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Studies of the antenna effect in polymer molecules. 27. Hydrogen evolution from water

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Abstract

The light-induced formation of hydrogen from water was studied using polyelectrolytes containing naphthalene antenna chromophores as sensitizer. Viologen compounds were employed as electron relay. In the presence of platinum catalyst, the systems produced hydrogen efficiently on irradiation with light at $\lambda = 300$ nm. Natural solar light can also be used to generate hydrogen in such systems. © 1998 Elsevier Science S.A.

Keywords: Antenna polymers; Hydrogen; Photoproduction of hydrogen; Polyelectrolytes; Solar energy; Viologen

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1. Introduction

The photochemical generation of hydrogen from water has recently been the subject of extensive research. This process is based on the production of a non-polluting fuel from water using solar light, and appears to be one of the more promising approaches to the conversion and storage of solar energy.

The essential components of the systems used for this purpose include a photosensitizer (S), an electron relay (R) and a catalyst [1]. The excitation of the photosensitizer leads to electron transfer via the reactions

$$S + h\nu \rightarrow S^* \qquad (1)$$

$$S^* + R \rightarrow S^+ + R^- \qquad (2)$$

In the presence of a catalyst, such as colloidal platinum, R^- reduces the hydrogen from a water molecule and undergoes re-oxidation

$$R^- + H_2O \rightarrow \tfrac{1}{2}H_2 + R + OH^- \qquad (3)$$

A sacrificial electron donor (D) is usually added to the solution in order to recover the photosensitizer

$$S^+ + D \rightarrow S + D^+ \qquad (4)$$

A number of such systems, varying in molecular organization and composition, have been developed and studied [1–28]. Homogeneous systems, which are much easier to prepare and can be well characterized, have relatively low efficiency. This is because of the need to carry out efficient primary charge separation (reaction (1)) in such a way that the back recombination reaction is suppressed. This problem can be solved by using microheterogeneous systems, but most of these systems are rapidly deactivated. For example, the semiconductors used for this purpose are known to undergo photocorrosion [24].

In previous papers in this series, it has been reported that water-soluble antenna polyelectrolytes, referred to as "photozymes", act as microheterogeneous photocatalysts [29–38]. They have been shown to be highly efficient and very stable. It has also been demonstrated that several photozymes containing naphthalene antenna units can act as sensitizers and electron donors in the photoreduction of viologen compounds [39].

This paper reports studies on the application of the photozymes containing naphthalene antenna chromophores for the generation of hydrogen from water.

2. Experimental section

2.1. Materials

The photosensitizers used in this work were synthesized and purified according to the methods described previously [29,37,38,40]: poly(sodium styrenesulfonate-*co*-2-vinylnaphthalene) (PSSS-VN)

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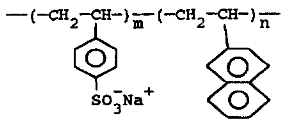
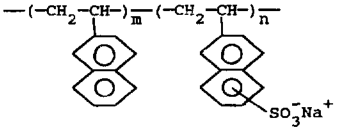
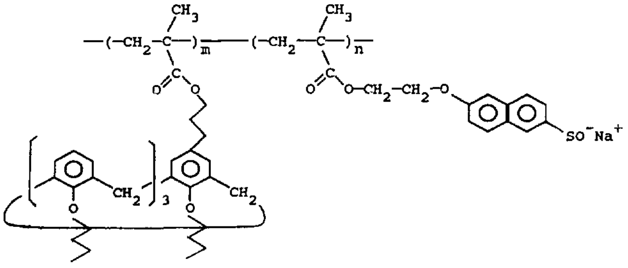


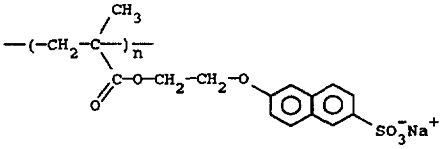
partially sulfonated poly(2-vinylnaphthalene) (SPVN)



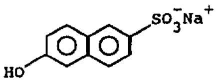
poly[(2-(6-sulfo-2-naphthoxy)ethyl methylacrylate)-*co*-(5-(3-(methacryloyloxy)propyl)-25,26,27,28-tetrabutoxy-calix[4]arene] (NS-CAL)



poly[2-(6-sodium sulfonate-2-naphthoxy)-ethyl methacrylate] (PNS)



2-(6-sulfo-2-naphthoxy)ethyl methacrylate sodium salt (NS)



Solutions were prepared using the following buffers: potassium biphthalate for pH 4, potassium biphthalate–sodium hydroxide for pH 5 and potassium phosphate monobasic–sodium hydroxide for pH 6 and 7. For the set of experiments in which the formation of hydrogen was followed by mass spectral (MS) analysis, the solutions were prepared in deionized water or in D_2O (Aldrich, 99.9 at.% D).

