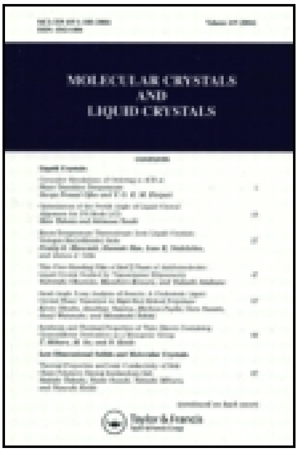

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THIRD-ORDER NONLINEAR OPTICAL PROPERTIES OF THIOPHENE OLIGOMERS AND DERIVATIVES

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Abstract A series of α, α'-thiophene oligomers and their α, α'-substituted derivatives such as formyl, bromine, and cyano have been prepared in order to discuss the effects of number of thiophene rings and introduction of functional groups on third-order nonlinear optical properties. Optical absorption spectra and optical third harmonic generation (THG) have been studied in vacuum-evaporated thin films or solid solution. The values of λ_{max}, linear polarizabilities and $\chi^{(3)}(-3\omega;\omega,\omega,\omega)$ obtained from THG measurement for thiophene oligomers increase with increasing number of thiophene rings. The introduction of electro-active groups and increasing the molecular planarity enhanced the linear polarizabilities and third-order nonlinear optical susceptibilities.

INTRODUCTION

There are various approaches to obtain processable third-order nonlinear optical materials which meet several requirement for waveguide application, *i.e.*, thin-film forming, thickness controlled, and pattering properties. Utilization of soluble conjugated polymers is a typical example[1] and that of glassy polymers doped with conjugated molecule infinite conjugation is alternative.[2] In the former case the polymer backbond offers extended conjugation path for delocalized π-electrons. Although the mechanical properties of polymer matrix is mainly used in the latter case, there is quite wide flexibility for material selection. Our current interests have been focused on development of novel conjugated molecules suitable for this application.[3]

Recently wide variety of research works on thiophene oligomer and related compounds have been carried out and their opto-electronic properties have been studied

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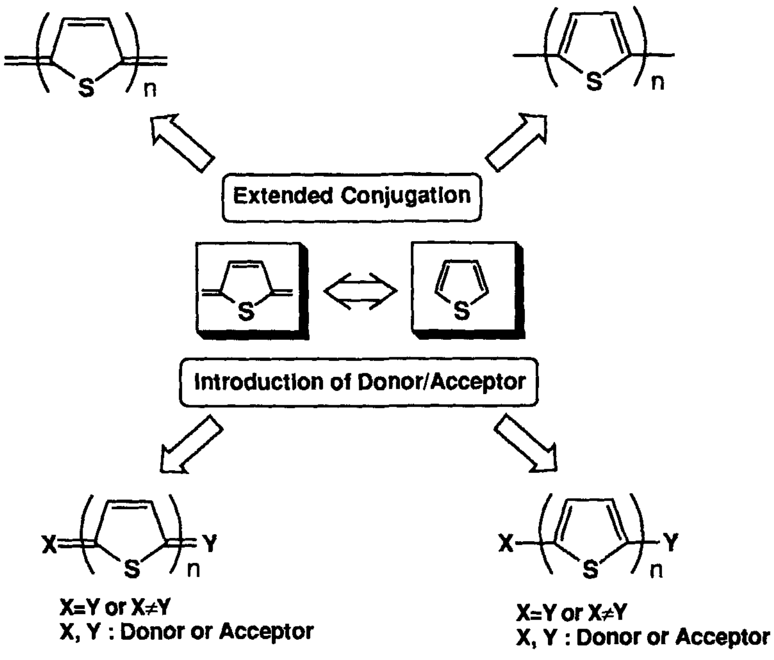
as a function of number of thiophene rings experimentally and theoretically.[4] From application view points, organic semiconductor devices such as field-effect transistors were developed based on vacuum-evaporated thin films of thiophene oligomer and their primary characteristics were elucidated.[5] From fundamental view points, on the other hand, thiophene oligomers are one of the typical target systems for molecular-level study for nonlinear optics. There was excellent study on nonlinear optical properties of partially alkylated soluble oligomers up to 11 thiophene rings to reduce torsion angles in α, α'-thiophene coupling.[6] Besides the increase in the number of repeating conjugated units, the polarizable structure by introducing electro-active groups[7, 8] and the increase of molecular planarity are alternative methods to extend the effective conjugation length. Scheme I indicates the molecules to elucidate effects of conjugation length and introduction of electro-active groups, that is, the increase in the number of thiophene rings or the extension of thienoquinonoid structures[9] and the introduction of donors (D) and/or acceptors (A). In this paper, we investigate the linear and nonlinear optical structure-property relationships in the molecular level and discuss the importance of molecular planarity on third-order nonlinear optical responses.

