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THE PREPARATION OF TAILORED LENGTH THIOPHENE-BENZOBISTHIAZOLE OLIGOMERS WITH SOLUBILIZING DECYLOXY PENDANTS FOR THIRD ORDER NONLINEAR OPTICAL PROPERTY CORRELATIONS

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Final Report for Period January 1990 to August 1991

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In an effort to better understand the relationship between molecular weight and third-order nonlinear optical (NLO) activity for condensation polymers, a series of thiophene containing benzobisthiazoles were synthesized via a trimethylsilylpolyphosphate (PPSE) catalysed condensation of a bis-o-aminothiophenol monomer and a didecyloxythiophene dicarboxylic acid. The physical and chemical characterization of these oligomers, including molecular weight determinations, are summarized. The enhancement of the bulk susceptibility and second molecular hyperpolarizability are demonstrated to increase with increasing oligomer length. Based on the data from femtosecond degenerate four-wave mixing (DFWM) experiments, the second hyperpolarizability of the oligomers is enhanced by two-photon resonance.

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FOREWORD

This report was prepared by the Polymer Branch, Nonmetallic Materials Division. The work was initiated under Project 2303, "Nonmetallic and Composite Materials," Task No. 2303Q3, Work Unit Directive 2303Q307, "Structural Resins." It was administered under the direction of the Materials Directorate, Wright Laboratory, Air Force Systems Command, Wright-Patterson Air Force Base, Ohio with Dr. Robert C. Evers as the Materials Directorate Project Scientist. Coauthors were Marilyn R. Unroe and Bruce A. Reinhardt, Materials Directorate (WL/MLBP). This report covers research conducted from January 1990 to August 1991. The authors thank the following personnel for their supporting contributions to this project: Ann Dillard and Charlie Benner, University of Dayton Research Institute, for synthesis and liquid chromatography, respectively; the personnel of the Materials Integrity Branch, WL/MLSA, for elemental analyses, mass spectroscopy and coordination of the vapor pressure osmometry work; Dr. Paul Russo, Department of Chemistry, Louisiana State University, for the plasma desorption mass spectroscopy work; and finally, the personnel of the Photonics Research Laboratory, SUNY Buffalo, especially Dr. Paras Prasad, for the DFWM evaluations.

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SECTION 1. INTRODUCTION

Within the past decade the interests of the Air Force in third-order nonlinear optical (NLO) activity have centered on the incorporation of the benzobisthiazole moiety in an optically active oligomer or polymer backbone for third-order effects. The problems with the use of such a fused ring heterocyclic unit include the typical phenomena encountered in the preparation of highly ordered and rigid-rod polymers: first, the use of strong acids such as polyphosphoric acid to prepare such polymers, and second, the insolubility and intractability of the final polymer in nonacidic media. Typical synthetic strategies to avoid the insolubility and intractability issues focused on the use of solubilizing pendants on the polymer backbones of rigid rods (References 1-3) and extended chains (Reference 4). One of the most successful pendants found which dramatically enhances solubility was the long chain n-alkoxy group. There are several examples of the use of long chain alkoxy pendants to enhance solubility in the recent literature (References 5, 6). Other variations on the solubility theme have employed sterically hindered tertiary alkyl and alkoxy groups as pendants (Reference 7).

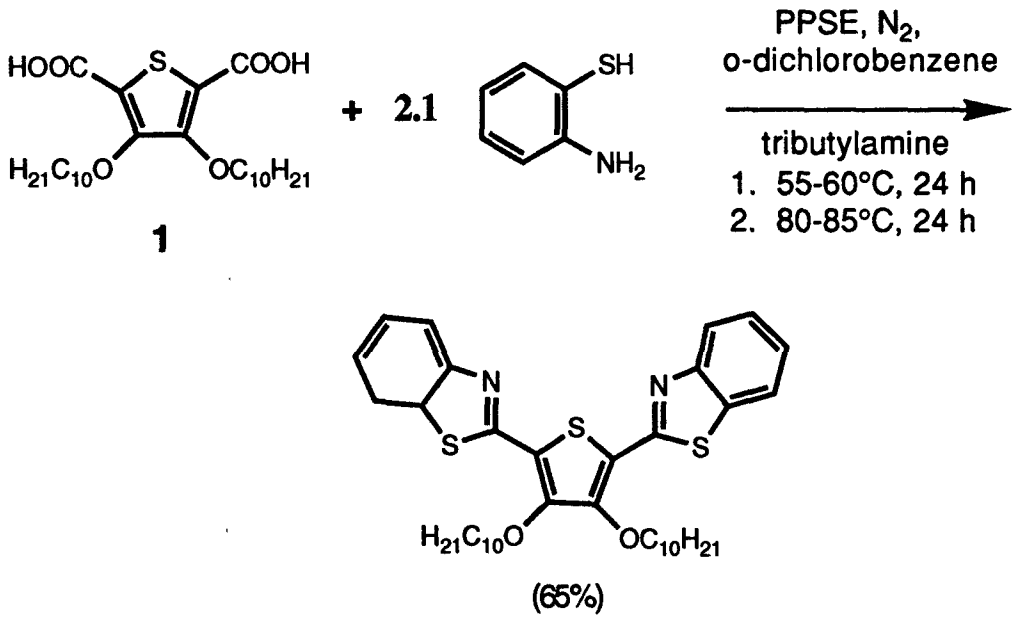
Recent synthetic designs of NLO active polymers and oligomers have also concentrated on the incorporation of short conjugation sequences in the electroactive species. Again, the reasoning behind the use of this construction parameter has included the circumvention of processing problems usually associated with highly conjugated systems, namely, poor solubility in common organic solvents such as chloroform and tetrahydrofuran (THF) or the formation of poor optical quality films. In addition to the avoidance of processing problems, the use of well-characterized polymers and oligomers of known chain length provides insight into the hypotheses of various workers (References 8-10) concerning the limitation of the second molecular hyperpolarizability, γ, with increasing chain length.

