Preparation and properties of poly(*p*-phenylene-1,3,5-hexatrienylene)

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Poly(*p*-phenylene-1,3,5-hexatrienylene) (**1P**) was prepared by the Wittig reaction of terephthalaldehyde with bis-ylide derived from *trans*-1,4-bis(triphenylphosphonium)-2-butene dichloride. The polymer was an orange-red powder with maximum absorption at 407 nm, and its degree of polymerization was found to be 4–9 by g.p.c. analysis. The ^{1}H n.m.r. and i.r. spectral data indicated that **1P** predominantly has an all-*trans* structure in its triene unit. The correlation between the u.v.–vis. absorption maximum and the conjugation length of **1P** was investigated, and the photochemical reactivity of **1P** was studied by means of u.v.–vis. absorption spectroscopy. The d.s.c. thermogram of **1P** showed an exothermic peak at 118°C, which was assignable to crystallization. A pellet of **1P** could be doped with iodine and its maximum electrical conductivity was 0.50 S cm^{-1}.

(Keywords: poly(*p*-phenylene-1,3,5-hexatrienylene); Wittig reaction; u.v.–vis. absorption spectroscopy; *cis–trans* isomerization; photodegradation; electrical conductivity)

INTRODUCTION

Conjugated polymers have been extensively studied because they are attractive from both theoretical and practical points of view. Of these polymers, poly(*p*-phenylene vinylene) (PPV) is one of the most interesting. It is not only highly conductive, like polyacetylene (PA), but is also stable in air, like poly(*p*-phenylene)[1,2]. Many studies have been devoted to chemical modification of PPV. Almost all of these studies have dealt with the introduction of side chains on benzene rings. Only a few papers have been concerned with modification of the main chains[3–5]. If we could obtain a conjugated polymer with a molecular structure between PA and PPV, it would be a new polymer which exhibits high conductivity.

In this paper, we report on the preparation and some properties of the conjugated polymer poly(*p*-phenylene-1,3,5-hexatrienylene) (**1P**) with a new backbone structure in the polymer main chain. While PPV could not be doped with iodine, **1P** was moderately conductive upon iodine-doping. In addition, **1P** showed interesting photochemical reactivity. We also prepared a monomer, 1,6-bis(4-formylphenyl)-1,3,5-hexatriene (**1M**), and compared its properties with those of **1P**.

EXPERIMENTAL

Materials

Trans-1,4-dichloro-2-butene, triphenyl phosphine, and terephthalaldehyde were purchased from Wako Pure Chemical Industries Ltd. and used without further purification.

Trans-*1,4-bis(triphenylphosphonium)-2-butene dichloride* (**3**). The salt **3** was prepared according to the method described in the literature[6].

3: ^{1}H n.m.r. (CDCl$_3$): δ 4.78 (2H, d, $J = 5.3$ Hz), 4.82 (2H, d, $J = 5.3$ Hz), 6.32 (2H, bs), 7.29–7.37 (6H, m), 7.62–7.87 (24H, m).

1,6-Bis(4-formylphenyl)-1,3,5-hexatriene (**1M**). Terephthalaldehyde **2** (2.0 g, 0.015 mol) and phosphonium salt **3** (4.7 g, 0.0072 mol) were dissolved in 250 ml of absolute ethanol. To this solution was added dropwise a sodium ethoxide solution (prepared from 0.35 g (0.015 mol) of sodium and 50 ml of absolute ethanol) 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 to yield 0.82 g (38%) of **1M** as yellow-orange granules. The product was purified by g.p.c. with chloroform elution. No peak due to impurity was detected in its ^{1}H n.m.r. spectrum.

All *trans* **1M**: M.p. 210–213°C (lit.[7] 207–208°C). ^{1}H n.m.r. (CDCl$_3$): δ 6.58–6.74 (4H, m), 6.98–7.11 (2H, m), 7.57 (4H, d, $J = 8.3$ Hz), 7.84 (4H, d, $J = 8.3$ Hz), 9.99 (2H, s). I.r. (KBr): 1689 (s), 1601 (m), 1568 (m), 1400 (w), 1305 (w), 1217 (m), 1162 (m), 1110 (w), 997 (s), 876 (w), 814 (m), 525 (w) cm^{-1}. U.v.–vis. (CHCl$_3$) λ max. 396 nm. Fluorescence emission spectrum (excitation at 394 nm in CHCl$_3$) 445, 470 nm.

