Synthesis and Nonlinear Optical Characterization of Copolymers Containing Alternating 3,4-Dialkoxythiophene and (1,3,4-Oxadiazolyl)benzene Units

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ABSTRACT: We report the synthesis and linear and third-order nonlinear optical (NLO) characterization of two novel copolymers containing alternating 3,4-dialkoxythiophene and 1,4-bis(1,3,4-oxadiazolyl)benzene units. The copolymers were synthesized with a precursor polyhydrazide route. Both copolymers exhibited fluorescence around 430 nm under the irradiation of UV light. The NLO measurements were made with the single-beam Z-scan technique with Nd:YAG nanosecond laser pulses at 532 nm. The nonlinear refractive index of the investigated copolymers was negative, and the magnitude was as high as 10^{-10} esu. The samples exhibited strong reverse saturation absorption and very good optical limiting properties at the wavelength used. The concentration dependence of third-order NLO parameters was studied. © 2007 Wiley Periodicals, Inc. J Appl Polym Sci 106: 3033–3039, 2007

Key words: conjugated polymers; optics; polycondensation; synthesis

INTRODUCTION

Polymers have been materials of interest for many researchers in the fields of photonics and optoelectronics in the past several years due to their large third-order nonlinear responses and related device applications.[1–3] A strong delocalization of π electrons along the polymeric chain is known to be the reason for their large third-order nonlinearity. These polymers offer good flexibility at both the molecular and bulk levels for the structural modifications that are necessary to optimize them for practical use.[4] Various conjugated polymers, such as polyacetylene, polydiacetylene, and poly(p-phenylene vinylene), have been studied extensively, and large values of third-order nonlinear optical susceptibility [$\chi^{(3)}$] have been measured.[4,5] However, the application of these materials may face problems in the areas processing or environmental stability; as a result, a number of other conjugated polymers have also been investigated for their third-order nonlinear optical (NLO) properties. Among these, polythiophenes are gaining considerable interest as materials for nonlinear optics because of their large third-order response, chemical stability, and processibility with suitable substituents.[6,7] Because the NLO response of these polymers is primarily determined by their molecular structure, one can employ molecular modeling and synthesis to design and prepare polymers with increased nonlinearity by introducing suitable substituents. In this report, we describe the synthesis of two copolymers containing alternating substituted thiophene and 1,4-bis(1,3,4-oxadiazolyl)benzene units and their third-order NLO characterizations. The third-order NLO measurements were performed with the single-beam Z-scan technique with Nd:YAG nanosecond laser pulses at 532 nm. The two copolymers possessed high values of the nonlinear refractive index (n_2) and $\chi^{(3)}$ and showed strong reverse saturation absorption. These copolymers demonstrated good optical limiting of nanosecond laser pulses. The concentration (C) dependence of NLO parameters is also reported.

EXPERIMENTAL

3,4-Dialkoxythiophene-2,5-carbonyldihydrazides (**1a** and **1b**) were synthesized from corresponding diethyl 3,4-dialkoxythiophene-2,5-dicarboxylates with an excess of hydrazine monohydrate in methanol.[8] We prepared terephthaloyl chloride (**2**) by refluxing terephthalic acid with thionyl chloride. IR spectra of the polymers were recorded on a Nicolet Avatar 330 Fourier transform infrared spectrometer (Thermo Electron Corp.,

Madison, WI). The ultraviolet–visible (UV–vis) spectra of the polymers were measured with a Varian CARY 500 spectrophotometer (Palo Alto, CA). Thermogravimetric analysis was carried out with a thermal analysis 2950 thermogravimetric analyzer (TA Instruments, New Castle, DE). ^{1}H-NMR spectra were obtained with an AMX 400-MHz Fourier transform nuclear magnetic resonance spectrometer with a tetramethylsilane/solvent signal (Aldrich Chemical Co., Milwaukee, WI) as an internal reference. Fluorescence spectra of the polymers were recorded with a PerkinElmer LS 50B luminescence spectrometer (Waltham, MA). Elemental analyses were performed on a Flash EA 1112 CHNS analyzer (Thermo Electron Corp.). The molecular weights of the polymers were determined with a Shimadzu gel permeation chromatograph (Kyoto, Japan) with tetrahydrofuran (THF) as an eluant against polystyrene standards.