Even more recent publications from a cooperative research group (References 11, 12) have demonstrated the use of the long chain decyloxy group as not only a solubilizing pendant but also as a moiety enhancing the value of γ of oligomers dissolved in THF solutions. The approach of the research reported here has been to combine the concept of improved solubility of oligomers containing the long chain n-alkoxy group with the concept of higher values of third order hyperpolarizability as molecular weight increases. The ultimate goal of the research was to find what was the molecular weight cutoff at which the third-order NLO activity reached its maximum for the series of substituted thiophene-benzobisthiazole oligomers.

SECTION 2. RESULTS AND DISCUSSION

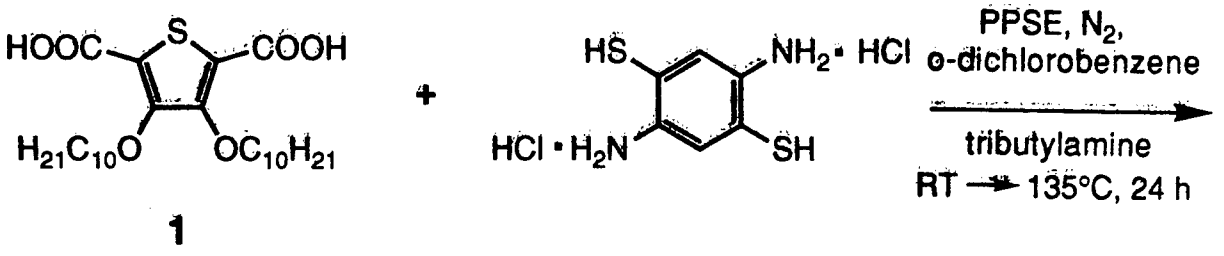
2.1. Synthetic Preparations

To prove the feasibility of the synthetic approach the model compound, 3,4-bis(decyloxy)-2,5-bis(benzothiazol-2-yl)thiophene, was prepared using a previously reported (Reference 11) condensation reaction in which trimethylsilylpolyphosphate (PPSE) catalyst and o-dichlorobenzene were the media of choice for the reaction of 3,4-bis(decyloxy)-2,5-thiophenedicarboxylic acid (1) with two equivalents of o-aminothiophenol.



The preparation of the diacid oligomer precursors of varying average chain length utilized monomer **1** and a bis-o-aminothiophenol monomer with the PPSE/o-dichlorobenzene media. Average chain length was optimized by adjusting the stoichiometry of the reactants to achieve the maximum amount of oligomers in each distribution mixture while the amount of high polymer produced was minimized (Experimental, 3.1). After isolation by precipitation, the diacid precursors were endcapped with an excess of two equivalents of

o-aminothiophenol using PPSE and o-dichlorobenzene to obtain the final benzothiazole capped oligomer distribution.



