene-2,6-dicarbohydrazide (**b**) by reacting it with excess hydrazine hydrate in methanol. The compound **b** was then condensed with 3,4-ethylene-dioxythiophene-2,5-dicarboxylic acid chloride (**c**) and 3,4-diphenyl-2,5-dicarboxylic acid chloride (**d**) to get the precursor polyhydrazides **PH1** and **PH2**, respectively, in the presence of anhydrous aluminum chloride with a trace amount of pyridine as a catalyst. Finally, the polyhydrazide was conveniently converted into target polyoxadiazoles, **P1** and **P2**, by cyclization with phosphorous oxychloride (POCl₃). The detailed experimental protocols used for the synthesis of intermediates, monomer,



SCHEME 1. Synthesis of polymers P1 and P2.

precursor polyhydrazides, and target polymers are given below.

SYNTHESIS OF NAPHTHALENE-2,6-DICARBOHYDRAZIDE (B)

Naphthalene-2,6-carboxylate (**a**, 0.5 g) was added to a solution of 10-mL hydrazine monohydrate in 15 mL of methanol. The reaction mixture was refluxed for 3 h. Upon cooling the solution to room temperature, a white precipitate was obtained. The precipitate was filtered, washed with petroleum ether, dried under vacuum, and finally recrystallized from ethanol to get white solid. Yield: 80%, FTIR (KBr, cm^{-1}): 3177, 3316 ($>\text{NHNH}_2$), 1654 ($>\text{C}=\text{O}$). ^1H NMR (400 MHz, CDCl_3). δ (ppm): 9.82 (t, 2H, $>\text{N}-\text{H}$), 7.48 (m, 6H, aromatic), 7.42 (s, 4H, $-\text{NH}_2$). Anal. Calcd. for $(\text{C}_{12}\text{H}_{12}\text{N}_4\text{O}_2)$: C, 59.01%;

H, 4.95%; N, 22.94%. Found: C, 58.94%; H, 4.88%; N, 22.83%.

SYNTHESIS OF PRECURSOR POLYHYDRAZIDES PH1 AND PH2

A mixture of 1 equiv of naphthalene-2,6-dicarbohydrazide, 2 equiv of anhydrous aluminum chloride, and 0.1 mL of pyridine was dissolved in 15 mL of NMP. To this a clear solution of 1 equiv of corresponding diacid chloride in 10 mL of NMP was added slowly at room temperature with stirring, and stirring was continued for 5 h. Furthermore, it was heated at 80°C for 12 h with stirring. After cooling to room temperature, the reaction mixture was poured into ice-cold water and the precipitate separated was collected by filtration. It was washed with water followed by acetone, and finally dried in

vacuum to get the polyhydrazides, **PH1** and **PH2**, with yield 80% and 82%, respectively.

PH1: FTIR (KBr, cm^{-1}): 3326 ($>\text{N-H}$), 1680 ($>\text{C=O}$). Anal. Calcd. for ($\text{C}_{20}\text{H}_{14}\text{N}_4\text{O}_6\text{S}$): C, 54.79%; H, 3.22%, N, 12.78%, S, 7.31%. Found: C, 54.66%; H, 3.14%, N, 12.67%, S, 7.22%.

PH2: FTIR (KBr, cm^{-1}): 3332 ($>\text{N-H}$), 1710 ($>\text{C=O}$). Anal. Calcd. for ($\text{C}_{30}\text{H}_{20}\text{N}_4\text{O}_4\text{S}$): C, 67.66%, H, 3.79%, N, 10.52%, S, 6.02%. Found: C, 67.53%, H, 3.64%, N, 10.38%, S, 5.88%.

SYNTHESIS OF POLYMERS P1 AND P2

A mixture of polyhydrazide (**PH1/PH1**, 0.5 g) and 20 mL of phosphorusoxychloride (POCl_3) was heated at 80°C for 10 h with stirring. The reaction mixture was then cooled to room temperature and poured to excess of ice. The resulting precipitate was collected by filtration, washed with excess amount of water followed by acetone, and dried in a vacuum oven to get the polymers, **P1** and **P2**. Their spectral and elemental analysis data are given below.

