Preparation and Nonlinear Optical Properties of Poly(2,5-diheptyl-1,4-phenylenehexa-1,3,5-trienylene)

Yoriko Sonoda,* Yasuzo Suzuki, Edward Van Keuren, and Hiro Matsuda

National Institute of Materials and Chemical Research, 1-1 Higashi,
Tsukuba, Ibaraki 305, Japan

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ABSTRACT: A new π-conjugated polymer, poly(2,5-diheptyl-1,4-phenylenehexa-1,3,5-trienylene) (HpPPHT) was synthesized by a Wittig reaction. The polymer was obtained as a red solid ($\lambda_{max} = 453$ nm in chloroform) that was easily soluble in common organic solvents, as a result of introducing long alkyl side chains onto the aromatic rings. The structure was confirmed by IR and NMR spectra. The degree of polymerization was shown by GPC and NMR peak integrals to be about 10. The third-order nonlinear susceptibility $\chi^{(3)}$ for a thin film of HpPPHT was evaluated to be 2.3×10^{-12} esu (1.98 μm, nonresonant region) by third-harmonic generation (THG). The value was about 3 times higher than that of poly(2,5-diheptyl-1,4-phenylenevinylene) (HpPPV) due to the more effective π-delocalization in HpPPHT.

Introduction

Conjugated polymers have been studied extensively because of their potential as third-order nonlinear optical (NLO) materials.[1,2] Among these polymers, the poly(arylenevinylene)s are one of the most interesting classes of polymers from the scientific and technological points of view, because they can easily be obtained as stable, high-quality films via the sulfonium salt pyrolysis. Third-order nonlinear susceptibility, $\chi^{(3)}$, for a film of poly(1,4-phenylenevinylene) (PPV, Figure 1a) was evaluated by THG measurement to be 7.8×10^{-12} esu at a fundamental wavelength of 1.85 μm.[3] The introduction of electron-donating alkoxy groups into the aromatic rings[4] or the replacement of phenylene with thienylene rings[5] reduced the energy band gap (Eg) of the polymer to enhance its nonlinear optical properties. Film stretching, which resulted in the red shift and/or sharpening of the absorption, also improved the nonlinearity of PPV.[6] These results show that the nonlinearity in PPV can be enhanced by various chemical modifications and mechanical (orientational) influences.

Poly(1,4-phenylenehexa-1,3,5-trienylene) (PPHT, Figure 1c) is a polymer with a structure intermediate between these of poly(acetylene) (PA) and PPV. PPHT is expected to show higher NLO activity than PPV because of its lower Eg due to the replacement of vinylene with hexa-1,3,5-trienylene units. Furthermore, it should be more stable than PA as a consequence of having phenylene groups in the polymer main chain. However, an attempt to obtain a high-quality film of PPHT by sulfonium salt pyrolysis was unsuccessful.[7] Polymerization did not appear to occur in methanol. Although the sulfonium salt prepolymer was obtained in water, the oxidation of the prepolymer during and/or after the thermal treatment prevented us from obtaining the final conjugated polymer of PPHT. On the other hand, a Wittig reaction of terephthalaldehyde and an ylide from the bisphosphonium salt of *trans*-1,4-dichloro-2-butene gave PPHT with formyl end groups (FPPHT).[8] However, it was obtained as a powder with a low degree of polymerization (DPn < 10). These results are attributed to the low solubility of PPHT due to its rigid structure.

Introduction of long side chains onto the aromatic rings of a polymer improves its solubility remarkably. Some PPV derivatives bearing long alkyl or alkoxy chains were prepared as soluble polymers with high molecular weights.[9−14] Poly(2,5-diheptyl-1,4-phenylenevinylene) (HpPPV, Figure 1b), which we previously synthesized by sulfonium salt pyrolysis,[15] was easily soluble in common organic solvents, in spite of its high degree of polymerization (DPn ∼ 150). Therefore, the solubility of PPHT is expected to be improved by introduction of the long heptyl chains. This article reports the preparation of poly(2,5-diheptyl-1,4-phenylenehexa-1,3,5-trienylene) (HpPPHT, Figure 1d), a ring-substituted derivative of PPHT, by a Wittig reaction. A value of $\chi^{(3)}$ for a thin film of HpPPHT was measured by the Maker fringe method of THG. Values of $\chi^{(3)}$ for PPV and HpPPV were also measured for comparison.

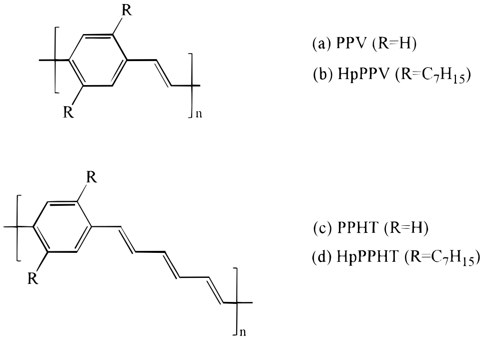

Figure 1. Structures of (a) PPV, (b) HpPPV, (c) PPHT, and (d) HpPPHT.