General procedure for the synthesis of polyhydrazides 3a and 3b

To a mixture of 1 equiv of the appropriate dihydrazide (0.5 g of **1a** and 1 g of **1b**), 2 equiv of anhydrous aluminum chloride (0.46 g for **3a** and 0.52 g for **3b**), 0.1 mL of pyridine, 20 mL of *N*-methylpyrrolidone (NMP), and 1 equiv of **2** (0.35 g for **3a** and 0.4 g for **3b**) was added slowly at room temperature. The reaction mixture was stirred at room temperature for 5 h. The resultant yellow solution was heated at 80°C with stirring for 20 h. After it was cooled to room temperature, the reaction mixture was poured into water to produce a precipitate. The precipitate was collected by filtration, washed with water followed by acetone, and finally dried in an oven.

3a: Yield: 85%. IR (KBr, ν, cm^{-1}): 3348, 2944, 2879, 1692, 1637, 1492, 1452, 1282, 1096, 862, 724.

3b: Yield: 80%. IR (KBr, ν, cm^{-1}): 3350, 2938, 2876, 1693, 1638, 1498, 1455, 1285, 1047, 910, 864, 718.

General procedure for the synthesis of polyoxadiazoles P1 and P2

A mixture of polyhydrazide (0.5 g) and 20 mL of poly(phosphoric acid) was heated at 100°C with stirring for 4 h. The reaction mixture was then cooled to room temperature and poured into an excess of water. The resulting precipitate was collected by filtration and was washed with water followed by acetone and dried *in vacuo*.

P1: ^{1}H-NMR [400 MHz, dimethyl sulfoxide (DMSO)-d^6, δ, ppm)]: 8.01 (s, 4H, Ar—H), 4.13 (q, J = 6.9 Hz, 4H, —OCH₂), 1.33 (t, J = 6.6 Hz, 6H, —CH₃). IR (KBr, ν, cm^{-1}): 2938, 2876, 1693, 1539, 1426, 1286, 1170, 998, 730. Anal. Calcd for C₁₈H₁₄N₄O₄S: C, 56.54%; H, 3.66%; N, 14.66%; S, 8.38%. Found: C, 56.23%; H, 3.54%; N, 14.79%; S, 8.55%.

P2: ^{1}H-NMR (400 MHz, DMSO-d^6, δ, ppm): 8.03 (s, 4H, Ar—H), 4.1 (t, J = 6.8 Hz, 4H, —OCH₂), 1.8–0.92 [m, 38H, —(CH₂)₈—CH₃]. IR (KBr, ν, cm^{-1}): 2928, 2856, 1693, 1538, 1489, 1373, 1278, 1174, 1052, 1012, 854, 728. Anal. Calcd for C₃₄H₄₆N₄O₄S: C, 67.33%; H, 7.59%; N, 9.24%; S, 5.28%. Found: C, 67.54%; H, 7.45%; N, 9.45%; S, 5.36%.