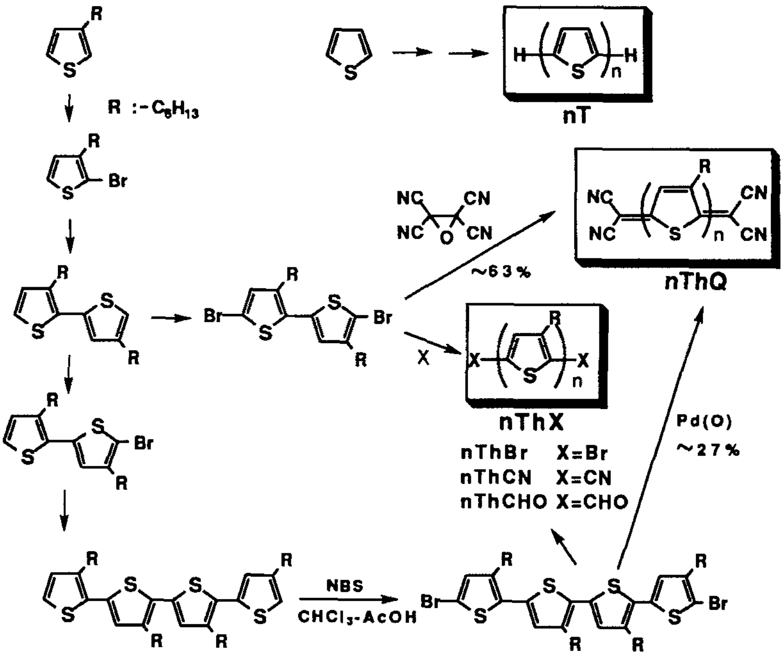


SCHEME I Thiophene and quinonoid structures for investigation of structure-property relationships.

EXPERIMENTAL

Samples

A series of thiophene oligomers (nTh, n=2, 4, 8) and derivatives (nThX, n=2, 4, 8 and X=CN, Br, CHO) were synthesized according to Scheme II. Thiophene with 3-hexyl substituent was selected as a conjugated repeating unit and showed good solubility into common organic solvents and polymers. Oligothienoquinonoid derivatives (nThQ) were also successfully synthesized in good yields. The details of synthetic procedures will be reported elsewhere.[10] Thin films of poly (methyl methacrylate) (PMMA) doped with various concentration of thiophene oligomers (about 0.1- 1μm thick) were prepared on a fused silica substrate by spin-coating of $CHCl_3$ polymer solution.



SCHEME II Synthesis of thiophene oligomers and derivatives.

Third Harmonic Generation Measurements

THG measurements were carried out at fundamental wavelength of 1907 nm in a vacuum of several Torr to eliminate the effect of air.[11] The THG Maker fringe pattern was obtained by rotating the film sample and analyzed by standard procedures[12] using a $\chi^{(3)}$ value for fused silica, 1.4 x10^{-14} esu as a reference.[13]

RESULTS AND DISCUSSION

Optical Absorption Spectra

In order to obtain highly soluble conjugated oligomers for above-described guest/host systems, oligothiophene and thienoquinonoid with 3-hexyl substituent were studied. However this 3-alkylation induced a twisted structure with large torsion angle along oligomer chain. We examined the effective conjugation length from optical spectra of solid solution, PMMA films doped with these 3-hexyl thiophene oligomers, in comparison with vacuum-deposited oligothiophene films. Figure 1 shows the optical absorption peaks λ_{max} for thiophene oligomers besides partially alkylated oligomers reported by Havinga et. al.[14] Although partially alkylated oligomers, especially $n \geq 6$, have the same values of λ_{max} as unsubstituted thiophene oligomers (nT), the blue shift of λ_{max} in 3-hexyl thiophene oligomers was obtained in this work presumably due to the twisted structures induced by 3-alkylation in the repeating units. In the case of α, α'-cyano derivatives (4ThCN), red shift of λ_{max}, was observed compared with that of 3-alkyl thiophenes. Moreover large difference was observed in thienoquinonoid structures with four cyano groups. Taking the effects of introduction of cyano groups in 3-alkyl thiophene oligomers into account, this large red shift can be explained by the additional effect of molecular planarity on effective conjugation length. Figure 2 summarizes the λ_{max}, of the absorption peak for α, α'-substituted quater thiophenes (4ThX). Introduction of electro-active groups obviously induced red shift in the order of Br<CN<CHO<<$(CN)_2$. This solvatochromism can be explained by the donor number of solvents.[10]