Methyl viologen dichloride hydrate (MV^{2+}, Aldrich, 98%) was used as received.

4,4′-Bipyridinium-1,1′-bis(trimethylenesulfonate) (SPV) was prepared according to the procedure described in the literature [18].

Triethanolamine (TEA, Aldrich, 98%) was distilled under reduced pressure.

Hydrogen hexachloroplatinate(IV) hydrate (Aldrich, 99.9%), ethylenediaminetetraacetic acid, disodium salt dihydrate (EDTA, Aldrich, better than 99%), citric acid, trisodium salt dihydrate (Aldrich, 99%), Carbowax 20 M (Chromatographic Specialties) and poly(vinyl alcohol) (PVA, Aldrich, 100% hydrolyzed, $M_w = 14\,000$) were used as received.

Colloidal platinum was prepared according to the procedure given in the literature [1,6]. The sol was protected with PVA (1% (w/w) solution) or with Carbowax 20 M. (PVA was generally dissolved in deionized water, except for the reaction carried out in D_2O solution, when PVA was dissolved in D_2O.) The Pt–PVA or Pt–Carbowax solution was centrifuged for 1 h and the dark gray supernatant was separated from the black deposit. The platinum content in the supernatant was determined from the absorption spectrum of the Pt–PVA sol ($\epsilon = 2.3 \times 10^3$ M^{-1} cm^{-1} at 450 nm) [1].

2.2. *Irradiation of samples*

Artificial source irradiation was performed using a 100 W high-pressure mercury lamp (Photon Technology International, PTI, USA). The beam was passed through 10 cm of water in order to cut-off the IR radiation, and then through a 313 nm interference filter. The incident light intensity was determined using a ferrioxalate actinometer [41] ($I_0 = 2.5 \times 10^{-8}$ einstein s^{-1}).

Alternatively, the samples were irradiated using a Rayonet Photochemical Reactor (Southern New England Ultraviolet Company, USA) equipped with ten RP-300 lamps.

The aqueous polymer solutions containing viologen and TEA were deaerated prior to irradiation by flushing with argon for 30 min. The required amount of the separately deaerated Pt sol was then added. The samples were mixed during irradiation using a small magnetic stirring bar.

Natural source irradiation was carried out using solar light. The experiments were performed in Toronto on bright sunny days in August 1994 between 10:00 a.m. and 3:00 p.m.

2.3. *UV spectra*

The UV spectra of the samples were measured using a Hewlett-Packard 8451 A diode array spectrophotometer.

2.4. *Gas chromatographic analysis*

The kinetics of hydrogen formation were measured by gas chromatography (GC). A GC-8A gas chromatograph (Shimadzu), equipped with a thermal conductivity detector and a Carbosieve 5 Å column, was used (column temperature, 30 °C). Helium (Canox, high purity) was used as the carrier gas. The flow rate was adjusted to 40 ml min^{-1}.

2.5. *Mass spectra*

Analysis of the gas evolved during the experiments was performed using a Vacuum Generators 70 S-250 mass spectrometer.

2.6. High performance liquid chromatography (HPLC) analysis

HPLC analysis was carried out using a Waters HPLC system equipped with a tunable absorbance detector and a ZORBAX ODS column (4.6 mm×15 cm). A mixture of methanol and water (10 : 90, v/v) was used as eluent.

3. Results and discussion

3.1. Production of hydrogen photosensitized by polymeric naphthalene chromophores

Irradiation of deaerated aqueous solutions containing polymers and viologen compounds with light absorbed only by the naphthalene polymeric units results in the photosensitized reduction of viologen, as demonstrated by monitoring the electronic absorption spectra. The increase in the absorption characteristic of partly reduced viologen [10,42] in the 300–800 nm range, with maxima around 395 and 600 nm, can be observed during irradiation. The changes can also be easily monitored visually because the solutions become blue. The process is especially efficient in the presence of a sacrificial electron donor (TEA), which reduces the naphthalene radical cation. It has been shown that the naphthalene chromophore in the excited state transfers an electron to the viologen compound. When methyl viologen (MV^{2+}) is used, the formation of $MV^{\cdot+}$ is observed, and $SPV^{\cdot-}$ is generated when SPV is present in the solution. A sacrificial electron donor, such as TEA (or EDTA), when added to the solution, reduces the naphthalene radical cation and restores the photocatalytic activity of the polymer.