Z-scan measurements

Z-scan is a simple and well-known technique based on the principle of self-focusing or self-defocusing.[9] It allows the simultaneous measurement of nonlinear absorption (NLA) and nonlinear refraction in a sample. A Gaussian beam is focused by a lens onto the sample, and the variation in the beam profile is observed at the far field as the sample is taken through the focus. Here the sample itself acts as a lens, and hence, it can be viewed as the placement of another lens in the path of the beam and a further change in the beam profile. Z-scan with no aperture (open aperture) is performed to determine the NLA, whereas Z-scan with an aperture (closed aperture) is performed to determine the nonlinear refraction in samples. A material with a negative n_2 gives a prefocal peak followed by a postfocal valley as a closed-aperture Z-scan signature. Similarly, a material with a positive n_2 gives a prefocal valley followed by a postfocal peak as the Z-scan signature. In the case of material with significant NLA, open-aperture Z-scan shows a suppressed peak and an enhanced valley signature. A detailed description of our experimental setup is given in ref. 10. The second harmonic output of a Q-switched Nd:YAG nanosecond laser was used as the source of light in our experiment. The output of the laser had a nearly Gaussian intensity (*I*) profile. The Z-scan data was obtained with a 50% (linear aperture transmittance (S) = 0.5) aperture and a pulse energy of 20 μJ, which corresponded to a peak irradiance of 4.44×10^8 W/cm^2. To avoid cumulative thermal effects, data were collected in single-shot mode.[11] Optical limiting was obtained when the sample was at focal plane by the variation of the input energy and the monitoring of the input and output energies simultaneously by two pyroelectric detectors connected to a Laser Probe Rj-7620 energy ratiometer (Laser Probe Inc., Utica, NY).

RESULTS AND DISCUSSION

Synthesis and initial characterization of the polymers

The synthetic routes of polymers **P1** and **P2** are shown in Scheme 1. Polyhydrazides (**3a** and **3b**) were prepared by the polycondensation reaction of **2** with the corresponding 3,4-dialkoxythiophene-2,5-carbonyldihydrazide in NMP in the presence of anhydrous aluminum chloride and pyridine. As observed
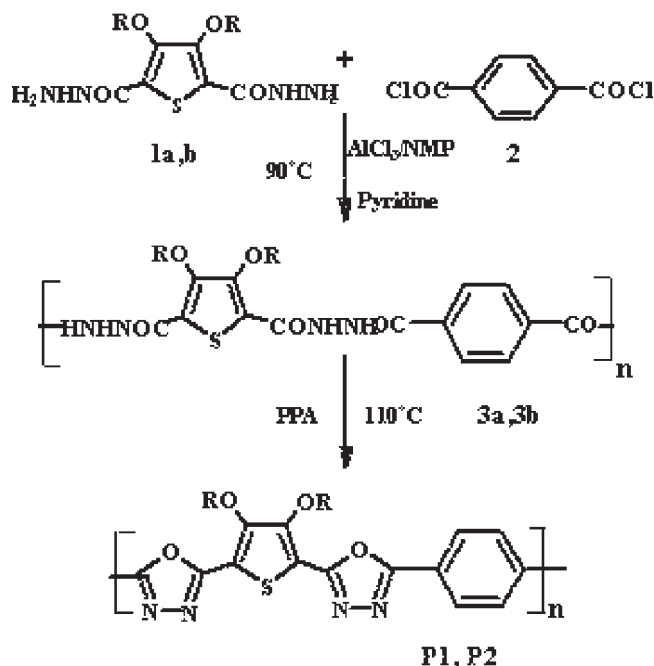
Scheme 1 Synthesis of the polymers.