Results and Discussion

Preparation of Aldehyde 3a and Bisphosphonium Salt 6. The preparation procedure for aldehyde **3a** and salt **6** is shown in Scheme 1. Although aldehyde **2** could be obtained by hydrolysis of the hexaminium salt of dichloride **1**, the reaction using 2-nitropropane gave a higher yield of product. Aldol reaction of aldehyde **2** gave compounds **3a** (15%) and **3b** (25%). In the aldol reaction of the parent terephthalaldehyde, the symmetrical diadduct could be selectively obtained in 42% yield. Only a trace amount of the unsymmetrical isomer was shown to be formed by a ^{1}H NMR spectrum of the reaction mixture. The higher yield of aldehyde **3b** relative to **3a** therefore should be attributed not to

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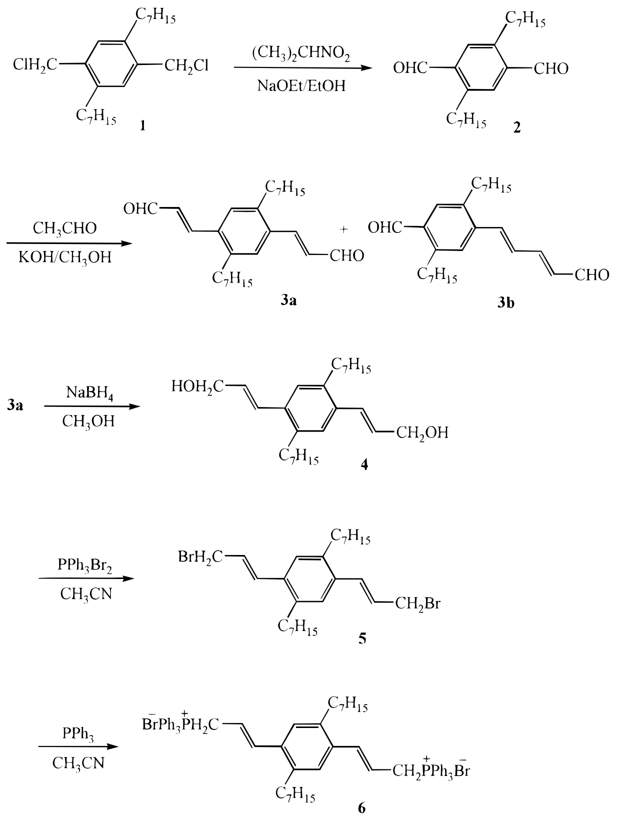
Scheme 1. Synthetic Route to Aldehyde 3a and Bisphosphonium Salt 6

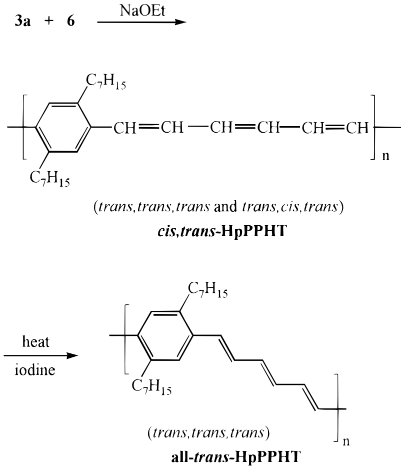


a higher intrinsic reactivity of cinnamaldehyde relative to benzaldehyde but to the steric hindrance of heptyl groups of aldehyde **2**. Aldehyde **3a** could be isolated from the reaction mixture, which contained a large amount of the starting compound, an intermediate with only one formyl group reacted, and high molecular weight red materials, by silica gel column chromatography. The reduction of aldehyde **3a** with $NaBH_4$ in methanol gave alcohol **4**. From this alcohol, dibromide **5** was obtained by a procedure similar to that given for 1,4-phenylene-3,3′-bis(allyl bromide).[7] Bromide **5** reacted with triphenylphosphine in acetonitrile to afford bisphosphonium salt **6**. The solubilities of aldehyde **3a** and salt **6** were much improved compared to the corresponding unsubstituted compounds.

Polymerization. HpPPHT was prepared by the Wittig reaction of dialdehyde **3a** and bisphosphonium salt **6** (Scheme 2). Since the reaction did not occur in ethanol at room temperature, we conducted the reaction at refluxing temperature using the same solvent to obtain HpPPHT as a red precipitate. However, the value of DPn was estimated from ^1H NMR peak integrals to be 4-5, which was rather lower than we had 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 in compounds **3a** and **6**.

