Preparation and Nonlinear Optical Properties of a Series of Linear π-Conjugated Oligomers

（一次元π共役オリゴマーの合成と非線形光学的性質）

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Yoriko Sonoda

Contents

1

General Introduction

1.1 Nonlinear Optical (NLO) Materials

Nonlinear Optics is expected to play a major role in the technology of photonics. Examples of NLO phenomena that are potentially useful for this purpose are the ability to change the frequency of light and to amplify one source of light with another, switch it, or change its transmission characteristics through a medium, depending on its intensity.

Compared to the more traditional inorganic NLO materials, history of organic NLO materials is quite new. Organic materials are increasingly being recognized as the materials of the future because their molecular nature can be used to optimize molecular structure to maximize NLO properties. Other benefits of organic materials are fast response time, mechanical strength and high processability. From these relative merits, it is clear that organic materials are promising group of NLO materials [1–3].

1.2 Molecular Design of Organic Polymers for Third-order NLO materials

Polarization Response of Materials in an Intense Electric Field

When a medium is subjected to an intense electric field such as that due to a laser pulse, the polarization response of the material ΔP can be expressed in a power series of the field strength E

$$\Delta P = \chi^{(1)} E + \chi^{(2)} EE + \chi^{(3)} EEE + \ldots \qquad (1.2.1)$$

In the above equation the term $\chi^{(1)} E$ describes the linear polarization of the material. The coefficient $\chi^{(2)}$ relating to the polarization to the square of the field strength E is called the second-order nonlinear susceptibility of the medium. Its magnitude describes the strength of second-order NLO process. The coefficient $\chi^{(3)}$ is referred to as the third-order nonlinear susceptibility describing third-order process. Similarly, high-order terms describe the high-order processes. For most materials, the high-order effects are extremely difficult to observe.

Second- and Third-Harmonic Generation

Second-order NLO effects can be visualized as a three-wave mixing process where the waves exchange energy with one another through the intercession of the nonlinear medium. In the optical field $\boldsymbol{E} = A\cos\omega$, the nonlinear polarization $P^{(2)}$ is given as

$$\begin{aligned} P^{(2)} &= \chi^{(2)} A_1 \cos(\omega_1 t)\, A_2 \cos(\omega_2 t) \\ &= (1/2)\chi^{(2)} A_1 A_2 [\cos(\omega_1+\omega_2)t + \cos(\omega_1-\omega_2)t] \qquad (1.2.2) \end{aligned}$$

Equation 1.2.2 clearly shows the production of new frequency ω_3 by the interaction of waves at frequencies ω_1 and ω_2. The susceptibility $\chi^{(2)}$ to describe this process is

$$\chi^{(2)}(-\omega_3; \omega_1, \omega_2)$$

where $\omega_3 = \omega_1 \pm \omega_2$. In the case where $\omega_1 = \omega_2 = \omega$, Equation 1.2.2 is simplified to

$$P^{(2)} = (1/2)\chi^{(2)} A_1 A_2[\cos(2\omega)t+1] \qquad (1.2.3)$$

The first term of this equation shows one of the best known effects in nonlinear optics, second-harmonic generation (SHG). For SHG the susceptibility is $\chi^{(2)}(-2\omega; \omega, \omega)$.

Similarly, third-order NLO effects can be described as four-wave mixing process where waves at frequencies ω_1, ω_2, ω_3 interact to produce ω_4. This coefficient is represented as

$$\chi^{(3)}(-\omega_4; \omega_1, \omega_2, \omega_3).$$

In the case where $\omega_1 = \omega_2 = \omega_3 = \omega$, third-harmonic generation (THG), it becomes $\chi^{(3)}(-3\omega; \omega, \omega, \omega)$.

Microscopic Nonlinearity

In discussing NLO properties, the polarization of the molecule by the radiation field is often approximated as the creation of an induced dipole by an electric field. Under the weak polarization limit, the expression for the dipole moment Δp induced on a molecule by the local field E is

$$\Delta p = \alpha E + \beta EE + \gamma EEE + ... \qquad (1.2.4)$$

In the above equation, the coefficient α is the polarizability of the molecule with respect to the optical field E. The polarizability term describes the linear interaction with the optical field and accounts for linear absorption and reflection behavior of the molecule. The coefficients β and γ are called first and second hyperpolarizabilities (second and third microscopic nonlinearities) and constitute the molecular origin of the second- and third-order NLO interactions, respectively.

Free-electron Model

There have been several semiempirical approaches to calculate the third-order NLO properties of organic molecules. For a conceptual understanding of the third-order nonlinearity γ in linear conjugated polymers, the free-electron model [4] is often used because of its simplicity. The expression for γ obtained by this model is

$$\gamma = 256L^{10}/(45a_o^3\, e^2\, \pi^6\, N^5) \qquad (1.2.5)$$

In the above equation $a_o = \hbar^2/me^2$ is the atomic Bohr radius, $\hbar$ is the Planck constant, e and m are the charge and mass of an electron, respectively. $2L$ is the length of the one-dimensional box in which the π-electrons are confined and $2N$ is the total number of π-electrons in the conjugated double bonds; N is also the number of repeating units. Assuming $N \propto L$, equation 1.2.5 suggests that $\gamma \propto N^5$.

The above model has been extended to calculate the dependence of $\chi^{(3)}$ on the band gap of the conjugated polymer. The band gap is the energy gap between the highest occupied π orbital and the lowest unoccupied π^* orbital of the molecule, and can be determined from the absorption spectrum of the molecule. The derived expression [1] is

$$\chi_{zzzz}^{(3)} = (2^5\, \pi^2\, e^{10}/45)(1/\sigma)(a_o/d)^3\, (1/Eg^5) \qquad (1.2.6)$$

In this equation, d is the average C–C distance, σ is the cross-sectional area per chain and Eg is the energy band gap. Equation 1.2.6 predicts that $\chi^{(3)}$ component along the conjugated polymer chain direction ($\chi_{zzzz}^{(3)}$) shows an inverse dependence on the 6th-power of π–π^* band gap.

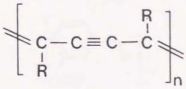
Structural Requirements for Third-order NLO Materials

Compared to the extensive amount of research on second-order NLO materials, the study of third-order NLO process has received relatively limited attention. Although the scope of synthesis and characterization of third-order NLO materials has considerably expanded recently, our theoretical understanding of third-order nonlinearity is very limited and guidelines for molecular structural requirements for enhancing the microscopic nonlinearity, γ, can be only crudely stated.

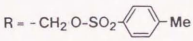
Large third-order optical nonlinearities are associated with π-electron systems. Since a polymeric backbone provides a structural framework for extensive π-electron delocalization, conjugated polymers have been the subject of intense interest for the study of third-order NLO processes. While earlier works focused mainly on the various polydiacetylenes (PDAs) [5–12], efforts have expanded to other classes of conjugated polymers recently [13–40]. Molecular structures and $\chi^{(3)}$ values of some selected examples are summarized in Table 1.2.1.

Among these polymers, poly(arylenevinylene)s are one of the most interesting classes of polymers from scientific and technological points of view, since they can easily be obtained as stable, high-quality films via a soluble precursor route. A value of $\chi^{(3)}$ for a thin film of poly(1,4-phenylenevinylene) (PPV) was estimated to be 5–10 x 10^{-12} esu [19]. The introduction of electron-donating alkoxy groups into the aromatic rings [23] or the replacement of phenylene with thienylene rings [30] reduced Eg of the polymer to enhance its NLO properties. Film stretching, which resulted in the sharpening and/or red-shift of the absorption, also improved the nonlinearity of PPV [20].

Table 1.2.1 Molecular structures and values of $\chi^{(3)}$ for some selected examples of conjugated polymers



PDA

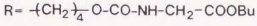


PTS

$\chi^{(3)} = 8.5 \times 10^{-10}$ esu [5]

Fundamental Wavelength: 1.89 μm

(Measurement Technique: THG)



Poly-4-BCMU

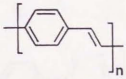
$\chi^{(3)} = 4.0 \times 10^{-10}$ esu [7]

0.605 μm (DFWM)

PA

$\chi^{(3)} = 1.3 \times 10^{-9}$ esu [13]

1.907 μm (THG)

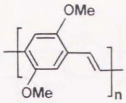


PPV

$\chi^{(3)} = 7.8 \times 10^{-12}$ esu [19]

1.85 μm (THG)

Table 1.2.1 (Continued)



DMPPV

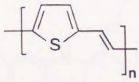
$\chi^{(3)} = 5.4 \times 10^{-11}$ esu [23]

1.85 μm (THG)

PT

$\chi^{(3)} = 4 \times 10^{-10}$ esu [28]

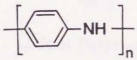
0.602 μm (DFWM)



PTV

$\chi^{(3)} = 3.2 \times 10^{-11}$ esu [30]

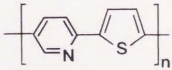
1.85 μm (THG)



PAn

$\chi^{(3)} = 9.0 \times 10^{-11}$ esu [32]

1.86 μm (THG)

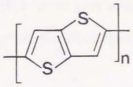


PTPY

$\chi^{(3)} = 1.5 \times 10^{-10}$ esu [34]

1.525 μm (THG)

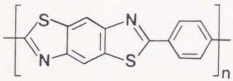
Table 1.2.1 (Continued)



PTT

$\chi^{(3)} = 2 \times 10^{-11}$ esu [35]

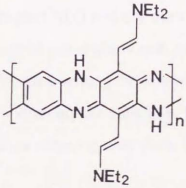
1.25–1.45 μm (THG)



PBT

$\chi^{(3)} = 5 \times 10^{-11}$ esu [36]

1.91 μm (THG)



Ladder Polymer

$\chi^{(3)} = 9.8 \times 10^{-10}$ esu [38]

0.532 μm (DFWM)

These results show that the NLO property of PPV can be enhanced by various chemical modifications which result in the decrease of Eg.

Poly(1,4-phenylenehexa-1,3,5-trienylene) (PPHT, Figure 1.2.2) is a polymer with an intermediate structure between polyacetylene (PA) and PPV. PPHT is expected

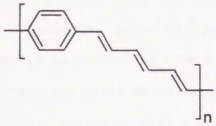


Figure 1.2.2 Structure of PPHT

to show higher NLO activity than PPV, because of its lower value of Eg due to the replacement of the vinylene with hexa-1,3,5-trienylene units. Although PA exhibits the highest $\chi^{(3)}$ value among the known conjugated polymers up to now [13-18], it is insoluble and extremely air sensitive. PPHT is expected to be more stable than PA as a consequence of having phenylene groups in the polymer main chain.

1.3 Measurements of Third-order Nonlinear Susceptibilities $\chi^{(3)}$ by Third-Harmonic Generation

The third-order NLO interactions produce a large number of phenomena, such as third-harmonic generation (THG), degenerate four-wave mixing (DFWM), electric-field induced second-harmonic generation, optical Kerr gate and self-focusing. Any of these phenomena can be used to obtain information on third-order optical nonlinearity. In this work, $\chi^{(3)}$ values were measured by the Maker fringe method of THG.

A typical experimental arrangement for THG is shown in Figure 1.3.1 [41]. For the THG measurement, a quartz substrate is generally taken as a reference. In this method, the path length of the sample (and the reference) is varied and third-harmonic

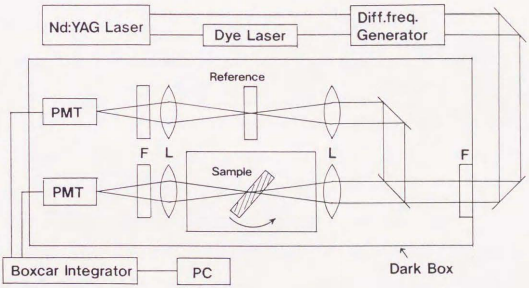


Figure 1.3.1 A typical experimental arrangement for THG

F : Optical Filter, L : Lens, PMT : Photomultiplier, PC : Personal Computer

signal is monitored as a function of the interaction length to obtain the fringes. The observed Maker fringe pattern is fitted using a computer program to obtain the co-

herence lengths for both the sample and the reference. The intensities of the third-harmonic signals for the sample and the reference for the same input intensity and the same interaction length are also determined from the experiment. The value of $\chi^{(3)}$ of the sample was obtained from Equation 5.1 (See General Experimental) [42].

1.4 Scope of This Thesis

Although there have been many reports on the third-order NLO properties of conjugated polymers, our microscopic understanding of optical nonlinearity is very limited. A more systematic study is needed in order to get such a fundamental understanding.

The purpose of this work is to clarify the relationship between the structures and third-order NLO properties for a series of linear π-conjugated oligomers whose structures can be clearly identified.

In Chapter 2, synthesis and characterization of all-*trans*-1,4-phenylenehexa-1,3,5-trienylene oligomers are described, and NLO properties of thin films of these oligomers are investigated. In Section 2.1, $\chi^{(3)}$ values of unsubstituted 1,4-phenylenehexa-1,3,5-trienylene oligomers are measured by the Maker fringe method of THG. Dependence of $\chi^{(3)}$ values on the degree of polymerization is studied. In Section 2.2.1, $\chi^{(3)}$ values of 1,4-phenylenehexa-1,3,5-trienylene oligomers with formyl end groups are reported. Effects of substitution with the formyl groups on the NLO properties are studied. In section 2.2.2, attempts to prepare a high-quality film of PPHT by the sulfonium salt pyrolysis are described. In Section 2.3, a value of $\chi^{(3)}$ for a thin film of a PPHT derivative bearing long alkyl side chains is reported.

In Chapter 3, synthesis and characterization of a new ring-substituted derivative of PPV with long alkyl side chains are described. A value of $\chi^{(3)}$ for a thin film of the polymer is measured and compared with that of the PPHT derivative described in Section 2.3. Effects of the introduction of the long side chains on the NLO properties of PPV is discussed.

In Chapter 4, the dependence of the measured $\chi^{(3)}$ values on Eg is clarified for the oligomers described in Chapters 2 and 3. The dependence obtained from the experiments is compared with that predicted by the free-electron model (Equation 1.2.6).

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2

Poly(1,4-phenylenehexa-1,3,5-trienylene) System

2.1 Synthesis and Characterization of the Dimer and Trimer of Poly(1,4-phenylenehexa-1,3,5-trienylene)

Introduction

There have been many theoretical studies on the chain-length dependence of the third-order NLO properties for conjugated polyenes [1-8]. The second hyperpolarizabilities γ of linear polyenes are theoretically predicted to increase rapidly with the increase in the chain-length, and then expected to attain saturation when the number of double bonds reaches about 20 [3,6,7].

Compared to a large number of theoretical studies, there have been only a few experimental studies to clarify the relationship between the chain-length and nonlinearity. In 1974, Hermann and Ducuing have reported a dramatic enhancement of γ with the increase in the chain-length for linear conjugated polyenes such as retinal and retinol [9]. Since this pioneering work, some systematic studies have been reported for conjugated compounds with well-defined structures [10-15]. For thiophene oligomers, the measured γ values in THF solution increased with the increase in the number of repeating unit by the hexamer (degree of polymerization DPn=1-6) [10] and saturated in the

range of DPn=6–10 [13].

This section describes the preparation and NLO properties of all-*trans*-1,4-bis(6-phenylhexa-1,3,5-trienyl)benzene (PHT2, Figure 2.1.1(b)) and 1,6-bis[4-(6-phenylhexa-1,3,5-trienyl)phenyl]hexa-1,3,5-triene] (PHT3, Figure 2.1.1(c)). Structures of these oligomers were confirmed by comparison of their IR spectra with that of the monomer, 1,6-diphenylhexa-1,3,5-triene (PHT1, Figure 2.1.1(a)). Values of $\chi^{(3)}$ for thin films of the obtained oligomers were measured by the Maker fringe method of THG.

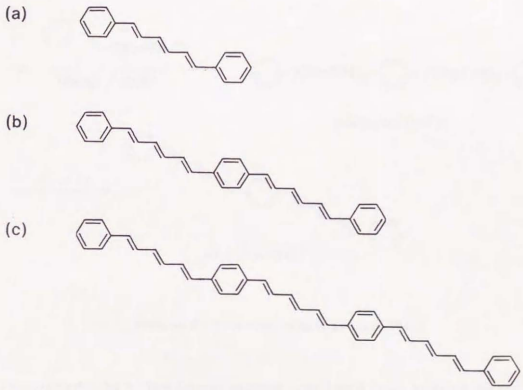


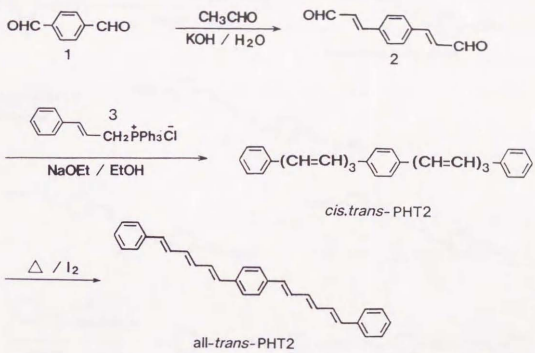
Figure 2.1.1 Structures of all-*trans*- (a)PHT1, (b)PHT2 and (c)PHT3

Results and Discussion

Preparation of PHT2

Although PHT2 has been synthesized previously by the Heck reaction [16], the yield was rather low and spectral characteristics of the compound are not known. In this

work, PHT2 was prepared from 1,4-phenylenediacrylaldehyde **2** and triphenylcinnamylphosphonium chloride **3**. The synthetic route is shown in Scheme 2.1.1. Aldehyde **2** was prepared by the aldol condensation between terephthalaldehyde **1** and acetaldehyde. The Wittig reaction was also carried out, yielding 24% of aldehyde **2** after reflux-

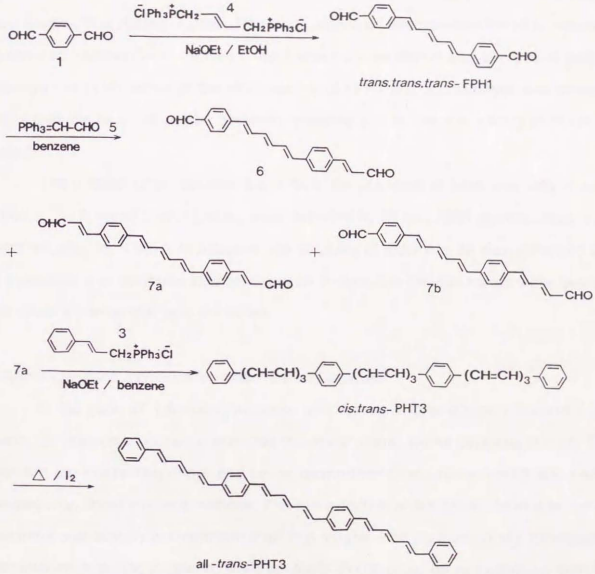


Scheme 2.1.1 Synthetic route to all-*trans*-PHT2

ing in benzene for 24 h. The former reaction was found more suitable for the preparation of aldehyde **2**, since the product was formed in higher yield under milder conditions. The Wittig reaction of compound **2** and the ylide prepared from salt **3** gave *cis*-containing PHT2 in high yield at room temperature. The ^{1}H NMR, IR and UV-vis spectra of the crude dimer indicated the presence of *cis*-bonds in the trienes. Both *trans*- and *cis*-double bonds are thus formed by the reaction.

Preparation of PHT3

The synthetic route to PHT3 is shown in Scheme 2.1.2. The Wittig aldehyde extension of 1,6-bis(4-formylphenyl)hexa-1,3,5-triene (FPH1) was carried out to obtain aldehyde **7a**. More than six different products were isolated by gel-permeation



Scheme 2.1.2 Synthetic route to all-*trans*-PHT3

chromatography (GPC). NMR spectroscopic analysis of the compounds clarified the structures of **6**, **7a** and **7b**. Some polymeric materials were also separated, whose NMR

spectra indicated the presence of a -CH=CH-CH=CH-CHO group formed by secondary reaction. A mixture of **7a** and **7b** was obtained after GPC separation, which could be further separated into each isomer by preparative TLC. The structures of **7a** and **7b** were established from their NMR and IR spectra. The UV-vis spectra of the two isomers were virtually identical, indicating that they had essentially the same conjugation lengths. The starting material FPH1 was recovered after reaction for 16 h. However, prolonged heating (24 h) caused undesirable polymerization and decreased yield of aldehyde **7a** (2 %). Although the aldol reaction of FPH1 and acetaldehyde was attempted, aldehyde **7a** could not be obtained, possibly due to the low affinity of FPH1 for water.

The reaction of compounds **3** and **7a** in the presence of base was very slow. In ethanol, unchanged formyl groups were detected by IR and NMR spectroscopy even after refluxing for 3 days. In benzene, the solubility of aldehyde **7a** was enhanced and the reaction was complete after refluxing for 2 days. *cis*-Double bonds were found in the crude trimer as well as in the dimer.

Thermal cis-trans *Isomerization under Iodine Catalysis*

In the case of 1,4-distyrylbenzene and 1,4-bis(4-phenylbuta-1,3-dienyl)benzene, *cis-trans* isomerization occurred thermally under iodine catalysis [17,18]. The present *cis*-containing dimer and trimer isomerized to all-*trans*-PHT2 and PHT3, respectively, under similar conditions. The isomerization of the crude dimer was carried out more successfully in chloroform than in *p*-xylene. The *cis,trans*-PHT2 appeared to decompose in boiling *p*-xylene, while all-*trans*-PHT2 could be recrystallized from the same solvent. The all-*trans* isomer may thus possibly be thermally more stable than the *cis*-containing product. The crude trimer also isomerized in boiling toluene or *p*-xylene. The IR spectrum of the resulting crystal indicated an all-*trans* structure shown as Figure 2.1.1(c). Although purification of all-*trans*-PHT3 was attempted, no solvent was found to be adequate for recrystallization.