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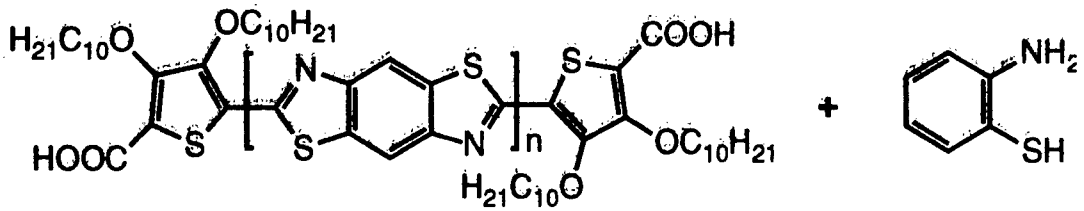
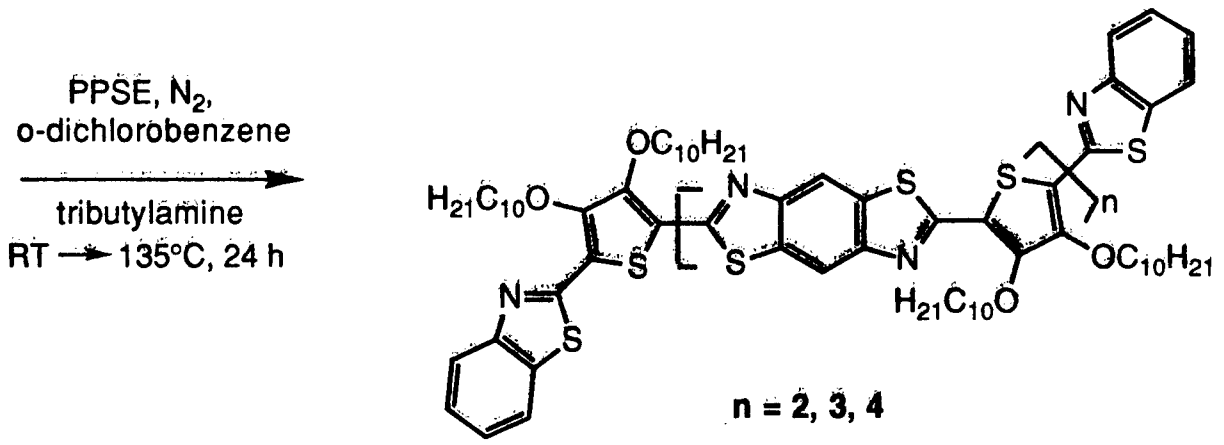
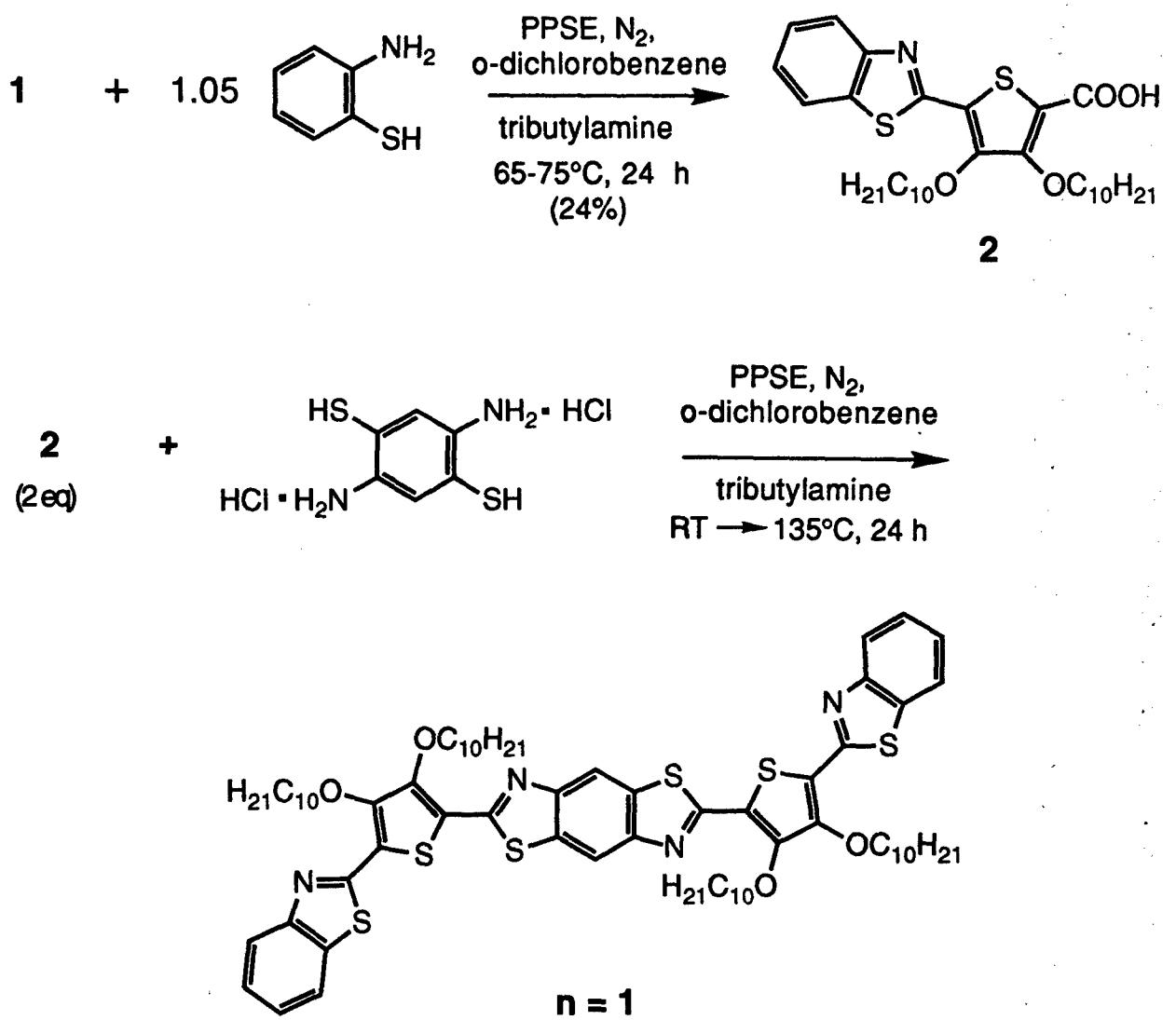


n = 2, 3, 4



n = 2, 3, 4

The oligomer n = 1 was prepared in 85 percent yield by a route in which the consideration of polydispersity was eliminated and a pure one component system was obtained. Compound **2** was prepared in low yield using the PPSE catalysed reaction of monomer **1** with a slight equivalent excess of o-aminothiophenol.