To obtain *cis*-**1M**, a solution of all-*trans* **1M** in chloroform (5×10^{-4} M) was irradiated with 437 nm light for 15 min. The pure *cis*-**1M** was separated by g.p.c. (chloroform elution) from the obtained solution of the geometric isomers.

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Cis-**1M**: ^{1}H n.m.r. ($CDCl_3$): δ 6.44–6.69 (4H, m), 6.89–6.99 (2H, m), 7.52 (2H, d, $J = 8.2$ Hz), 7.55 (2H, d, $J = 8.3$ Hz), 7.83 (2H, d, $J = 8.4$ Hz), 7.89 (2H, d, $J = 8.4$ Hz), 9.97 (1H, s), 10.02 (1H, s). U.v.–vis. ($CHCl_3$) λ max. 296, 394 nm.

*Poly(*p*-phenylene-1,3,5-hexatrienylene)* (**1P**). Terephthalaldehyde **2** (2.0 g, 0.015 mol) and phosphonium salt **3** (4.7 g, 0.0072 mol) were dissolved in 250 ml of absolute ethanol. To this solution was slowly added a solution of sodium ethoxide (prepared from 0.35 g of sodium and 50 ml of absolute ethanol) under an argon atmosphere. After stirring the mixture for 2 days in the dark, an additional solution of salt **3** (4.7 g in 50 ml of ethanol) was poured into the reaction mixture, whereupon 50 ml of a sodium ethoxide solution (0.3 M) was added dropwise. After the mixture had been stirred for another 5 days, the orange-red precipitate was filtered, washed three times with ethanol, and dried *in vacuo* at 55°C to afford 0.46 g of **1P** in 20% yield (calculated for repeating units of $C_{12}H_{10}$). The product was purified by g.p.c. with chloroform elution.

1P: M.p. >300°C. ^{1}H n.m.r. ($CDCl_3$): δ 6.15–6.70 (4H, m), 6.70–7.02 (2H, m), 7.36 (4H, bs). I.r. (KBr): 1678 (s), 1605 (s), 1268 (m), 1173 (m), 1110 (s), 997 (s), 876 (m), 818 (m), 546 (m) cm^{-1}. U.v.–vis. ($CHCl_3$) λ max. 407 nm. Fluorescence emission spectrum (excitation at 405 nm in $CHCl_3$) 510 nm.

Photolysis

U.v.–vis. absorption spectral measurements. A solution of **1M** (3×10^{-4} M) or **1P** (1 mg/10 ml) in chloroform was irradiated for 2 h in a quartz cell (10 mm optical length) at room temperature under air. A high pressure mercury lamp or a spectroirradiator was used as a light source. The u.v.–vis absorption spectra were recorded during irradiation.

^{1}H n.m.r. spectral measurements. A solution of **1M** (7×10^{-4} M) in chloroform-d was irradiated in a n.m.r. sample tube with 437 nm light for 15 min at room temperature under air. A spectroirradiator was used as a light source. The *cis–trans* isomerization of **1M** was studied by ^{1}H n.m.r. spectroscopy. In order to follow the photodegradation of **1M**, the solution was irradiated with 305 nm light for 120 min.

Preparative experiments. A solution of **1M** (1×10^{-3} M) or **1P** (1 mg/10 ml) in chloroform was irradiated in a Pyrex glass for 2 h at room temperature under air. A high pressure mercury lamp was used as a light source. The photolysed solution was analysed by g.p.c. (chloroform).

Measurements

Differential scanning calorimetry (d.s.c.). The d.s.c. measurements of **1M** and **1P** were carried out in air between 30 and 410°C for 2.00 mg of each sample in an aluminium sample pan. The heating and cooling rates were 10°C min^{-1}.

Thermogravimetric analysis (t.g.a.). The t.g.a. measurements were carried out from 30 to 410°C under flowing air for 5.00 mg of each sample in a platinum sample pan. The heating rate was 10°C min^{-1}.

