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Third Harmonic Generation Study of  $\alpha$ -Thiophene Oligomers: Monomer to Octamer

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## Third Harmonic Generation Study of $\alpha$ -Thiophene Oligomers: Monomer to Octamer

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### Abstract

The second hyperpolarizabilities,  $\langle\chi(-3\omega; \omega, \omega, \omega)\rangle$ , of  $\alpha$ -thiophene oligomers up to the octamer have been measured with third harmonic generation experiments. Measurements in THF solutions with 1.91  $\mu\text{m}$  fundamental radiation found significantly lower nonlinearity and conjugation length dependence in comparison to reported results obtained from DC electric field induced second harmonic generation and degenerate four wave mixing measurements. Previously reported nonlinearity saturation for the extended oligomers was also not evident in the current study.

### Introduction

The nonlinear optical properties of conjugated polymers are of considerable current interest because of the potential for realizing polymeric photonic devices. One dimensional delocalization and correlation of their  $\pi$  electrons lead to the relatively large third order optical nonlinearities in these polymers. Oligomeric models were

often used both theoretically and experimentally to elucidate the development of large optical nonlinearity with increasing conjugation. Of interest are the conjugation length scaling parameter of the molecular second hyperpolarizability and the eventual saturation of the nonlinearity due to finite delocalization length of the  $\pi$  electrons.

For oligothiophenes, many attempts have been carried out both experimentally and theoretically to characterize their third order optical nonlinearities. Zhao *et al.*<sup>1</sup> investigated the  $\langle\chi(-\omega; \omega, -\omega, \omega)\rangle$  of monomer to hexamer with femtosecond degenerated four wave mixing (DFWM) at 602 nm in THF solution. They reported strong length dependence with experimental length scaling parameter of  $\sim 4$ . Thienpont *et al.*<sup>2</sup> used DC electric field induced second harmonic generation (EFISH) at 1.06  $\mu\text{m}$  to examine the length dependence and nonlinearity saturation on  $\langle\chi(-2\omega; \omega, \omega, 0)\rangle$  with oligomers (up to 11 repeated units) in PMMA composite. A strong length dependence which saturates at seven repeated units was reported. Fichou *et al.*<sup>3</sup> revealed conformational disorder in the solid state by absorption spectroscopy. They also studied the dispersion of  $\langle\chi(-3\omega; \omega, \omega, \omega)\rangle$  of oligothiophene thin films with wavelength dependent third harmonic generation (THG) experiments. Conformational disorder was concluded to be the reason for the relatively low nonlinearities observed. Charra *et al.*<sup>4</sup> investigated the second hyperpolarizability of oligothiophene computationally at the CNDO level and reported a power law length dependence with exponent  $\sim 4$  and saturation at

about 16 repeated units for planar conformation. A strong dihedral angle dependence was also noted.

We present in this paper results obtained on the scalar part of the second hyperpolarizabilities of trimethylsilyl end capped  $\alpha$ -thiophene oligomers up to the octamer with THG experiments. Measurements were carried out in THF solutions with 1.9  $\mu\text{m}$  fundamental radiation. THG represents the most direct characterization of the electronic third order optical response of materials. It is free from nuclear, population, and thermal responses which tends to complicate data reductions in other measurements. When solubility allows, solution measurements minimize conformational disorder which complicates interpretation in the solid state measurements. Well defined molecular parameters can be extracted with well accepted local field and binary mixture models. The oligomers are obtained with trimethylsilyl end groups and are reasonably soluble in THF. The synthetic procedure and linear optical properties of the oligomers have been reported<sup>5</sup> and the later is summarized below for convenience. The experimental geometry and apparatus used in our measurement have been reported in detail<sup>6</sup> previously<sup>6</sup> and will be briefly described.

## Experimental

Figure 1 depicts the structures of trimethylsilyl end capped thiophene oligomers from the monomer to the octamer. The terminal trimethylsilyl groups allows the monomer, dimer, and trimer to be

freely soluble in numerous organic solvents. The higher homologs,

*tetramer*  
~~trimer~~ through octamer have, in addition to the terminal

trimethylsilyl groups, methyl groups symmetrically substituting ~~one~~ two *X* or more of the thiophene units in order to enhance the solubility of the systems. The UV spectroscopic data, obtained in chloroform solutions, for the oligo- $\alpha$ -thiophenes are summarized in Table 1 and Figure 2. The values of  $\lambda_{\text{max}}$  and  $\epsilon_{\text{max}}$  increase with conjugation length without an apparent saturation. When compared to the unsubstituted derivatives, there is little disruption in the conjugation as a result of the methyl or trimethylsilyl substitution.