2.2. Physical Characterization

The physical characteristics of the oligomers are summarized in Table 1. Yields ranged from a high of 85 percent for the n = 1 oligomer to a low of 41 percent for the n = 4 oligomer. The decrease in yield as molecular weight increased was not an unusual observation for this phenomena was also observed in the synthesis of a series of substituted polyphenylenes which were prepared by another synthetic route (Reference 13). The appearance of the oligomers changed from a light green-beige powder for the n = 1 oligomer to dark green iridescent powders for the higher oligomers. There was a predictable trend in solubility observed in which the n = 1 oligomer was totally soluble in

Table 1. Characterization of Substituted Thiophene - Benzobisthiazole Oligomers

OLIGOMER	YIELD[1] (%)	ELEM. ANAL. Calc'd (Found)	EMPIRICAL FORMULA (FW)	APPEARANCE	SOLUBILITY IN THF (%)[2]
n = 1	85	C 67.37 (67.01) H 7.59 (7.54) N 4.49 (4.52) S 15.42 (15.17) P 0.00 (0.07)	$C_{70}H_{94}N_4O_4S_6$ (1247.83)	light beige-green powder	total; (bright yellow-green soln)
n = 2	67	C 66.84 (63.15) H 7.59 (7.05) N 4.59 (4.75) S 15.74 (15.54) P 0.00 (0.59)	$C_{102}H_{138}N_6O_6S_9$ (1832.69)	dark green iridescent powder	10% (wt/vol); (yellow soln)
n = 3	54	C 66.57 (61.36) H 7.59 (6.41) N 4.64 (5.29) S 15.91 (16.83) P 0.00 (0.75)	$C_{134}H_{182}N_8O_8S_{12}$ (2417.55)	dark green iridescent powder	10% (wt/vol); (med yellow soln)
n = 4	41	C 66.40 (60.09) H 7.59 (6.17) N 4.66 (5.79) S 16.02 (17.36) P 0.00 (0.99)	$C_{166}H_{226}N_{10}O_{10}S_{15}$ (3002.42)	dark green iridescent powder	partial (<10%); (yellow-orange soln)

[1] Purified yield.

[2] All oligomers were dissolved into THF (1 mL) at room temperature at 1% (wt/vol) increments until turbidity was observed.

THF at room temperature and the n = 4 oligomer was only partially soluble in THF. The n = 2 and n = 3 oligomer distributions were intermediate in solubility up to 10 percent (wt/vol) in THF. There are several explanations for the wide deviations from the theoretically calculated values in the elemental analyses. First of all, it is known from previous experience in this laboratory that polybenzobisazole polymers are difficult to characterize by elemental analysis because of incomplete combustion of the thermally stable heterocyclic fused rings. Second, a phosphorus analysis of each oligomer sample indicated an increasing phosphorus content with increasing molecular weight. This high phosphorus content is directly attributable to the PPSE catalyst and is not completely released in the

aqueous acid wash of the work up. Although there is no direct analytical proof, either a PPSE-oligomer complex or a micellular effect is suspected to exist as molecular weight increases which fouls the elemental analysis data.

A sample of the n = 2 oligomer was also evaluated by differential scanning calorimetry (DSC, ΔT = 10°C/min, helium) to determine any unique thermoanalytical data for the oligomers. The DSC of the n = 2 oligomer indicated a softening transition at 180-190°C, but there were no indications of a polymerization exotherm up to 450°C.

Several standard techniques were attempted to obtain an assignment of number and weight average molecular weights (M_n and M_w respectively) to the oligomer distributions (Table 2).

Table 2. Characterization of Molecular Weight Distribution

OLIGOMER	FORMULA WEIGHT (g/mol)	M_w GPC	M_n Calc'd	M_n VPO[1]	M_n PDMS[2]
n =1	1247.83	1247.83, one component n = 1	1247.83	N/A	1248.1 (M^+)
n = 2	1832.69	2600, multi-component n = 1, 2, 3, 4, polymer	1826.77	N/A	1446.96
n = 3	2417.55	unresolved	2554.41	N/A	unresolved
n = 4	3002.42	unresolved	3284.24	N/A	1247.83 43 (M^+)

1 Attempts by two separate organizations to use this technique with THF solutions were unsuccessful.

2 Plasma desorption mass spectroscopy performed by Louisiana State University, Department of Chemistry.

Vapor pressure osmometry (VPO) was not an acceptable method of analysis even though the method is usually reliable for molecular weight determinations up to 20,000. Likewise, the use of size separation chromatography techniques such as gel permeation chromatography (GPC) were unsuccessful for the higher molecular weight oligomers. Good resolution for the n = 1 and n = 2 oligomers was obtained and is graphically shown in Figure 1. The technique that was more successful for full characterization of molecular weight distribution was plasma desorption mass spectroscopy (PDMS). However, PDMS was not successful for the location of higher molecular weight parent ions of the n = 3