We thus conducted the reaction 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 about 10 mg/mL. Its DPn was estimated to be 9−10 from ^1H NMR peak integrals. GPC analysis (chloroform elution) showed that its molecular weight was $\bar{M}_n = 3900$ (DPn = 10−11) and $\bar{M}_w/\bar{M}_n = 2.0$ (polystyrene standard). Although DPn of HpPPHT was not enhanced significantly compared with FPPHT,[8] the solubility was much improved by the introduction of the long alkyl groups.

Scheme 2. Synthesis of HpPPHT by the Wittig Reaction of Compounds 3a and 6



***cis*−*trans* Thermal Isomerization.** As will be shown later in this article, IR and ^1H NMR spectra of the crude HpPPHT showed the presence of a considerable amount of *trans,cis,trans*-trienes. Similar findings were observed for the dimer (PHT2) and trimer (PHT3) of PPHT, which we had previously synthesized as model compounds for the polymer.[16] Pure *all-trans* isomers of PHT2 and PHT3 were obtained by heating crude products having *trans,cis,trans*-trienes in appropriate solvents with a trace of iodine. Thus, we conducted a similar heat treatment for the present *cis*-containing crude polymer (*cis,trans*-HpPPHT) to obtain HpPPHT with a predominantly *trans,trans,trans* structure (*all-trans*-HpPPHT, Scheme 2). The solubility of the polymer decreased somewhat after the isomerization.

In the preparation of FPPHT by the Wittig reaction of terephthalaldehyde and the bisphosphonium salt of *trans*-1,4-dichloro-2-butene,[8] the polymer was expected to have *cis,trans,trans*(and *cis,trans,cis*)-trienes, since double bonds at the 1 and 5 positions of the trienes were newly formed. Actually, however, the IR and NMR spectra of the polymer obtained showed only a small amount of *cis* double bonds. Since *cis,trans,trans*-1,6-bis(4-formylphenyl)hexa-1,3,5-triene isomerized to its *trans,trans,trans* form in the dark at room temperature,[8] FPPHT having *cis,trans,trans*-trienes possibly thermally isomerized to that with an *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. *cis,trans,trans*-1,6-Diphenylhexa-1,3,5-triene (*cis,trans,trans*-DPH) is theoretically predicted to be a nonplanar structure due to the steric hindrance between the phenyl groups and *cis* double bonds, while a planar structure is predicted for *trans,cis,trans*-DPH.[17] Therefore, the thermal stabilities of these isomers are expected to be *trans,trans,trans*-DPH > *trans,cis,trans*-DPH > *cis,trans,trans*-DPH. The *cis, trans* geometries of trienes in the crude products of PHT2, PHT3, FPPHT, and HpPPHT can thus be explained by the different thermal stabilities between *trans,cis,trans*- and *cis,trans,trans*-trienes. Furthermore, in the case of HpPPHT, the steric hindrance of

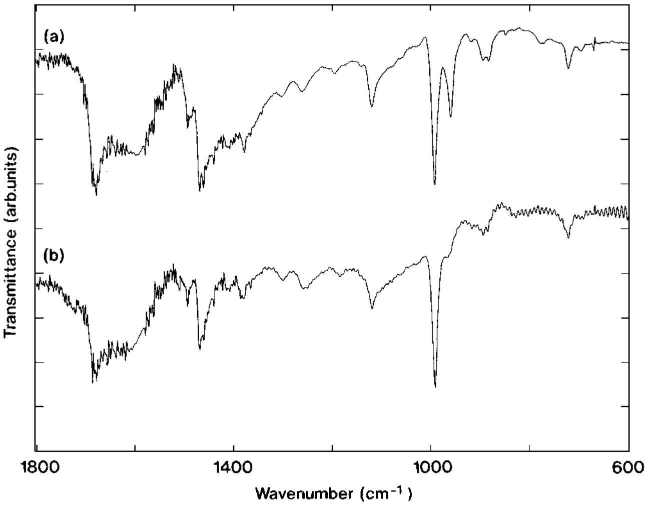


Figure 2. IR spectra of (a) *cis,trans*- and (b) *all-trans*-HpPPHT prepared in benzene (KBr disk).

the heptyl groups would suppress the *cis*−*trans* thermal isomerization.