To extract  $\langle \chi(-3\omega; \omega, \omega, \omega) \rangle$ , a set of linear and nonlinear optical measurement is carried out for THF solutions of each oligomer. These included measurements of density, indices of refraction at several wavelengths, THG amplitude and coherence length. These measurements respectively determine the specific volume of a solute molecule in solution, solution dispersion, and the THG nonlinear susceptibilities for each solution. The THG experimental setup consists of a 20 Hz Nd:YAG laser with 10 ns pulses of 0.4 J in energy. The 1.06  $\mu\text{m}$  output pumps a hydrogen Raman shifter, providing up to 120 mW of Stokes-shifted radiation at 1.91  $\mu\text{m}$ . This radiation serves as the fundamental frequency for the THG experiments, with the harmonic wavelengths at 636 nm. For all the thiophene oligomers which have absorption edge at wavelengths below 600 nm, the measurement can be considered as off-resonance.

THG experiments are carried out with an unconventional technique in which the harmonic amplitudes and coherence lengths are measured separately. The laser beam is divided three ways; an intensity normalization reference branch, a coherence length measurement branch, and a harmonic amplitude measurement branch. The third harmonic signals from all three branches are detected with photomultiplier tubes, and collected through gated integrators. For the determination of harmonic amplitude, we adopted a tight focusing geometry with which the focal region of the laser beam is placed at the window-liquid interface of a "single interface" sample cell. The sample cell is equipped with a thick (2 cm) front optical window and two adjacent liquid chambers (3 cm path length) holding a reference liquid and a sample solution for comparative measurement. This way, harmonic amplitude due to the air-window interfaces can be ignored. For the coherence length, a wedged liquid cell consisting of two crystalline quartz windows is used.  $\langle \gamma(-3\omega; \omega, \omega, \omega) \rangle$  is calculated from the measured solution properties, following the full Onsager local field model and taking the infinite dilution limit for all concentration dependent quantities.

## Results and Discussion

Two detailed experimental studies of the spectroscopy and third order optical nonlinearity of oligothiophenes have been carried out. Zhao *et al.*<sup>1</sup> investigated the  $\langle \gamma(-\omega; \omega, -\omega, \omega) \rangle$  of unsubstituted monomer to hexamer with femtosecond DFWM experiments at 602 nm in THF solution and Thienpont *et al.*<sup>2</sup> used EFISH experiments at

1.06  $\mu\text{m}$  to determine  $\langle\gamma(-2\omega; \omega, \omega, 0)\rangle$  with alkylated oligomers (up to 11 repeated units) in PMMA composite. Both studies found rapidly decreasing band gap and increasing nonlinearity with oligomeric size. We will compare our results with these earlier works and try to point out discrepancies as well as suggest possible explanations.

Table 1 summarizes all our measurement results for the trimethylsilyl end capped thiophene oligomers. Our spectroscopic data are in reasonable agreement with those obtained in previous works. The dominant low energy transition of the trimethylsilyl end capped oligomers has a generally red-shifted  $\lambda_{\text{max}}$  (by about 10 nm) and a comparable  $\epsilon_{\text{max}}$  in  $\text{CHCl}_3$  solution in comparison with the unsubstituted thiophene values obtained in THF. <sup>(5)</sup> The agreement in  $\lambda_{\text{max}}$  with the alkylated uncapped thiophenes is less satisfactory. The trimer values differ by 24 nm with our value red-shifted. Our octamer value is 6 nm red-shifted from their  $\lambda_{\text{max}}$  value for the oligomer with 11 repeated units. The disagreement may however be due to the less polar PMMA matrix used for the uncapped oligomers. Therefore, it is reasonable to conclude that the thiophene oligomers used in the three studies have similar  $\pi$  electronic properties.