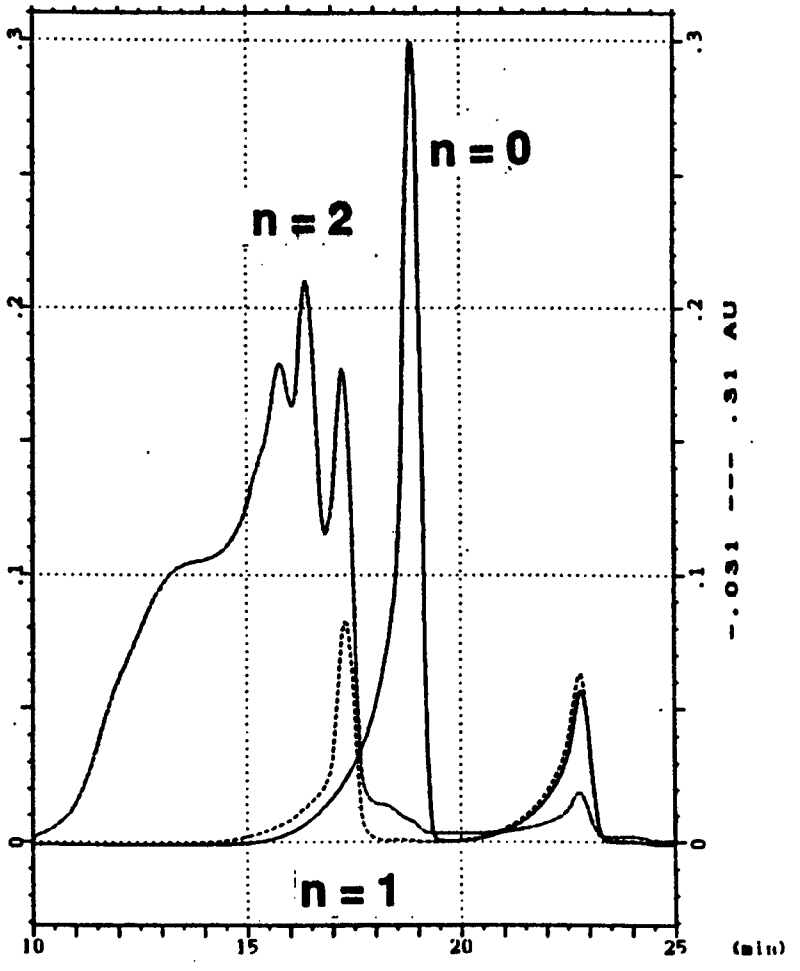


Figure 1. GPC Chromatogram of n = 0, n = 1 and n = 2 Oligomers. All Samples Were Spiked With Toluene As a Marker (Toluene Retention Time = 23 min)

and n = 4 oligomers. In addition, no higher molecular weight parent ions were detected in the n = 2 sample despite the resolution of higher molecular weight species in the GPC chromatogram.

Characterization of the distribution of oligomers was therefore easily performed for lower molecular weight oligomers using GPC or PDMS. Although PDMS techniques will accurately detect the lower molecular weight species in a higher molecular weight distribution and provide a reasonable calculation of the M_n, this technique was not acceptable for higher molecular weight determinations.

2.3 Summary of DFWM Experiments

The measurements of the third-order NLO activity were performed using femtosecond DFWM in varying concentrations of dilute THF solutions. These data are summarized in Table 3 together with the ultraviolet/visible (UV/VIS) spectra of the oligomers. The advantages of using dilute solutions versus the film technique for third-order NLO measurements by DFWM include the avoidance of occlusions and nonuniformities in films which skew the measurements of γ. From the calculation of the bulk third order susceptibility ($\chi^{(3)}$) it was observed that $\chi^{(3)}$ increased with increasing molecular weight. The graphic representation of the bulk susceptibility versus molecular weight demonstrated this increase in $\chi^{(3)}$ (Figure 2). Agreement of the smooth curve fit with the experimental values of $\chi^{(3)}$ on the raw data line of Figure 2 demonstrated high reliability of the lower molecular weight data. By the point high n = 4 oligomer content in the mixtures was achieved, a leveling of the smooth curve data was approached. Therefore, $\chi^{(3)}$ may be approaching its maximum near the n = 4 or n =5 repeat unit for these molecular constructs. Unfortunately, the lack of good characterization techniques for oligomer distributions that approach high polymers limit the utility of the synthetic method for continuing beyond the preparation of the n = 4 mixture.

Table 3. Data of DFWM Experiments Upon THF Solutions of Oligomers

OLIGOMER	UV/VIS λ_{max} (nm)	γ (real) (esu)	γ (im) (esu)	$\chi^{(3)}$
n = 0	390	$+3.90 \times 10^{-34}$		2.60×10^{-12}
n = 1	438	-3.49×10^{-32}	5.26×10^{-32}	1.64×10^{-10}
n = 2	447	-8.68×10^{-32}	13.67×10^{-32}	2.89×10^{-10}
n = 3	460	-13.92×10^{-32}	21.85×10^{-32}	3.48×10^{-10}
n = 4	450	-47.97×10^{-32}	40.96×10^{-32}	6.76×10^{-10}