^{1}H NMR Spectra

The NMR spectra of *cis,trans*-PHT2 and PHT3 were obtained in deuteriochloroform at room temperature. *cis*-Double bonds in these oligomers are expected to be in *trans,cis,trans* trienes, since the central double bonds of trienes are newly formed by the reactions. Therefore, NMR spectra of *trans,trans,trans*- and *trans,cis,trans*-PHT1 were measured for analysis of those of the oligomers. The two isomers of PHT1 gave the following spectra: *trans,trans,trans*-PHT1: $\delta(CDCl_3)$ 7.18–7.46 (10H, m, phenyl), 6.89 (2H, ddd, *J* 15.4, 7.0, 2.9, triene H_2, H_5), 6.60 (2H, d, *J* 15.6, triene H_1, H_6) and 6.53 (2H, dd, *J* 7.0, 3.1, triene H_3, H_4). *trans,cis,trans*-PHT1: $\delta(CDCl_3)$ 7.45–7.51 (4H, m, phenyl H_2, $H_{2'}$, H_6, $H_{6'}$), 7.38–7.45 (2H, m, triene, H_2, H_5), 7.30–7.38 (4H, m, phenyl H_3, $H_{3'}$, H_5, $H_{5'}$), 7.21–7.30 (2H, m, phenyl H_4, $H_{4'}$), 6.62 (2H, d, *J* 15.9, triene H_1, H_6) and 6.19–6.31 (2H, m, triene H_3, H_4). The multiplet at δ6.19–6.31 was found to be characteristic of *trans,cis,trans* trienes. In the spectra of *cis,trans*-PHT2 and PHT3, four multiplets were observed at δ7.10–7.52, 6.82–6.97, 6.50–6.67 and 6.21–6.28, and δ7.01–7.54, 6.83–6.95, 6.46–6.65 and 6.18–6.27, respectively. Of these signals, multiplets at δ6.2–6.3 showed the presence of *trans,cis,trans* trienes in the compounds.

All-*trans*-PHT2 and PHT3 were much less soluble than the corresponding *cis*-containing isomers. The NMR spectrum of neither all-*trans*-PHT2 nor PHT3 was obtained in deuteriochloroform. The solubility of all-*trans*-PHT2 in chloroform was 3–4 mg dm^{-3} at room temperature. All-*trans*-PHT3 was less soluble than the dimer.

IR Spectra

Figure 2.1.2 shows the IR spectra of all-*trans* isomers of (a)PHT1, (b)PHT2 and (c)PHT3. *cis,trans*-PHT2 and PHT3 showed peaks at 962, 1001, 963 and 999 cm^{-1}, respectively [Figure 2.1.2(b)' and (c)']. These are assignable to the C–H out-of-plane vibration of *cis*-containing trienes [19,20]. After isomerization, the peak at 960 cm^{-1}

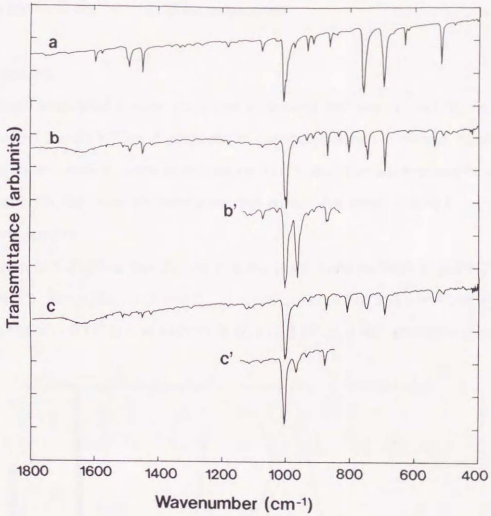


Figure 2.1.2 IR spectra of all-*trans*- (a)PHT1, (b)PHT2 and (c)PHT3 (KBr)

Two characteristic peaks of *cis,trans*-PHT2 and PHT3 are shown in (b') and (c'), respectively

completely disappeared and only a strong peak at 1000 cm^{-1} was observed. This peak at 1000 cm^{-1} is attributed to the C-H out-of-plane vibrations which are characteristic of all-*trans* trienes [19,20]. The peaks at 690 and 745 cm^{-1} are due to the C-H out-of-plane vibration of monosubstituted benzene rings. The spectra of PHT2 and PHT3 showed peaks of 1,4-disubstituted benzene rings at about 800 cm^{-1}. Broad absorptions due to C=C stretching vibration of polyenes were observed at around 1635 cm^{-1} in the

spectra of PHT2 and PHT3. All-*trans*-PHT1, PHT2 and PHT3 showed peaks at 3013 cm^{-1}, which were assignable to the C-H stretching vibrations of =CH-. The origin of the peaks at 860-870 cm^{-1} could not be determined.

UV-vis Spectra

Small absorptions were observed at around 340 nm in the UV-vis spectra of *cis,trans*-PHT2 and PHT3 and attributed to *cis* double bonds in trienes. Similar absorptions, called '*cis*-peaks', were observed for PHT1 and 1,4-bis(4-phenylbuta-1,3-dienyl)benzene [21,22]. After isomerization, the dimer and trimer showed no '*cis*-peak' in the UV-vis spectra.

Figure 2.1.3 shows the UV-vis spectra of all-*trans* isomers of (a)PHT1, (b)PHT2 and (c)PHT3. Absorption maxima (λ_{max}) were observed at 358 nm (3.46 eV) (PHT1), 419 nm (2.96 eV) (PHT2) and 443 nm (2.80 eV) (PHT3), which shifted to a longer

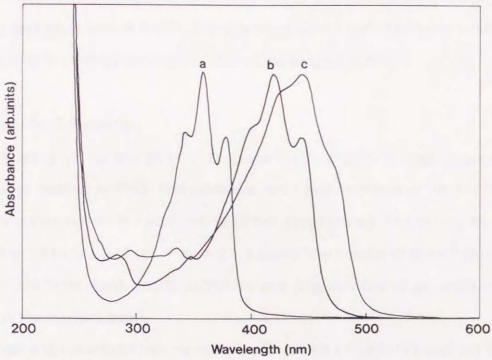


Figure 2.1.3 UV-vis spectra of all-*trans*- (a)PHT1, (b)PHT2 and (c)PHT3 ($CHCl_3$)

wavelength with the increase in the degree of polymerization (DPn). 1,4-Phenylenevinylene oligomers show their λ_{max} at 310 nm (DPn=1), 355 nm (DPn=2) and 385 nm (DPn=3) in chloroform [23]. In the case of 1,4-phenylenebuta-1,3-dienylene oligomers, λ_{max} values are 334 and 389 nm for 1,4-diphenylbuta-1,3-diene (DPn=1) and 1,4-bis(4-phenylbuta-1,3-dienyl)benzene (DPn=2), respectively [21,24] These spectral data indicate that the shifts in the λ_{max} of PHT1, PHT2 and PHT3 can be attributed to the increase in conjugation length.

In the spectrum of all-*trans*-PHT2, λ_{max} was found at 421 nm in benzene. Diphenyldodecahexaene, having the same number of double bonds as PHT2, showed λ_{max} at the same wavelength (420 nm) in benzene [24]. It thus follows that middle phenylene rings do not largely interrupt the conjugation system in all-*trans*-PHT2. Similar findings were observed for diphenyloctatetraene (λ_{max}=384 nm [24]) and 1,4-bis(4-phenylbuta-1,3-dienyl)benzene (λ_{max}=389 nm [21]).

Vibrational fine structures were observed in the spectra of all-*trans*-PHT2 and PHT3 as well as in that of PHT1. The spacings were 1300-1400 cm^{-1}, which should correspond to the energy gaps of vibration in the excited states.

Third-order NLO Properties

Values of $\chi^{(3)}$ for thin films of all-*trans*-PHT1 and PHT2 were measured by the Maker fringe method of THG. The refractive index and thickness of the PHT1 film used in the measurement were 1.493 and 1670 nm, respectively. The values for the film of PHT2 were 1.715 and 240 nm. Figure 2.1.4 shows the measured third-harmonic intensities for (a)a 1mm-thick quartz substrate and (b)a thin film of all-*trans*-PHT2 as a function of the incident angle.

Figure 2.1.5 shows the measured $\chi^{(3)}$ values of (a)PHT1 and (b) PHT2 as a function of the fundamental light wavelength. PHT1 showed a similar $\chi^{(3)}$ value at each wavelength, while the $\chi^{(3)}$ values of PHT2 increased as the wavelength decreased.

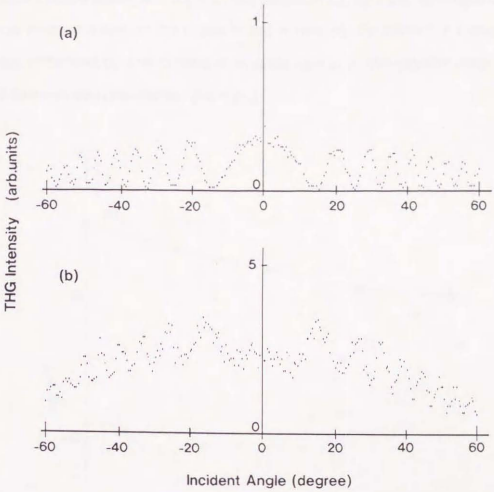


Figure 2.1.4 Measured third-harmonic intensities at 1.62 μm as a function of the incident light angle for (a)a quartz substrate of 1-mm thickness and (b)an all-*trans*-PHT2 thin film of 240 nm thickness

The effect of resonance enhancement on third-order nonlinearity is theoretically predicted [25,26]. Using the sum-over-states (SOS) approach [25], the second hyper-polarizability $\gamma(-3\omega;\omega,\omega,\omega)$ responsible for THG is expressed as

$$\gamma(-3\omega;\omega,\omega,\omega) = p\sum_{n_1 n_2 n_3} \frac{e^4}{4\hbar^3} \frac{r_{gn_3} r_{n_1 n_2} r_{n_2 n_1} r_{n_1 g}}{(\omega-\omega_{n_1 g})(2\omega-\omega_{n_2 g})(3\omega-\omega_{n_3 g})} \qquad (2.1.1)$$

In this expression, ω is the frequency of the electric field, g and n refer to the ground

and various excited states with $\omega_{ng} = \omega_n - \omega_g$, respectively, and $er_{nn'}$ corresponds a transition dipole moment between the states n and n' ($n \neq n'$). Equation 2.1.1 shows that γ is resonance enhanced by one-photon resonance ($\omega = \omega_{ng}$), two-photon resonance ($2\omega = \omega_{ng}$) and three-photon resonance ($3\omega = \omega_{ng}$).

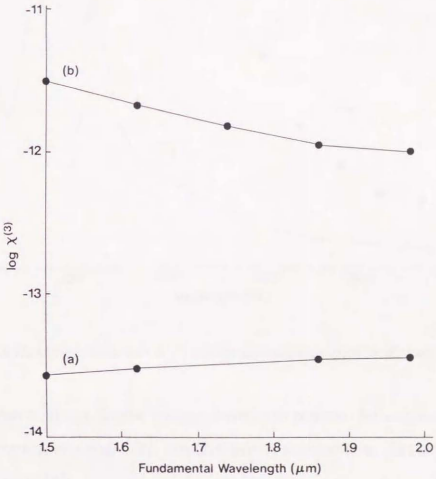


Figure 2.1.5 Measured $\chi^{(3)}$ values for thin films of all-*trans*- (a)PHT1 and (b)PHT2 as a function of the fundamental light wavelength

Figure 2.1.6 shows wavelength dispersion of $\chi^{(3)}$ and the absorption spectrum of the PHT2 film. This clearly shows that the observed increase in $\chi^{(3)}$ values at shorter wavelength is attributed to the resonance effect corresponding to the three-photon absorption. This means that a $\chi^{(3)}$ value of PHT2 is expected to be higher at a shorter-

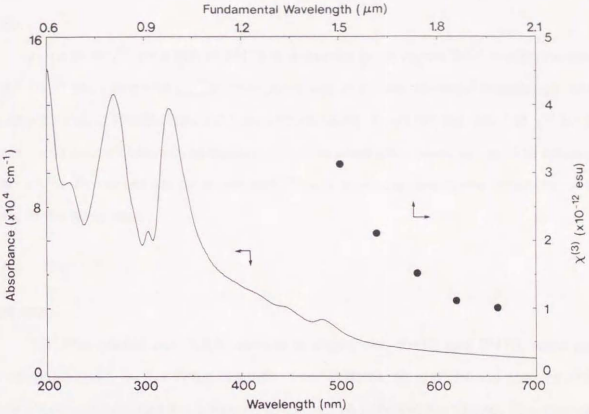


Figure 2.1.6 Wavelength dispersion of $\chi^{(3)}$ and the absorption spectrum for all-*trans*-PHT2 film

wavelength than 1.50 μm. Similar findings have been reported for polydiacetylene [27], poly(2,5-thienylenevinylene) [28], poly(1,4-phenylenevinylene) [29] and its 2,5-dimethoxy derivative [30].

Values of $\chi^{(3)}$ for all-*trans*-PHT1 and PHT2 at fundamental wavelength 1.98 μm (non-resonant region) were estimated to be 3.6 x 10^{-14} and 1.0 x 10^{-12} esu, respectively. The $\chi^{(3)}$ value of PHT1 is as the same order as that of a quartz substrate (1 x 10^{-14} esu [31]), showing that the monomer has very little NLO optical activity. The $\chi^{(3)}$ value of PHT2 is about 30 times higher than that of PHT1. The band gap energies (Eg) of PHT1 and PHT2 determined from λ_{max} in chloroform were 3.46 and 2.96 eV, respectively. The value of Eg for PHT2 is thus smaller than that for PHT1 by 0.50 eV, due to the extended

π-conjugation system. Since a value of $\chi^{(3)}$ shows a strong dependence on Eg (Chapter 1, Equation 1.2.6), the higher value of $\chi^{(3)}$ for PHT2 can be attributed to its smaller value of Eg.

A value of $\chi^{(3)}$ for a film of PHT3 is expected to be higher than that of the dimer (1.0×10^{-12} esu), since its λ_{max} in chloroform was observed at longer wavelength compared with that of PHT2 (Figure 2.1.3). Unfortunately, however, the value of $\chi^{(3)}$ for the trimer could not be obtained, because neither the absorption spectrum nor the refractive index of the film could not be measured. This is probably due to the instability of the trimer in the solid state.

Summary

1,4-Phenylenehexa-1,3,5-trienylene oligomers, PHT2 and PHT3, were prepared respectively by the Wittig reaction. The ^{1}H NMR, IR and UV-vis spectra of the crude oligomers indicated the presence of *cis* double bonds in the trienes. The *cis-trans* isomerization of these oligomers was carried out by heating the *cis*-containing crude product in an appropriate solvent under iodine catalysis. The structures of PHT2 and PHT3 were confirmed by comparison of their IR spectra with that of PHT1. The absorption maximum in chloroform was observed at longer wavelength as the number of repeating unit increased, indicating that the conjugation length increased successfully in this system.

Values of $\chi^{(3)}$ for thin films of PHT1 and PHT2 were estimated by THG measurements to be 3.6×10^{-14} and 1.0×10^{-12} esu (non-resonant region), respectively. The $\chi^{(3)}$ value of PHT2 was found to be about 30 times higher than that of PHT1. This is attributed to a smaller Eg of the dimer due to the extended π-conjugated system. The $\chi^{(3)}$ value of PHT3 could not be obtained, because of the instability of the film in air.

Experimental

Terephthalaldehyde **1** was purchased from Aldrich and recrystallized from water before use. Triphenylcinnamylphosphonium chloride **3** and *trans*-1,4-bis(triphenyl phosphonio)-2-butene dichloride **4** were prepared according to the literature [18]. (Triphenylphosphoranylidene)acetaldehyde **5** was obtained from Aldrich and used without further purification. Isomers of *trans,trans,trans*- and *trans,cis,trans*-PHT1 were prepared according to the literature [21].

1,4-Phenylene-diacrylaldehyde 2

(a)Aldol condensation

Aldehyde **2** was prepared according to the literature [32]. Yield 42 % (lit.[32] 49 %). M.p. 159-162 °C (lit.[32] 162.5-164 °C); $\delta(CDCl_3)$ 9.75 (2H, d, *J* 7.7), 7.64 (4H, s), 7.49 (2H, d, *J* 16.1), 6.77 (2H, dd, *J* 16.1, 7.7); ν_{max}(KBr)/cm^{-1} 1666s, 1621m, 1421m, 1394w, 1298m, 1252w, 1129s, 1014w, 978s, 799s, 582w and 525w.

(b) Wittig condensation

A solution of compounds **1** (1.0 g, 7.5 mmol) and **5** (4.5 g, 15 mmol) in benzene (95 cm^3) was heated at reflux for 24 h under a nitrogen atmosphere. Water was added to the reaction mixture and the products were extracted with diethyl ether. Evaporation of the extract gave a brown oil, which crystallized from ethanol in water (60 %, 50 cm^3) to afford dialdehyde **2** (0.33 g, 24 %). The NMR spectrum of the product was identical with that of aldehyde **2** obtained by procedure *(a)*.

cis-Containing-1,4-bis(6-phenylhexa-1,3,5-trienyl)benzene *cis,trans*-PHT2

To a suspension of aldehyde **2** (0.50 g, 2.7 mmol) and salt **3** (2.5 g, 5.9 mmol) in absolute ethanol (30 cm^3) was added a solution of sodium ethoxide (0.25 mol dm^{-3}, 24 cm^3) over a period of 30 min under a nitrogen atmosphere. After the suspension had been stirred in the dark for 3 days, ethanol in water (60 %, 120 cm^3) was added and the

mixture was stirred for 10 min. The resulting precipitate was filtered and washed with water (50 cm^3) and absolute ethanol (50 cm^3). The crude 1,4-bis(6-phenylhexa-1,3,5-trienyl)benzene (0.93 g, 90 %) was obtained as yellow crystals; ν_{max}(KBr)/cm^{-1} 3014m, 1591w, 1508w, 1490m, 1447m, 1073w, 1001s, 962s, 873m, 803w, 783w, 748s, 691s, 537w and 517m.

All-*trans*-1,4-bis(6-phenylhexa-1,3,5-trienyl)benzene all-*trans*-PHT2

A solution of *cis,trans*-PHT2 (20 mg) in chloroform (100 cm^3) was heated at reflux for 15 h in the dark with a trace of iodine. After evaporation of the solvent under reduced pressure, the residue was recrystallized from *p*-xylene (15 cm^3) to give all-*trans*-PHT2 as bright orange leaflets (8 mg); m.p. 257-262 °C (Found: C,92.78; H,6.77; M^+,386.2022. Calc. for $C_{30}H_{26}$: C,93.22; H,6.78 %; *M*, 386.2035); ν_{max}(KBr)/cm^{-1} 3013w, 1636w, 1486w, 1446w, 996s, 933w, 913w, 868m, 833w, 802m, 745m, 691s, 537m and 509w; λ_{max}($CHCl_3$)/nm 419 (ε=8.0x10^4).

1,6-Bis(4-formylphenyl)hexa-1,3,5-triene FPH1

To a solution of aldehyde **1** (2.0 g, 15 mmol) and salt **4** (4.7 g, 7.2 mmol) in absolute ethanol (250 cm^3) was added dropwise a sodium ethoxide solution (30 mmol, 50 cm^3) under an argon atmosphere over a period of 30 min. After the mixture had been stirred for 2 days in the dark at room temperature, the resulting yellow-orange precipitate was collected by filtration, washed with ethanol, and dried *in vacuo* at 55 °C. FPH1 (0.82 g, 38 %) was obtained as a yellow-orange solid. The product was recrystallized from acetonitrile and further purified by GPC (chloroform). M.p. 212-214 °C (lit.[33] 207-208 °C) (Found: M^+,288.1136. Calc.for $C_{20}H_{16}O_2$: *M*, 288.1149); δ_H($CDCl_3$) 9.98 (2H, s), 7.84 (4H, d, *J* 8.4), 7.57 (4H, d, *J* 8.2), 7.05 (2H, ddd, *J* 15.4, 7.0, 2.8), 6.69 (2H, d, *J* 15.6) and 6.63 (2H, dd, *J* 7.0, 2.8); ν_{max}(KBr)/cm^{-1} 1689s, 1601m, 1568m, 1400w, 1305w, 1217m, 1162m, 1110w, 997s, 876w, 814m and 525w; λ_{max}($CHCl_3$)/nm 418(ε=7.0x10^4), 397(ε=8.7x10^4) and 376(ε=6.2x10^4).

Reaction of compound 5 and FPH1

A solution of FPH1 (0.20 g, 0.69 mmol) and (triphenylphosphoranylidene)acetaldehyde **5** (0.43 g, 1.4 mmol) was heated at reflux for 16 h in benzene (10 cm^3). After the reaction mixture had been cooled to room temperature, water (100 cm^3) was added to it. The products were extracted with dichloromethane (200 cm^3) and the extract was evaporated under reduced pressure. To the residue was added ethanol in water (60%, 40 cm^3) to precipitate a bright yellow solid (0.22 g).

The crude products were subjected to GPC analysis. Aldehyde **6** (22 mg, 10 %), the isomeric mixture of aldehydes **7a** and **7b**, and some polymeric materials (85 mg, 39 % w/w) were obtained. The starting material FPH1 was recovered (34 mg, 17 %). The mixture of aldehydes **7a** and **7b** was separated into each isomer [**7a**(53 mg, 22 %), **7b**(23 mg, 10 %)] by preparative TLC (dichloromethane).