While we also observed a strong increase of normalized molecular nonlinearity with oligomeric size (Figure 3), the magnitude of  $\langle\gamma(-3\omega; \omega, \omega, \omega)\rangle$  and its rate of increase are found to be considerably smaller than the previous results obtained by DFWM and by EFISH.

Accounting for the degeneracy factors due to the differing experiments ( $3\gamma_{\text{THG}} = \gamma_{\text{DFWM}}$  and  $6\gamma_{\text{THG}} = \gamma_{\text{EFISH}}$ ), our heptamer value is

about a factor of 3 lower than the DFWM value and a factor of 7 lower than the EFISH value. The conjugation length scaling parameter,  $\eta$ , defined according to  $\gamma \sim N^\eta$ , where  $N$  is the number of thiophene unit<sup>3</sup>, can be obtained from a log-log plot. A value of 2.8 is obtained from our THG results. This value is considerably lower than the 4.05 and 4.54 obtained from DFWM and EFISH studies respectively. No obvious saturation of  $\langle \gamma(-3\omega; \omega, \omega, \omega) \rangle$  was observed up to the octamer which is also in disagreement with the EFISH results. In good agreement with our result, a value of  $\eta \sim 3$  was obtained on  $\chi^{(3)}(-3\omega; \omega, \omega, \omega)$  by Kajzar<sup>8</sup> in his THG studies of the trimer, heptamer and hexamer oligothiophene solutions. X

A likely explanation for the disagreements is the strong dispersion of  $\gamma$ . Due to the different fundamental and harmonic wavelengths involved in these experiments, results are strongly affected by dispersion and resonance enhancement. From the spectra in Figure 1, strong two-photon enhancement must be present for the DFWM experiment where 602 nm fundamental, with two-photon wavelength at 301 nm, was used. Likewise, for the EFISH studies where 1.06  $\mu\text{m}$  fundamental was used,  $\langle \gamma(-2\omega; \omega, \omega, 0) \rangle$  must be strongly influenced by two-photon resonance in the longer oligomers whose absorption cut-off's extend well beyond the second harmonic at 533 nm. Therefore, resonance enhancement may be attributed to the high scaling parameters measured. For THG, since 1.91  $\mu\text{m}$  fundamental was used to generate a third harmonic at 636 nm, which is significantly below the absorption cut-off of all the

oligomers, the measured  $\langle \gamma(-3\omega; \omega, \omega, \omega) \rangle$  is less influenced by three-photon resonances.

In addition, despite the 400 fs duration of the 602 nm light pulses used in the DFWM experiments, measurement of  $\chi^{(3)}_{1111}$  with parallel polarized laser beams does not insure purely electronic response. Short-lived one- and two-photon excitations as well as orientational response due to the strong anisotropic polarizabilities of the oligomers may contribute to the DFWM signal. In fact, when 60 fs pulses were used in a DFWM study of a polythiophene, a six-fold smaller nonlinearity was measured in comparison to the value obtained with 400 fs pulses. In the EFISH study, since a polymeric matrix was used, it is difficult to obtain an accurate value of the DC field due to potential ionic conductivity and charge injection variation among the different samples. A solution measurement with proper referencing may improve the accuracy of the EFISH measurement.

Using a self-consistent field CNDO computations (including mono-excited states and configuration interactions) on unsubstituted oligomers with planar geometries, a theoretical scaling parameter of  $\eta = 4$  was obtained by Charra *et al.* significantly higher than the THG values. They also reported a strong decrease of  $\gamma$  with increasing torsional distortion. Spectroscopic evidence of conformational disorder and the presence of "rotamer" with preferred torsional angles has also been reported in solid thin films of thiophene oligomers. These spectral features occur at a wavelengths up to 130

nm red-shifted from the solution  $\lambda_{\max}$ , with the longest spectral feature likely corresponding to the planar conformation.

