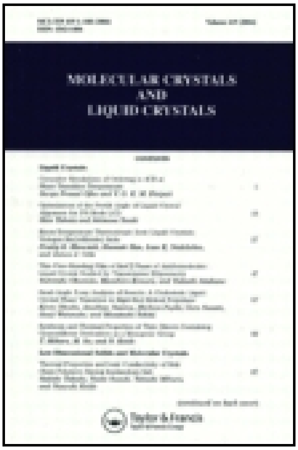

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Nonlinear Optical Properties of a Novel Polythiophene Derivative Determined by Third Harmonic Generation, Z-scan and Degenerate Four-Wave Mixing

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Nonlinear Optical Properties of a Novel Polythiophene Derivative Determined by Third Harmonic Generation, Z-scan and Degenerate Four-Wave Mixing.

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The linear and third order nonlinear optical properties of a polythiophene derivative incorporating 5,6-dialkoxy-thieno[3,4-b]pyrazine units were investigated. This low band gap material has a large oscillator strength, weak photoluminescence and strong enhancement of the Raman bands. We surmise that the long conjugation length of the polymer backbone, as well as the effect of the substituents on the π-electrons, give rise to a large value of the third order nonlinear susceptibility, $\chi^{(3)}$. Measurements by Z-scan and third harmonic generation (THG) corroborate earlier results from degenerate four wave mixing (DFWM) experiments. The $\chi^{(3)}$ values from Z-scan with 20 ps pulses were over 10^{-7} esu near the lowest energy absorption band.

Keywords: nonlinear optics; conjugated polymers; polythiophene

INTRODUCTION

Since the discovery of large third order nonlinear optical (NLO) susceptibilities in materials such as polydiacetylene (PDA) and polyacetylene (PA)[1,2], a great deal of experimental and theoretical work has been done on conjugated polymers for NLO.[3] The π-electrons of the polymer main chain plays an important role in giving large NLO properties and fast response times, as well as other affecting other characteristics such as linear absorption and chemical stability. While the large, fast nonlinearities in these materials are interesting for all-optical switching applications, basic problems have persisted in further increasing the $\chi^{(3)}$ values as well as decreasing the linear absorption coefficients α, with values of the figure of merit (FOM), $\chi^{(3)}/\alpha$, still one to several orders of magnitude smaller than that needed for practicable device fabrication. Furthermore, polymers such as PA and PDA may have other drawbacks, such as poor processability or lack of environmental stability.

In recent years, a number of modified conjugated polymers have been developed as third order NLO materials[3] as well as for various other applications.[4-6] For several years we have been investigating[7-10] novel polythiophene (PT) derivatives produced by the method of Stille coupling.[11] This research has been carried out in the framework of the MITI- sponsored project "Nonlinear Photonics Materials", so we have been primarily concerned with improving the third order NLO properties of these polymers. In addition, we have tried to develop models of the structure/property relation regarding the effects of substitution and polymer structure on the optical properties. For copolymers incorporating unsubstituted thiophene or bithiophene "spacers"

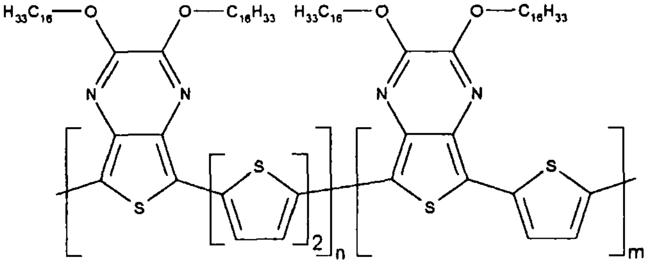

FIGURE 1 Polythiophene derivative random copolymer (n:m = 80:20)

and 5,6-dialkoxy-thieno[3,4-b]pyrazines (Fig. 1), good values have been obtained[10] for the third order NLO susceptibility, $\chi^{(3)}$. In this report, after a brief review of the synthetic method, we will give a detailed picture of the optical properties of this material. THG and Z-scan results will be discussed, incorporating information from absorption, photoluminescence and Raman spectra as well as earlier measurements of $|\chi^{(3)}|$ by DFWM.