IR Spectra. Figure 2a 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.[16,18,19] After the heat treatment, the peak at 958 cm^{-1} disappeared and only a strong peak was observed at 990 cm^{-1} (Figure 2b). Since this peak is characteristic of *trans,trans,trans*-trienes,[16,18,19] this observation clearly shows that the *cis,trans*-HpPPHT isomerized to the polymer with *all-trans* structure by the treatment. The broad absorption at around 1600 cm^{-1} can be attributed to the C=C stretching vibration of trienes.[16,18,19] A similar strong absorption was observed in the spectrum of FPPHT.[8] In the spectra of PHT2 and PHT3,[16] however, the corresponding peaks were very weak. This is probably due to the more highly symmetrical structures of PHT2 and PHT3 than those of HpPPHT and FPPHT, since the intensity of the peaks due to C=C double bonds is expected to diminish when the molecule becomes more symmetrical.[20] The strong peak at 1677 cm^{-1} is attributed to the C=O vibration of carbonyl groups conjugated with double bonds, indicating that the end groups of HpPPHT prepared in benzene are CH=CHCHO groups. No peak due to monosubstituted benzene rings was observed. For the polymer prepared in ethanol, on the other hand, two characteristic peaks due to benzene rings were observed at 690 and 744 cm^{-1}, in addition to the carbonyl peak at 1677 cm^{-1}. These peaks suggest the presence of the two kinds of end groups, $CH{=}CHCH_2{}^{+}PPh_3Br^{-}$ and CH=CHCHO, in the polymer. Other characteristic peaks are assigned as follows: 3029 (C−H stretching vibration of =CH), 2954 and 2924 (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 721 cm^{-1} (wagging vibration of methylenes).

^{1}H NMR Spectra. Figure 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 trienes were newly formed by the polymerization. From comparison with the spectra of authentic *trans,trans,trans*- and *trans,cis,trans*-DPH,[21] peaks due to the trienes in the polymer can be assigned as follows: δ 7.3−7.4 (*trans,cis,trans,* H_2 and H_5), 6.7−7.0 (*trans,trans,trans*, H_1, H_2, H_5, and H_6; *trans,cis,trans,* H_1 and H_6), 6.4−6.7 (*trans,trans,trans*, H_3 and H_4), and 6.2−6.4 (*trans,cis,trans*, H_3 and H_4). The ratio of *trans,trans,trans*-:*trans,cis,trans*-trienes was estimated to be 2:1 from peak integrals. The peaks of H_1 and H_6 of *trans,trans,trans*- and *trans,cis,trans*-trienes in *cis, trans*-HpPPHT are located at lower magnetic fields by 0.2−0.3 ppm than those of the corresponding protons in the *trans,trans,trans* and *trans,cis,trans* isomers of DPH.[21] 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.[22] Our observation described earlier therefore can be attributed to the steric hindrance between H_1 and H_6 of the trienes and H_1 of the heptyl groups in the polymer. Figure 3 (inset) also shows the spectrum of *all-trans*-HpPPHT prepared in benzene. Intensities of the peaks of *trans,cis,trans*-trienes at δ 7.3−7.4 and 6.2−6.4 decreased significantly, supporting the peak assignments for *cis,trans*-HpPPHT described earlier. Although the IR peak due to *cis* double bonds was very weak for the polymer after heating (Figure 2b), ^{1}H NMR peak integrals showed the ratio of *trans,trans,trans*:*trans,cis,trans* to be 85:15.

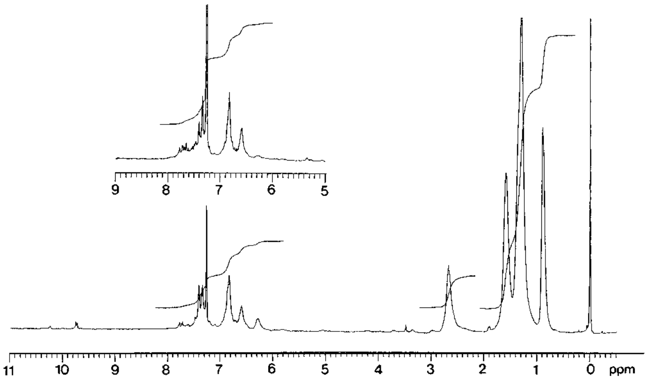


Figure 3. ^{1}H NMR spectra of *cis,trans*- and (inset) *all-trans*-HpPPHT prepared in benzene ($CDCl_3$).

In the spectra of *cis,trans*- and *all-trans*-HpPPHT prepared in ethanol, peaks due to CH=CHCHO and $CH{=}CHCH_2{}^{+}PPh_3Br^{-}$ end groups were observed at δ 9.68−9.76 (CH=CHC*H*O), 7.62−7.98 ($CH{=}CHCH_2$-$^{+}PPh_3Br^{-}$ and C*H*=CHCHO), 5.86−6.00 ($CH{=}CHCH_2$-$^{+}PPh_3Br^{-}$), and 5.04−5.17 ($CH{=}CHCH_2{}^{+}PPh_3Br^{-}$). The polymer thus was shown to have the two kinds of end groups. Integrals of these peaks indicated that the ratio of the end groups $CH{=}CHCHO{:}CH{=}CHCH_2{}^{+}PPh_3Br^{-}$ was 65:35. For the polymer prepared in benzene, however, peaks of $CH{=}CHCH_2{}^{+}PPh_3Br^{-}$ groups were very weak, indicating that only CH=CHCHO groups were contained as the end groups in the polymer. These findings agreed with those from the IR spectra.