Thermochromic behavior in polythiophene solution showing strong red-shifted spectra have also been reported.<sup>10</sup> From these considerations, it is likely that non-zero torsional angles in solution contributes to reduce the nonlinearity and scaling parameters obtained in our measurements. X

### Conclusion

The second hyperpolarizabilities of trimethylsilyl end capped  $\alpha$ -thiophene oligomers up to the octamer have been measured with third harmonic generation experiments. Measurements in THF solutions with 1.9  $\mu\text{m}$  fundamental radiation found significantly lower nonlinearity and conjugation length dependence in comparison to reported results obtained from DC electric field induced second harmonic generation and degenerate four wave mixing measurements. We believe our THG results are more reliable since they are not encumbered by non-electronic responses and less influenced by multi-photon resonances in the current study. The reduced length scaling is likely a result of the non-planar geometries of the oligothiophenes in solution.

See Acknowledgments for NSF + ONR.

Table 1: Spectroscopic and nonlinear optical results for oligothiophenes ( $\lambda_{\max}$  and  $\epsilon_{\max}$  are obtained in  $\text{CHCl}_3$  solutions;  $\langle\gamma\rangle$  from THF solutions)

N	$\lambda_{\max}$ (nm)	$\epsilon_{\max}$ ( $\text{mol}^{-1}\text{cm}^{-1}$ )	$\langle\gamma(-3\omega; \omega, \omega, \omega)\rangle$ ( $\times 10^{-36}$ esu)
1	248	1.1	6
2	320	1.7	15
3	368	2.7	41
4	396	3.5	142
5	418	3.7	249
6	430	4.1	320
7	446	4.6	450
8	458	6.1	620

Did you record these values yourself?

In our final published version of ref 5, we report for this compound  $\lambda_{\max} = 448$ , but we didn't have enough for a good  $\epsilon_{\max}$  determination,  $\therefore$  we left it blank.

## Figure Caption

Figure 1: Molecular structures of trimethylsilyl end capped  $\alpha$ -thiophene oligomers.

Figure 2: Absorption spectra of trimethylsilyl end capped  $\alpha$ -thiophene oligomers in Chloroform solution.

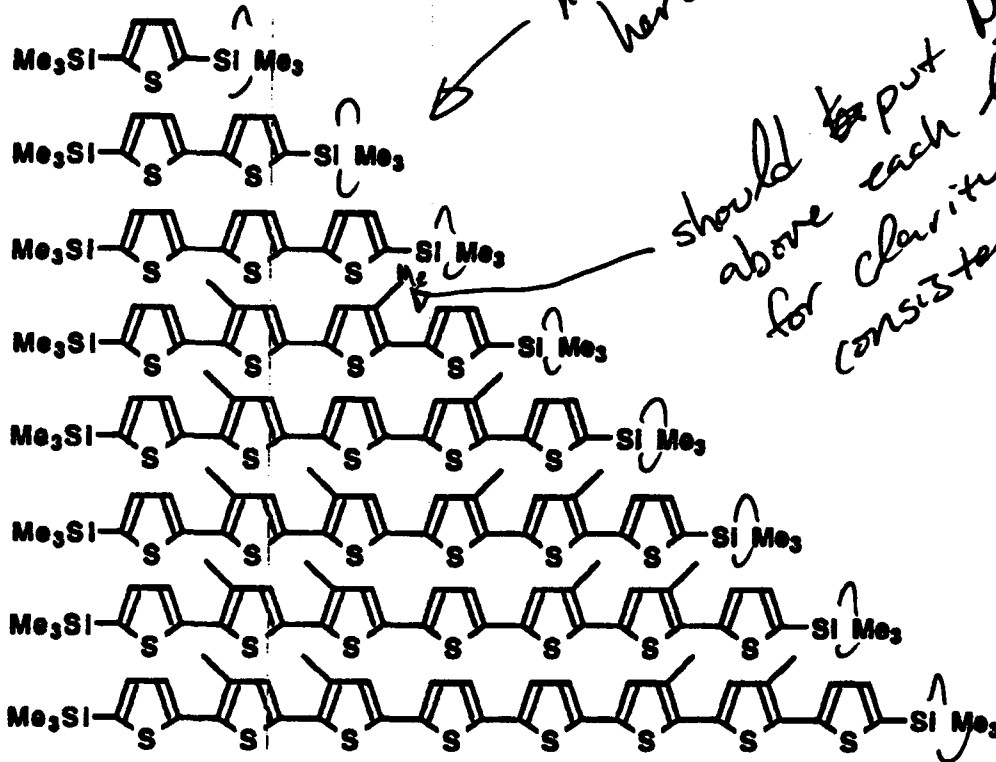
Figure 3: Normalized second hyperpolarizabilities of trimethylsilyl end capped  $\alpha$ -thiophene oligomers.