for other polyhydrazides, these polyhydrazides were also insoluble in common organic solvents. The polyhydrazides were converted into the corresponding polyoxadiazoles via a cyclodehydration reaction with poly(phosphoric acid). The successful conversion of polyhydrazides into polyoxadiazoles was confirmed by Fourier transform infrared spectra. The stretching bands of C=O and N—H groups in the polyhydrazides around 1637 and 3350 cm^{-1}, respectively, disappeared, and a peak around 1538 cm^{-1} corresponding to imine in an oxadiazole ring was newly generated. Both the polymers were partially soluble in conven-
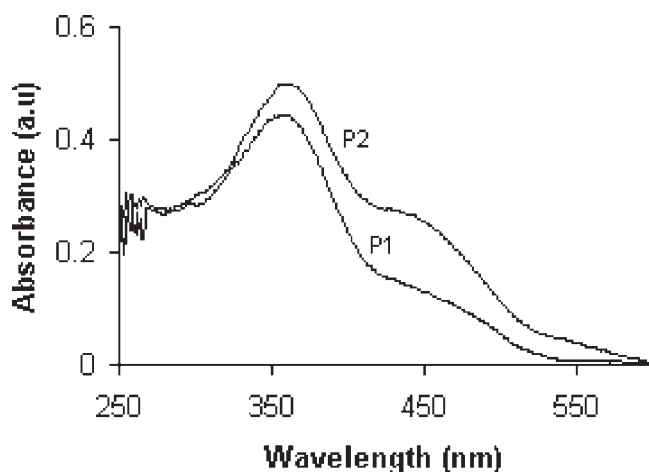
tional solvents, such as CHCl$_3$ and THF, but were readily soluble in DMF, DMSO, and NMP and in strong organic acids, such as trifluoroacetic acid. The chemical structures of the polymers were confirmed by CHNS analysis and ^{1}H-NMR spectroscopy. The elemental analysis results for the polymers were in agreement with their empirical formulas, as given in the Experimental part. In the ^{1}H-NMR spectra, both the polymers showed a singlet peak around $\delta = 8.01$ due to the protons on the benzene ring. In addition, peaks corresponding to the protons of the alkoxy groups at 3 and 4 positions of the thiophene ring were also observed. The number-average molecular weights (M_n's) of the THF soluble parts of the polymers were measured to be 3786 for **P1** (weight-average molecular weight/M_n = 1.48) and 4268 for **P2** (weight-average molecular weight/M_n = 1.43). Thermogravimetric analysis of the polymers was carried out under a nitrogen atmosphere at a heating rate of 5°C/min. The polymers were thermally stable up to about 300°C.

UV–vis absorption and fluorescence emission spectroscopy

The UV–vis absorption and fluorescence spectra of the polymers were measured in dilute DMF solutions (ca. 10^{-5}). As shown in Figure 1, the absorption maxima were 352 nm for **P1** and 360 nm for **P2**. These absorption maxima were comparable to those of some thiophene–1,3,4-oxadiazole copolymers.[12,13] Compared with **P1**, **P2** showed a redshift in the absorption spectra. This may have been due to an increase in the electron-donating properties of the alkoxy group with increasing chain length. As shown in Figure 2, polymers **P1** and **P2** showed emission maxima at 432 and 434 nm, respectively. The Stokes shift was determined to be
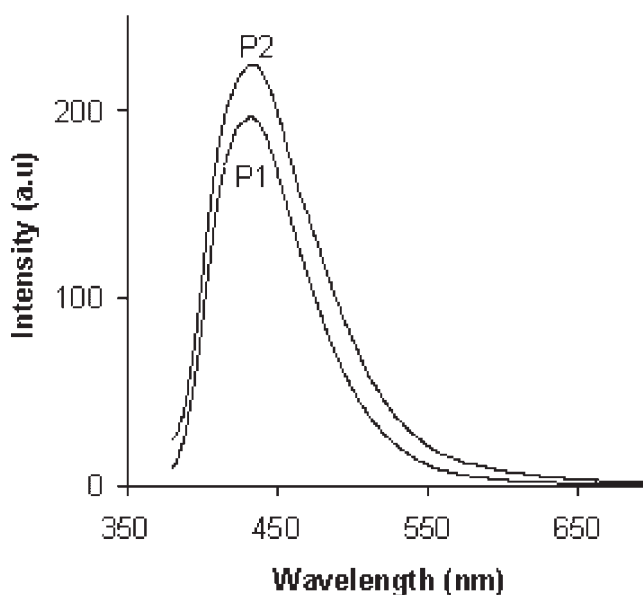

Figure 1 Linear absorption spectra of the polymers. The extinction coefficients were 44,000 and 50,000 L mol^{-1} cm^{-1} for **P1** and **P2,** respectively.

Figure 2 Fluorescence emission spectra of the polymers.

TABLE I
Determined Values of the Linear Optical and NLO Parameters

Polymer	n_0	α (cm^{-1})	n_2 ($\times 10^{-10}$ esu)	β (cm/GW)	Re $\chi^{(3)}$ ($\times 10^{-12}$ esu)	Im $\chi^{(3)}$ ($\times 10^{-12}$ esu)
P1	1.408	0.013	−0.884	14.52	−0.931	0.218
P2	1.402	0.0514	−1.012	19.96	−1.06	0.295

80 nm for **P1** and 78 nm for **P2**. These results indicate that the polymers could be used as light-emitting materials in devices.