SYNTHESIS

The method of Stille coupling as applied to polythiophene derivatives, schematically represented in Fig. 2, allows one to obtain polymers with minimal structural defects, doping or overoxidation. In addition, the method allows the use of a much wider variety of functional groups than in standard PT synthesis. Finally, the method has the advantage of enabling the synthesis of polymers with alternation of rings with different substitution patterns (substituted and unsubstituted at positions 3 and 4) or even copolymers with two different thiophene units. While Stille coupling is being used for producing other types of polymer heterocycles as well as thiophene oligomers,[12,13] this is the first application we are aware of for the synthesis of PTs using this reaction.

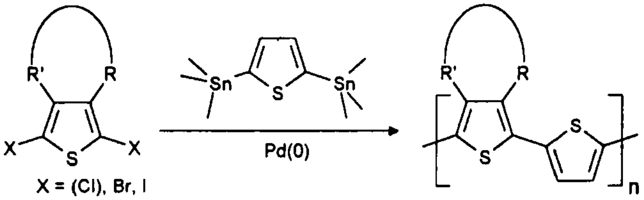

FIGURE 2 Schematic diagram of the Stille reaction.

One of the most interesting groups of PT derivatives for NLO was found to be that incorporating thieno[3,4-b]pyrazine. Both the substituents on the pyrazine ring as well as the alternation pattern of substituted and unsubstituted thiophene units have fundamental effects on the electronic and optical properties of the polymers. Related low band gap PTs incorporating these pyrazine blocks have been synthesized[14] and predicted to have quinoidal ground state conformations.[15]

The details of the synthesis may be found elsewhere.[8] By a copolymerization of the 2,3-dialkoxy-5,7-dihalothieno[3,4-b]pyrazine with 2,5-bis(trimethyltin)thiophene (20%) and 2,5-bis(trimethyltin)-2,2'-bithiophene (80%) the material which we will refer to as PTP (Fig. 1) was synthesized. PTP1 was synthesized using Br-coupling, while PTP2 was synthesized with I-coupling. Using a casting method, thin films were prepared with relatively good optical quality. The linear and nonlinear optical properties of film samples left in air at room temperature were measured several times over a period of several months to one year after fabrication. Only negligible changes were observed, suggesting good environmental stability.

EXPERIMENTAL

Raman spectra were recorded using a Fourier-Transform spectrometer Bruker RFA 106 equipped with a cw Nd-YAG laser (1064 nm) integrating a sample area of 10^{-2} mm^2. In order to investigate the chemical homogeneity of the thin films on a μm scale a Raman microscope (Dilor Labram) was used. Absorption spectra were measured with a visible--near-infrared (VIS-NIR) grating spectrometer (Instruments Systems), while the film thickness and the surface roughness were determined by an alpha stepper (Tencor 200).

THG measurements were done using the output of an β-Barium-Borate based optical parametric oscillator pumped by the frequency-tripled output (355 nm) of a Nd:YAG laser. Pulses in the wavelength range 1200 ~

2100 nm with 2~4 ns duration and energies up to 15 mJ/pulse could be produced. The Maker fringe technique was used with standard analysis of the output[16] and a value of $\chi^{(3)} = 0.95\times10^{-14}$ esu for the quartz reference.[17] The data were corrected for absorption at the third harmonic wavelength.

The Z-scan apparatus was based on an optical parametric generator/amplifier (OPG/A) (EKSPLA model PG401VIR) pumped by the third harmonic (λ=355 nm) of a Nd:YAG (EKSPLA model PL2143A) laser with 30 ps pulse width and pulse energies around 10 mJ. The output of the OPG/A can be tuned in the wavelength ranges from 420 nm to 680 nm (signal) and from 740 nm to 1800 nm (idler). The pulse width was found to be 20 ps from self-diffraction measurements on CS_2 and ZnSe.