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Fig 2

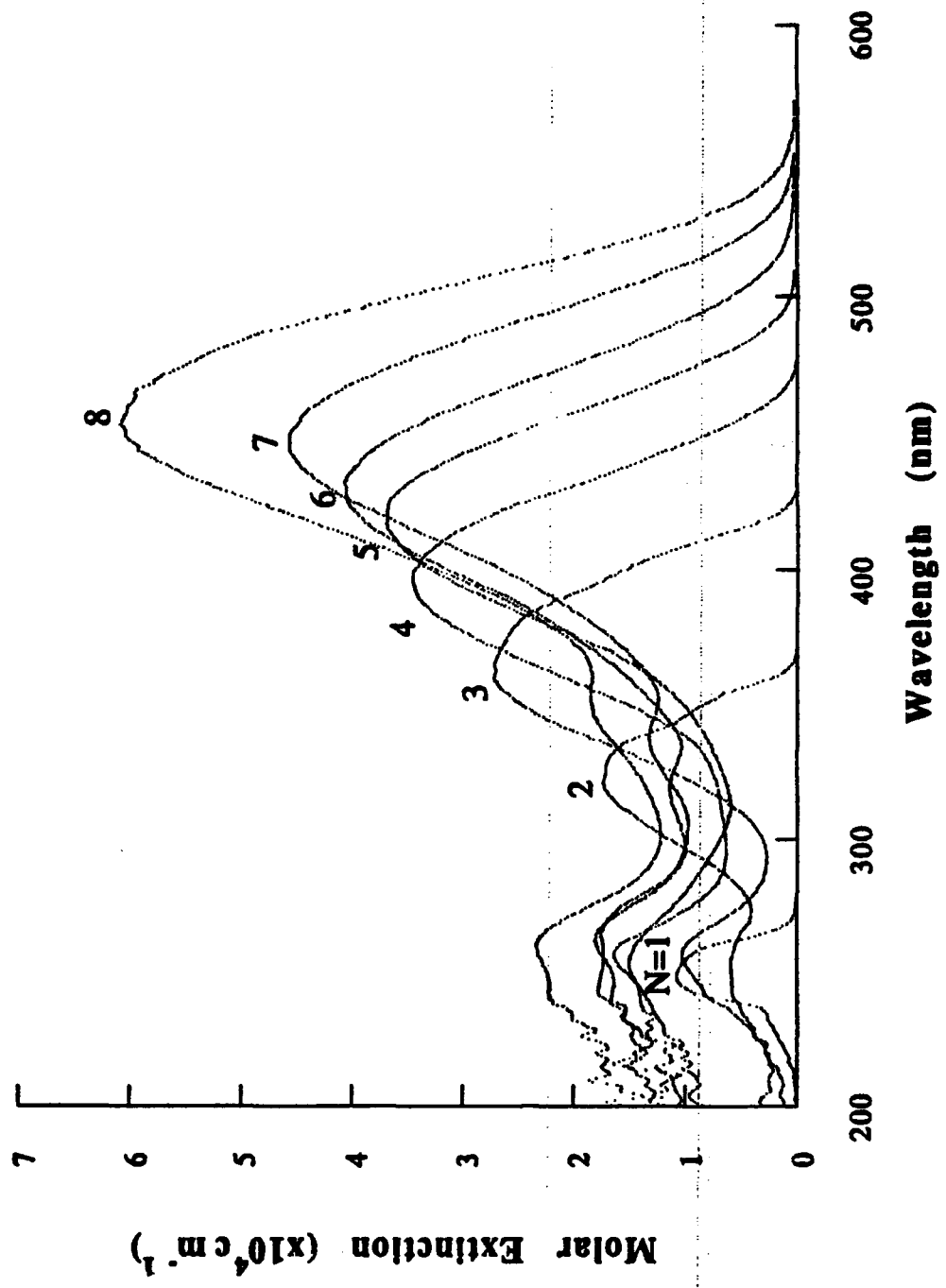


Fig 3