Z-scan measurements

The linear absorption spectra of the copolymers showed that 532 nm was close to one of the absorption edges. Small absorption tails at 532 nm gave the linear absorption coefficients (α's) for the copolymers, which are tabulated in Table I. Figure 3 shows the normalized transmission (T) without aperture at 532 nm (open aperture) as a function of distance along the lens axis for **P2**. The transmission was symmetric about the focus [position of the sample (z) = 0], where it had a minimum transmission; thus, an I-dependent absorption effect was observed. T for the open-aperture condition is given by[14]

$$T(z) = 1 - \frac{q_0}{2\sqrt{2}}_{\text{for } |q_0| < 1} \tag{1}$$

where q_0 is a free factor defined as

$$q_0 = \frac{\beta I_0(1 - \exp^{-\alpha L})}{(1 + z^2/z_0^2)\alpha}$$

where L is the length of the sample, I_0 is the intensity of the laser beam at the focus, and z_0 is the Rayleigh range of the lens. A fit of eq. (1) to the open-aperture data yielded a value of NLA of $\beta = 1.996 \times 10^{-10}$ m/W for **P2**. The excited-state absorption cross-section (σ_{ex}) was measured from the normalized open-aperture Z-scan data.[14] We assumed that the molecular energy levels could be reduced to a three-level system to calculate σ_{ex}. Molecules are optically excited from
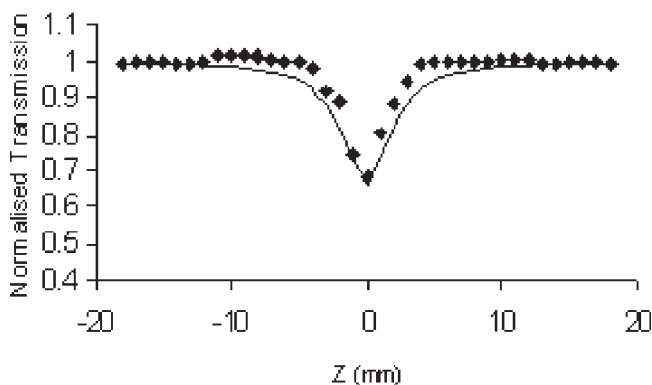
the ground state to the singlet-excited state, and from this state, they relax either to the ground state or the triplet state, when excited-state absorption can occur from the triplet to the higher triplet excited state.

The change in I of the beam as it passes through the material is given by

$$dI/dz = \alpha I - \sigma_{\text{ex}}N(t)I$$

where I is the intensity, N is the number of molecules in the excited state, and t is time. The excited-state density of molecules appears as a result of a NLA process whose I dependence can be obtained from

$$dn/dz = \sigma_{\text{ex}}I/h\nu$$

where n is the number of molecules in the excited state, h is planck's constant, and ν is the frequency of the laser. When the previous two equations are combined and one solves for the fluence of the laser (F_0) and integrates over the spatial extent of the beam, the T for open aperture is given as

$$T = \ln\left(1 + \frac{q_0}{1+x^2}\right) \Big/ \frac{q_0}{1+x^2} \tag{2}$$

where

$$q_0 = \sigma_{\text{ex}}F_0 L_{\text{eff}}/2h\nu$$

where L_{eff} is the effective length of sample.