^{13}C NMR Spectra. *cis,trans*-HpPPHT prepared in benzene gave the following ^{13}C NMR data in deuteriochloroform: δ 138.6 and/or 138.3 (arom, C_1 and C_4), 134.9 (arom, C_2 and C_5), 133.9 (*trans,trans,trans*-triene, C_3 and C_4), 130.8 (*trans,trans,trans*-triene, C_1 and C_6), 129.8 (*trans,trans,trans*-triene, C_2 and C_5), and 126.7 and/or 126.4 (arom, C_3 and C_6). Peaks due to the carbon atoms of methylene and methyl groups of the heptyl chains were observed in the region of δ 14−34. The peak of C_2 and C_5 and that of C_3 and C_4 of the *trans,trans,trans*-trienes in the polymer had almost the same chemical shifts as the corresponding peaks of the

Table 1. Values of Energy Band Gaps Determined from λ_{max} (Eg), Thicknesses (*t*), Refractive Indices at 633 nm (*n*), and Third-Order Nonlinear Susceptibilities at 1.98 μm ($\chi^{(3)}$) for Thin Films of HpPPHT, HpPPV, and PPV

polymers	DPn	Eg (eV)	*t* (nm)	*n*	$\chi^{(3)} \times 10^{12}$ (esu)
cis,trans-HpPPHT[a]	4	2.96	19	1.90	3.5
cis,trans-HpPPHT[b]	10	3.08	17	1.80	2.3
HpPPV	150	3.43	217	1.72	0.74
PPV	100	2.72	30	2.41	9.7

[a] HpPPHT prepared in ethanol. [b] HpPPHT prepared in benzene.

authentic *trans,trans,trans*-DPH.[23] However, the peak of C_1 and C_6 of the trienes was located at a higher magnetic field by 1.6 ppm than that of the corresponding carbons of DPH.[23] The steric hindrance of H_1 and H_6 of the triene and H_1 of the heptyl groups caused the increase in the electron density of C_1 and C_6 of the trienes. This resulted in a shift to the higher magnetic field of the peak in the ^{13}C NMR spectrum. The peak due to C_3 and C_4 of the *trans,cis,trans*-trienes of the polymer was observed at δ 124.7, which was located at a higher magnetic field than the corresponding peak of the *trans,trans,trans*-trienes by 9.2 ppm. Similar upshield of the peak due to the carbon atoms of *cis* double bonds was reported for *cis*-poly(acetylene).[24]

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 in chloroform. The spectrum of *all-trans*-HpPPHT (λ_{max} = 457nm) was practically identical to that of the *cis,trans* polymer. Also in the case of DPH, the difference in λ_{max} between *trans,trans,trans* and *trans,cis,trans* isomers was reported to be very small.[25] 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 are considered to have planar structures.[17] For *all-trans*-DPH, PHT2, PHT3,[16] and HpPPHT prepared in ethanol, λ_{max} values were observed at 358, 419, 443, and 457 nm in chloroform, respectively. The π-conjugation system increased as the degree of polymerization increased, suggesting that HpPPHT prepared in ethanol had little or no structural defects in the polymer main chain. As for HpPPHT prepared in benzene, however, λ_{max} values were observed at 453 nm for both *cis,trans* and *all-trans* polymers in chloroform. In spite of the higher degree of polymerization, these values were essentially the same as that for the polymer prepared in ethanol. Although no peak due to $CH{=}CHCH_2{}^+PPh_3Br^-$ end groups was observed in the NMR or IR spectra, ICP spectrochemical analysis showed that the polymer contained 0.13% of phosphorus. The phosphorus therefore should be derived from phosphorus-containing groups in the polymer main chain, which were possibly formed by undesirable side reactions that occurred during the polymerization. These structural defects would interrupt the conjugation of the polymer, resulting in the blue shift of λ_{max} in the UV–vis spectrum.