The beam from the OPG/A was spatially filtered and apertured to get beam with an approximately Gaussian profile and focused to a spot size of about 30 μm. After passing through the sample, the beam was split and both the total transmission and the transmission through an aperture were measured. The nonlinear refractive index, n_2, and nonlinear absorption coefficient, α_2 were determined from the ratio of the closed to open aperture signals and open aperture signal alone, respectively, using the expressions given in the literature.[18] Both signals could be consistently fit as long as there was no saturation, which manifested itself as a broadening of the absorption change vs. sample position as well as intensity dependent values of n_2 and α_2. In the case of saturation, a more complex analysis is required.[19] We measured at several pulse energies to determine the effects from saturation, the values of the nonlinearities determined at the lowest pumping energy are given in cases where saturation was evident. The values of the real and imaginary part of the third order susceptibility were calculated from n_2 and α_2 using a value of 1.7 for the refractive index of the polymer.

DFWM-measurements were performed in the forward wave geometry using ~100 femtosecond pulses from an optical parametric amplifier pumped by a Ti:sapphire laser, or with pulses directly from the laser itself. In this way, the nonlinearities at wavelengths from 500 nm to 700 nm (OPA) and from 750 nm to 910 nm (Ti:sapphire laser) could be determined. More details of the experimental arrangement and data analysis are given elsewhere.[10]

RESULTS AND DISCUSSION

The linear absorption and photoluminescence (PL) spectra are shown in Fig. 3. The absorption peaks at around 1.8 eV (680 nm) for both PTP1 and 2, with the I-coupled material (PTP2) having a slightly lower band gap and higher absorption coefficient. The PL quantum yield is very low, on the order of $<10^{-5}$. It has been proposed that the weakness of PL in conjugated polymers may be due to the lowest energy state of the polymer being the two

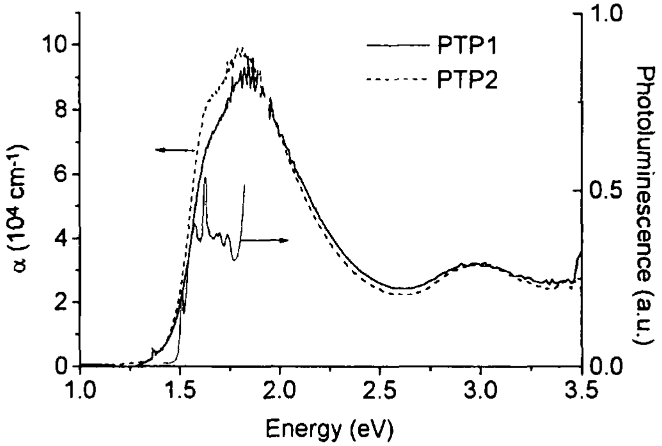

FIGURE 3 Absorption and PL spectra of polythiophene derivatives.

photon-allowed $2A_g$ rather than the $1B_u$.[20] From the figure, one can observe some vibronic progression, as well as very little Stokes shift (independent of the excitation wavelength), indicating that the lowest dipole allowed excitation is reached via a 0-0 transition. This contrasts with the case of alkyl-substituted PTs[21], as well as a number of other conjugated polymers, and suggests that the conformational changes in the excited state are minimal. Stokes shifts in various PTs have been attributed to relaxation of torsional strain in the excited state[21]. The predicted planar ground state of similar polymers[15] leads us to believe that a planar conformation of our polymers leads to little torsional strain in the ground state.

The Raman spectrum is dominated by the C=C stretching mode line at 1420 cm^{-1} and the C-C line at about 1055 cm^{-1}. The strengths of these two lines relative to lines due to the vibrational modes of the substituents were large compared to similar substituted PTs. This is due to the large oscillator strength of the transition seen in the linear absorption spectrum as well as strong electron-phonon coupling. Large Raman cross sections have been predicted to give a large contribution to the third order optical nonlinearity of the nuclear relaxation.[22]