$$L_{\text{eff}} = (1 - \exp^{-\alpha L})/\alpha$$

Figure 3 Open-aperture Z-scan curve for **P2**. The solid line was fitted to the data from eq. (1) with $\beta = 19.96$ cm/GW.
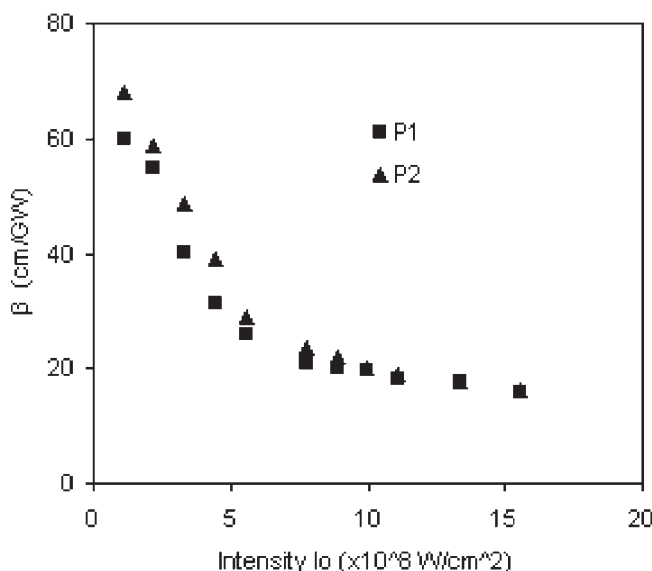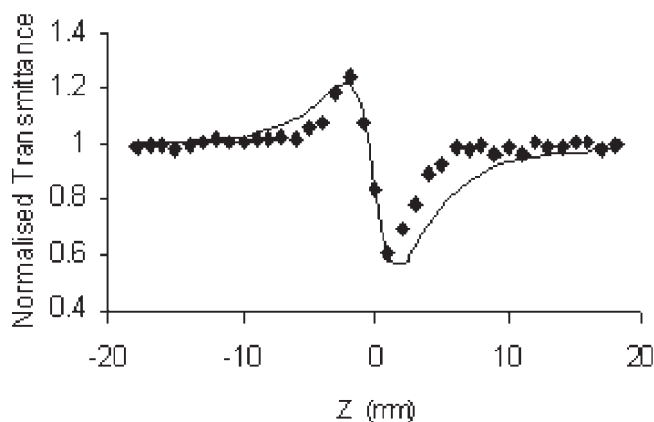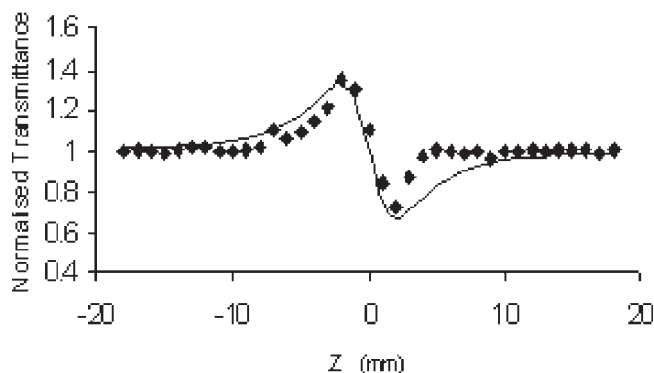

Figure 4 β versus I_0.

Figure 5 Closed-aperture Z-scan curve for **P2**. The solid line was fitted with $\Delta\phi_0 = 1.6$.

A fit of eq. (2) to the open-aperture data at 532 nm with q_0 yielded a value of σ_{ex} of 2.805×10^{-17} cm² for copolymer **P2**. The ground-state absorption cross-section (σ_g) can be calculated from

$$\alpha = \sigma_g N_a C$$

where N_a is Avogadro's number and C is the concentration (mol/cm³). σ_g was calculated to be 8.534×10^{-18} cm². The value of σ_{ex} was larger than the value of σ_g, which was in agreement with the condition for observing reverse saturable absorption.[14,15] Reverse saturable absorption generally arises in a molecular system when σ_{ex} is larger than σ_g. Figure 4 shows a plot of β versus I_0 for copolymers **P1** and **P2** in DMF. Generally, NLA can be caused by free carrier absorption, saturated absorption, direct multiphoton absorption, or excited-state absorption. If the mechanism belongs to the simple two-photon absorption, β should be a constant that is independent of the on-axis irradiance I_0.[16] However, the graph in Figure 4 shows that β decreased with increasing I_0. The fall-off of β with increasing I_0 was a consequence of the reverse satura-

tion absorption.[15] A small linear absorption at 532 nm and the measured σ_{ex} values indicated that there was a contribution from the excited-state absorption to the observed NLA. Therefore, we attributed this observed NLA to a reverse saturation absorption.