Third-Order NLO Properties. Values of $\chi^{(3)}$ were measured for thin films of *cis,trans*-HpPPHT by the Maker fringe method of THG. Measurements were also conducted for thin films of HpPPV and PPV under the same conditions for comparison. The values of $\chi^{(3)}$, energy band gaps (Eg), refractive indices (*n*), and thicknesses (*t*) of the films of these polymers are listed in Table 1. Figure 4 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 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. HpPPHT prepared in ethanol showed a similar wavelength dependence of $\chi^{(3)}$. The resonant effect was also reported for conjugated polymers such as PPV[3], 2,5-alkoxylated PPV,[4] and poly(2,5-thienylenevinylene).[5]

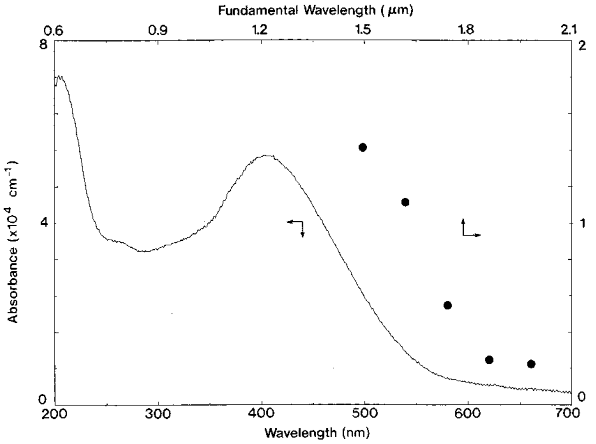


Figure 4. Measured $\chi^{(3)}$ values and the absorption spectrum for a thin film of *cis, trans*-HpPPHT prepared in benzene.

As shown in the table, HpPPHT prepared in ethanol exhibited a little higher value of $\chi^{(3)}$ than that of the polymer prepared in benzene. Since $\chi^{(3)}$ for a conjugated polymer is enhanced with the decrease in Eg, the higher value of $\chi^{(3)}$ for the former can be attributed to its smaller Eg than that of the latter by 0.12 eV. The measured $\chi^{(3)}$ value of HpPPV (DPn ~ 150)[15] was 7.4×10^{-13} esu at 1.98 μm, which was much lower than the value of PPV. This can be attributed to the increase in Eg from the torsion of the main chain and the decrease in the π-electron density due to the steric hindrance and volume effect of the heptyl side chains, respectively. In spite of the low degree of polymerization, the nonresonant $\chi^{(3)}$ value of HpPPHT prepared in ethanol was about 5 times higher than that of the high molecular weight HpPPV. This is attributed to the smaller Eg for the film of HpPPHT than that of HpPPV by as much as 0.47 eV. Due to the smaller steric hindrance of the heptyl side chains, the main chain of HpPPHT was considered to be less strongly distorted. This led to the more effective π-electron delocalization in HpPPHT, which resulted in the higher value of $\chi^{(3)}$ for the polymer.

Summary

A new conjugated polymer, HpPPHT, was prepared by a Wittig reaction. It was easily soluble in organic solvents as a result of introducing long alkyl side chains. The structure was confirmed by IR, ^{1}H NMR, ^{13}C NMR, and UV–vis spectroscopies. In spite of its low degree of polymerization, the polymer exhibited a relatively high value of $\chi^{(3)}$ due to its highly conjugated structure.

Experimental Section

2,5-Diformyl-1,4-diheptylbenzene (2). The preparatory procedure for 2,5-bis(chloromethyl)-1,4-diheptylbenzene (**1**) has already been described.[15] 2-Nitropropane (2.4 mL, 27 mmol) was added to a solution of sodium ethoxide (1.0 mol/L, 27 mL) to give the sodium salt of 2-nitropropane as a white precipitate. To this suspension was added a hot solution (60 °C) of dichloride **1** (5.0 g, 13.5 mmol) in ethanol (110 mL), 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 diethyl ether (200 mL) and water (300 mL), respectively. The ether layer was washed with aqueous sodium hydroxide (5%, 100 mL) to remove any acetoxime and excess 2-nitropropane and then washed with water (100 mL). 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 **2** (4.3 g, 97%): mp 57.0−58.0 °C; ^{1}H NMR (270 MHz, $CDCl_3$) δ 10.36 (s, 2H), 7.73 (s, 2H), 2.92−3.10 (m, 4H), 1.48−1.72 (m, 4H), 1.07−1.48 (m, 16H), and 0.88 (t, $J = 6.7$ Hz, 6H). Anal. Calcd for $C_{22}H_{34}O_2$: C, 79.95; H, 10.37 (M, 330.2556). Found: C, 79.75; H, 10.41 (M^+, 330.2555).

Aldol Reaction of Dialdehyde 2 and Acetaldehyde. A solution of dialdehyde **2** (3.0 g, 9.2 mmol) and potassium hydroxide (2.0 g) in methanol (600 mL) was stirred for 3 h at 0−5 °C under bubbling with nitrogen. To this solution was added dropwise a solution of acetaldehyde (90% in water, 2.5 mL) in methanol (15 mL) at room temperature under a nitrogen atmosphere. After the mixture had been stirred for 2 days at room temperature, aqueous ammonium chloride (0.5%, 1.0 L) was added to the reaction mixture, and the products were extracted with diethyl ether (900 mL). The extract was dried over $MgSO_4$, and the solvent was evaporated under reduced pressure to give an orange oil (3.73 g). The crude products were subjected to silica gel column chromatography (hexane:diethyl ether = 9:1). Aldehydes **3a** (0.51 g, 15%) and **3b** (0.85 g, 25%) were isolated. Aldehyde **3a** was purified further by recrystallization from hexane.