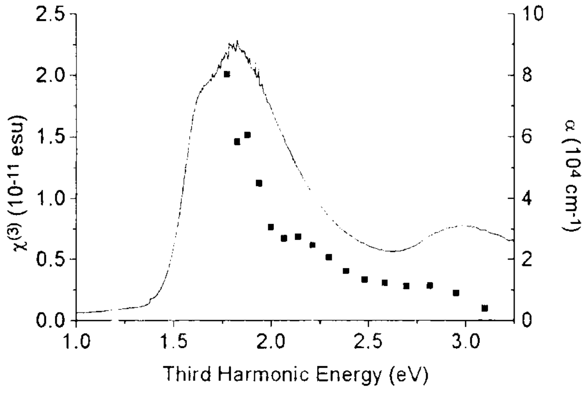

FIGURE 4 $\chi^{(3)}$ values from THG (PTP2).

The THG measurement results are displayed in Figure 4. The values measured for $\chi^{(3)}(-3\omega;\omega,\omega,\omega)$ follow the linear absorption, showing the strong effect of resonance enhancement. The value of $\chi^{(3)}(-3\omega;\omega,\omega,\omega)$ seems to peak at the low energy side of the absorption band, although without data at longer wavelengths this is difficult to confirm.

The Z-scan results from sample PTP1 are shown in Fig. 5. The peak $|\chi^{(3)}|$ values (at E=1.59 eV; λ=780 nm) were on the order of 1.3×10^{-7} esu. Both the real and imaginary parts of $\chi^{(3)}$ have pronounced peaks on the low energy side of the resonance. The nonlinear absorption shows a clear change from saturable to induced absorption at around 1.51 eV (820 nm).

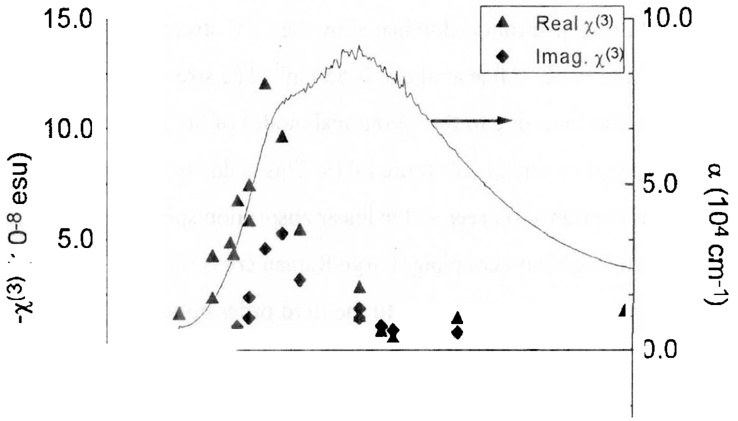

FIGURE 5 Real and imaginary parts of $\chi^{(3)}$ for PTP1

From the DFWM experiment, the magnitude and the relaxation behavior of the $\chi^{(3)}$ nonlinearity were determined. Resonant DFWM curves are shown in Fig. 6 for the sample PTP1 at a number of wavelengths. Both polymers showed a similar ultrafast relaxation being characterized by two time constants of 200 fs and about 1.5 ps. As seen in Fig. 6, changes in the decay times with wavelength across the absorption band were not observed. The

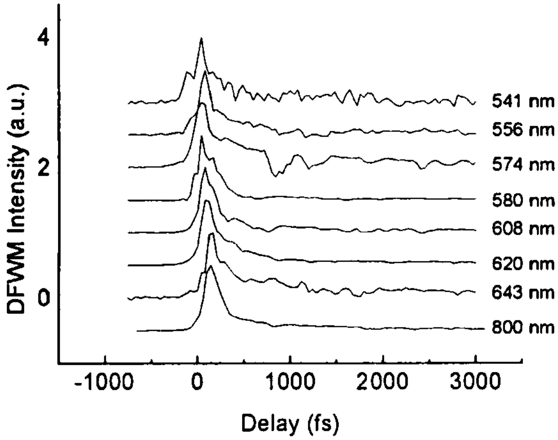

FIGURE 6 DFWM signals vs. λ for sample PTP1.