The properties of the system change dramatically on addition of Pt sol. The blue color disappears and gas bubbles are formed. It is known that, in the presence of a Pt catalyst, $MV^{\cdot+}$ is re-oxidized by water with the generation of hydrogen. GC and MS analyses have confirmed that, during the irradiation of aqueous solutions of several naphthalene antenna polyelectrolytes with MV^{2+} or SPV in the presence of TEA and Pt sol, hydrogen is efficiently produced.

Fig. 1 shows the mass spectra for the gas produced during irradiation of PSSS-VN + MV^{2+} + TEA + Pt sol dissolved in water and in D_2O. The reactions were carried out at pH 7 (no buffer added). The spectra clearly show that hydrogen (H_2) is formed during irradiation in water and deuterium (D_2) when D_2O is used as solvent, confirming that the gas formed originates from the solvent and not from other components in the system.

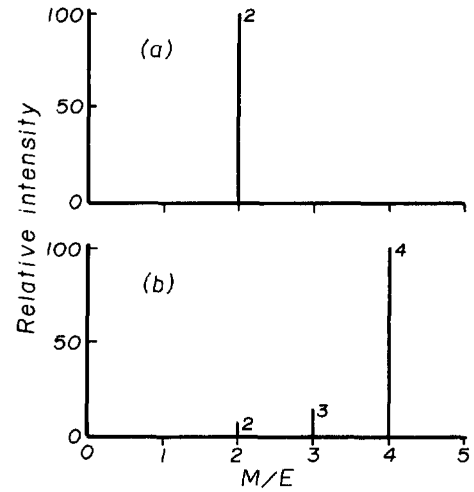


Fig. 1. Mass spectra of the gas formed during irradiation of solutions of PSSS-VN + MV^{2+} + TEA + Pt sol in water (a) and in D_2O (b) for 2 h with light at 300 nm.

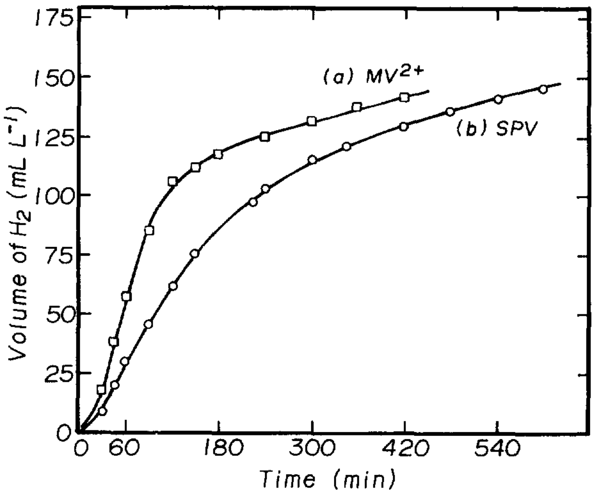


Fig. 2. Kinetic curves for hydrogen production during irradiation of PSSS-VN + MV^{2+} + TEA + Pt sol and PSSS-VN + SPV + TEA + Pt sol at pH 4 with light at 300 nm.

Fig. 2 shows the typical hydrogen production curves obtained during irradiation of aqueous solutions of PSSS-VN + MV^{2+} and PSSS-VN + SPV in the presence of TEA and Pt catalyst at 300 nm and pH 4. After an induction time of several minutes, hydrogen is generated at approximately constant rates (56 and 30 ml l^{-1} h^{-1} when MV^{2+} and SPV are used as electron relays respectively). After about 2–3 h, the rates decrease slightly. The curves for hydrogen formation in all of our systems are qualitatively similar. The observed decrease in the rate of hydrogen generation may be induced by the relatively high partial pressure of hydrogen, because it is not removed from the system during irradiation. The growing partial pressure of hydrogen can influence the redox equilibrium in the aqueous polymer solution. The hydrogen can also participate in the hydrogenation of both oxidized and partly reduced viologen (e.g. MV^{2+} and $MV^{\cdot+}$) [14,23].