Electrical conductivity. The conductivity of **1P** was measured according to the conventional four-probe method. The pellet sample used for the measurement was prepared from 25 mg of **1P** under a pressure of 200 kg cm^{-2}. This pellet, measuring ~10 mm × 5 mm × 0.2 mm, was mounted on a four-probe conductivity device in an evacuation vessel, and exposed to iodine vapour for doping.

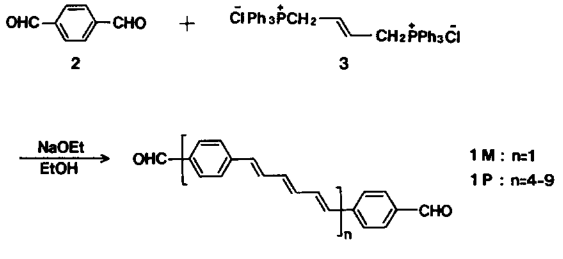
Apparatus

^{1}H n.m.r. spectra were recorded on a Jeol GSX 270 spectrometer operating at 270 MHz. I.r. and u.v.–vis. spectra were recorded on a Perkin–Elmer 1720 and a Hitachi U-3400 absorption spectrometer, respectively. Fluorescence spectra were recorded on a Hitachi MPF-4 spectrophotometer. The melting point was determined on a Laboratory Device Mel-Temp melting point apparatus and was uncorrected. Purification of the sample and the measurement of the degree of polymerization were carried out on an LC-908 gel permeation liquid chromatograph (Japan Analytical Industry Co. Ltd). Irradiation was carried out with an Ushio USH-500-D 500W high pressure mercury lamp or a CRM-FA 2KW spectroirradiator (Japan Spectroscopic Co. Ltd). In the use of the former, the light was filtered by an HA-30 glass filter ($\lambda > 320$ nm) in every case. D.s.c. and t.g.a. were carried out on a Seiko Densi SSC-5000 DSC/TGA analyser.

RESULTS AND DISCUSSION

Synthesis

1M and **1P** were prepared by the Wittig reaction from terephthalaldehyde **2** and *trans*-1,4-bis(triphenylphosphonium)-2-butene dichloride **3** (*Scheme 1*).



Scheme 1 Synthesis of **1M** and **1P**

The resulting polymer was an orange-red powder, which was mostly soluble in chloroform but only slightly soluble in common organic solvents, such as benzene, ether and acetone. Both **1M** and **1P** should be treated in darkness because of their high photosensitivity.

^{1}H n.m.r. spectroscopy

Figures 1a and *1b* show the ^{1}H n.m.r. spectra of **1M** and **1P**, respectively. The multiplet signals at 6.58–6.74 and 6.98–7.11 ppm in *Figure 1a* are due to the hexatriene moiety in the all-*trans* structure. Signals at 6.15–6.70 and 6.70–7.02 ppm in *Figure 1b* correspond to the all-*trans* hexatriene units in **1P**. However, weak peaks at around 5.95 ppm indicate that **1P** contains a small amount of *cis* double bonds. Small peaks due to aldehyde protons were observed at about 10 ppm in *Figure 1b*, and no peak due to the methylenes of $-CH_2-\overset{+}{P}Ph_3\overset{-}{Cl}$ was detected in the region 4.0–5.0 ppm. These findings suggest that the