1-(4-Formylphenyl)-6-[4'-(2-formylvinyl)phenyl]hexa-1,3,5-triene 6

M.p. 198.5-200 °C. (Found: M^+,314.1286. Calc.for $C_{22}H_{18}O_2$: *M*,314.1307); $\delta_H(CDCl_3)$ 9.98 (1H, s), 9.71 (1H, d, *J* 7.7), 7.84 (2H, d, *J* 8.2), 7.56 (2H, d, *J* 8.2), 7.55 (2H, d, *J* 8.2), 7.48 (2H, d, *J* 8.4), 7.46 (1H, d, *J* 16.1), 6.94-7.10 (2H, m), 6.72 (1H, dd, *J* 15.8, 7.9) and 6.57-6.71 (4H, m); $\nu_{max}(KBr)/cm^{-1}$ 3016w, 1691s, 1685sh, 1666s, 1621w, 1597m, 1562m, 1420w, 1394w, 1295w, 1213m, 1160m, 1132s, 1106w, 998s, 975m, 926w, 872w, 806s, 797sh, 662w, 588w and 526m; $\lambda_{max}(CHCl_3)$/nm 411 (ε=7.9x10^4).

1,6-Bis[4-(2-formylvinyl)phenyl]hexa-1,3,5-triene 7a

M.p. 218-219 °C (Found: M^+, 340.1458. Calc.for $C_{24}H_{20}O_2$: 340.1463); δ_H ($CDCl_3$) 9.71 (2H, d, *J* 7.7), 7.54 (4H, d, *J* 8.2), 7.48 (4H, d, *J* 8.4), 7.45 (2H, d,*J* 16.1), 6.99 (2H, ddd, *J* 15.4, 6.9, 3.0), 6.72 (2H, dd, *J* 16.1, 7.9), 6.64 (2H, d, *J* 15.6) and 6.60

(2H, dd, *J* 7.3, 3.0); ν_{max}(KBr)/cm^{-1} 3017w, 1692s, 1670sh, 1621s, 1594s, 1553w, 1507w, 1421m, 1296m, 1255w, 1127s, 1107m, 1009s, 1002sh, 967s, 879m, 804s, 585w and 536m; λ_{max}($CHCl_3$)/nm 424 (ε=6.9x10^4).

1-[4-(4-Formyl-1,3-butadienyl)phenyl]-6-(4'-formylphenyl)hexa-1,3,5-triene 7b

M.p. 214-216 °C (Found: M$^+$, 340.1458. Calc.for $C_{24}H_{20}O_2$: *M*, 340.1463); δ_H(CD_2Cl_2) 9.89 (1H, s), 9.54 (1H, d, *J* 7.9), 7.76 (2H, d, *J* 8.2), 7.52 (2H, d, *J* 7.9), 7.43 (2H, d, *J* 6.9), 7.39 (2H, d, *J* 8.9), 7.23 (1H, ddd, *J* 15.0, 7.6, 2.8), 6.85-7.10 (4H, m), 6.51-6.70 (4H, m) and 6.18 (1H, dd, *J* 15.0, 8.3); ν_{max}(KBr)/cm^{-1} 3018w, 1691s, 1669s, 1618s, 1593s, 1561w, 1457w, 1396m, 1301w, 1261w, 1212m, 1162s, 1153s, 1116s, 998s, 987s, 871m, 822w, 806m, 585w and 531w; λ_{max}($CHCl_3$)/nm 423 (ε=3.4x10^4).

***cis*-Containing-1,6-bis[4-(6-phenyl-1,3,5-hexatrienyl)phenyl]hexa-1,3,5-triene *cis,trans*-PHT3**

A solution of sodium ethoxide (0.30 mol dm^{-3}; 1.1 cm^3) was added to one of aldehyde **7a** (50 mg, 0.15 mmol) and salt **3** (134 mg, 0.32 mmol) in benzene (14 cm^3). This solution was heated at reflux in the dark for 2 days, and then ethanol in water (60 %, 15 cm^3) was added to crystallize the crude trimer. The resulting red crystals were filtered and dried under reduced pressure. Yield 22 mg (28 %); ν_{max}(KBr)/cm^{-1} 3014w, 1636w, 1508w, 1490w, 1457w, 1447w, 1420w, 1110w, 1073w, 999s, 963m, 930w, 873m, 809m, 745s, 691s, 541m and 511w.

All-*trans*-1,6-bis[4-(6-phenyl-1,3,5-hexatrienyl)phenyl]hexa-1,3,5-triene all-*trans*-PHT3

A solution of *cis,trans*-PHT3 in toluene or *p*-xylene was heated at reflux for 1.5 h with a trace of iodine. The red crystals were collected, washed with absolute ethanol, and dried under reduced pressure. M.p. >250 °C(decomp.) (Found: M$^+$, 540.2803.

Calc.for $C_{42}H_{36}$: *M*, 540.2817); ν_{max}(KBr)/cm^{-1} 3013w, 1635w, 1508w, 1488w, 1457w, 1446w, 1121w, 1109w, 1072w, 1000s, 930w, 872m, 807m, 747m, 691m, 537m and 509w; λ_{max}($CHCl_3$)/nm 443. The molar extinction coefficient could not be determined due to the low solubility.

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2.2 Synthesis and Characterization of Poly(1,4-phenylenehexa-1,3,5-trienylene)

2.2.1. Wittig Reaction

Introduction

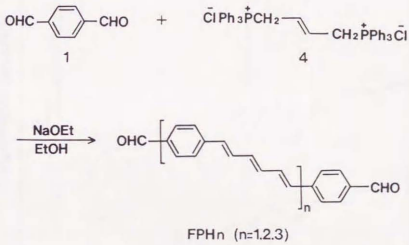
In the previous section, synthesis and characterization of the dimer (PHT2) and trimer (PHT3) of PPHT have been described. These oligomers, although sparingly soluble in common organic solvents, could be clearly identified by IR spectroscopy. The absorption maxima in chloroform were observed at longer wavelengths as the number of repeating unit increased, indicating the elongation of the conjugation length. A value of $\chi^{(3)}$ for a thin film of the dimer was estimated to be 1.0×10^{-12} esu (non-resonant region), which was about 30 times higher than that for the monomer (PHT1). This is derived from the fact that the energy band gap of PHT2 was smaller than that of PHT1 by 0.50 eV.

In order to gain a deeper insight into the relationship between the degree of polymerization (DPn) and third-order NLO properties in this system, it is desirable to obtain a 1,4-phenylenehexa-1,3,5-trienylene oligomer with higher molecular weight. This section describes the Wittig reaction of terephthalaldehyde **1** and the ylide from *trans*-1,4-bis(triphenylphosphonio)-2-butene dichloride **4**. Values of $\chi^{(3)}$ for thin films of the obtained compounds were measured by the Maker fringe method of THG.

Results and Discussion

*The Wittig Reaction of Terephthalaldehyde **1** and the Ylide from* trans-*1,4-Bis(triphenylphosphonio)-2-butene Dichloride **4***

The reaction of aldehyde **1** and the ylide from salt **4** gave a mixture of 1,4-phenylenehexa-1,3,5-trienylene oligomers with formyl end groups (FPHn) as an orange-red precipitate in low yield (Scheme 2.2.1). Methanol, 1-propanol, dichloromethane or chloroform as a solvent did not improve the yield. Reactions at elevated temperatures gave only a trace of the oligomers. NMR spectrum of a crude product showed the presence of a large amount of ethoxy groups. A bis-phosphonium salt, when treated with base, occasionally undergoes Hoffmann elimination with the formation of triphenylphosphine and a mono-phosphonium salt [1-3]. The low yield of the oligomers can therefore be attributed to the decomposition of salt **4** into triphenylbuta-1,3-dienylphosphonium chloride with the elimination of triphenylphosphine. The resulting mono-phosphonium salt possibly reacted with ethoxide ions to give compounds having ethoxy groups, which were found in the crude product.



Scheme 2.2.1 Synthesis of FPHn by the Wittig reaction

The mixture of FPHn oligomers was partially soluble in chloroform but only slightly soluble in other common organic solvents such as benzene, ether and acetone. Degree of polymerization for the chloroform-soluble part of the mixture of the oligomers was shown to be DPn < 10 by gel-permeation chromatography (GPC) (polystyrene

standard). The monomer (FPH1), dimer (FPH2) and trimer (FPH3) could be isolated from the oligomeric mixture. The degree of polymerization for each oligomer was confirmed by ^{1}H NMR peak integrals and high-resolution mass spectroscopy. Oligomers with DPn > 3 could not be isolated by GPC.

IR Spectra

Figure 2.2.1 shows the IR spectra of (a)FPH1, (b)FPH2 and (c)FPH3. The strong absorption observed at 1690 cm^{-1} in each spectrum was attributed to C=O stretching

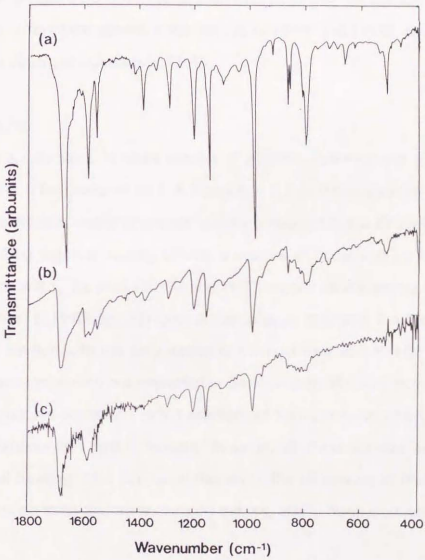


Figure 2.2.1 IR spectra of (a)FPH1, (b)FPH2 and (c)FPH3 (KBr)

vibration of aldehydes. This suggested that the end groups of these oligomers were -CHO. The sharp peaks at 998 cm^{-1} are assigned to the C-H out-of-plane bending vibration of double bonds, which are characteristic of all-*trans* trienes [4,5]. The absorptions at 800-820 cm^{-1} are due to the C-H out-of-plane bending vibration of the 1,4-disubstituted benzene ring. Corresponding absorptions due to all-*trans* trienes and aromatic rings were observed at almost the same positions in the spectra of all-*trans*-PHT1, PHT2 and PHT3 (Figure 2.1.2). The strong peaks at 1600 cm^{-1} can be assigned to the C=C stretching vibration of trienes [4,5]. Weak absorptions due to methylene and/or methyl groups were observed at 2921 and 2850 cm^{-1} in the spectrum of FPH3. These peaks, which were absent in the spectra of FPH1 and FPH2, showed the presence of some structural disorders in FPH3.

^{1}H NMR Spectra

Figure 2.2.2 shows ^{1}H NMR spectra of (a)FPH1, (b)FPH2 and (c)FPH3 in deuteriochloroform. The peaks at δ6.2-6.7 and 6.7-7.1 in these spectra are due to the hexatriene moiety in all-*trans* structures, which correspond to the IR peak at 998 cm^{-1}.

The Wittig reaction usually affords a mixture of *trans* and *cis* isomers [6]. As shown in Section 2.1, the crude PHT2 and PHT3 contained *cis* double bonds, and the all-*trans* isomers of PHT2 and PHT3 could be obtained only after the thermal treatment under iodine catalysis. In the preparation of FPH1, FPH2 and FPH3, *trans,trans,cis* and/or *cis,trans,cis* trienes are expected to be formed in addition to *trans,trans,trans* trienes, since double bonds at 1 and 3 positions of the trienes are newly formed by the reaction of compounds **1** and **4**. Actually, however, all-*trans* isomers were mainly obtained without heating. This can be attributed to the difference in thermal stabilities between *trans,cis,trans* and *trans,trans,cis* trienes, and is discussed later in this thesis (Section 2.3).

Peaks due to the aldehyde protons were observed at δ10, but there was no

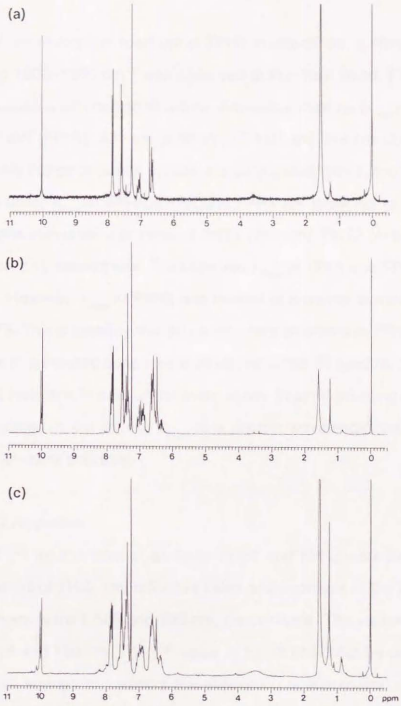


Figure 2.2.2 ^{1}H NMR spectra of (a)FPH1, (b)FPH2 and (c)FPH3 ($CDCl_3$)

peak due to the methylenes of $-CH_2\overset{+}{P}Ph_3\bar{C}l$ in the region of δ4.0–5.0. This showed that $-CH_2\overset{+}{P}Ph_3\bar{C}l$ end groups derived from salt **4** were absent in these oligomers.

UV-vis Spectra

In the UV-vis absorption spectrum of FPH1 in chloroform, a vibrational structure with the spacing 1200-1300 cm^{-1} was observed in the main band. FPH2 and FPH3 gave broad absorptions with no fine structure. Absorption maxima (λ_{max}) were observed at 397 nm (3.12 eV) (FPH1), 431 nm (2.88 eV) (FPH2) and 413 nm (3.00 eV) (FPH3). Since C=O double bonds of formyl groups are conjugated with 1,4-phenylenehexa-1,3,5-trienylene units, λ_{max} of FPH1, FPH2 and FPH3 are expected to be observed at longer wavelengths compared with those of PHT1 (358 nm), PHT2 (419 nm) and PHT3 (442 nm) (Section 2.1), respectively. The observed λ_{max} of FPH1 and FPH2 agreed with this expectation. However, λ_{max} of FPH3 was located at a shorter wavelength by 30 nm than that of PHT3. This is possibly due to the structural disorders in FPH3, because the small peaks due to saturated bonds were observed in the IR spectra. Such structural disorders would lead to a torsion of the main chain, thus interrupting its conjugation system. This resulted in the shift of λ_{max} to a shorter wavelength than expected for FPH3 with pure all-*trans* structure.

Third-order NLO Properties

Values of $\chi^{(3)}$ for thin films of all-*trans*-FPH1 and FPH2 were measured by the Maker fringe method of THG. The refractive index and thickness of the FPH1 film used in the measurement were 1.528 and 335 nm, respectively. The values for the film of FPH2 were 1.618 and 160 nm. The $\chi^{(3)}$ value of FPH3 could not be determined, because a good film enough to measure the absorption spectrum and refractive index could not be obtained. This is probably due to the instability of the trimer in the solid state.

Figure 2.2.3 shows the measured third-harmonic intensities for (a)a quartz substrate and (b)a thin film of FPH2 as a function of the incident angle. Figure 2.2.4 shows the measured $\chi^{(3)}$ values of (a)FPH1 and (b)FPH2 as a function of the fundamental light

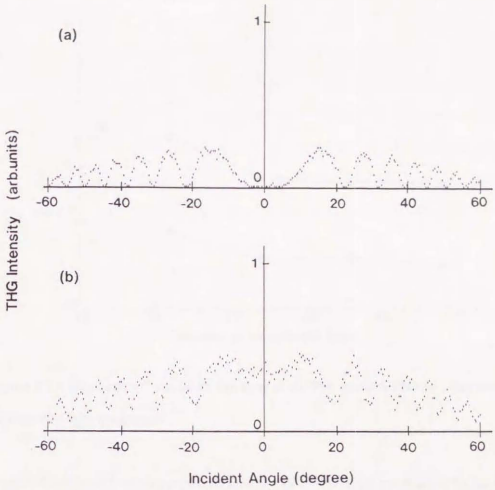


Figure 2.2.3 Measured third-harmonic intensities at 1.86 μm as a function of the incident angle for (a)a quartz substrate of 1-mm thickness and (b)a FPH2 thin film of 160 nm thickness

wavelength. Similar to the case of PHT2, the near-resonant effect due to three-photon absorption was observed for FPH2. The measured $\chi^{(3)}$ value of FPH1 was 2.0 x 10^{-13} esu at fundamental wavelength 1.98 μm (non-resonant region), which was about six times higher than that of PHT1. The energy band gap (Eg) of FPH1 determined from λ_{max} in chloroform was 3.12 eV, which was smaller than that of PHT1 by 0.34 eV. This is clearly due to the extension of conjugated length as a result of introduction of the formyl groups. The higher $\chi^{(3)}$ value of FPH1 can therefore be attributed to its smaller value of Eg than that of PHT1. From the Finite Field semiempirical Austin Model 1

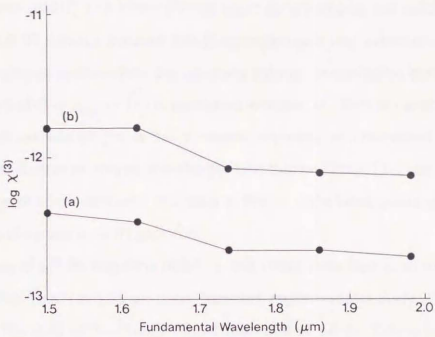


Figure 2.2.4 Measured $\chi^{(3)}$ values for thin films of (a)FPH1 and (b)FPH2 as a function of the fundamental light wavelength

(AM1) calculation, second hyperpolarizability γ of FPH1 was evaluated to be 422 x 10^{-36} esu, which was 1.5 times higher than the calculated value of PHT1 [7]. The present experimental results show that the observed substitution effect of the formyl group on $\chi^{(3)}$ is somewhat larger than the effect on γ which predicted by the AM1 calculation.

A $\chi^{(3)}$ value of FPH2 was estimated to be 7.4 x 10^{-13} esu at 1.98 μm (non-resonant region). This was 3-4 times higher than that of FPH1, corresponding to the lower value of Eg for FPH2 due to the extended π-delocalization.

Summary

The Wittig reaction of aldehyde **1** and the ylide from salt **4** gave a mixture of 1,4-phenylenehexa-1,3,5-trienylene oligomers with formyl end groups (FPHn). Due to the

low solubility of FPHn, the degree of polymerization was low (DPn <10). The monomer (FPH1), dimer (FPH2) and trimer (FPH3) could be isolated as red solids by GPC. The ^{1}H NMR and IR spectra showed that these oligomers had predominantly all-*trans* structures, a result perhaps from the *cis-trans* thermal isomerization during polymerization. The red-shift of λ_{max} of FPH2 compared with that of FPH1 showed that the conjugation length became longer as the number of repeating unit increased. However, λ_{max} of FPH3 was located at shorter wavelength than that of FPH2. This can be attributed to the presence of some structural disorders in FPH3, since weak peaks due to saturated bonds were observed in its IR spectrum.

Values of $\chi^{(3)}$ for thin films of FPH1 and FPH2 were estimated to be 2.0 x 10^{-13} and 7.4 x 10^{-13} esu (at 1.98 μm, non-resonant region), respectively. The $\chi^{(3)}$ value of FPH2 was found to be 3-4 times higher than that of FPH1. This is attributed to the lower Eg of FPH2 due to the extension of π-delocalization. The value of FPH1 was about six times higher than that of PHT1, corresponding to the decrease in Eg as a result of introducing electron-withdrawing formyl groups. The $\chi^{(3)}$ value of FPH3 could not be measured, because of the instability of the film in air.

Experimental

Reaction of terephthalaldehyde 1 and bis-phosphonium salt 4

To a solution of aldehyde **1** (2.0 g, 15 mmol) and salt **4** (4.7 g, 7.2 mmol) in absolute ethanol (250 cm^3) was slowly added a solution of sodium ethoxide (0.30 mol dm^{-3}, 50 cm^3) under an argon atmosphere. After the mixture had been stirred for 2 days in the dark, an additional solution of the salt (4.7 g in 50 cm^3 of ethanol) was poured into the reaction mixture, whereupon a sodium ethoxide solution (0.30 mol dm^{-3}, 50 cm^3) was added dropwise. After the mixture had been stirred for another 2 days, the resulting orange-red precipitate was collected, washed with water and then three times with ethanol, and dried *in vacuo* at 55 °C. A mixture of FPHn oligomers was obtained [0.46

g, 20 % yield (calculated for repeating units of $C_{12}H_{10}$)]. FPH2 and FPH3 were isolated from the mixture by GPC (chloroform).

1,4-Bis{6-(4-formylphenyl)hexa-1,3,5-trienyl}benzene FPH2

M.p.>280 °C (Found:M^+, 442.1908. Calc.for $C_{32}H_{26}O_2$:*M*, 442.1934); $\delta_H(CDCl_3)$ 9.97-10.02 (2H, m), 7.8-7.9 (4H, m), 7.5-7.6 (4H, m), 7.3-7.5 (4H, m), 6.8-7.1 (4H, m) and 6.2-6.7 (8H, m); ν_{max}(KBr)/cm^{-1} 1691s, 1603m, 1303w, 1210m, 1164m, 1106w, 996s, 872w, 804m and 517w.

1,6-Bis{4-[6-(4-formylphenyl)hexa-1,3,5-trienyl]phenyl}hexa-1,3,5-triene FPH3

$\delta_H(CDCl_3)$ 9.9-10.0 (2H, m), 7.8-7.9 (4H, m), 7.5-7.6 (4H, m), 7.3-7.5 (4H, m), 6.8-7.1 (4H, m) and 6.2-6.7 (8H, m); ν_{max}(KBr)/cm^{-1} 1691s, 1595m, 1305w, 1263w, 1213m, 1166m, 1113w, 998s, 964w and 826m.