P1: FTIR, (cm^{-1}): 2918–2850 (C–H), 1581–1519 ($-\text{C=N}-$), 1482, 1381 (aromatic), 1048 (C–O–C). ^1H NMR (400 MHz, CDCl_3) δ (ppm): 7.96–7.50 (m, 6H, naphthalene) 4.68 (s, 4H, $-\text{OCH}_2\text{CH}_2\text{O}-$) Anal. Calcd. for $\text{C}_{20}\text{H}_{10}\text{N}_4\text{O}_4\text{S}$: C, 59.70%; H, 2.50%; N, 13.92%, S, 7.97%. Found: C, 59.58%; H, 2.36%; N, 13.80%, S, 7.83%. Molecular weight (weight average, M_w) 4208 and (number average, M_n) 3568, polydispersity (PD) = 1.18.

P2: FTIR, (cm^{-1}): 2923–2855 (C–H), 1585–1520 ($-\text{C=N}-$), 1485–1388 (aromatic), 1055(C–O–C). ^1H NMR (400 MHz, CDCl_3) δ (ppm): 7.00–8.75 (m,

16H, phenyl and naphthalene). Anal. Calcd. for $\text{C}_{30}\text{H}_{16}\text{N}_4\text{O}_2\text{S}$: C, 72.57%; H, 3.25%, N, 11.28%; S, 6.46%. Found: C, 72.39%; H, 3.42%, N, 11.19%; S, 6.33%. Molecular weight (weight average, M_w) 5240 and (number average weight, M_n) 4200, PD = 1.25.

Results and Discussion

The newly synthesized monomer, precursor polyhydrazides, and the final polymers were characterized by spectral and elemental analyses. FTIR spectrum of naphthalene-2,6-dicarbohydrazide (**b**) showed (Fig. 2) absorption bands for hydrazide ($3177, 3316 \text{ cm}^{-1}$ for $>\text{NHNH}_2$) and carbonyl stretching at 1654 cm^{-1} . ^1H NMR spectrum of it displayed a singlet peak at $\delta 9.82 \text{ ppm}$, which corresponds to $>\text{N-H}$ protons and a set of multiple peaks at $\delta 7.48 \text{ ppm}$ that corresponds to six aromatic protons. Furthermore, the elemental analysis data are in agreement with its expected molecular formula (**b**).

The formation of a precursor polyhydrazide was evidenced by its FTIR spectral and elemental analyses. The FTIR spectrum of polyhydrazide **PH1** (Fig. 3) exhibited sharp peaks at 3326 and 1680 cm^{-1} accounting for $-\text{N-H}$ and $-\text{C=O}$ groups, respectively. Furthermore, the successful conversion of polyhydrazide **PH1** into polyoxadiazole **P1** was confirmed by its FTIR spectrum (Fig. 3). In its FTIR spectrum, disappearance of $-\text{C=O}$ and $-\text{N-H}$ stretching absorption bands, and the appearance of a sharp peak at around 1585 cm^{-1} was mainly due to the $-\text{C=N}$ group. This clearly indicates the

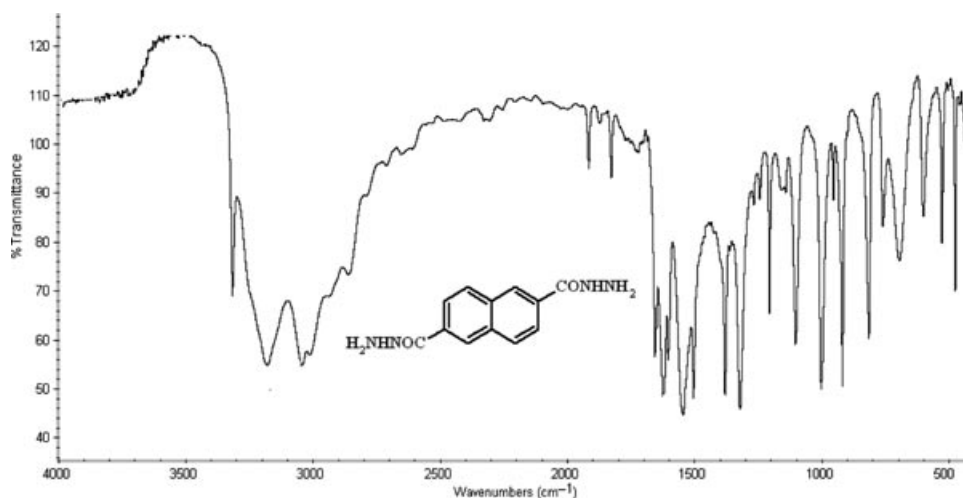


FIGURE 2. FTIR spectrum of naphthalene-2,6-dicarbohydrazide (**b**).