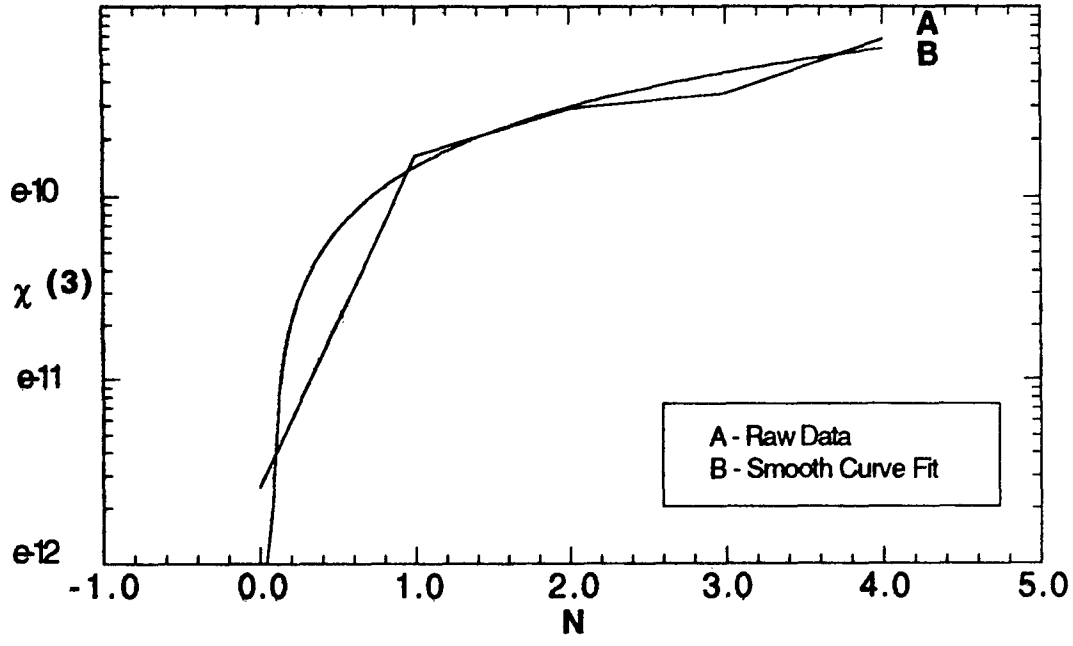


Figure 2. Plot of Bulk Third Order Susceptibility Versus Oligomer Length (Table 3)

A two-photon resonance enhancement of $\chi^{(3)}$ was also observed for the series of oligomers and was demonstrated by the appearance of an imaginary component of γ. The existence of an imaginary component corresponds to a contribution to the nonlinear response from modes at a frequency close to 2ω. The instructional caveat was the positive real γ value of the model n = 0 with no imaginary component. Thus the simplest model demonstrated no two-photon enhancement and was not representative of the values to be

obtained on the oligomers for real γ's. In addition, the $\chi^{(3)}$ value for the model was almost two orders of magnitude below the values obtained for the oligomer mixtures. Table 3 data also indicated an expected red shift in the λ_{max} of the UV/VIS as molecular weight increased. The red shift was due to the increase in conjugation length with increasing molecular weight. As molecular weight increased, the resolution of the spectra to determine λ_{max} became less accurate and there was a noticeable broadening of the spectra. This leveling off of λ_{max} as molecular weight increased was also observed for the polyphenyls mentioned earlier (Reference 14).

2.4 Conclusions

Reasonable molecular weight determinations were achieved for lower molecular weight decyloxy substituted thiophene-benzobisthiazole oligomers prepared by a previously reported condensation reaction in nonacidic media. However, existing techniques such as VPO, GPC, and newer characterization techniques such as PDMS were still unsuccessful in determining average molecular weight for higher oligomer distributions. DFWM experiments on dilute solutions of oligomers in THF confirmed an expected rise in bulk susceptibility and λ_{max} as molecular weight increased. All oligomers prepared showed an imaginary component of γ and negative real components of γ which indicated the oligomers exhibit two photon resonance enhancement by modes at a frequency close to 2ω. In contrast, the model system displayed only a positive real component to γ and was not truly representative of γ_{real} values for the oligomers. The limitations of reliable characterization of oligomers that approach high polymers led to the cessation of the work at the n = 4 repeat unit. From the plot of $\chi^{(3)}$ versus the oligomer repeat unit, the limit of the molecular weight cutoff for $\chi^{(3)}$ maximum was not able to be determined. However, the experimental work up to the n = 4 repeat unit which was performed, though, appeared to approach the maximum $\chi^{(3)}$ based on the smooth curve fit of Figure 2.

SECTION 3. EXPERIMENTAL

3.1 Synthesis

All solvents used were reagent or HPLC grade and used without further purification. The PPSE was purchased from Fluka AG. The monomer, 2,5-diamino-1,3-benzenedithiol dihydrochloride (PBT monomer), was obtained in monomer grade from SRI International, Palo Alto, CA and used without further purification. The capping reagent, o-amino-thiophenol, was purchased from Aldrich and was distilled in vacuo before use.