wavelength dispersion of the $\chi^{(3)}$ values of PTP2 are shown in Fig. 7, and are nearly an order of magnitude lower than those measured in Z-scan. The pulse duration in the Z-scan measurement (20 ps), though, was longer than the relaxation time of the nonlinearity, while it was shorter in the DFWM measurement. The Z-scan results are then comparable to the continuous wave $\chi^{(3)}$ measured with a pulse width longer than the characteristic decay time. The nonlinearity measured in an experiment with a

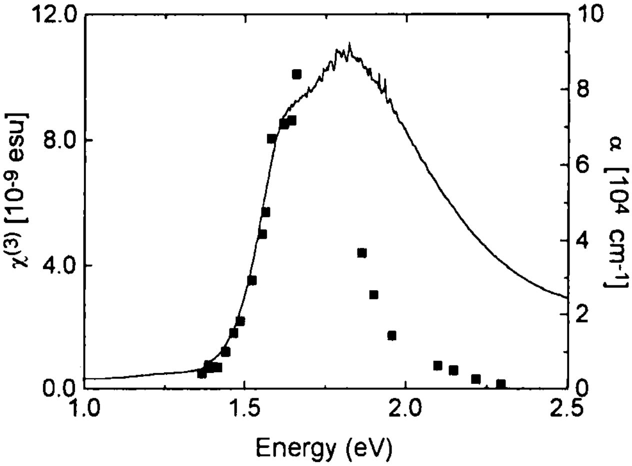

FIGURE 7 $\chi^{(3)}$ (DFWM) vs. wavelength (PTP2).

shorter pulse width will be reduced by a factor on the order of T_1/t_0, where T_1 is the relaxation time and t_0 is the pulse width. Using $T_1 \sim 1$ ps and $t_0 \sim 100$ fs, we get a scaling factor of 10, which agrees roughly with the results.

As seen in Figure 7, $\chi^{(3)}$ scales roughly with the absorption coefficient at energies below the resonance, while above it the FOM, $\chi^{(3)}/\alpha$, drops off considerably. In this region we find a power-law relation of $\chi^{(3)}$ to α with exponent of about 3.3. An approximately linear scaling between $\chi^{(3)}$ and α below the band gap has been seen in other conjugated polymers[23] and predicted theoretically.[24] However, the theoretical prediction for the scaling above resonance is for a power-law with exponent of only 1.7. The Z-scan data are also show a similar dispersion, although the off-resonant value of the FOM is larger.

The identical time decay above and below resonance suggests that the physical processes are the same. One possible origin of this effect may be the distribution of conjugation lengths. The shape of this distribution is a complex function of polymerization grade, local steric hindrance of chains leading to imperfect π-electron overlap and local monomer sequence, etc., and may affect the linear and nonlinear optical properties differently. The effect of electron-phonon coupling is also expected to play a significant role.

CONCLUSIONS

Evaluation of the NLO properties of a novel polythiophene derivative was done by wavelength dispersive third harmonic generation, Z-scan and degenerate four wave mixing. Maximum values of $|\chi^{(3)}|$ measured by Z-scan were greater than 10^{-7} esu on resonance, with strong saturation of the nonlinear absorption near the resonance crossing over to induced absorption near 1.52 eV (815 nm), just at the absorption edge. The dispersion of the $|\chi^{(3)}|$ values from the DFWM measurement showed different power-law scaling with α above and below the resonance. The $|\chi^{(3)}|$ maximum from DFWM was also at the absorption edge and had a value of over 10^{-8} esu. Two characteristic relaxation times (100 fs and 1.5 ps) were observed. Wavelength dependent THG measurements also seem to exhibit a maximum at the low energy side of the absorption band.