The sequence of processes leading to hydrogen generation can be described by the following scheme

$$N^{*} + MV^{2+} \rightarrow N^{\cdot+} + MV^{\cdot+} \quad (5)$$

$$N^{\cdot+} + TEA \rightarrow N + TEA_{OX} \quad (6)$$

$$MV^{\cdot+} + H_2O \xrightarrow{Pt} MV^{2+} + \tfrac{1}{2}H_2 + OH^{-} \quad (7)$$

The efficiency of hydrogen generation is expected to be dependent on several factors, such as the type of polymer used, pH of the solution, concentrations of the polymer, viologen compound and Pt in the irradiated solution, type of sacrificial electron donor and type of support used to protect the Pt sol.

3.2. Effect of agent used to protect the Pt sol

In this work, the PVA-protected Pt sol was a much more efficient catalyst than that protected with Carbowax. Pt protected by PVA generally displays a higher catalytic activity [16]. However, the drastically reduced activity of the Pt sol protected with Carbowax in our systems probably results from its hydrophobicity. The Carbowax–Pt particles are hydrophobic and are probably solubilized in hydrophobic pockets created within the polymer chains. This explanation is consistent with the observation that the Pt sol protected with Carbowax is a better catalyst when the NS polymer is used as sensitizer than when PSSS-VN is applied. PSSS-VN displays a much higher solubilizing ability towards hydrophobic molecules dispersed in water than does the NS polymer [40].

3.3. Effect of the photosensitizer and viologen compound used

The rates of hydrogen production determined after 60 min of irradiation of several polymer systems are given in Table 1. The quantum yields for electron transfer from naphthalene chromophores to MV^{2+} determined in separate experiments (in the absence of Pt) are also included. It can be observed that these values correlate quite well. The production of hydrogen is faster in the systems in which the efficiency of formation of $MV^{\bullet +}$ is higher. The high performance of the PSSS-VN photozyme reflects the importance of the separation of the radical ion pair ($N^{\bullet +}$ and $MV^{\bullet +}$) formed in the primary photochemical event.

Table 1
Rates of hydrogen production in reactions photosensitized by the various naphthalene antenna polymers [a] and the quantum yields of electron transfer from polymeric naphthalene chromophores to MV^{2+} [b]

Polymer	V_{H_2} ($ml\ l^{-1}\ h^{-1}$)	$\phi(\pm 5\%) \times 10^3$
PNS	14	2.5
NS-CAL	46	3.3
SPVN	48	1.4
PSSS-VN	56	1.8
NS [c]	5	0.1

[a] $c_{naphthalene\ units} = 1.5 \times 10^{-3}$ M, $c_{MV^{2+}} = 1 \times 10^{-3}$ M, $c_{TEA} = 5 \times 10^{-2}$ M, $c_{Pt} = 5$ mg l^{-1}, pH 4, $\lambda_{irr} = 300$ nm.
[b] Experiments carried out in the absence of Pt catalyst, $\lambda_{irr} = 313$ nm.
[c] Data obtained using the low-molecular-weight model compound (NS) included for comparison.

The quantum yields of hydrogen production photosensitized by the PSSS-VN photozyme were estimated to be 0.15 ± 0.02 when MV^{2+} was used as electron relay and 0.08 ± 0.01 when SPV was used. This indicates that the efficiency of hydrogen production is determined by the efficiency of irreversible formation of MV^{2+}.

However, in spite of the higher hydrogen yields with MV^{2+}, the quantum yields of formation of $SPV^{\bullet -}$ were generally much higher than those for $MV^{\bullet +}$ [39]. This effect is probably caused by the fact that the redox potential for MV^{2+} is lower than that for SPV.

Stramel and Thomas [43] have reported that poly(sodium styrenesulfonate) (PSSS) forms a complex with viologen in which the absorption spectrum is shifted to longer wavelengths, resulting in the direct excitation of viologen by near-visible light. In the presence of TEA, this would also be expected to produce hydrogen. In a control experiment in which the only change was the replacement of PSSS-VN by PSSS, the presence of reduced viologen (MV^{+}) was detected after prolonged irradiation, but at a concentration more than an order of magnitude lower than that obtained with PSSS-VN under similar conditions. It therefore appears that the naphthalene antenna groups and the hydrophobic domains created by them play an essential role in increasing the efficiency of hydrogen generation in the photozyme system.

3.4. Dependence on pH

The rates of hydrogen formation during irradiation of polymer solutions at different pH are given in Table 2. It can be seen that there is a strong dependence on the pH of the solution, and the evolution of hydrogen is faster at low pH.