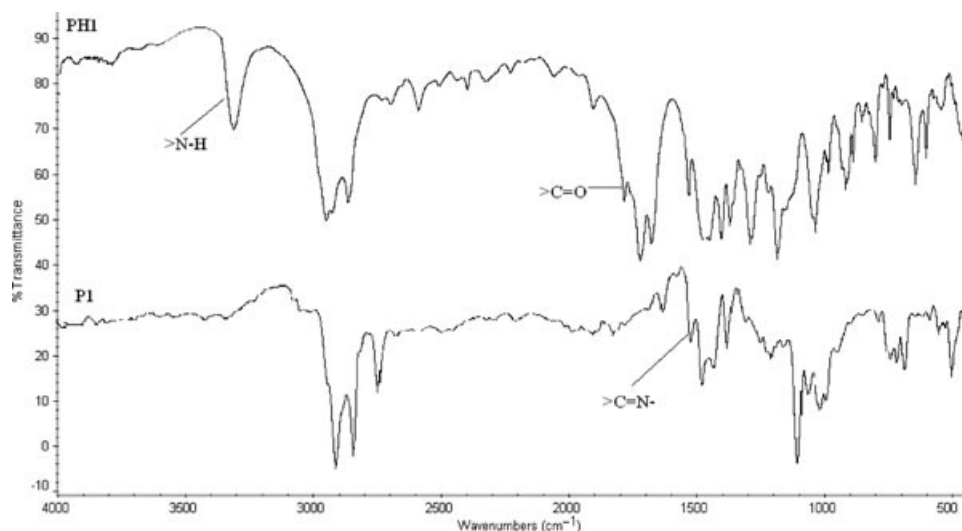


FIGURE 3. FTIR spectrum of polyhydrazide **PH1** and polymer **P1**.

cyclization of polyhydrazide **PH1** into polyoxadiazole **P1**.

The chemical structure of the **P1** was further confirmed by its ^1H NMR spectroscopy and elemental

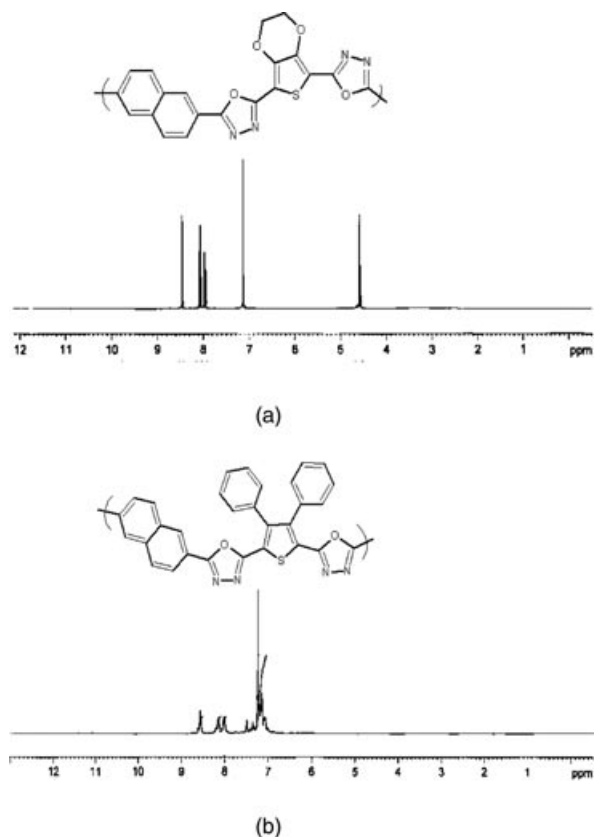


FIGURE 4. (a) ^1H NMR spectrum of the polymer **P1** and (b) ^1H NMR spectrum of the polymer **P2**.

analysis. The ^1H NMR spectra of the polymer **P1** (Fig. 4a) showed a multiplet at δ 7.96–7.50 ppm, due to the six protons of the naphthalene ring. Also, peaks corresponding to the four protons of the ethylene-dioxy ($-\text{OCH}_2\text{CH}_2\text{O}-$) group at 3 and 4-positions of the thiophene ring resonated as singlet at δ 4.68 ppm.