2,5-Diheptyl-1,4-phenylene Diacrylaldehyde (3a): mp 95.0−97.0 °C; ^{1}H NMR ($CDCl_3$) δ 9.76 (d, $J = 7.4$ Hz, 2H), 7.75 (d, $J = 15.8$ Hz, 2H), 7.46 (s, 2H), 6.72 (dd, $J = 15.6$, 7.7 Hz, 2H), 2.76 (t, $J = 7.8$ Hz, 4H), 1.47−1.66 (m, 4H), 1.15−1.47 (m, 16H), and 0.87 (t, $J = 6.3$ Hz, 6H). Anal. Calcd for $C_{26}H_{38}O_2$: M, 382.2870. Found: M^+, 382.2880.

2-(4-Formylbuta-1,3-dienyl)-5-formyl-1,4-diheptylbenzene (3b): Oil; ^{1}H NMR ($CDCl_3$) δ 10.26 (s, 1H), 9.67 (d, $J = 7.9$ Hz, 1H), 7.66 (s, 1H), 7.46 (s, 1H), 7.34 (dd, $J = 15.1$, 11.0 Hz, 1H) 7.28 (d, $J = 15.3$ Hz, 1H), 7.04 (dd, $J = 15.7$, 10.7 Hz, 1H), 6.35 (dd, $J = 15.1$, 7.9 Hz, 1H), 3.00 (t, $J = 7.8$ Hz, 2H), 2.74 (t, $J = 7.8$ Hz, 2H), 1.46−1.69 (m, 4H), 1.16−1.46 (m, 16H), and 0.88 (t, $J = 6.7$ Hz, 6H).

2,5-Bis(3-hydroxy-1-propenyl)-1,4-diheptylbenzene (4). A mixture of dialdehyde **3a** (0.50 g, 1.3 mmol) and $NaBH_4$ (0.050 g, 1.3 mmol) was stirred in methanol (10 mL) for 24 h at 40 °C. This solution was quenched with aqueous sodium carbonate (0.2%, 200 mL). The products were extracted with diethyl ether (500 mL). The extract was dried over $MgSO_4$ and evaporated under reduced pressure to give a yellow oil (0.43 g). Recrystallization of this oil from hexane gave dialcohol **4** (0.23 g, 46%) as pale yellow crystals: mp 72.0−73.5 °C; ^{1}H NMR ($CDCl_3$) δ 7.24 (s, 2H), 6.82 (d, $J = 15.8$ Hz, 2H), 6.26 (dt, $J = 15.5$, 5.9 Hz, 2H), 4.34 (dd, $J = 5.9$, 1.5 Hz, 4H), 2.62 (t, $J = 7.9$ Hz, 4H), 1.45−1.67 (m, 4H), 1.18−1.41 (m, 16H), and 0.88 (t, $J = 6.8$ Hz, 6H). The OH protons were not detected. Anal. Calcd for $C_{26}H_{42}O_2$: M, 386.3183. Found: M^+, 386.3188.

2,5-Bis(3-bromo-1-propenyl)-1,4-diheptylbenzene (5). A solution of bromine (8%, w/w) in acetonitrile was added dropwise to a solution of triphenylphosphine (0.28 g, 1.1 mmol) in acetonitrile (10 mL) 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 **4** (0.20 g, 0.52 mmol) in acetonitrile (10 mL) was added, and the mixture was stirred for an additional 1 h at room temperature. The solvent was evaporated under reduced pressure. Ethanol in water (60%, 100 mL) was added to the residue, and the resulting precipitate was filtered and dried at room temperature to give dibromide **5** as pale yellow crystals (0.19 g, 71%): mp 60.0−62.0 °C; ^{1}H NMR ($CDCl_3$) δ 7.23 (s, 2H), 6.85 (d, $J = 15.5$ Hz, 2H), 6.29 (dt, $J = 15.5$, 7.8 Hz, 2H), 4.18 (dd, $J = 7.8$, 0.8 Hz, 4H), 2.61 (t, $J = 7.8$ Hz, 4H), 1.46−1.59 (m, 4H), 1.21−1.40 (m, 16H), and 0.89 (t, $J = 6.8$ Hz, 6H). Anal. Calcd for $C_{26}H_{40}Br_2$: M, 510.1496. Found: M^+, 510.1496.