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2.2 Synthesis and Characterization of Poly(1,4-phenylenehexa-1,3,5-trienylene)

2.2.2. Sulfonium Salt Pyrolysis

Introduction

As described in the previous section, 1,4-phenylenehexa-1,3,5-trienylene oligomers with formyl end groups (FPHn) were obtained by the Wittig reaction of aldehyde **1** and the ylide from salt **4**. However, they were sparingly soluble in common organic solvents and the degree of polymerization was low, a result perhaps of its rigid structure. This problem made it impossible to prepare PPHT with high molecular weight.

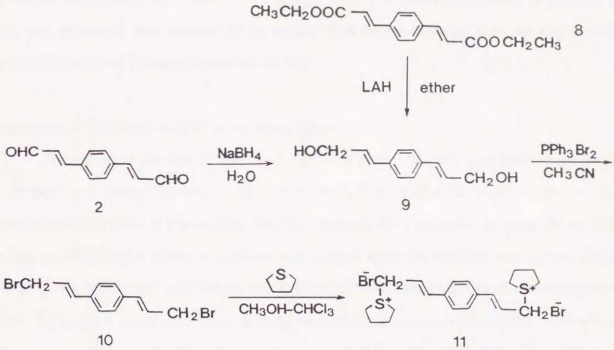
High molecular weight films of poly(arylenevinylene)s can be readily obtained from sulfonium salt prepolymers, which are soluble in polar solvents, by pyrolysis. Since poly(1,4-phenylenevinylene) (PPV) [1] and its 2,5-disubstituted derivative [2] were so prepared ($\overline{M}n$ values > $3x10^4$) and also poly(2,5-thienylenevinylene) (PTV) [3], poly(2,5-furylenevinylene) [4], poly(1,4-naphthalenevinylene) [5] and poly(2,5-selenophenediylvinylene) [6], I hoped to apply the same method to the synthesis of PPHT.

This section describes the preparation of *p*-phenylene-3,3'-bis(1-allyltetrahydrothiophenium) dibromide **11**, and its reactions upon treatment with aqueous and methanolic sodium hydroxide.

Results and Discussion

*Preparation of Sulfonium Salt **11***

The synthetic route to salt **11** is shown in Scheme 2.2.2. Although diester **8** failed to react with lithium aluminium hydride (LAH) in benzene, in diethyl ether it was con-



Scheme 2.2.2 Synthetic route to salt **11**

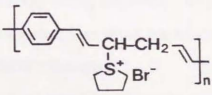
verted into dialcohol **9** (40 %).

However, since a side reaction resulted in the reduction of double bonds and production of by-products containing 3-hydroxypropyl groups, the reduction of aldehyde **2** was attempted under the same conditions. While the reduction of cinnamaldehyde, a model compound, in benzene gave cinnamylalcohol in high yield, no reaction occurred between dialdehyde **2** and LAH under similar conditions. The reduction of the dialdehyde to give diol **9** (73 %) was eventually achieved with sodium borohydride ($NaBH_4$) in water; methanol as solvent gave a lower yield of the product. In addition to the dialcohol, the reaction mixture contained much material with only one reduced carbonyl group. Attempts to obtain higher yields at elevated temperatures (70 °C), or using a greater concentration of the dialdehyde were unsuccessful. Dibromide **10** was prepared from the dialcohol by a similar procedure to that given for cinnamyl bromide

[7]. Reaction of this dibromide with tetrahydrothiophene (THT) in methanol–chloroform afforded the desired sulfonium salt **11** in high yield. The salt was somewhat unstable in air, and gradually decomposed to an unidentified brown material over several months even when stored at low temperature (5 °C).

*Reaction of Sulfonium Salt **11** in Aqueous Base*

An aqueous solution of salt **11** (0.050 mol dm^{-3}, 10 cm^3) was treated dropwise with aqueous sodium hydroxide (0.10 mol dm^{-3}, 5 cm^3) at 0 °C under a nitrogen atmosphere. The color of the reaction mixture changed from colorless to deep yellow after a few minutes, and a yellow precipitate was formed when the mixture was further stirred for 1 h. The precipitate was filtered and dried under reduced pressure at room temperature. Although a small amount of a sticky red material remained insoluble, most of the precipitate slowly dissolved in methanol, suggesting that the precipitate was a polymer. Based on the structure of the prepolymer of PPV, the obtained polymer was considered to be poly[*p*–phenylene{3–(tetrahydrothiophen–1–io)hexa–1,5–dien–1,6–ylene} bromide] **12** (Figure 2.2.5).



12

Figure 2.2.5 Structure of polymer **12**

Figure 2.2.6(a) shows the UV–vis spectrum of polymer **12**. An absorption maximum (λ_{max}) was found at 292 nm in methanol, which was essentially the same as that of salt **11** (299 nm). This finding agreed with the expectation that the salt and polymer would differ little in the length of their chromophores. The weak absorption at

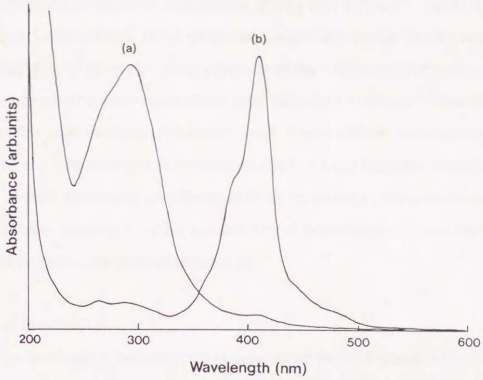


Figure 2.2.6 UV-vis spectra of (a)polymer **12** and (b)compound **X** (CH_3OH)

408 nm in the spectrum of the polymer but absent in that of the salt was attributed to the presence of an intermediate formed during polymerization. This is similar to the strong absorption at 412 nm which was observed when the reaction was conducted in basic methanol, and is discussed later in this section.

The ^{1}H NMR spectrum of polymer **12** was measured in deuteriomethanol. A peak due to aromatic protons was observed at δ7.5 as a broad singlet. Olefinic protons gave broad peaks at δ6.6, 6.3 and 6.0. The multiplets at δ3.4–3.6 and 2.2–2.5 were assigned to the methylenes of the THT rings. The broad absorption at δ2.5–3.0 should be due to the methylene protons of the polymer main chain. A methine signal was expected in the ^{1}H NMR spectrum (observed at δ5.05) [8] but was not observed. Consideration of the effect of double bonds on the chemical shift of the methine peak led me to expect this signal to be at approximately δ4.7, but the two strong resonances due to the solvent at

δ4.7 and 4.9 prevented this.

Polymer **12** showed IR absorptions at 810 and 971 cm^{-1} (C–H deformation vibrations of 1,4–disubstituted benzene rings and *trans* double bonds, respectively), 2923 and 2856 cm^{-1} (C–H stretching vibrations of the methylene and methine groups in the THT rings and polymer main chain) and 1601 and 1168 cm^{-1} (new absorptions observed after polymerization but unassigned). There was no carbonyl absorption at 1670–1730 cm^{-1}, indicating the absence of CHO or CO_2H groups. Although the assignment of each NMR peak was restricted to some extent by the peak broadness and the low S/N ratio resulting from the low solubility of the polymer, UV–vis and IR spectra support the proposed structure of polymer **12**.

Pyrolysis of Polymer 12

In the expectation that pyrolysis of polymer **12** would produce a film of PPHT, as in the case of PPV, its methanol solution was cast on a glass plate which was then heated at 250 °C for 2–4 h at 10^{-3} Torr. A yellow solid was obtained as a thermal product. Its IR spectrum showed absorption at 996 cm^{-1} (C–H out–of–plane vibration of trienes), although the intensity was low. The peak at 1675 cm^{-1}, together with that due to the *trans*–vinylene groups at 962 cm^{-1}, indicated the presence of –CH=CH–CHO groups. Since polymer **12** was free of carbonyl groups before pyrolysis (IR analysis), these were assumed to be formed either by decomposition of polymer **12** during pyrolysis, or by oxidation of PPHT in air after pyrolysis. If the former is the case then the source of oxygen must be residual water and/or hydroxide ion used in the polymerization and not oxygen gas from air, since the pyrolysis was conducted *in vacuo*. Since these carbonyl groups must be formed by the cleavage of the main chain of polymer **12** or PPHT, it might be expected that there would be some soluble components formed in the process. However, no thermal product was found to be soluble in dichloromethane or methanol.

Similar findings have been reported in the preparation of PTV. Carbonyl com–

pounds were found after pyrolysis even at 10^{-6} Torr [9]. In order to prevent the formation of these compounds, PTV was prepared by pyrolysis of the 'methoxy precursor polymer' with catalytic amounts of hydrochloric acid [9]. Unfortunately, in this case, the sulfonium groups of polymer **12** could not be substituted with methoxy groups. For example, no change was detected in the NMR spectrum even after a methanol solution of the polymer had been stirred at room temperature. The polymer when stirred in methanol at reflux gave a product insoluble in methanol but soluble in chloroform. Its molecular weight was found to be 2,000–3,000 by gel-permeation liquid chromatography (polystyrene standard). However, the IR spectrum of the product was virtually the same as that obtained after pyrolysis at 250 °C.

*Reaction of Sulfonium Salt **11** in Basic Methanol*

Polymer **12** was obtained by the reaction of salt **11** with aqueous sodium hydroxide. However, the polymer proved to be water-insoluble and no further polymerization appeared to occur. It was considered that the reaction of the salt **11** in basic methanol would give a polymer with higher molecular weight than that obtained in water, since both compounds **11** and **12** were soluble in methanol.

On adding a solution of sodium hydroxide (0.10 mol dm^{-3}, 1 cm^3) at 0° C to a solution of salt **11** (0.01 mol dm^{-3}, 10 cm^3) in methanol, the reaction mixture soon turned from colorless to intense yellow, a process followed by UV-vis spectroscopy. The absorption of the salt at 299 nm disappeared and a new absorption emerged at 412 nm as the amount of added sodium hydroxide increased (Figure 2.2.7). When the solution was stirred at 0 °C for 2 h after the complete disappearance of the absorption at 299 nm, it gave no further spectral change; however, slow discoloration was noted over a long period (4–5 h) with λ_{max} changing from 412 nm to 265 nm. The λ_{max} of this yellow material **X** was observed at a different wavelength to that of polymer **12** (Figure 2.2.6(b)). If compound **X** is an unknown polymer, the λ_{max} should shift gradually to longer wavelength as polymerization proceeds. Actually, isosbestic points were ob-

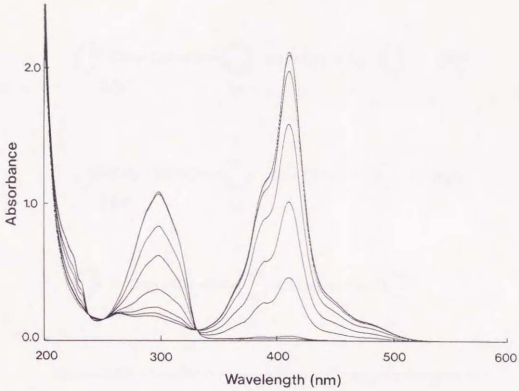
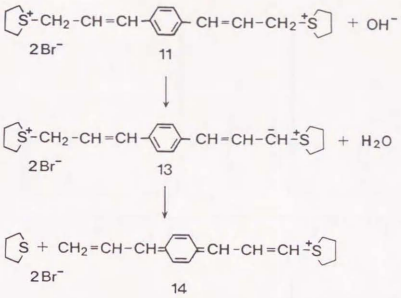


Figure 2.2.7 Changes in UV–vis spectra during the reaction of salt **11** with sodium hydroxide in methanol at 0 °C

served at 332, 252 and 239 nm. Compound **X** was thus not a polymer but a low molecular weight material.

For the polymerization of the sulfonium salt monomer of PPV the 'Wessling mechanism' has been proposed, which includes a mono–ylide and a *p*–xylylene derivative as reaction intermediates [10–12]. Therefore, compound **X** may possibly have the structure of either mono–ylide **13** or *p*–xylylene derivative **14** (Scheme 2.2.3).

For further clarification of the structure of compound **X**, the reaction was also followed by ^{1}H NMR spectroscopy. Measurements were carried out in deuteriomethanol at room temperature. When a solution of sodium hydroxide (1.6 mol dm^{-3}, ca. 0.05 cm^3) was added to one of salt **11** (0.01 mol dm^{-3}, 0.7 cm^3), the spectrum showed the disappearance of the salt coincident with growth of new peaks at δ6–8 and those due to eliminated THT (δ1.85–1.95m and 2.70–2.80m) (Figure 2.2.8). The two sets of multi–



Scheme 2.2.3 Formation of mono-ylide **13** and *p*-xylylene derivative **14**

plets at δ2.2–2.5 and 3.4–3.7 were tentatively assigned to the methylene groups of the THT rings in compound **X**. Peak integrals of these signals showed that equimolecular amounts of compound **X** and free THT were formed from the salt. Although further experiments are required to confirm the peak assignments, these observations suggest that compound **X** is not mono-ylide **13** formed by mere deprotonation of the salt, but actually *p*-xylylene derivative **14** which should be formed from the ylide with elimination of THT. Compound **X** was quite stable so that the UV-vis and NMR spectra could be obtained even in air at room temperature. This agreed with the expectation that compound **14** is predicted to be stabilized by the long conjugated system.

While salt **11** produced polymer **12** in aqueous base, it gave no polymer in methanol. The failure of the polymerization in methanol is attributed to either the low solubility of the salt, or to the higher stability of the reaction intermediate resulting in a stopped reaction.

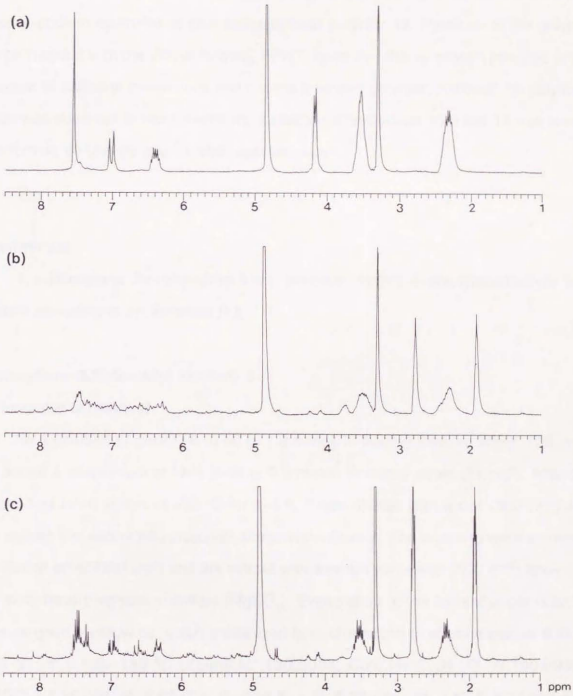


Figure 2.2.8 Changes in NMR spectra during the reaction of salt **11** with sodium hydroxide in deuteriomethanol at room temperature. (a)Before reaction, (b)reaction time 10 min, and (c)40 min

Summary

Bis-sulfonium salt **11** was prepared from dialdehyde **2**. This salt reacted with aqueous sodium hydroxide to give sulfonium salt polymer **12**. Pyrolysis of the polymer was carried out with the aim of forming PPHT, however, this approach resulted in the formation of carbonyl compounds and not the intended polymer. Although no polymerization was observed in basic methanol, a reaction intermediate from salt **11** was shown to be formed by UV-vis and ^{1}H NMR spectroscopy.

Experimental

1,4-Phenylene diethylacrylate **8** was prepared from 1,4-phenylenediacrylic acid (Aldrich) according to the literature [13].

p-Phenylene-3,3'-bis(allyl alcohol) 9

*(a) Reduction of diester **8***

To a solution of diester **8** (0.50 g, 1.8 mmol) in freshly distilled ether (100 cm^3) was added a suspension of LAH (0.35 g, 9.1 mmol) in diethyl ether (35 cm^3). After the mixture had been stirred at -20 °C for 3-4 h, it was diluted with water (300 cm^3) and then poured into saturated solution of ammonium chloride. The products were extracted with diethyl ether (500 cm^3) and the extract was washed with water (500 cm^3) and dried over anhydrous magnesium sulfate ($MgSO_4$). Evaporation of the solvent under reduced pressure gave a yellow oil, which crystallized from chloroform to afford dialcohol **9** (0.14 g, 40 %); m.p.135-136 °C (Found:M$^+$,190.0994. Calc.for $C_{12}H_{14}O_2$:*M*,190.0993); δ_H($CDCl_3$) 7.35 (4H, s), 6.60 (2H, dt, *J* 15.8, 1.3), 6.37 (2H, dt, *J* 15.8, 5.6) and 4.33 (4H, dd, *J* 5.6, 1.3). The OH protons were not detected; ν_{max}(KBr)/cm^{-1} 3367s, 2920w, 2856w, 1654m, 1511m, 1085s, 1007s, 972sh, 967s, 855m and 776m.

(b) Reduction of dialdehyde ***2***

A mixture of dialdehyde **2** (0.50 g, 2.7 mmol) and $NaBH_4$ (0.13 g, 3.4 mmol) was stirred in water (25 cm^3) for 20 h at 40 °C. This suspension was diluted with water (250 cm^3) and then quenched with saturated aqueous sodium carbonate (250 cm^3). The products were extracted with diethyl ether (500 cm^3) and the extract was dried over $MgSO_4$ and evaporated under reduced pressure. Recrystallization of the residue from benzene gave dialcohol **9** (0.37 g, 73 %), the NMR spectrum of which was identical with that of the alcohol obtained from the diester.

p–Phenylene–3,3'–bis(allyl bromide) 10

A solution of bromine (8 % w/w) in acetonitrile was added dropwise to a solution of triphenylphosphine (0.83 g, 3.2 mmol) in acetonitrile (30 cm^3) at 0 °C until the resultant solution was slightly yellow. Addition of a little triphenylphosphine turned the solution colorless. After the mixture had been stirred for 1 h, a solution of dialcohol **9** (0.30 g, 1.6 mmol) in acetonitrile (150 cm^3) was added to it and the mixture was stirred for a further 1 h at room temperature. The solvent was evaporated under reduced pressure. Ethanol in water (60%, 150 cm^3) was added to the residue and the resulting precipitate was filtered and dried at room temperature to give pure dibromide **10** as pale yellow crystals (0.35 g, 69 %); m.p.160–162 °C (Found:M^+,313.9338. Calc.for $C_{12}H_{12}Br_2$:*M*,313.9306); $\delta_H(CDCl_3)$ 7.35 (4H, s), 6.63 (2H, d, *J* 15.5), 6.41 (2H, dt, *J* 15.5, 7.8) and 4.17 (4H, dd, *J* 7.8, 0.8); ν_{max}(KBr)/cm^{-1} 1642w, 1436w, 1412w, 1213sh, 1200s, 1139w, 972s, 966s, 810s, 585m and 514m.

p–Phenylene–3,3'–bis(1–allyltetrahydrothiophenium) Dibromide 11

THT (0.61 g, 6.9 mmol) was added dropwise to a solution of dibromide **10** (0.10 g, 0.32 mmol) in chloroform (15 cm^3) and methanol (35 cm^3). The mixture was stirred at 0 °C for 30 min and then at room temperature for 7 h. After concentration of the mixture

under reduced pressure, acetone (50 cm^3) was added to it. The resulting precipitate was filtered and dried at room temperature to give sulfonium salt **11** as a pale yellow solid (0.12 g, 76 %); m.p.164 °C (decomp.); $\delta_H(CD_3OD)$ 7.55 (4H, s), 7.01 (2H, d, *J* 16.1), 6.40 (2H, dt, *J* 15.4, 7.7), 4.16 (4H, d, *J* 7.4), 3.41–3.66 (8H, m) and 2.19–2.47 (8H, m); $\delta_C(CD_3OD)$ 142.5, 138.2, 129.5, 118.1, 46.8, 44.2 and 30.7; ν_{max}(KBr)/cm^{-1} 3025w, 2969m, 2950m, 1644m, 1510w, 1413s, 1313m, 1261w, 1072m, 988s, 910w, 863w, 814w, 625w and 520m.

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2.3 Synthesis and Characterization of Poly(2,5-diheptyl-1,4-phenylenehexa-1,3,5-trienylene)

Introduction

The Wittig reaction of aldehyde **1** and the ylide from bis-phosphonium salt **4** gave a mixture of 1,4-phenylenehexa-1,3,5-trienylene oligomers with formyl end groups (FPHn). However, it was obtained as a powder with low degree of polymerization (Section 2.2.1). Attempts to obtain PPHT with high molecular weight by the sulfonium salt pyrolysis were unsuccessful (Section 2.2.2). Although the sulfonium salt prepolymer was obtained in water, the oxidation of the prepolymer during and/or after the thermal treatment prevented me from obtaining the final conjugated polymer. These results are attributed to the low solubility of PPHT due to its rigid structure.

Introduction of long side chains into the aromatic rings of a polymer improves its solubility remarkably. Some of PPV derivatives bearing long alkyl or alkoxy chains were prepared as soluble polymers with high molecular weights [1-5]. The solubility of PPHT is thus expected to be enhanced by introduction of long side chains. This section describes the preparation of poly(2,5-diheptyl-1,4-phenylenehexa-1,3,5-trienylene) (HpPPHT, Figure 2.3.1), a ring-substituted derivative of PPHT. A value of $\chi^{(3)}$ for a thin film of HpPPHT was measured by the Maker fringe method of THG.