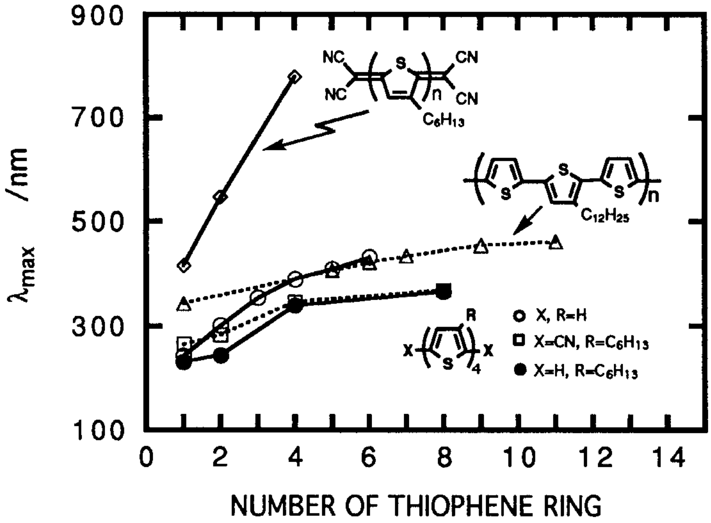


FIGURE 1 Optical absorption peaks λ_{max} for thiophene oligomers and derivatives.

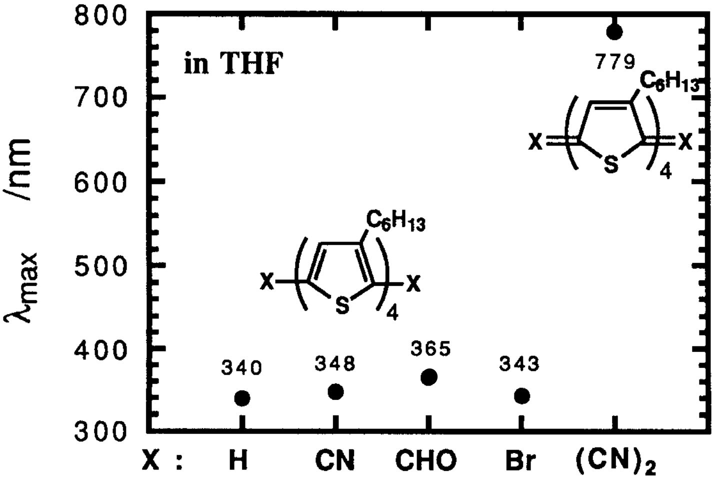


FIGURE 2 Optical absorption peaks λ_{max} for α, α'-substituted quarter thiophene derivatives and quinonoid.

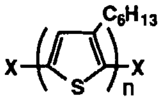
Linear Polarizabilities

Isotropically averaged molecular polarizability <α> can be expressed by the following equation:

$$\langle\alpha\rangle=\alpha_x+\alpha_y+\alpha_z \tag{1}$$

In the case of guest/host systems the overall polarizability is a sum of guest molecules and host matrix contributions. Assuming the Lorentz model, we can calculate polarizability using the values of refractive indices. Figure 3 shows the concentration dependence of refractive indices at a wavelength of 632.8 nm for 4Th/PMMA films, and linear relationship was obtained. <α> values obtained are summarized in Table I. Introduction of electro-active groups enhanced the values of <α> in the order of CN<Br<CHO in the quater thiophene derivatives. Assuming the monotonic increase of <α> values between n=4 and n=8 of 3-hexyl thiophene oligomers, α, α'-substitution enhances effective conjugation length: CN- and CHO-substituted quater 3-hexyl oligomers have similar <α> values corresponding to n=5 and n=6 unsubstituted 3-hexyl thiophene oligomers, respectively.

TABLE I Linear polarizabilities for thiophene oligomers and derivatives.



	X	< α > ($10^{-23}cm^3$)
n=4	H	1.9
	Br	2.8
	CN	2.6
	CHO	3.1
n=8	H	5.0

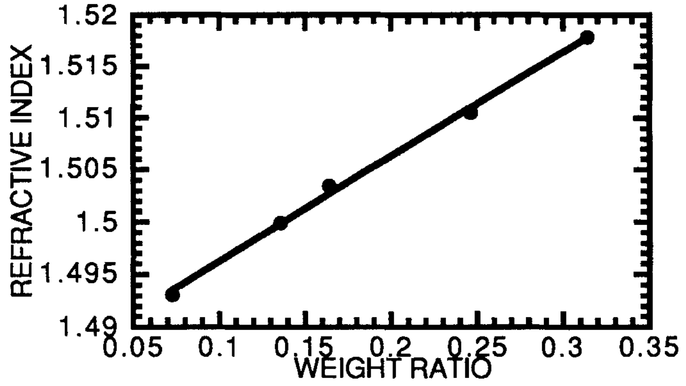


FIGURE 3 Concentration dependence of refractive indices at a wavelength of 632.8 nm for 4Th/PMMA films.