The structure of the polymer **P2** was confirmed by its ^1H NMR spectroscopy and elemental analysis. The ^1H NMR spectra of **P2** (Fig. 4b) showed multiplet peaks at δ 7.00–8.75 ppm due to the presence of 16 protons of naphthalene and phenyl rings. The results of elemental analysis of polymers were in agreement with its expected empirical formula. The THF soluble part of the polymer was taken for molecular weight analysis. The weight average (M_w) and number average (M_n) molecular weight of **P1** were found to be 4208 and 3568, respectively. Its PD was estimated to be 1.18. Low molecular weights of the polymers may be attributed to lower solubility of the polymer in THF. According to thermogravimetric analysis, the newly synthesized polymers were found to be thermally stable up to about 330°C. The thermogravimetric trace of the polymer **P1** is shown in Fig. 5.

REDOX STUDIES OF THE POLYMERS

Cyclic voltammetry was employed to determine redox potentials of new polymers and then to estimate the HOMO and LUMO, which is of importance to determine the band gap. The cyclic voltammogram of the polymers coated on a glassy carbon

TABLE I
Electrochemical Potentials, Energy Levels of the Polymers P1 and P2

Polymer	E_{Oxd}	E_{red}	E_{Oxd} (onset)	E_{red} (onset)	E_{HOMO} (eV)	E_{LUMO} (eV)	E_g (eV)
P1	1.25	-1.10	1.16	-0.82	-5.56	-3.58	1.98
P2	1.20	-1.15	1.12	-0.76	-5.52	-3.64	1.88

electrode was measured using AUTOLAB PGSTAT-30 electrochemical analyzer, using a Pt counter electrode and an Ag/AgCl reference electrode, immersed in the electrolyte [0.1M (*n*-Bu)₄NClO₄ in acetonitrile] at a scan rate of 25 mV/s. Electrochemical data of P1 and P2 are summarized in Table I.

While sweeping cathodically, the polymers P1 (Fig. 6a) and P2 (Fig. 6b) showed reduction peaks at -1.10 and -1.15 V, respectively. These reduction potentials are lower than those of 2-(4-*tert*-butyl phenyl)-1, and 3,4-oxadiazole, one of the most widely used electron-transporting materials. In the anodic sweep (Figs. 6a and 6b), polymers showed an oxidation peak at around 1.20 V, which is comparable with some donor-acceptor-type conjugated polymers containing oxadiazole moieties reported in the literature. The following equations reported in the literature^{18–20} were used for the calculation of HOMO and LUMO energy levels of our polymers. $E_{\text{HOMO}} = -[E_{\text{onset}}^{\text{oxd}} + 4.4 \text{ eV}]$ and $E_{\text{LUMO}} = -[E_{\text{onset}}^{\text{red}} - 4.4 \text{ eV}]$, where $E_{\text{onset}}^{\text{oxd}}$ and $E_{\text{onset}}^{\text{red}}$ are the onset potentials versus SCE for the oxidation and reduction of the material, respectively.

The HOMO energy level of the polymers P1 and P2 were estimated to be -5.56 and -5.52 eV, respec-

tively. The HOMO energy levels (-5.56 and -5.52 for P1 and P2, respectively) are comparable with CN-PPV and some reported polyoxadiazoles. The LUMO energy levels (-3.58 and -3.64 eV for the polymers P1 and P2, respectively) are lower than those of PPV and some conjugated polyoxadiazoles reported earlier.^{16,21} This can be attributed to the presence of electron-withdrawing 1,3,4-oxadiazole ring along with the additional conjugative