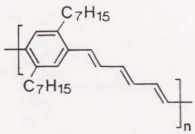
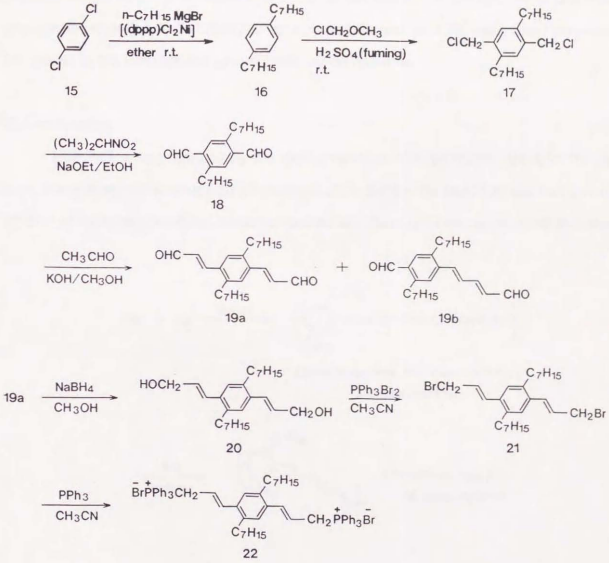


Figure 2.3.1 Structure of HpPPHT

Results and Discussion

*Preparation of Aldehyde **19a** and Bis-phosphonium Salt **22***

The preparation procedure for aldehyde **19a** and salt **22** is shown in Scheme 2.3.1. Although aldehyde **18** could be obtained by hydrolysis of the hexaminium salt of dichloride **17**, the reaction using 2-nitropropane gave a higher yield of product. Aldol reaction of aldehyde **18** gave compounds **19a** (15 %) and **19b** (25 %). Aldehyde **19b**

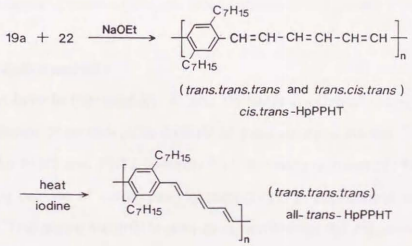


Scheme 2.3.1 Preparation procedure for aldehyde **19a** and bis-phosphonium salt **22**

(and/or its optical isomer, not shown in the Scheme) was obtained in higher yield than **19a**, due to the steric hindrance of heptyl groups of aldehyde **18**. Aldehyde **19a** could be isolated from the reaction mixture, which contained a large amount of the starting compound, an intermediate with only one formyl group reacted and high molecular weight red materials, by silica-gel column chromatography. The reduction of aldehyde **19a** with $NaBH_4$ in methanol gave alcohol **20**. From this alcohol dibromide **21** was obtained by a similar procedure to that given for *p*-phenylene-3,3'-bis(allylbromide) **10** (Section 2.2.2). Bromide **21** reacted with triphenylphosphine in acetonitrile to afford bis-phosphonium salt **22**. Solubility of aldehyde **19a** and salt **22** were much improved compared to the corresponding unsubstituted compounds.

Polymerization

HpPPHT was prepared by the Wittig reaction of dialdehyde **19a** and the ylide from bis-phosphonium salt **22** (Scheme 2.3.2). Since the reaction did not occur in ethanol at room temperature, it was conducted at refluxing temperature using the same



Scheme 2.3.2 Synthesis of HpPPHT by the Wittig reaction

solvent to obtain HpPPHT as a red precipitate. However, its degree of polymerization (DPn) was estimated from ^{1}H NMR peak integrals to be 4–5, which was rather lower than expected. This is attributed to a reduced polymerization rate due to the low solubility of the polymer in ethanol, in addition to the steric hindrance of the heptyl groups of compounds **19a** and **22**.

The reaction was thus conducted in benzene, in which the polymer was expected to be more soluble. No precipitate was produced in this case, even after refluxing for 2 days. After the evaporation of the solvent and addition of ethanol to the residue, a red precipitate was obtained. This was easily soluble in common organic solvents such as chloroform, toluene and acetone. The solubility in chloroform was 7–10 mg cm^{-3}. Its DPn was estimated to be 9–10 from ^{1}H NMR peak integrals. GPC analysis (chloroform) showed that the molecular weight was $\overline{M}n$=3,900 (DPn=10–11) and $\overline{M}w/\overline{M}n$=2.0 (polystyrene standard). Although DPn of HpPPHT was not so much enhanced compared with that of FPHn oligomers (DPn<10) (Section 2.2.1), the solubility of HpPPHT was much improved by introduction of the long alkyl groups. Moreover, HpPPHT was appeared to be more stable than PHT3 and FPH3. This is probably because the steric hindrance of the heptyl groups suppressed the oxidation of the trienes in air.

cis,trans–*Thermal Isomerization*

As shown later in this section, IR and ^{1}H NMR spectra of the crude HpPPHT showed the presence of considerable amount of *trans,cis,trans* trienes. Similar findings were observed for PHT2 and PHT3 (Section 2.1). All–*trans* isomers of PHT2 and PHT3 were obtained by heating of *cis*–containing compounds in appropriate solvents with a trace of iodine. The same treatment was thus conducted for *cis*–containing crude polymer (*cis,trans*–HpPPHT) to give HpPPHT with predominantly all–*trans* structure (all–*trans*–HpPPHT, Scheme 2.3.2). The solubility of the polymer decreased somewhat after the isomerization.

In the preparation of FPHn oligomers by the Wittig reaction of aldehyde **1** and the ylide from salt **4**, the products were expected to have *trans,trans,cis* (and *cis,trans,cis*) trienes, since double bonds at 1 and 5 positions of the trienes were newly formed by the reaction. Actually, however, IR and NMR spectra showed the presence of only a small amount of *cis* double bonds in the products. *trans,trans,cis*-FPH1 was observed to isomerize to *trans,trans,trans*-FPH1 in the dark at room temperature. Therefore, FPHn oligomers having *trans,trans,cis* trienes possibly isomerized thermally to those with all-*trans* structure during the polymerization. On the other hand, *trans,cis,trans* trienes in PHT2, PHT3 and HpPPHT were thermally more stable and did not isomerize easily without iodine catalysis.

trans,trans,cis-1,6-Diphenylhexa-1,3,5-triene (*trans,trans,cis*-PHT1) is theoretically predicted to be a non-planar structure due to the steric hindrance between the protons of phenyl groups and *cis*-double bonds, while planar structures are predicted for *trans,trans,trans*- and *trans,cis,trans*-PHT1 [6]. This suggests that the thermal stabilities of these isomers are *trans,trans,trans*- > *trans,cis,trans*- > *trans,trans,cis*-PHT1. The *cis,trans* geometries of trienes in the crude products of PHTn, FPHn oligomers and HpPPHT can similarly be explained by the difference in the thermal stabilities between *trans,cis,trans* and *trans,trans,cis* trienes. Furthermore, in the case of HpPPHT, the steric hindrance of the heptyl groups would suppress the isomerization.

IR Spectra

Figure 2.3.2(a) shows the IR spectrum of the crude HpPPHT prepared in benzene. The peaks at 958 and 990 cm^{-1} are attributed to the C-H out-of-plane vibration of *cis*-containing trienes [7,8]. After the thermal treatment, the peak at 958 cm^{-1} disappeared and only a strong peak was observed at 990 cm^{-1} (Figure 2.3.2(b)). Since this peak is characteristic of *trans,trans,trans* trienes [7,8], the observation clearly shows that *cis,trans*-HpPPHT isomerized to all-*trans*-HpPPHT by the heat treatment.

The broad absorption at around 1600cm^{-1} can be attributed to the C=C stretch-

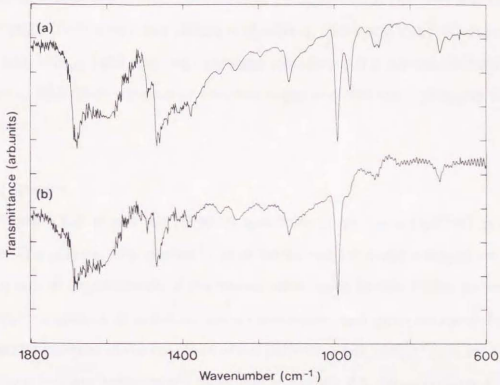


Figure 2.3.2 IR spectra of (a)*cis,trans*- and (b)all-*trans*-HpPPHT prepared in benzene (KBr)

ing vibration of trienes [7,8]. Similar strong absorptions were observed for FPH1, FPH2 and FPH3 (Section 2.2.1). In the spectra of PHT2 and PHT3, however, the corresponding peaks were very weak (Section 2.1). This is probably due to the higher symmetrical structures of PHT2 and PHT3 than that of HpPPHT, since the intensity of the peaks due to C=C double bonds is expected to diminish when the molecule becomes more symmetrical [9].

The strong peak at 1677 cm^{-1} is attributed to the C=O vibration of carbonyl groups conjugated with double bonds, showing that the end groups of HpPPHT prepared in benzene were *trans*-2-formylvinyl groups. For the polymer prepared in ethanol, peaks of mono-substituted benzene rings were observed at 690 and 744 cm^{-1} in addition to the carbonyl peak at 1677 cm^{-1}. These peaks showed the presence of tri-

phenylphosphonium groups in the polymer.

Other characteristic peaks observed in the spectrum of HpPPHT are assigned as follows: 3029 (C–H stretching vibration of =CH–), 2954 and 2927 (C–H vibration of $-CH_2-$ and $-CH_3$), 1486 and 1467 (skeletal vibration of 1,2,4,5–tetrasubstituted benzene rings), 892 (C–H vibration of benzene rings) and 723 cm^{-1} (wagging vibration of methylenes).

^{1}H NMR Spectra

Figure 2.3.3 shows the ^{1}H NMR spectrum of *cis,trans*–HpPPHT prepared in benzene. The polymer is expected to have *trans,trans,trans* and *trans,cis,trans* trienes, since the central double bonds of the trienes were newly formed by the polymerization. Therefore, the spectra of authentic *trans,trans,trans*– and *trans,cis,trans*–PHT1 were measured for analysis of the spectrum of the polymer. Peak assignments for the spectra of these two isomers were already described in Section 2.1. Since protons at 2,3,4 and 5 positions of *trans,trans,trans* and *trans,cis,trans* trienes in *cis,trans*–HpPPHT are far from the aromatic rings, the steric effect of the heptyl groups on their chemical shifts is considered to be small. Therefore, the peaks of these protons in the polymer are expected to be observed at similar positions to those in the spectrum of *trans,trans,trans*– or *trans,cis,trans*–PHT1. From these expectations together with the peak integrals, each peak in the spectrum of *cis,trans*–HpPPHT can be assigned as shown in Table 2.3.1.

Table 2.3.1 ^{1}H NMR peak assignments for the spectrum of *cis,trans*–HpPPHT prepared in benzene

		trans,trans,trans	*trans,cis,trans*
arom.	$H_{3,6}$	δ7.35	7.4
triene	$H_{1,6}$	6.7–7.0	6.7–7.0
	$H_{2,5}$	6.7–7.0	7.4
	$H_{3,4}$	6.4–6.7	6.2–6.4

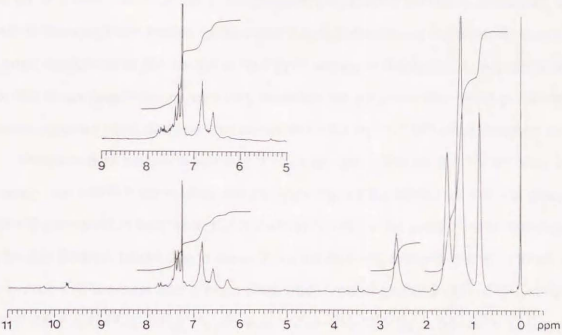


Figure 2.3.3 ^{1}H NMR spectra of *cis,trans*– and all–*trans*–HpPPHT (the inset) prepared in benzene ($CDCl_3$)

The ratio of *trans,trans,trans* : *trans,cis,trans* trienes was estimated to be 2:1 from peak integrals. Comparison of the spectrum of *cis,trans*–HpPPHT with those of *trans,trans,trans*– and *trans,cis,trans*–PHT1 showed that the peaks due to the protons at 1 and 6 positions of *trans,trans,trans* and *trans,cis,trans* trienes in *cis,trans*–HpPPHT were located at lower magnetic fields by 0.2–0.3 ppm than those of the corresponding protons in *trans,trans,trans*– and *trans,cis,trans*–PHT1. When a strong steric hindrance exists between a proton and a neighboring group, the electron cloud around the proton is predicted to be deformed. The decreased spherical symmetry of the electron distribution causes a paramagnetic contribution, which results in a shift to a lower magnetic field [10]. The observation for *cis,trans*–HpPPHT described above can therefore be attributed to the steric hindrance between the olefinic protons at 1,6–positions of the trienes and the α–protons of the heptyl groups.

Figure 2.3.3 (the inset) shows the spectrum of all-*trans*-HpPPHT obtained by the thermal isomerization of the crude polymer prepared in benzene. Intensities of the peaks of *trans,cis,trans* trienes at δ7.4 and 6.2–6.4 decreased significantly, supporting the peak assignments for *cis,trans*-HpPPHT shown in Table 2.3.1. Although the IR peak due to *cis* double bonds was very weak for the polymer after heating, the ratio of *trans,trans,trans* : *trans,cis,trans* was shown to be 5:1 by ^{1}H NMR peak integrals.

Peaks due to the triphenylphosphonium groups in Figure 2.3.3 were very weak, indicating that *trans*-2-formylvinyl groups were mainly contained as the end groups in HpPPHT prepared in benzene. On the other hand, in the spectrum of the polymer prepared in ethanol, peaks due to *trans*-2-formylvinyl and *trans*-3-triphenylphosphonium-1-propenyl bromide end groups were observed at δ9.68–9.76 (-CH=CH-C*H*O), 7.62–7.98 (-CH=CH-$CH_2\overset{+}{P}Ph_3\overset{-}{B}r$ and -C*H*=CH-CHO), 5.86–5.90 (-CH=C*H*-$CH_2\overset{+}{P}Ph_3\overset{-}{B}r$) and 5.04–5.17 (-CH=CH-C$H_2\overset{+}{P}Ph_3\overset{-}{B}r$). The polymer was thus shown to have two kinds of end groups, which agreed with the findings from the IR spectra. Integrals of these peaks indicated the ratio of the end groups -CH=CH-CHO : -CH=CH-$CH_2\overset{+}{P}Ph_3\overset{-}{B}r$ was 65:35.

^{13}C NMR Spectra

cis,trans-HpPPHT prepared in benzene gave the following ^{13}C NMR data in deuteriochloroform: δ138.6 and/or 138.3 (arom., C_1 and C_4), 134.9 (arom., C_2 and C_5), 133.9 (triene, C_3 and C_4), 130.8 (triene, C_1 and C_6), 129.8 (triene, C_2 and C_5), 126.7 and/or 126.4 (arom., C_3 and C_6) and 124.7 (triene, C_3 and C_4). Peaks due to the carbons of methylene and methyl groups of the heptyl chains were observed in the region of δ14–34. A peak of the carbons at 2 and 5 positions of the trienes of the polymer had almost the same chemical shifts as those of the authentic *trans,trans,trans*-PHT1 (δ129.3) [11] and *trans,cis,trans*-PHT1 (δ130.0). The peaks at δ133.9 and 124.7 can be assigned to the carbons at 3 and 4 positions of *trans,trans,trans* and *trans,cis,trans* trienes of the polymer, respectively, because the corresponding peaks were observed at

similar positions in the spectra of *trans,trans,trans*-PHT1 (δ133.8) [11] and *trans,cis,trans*-PHT1 (δ124.2). Similar upshield of the peak due to the carbons of *cis* double bonds was reported for *cis*-polyacetylene [12]. However, the peak due to the carbons of 1 and 6 positions of the trienes in HpPPHT was located at a higher magnetic field by 2-3 ppm than that of *trans,trans,trans*- and *trans,cis,trans*-PHT1. The steric hindrance between the olefinic carbons at 1,6-positions of the trienes and the aliphatic carbons at α-positions of the heptyl groups caused the decrease in the electron density of the triene protons at 1,6-position and the increase in that of the carbons at 1,6-positions of the trienes. The latter resulted in the shift to the higher magnetic field of the peak in the ^{13}C NMR spectrum.

UV-vis Spectra

In the UV-vis spectrum of *cis,trans*-HpPPHT prepared in ethanol, the absorption maximum (λ_{max}) was observed at 454 nm (2.73 eV). The spectrum of all-*trans*-HpPPHT (λ_{max} = 457 nm (2.71 eV)) was practically identical to that of the *cis,trans* polymer. Also in the case of PHT1, the difference in λ_{max} between *trans,trans,trans* and *trans,cis,trans* isomers was reported to be very small [13]. These observations agreed with the expectation that *trans,trans,trans* and *trans,cis,trans* trienes would differ little in the length of the chromophores, because they were considered to have planar structures [6].

As for HpPPHT prepared in benzene, λ_{max} were observed at 453 nm (2.73 eV) for both *cis,trans* and all-*trans* polymers. In spite of the higher DPn, λ_{max} of HpPPHT prepared in benzene was essentially the same as that for the polymer prepared in ethanol. This suggested that λ_{max} was no longer sensitive to the increase in DPn in the region of DPn>4. The λ_{max} of HpPPHT was located at longer wavelength than those of PHT2 and PHT3, clearly due to the extension of π-conjugation system.

Although λ_{max} in chloroform were observed at almost the same wavelength for both of the polymers, λ_{max} of the films on quartz substrates were 419 nm (2.96 eV) and

403 nm (3.08 eV) for those prepared in ethanol and benzene, respectively. This suggests that the higher DPn caused the decrease in the effective conjugation length of HpPPHT in the solid states because of the steric hindrance of the heptyl groups.

Third-order NLO Properties

Values of $\chi^{(3)}$ were measured for thin films of *cis,trans*-HpPPHT prepared in ethanol and benzene. For the polymer prepared in ethanol, the refractive index and thickness of the film were 1.896 and 19 nm, respectively. The values were 1.799 and 17 nm for the film of the polymer prepared in benzene. Figure 2.3.4 shows the measured

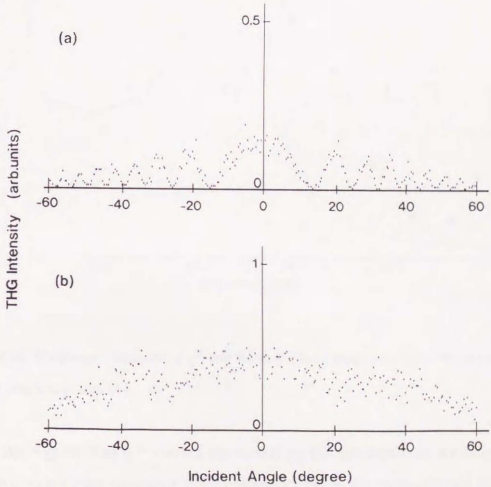


Figure 2.3.4 Measured third-harmonic intensities at 1.86 μm as a function of the incident light angle for (a)a quartz substrate of 1-mm thickness and (b)a thin film of *cis,trans*-HpPPHT prepared in benzene (thickness 17 nm)

third-harmonic intensities for (a)a 1-mm thick quartz substrate and (b)a thin film of *cis,trans*-HpPPHT prepared in benzene, as a function of the incident angle. Figure 2.3.5 shows the measured $\chi^{(3)}$ values of *cis,trans*-HpPPHT prepared in benzene as a function of the fundamental light wavelength. The absorption spectrum of the film is also

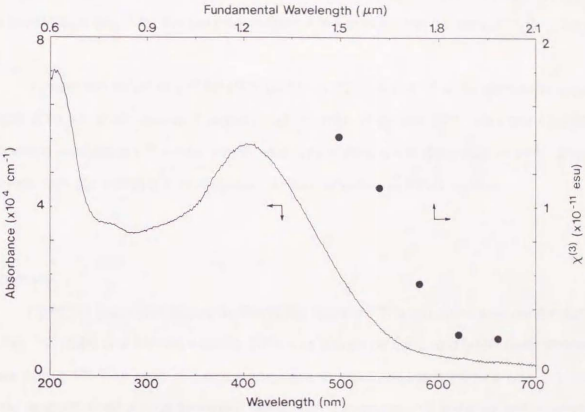


Figure 2.3.5 Wavelength dispersion of $\chi^{(3)}$ and the absorption spectrum for a thin film of *cis,trans*-HpPPHT prepared in benzene

shown in the Figure. The $\chi^{(3)}$ values increased as the fundamental wavelength decreased, due to the near-resonant effect corresponding to the three-photon absorption. The polymer prepared in ethanol showed a similar wavelength dependence of $\chi^{(3)}$.

Values of $\chi^{(3)}$ were estimated to be 3.5×10^{-12} and 2.3×10^{-12} esu (at 1.98 μm, non-resonant region) for *cis,trans*-HpPPHT prepared in ethanol and benzene, respec-

tively. The polymer prepared in ethanol exhibited a higher value of $\chi^{(3)}$ than that of the polymer prepared in benzene. From λ_{max} in the spectra of the films, energy band gaps (Eg) were determined to be 2.96 and 3.08 eV for the polymers prepared in ethanol and benzene, respectively. Therefore, Eg for the film of HpPPHT prepared in benzene was larger by 0.12 eV than that for the polymer prepared in ethanol. Since a value of $\chi^{(3)}$ for a conjugated polymer is enhanced with the decrease in Eg (Chapter 1, Equation 1.2.6), the lower value of $\chi^{(3)}$ for the polymer prepared in benzene can be attributed to its larger Eg.