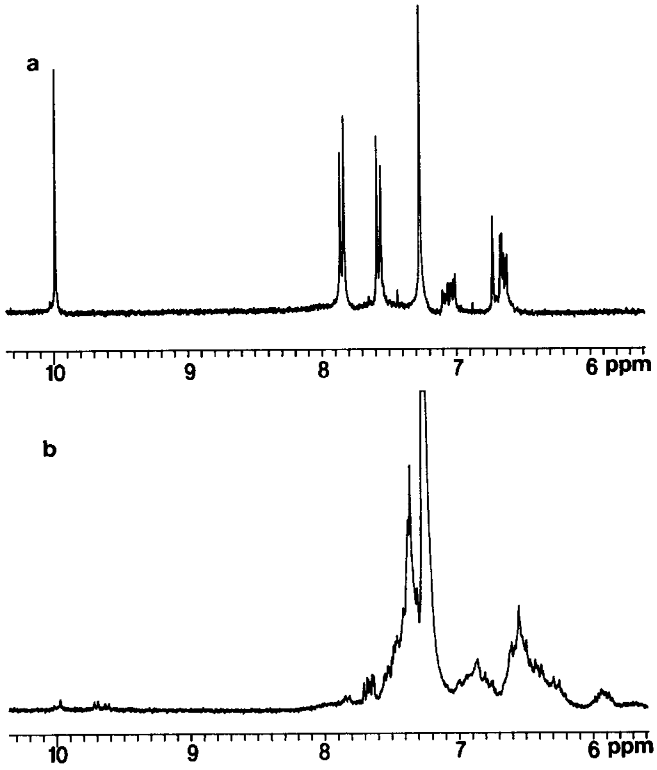


Figure 1 ^1H n.m.r. spectra of (a) **1M** and (b) **1P** in $CDCl_3$

end groups of **1P** do not contain $-CH_2-\overset{+}{P}Ph_3\overset{-}{Cl}$ derived from the salt **3**.

I.r. spectroscopy

Figures 2a and *2b* show the i.r. spectra of **1M** and **1P**, respectively. In the spectrum of **1P**, a strong absorption band was observed at 1678 cm^{-1}, which was attributed to C=O stretching vibration of aldehydes. The sharp absorption band at 997 cm^{-1} and the weaker one at 1605 cm^{-1} are assigned, respectively, to the C–H out-of-plane bending and the C=C stretching vibration of double bonds, both of which are characteristic of all-*trans* trienes[8–10]. The absorption at 818 cm^{-1} is due to the C–H out-of-plane bending vibration of the 1,4-disubstituted benzene ring.

In the spectrum of **1M**, these bands appeared at 1689, 997, 1601 and 814 cm^{-1}. These i.r. data together with ^1H n.m.r. data indicate that **1M** and **1P** have the all-*trans* structure shown in *Scheme 1*. The ratio of the peak intensities of C–H bending of trienes to the C=O stretching vibration of aldehydes was larger in **1P** than in **1M**, indicating that polymerization took place.

Degree of polymerization

In order to follow the progress of the polymerization, the chloroform-soluble part of the product was analysed by g.p.c. The higher molecular weight portion increased with increases in the total amount of added salt and reaction time (*Figure 3*). This fact supports the theory that the end group is –CHO during the polymerization. The degree of polymerization was 4–9 after 7 days, and did not increase further.

U.v.–vis. spectroscopy

Figure 4a shows the u.v.–vis. absorption spectrum of **1M**, with a maximum at 396 nm. A vibrational fine structure was observed in the main band, and the spacing was 1200–1300 cm^{-1}.

The spectrum of **1P**, on the other hand, shows a broad absorption band, with a maximum at 407 nm and an onset at 550 nm (*Figure 5a*). In spite of its low degree of polymerization, the absorption maximum of **1P** is red-shifted by 19 nm over that of oligomeric powder of PPV, with a polymerization degree[11] of 5–7. This may