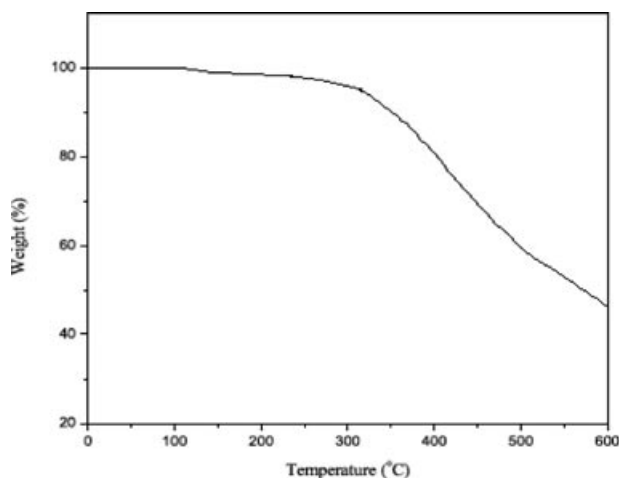
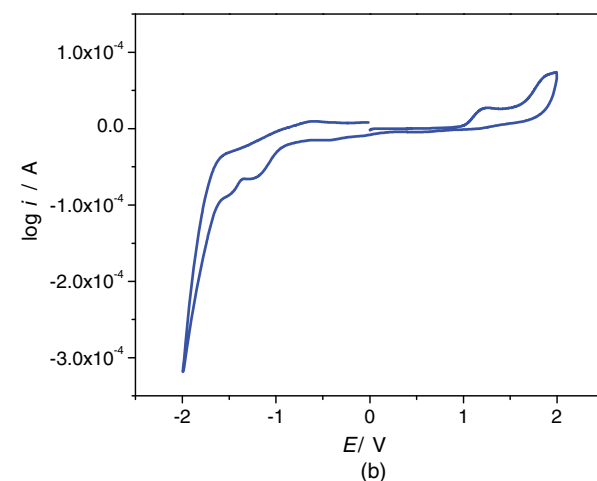
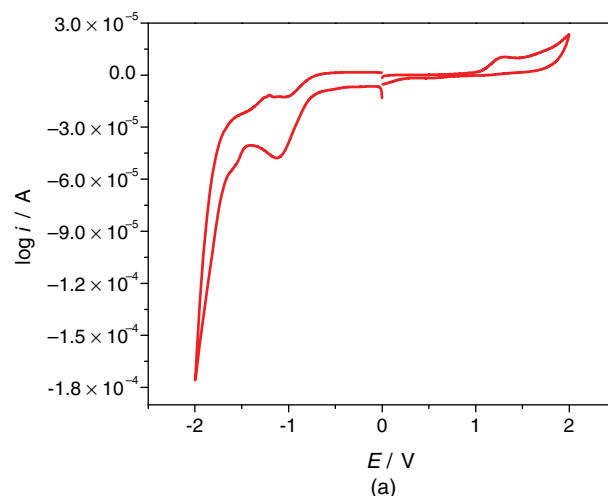
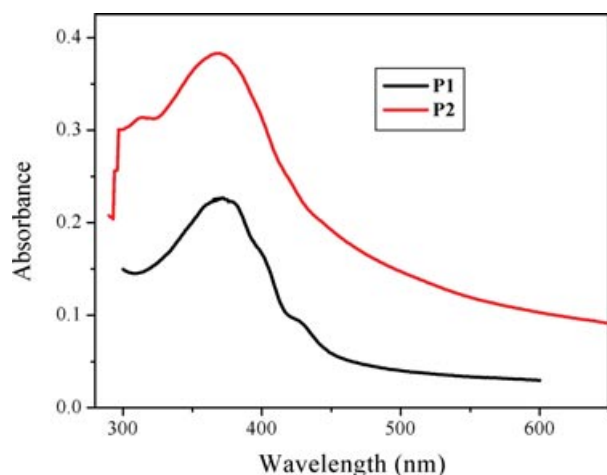
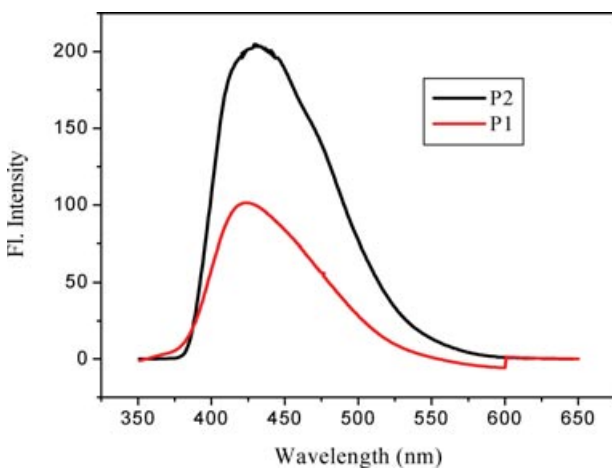
**FIGURE 5.** Thermogravimetric trace of the polymer P1.**FIGURE 6.** (a) Cyclic voltammogram for the polymer P1 and (b) cyclic voltammogram for the polymer P2.