A reported value of $\chi^{(3)}$ for PPV (DPn $\sim$100) is 5 x10^{-12} at fundamental wavelength 2.10 μm (non-resonant region) [14]. In spite of its low DPn, *cis,trans*-HpPPHT showed a moderate $\chi^{(3)}$ value, which was only a little lower than that of PPV. This is derived from the fact that π-conjugation is more effective in PPHT system.

Summary

HpPPHT was synthesized by the Wittig reaction. The structure was confirmed by IR, ^{1}H, ^{13}C NMR and UV-vis spectra. DPn was shown by GPC and NMR peak integrals to be about 10. The ratio of *trans,trans,trans* to *trans,cis,trans* trienes was 2:1 for a crude product. After a heat treatment under iodine catalysis, the polymer with predominantly all-*trans* structure could be obtained. Solubility of the polymer was much improved compared with that of PHT3 and FPH3, due to the introduction of the long alkyl side chains into the aromatic rings. Moreover, it appeared to be more stable than these trimers, probably because the steric hindrance of the heptyl groups suppressed the oxidation of the trienes in air.

A value of $\chi^{(3)}$ for a thin film of HpPPHT was estimated to be 2.3 x 10^{-12} esu (1.98 μm, non-resonant region). In spite of its low DPn, HpPPHT showed relatively high nonlinearity due to its highly conjugated structure.

Experimental

trans,cis,trans-PHT1 was prepared according to the literature [15].

1,4-Diheptylbenzene 16

Heptylmagnesium bromide was prepared by adding heptyl bromide (91.3 g, 0.51 mol) in dry ether (180 cm^3) to magnesium (13.6 g, 0.56 mol) in ether (10 cm^3) under mild refluxing. The mixture was heated at reflux for 3 h. This Grignard reagent was added dropwise to a solution of 1,4-dichlorobenzene **15** (30 g, 0.204 mol) and dichloro[1,3-(diheptylphosphino)propane]nickel(II) (0.24 g) in dry ether (150 cm^3) at room temperature over a period of 60 min. After the mixture had been stirred for 20 h, the usual work-up and distillation under reduced pressure gave 1,4-diheptylbenzene **16** (40 g, 72 %); b.p. 148 °C (0.4 mmHg).

2,5-Bis(chloromethyl)-1,4-diheptylbenzene 17

To a solution of 1,4-diheptylbenzene **16** (20 g, 0.104 mol) and chloromethyl-methyl ether (23.3 g, 0.29 mol) was added fuming sulfuric acid (60 %, 15.8 g) over a period of 20 min at below 10 °C. After the reaction mixture had been stirred for 22 h at room temperature, it was poured into ice water (200 cm^3). The resulting crystals were separated and purified by silica-gel column chromatography (hexane). Subsequent recrystallization from hexane gave 2,5-bis(chloromethyl)-1,4-diheptyl benzene **17** (19 g, 49 %) as white crystals; m.p. 78.0-79.5 °C; $\delta_H(CDCl_3)$ 7.15 (2H, s), 4.56 (4H, s), 2.66 (4H, t, *J* 6.6), 1.52-1.68 (4H, m), 1.18-1.46 (16H, m) and 0.88 (6H, t, *J* 6.6); δ_C 139.5, 135.5, 131.4, 43.8, 31.8, 31.7, 31.1, 29.6, 29.1, 22.6 and 14.0; ν_{max}(KBr)/cm^{-1} 3009w, 2952s, 2923s, 2850s, 1511w, 1497w, 1468s, 1406w, 1376w, 1341w, 1260s, 1198w, 1127w, 1119w, 1032w, 922w, 908m, 901m, 835w, 809w, 766w, 751m, 723m, 701s, 607s and 500w.

2,5-Diformyl-1,4-dihepthylbenzene 18

2-Nitropropane (2.4 cm^3, 27 mmol) was added to a solution of sodium ethoxide (1.0 mol dm^{-3}, 27 cm^3) to give the sodium salt of 2-nitropropane as a white precipitate. To this suspension was added a hot solution (60 °C) of dichloride **17** (5.0 g, 13.5 mmol) in ethanol (110 cm^3), and the mixture was heated at reflux for 4 h. After the reaction mixture had been cooled to room temperature, sodium chloride was filtered off and the solvent was evaporated under reduced pressure. The residue of product and sodium chloride was dissolved in ether (200 cm^3) and water (300 cm^3), respectively. The ether layer was washed with aqueous sodium hydroxide (5 %, 100 cm^3) to remove any acetoxime and excess 2-nitropropane, and then washed with water (100 cm^3). The extract was dried over anhydrous magnesium sulfate ($MgSO_4$), and the solvent was evaporated under reduced pressure. The resulting pale yellow solid was recrystallized from hexane to afford dialdehyde **18** (4.3 g, 97 %); m.p. 57.0-58.0 °C (Found: C, 79.75; H, 10.41 %; M^+,330.2555. Calc.for $C_{22}H_{34}O_2$: C,79.95; H,10.37 %; *M*,330.2556); $\delta_H(CDCl_3)$ 10.36 (2H, s), 7.73 (2H, s), 2.92-3.10 (4H, m), 1.48-1.72 (4H, m), 1.07-1.48 (16H, m) and 0.88 (6H, t, *J* 6.7); ν_{max}(KBr)/cm^{-1} 2956m, 2921s, 2873m, 2852s, 1684s, 1675s, 1467m, 1459m, 1404m, 1313w, 1159m, 919w, 907w, 872w and 720m.

Aldol reaction of dialdehyde 18 and acetaldehyde

To a solution of dialdehyde **18** (3.0 g, 9.1 mmol) and potassium hydroxide (2.0 g) in methanol (600 cm^3) was added dropwise a solution of acetaldehyde (90 % in water, 2.5 cm^3) in methanol (15 cm^3) at room temperature under a nitrogen atmosphere. After the mixture had been stirred for 2 days, aqueous ammonium chloride (0.5 %, 900 cm^3) was added to the reaction mixture and the products were extracted with diethyl ether (900 cm^3). The extract was dried over $MgSO_4$ and the solvent was evaporated under reduced pressure to give an orange oil (3.7 g).

The crude products were subjected to silica-gel column chromatography (hexane : diethyl ether = 9:1). Aldehydes **19a** (0.51 g, 15 %) and **19b** (0.84 g, 25 %)

were isolated. Aldehyde **19a** was further purified by recrystallization from hexane.

2,5-Bis(2-formylvinyl)-1,4-diheptylbenzene 19a

M.p.95.0-97.0 °C (Found: M^+,382.2880. Calc.for $C_{26}H_{38}O_2$:*M*,382.2870); $\delta_H(CDCl_3)$ 9.76 (2H, d, *J* 7.4), 7.75 (2H, d, *J* 15.8), 7.46 (2H, s), 6.72 (2H, dd, *J* 15.6, 7.7), 2.76 (4H, t, *J* 7.8), 1.47-1.66 (4H, m), 1.15-1.47 (16H, m) and 0.87 (6H, t, *J* 6.3); ν_{max}(KBr)/cm^{-1} 2949m, 2919s, 2868w, 2852s, 2821w, 1669s, 1612s, 1496w, 1467s, 1323m, 1205m, 1162m, 1119s, 970s, 879w, 849m and 724m; Rf = 0.77 (hexane : diethyl ether = 1 : 1).

2-(4-Formylbuta-1,3-dienyl)-5-formyl-1,4-diheptylbenzene 19b

Oil; $\delta_H(CDCl_3)$ 10.26 (1H, s), 9.67 (1H, d, *J* 7.9), 7.66 (1H, s), 7.46 (1H, s), 7.34 (1H, dd, *J* 15.1, 11.0) 7.28 (1H, d, *J* 15.3), 7.04 (1H, dd, *J* 15.7, 10.7), 6.35 (1H, dd, *J* 15.1, 7.9), 3.00 (2H, t, *J* 7.8), 2.74 (2H, t, *J* 7.8), 1.46-1.69 (4H, m), 1.16-1.46 (16H, m) and 0.88 (6H, t, *J* 6.7); Rf=0.32 (hexane : diethyl ether = 1 : 1).

2,5-Bis(3-hydroxy-1-propenyl)-1,4-diheptylbenzene 20

A mixture of dialdehyde **19a** (0.50 g, 1.3 mmol) and $NaBH_4$ (0.050 g, 1.3 mmol) was stirred in methanol (10 cm^3) for 24 h at 40 °C. This solution was quenched with aqueous sodium carbonate (0.2%, 200 cm^3). The products were extracted with diethyl ether (500 cm^3). The extract was dried over $MgSO_4$ and evaporated under reduced pressure to give an orange oil (0.43 g). Recrystallization of this oil from hexane gave dialcohol **20** (0.23 g, 45 %) as pale yellow crystals; m.p.72.0-73.5 °C (Found: M^+, 386.3188. Calc.for $C_{26}H_{42}O_2$:*M*, 386.3183); $\delta_H(CDCl_3)$ 7.24 (2H, s), 6.82 (2H, d, *J* 15.8), 6.26 (2H, dt, *J* 15.5, 5.9), 4.34 (4H, dd, *J* 5.9, 1.5), 2.62 (4H, t, *J* 7.9), 1.45-1.67 (4H, m), 1.18-1.41 (16H, m) and 0.88 (6H, t, *J*6.8). The OH protons were not detected; ν_{max}(KBr)/cm^{-1} 3367s, 3276sh, 3040w, 3018w, 2956s, 2924s, 2851s, 1674m, 1618w, 1493m, 1467s, 1444m, 1357m, 1097s, 1022s, 959s, 894m and 722m.

2,5-Bis(3-bromo-1-propenyl)-1,4-diheptylbenzene 21

A solution of bromide (8 % w/w) in acetonitrile was added dropwise to a solution of triphenylphosphine (0.29 g, 1.1 mmol) in acetonitrile (10 cm^3) at 0°C until the resultant solution was slightly yellow. Addition of a small amount of triphenylphosphine turned the solution colorless. After the mixture had been stirred for 1 h, a solution of dialcohol **20** (0.20 g, 0.52 mmol) in acetonitrile (10 cm^3) was added to it and the mixture was stirred for a further 1 h at room temperature. The solvent was evaporated under reduced pressure. Ethanol in water (60 %, 100 cm^3) was added to the residue and the resulting precipitate was filtered and dried at room temperature to give dibromide **21** as pale yellow crystals (0.19 g, 71 %); m.p. 60.0-62.0 °C (Found: M^+, 510.1496. Calc.for $C_{26}H_{40}Br_2$: *M*, 510.1496; $\delta_H(CDCl_3)$ 7.23 (2H, s), 6.85 (2H, d, *J* 15.5), 6.29 (2H, dt, *J* 15.5, 7.8), 4.18 (4H, dd,*J* 7.8, 0.8), 2.61 (4H, t, *J* 7.8), 1.46-1.59 (4H, m), 1.21-1.40 (16H, m) and 0.89 (6H, t, *J* 6.8); ν_{max}(KBr)/cm^{-1} 3043w, 3020w, 2953s, 2922s, 2852s, 1634m, 1491w, 1468m, 1201s, 963s, 895w, 853w and 723w.

2,5-Bis(3-triphenylphosphonio-1-propenyl)-1,4-diheptylbenzene dibromide 22

A solution of dibromide **21** (0.15 g, 0.29 mmol) and triphenylphosphine (0.21 g, 0.80 mmol) in acetonitrile (50 cm^3) was heated at reflux for 24 h. After the solvent had been evaporated under reduced pressure, toluene (20 cm^3) was added to the residue to give a precipitate. This was filtered and dried at room temperature to afford bisphosphonium salt **22** (0.27 g, 89 %) as a pale yellow solid; m.p. 226-230 °C (decomp.); $\delta_H(CDCl_3)$ 7.59-8.00 (30H, m), 6.94 (2H, s), 6.87 (2H, dd, *J* 15.7, J_{P-H} 5.8), 5.80-5.95 (2H, m), 5.10 (4H, dd, *J* 7.6, J_{P-H} 14.8), 2.27 (4H, t, *J* 7.9), 1.48-1.62 (4H, m), 1.11-1.36 (16H, m) and 0.88 (6H, t, *J* 6.8); ν_{max}(KBr)/cm^{-1} 3051w, 3007w, 2953m, 2924s, 2853s, 1624m, 1587m, 1486m, 1466m, 1437s, 1113s, 996m, 973m, 895w, 855w, 741s, 723s and 691s.

Wittig reaction of dialdehyde 19a and the ylide from bis-phosphonium salt 22

(a) Reaction in ethanol

To a solution of dialdehyde **19a** (100 mg, 0.26 mmol) and bis-phosphonium salt **22** (270 mg, 0.26 mmol) in absolute ethanol (75 cm^3) was added a solution of sodium ethoxide (0.10 mol dm^{-3}, 5.2 cm^3) under a nitrogen atmosphere. After the solution had been heated at reflux in the dark for 24 h, the resulting red precipitate was filtered and washed with ethanol (50 cm^3). *cis,trans*-HpPPHT (53 mg, 29 %) was obtained as a red solid; ν_{max}(KBr)/cm^{-1} 3029w, 2951m, 2924s, 2850s, 1677s, 1618m, 1486m, 1467s, 1457sh, 1438m, 1411w, 1377w, 1299w, 1258w, 1194w, 1116s, 1054w, 990s, 958s, 892m, 744w, 721m and 690m.

Thermal isomerization

A solution of *cis,trans*-HpPPHT prepared in ethanol (20 mg) in chloroform (30 cm^3) was heated at reflux for 16 h in the dark with a trace of iodine. After evaporation of the solvent under reduced pressure, the residue was dissolved in chloroform and reprecipitated into ethanol to give all-*trans*-HpPPHT as a red solid (5-10 mg); ν_{max}(KBr)/cm^{-1} 3025w, 2953m, 2924s, 2851s, 1676s, 1618m, 1491m, 1466m, 1459m, 1438w, 1406w, 1376w, 1300w, 1116s, 1030sh, 991s, 968w, 892w, 823m, 756w, 722m and 691m.

(b) Reaction in benzene

The reaction was conducted in a similar manner to that described above. After the reaction mixture had been heated at reflux for 2 days, the solvent was evaporated under reduced pressure and ethanol was added to the residue. The resulting precipitate was filtered, washed with ethanol and dried at room temperature to give *cis,trans*-HpPPHT (55 %) as a red solid; m.p. 120-126 °C; δ_C($CDCl_3$); 138.6, 138.3, 134.9, 133.9, 130.8, 129.8, 128.7, 126.7, 126.4, 124.7, 33.2, 31.8, 31.4, 29.6, 29.2, 22.7 and 14.1; ν_{max}(KBr)/cm^{-1} 3030w, 2953m, 2923s, 2851s, 1676s, 1596m, 1491m, 1466s, 1459s, 1376w, 1302w, 1261w, 1194w, 1118m, 990s, 958m, 892m, 881m, 776w and

721m.

Thermal isomerization

A solution of *cis,trans*-HpPPHT prepared in benzene (20 mg) in chloroform (30 cm^3) was heated at reflux for 40 h in the dark with a trace of iodine. After evaporation of the solvent under reduced pressure, the residue was dissolved in chloroform and reprecipitated into ethanol to give all-*trans*-HpPPHT as a red solid (5-10 mg); ν_{max}(KBr)/cm^{-1} 3030w, 2953m, 2924s, 2851s, 1676s, 1610s, 1491m, 1466s, 1459sh, 1384w, 1299w, 1258w, 1184w, 1118m, 990s, 965sh, 893m and 721m.

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3

Poly(1,4-phenylenevinylene) System

3.1 Synthesis and Characterization of Poly(2,5-diheptyl-1,4-phenylenevinylene)

Introduction

Among the conjugated polymers exhibiting large nonlinearities, poly(1,4-phenylenevinylene) (PPV) is one of the most interesting from scientific and technological points of view, since it can easily be obtained as a high-quality film via the sulfonium salt pyrolysis procedure [1]. NLO properties of PPV can be enhanced by various chemical modifications. The introduction of the electron-donating alkoxy groups into the aromatic rings [2] or the replacement of phenylene with thienylene rings [3] reduced the energy band gap (Eg) of the polymer to improve its NLO properties considerably.

On the other hand, little attention has been paid on the NLO properties of alkylated PPV derivatives, since no decrease in Eg is expected in this case. However, in order to clarify the steric effect of long side chains on the NLO properties of PPV, it would be more helpful to study the properties of alkylated derivatives.

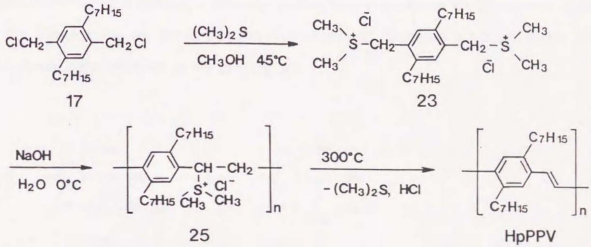
This section describes the preparation of a new PPV derivative, poly(2,5-diheptyl-1,4-phenylenevinylene) (HpPPV). A $\chi^{(3)}$ value for a thin film of HpPPV was

measured by the Maker fringe method of THG, and compared with that of HpPPHT described in Section 2.3.

Results and Discussion

Preparation of HpPPV

The synthetic route to HpPPV is shown in Scheme 3.1.1. The reaction of dichloride **17** with dimethyl sulfide afforded a stable salt **23** in a considerably high yield. In the preparation of PPV, tetrahydrothiophene (THT) gives a higher polymerization rate and polymer yield than dimethyl sulfide [4]. Thus, instead of dimethyl sulfide, THT was also



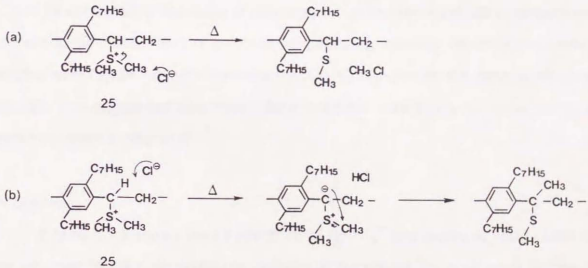
Scheme 3.1.1 Synthetic route to HpPPV

used for the preparation of a bis(sulfonium salt) monomer. However, the bis(sulfonium salt) **24** from THT was unstable and gradually returned to dichloride **17** and THT at room temperature. This is attributed to the steric hindrance between the bulky THT and heptyl groups, since dimethyl sulfide afforded the stable salt.

Monomer salt **23** was polymerized in an aqueous base to give sulfonium salt prepolymer **25** as a greenish-yellow gummy material. After dialysis of the reaction mix-

ture in a neutralized solution, the prepolymer was separated and used for the pyrolysis without drying completely, since it was unstable in the dry state. A solution of the prepolymer in 1-butanol was cast on a glass plate and heated. After pyrolysis, HpPPV was obtained as a high-quality freestanding film emitting strong green fluorescence. The pyrolysis was conducted at 200 or 300 °C. The products obtained at both temperatures showed completely identical NMR and IR spectra. The products were purified by reprecipitation into methanol. However, no change was detected in the NMR and IR spectra of the polymers after the reprecipitation.

Elemental analysis of HpPPV indicated the presence of a small amount of sulfur in the polymer. Since the sulfur content was almost the same for the polymers obtained by pyrolysis at 200 and 300 °C, the residual sulfur should be due to the elimination of monochloromethane instead of dimethyl sulfide from prepolymer **25** (Scheme 3.1.2(a)), or the Stevens rearrangement of the methyl groups (Scheme 3.1.2(b)), rather than incomplete decomposition of the prepolymer.



Scheme 3.1.2 Possible side reactions of prepolymer **25** on pyrolysis

As a result of having the flexible side chains, HpPPV is soluble in common organic solvents such as chloroform, dichloromethane, 1,1,2,2-tetrachloroethane and toluene. Solubility of the polymer obtained by pyrolysis at 200 °C was 50 mg cm^{-3} (chloroform). The product obtained by pyrolysis at 200 °C was more soluble than that obtained at 300°C. While almost all of the product at 200 °C was soluble in chloroform, only 70-75 % of the product at 300 °C was soluble. The 25-30 % residue was yellow-brown solid emitting no fluorescence. It was insoluble in chloroform even at elevated temperatures, suggesting that crosslinking took place during pyrolysis. However, IR spectra showed no clear difference between the soluble and insoluble parts.

Molecular weight of the chloroform-soluble part of HpPPV was measured by gel permeation chromatography. Calibration with polystyrene standards showed that molecular weight of HpPPV prepared at 200 °C were $\bar{M}_n$=3.8x10^4, $\bar{M}_w$=1.4x10^5 and $\bar{M}_w/\bar{M}_n$=3.7. Molecular weights of the polymer prepared at 300 °C were $\bar{M}_n$=4.7x10^4, $\bar{M}_w$=1.8x10^5 and $\bar{M}_w/\bar{M}_n$=3.8. These values are 4.5-5.5 times higher than those of an alkoxylated PPV derivative prepared by the McMurry process [5]. The molecular weight should be controlled at the stage of condensation of monomer salt **23** to prepolymer **25** and should be independent of pyrolysis temperatures. Actually, however, the molecular weights were higher for HpPPV obtained at 300 °C than that for the polymer obtained at 200 °C. This suggested that crosslinking reactions took place more frequently at a higher pyrolysis temperature.