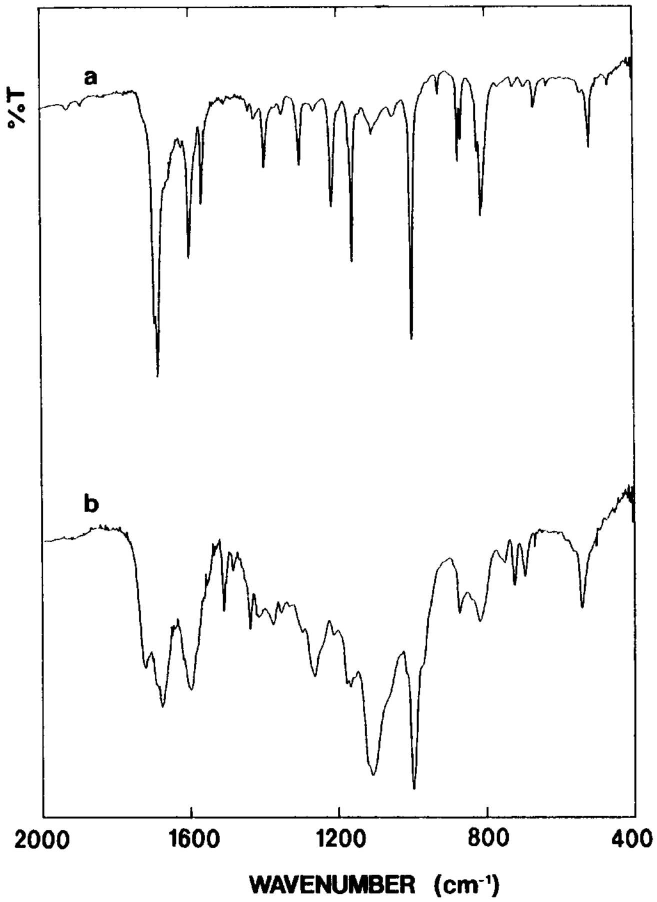


Figure 2 I.r. spectra of (a) **1M** and (b) **1P**

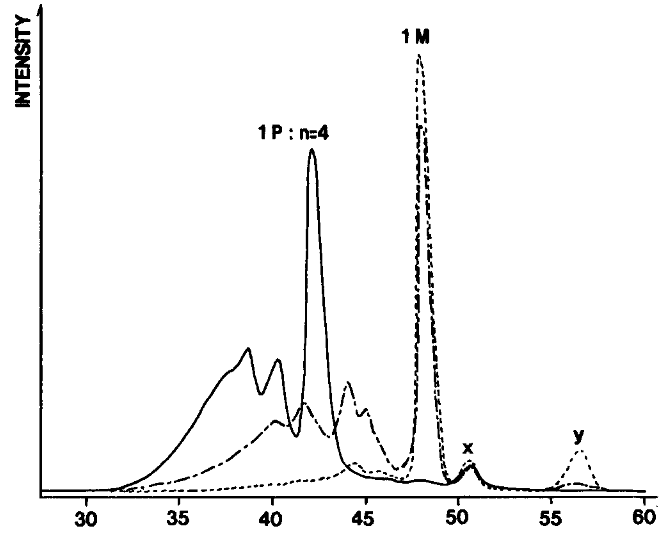


Figure 3 Gel permeation chromatogram of **1M** and **1P**. Total reaction time and amount of **3**: - - -, 2 days, 0.5 eq; — — — —, 4 days, 1.0 eq; ——, 7 days, 1.0 eq; x = triphenylphosphine oxide; y = terephthalaldehyde

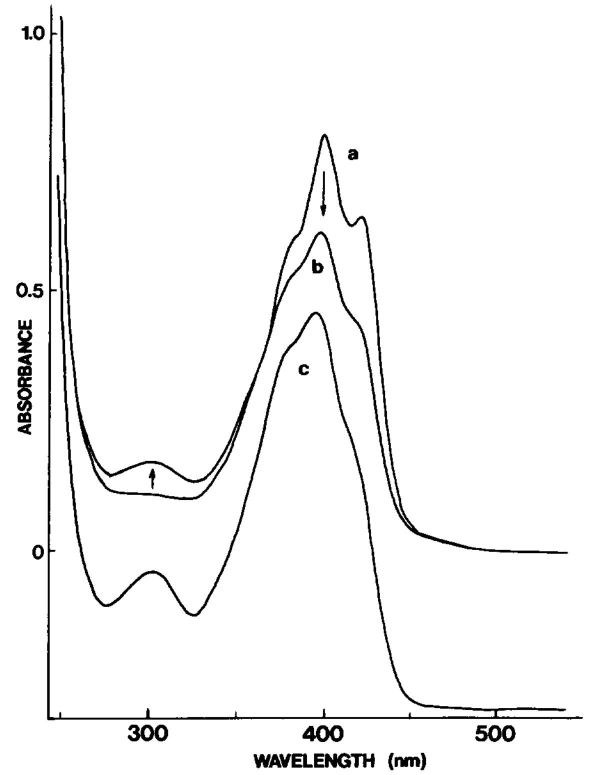


Figure 4 U.v.–vis. absorption spectra of **1M** in chloroform: (a) all-*trans* form before irradiation; (b) mixture of geometric isomers after 10 min irradiation with 437 nm light; (c) *cis*-**1M** obtained by g.p.c. purification. The spectrum (c) is shifted downwards by 0.30 of absorbance for clarity