3.1.1 Preparation of 3,4-bis(decyloxy)-5-(benzothiazol-2-yl)thiophene-1-carboxylic acid (2). A solution of monomer **1** (5.00 g, 10.32 mmol) (Reference 11), o-aminothiolphenol (1.36 g, 10.83 mmol) and o-dichlorobenzene (11 mL) was stirred under a nitrogen atmosphere for 0.25 h before the addition of PPSE (12.38 g) and enough o-dichlorobenzene (20 mL) to maintain a 40% concentration of PPSE to solvent. Tri-n-butylamine (2.68 g, 14.44 mmol) was added by dropping funnel over a period of 0.25 h at room temperature and the flask was gradually heated to an internal temperature of 65-75°C where the temperature was maintained for 24 h. The flask was allowed to cool to room temperature, the reaction was washed in water (200 mL) and the organic layer was separated from the aqueous layer. The solvent was removed by evaporation, and the residue was chromatographed on a silica gel column (Woelm DCC, 2.5 cm dia X 58 cm H) using 3:1 chloroform:heptane to remove the disubstituted contaminant and 4:1 chloroform:heptane to remove **2**. The crude product was recrystallized in 3:2 petroleum ether:toluene (50mL) which was cooled in the refrigerator to afford **2** as very pale yellow needles (1.42 g, 24%): mp 141-143°C (uncorrected).

Elem. Anal. calc'd for $C_{32}H_{47}NO_4S_2$: C, 66.98; H, 8.26; N, 2.44; S, 11.17. Found: C, 67.01; H, 8.34; N, 2.56; S, 11.05. GCMS: m/z = 574 (2, M^+), 43 (100, $(C_3H_7)^+$).

3.1.2 Preparation of n = 1 oligomer. A solution of **2** (1.83 g, 3.19 mmol), PBT monomer (0.39 g, 1.59 mmol), o-dichloro-benzene (19 mL) and PPSE (7.65 g) were stirred under nitrogen for 0.25 h before the dropwise addition of tri-n-butylamine (1.42 g, 7.64

mmol). The internal temperature was slowly raised to 135°C over 3 h at which temperature the flask was maintained for 24 h. The color of the reaction changed from a light yellow to a clear chartreuse upon heating. After the flask was allowed to cool to room temperature, the solvent was removed in vacuo and the residue suspended into methylene chloride. The organic solution was washed with 3 percent aqueous hydrochloric acid (100 mL), water (200 mL), and separated. The solvent was evaporated in vacuo and the residue was precipitated into THF:80% aqueous methanol to afford the crude product. The solid was purified in a continuous extraction apparatus using 95 percent ethanol for 72 h. The solid was dried in vacuo for 48 h at 200°C to afford pure n = 1 oligomer as a beige-green powder (1.60 g).

3.1.3 Representative two-step preparation of oligomer distributions n = 2, n = 3 and n = 4: preparation of diacid n = 2. A 150 mL polymerization flask was charged with an exact solution of **1** (3.029 g, 6.25 mmol), PBT monomer (0.981 g, 4.00 mmol), o-dichlorobenzene (70 mL) and PPSE (15.0 g). After strring under a nitrogen atmosphere for 0.25 h, tri-n-butylamine (7.12 g, 38.4 mmol) was added by dropping funnel at a drip rate of a drop per second. The color of the solution changed from a clear yellow to an opaque green-red-brown upon heating of the flask to an internal temperature of 135°C. After maintaining the internal temperature at 135°C for 24 h, the flask was allowed to cool to room temperature and the solvent was removed in vacuo. The residue was washed, precipitated, and isolated as previously described in Section 3.1.2 to afford a dark brown solid (2.23 g, 78%).

Preparation of n = 2 capped oligomer. Likewise, as previously descibed for the preparation of the diacid precursor, a solution of the n = 2 diacid (2.20 g, 1.33 mmol), o-aminothiophenol (0.33 g, 2.66 mmol), o-dichlorobenzene (8 mL) and PPSE (3.19 g) were stirred for 0.5 h under nitrogen before the dropwise addition of tri-n-butylamine (0.69 g, 3.72 mmol). The flask was heated over a period of an hour to an internal temperature of

135°C. The temperature was maintained at 135°C for 24 h. Washing and isolation procedures similar to those that were described in Section 3.1.2 afforded a dark green iridescent solid (1.64 g, 67%, Table 1).

3.2 DFWM measurements. The system used for measurements of the second hyperpolarizabilities was previously described in another publication (Reference 15). Measurements were carried out on THF solutions of the oligomers using DFWM in a standard time resolved backward beam geometry. The system delivered amplified nearly transform limited 400-femtosecond limited pulses at 602 nm with a repetition frequency of 30 Hz and maximum energy of 0.4 mJ/pulse. Sets of beam splitters and mirrors were used to obtain a series of three synchronous beams that were simultaneously incident upon the sample by delay lines. Peak power at the sample was on the order of 1-20 GW/cm^2. However, one of the synchronous beams was delayed in the backward geometry with respect to the other two beams so that a temporal profile of the DFWM signal was recorded. The signal was observed as the phase conjugate of the probe beam in backward geometry. The signal was monitored with a photodiode and processed with a boxcar averager.