IR Spectra

Figure 3.1.1 shows the IR spectrum of HpPPV. The peaks at 2800-3000 cm^{-1} are assigned to the C-H stretching vibration of the methyl and methylene groups. The peaks at 1378, 1467 and 1498 cm^{-1} are due to the skeletal vibration of a 1,2,4,5-tetrasubstituted benzene ring. The corresponding C-H out-of-plane vibration was observed at 892 cm^{-1}. These were observed at almost the same positions as the corre-

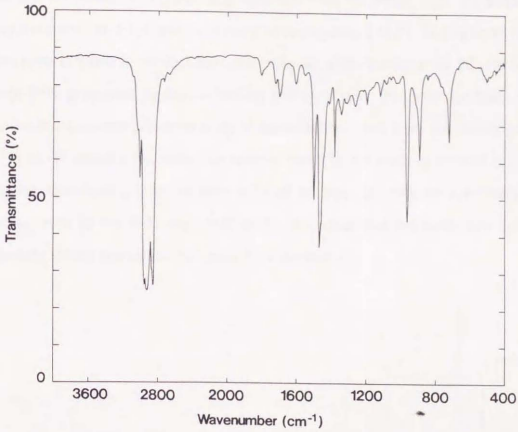


Figure 3.1.1 IR spectrum of HpPPV (film)

sponding peaks of HpPPHT (Section 2.3). The strong peak at 963 cm^{-1} is assigned to *trans* double bonds. A peak due to *cis* bonds was expected to appear at approximately 730 cm^{-1} [6]. Unfortunately, however, it is not clear from this spectrum whether *cis* bonds are present in the polymer, since a strong peak due to the wagging vibration of the methylene groups is located at 722 cm^{-1} [6].

NMR Spectra

Figure 3.1.2 shows the ^1H NMR spectrum of HpPPV measured in deuterio-chloroform. The peaks at δ7.42 and 6.86 are assigned to the aromatic protons of the *trans* and *cis* repeating units, respectively. The peaks at δ7.25 and 6.75 are assigned, respectively, to the olefinic protons of the *trans* and *cis* repeating units. These assign-

ments are consistent with previously reported ones for *trans*- and *cis*-stilbenes, 1,4-distyrylbenzene, and 1,4-phenylenevinylene oligomers [5,7]. The ratio of *trans* to *cis* olefinic units is found to be 93:7 from the integrals of the peaks at δ7.25 and 6.75. In the case of PPV prepared by the sulfonium salt pyrolysis, the polymer main chain was assumed to be consist predominantly of *trans* olefinic units from the strong peak at 965 cm^{-1} in its IR spectra [1]. Now the ratio of *trans* to *cis* olefinic units is quantitatively estimated. Considering that the ratio is 71:29 for poly(2,5-dihexyl-1,4-phenylenevinylene) prepared by the McMurry's method [5], it is clear that the sulfonium salt pyrolysis is excellent for the preparation of *trans* PPV derivatives.

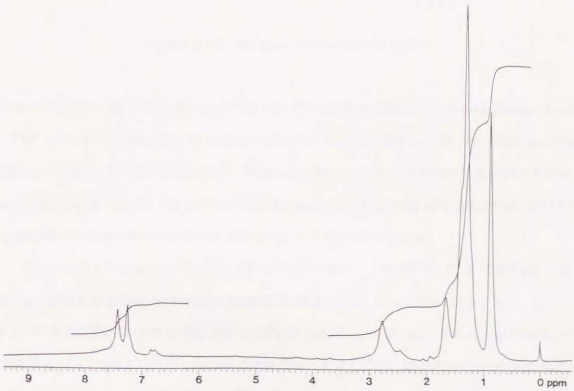


Figure 3.1.2 ^{1}H NMR spectrum of HpPPV ($CDCl_3$)

The peak at δ2.77 and the smaller one at δ2.43 are assigned to the protons of α-methylenes of heptyl groups. The ratio of their integrals was 9:1. These two peaks are tentatively assigned to two kinds of stereochemically different α-methylenes. The possible structures are shown in Figure 3.1.3. While the peak at δ2.77 is due to the

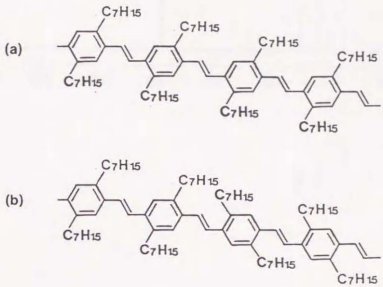


Figure 3.1.3 Two possible structures of HpPPV

regular structure (a), the peak at δ2.43 can be assigned to the more crowded structure (b). Two similar peaks due to α-methylenes were observed in ^{1}H NMR spectra of poly(3-alkyl-2,5-thiophene)s [8,9]. The smaller peaks at higher magnetic fields are considered to be due to the α-methylenes with more crowded structures, which was associated with the head-to-head bondings of thiophene rings.

Figure 3.1.4 shows ^{1}H-^{13}C COSY spectrum of HpPPV. It is clarified that the peak at δ126.9 is assigned to the carbons at 3 and 6 positions of the aromatic rings. The peak at δ127.2 is due to the *trans* olefinic carbons. Although the assignments of the peaks at δ135.6 and 138.5 are not clear from the COSY spectrum, comparison with spectra of compounds **17, 23** and **25** indicates that the peak at δ135.6 is due to the carbons at 2 and 5 positions of the aromatic rings. The other peak at δ138.5 must therefore be due to the carbons at 1 and 4 positions. The ^{13}C peak at δ33.4 corresponds to the ^{1}H peak due to the α-methylenes at δ2.77. The ^{13}C peak corresponding to the ^{1}H peak at δ2.43 would be too weak to be observed.

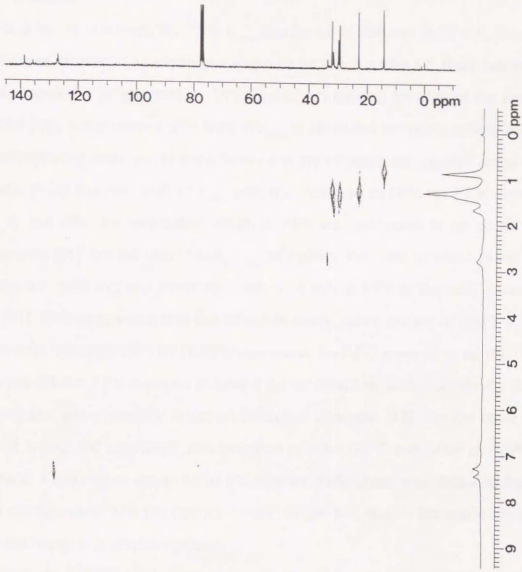


Figure 3.1.4 $^{1}H-^{13}C$ COSY NMR spectrum of HpPPV ($CDCl_3$)

UV-vis Spectra

Absorption maximum (λ_{max}) for a thin film of HpPPV was observed at 362 nm (3.43 eV), which was located at shorter wavelength by 30–40 nm than that in chloroform. This can be attributed to the fact that the conjugation system derivated from the coplanar configuration in the solid state due to the steric hindrance of the heptyl groups. In solution, the molecule can be more planar because the free-rotation of the heptyl

groups is possible.

For a film of unsubstituted PPV, λ_{max} was found at 456 nm (2.72 eV). Thus λ_{max} of HpPPV was located at shorter wavelength by as much as 94 nm than that of PPV. Since the degrees of polymerization (DPn) were high enough for both of the polymers (DPn > 100 [10]), the observed difference in λ_{max} is attributed not to the difference in the number of repeating units, but to the difference in the effective conjugation length in the solid state. From the red-shift of λ_{max} with the increase in DPn for PPV oligomers (DPn=1-6), the effective conjugation length of PPV was estimated to be about 10-17 repeating units [11]. On the other hand, λ_{max} of HpPPV film was between those of the dimer (358 nm, 3.46 eV) and trimer (395 nm, 3.14 eV) of PPV in the solid states (KBr pellets) [11]. This suggested that the effective conjugation length of HpPPV is 2-3 monomer units, although DPn for HpPPV was shown by GPC analysis to be 130-170.

Unsubstituted PPV is shown to have a planar structure both theoretically (MNDO calculation) and experimentally (electron diffraction analysis) [12]. On the other hand, analysis of X-ray and ultraviolet photoelectron spectra (XPS and UPS) of HpPPV by Austin Model 1 calculation showed that the polymer main chain was derivated from the coplanar configuration with the optimal torsion angle 34°, due to the steric hindrance between the heptyl and vinylene groups.

Introduction of the heptyl side chains improved the solubility of PPV and PPHT remarkably. In PPV, however, the steric hindrance of the side chains caused the torsion of the polymer main chain, and decreased its effective conjugation length considerably. On the other hand, λ_{max} of the tetramer of HpPPHT was located at longer wavelength than that of PHT3 in chloroform, indicating that the conjugation length increased with the increase in DPn. This is because the steric hindrance between the two adjacent heptyl groups was smaller in PPHT system.

Third-order NLO Properties

A value of $\chi^{(3)}$ for a thin film of HpPPV was measured by the Maker fringe

method of THG. The refractive index and thickness of the film used in the experiment were 1.723 and 220 nm, respectively. Figure 3.1.5 shows the measured third-harmonic

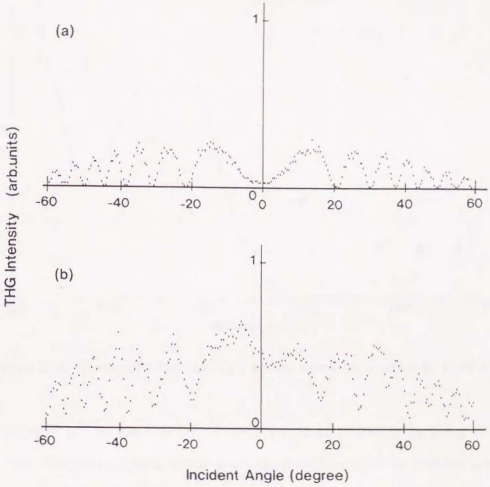


Figure 3.1.5 Measured third-harmonic intensities at 1.86 μm as a function of the incident light angle for (a)a quartz substrate of 1-mm thickness and (b)a HpPPV thin film of 220 nm thickness

intensities for (a)a quartz substrate and (b)a thin film of HpPPV as a function of the incident angle. Figure 3.1.6 shows the measured $\chi^{(3)}$ values of HpPPV as a function of the fundamental wavelength, together with the absorption spectrum of the film. The $\chi^{(3)}$ values increased somewhat as the wavelength decreased. This can be attributed to the near-resonance effect corresponding to the three-photon absorption.

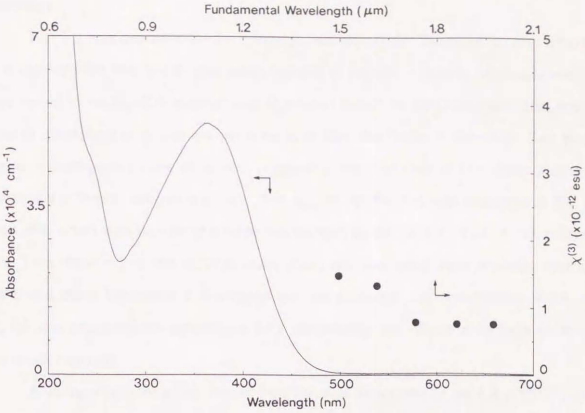


Figure 3.1.6 Wavelength dispersion of $\chi^{(3)}$ and the absorption spectrum for HpPPV film

A value of $\chi^{(3)}$ for the thin film of HpPPV was estimated to be 7.4 x 10^{-13} esu (at 1.98 μm, non-resonant region), which was about one-seventh of that for unsubstituted PPV (5 x 10^{-12} esu at 2.1 μm [13]). Following two reasons are possible to explain this result: (1) Eg of HpPPV and PPV films were determined from λ_{max} to be 3.43 and 2.72 eV, respectively. The larger Eg of HpPPV resulted in the lower $\chi^{(3)}$ value of the polymer; (2) π-Electron density of HpPPV was diluted with the bulky heptyl groups, and would be lower than that of PPV. The lower π-electron density also causes the decrease in the value of $\chi^{(3)}$.

In spite of its higher DPn, the $\chi^{(3)}$ value of HpPPV was one-fifth to one-third of that of HpPPHT. Eg of HpPPV was larger than that of HpPPHT by 0.47 eV, due to the larger torsion of the main chain. This resulted in the lower $\chi^{(3)}$ value of HpPPV.

Summary

HpPPV was prepared by the sulfonium salt pyrolysis. The polymer was obtained as a high-quality film, which was easily soluble in organic solvents. Molecular weights were found to be $\overline{M}_n$=3.8-4.7x10^4 and $\overline{M}_w$=1.4-1.8x10^5 by GPC analysis. The ratio of *trans* to *cis* olefinic units was shown to be 93:7 from the ^{1}H NMR spectrum. Two peaks due to α-methylenes were observed, suggesting the presence of two kinds of stereo-chemically different methylene groups. The λ_{max} of HpPPV film was observed at 362 nm (3.43 eV), which was located at shorter wavelength by 94 nm than that of unsubstituted PPV. This showed that the polymer main chain was derivated from coplanar structure due to the steric hindrance of the heptyl groups. Although the introduction of the long alkyl chains improved the solubility of PPV remarkably, the effective conjugation length was much reduced.

A value of $\chi^{(3)}$ for a thin film of HpPPV was estimated to be 7.4 x 10^{-13} (non-resonant region), which was about one-seventh of that of PPV. This is attributed to the larger Eg and lower π-electron density due to the steric hindrance and volume effect of the long side chains, respectively. The $\chi^{(3)}$ value of HpPPV was much lower than that of HpPPHT, because of the larger Eg of HpPPV. The delocalization of π-electrons was thus found to be more effective in PPHT system.

Experimental

Unsubstituted PPV was prepared according to the literature [4].

Bis(sulfonium salt) monomer 23

Dimethyl sulfide (1.6 cm^3, 22 mmol) was added to a solution of dichloride **17** (2.1 g, 5.5 mmol) in methanol (20 cm^3). After the mixture had been stirred at 45°C for 23 h, methanol and excess dimethyl sulfide were distilled off. Acetone (100 cm^3) was added

to the residue and the resulting solid was washed with ether and dried at room temperature to give sulfonium salt **23** as a white solid (2.2 g, 79 %); m.p. 187.0°C; $\delta_H(D_2O)$ 7.21 (2H, s), 4.48 (4H, s), 2.67 (12H, s), 2.54 (4H, t, *J* 7.8), 1.36–1.50 (4H, m), 0.99–1.16 (16H, m) and 0.64 (6H, t, *J* 7.0); $\delta_C(CD_3OD)$ 143.7, 135.9, 130.1, 48.5, 33.8, 33.6, 33.3, 31.3, 31.2, 25.9, 24.5 and 15.3; ν_{max}(KBr)/cm^{-1} 2923s, 2853s, 1653w, 1506m, 1467s, 1450s, 1420s, 1395m, 1379m, 1333w, 1307w, 1260s, 1203w, 1179w, 1148m, 1061s, 1022s, 951m, 907w, 835w, 763w, 724m, 701m, 672m, 607w and 464w.

Bis(sulfonium salt) monomer 24

Tetrahydrothiophene (THT) (1.0 cm^3, 11 mmol) was added to a solution of dichloride **17** (1.0 g, 2.7 mmol) in methanol (10 cm^3) and chloroform (1.0 cm^3). After the mixture had been stirred at 45 °C for 25 h, the solvents and excess THT were distilled off. Acetone (50 cm^3) was added to the residue and the resulting white solid was washed with ether and dried at room temperature to give sulfonium salt **24** (0.76 g, 52 %); $\delta_H(D_2O)$ 7.24 (2H, s), 4.40 (4H, s), 3.11–3.48 (8H, m), 2.60 (4H, t, *J* 7.6), 2.05–2.37 (8H, m), 1.38–1.57 (4H, m), 1.01–1.24 (16H, m) and 0.68 (6H, t, *J* 6.6).

Sulfonium salt prepolymer 25

To a solution of salt **23** (5.0 g, 10 mmol) in water (50 cm^3) was added an aqueous sodium hydroxide (0.20 mol dm^{-3}, 55 cm^3, 11 mmol) at 0°C over a period of 40 min. After the mixture had been stirred for 2 h, a diluted solution of hydrogen chloride was added to the reaction mixture to adjust pH to 7. After this solution was subjected to dialysis for 4 days, prepolymer **25** was separated from the solution as faint yellow-green powder. The dialysis was continued until no chloride ion was detected with silver nitrate. ν_{max}(KBr)/cm^{-1} 3018w, 2957s, 2927s, 2855s, 1688m, 1642m, 1503m, 1467m, 1429m, 1379w, 1314w, 1216s, 1096m, 1048m, 1021m, 928w, 759s and 669m.

Poly(2,5-diheptyl-1,4-phenylenevinylene) HpPPV

A saturated solution of prepolymer **25** in 1-butanol was cast on a glass plate and dried at room temperature overnight. The film on the glass plate was heated at 200 or 300 °C for 4 h *in vacuo*. HpPPV was obtained as a film emitting yellow-green fluorescence, which was dissolved in chloroform and purified by reprecipitation with methanol. The yield of HpPPV was 77 % based on monomer salt **23**. M.p. 355-365 °C (decomp.) (Found for HpPPV obtained by pyrolysis at 300 °C: C, 88.34; H, 11.56; S, 1.50 %. For HpPPV obtained by pyrolysis at 200 °C: C, 86.78; H, 10.98; S, 1.40 %. Calc.for $C_{22}H_{34}$: C, 88.52; H; 11.48; S, 0 %); $\delta_H(CDCl_3)$ 7.42 (2H, s), 7.25 (2H, s), 2.30-2.95 (4H, m), 1.66 (4H, bs), 1.00-1.51 (16H, m) and 0.88 (6H, bs); $\delta_C(CDCl_3)$ 138.5, 135.6, 127.2, 126.9, 33.4, 31.9, 31.4, 29.7, 29.2, 22.7 and 14.1; ν_{max}(film)/cm^{-1} 3008m, 2921s, 2854s, 1802w, 1695w, 1603w, 1498s, 1467s, 1378m, 1340w, 1259w, 1193w, 1118w, 963s, 892m, 722m and 504w.

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4

Dependence of Third-order Nonlinear Susceptibilities on Energy Band Gaps

Introduction

For a fundamental understanding of nonlinear optical (NLO) effects in conjugated molecules, it would be helpful to study the structure-property relationship for a series of conjugated oligomers with well-defined structures. There have been some experimental studies on the chain-length dependence of NLO properties for conjugated oligomers [1-7]. For thiophene oligomers, measured values of second hyperpolarizabilities, γ, showed a dependence on the 4-5th-power of the number of repeating unit [2,5]. This is in good agreement with that from the free-electron model (Chapter 1, Equation 1.2.5). As for the dependence of $\chi^{(3)}$ on energy band gaps (Eg), the model predicted that values of $\chi^{(3)}$ in non-resonant region showed an inverse dependence of the 6th-power of Eg (Equation 1.2.6) [8,9]. However, there has been few experimental report on the Eg-dependence of $\chi^{(3)}$, at least for organic compounds in the solid states.

In this chapter, the Eg-dependence of the measured $\chi^{(3)}$ values is studied for 1,4-phenylenehexa-1,3,5-trienylene and 1,4-phenylenevinylene oligomers described in the previous chapters. The result is compared with the theoretical prediction using the free-electron model.

Results and Discussion

Figure 4.1 shows the structures of the oligomers and polymers studied in this work. The measured Eg determined from the absorption maxima (λ_{max}) in chloroform, refractive indices at 633 nm, thicknesses of the films used in the THG measurements and $\chi^{(3)}$ values (non-resonant region) are listed in Table 4.1.

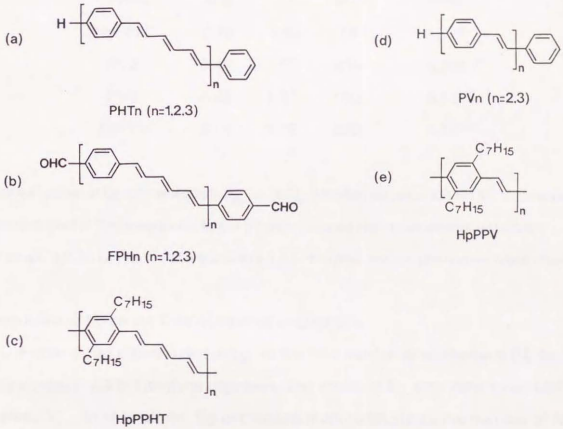

Figure 4.1 Structures of the oligomers and polymers in 1,4-phenylenehexa-1,3,5-trienylene and 1,4-phenylenevinylene systems

Compounds	Eg (eV)	n	t (nm)	$\chi^{(3)}$ ($\times 10^{-12}$ esu)
PHT1	3.46	1.49	1670	0.036 [(a)]
PHT2	2.96	1.72	240	1.0 [(a)]
PHT3	2.80	----	---	----
FPH1	3.12	1.53	340	0.20 [(a)]
FPH2	2.88	1.62	160	0.74 [(a)]
FPH3	3.00	----	---	----
HpPPHT	2.73	1.90	19	3.5 [(a)]
PV2	3.49	1.50	230	0.039 [(b)]
PV3	3.23	1.53	160	0.14 [(b)]
HpPPV	3.26	1.72	220	0.74 [(a)]

Table 4.1 Values of Eg determined from λ_{max} in $CHCl_3$, refractive indices at 633 nm (n), thicknesses (t) of the films used in THG measurements and $\chi^{(3)}$ (non-resonant region, fundamental wavelength: (a)1.98 μm; (b)1.50 μm) for 1,4-phenylenehexa-1,3,5-trienylene and 1,4-phenylenevinylene oligomers

Dependence of Eg on the Total Number of π-Electrons

Figure 4.2(a) shows a plot of Eg vs the total number of π-electrons (N) for 1,4-phenylenehexa-1,3,5-trienylene oligomers. The values of Eg were determined from the observed λ_{max} in chloroform. Eg decreased monotonously as the number of N increased, although it seemed to begin to level off from the tetramer (N~50). A plot of Eg vs N for 1,4-phenylenevinylene oligomers is shown in Figure 4.2(b) for comparison. The values of Eg were determined from the observed λ_{max} (for PV1, PV2 and PV3) or taken from the reported ones (for PV4, PV5 and PV6) [10] in chloroform. The measured Eg for these 1,4-phenylenevinylene oligomers agreed well with those obtained from VEH calculation [11,12]. Figures 4.2(a) and (b) show that Eg of a 1,4-phenylenehexa-1,3,5-trienylene oligomer is smaller than that of the 1,4-phenylenevinylene oligomer

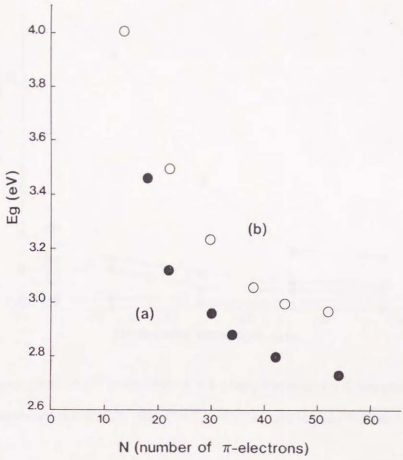

Figure 4.2 Plots of Eg vs the total number of π-electrons (N) for the oligomers in (a)1,4-phenylene-hexa-1,3,5-trienylene and (b)1,4-phenylenevinylene systems

having the same number of π-electrons. This indicates a more effective π-electron delocalization for the oligomers in 1,4-phenylenehexa-1,3,5-trienylene system.