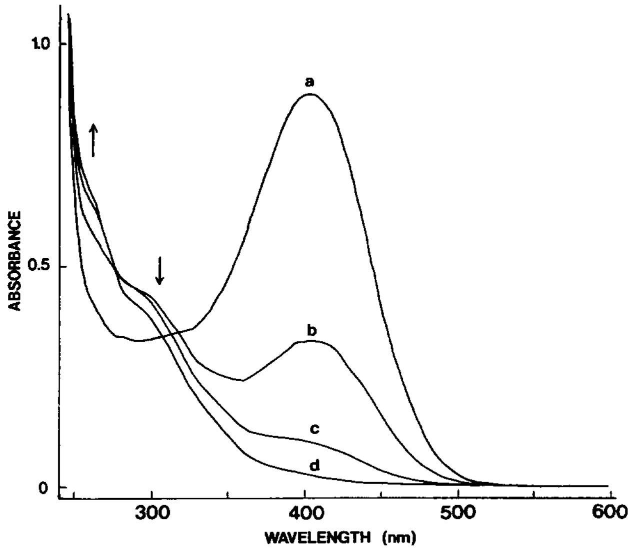


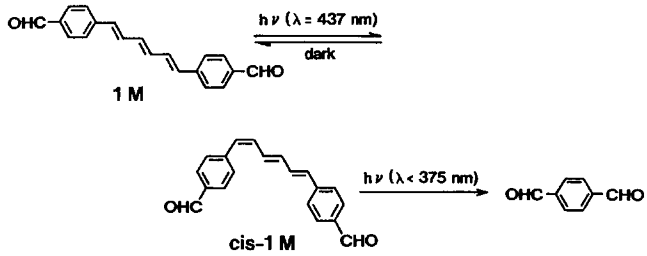
Figure 5 U.v.–vis. absorption spectra obtained after continuous irradiation ($\lambda > 320$ nm) of all-*trans* **1P** for (a) 0, (b), 18, (c) 36 and (d) 54 min in chloroform

be attributed to the longer effective conjugation length of **1P**.

In order to clarify the correlation between the absorption maximum and the degree of polymerization, **1P** was fractionated by g.p.c. by the degree of polymerization and the spectrum was measured for each fraction. It was found that the absorption maximum was almost independent of the degree of polymerization, and that the absorption onset rather than the maximum was shifted towards the red part of the spectrum with increases in the degree of polymerization. This was rather unexpected, because it is generally believed that the absorption maximum of the energetically lowest π–π^* transition in a conjugated compound is shifted to lower energy in the spectrum as the conjugation length becomes longer. However, similar results have been reported with PPV[11–14]. Obrzut and Karasz[13] interpreted their experimental results in terms of the assumption that the maximum absorption band in PPV can be attributed to overlapping transitions from localized energy levels rather than from an effect of an extended conjugation. This type of strong electronic–vibrational coupling must also play an important role with **1P**.

Photoreactivities of 1M and 1P

All-*trans* **1M** was isomerized on exposure to visible light to *cis*-**1M**, which subsequently yielded terephthalaldehyde by oxidative cleavage caused by u.v. light irradiation (*Figure 6* and *Scheme 2*).



Scheme 2 Photoreactions of **1M** in chloroform

The presence of *cis* double bonds could be detected by the emergence of a small '*cis*-peak' with an absorption maximum at 296 nm in chloroform (*Figure 4b*). The fine structure, which was observed in the spectrum of the all-*trans* **1M**, disappeared in that of the *cis* isomer. The absorption maximum of the main peak was slightly blue-shifted with a decrease in absorption intensity. The