The intensities of the THF solutions of oligomers were compared to a reference sample of THF under similar conditions so that the following equation described the bulk susceptibility of the oligomers:

$$\chi(3) = (n / n_r)^2 (I / I_r)^{1/2} (l/l_r) (\chi_r^{(3)}) F \qquad (1)$$

where I stands for the DFWM intensity, n is the refractive index of the medium, l is the interaction length, the subscript r refers to the reference sample and F is the correction factor needed to account for absorption losses. The value of $\chi_r^{(3)}$ for the the THF standard has been determined after rigorous comparisons of other reference solvents to be

3.3×10^{-14} esu and is an adopted value for THF at the Photonics Laboratory of SUNY Buffalo. Since the existence of contributions of the solute and solvent to the DFWM measurement contribute to equation (1), the sum of the two contributions may be stated as such:

$$\chi^{(3)} = L^4(N_S\gamma_S + N_x\gamma_x) \qquad (2)$$

where γ_S and γ_X stand for the second hyperpolarizabilities of the solvent and solute respectively, N_S and N_X specify the respective molecular densities, and L is the local field factor in solution which is approximated by using the Lorentz expression. The refractive index, n, in the Lorentz expression was measured using an Abbe refractometer at the sodium line (589 nm). However, this equation only holds true for coherent contributions by both solvent and solute to the real components of the hyperpolarizabilities.

When soluble compounds are measured for their second hyperpolarizabilities, dilute solutions of oligomers at various set concentrations are usually prepared and the $\chi^{(3)}$ values are obtained using equation (1) and then solving equation (2) with a least squares fit to get solute γ values. When no imaginary contribution to $\chi^{(3)}$ is assumed for THF, the following equation must be used:

$$\chi^{(3)}_{\text{eff}} = L^4((N_1\gamma_{1r} + N_2\gamma_2)^2 + (N_1\gamma_{1i})^2)^{1/2} \qquad (3)$$

where γ_{1r} and γ_{1i} are the real and imaginary components respectively of the second hyperpolarizability of the solute and γ_2 is the second hyperpolarizability of THF. Equation (3) was the preferred equation to determine $\gamma_{(\text{real})}$ and $\gamma_{(\text{im})}$ in this study.

SECTION 4. REFERENCES

1(a). T. T. Tsai and F. E. Arnold, *Polym. Prepr.* **1986** *27* (2), 221.

1(b). J. Burkett and F. E. Arnold, *Polym. Prepr.* **1987** *28* (2), 278 .

2. J. F. Wolfe and F. E. Arnold, *Macromolecules* **1981** *14* (4), 909.

3. H. Ringsdorf and P. Tschirner, *Makromol. Chem.* **1987** *188*, 1431.

4 P. W. Morgan, S. L. Kwolek and T. C. Pletcher, *Macromolecules* **1987** *20* (4), 729.

5(a). M. Ballauff, *Makromol. Chem., Rapid Commun.* **1986** *7*, 407.

5(b). M. Wentzel, M. Ballauff and G. Wegner, *Makromol. Chem.* **1987** *188*, 2865.

6. K.-S. Lee and J. C. Won, *Makromol. Chem.* **1989** *190*, 1547.

7. C. Spangler, P.-K. Liu, T. A. Kelleher, M. L. Saindon and E. G. Nickel, "Substituent Effect in the Design of New NLO Materials," *Proc. SPIE - Int. Soc. Opt. Eng.: 1992 OE/LASE*, Paper No. 1626-46, Los Angeles, CA, January 22, 1992.

8. G. P. Agrausl, C. Cojan and C. Flytzanis, *Phys. Rev. B* **1978** *17*, 776.

9(a). A. F. Garito, J. R. Heflin, K. Y. Yang and O. Zamani-Khamire, "Enhancement of Nonlinear Optical Properties of Conjugated Linear Chains Through Lowered Symmetry," Organic Materials for Nonlinear Optics, 16-27, Royal Soc. Chem., London, 1989.

9(b). P. Prasad, "Studies of Ultrafast Third-order Non-linear Optical Processes in Polymer Films," Organic Materials for Nonlinear Optics, 264-274, Royal Soc. Chem., London, 1989.

10. C. Spangler, T. J. Hall, K. O. Havelka, D. W. Polis, L. S. Sapochak and L. R. Dalton, *Proc. SPIE - Int. Soc. Opt. Eng.: Nonlinear Optical Properties of Organic Materials III* **1990** *1337*, 125.

11. M. Zhao, M. Samoc, P. Prasad, B. Reinhardt, M. Unroe, M. Prazak, R. Evers, J. Kane, C. Jariwala and M. Sinsky, *Chem. Mater.* **1990** *2*, 670.

12. B. Reinhardt, M. Unroe, R. Evers, M. Zhao, M. Samoc, P. Prasad, and M.

Sinsky, *Chem. Mater.* **1991** *3*, 865.

13. M. R. Unroe and B. A. Reinhardt, *Synthesis* **1987** *(11)*, 981.

14. M. Zhao, Y. Cui, M. Samoc, P. Prasad, M. Unroe and B. Reinhardt, *J. Chem. Phys.* **1991** *95* (6), 3991.

15. D. N. Rao, J. Swiatkiewicz, P. Chopra, S. K. Ghoshal and P. N. Prasad, *Appl. Phys. Lett.* **1986** *48*, 1187.

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