TABLE II
Linear and Nonlinear Optical Parameters for the Polymers

Sample	Linear Optical Properties			Z-scan		
	Absorption λ_{\max}	Emission λ_{\max}	Optical Band Gap E_g (eV)	n_0^a	α^b (m^{-1})	I_s ($\times 10^{13} \text{Wm}^{-2}$)
P1	372	423	2.00	1.434	693.15	6.8
P2	374	428	2.00	1.430	673.34	1.4

^a n_0 Refractive index of polymer solution.^b α Linear absorption coefficient.

naphthalene spacers within the polymer backbone. From the onset potentials of oxidation and reduction process, the band gap of the polymers **P1** and **P2** was estimated to be 1.98 and 1.88 eV, respectively.

**FIGURE 7.** UV-vis absorption spectra of the polymers in solution.**FIGURE 8.** Fluorescence emission spectra of the polymers in solution.

LINEAR OPTICAL PROPERTIES

The UV-visible absorption and fluorescence spectra of the polymers were recorded in dilute DMF solution, and the spectral data are given in Table II. As shown in Fig. 7, the absorption maxima of the polymers in dilute DMF solutions are at 372 and 374 nm for **P1** and **P2**, respectively. The fluorescence emission spectra of these polymers in solution are shown in Fig. 8. The emissive maxima (excitation wavelength 370 nm) of the polymers in dilute DMF solution are at 423 and 428 nm for the polymers **P1** and **P2**, respectively. These results indicate that the polymers emit intense bluish-green light by the irradiation of UV light. The optical band gaps of the polymers were determined to be 2.00 eV for both the polymers. These results are in good agreement with the band gap obtained from the electrochemical method.

The newly synthesized polymers showed enhanced UV-vis and fluorescence maxima, and this can be attributed to the increased conjugation and planarity imparted by the naphthalene spacers. It was observed that the introduction of substitutions at 3,4-positions of the thiophene ring with ethylenedioxy (**P1**) and diphenyl (**P2**) moieties caused a significant change in their optical property when compared to unsubstituted polymers. However both of them showed almost same absorption and emission maxima. This clearly indicates that phenyl rings exhibit similar electronic effects on conjugation as the ethylenedioxy group acts on a polymer chain.

NONLINEAR OPTICAL PROPERTIES

From the absorption spectrum, it can be seen that the excitation wavelength of 532 nm is close to the long wavelength absorption edge. The sample solutions had transmission values close to 50% when taken in a 1-mm thick cuvette. The linear absorption coefficient for the polymers **P1** and **P2** are given in Table II. As seen from Figs. 9a and 9b, the samples