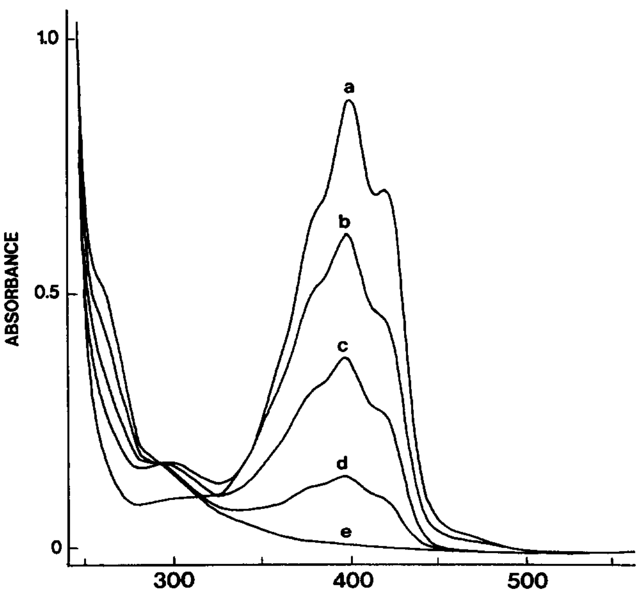
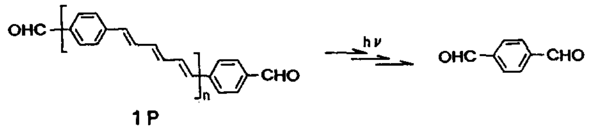


Figure 6 U.v.–vis. absorption spectra obtained after continuous irradiation ($\lambda > 320$ nm) of all-*trans* **1M** for (a) 0, (b) 20, (c) 40, (d) 60 and (e) 80 min in chloroform

cis–trans isomerization of **1M** was followed by means of ^{1}H n.m.r. and u.v.–vis. spectroscopy, and was found to be reversible. *Cis* double bonds in *cis*-**1M** completely returned to the *trans*-form upon standing in chloroform for 20 h in the dark. This was in contrast to the fact that the *cis* isomer of 1,6-diphenylhexatriene returned to the all-*trans* form upon irradiation in the presence of iodine[15]. Furthermore, the mixture of all-*trans* and *cis*-**1M** was separated into the pure isomers by g.p.c., and the u.v.–vis. spectrum of the *cis* isomer was obtained (*Figure 4c*). *Cis*-**1M** showed two singlet peaks due to aldehyde protons at 9.97 and 10.02 ppm in its ^{1}H n.m.r. spectrum. A *cis*-peak in a u.v.–vis. spectrum is characteristic of *cis–trans–trans* or *trans–cis–trans* 1,6-diphenylhexatrienes[15], and the two peaks of aldehyde protons in the n.m.r. spectrum show an asymmetric structure of *cis*-**1M**. These spectral data indicate that *cis*-**1M** has the *cis–trans–trans* structure shown in *Scheme 2*.

Although all-*trans* **1P** was isomerized to *cis*-**1P** upon visible light irradiation (*Figure 5b*), it did not return to the *trans* isomer upon irradiation or heating in the dark. **1P** was decomposed to give terephthalaldehyde even by visible light irradiation and, therefore, no reversible *cis–trans* isomerization could be observed (*Figure 5* and *Scheme 3*).



Scheme 3 Photoreactions of **1P** in chloroform

Terephthalaldehyde, the main photoproduct of **1M**, was identified by its u.v.–vis. absorption and ^{1}H n.m.r. spectra after g.p.c. separation. **1M** gave another product besides terephthalaldehyde upon u.v. light irradiation. It was a volatile material with low molecular weight ($\sim$80) and remained unidentified. The photoproduct of **1P** was a complex mixture and only terephthalaldehyde could be identified.

D.s.c. and t.g.a.

In the thermogram of **1M**, an endothermic peak was observed at 210°C, corresponding to its melting point, followed by an exothermic peak characteristic of thermal decomposition.

1P showed an exothermic peak (45 mJ mg^{-1}) at 118°C (*Figure 7*). This peak corresponds to the crystallization phenomenon, as no weight loss was observed at 118°C in its t.g.a. curve, and in the d.s.c. thermogram neither an exothermic nor an endothermic peak appeared during the subsequent process of cooling to 30°C and reheating to 120°C. This interpretation is supported by the observation that no change could be detected in its i.r. spectrum after annealing at 118°C for 2 h. The broad exothermic peak observed at around 200–270°C possibly corresponds to the thermal decomposition, since a weight loss was observed above 200°C in the t.g.a. curve. An endothermic peak was observed at 305°C, which was assignable to its melting point. However, **1P** had no peak at around 305°C when heating at a diminished rate in the range 200–270°C. This is explained in terms of the thermal decomposition of the sample during this slow heating. T.g.a. showed that decomposition started at 162°C for **1M** and at 194°C for **1P**. However, at 400°C, **1M** and **1P** underwent 22% and 40% weight loss, respectively, indicating that **1P** is less stable than **1M** at high temperatures.