Figure 5 shows T for the closed-aperture Z-scan for **P2**. The pure nonlinear refraction curve, shown in Figure 6, was obtained by the division of the closed-aperture data by the open-aperture data. The Z-scan signature showed a large negative nonlinearity (self-defocusing) for both polymers. The experimental data was fitted with the following equation as described by Bahae et al.[9] For the closed-aperture condition, T is given by

$$T(z) = 1 - \frac{4\Delta\phi_0 x}{(1+x^2)(9+x^2)} \tag{3}$$

where $\Delta\phi_0$ is the phase change and is given by

$$\Delta\phi_0 = \Delta T_{p-v}/[0.406(1-S)^{0.25}]$$

for $|\Delta\phi_0| \leq \pi$. ΔT_{p-v} is the difference between the peak and valley of the normalized transmission. The real part of the third-order nonlinear susceptibility [Re $\chi^{(3)}$] is related to n_2 and γ (m²/W) through

$$\text{Re } \chi^{(3)} = 2n_0^2 c\varepsilon_0\gamma$$
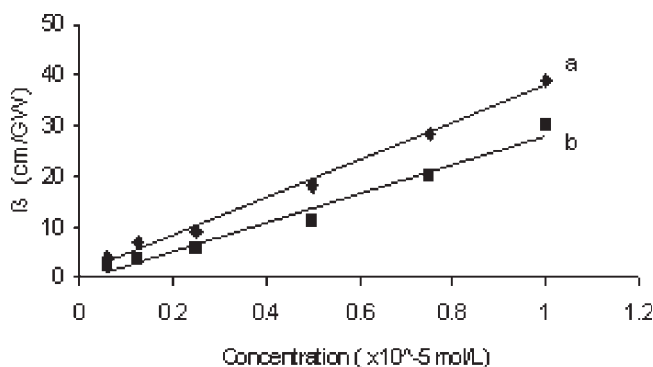
where γ is nonlinear refractive index expressed in SI units, i.e. in m²/W, n_0^2 is linear refractive index, and c is the velocity of light. The imaginary part of the third-order nonlinear susceptibility [Im $\chi^{(3)}$] is related to the NLA through

$$\text{Im } \chi^{(3)} = n_0^2 c\varepsilon_0\lambda\beta/2\pi$$

where ε_0 is the permittivity of free space, and λ is laser wavelength. n_2 is related to γ by

$$n_2(\text{esu}) = (cn_0/40\pi) \times \gamma(\text{m}^2/\text{W})^9$$

The value of n_2 was on the order of 10^{-10} esu for both copolymers, which was nearly two orders larger than the n_2 values reported for thiophene oligomers by Hein et al.[17] The obtained $\chi^{(3)}$ values were comparable
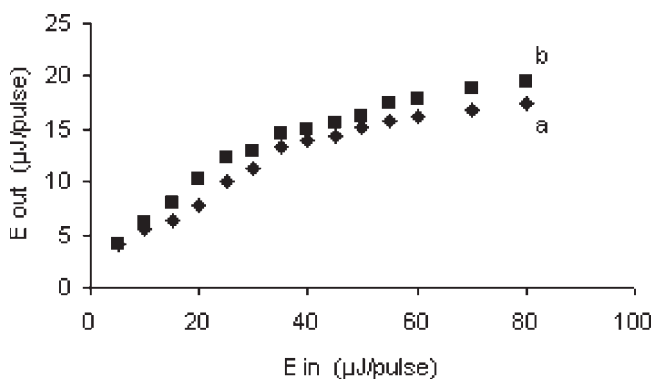

Figure 6 Pure nonlinear refraction curve obtained through the division method for **P2**. The solid line was fitted to the data from eq. (3) with $\Delta\phi_0 = 1.6$.