Eg-Dependence of $\chi^{(3)}$

Figure 4.3 shows measured values of $\chi^{(3)}$ for thin films of 1,4-phenylenehexa-1,3,5-trienylene oligomers as a function of the incident light wavelength. The $\chi^{(3)}$ values of PHT2, FPH2 and HpPPHT increased as the fundamental wavelength decreased.

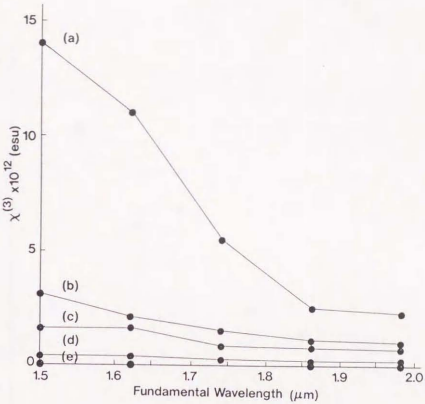

Figure 4.3 Measured values of $\chi^{(3)}$ for thin films of 1,4-phenylenehexa-1,3,5-trienylene oligomers as a function of the incident light wavelength; (a)HpPPHT, (b)PHT2, (c)FPH2, (d)FPH1 and (e)PHT1

This is attributed to the enhancement effect near the wavelength region of the third-harmonic resonance, as described in Sections 2.1, 2.2.1 and 2.3.

Third-order nonlinearity of a conjugated molecule is derived from its delocalized π-electrons. Since the degree of the delocalization is reflected to the optical absorption, the nonlinearity of the molecule must be closely related with its absorption spectrum. Figure 4.4 shows a plot of log $\chi^{(3)}$ (non-resonant) vs Eg. Values of log $\chi^{(3)}$ correlated well with Eg. No large difference was found between the correlation for the oligomers in 1,4-phenylenehexa-1,3,5-trienylene and that for the oligomers in 1,4-phenylene-vinylene systems.

The value of log $\chi^{(3)}$ was plotted vs log Eg in Figure 4.5. A simple least square fit showed the inclination of the plot to be −18. This means that the measured $\chi^{(3)}$ values

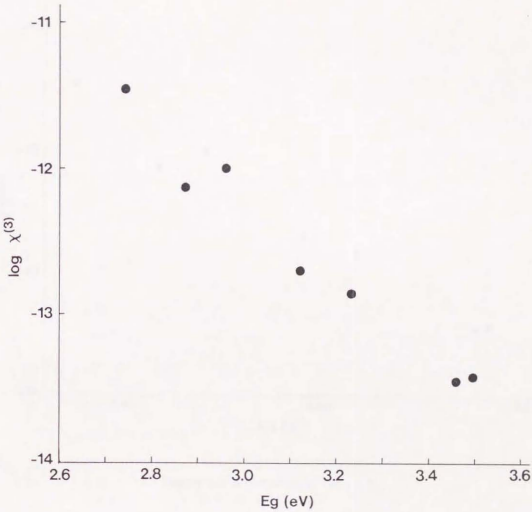

Figure 4.4 A plot of log $\chi^{(3)}$ vs Eg

show an inverse dependence on the 18th-power of Eg. Therefore, at least for the vacuum-deposited thin films of the oligomers studied in this work, the observed Eg-dependence of $\chi^{(3)}$ is found to be much stronger than that estimated from the free-electron model. This suggests that the interactions between π-electrons, which are neglected in the model, play an important role in exhibiting nonlinearities for thin films of linear π-conjugated compounds with finite chain-length.

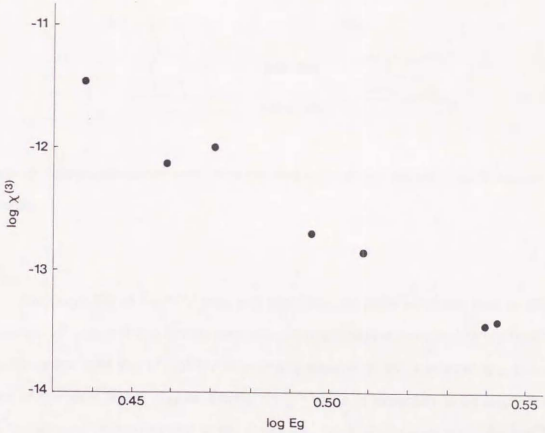

Figure 4.5 A plot of log $\chi^{(3)}$ vs log Eg

Difference in Eg-Dependence of $\chi^{(3)}$ between Vacuum-deposited and Cast Films

In the linear optical spectra of the vacuum-deposited thin films of PV2, PV3, PHT2, FPH1 and FPH2, very weak but clear absorptions were observed at 397, 434, 483, 449 and 498 nm, respectively. This suggests that the vacuum-deposited films are possibly oriented to some extent, because such absorptions were not detected in the solution spectra of the oligomers, or in the spectra of the cast films of HpPPHT and HpPPV. Since the vacuum-deposited films are probably oriented perpendicular to the substrate (Figure 4.6(a)), the molecules of PV2, PV3, PHT2, FPH1 and FPH2 should be perpendicular to the electric vector of the laser beam. The measured $\chi^{(3)}$ values of these oligomers may therefore be smaller than those expected for their non-oriented

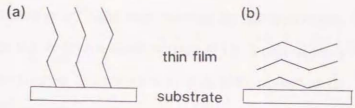

Figure 4.6 Possible orientations for thin films prepared by (a)vacuum deposition and (b)casting from solutions

films.

Although Eg of HpPPV was not significantly different from that of PV3, the measured $\chi^{(3)}$ value of the former was about 5 times higher than that of the latter (Table 4.1). Since the cast film of HpPPV is probably parallel to the substrate and the electric vector of the laser beam (Figure 4.6(b)), its $\chi^{(3)}$ value is expected to be larger than that for a film oriented perpendicular to the substrate. The higher value of $\chi^{(3)}$ for HpPPV can therefore be attributed to the difference in the orientations between the cast film of HpPPV and the vacuum-deposited film of PV3. However, there is another possibility that a transition from the ground state (S_o) to a higher excited state (S_n, $n \geq 2$), which can not be observed in the absorption spectrum, is more important in exhibiting the nonlinearity of HpPPV. If this is the case, the difference in $\chi^{(3)}$ values between HpPPV and PV3 can not simply be explained in terms of Eg determined from λ_{max} in the absorption spectra.

Summary

Chain-length dependence of Eg was investigated for a series of 1,4-phenylene-hexa-1,3,5-trienylene and 1,4-phenylenevinylene oligomers. Plots of Eg vs the total

number of π-electrons clearly indicated the more effective π-conjugation in the hexatrienylene system.

Eg-Dependence of $\chi^{(3)}$ was also clarified for the oligomers. The value of log $\chi^{(3)}$ correlated well with Eg. A simple least square fit for a plot of log $\chi^{(3)}$ - log Eg revealed that $\chi^{(3)}$ showed an inverse dependence on the 18th-power of Eg. The dependence is much stronger than the conventional free-electron model predicted, suggesting that the electron-electron interactions play an important role in exhibiting nonlinearities for thin films of linear π-conjugated oligomers with finite chain-length.

Weak absorptions observed at longer wavelengths in the spectra of the vacuum-deposited thin films of PV2, PV3, FPH1, FPH2 and PHT2 suggested the possibility that these films were oriented to some extent. The measured $\chi^{(3)}$ values of these oligomers may therefore be smaller than expected for their non-oriented films.

Although Eg of HpPPV was almost the same as that of PV3, the measured $\chi^{(3)}$ value of HpPPV was about 5 times higher than the value of PV3. This is probably due to the difference in the orientations between the cast and vacuum-deposited films.

Experimental

trans,trans-1,4-Distyrylbenzene (all-*trans*-PV2) and *trans,trans,trans*-4,4'-distyrylstilbene (all-*trans*-PV3) were prepared according to the literatures [13,14], and purified by recrystallization from toluene.

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5

Concluding Remarks

In the preceding chapters, I have described my studies on the preparation and third-order NLO properties of a series of π-conjugated oligomers in 1,4-phenylene-hexa-1,3,5-trienylene and 1,4-phenylenevinylene systems. For molecular design of organic materials with enhanced NLO properties, a fundamental understanding of non-linearity for conjugated compounds is needed. I believe my present work gives some basic and important findings for such an understanding. Finally, the remaining problems will be summarized.

In Chapter 2, I have described the preparation of 1,4-phenylenehexa-1,3,5-trienylene oligomers, and the measurements of $\chi^{(3)}$ for these oligomers in the solid states. In Section 2.1, the preparation of the dimer (PHT2) and trimer (PHT3) has been described. The energy band gap (Eg) determined from the absorption maximum (λ_{max}) decreased with the increase in the degree of polymerization (DPn). PHT2 showed a $\chi^{(3)}$ value of 1.0×10^{-12} esu in non-resonant region, which was as much as 30 times higher than that of the monomer (PHT1). Since Eg of PHT3 was somewhat lower than that of PHT2, the $\chi^{(3)}$ value of the trimer was expected to be higher than that of the dimer. However, PHT3 was unstable in air in the solid state, and its $\chi^{(3)}$ could not be measured. Moreover, it was rather intractable, because the solubility of PHT3 was very low.

In Section 2.2.1, the Wittig reaction of aldehyde **1** and the ylide from salt **4** has been described. The product was a mixture of oligomers with low DPn. This is due to the low solubilities of these oligomers. The monomer (FPH1), dimer (FPH2) and trimer (FPH3) with formyl end groups could be isolated from the mixture by GPC. However, FPH3 was shown to have some structural disorders, and the film was unstable in air as well in the case of PHT3. The instabilities of PHT3 and FPH3 are appeared to be derived from the fact that the conjugated double bonds are easily oxidized with molecular oxygen and/or water in air at room temperature.

Among the known organic polymers, polyacetylene (PA) has the highest record of $\chi^{(3)}$ up to now, but it is extremely unstable in air. Poly(1,4-phenylenevinylene) (PPV) is much more stable, but its $\chi^{(3)}$ value is moderate. Thus I have designed a new conjugated polymer, PPHT, with the expectation that it would show high nonlinearity as PA and high stability as PPV. Actually, however, PHT3 and FPH3 showed low stabilities as PA, and PHT2 and FPH2 showed lower values of $\chi^{(3)}$ than that of PPV. In order to overcome these undesirable properties of PPHT, it is necessary to introduce some suitable substituents into the aromatic rings of the polymer.

In Section 2.3, the preparation of poly(2,5-diheptyl-1,4-phenylenehexa-1,3,5-trienylene) (HpPPHT) has been described. Solubility of the polymer was much improved by introduction of the long alkyl side chains. However, DPn of HpPPHT was not so much enhanced. This can be attributed to the reduced polymerization rate due to the steric hindrance of the heptyl groups. The λ_{max} for the tetramer of HpPPHT was observed at longer wavelength than that of PHT3, showing that the conjugation length increased as DPn increased. However, little difference was found between λ_{max} of the tetramer and decamer of HpPPHT. This indicated that λ_{max} was no longer sensitive to the increase in DPn in the region of DPn > 4. In spite of its low DPn, the tetramer of HpPPHT showed a non-resonant $\chi^{(3)}$ value of 3.5×10^{-12} esu, which was only a little lower than that of PPV (5×10^{-12} esu) with high molecular weight ($\overline{M}n$=ca.30,000). Moreover, HpPPHT seemed to be more stable than PHT3 and FPH3. This is probably

due to the fact that steric hindrance of the heptyl groups suppressed the oxidation of the trienes in air. For more enhancement of the nonlinearity of HpPPHT, quantum coherent states such as J-aggregates should be made by introduction of electron-donating and accepting groups into the both ends of the polymer.

In Chapter 3, preparation of a new ring-substituted derivative of PPV, poly(2,5-diheptyl-1,4-phenylenevinylene) (HpPPV) has been described. The λ_{max} of HpPPV film was located at much shorter wavelength than that of the unsubstituted PPV. This is attributed to the torsion of the main chain due to the steric hindrance of the heptyl side chains. The introduction of the long alkyl side chains improved the solubility of PPV remarkably, however, its conjugation length was much reduced. A value of $\chi^{(3)}$ for the thin film of HpPPV was estimated to be about one-seventh of that for PPV in non-resonant region. This can be attributed to the higher Eg and lower π-electron density, which were respectively due to the steric and volume effects of the long side chains.

In Chapter 4, the Eg-dependence of $\chi^{(3)}$ for these oligomers has been described. The value of log $\chi^{(3)}$ correlated well with Eg. A conventional free-electron model predicted that $\chi^{(3)}$ showed an inverse dependence on the 6th-power of Eg. However, the plot of log $\chi^{(3)}$ vs log Eg for the experimental results indicated that the measured values of $\chi^{(3)}$ showed an inverse dependence on the 18th-power of Eg. Therefore, at least for the thin films of the oligomers studied in this work, the Eg-dependence of $\chi^{(3)}$ was found to be much stronger than the model had predicted. This suggests that the electron-electron interactions, which are neglected in the model, play an important role in exhibiting nonlinearities for thin films of conjugated molecules with finite chain-length. Although further experiments are required to confirm the generality and limitation of the correlation between $\chi^{(3)}$ and Eg, this finding can be fundamental for understanding of the origin of nonlinearities of conjugated compounds in the solid states.

Weak absorptions observed at longer wavelengths in the spectra of the vacuum-deposited films of PV2, PV3, PHT2, FPH1 and FPH2 suggested the possibility that these films were oriented to some extent. Since the vacuum-deposited films are con-

sidered to be oriented perpendicular to the substrates and the electric vector of the laser beam, the measured $\chi^{(3)}$ values of these oligomers may be smaller than those expected for their non-oriented films.

Although Eg of HpPPV was not significantly different from that of PV3, the value of $\chi^{(3)}$ was about 5 times higher than the value of PV3. This is probably due to the difference in the orientations between the cast film of HpPPV and the vacuum-deposited film of PV3. However, there is another possibility that a transition from the ground state to a higher excited state is more important in exhibiting the nonlinearity of HpPPV. This may give more interesting findings for understanding the NLO properties of π-conjugated polymers with high molecular weights.

General Experimental

Melting points were determined on a Laboratory Device Mel-Temp melting point apparatus and are reported uncorrected. High resolution mass spectra were obtained using a Hitachi M-80B instrument. Elemental analysis were performed with a CHNS-O EA1108-Elemental Analyzer (Carlo Erba Instruments). ^{1}H, ^{13}C and COSY spectra were recorded on a JEOL GSX 270 spectrometer with tetramethylsilane as internal reference; *J* values are given in Hz. IR spectra were recorded on a Perkin-Elmer 1720 spectrometer. UV-vis spectra of solutions and thin films were measured using a Hitachi U-3210 and a Shimadzu UV-3100S spectrometer, respectively. Isolation of products and determination of the molecular weights of the oligomers and polymers were conducted using an LC-908 gel-permeation liquid chromatograph (Japan Analytical Industry Co.Ltd.). Film thicknesses were measured with an Alpha-Step 300 Step-Height Profiler (Tencor Instruments). Refractive indices were measured at 633 nm using a Shimadzu AEP-100 ellipsometer. Wavelength dispersion of the refractive indices was calculated from the absorbance data using the Kramers-Kronig relation.

Measurement of Third-order Nonlinear Susceptibilities $\chi^{(3)}$

Thin films of PHT1, PHT2, PHT3, FPH1, FPH2, PV2 and PV3 were prepared on quartz glasses by vacuum deposition. Films of FPH3 and HpPPHT were prepared by casting from saturated solutions in toluene. A thin film of HpPPV was obtained by pyrolysis of the corresponding prepolymer which was cast on a quartz plate by spin-coating.

Third-harmonic generation (THG) measurements were carried out between 1.50-1.98 μm of fundamental wavelengths, which was generated by mixing beams from a Q-Switched Nd:YAG laser and a tunable dye laser using a $LiNbO_3$ crystal (Spectra-Physics, DCR-10). The pulse width was approximately 5 ns and the repetition rate was 10 Hz. The incident energy on a sample was roughly 2 mJ per pulse. A thin film sample

on a quartz glass substrate (1mm-thick) was mounted on a goniometer and rotated around an axis perpendicular to the laser beam. The apparatus was automatically controlled by a personal computer. The THG intensity of the sample film was measured as a function of laser incident angle. THG from the quartz glass was also measured as a control.

The observed THG was analyzed by the Maker fringe method. A value of $\chi^{(3)}$ was determined by fitting to the following equation reported in the literature [1]. A reference value of $\chi^{(3)} = 1 \times 10^{-14}$ esu was used for a fused quartz glass at all fundamental wavelength [2].

Equation for the determination of $\chi^{(3)}$

$$I_{3\omega} = \left| T_1 \frac{|\chi_s^{(3)}|}{\Delta\varepsilon_s} e^{-i\Delta\psi s/2} \sin\frac{\Delta\psi_s}{2} + T_2 \frac{|\chi_f^{(3)}| e^{-i\phi}}{\Delta\varepsilon_f} e^{-i\Delta\psi f/2} \sin\frac{\Delta\psi_f}{2} \right|^2 I_\omega^{\,3} \qquad (5.1)$$

where: ϕ is the phase of $\chi^{(3)}$ of the film, $\Delta\varepsilon = \varepsilon(\omega)-\varepsilon(3\omega) = n_\omega^{\,2}-n_{3\omega}^{\,2}$, $\Delta\psi = 6\pi t/\lambda_\omega(n_\omega\cos\theta_\omega - n_{3\omega}\cos\theta_{3\omega})$ is the phase mismatch between the waves at ω and 3ω in the medium, $n_{\omega,3\omega}$ is the refractive index, t is the film thickness, $\theta_{\omega,3\omega}$ is the angle the wave inside the material makes with the normal, $T_{1,2}$ are transmission factors depending on the boundary conditions and *f,s* refer to the film and substrate, respectively.

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Guide to Tables and Figures

1. General Introduction

2. Poly(1,4-phenylenehexa-1,3,5-trienylene) System

3. Poly(1,4-phenylenevinylene) System

4. Dependence of Third-order Nonlinear Susceptibilities on Energy Band Gaps

List of Publications

[1] "Preparation of Poly(2,5-diheptyl-1,4-phenylenevinylene) by Sulfonium Salt Pyrolysis"
Yoriko Sonoda and Kyoji Kaeriyama
Bull.Chem.Soc.Jpn., 1992,**65**,853.

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Yoriko Sonoda and Kyoji Kaeriyama
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Yoriko Sonoda and Yasuzo Suzuki
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[6] "Preparation and Nonlinear Optical Properties of Poly(2,5-diheptyl-1,4-phenylene-hexa-1,3,5-trienylene)"

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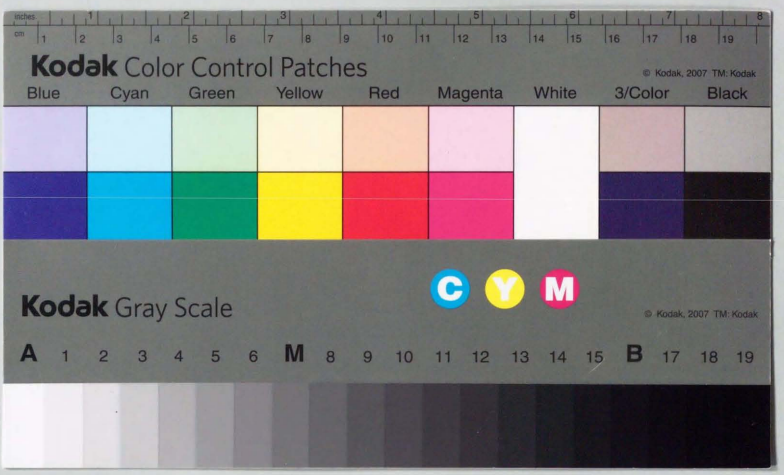
Macromolecules, (submitted)

[7] "Dependence of Third-order Nonlinear Susceptibilities on Energy Band Gaps for a Series of Linear π-Conjugated Oligomers"
Yoriko Sonoda, Kiyoshi Yase, Edward Van Keuren, Yasuzo Suzuki and Hiro Matsuda
Chem.Phys.Lett., (submitted)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