Third-order Nonlinear Optical Susceptibilities

The off-resonant third order optical susceptibility $\chi^{(3)}{}_{1111}(-3\omega;\ \omega,\omega,\omega)$ determined by third harmonic generation (THG) is directly related to $<\gamma>$ of the conjugated compound through local field factors f expressed in terms of the refractive indices n_ω and $n_{3\omega}$ as

$$\chi^{(3)}_{1111}(-3\omega;\omega,\omega,\omega)=Nf^{3\omega}f^{\omega}f^{\omega}f^{\omega}\langle\gamma\rangle(-3\omega;\omega,\omega,\omega) \qquad (2)$$

where N is the number of molecules per unit volume. Figure 4 shows the curve fitting of Maker fringes for typical samples of 4T and 6T thin films. The values of $\chi^{(3)}(-3\omega;\ \omega,\omega,\omega)$ for nT and nTh/PMMA with the same concentration series increase with increasing number of thiophene rings. From the concentration dependence (less than about 10 wt %) the values of $<\gamma>$ were obtained. Table II summarizes the $<\gamma>$ value. The enhancement of $<\gamma>$ value by introduction of α, α'-substitution was obtained and the similar enhancement of effective conjugation length to the linear polarizabilities was also observed: $<\gamma>$ values for CN- and CHO-substitution corresponds to those of n=5 and n=6 unsubstituted 3-hexyl thiophene oligomers, respectively. It should be noted that in the case of ThQ, THG was obtained under the resonant condition, and the huge enhancement of $<\gamma>$ values was observed. In conclusion, from optical absorption and linear polarizabilities results, the molecular planarity affected third-order nonlinear optical responses rater than the increase in the number of repeating conjugated units.

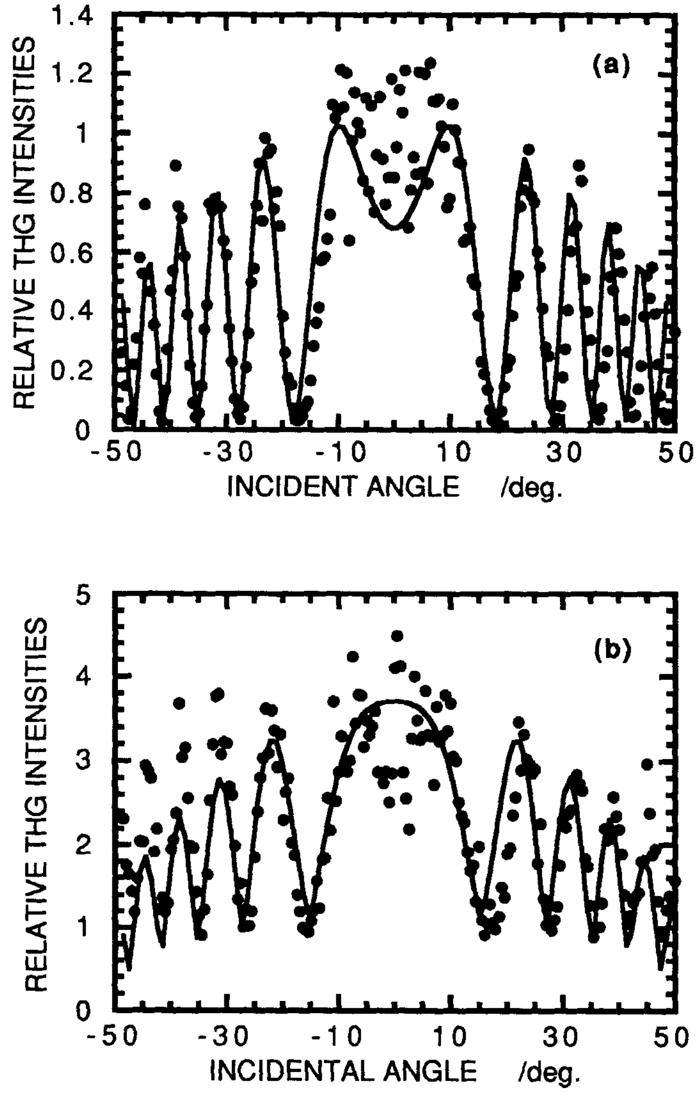
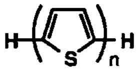
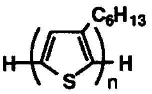
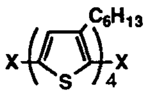


FIGURE 4 Typical Maker fringe patterns of 4T (a) and 6T (b) thin films.

TABLE II Nonlinear optical susceptibilities for thiophene oligomers and derivatives.

compound	n	$\chi^{(3)}$ (10^{-14}esu)	$<\gamma>$ (10^{-36}esu)
	4	7	
	6	60	
	8	350	
	4		68
	8		320
	X=Br		190
	X=CN		170
	X=CHO		300

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