Figure 7 C dependence of β of **P1** and **P2.**

with that obtained for poly(3-dodecyloxymethylthiophene) by Sasabe et al.,[18] which was 5×10^{-12} esu. The values of n_2 and $\chi^{(3)}$ are given in Table I.
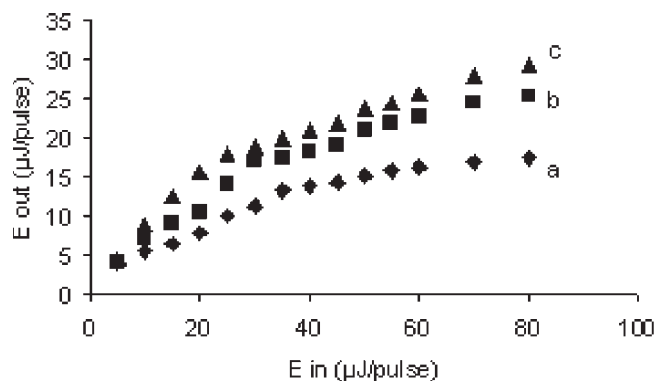
C dependencies of NLO properties can be analyzed to extract information on the NLO properties of the solute. *C* of the solutes in solution was varied, and Z-scans were repeated on solutions at each *C* to study the variation of nonlinear response. Figure 7 shows the dependence of β on *C* of **P1** and **P2** in solution. β varied almost linearly with sample *C*. The NLA and the nonlinear refraction decreased as *C* in the solution decreased from 1×10^{-5} to 2.5×10^{-6} mol/L. Thus, the observed decrease in the nonlinear response was directly related to *C* of the samples.

On the basis of strong reverse saturation absorption, good optical limiting properties could be expected for **P1** and **P2**. Optical limiters have been used in a variety of circumstances where decreasing transmission with increasing excitation is desirable. However, one of the most important applications is eye and sensor protection in optical systems.[15] Figure 8 demonstrates the optical limiting behavior of **P1** and **P2**. The best limiting behavior was observed with **P2**, which exhibited the strongest NLA. For incident energies less than 20 μJ/pulse, the output linearly increased with the input. However, for energies more than 20 μJ/pulse, an optical limiting of pulses was observed. The optical limiting behavior of **P2** at different *C*s is shown in Figure 9. The limiting threshold increased with decreasing *C* of the sample in DMF solution. Although both NLA and scattering could have contributed to optical limiting, we did not observe any significant scattering from the samples during our experiment within the energy limit used.

The copolymers contained alternating electron-donating (thiophene) and electron-withdrawing (oxadiazole) groups in their chain. OR refers to the alkoxy group. The lengths of the alkoxy groups at the 3,4 positions of the thiophene rings played an important role in the third-order nonlinear response of the copolymers. Copolymer **P2** showed a higher nonlin-

Figure 9 Optical limiting behavior of **P2** at *C*s of (a) 1×10^{-5}, (b) 0.5×10^{-5}, and (c) 0.25×10^{-5} mol/L. E in is input intensity and E out is output energy.

ear response than **P1**. This could have been due to the higher electron-donating ability of the decyloxy groups compared to ethyloxy groups. Therefore, we attributed the enhancement in third-order nonlinear response to the increased π-electron delocalization in the copolymer.

CONCLUSIONS

Synthesis of two novel copolymers containing alternating substituted thiophene and (1,3,4-oxadiazolyl)benzene units has been reported. Both polymers showed blue fluorescence under the irradiation of UV light. The third-order NLO measurements made with the single-beam Z-scan technique showed that copolymers possessed high $\chi^{(3)}$ values that were comparable with those obtained for poly(3-dodecyloxymethylthiophene) and poly(*p*-phenylenevinylene) copolymers. The dependence of NLO parameters on the length of the alkoxy substituents present in the copolymers indicated the electronic origin of nonlinearity. Both copolymers showed strong reverse saturation absorption and good optical limiting properties at 532 nm and, hence, may be used in optical limiting applications.

Figure 8 Optical limiting behavior of (a) **P2** and (b) **P1**. E in is input intensity and E out is output energy.

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