There are two major reasons for the observed pH dependence. The first is simply the dependence of the redox potential of hydrogen (E_{H^+/H_2}) on the activity of hydrogen ions a_{H^+}, and the second is the difference in stability of the system at different pH values.

The elementary process of hydrogen reduction is given as follows

$$H^+ + e^- \rightarrow \tfrac{1}{2}H_2 \qquad (8)$$

and

$$E_{H^+/H_2} = (RT/F)\ \ln a_{H^+} \qquad (9)$$

Table 2
Rates (V_{H_2}) and quantum yields (ϕ) of hydrogen production in PSSS-VN + MV^{2+} + TEA + Pt solutions at various pH values [a]

pH	V_{H_2} ($ml\ l^{-1}\ h^{-1}$)	ϕ (±10%)
4	56	0.150
5	30	0.075
6	23	0.057
7	6	0.015

[a] $c_{naphthalene\ units} = 1.5 \times 10^{-3}$ M, $c_{MV^{2+}} = 2 \times 10^{-3}$ M, $c_{TEA} = 5 \times 10^{-2}$ M, $c_{Pt} = 5$ mg l^{-1}, $\lambda_{irr} = 300$ nm.

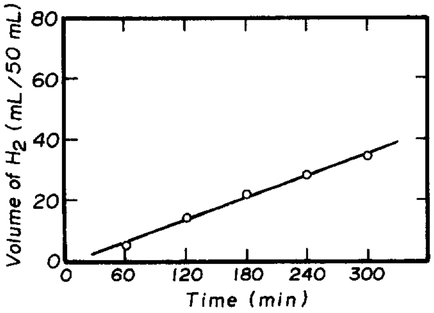


Fig. 3. Dependence of the volume of hydrogen formed on the exposure time of the PSSS-VN + MV^{2+} + TEA + Pt system to natural solar light.

At constant temperature E_{H^+/H_2} is dependent only on $[H^+]$, e.g. at 25 °C

$$E_{H^+/H_2} \approx -0.059 \times \mathrm{pH}\ (\mathrm{V}) \qquad (10)$$

The redox potentials for viologens measured vs. the normal hydrogen electrode (NHE) are as follows: for MV^{2+}, $E^0_{MV^{2+}/MV^+} = -0.44$ V; for SPV, $E^0_{SPV/SPV^-} = -0.37$ V [18]. The difference between the values of the redox potential for hydrogen and for MV^{2+} (or SPV) is the driving force for hydrogen generation. It is obvious that the difference decreases with increasing pH value.

The second important factor influencing the overall efficiency of hydrogen production is the photochemical and chemical stability of the reactants under the experimental conditions. The polyelectrolytes used as sensitizers in our experiments display very high stability. The stability of viologens during irradiation was tested by HPLC. It was shown that the stability of both MV^{2+} and SPV decreases considerably with increasing pH of the irradiated solution. An attempt to obtain quantitative data was not successful due to the relatively poor separation of the reaction mixture under our experimental conditions. The observed consumption of the viologens can be explained by considering their hydrogenation. The platinum-dependent hydrogenation of MV^{2+} has been the subject of several studies [12,14,23,43]. The process results in the formation of *N,N′*-dimethyl-4,4′-bipiperidine [44].

3.5. Production of hydrogen driven by natural solar light

It has been shown that the exposure of an aqueous solution of PSSS-VN + MV^{2+} + TEA + Pt sol to natural solar light results in the generation of hydrogen. Fig. 3 shows a typical curve for hydrogen production under these conditions.

4. Conclusions

These experiments demonstrate that polyelectrolytes containing naphthalene antenna chromophores can act as efficient photosensitizers for hydrogen evolution from water. The efficiency of hydrogen formation correlates well with the quantum yields of photoreduction of the viologen compounds. The high performance of PSSS-VN and SPVN indicates the importance of the separation of the radical ion pair formed as a result of electron transfer from the naphthalene chromophore to viologen. At low pH, the system consisting of PSSS-VN and SPV can produce the largest total amount of hydrogen. We propose that this is due to two cooperative effects: the specific conformation of the PSSS-VN chain which leads to the location of the naphthalene chromophores inside the hydrophobic microdomains of the polymer, thus separating them from $SPV^{\bullet-}$ present in the aqueous phase, and the electrostatic interactions between the negatively charged sulfonic groups in PSSS-VN or SPVN and the reduced $SPV^{\bullet-}$ radical ions.

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