

Poly(*p*-phenylene)-catalysed Photoreduction of Water to Hydrogen

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Irradiation ($\lambda > 290$ nm) of an aqueous suspension of poly(*p*-phenylene) leads to photocatalytic H₂ evolution in the presence of triethylamine or diethylamine.

Since doping of *cis*- and *trans*-polyacetylenes with electron acceptors or electron donors was found to induce a marked increase in electric conductivity,¹ a number of organic polymers with conjugated π -electrons have been synthesized and some novel conducting polymers, electrochromic polymers, and gas-sensitive polymers have been successfully developed.²⁻⁴ Among conjugated polymers, linear polymers were reported to have band gaps which range from 2 to 5 eV.⁵ However, such organic semiconductors have not yet been investigated with respect to the chemical conversion and storage of light energy. We report here that poly(*p*-phenylene) (PPP) prepared by polymerization of the Grignard reagent obtained from 1,4-dibromobenzene and magnesium, catalyses the photoreduction of water to H₂ in the presence of an appropriate electron donor.

According to Yamamoto's method,⁶ pale yellow porous PPP consisting of about 13 monomer units was prepared. It consists of a linear sequence of phenyl rings and is terminated at each end with 4-bromophenyl groups. The surface area was determined to be 39.1 m² g⁻¹ by the Brunauer-Emmett-Teller method. Based on its photoacoustic spectrum,⁷ the band gap was estimated to be 2.9 eV, which is slightly smaller than the calculated value of 3.2 eV.⁵ The absorption spectrum of suspended PPP in methanol shows a maximum at 300 nm with a shoulder at ~ 380 nm. We attempted to use PPP as a photocatalyst in reductive hydrogen evolution from aqueous diethylamine under irradiation ($\lambda > 290$ nm).

In a 4 cm³ quartz cubic cell equipped with a three-way stopcock were placed 1 cm³ of doubly distilled water, 3 cm³ of diethylamine, and 10 mg of PPP. After purging with argon, the cell was closed under atmospheric pressure, and the magnetically stirred mixture was irradiated at 313 nm using a 300 W high-pressure mercury arc lamp. The gas inside the tube was analysed at appropriate intervals by g.l.c. as previously reported⁸ and results are plotted in Figure 1. H₂ evolution catalysed by commercial microcrystalline ZnS (Nakarai GR grade)⁹ is also plotted for comparison. H₂ was generated continuously with PPP, with a slight tendency to level off, although the efficiency is less than that of ZnS. The PPP did not decompose under the reaction conditions; no change was observed in the colour and i.r. spectrum of the PPP which was isolated from the resulting reaction mixture by filtration, and bromide anion and soluble aromatic compounds were found negligible in the filtrate.† The slight decrease in H₂ generation on long irradiation may be attributable to the gradual decomposition of the active site of the PPP.

As shown in Table 1, a substantial amount of H₂ was evolved on irradiation at $\lambda > 290$ nm, but the apparent quantum yield was < 0.04 . Without PPP, no H₂ was produced.

H₂ was also produced on irradiation at 366 nm, but H₂ production was negligible for $\lambda > 400$ nm. H₂ evolution was also confirmed by irradiation of the inhomogeneous mixture of triethylamine and water in the presence of PPP. A lower molecular weight PPP consisting of 6 monomer units which is soluble in hot toluene did not show photocatalytic activity under comparable conditions. Hexane, 2,3-dihydrofuran, and methanol did not act as electron donors in the PPP-catalysed system.

In order to clarify the source of the hydrogen atoms, irradiation was performed in the presence of equal amounts of D₂O and triethylamine as a sacrificial electron donor. The D₂:DH:H₂ and/or D ratios from the mass spectrum were 36:5:2, indicating that hydrogen was formed by the reduction of the bulk water.

The formation of CO₂, CO, and O₂ was not observed even after prolonged irradiation. G.l.c. analysis of the liquid products from triethylamine indicated the presence of the same dimeric products as observed in the photoreaction in the presence of ZnS.⁸

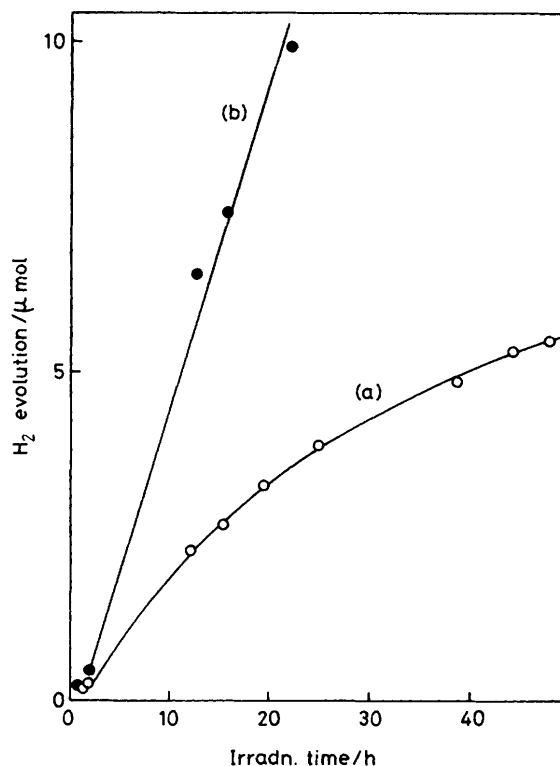


Figure 1. Hydrogen evolution by irradiation (at 313 nm) of (a) a suspension of PPP containing diethylamine (3 cm³), water (1 cm³), and PPP (10 mg), and (b) a suspension of ZnS containing diethylamine (3 cm³), water (1 cm³), and ZnS (15 mg).

† The absence of soluble aromatic compounds, which might be formed by photodecomposition, is based on the i.r. spectrum of the concentrated filtrate. When the reaction mixture was left for more than one month, bromide anion was found to be liberated.

Table 1. Hydrogen evolution in the photocatalytic reaction using poly(*p*-phenylene).

Organic electron donor (vol./cm ³)	H ₂ O (vol./cm ³)	PPP (wt./mg)	λ/nm ^a	Irradn. time/min	μmol of H ₂	Quantum yield, ^b Φ(1/2H ₂)
Diethylamine (2)	2	20	>290	240	8.30	—
Diethylamine (3)	1	10	313	1172	3.29	0.0335
Diethylamine (3)	1	10	366	240	0.45	0.0060
Diethylamine (3)	1	10	>400	125	0.06	0
Triethylamine (2)	2	10	313	200	0.93	0.0082
Triethylamine (2)	2	10	366	240	0.95	0.0048
n-Hexane (4)	0	15	313	1070	0.02	0
2,3-Dihydrofuran (3)	1	15	313	1160	0.03	0
Methanol (3)	1	15	313	240	0.04	0.0004

^a 313 nm light was obtained by using aqueous potassium chromate and potassium hydrogen phthalate as filters, and 366 nm light by a combination of Toshiba UV-35 and UV-D36C glass filters. ^b Quantum yields were determined using a hexan-2-one actinometer by assuming that two photons produce one molecule of H₂, and were corrected for light absorption by the suspended catalyst.

In conclusion, this is the first report on H₂ evolution photocatalysed by an organic semiconductor in sacrificial systems.

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