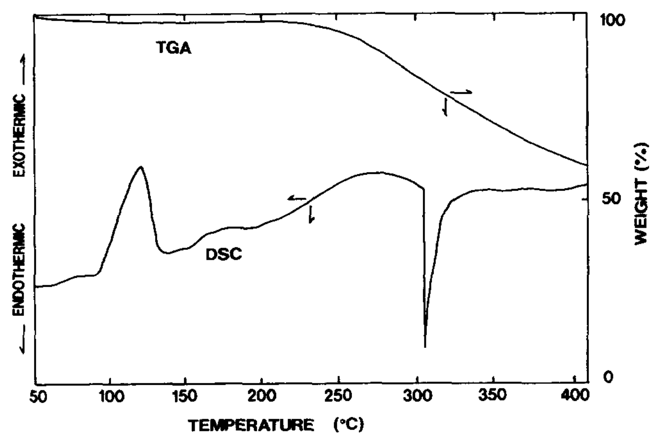


Figure 7 D.s.c. and t.g.a. thermograms of **1P**

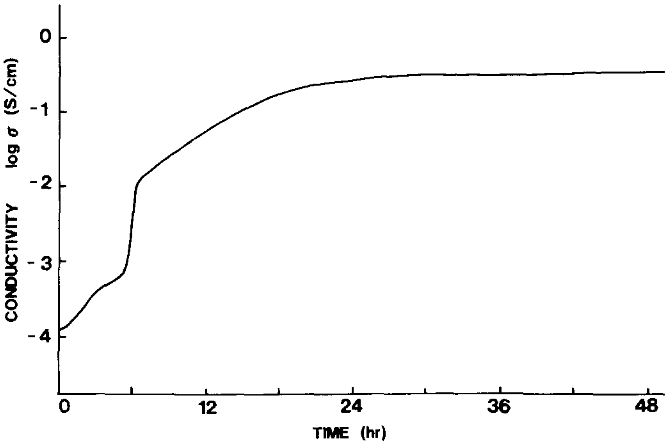


Figure 8 Doping effect of iodine on the electrical conductivity of **1P**

Electrical conductivity

The electrical conductivity of the iodine-doped PPV was reported to be 3.7×10^{-7} S cm^{-1} for the sample of all-*trans* oligomeric powder and 10^{-2} S cm^{-2} for that of oriented film[16]. This indicates that the electrical conductivity of PPV is not improved much by iodine-doping. We found that a pellet of **1P** could be doped with iodine, obtaining a maximum conductivity of 0.50 S cm^{-1} (*Figure 8*). This shows that the affinity of **1P** with iodine, which is a dopant with relatively low electron affinity, was enhanced by replacing vinylene with hexatrienylene units. The dopability of **1P** with iodine was, therefore, improved to yield higher electrical conductivity.

CONCLUSIONS

A new conjugated polymer **1P** has been prepared by the Wittig reaction; its structure was identified by comparing its ^{1}H n.m.r. and i.r. spectra with those of the monomer **1M**. *Cis–trans* isomerization of **1M** was found to be completely reversible, and the degradation to terephthalaldehyde was caused only by u.v. light irradiation. **1P** was degraded even by visible light and therefore reversible isomerization could not be observed. A pellet of **1P** was successfully doped with iodine. This shows that the replacement of vinylene units in PPV with hexatrienylene units enhanced the affinity of **1P** for iodine to give **1P** higher conductivity. Although **1P** was a powder with a relatively low molecular weight, it exhibited moderate conductivity. Since the present polymer has a stiff main chain, only its low molecular weight part was soluble in organic solvents. Studies are now in progress to prepare a soluble, high molecular weight polymer with long side chains on benzene rings.

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