It is clear that the structure of these novel substituted polythiophene derivatives has a profound effect on the linear and nonlinear optical properties. We believe that the alternation pattern of the thiophene and bithiophene with the substituted thiophene units reduces the steric hindrance of the alkoxy sidechains, causing less torsion and increasing the conjugation lengths, thereby lowering the band gap and improving the NLO properties. In addition, this pattern of substituted/unsubstituted thiophene will have a strong effect on the electronic potential that the π-electrons encounter, which we expect to also play a role in the large nonlinearities observed for these samples. Using the synthetic method of Stille coupling, we have a means to control and optimize the optical properties of these polythiophene derivatives and are continuing our efforts to produce new and interesting materials.

Acknowledgments

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References

[1.] C. Sauteret, J.-P. Hermann, R. Frey, F. Pradere, J. Ducuing R. Baughman, R. Chance, Phys. Rev. Lett. **36**, 956 (1976).
[2.] F. Kajzar, S. Etemad, G. Baker, J. Messier, Synth. Met. **17**, 563 (1987).
[3.] P. Prasad, D. Williams, Introduction to Nonlinear Optical Effects in Molecules and Polymers, (John Wiley and Sons Inc. 1991).
[4.] Ch. Bosshard, K. Sutter, Ph. Prêtre, J. Hullinger, M. Flörsheimer, P.Kaatz, P. Günter, Organic Nonlinear Optical Materials, (Gordon and Breach, 1995).
[5.] D. Bradley, Synth. Met. **54**, 401 (1993).
[6.] H. Naarman, in Conjugated Polymeric Materials: Opportunities in Electronics, Optoelectronic and Molecular Electronics, ed. by Bredas and Chance (Kluwer Academic Publ. 1990) pg. 11.
[7.] H. Möhwald, V. Belov and W. Schrof, Polymer Preprints, Japan, **45**, 79 (1996).
[8.] W. Schrof, H. Möhwald, V. Belov, E. Mayer, E. Van Keuren, German patent application no. DE-P 196 08 700.7, March 1996.
[9.] E. Van Keuren, V. Belov, W. Schrof, E. Mayer, S. Rozouvan, H. Saitoh, T. Hartmann, H. Möhwald, Mol. Cryst. Liq. Cryst., **294**, 287 (1997).
[10.] W. Schrof, S. Rozouvan, T. Hartmann, H. Möhwald, V. Belov, E. Van Keuren, Journ. Opt. Soc. Am. B, in press.
[11.] J. K. Stille, Angew. Chem. Int. Ed. Engl., **25**, 508 (1986).
[12.] Z. Bao, L. Yu, W. Chan, Journ. Am. Chem. Soc., **117** , 12426 (1995).
[13.] C. Kitamura, S. Tanaka, Y. Yamashita, Chem. Mater., **8**, 570 (1996).
[14.] M. Pomerantz, B. Chaloner-Gill, L. Harding, J. Tseng, W. Pomerantz, Synth. Met., **55-57**, 960 (1993).
[15.] K. Nayak, D. Marynick, Macromol., **23**, 2237 (1990).
[16.] F. Kajzar, J. Messier, Phys. Rev. A, **32**(4), 2352 (1985).
[17.] A. Mito, K. Hagimoto, C. Takahashi, Nonlinear Optics **13**, 3 (1995).
[18.] M. Sheik-bahae, A. Said, T. Wei, D. Hagan, E. Van Stryland, IEEE J. Quant. Electr., **26**(4), 760 (1990).
[19.] R. Rangel-Rojo, A. Kar, B. Wherret, M. Carroll, G. Cross, D. Bloor, Revista Mexicana de Fisica, **41**(6), 832 (1995).
[20.] Z. Soos, S. Ramasesha, D. Galvão, R. Kepler, S. Etemad, Synth. Met., **54**, 35 (1993).
[21.] B. Xu, S. Holdcroft, Macromol., **26**, 4457 (1993).
[22.] C. Castiglioni, M. Del Zoppo, G. Zerbi, J. Raman Spectr., **24**, 485 (1993).
[23.] C. Bubeck, A. Kaltbeitzel, A. Grund and M. Le Clerc, Chem. Phys., **154**, 343 (1991).
[24.] V. A. Shakin, S. Abe, T. Kobayashi, Phys. Rev. B, **53**, 10656 (1996).