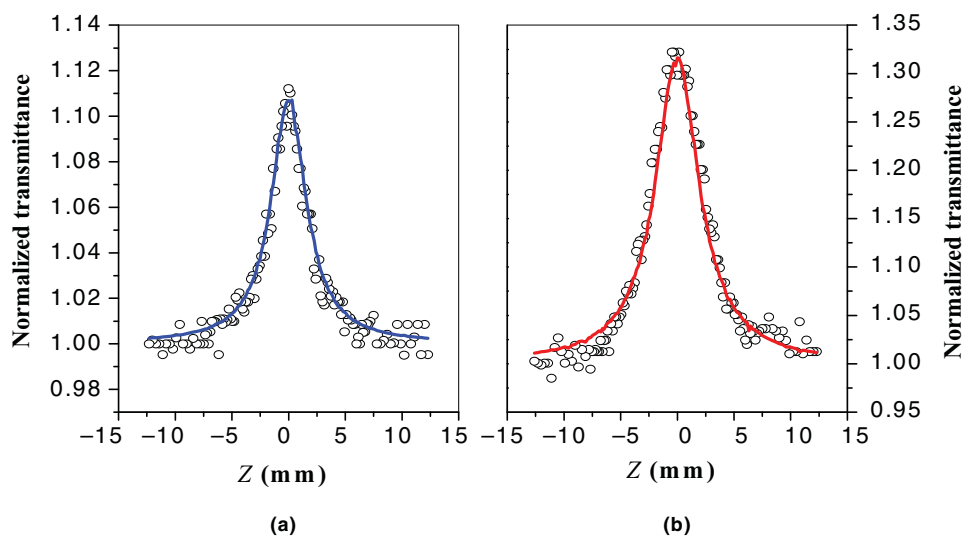


FIGURE 9. Open aperture z-scan curve for polymers P1 and P2.

show saturable absorption behavior when excited with 5-ns laser pulses at 532 nm. The z-scan curve can be fitted numerically to the saturation absorption equation. In this case, the nonlinear absorption coefficient²² can be represented as

$$\alpha_{\text{NL}} = \alpha_0 \left(\frac{1}{1 + (I_{\text{in}}/I_s)} \right) \quad (1)$$

where α_0 is the linear absorption coefficient, I_{in} is the incident intensity, and I_s is the saturation intensity (intensity at which the absorption becomes half of the linear absorption). The transmitted intensity I can now be calculated using the relation,

$$I = I_{\text{in}} e^{-\alpha_{\text{NL}}L} \quad (2)$$

where L is the length of the sample.

The obtained z-scan curve is fitted with numerically simulated results using Eqs. (1) and (2). The saturation intensity values obtained from the fits are presented in Table II.

Our open aperture z-scan profile shows a typical peak, symmetric about the focus, which is known to be the signature of saturable absorption. The peak appears at the focal point where the laser pulse has the strongest fluence. A similar type of saturable absorption in the near-field transmission curve was reported for inorganic materials.²³ Figures 9a and 9b show the open aperture z-scan curves for the polymers P1 and P2, respectively. The open circles denote experimental data points, and the solid line is a theoretical fit with the Eq. (1). As shown in Fig. 9, the normalized energy trans-

mittance displays an increased transmittance at the focus indicating saturable absorption.

In π -conjugated polymeric systems, electrons can move in large molecular orbitals which results from the linear superposition of the carbon p_z atomic orbitals. This extended conjugation leads to a very high optical nonlinearity, which generally increases with the conjugation length.²⁴ In polymers P1 and P2, the presence of electron-withdrawing 1,3,4-oxadiazole and electron-releasing 3,4-disubstituted thiophene units along the rigid polymer backbone renders the polymer chain a push-pull (donor- π -acceptor) electron system. Furthermore, the introduction of spacer naphthalene ring system contributes effectively in enhancing the conjugation length. As a result, an increased saturable NLO response was observed in our polymers. Thus, it can be concluded that our polymers are good saturable absorbers mainly due to their rigid backbone structure carrying donor-acceptor aromatic segments with extended conjugation. Evidently, saturable absorbers are important for many photonic applications, such as Q-switching and mode-locking of lasers, pulse shaping, optical switching, and so forth.²⁵ The fact that these polymers can be easily incorporated into thin films makes them better candidates for device applications.

Conclusions

In conclusion, we developed a method for the synthesis of new donor-acceptor-type conjugated

polythiophenes carrying oxadiazole and naphthalene moieties in the polymer backbone. The structures of newly synthesized intermediates and polymers (**P1** and **P2**) were confirmed by different spectroscopic techniques and elemental analysis. Their thermogravimetric and GPC studies reveal that they are thermally stable, and their PD is in the range of 1.18–1.25. The electrochemical band gaps of the polymers were found to be 1.98 and 1.88 eV, respectively, and their optical bands gaps were shown to be 2.00 eV. The polymers emit bluish-green fluorescence under the irradiation of UV light. Their NLO results indicate that the operating nonlinear mechanism observed with these polymers is saturable absorption. Here, the large saturable absorption of these polymers arises due to the strong delocalization of π -electrons along the polymer chain in addition to donor-acceptor-type of structural arrangement. Hence, the polymers investigated here are promising materials for their applications in photonic switching devices.

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