2,5-Bis[3-(triphenylphosphonio)-1-propenyl]-1,4-diheptylbenzene Dibromide (6). A solution of dibromide **5** (0.15 g, 0.29 mmol) and triphenylphosphine (0.21 g, 0.80 mmol) in acetonitrile (50 mL) was heated at reflux for 24 h. After the solvent had been evaporated under reduced pressure, toluene (20 mL) was added to the residue to give a precipitate. This was filtered off and dried at room temperature to afford bisphosphonium salt **6** (0.27 g, 90%) as a pale yellow solid: mp 226−230 °C (dec); ^{1}H NMR ($CDCl_3$) δ 7.59−8.00 (m, 30H), 6.94 (s, 2H), 6.87 (dd, $J = 15.7$ Hz, $J_{P-H} = 5.8$ Hz, 2H), 5.80−5.95 (m, 2H), 5.10 (dd, $J = 7.6$ Hz, $J_{P-H} = 14.8$ Hz, 4H), 2.27 (t, $J = 7.9$ Hz, 4H), 1.48−1.62 (m, 4H), 1.11−1.36 (m, 16H), and 0.88 (t, $J = 6.8$ Hz, 6H).

Wittig Reaction of Dialdehyde 3a and Bisphosphonium Salt 6. (a) Reaction in Ethanol. To a solution of dialdehyde **3a** (100 mg, 0.26 mmol) and bisphosphonium salt **6** (270 mg, 0.26 mmol) in absolute ethanol (75 mL) was added a solution of sodium ethoxide (0.10 mol/L, 5.2 mL) under a nitrogen atmosphere. After the solution had been heated at reflux in the dark for 24 h, the resulting red precipitate was filtered off and washed with ethanol (50 mL). *cis,trans*-HpPPHT (53 mg) was obtained as a red solid.

Thermal Isomerization. A solution of *cis,trans*-HpPPHT (20 mg) in chloroform (30 mL) 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 with ethanol to give *all-trans*-HpPPHT as a red solid (5−10 mg).

(b) Reaction in Benzene. The reaction was conducted in a manner similar to that described earlier. 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 off, washed with ethanol, and dried at room temperature to give *cis,trans*-HpPPHT (100 mg) as a red solid: mp 120−126 °C (dec).

Thermal Isomerization. A solution of *cis,trans*-HpPPHT (benzene) (20 mg) in chloroform (30 mL) 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 reprecipitated with chloroform−ethanol to give *all-trans*-HpPPHT as a red solid (5−10 mg).

Characterization. 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 and ICP spectrochemical analyses were performed with a CHNS-O EA1108 elemental analyzer (Carlo Erba Instruments) and an SPS-1200VR sequential ICP spectrochemical analyzer (Seiko Densi Kogyo), respectively. ^{1}H and ^{13}C NMR spectra were recorded on a JEOL GSX 270 spectrometer with tetramethylsilane as the internal reference. IR spectra were recorded on a Perkin-Elmer 1720 spectrometer. UV−vis spectra of chloroform solutions and thin films of the polymers were measured using Hitachi U-3210 and Shimadzu UV-3100S spectrometers, respectively. Isolation of the products and determination of the molecular weight of the polymers were conducted using an LC-908 gel permeation liquid chromatograph (Japan Analytical Industry Co. Ltd.). 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 by using the Kramers−Kronig relation. Film thicknesses were measured with an Alpha-Step 300 step-height profiler (Tencor Instruments).

Measurement of Third-Order Nonlinear Susceptibilities, $\chi^{(3)}$. A saturated solution of *cis,trans*-HpPPHT in toluene was cast on a 1 mm thick quartz substrate and dried at room temperature overnight. Thin films of HpPPV and PPV were obtained by pyrolysis of the corresponding sulfonium salt prepolymers,[15,26] which were cast on quartz substrates by spin coating.

THG measurements were carried out between 1.50 and 1.98 μm fundamental wavelengths, which were 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. The observed THG was analyzed by the Maker fringe method. The apparatus was automatically controlled by a personal computer. Values of $\chi^{(3)}$ were determined by fitting to the following equation.[27] A reference value $\chi^{(3)} = 1 \times 10^{-14}$ (esu) was used for fused quartz glass at all fundamental wavelengths.[28]

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

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

where ϕ is the phase of $\chi^{(3)}$ of the film, $\Delta\epsilon = \epsilon(\omega) - \epsilon(3\omega) = n_\omega^{\,2} - n_{3\omega}^{\,2}$, $\Delta\psi = 6\pi t/\lambda_\omega(n_\omega \cos\theta_\omega - n_{3\omega}\cos\theta_{3\omega})$ 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 and s refer to the film and substrate, respectively.

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References and Notes

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