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# Preparation of Photoactive Polythiocyanogens via Oxidation of Thiocyanates by Iodine in Water

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Several simple methods are known for the preparation of polythiocyanogens of molecular formula $(SCN)_x$. They can be prepared in good yield by heating $(SCN)_2$-containing solutions [1–3], by oxidation of thiocyanates in melts [4–6] or in solutions [7–11], and by electrochemical oxidation of thiocyanates in melts [12–14] or in solutions [15–18], as well. Although the first polythiocyanogens had already been prepared in 1919 [1], their structures and properties remained unknown up till now [19]. The intensive light absorption suggests a conjugated double bond structure, and interesting photophysical and photochemical properties for the polythiocyanogens. This expectation is supported by the observations of Pucciarelli *et al.* [20], who have found that the material precipitated on the platinum electrode in the anodic oxidation of thiocyanate melts is photoactive. The photoactivity was attributed to the unstable species $(SCN)_3^-$ and $[(SCN)_3]_x$ [14]. However, the electrodes maintained their photoactivity only for several days, and they lost the activity completely when kept in water [14].

We report here that the polythiocyanogens formed in the reaction of thiocyanates and iodine in water show photoactivity even in aqueous solutions, thus they may be considered for the senzitization of water-splitting by light. The polythiocyanogens were prepared on the basis of Yakovlev's work [8]. He has studied the solubility of iodine in thiocyanate solutions and found precipitation of a brown material with the composition of $(SCN)_x$ on heating concentrated thiocyanate solutions containing iodine.

## Experimental

The polythiocyanogens were prepared by the following methods:

*Method A*: 16.7 g $I_2$ were dissolved in a solution of 10 g $NH_4SCN$ in 6 cm$^3$ water. The red solution was stirred and heated at temperatures given in Table I for 8 h. After cooling, the reaction mixture was filtered, the precipitate was washed with 10 cm$^3$ water and 5 cm$^3$ acetone, and dried *in vacuo* at 100 °C over $P_2O_5$.

*Method B*: To a solution of 10 g $NH_4SCN$ in 6 cm$^3$ water small portions of 4.1 g $I_2$ were added slowly under reflux and stirring. After 4 h as the last portion of iodine had been added, the reaction mixture was cooled, filtered, and the precipitate was washed with water and acetone, dried on air at 140–150 °C for 4 h.

The photoelectrochemical measurements were made in a thermostated glass reactor. A bright platinum electrode of 2 × 0.5 cm$^2$ area and 1 molar calomel electrode was used as working and reference electrode, respectively. The potential of the working electrode was measured by an OP-205/1 type poten-

TABLE I. Characteristic Data of Polythiocyanogens Prepared under Different Conditions

| No. | T (°C) | Yield (%) | Colour | Analysis (%) | | |
|---|---|---|---|---|---|---|
| | | | | N | S | I |
| 1 | 70 | 14.9 | reddish yellow | 17.22 | 37.92 | 28.33 |
| 2 | 75 | 16.4 | reddish yellow | | | |
| 3 | 80 | 45.9 | dark red | 13.56 | 31.42 | 44.40 |
| 4[a] | | | orange | 20.24 | 46.35 | 13.50 |
| 5 | 85 | 53.7 | dark red | | | |
| 6 | 90 | 49.8 | ochre yellow | 20.17 | 48.58 | 12.87 |
| 7 | 95 | 47.0 | ochre yellow | | | |
| 8 | 100 | 44.6 | orange | 22.05 | 49.47 | 7.63 |
| 9[b] | 100 | 73.4 | brick-red | | | |
| 10[c] | 100 | 38.7 | orange | | | |
| 11[d] | 100 | 45.4 | orange | 24.14 | 50.50 | |

Method A, $n_{SCN}:n_I$ = 1:1. [a]1 g no. 3 was stirred in 50 cm$^3$ water for 40 h. [b]$n_{SCN}:n_I$ = 1:2. [c]$n_{SCN}:n_I$ = 2:1. [d]Prepared by Method B.

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tiometer (RADELKIS), and was registered by an OH-804/1 type potentiometric recorder (RADELKIS). An air-ventilated 1000 W halogen lamp (TUNGSRAM) served as light-source, with a 10 cm water-filter to cut off the IR radiation. The distance of the light source and the glass reactor was 50 cm. The illumination at the outside of the reactor was approx. 18 000 lx. The photoelectrochemical measurements were made mainly in 0.1 M phosphate-buffer (pH = 6.86).

Pretreatment of the working electrode: a bright platinum electrode washed successively with conc. sulphuric acid, water and acetone, was immersed into a stirred suspension of 25 mg finely powdered polymer in 30 cm$^3$ water for 6 h. Before use the working electrode was washed with water, and after use it was stored in water.

## Results and Discussion

Data in Table I show that the yield of the reaction and the colour of the products depend on the method of the preparation (A or B), on the mole ratio of the reagents, and change dramatically with the temperature. The essential difference of the products obtained under different conditions lies in their iodine content. The iodine content of the polymers did not change on extraction with carbontetrachloride or acetone, and decreased only by a few percent on reflux with carbondisulphide. However, in the case of an iodine-rich compound (no. 3) stirred in water for 40 h a significant decrease in the iodine content (from 44.40% to 13.50%) was observed, and iodide was detected in the liquid phase.

IR spectra of the polymers from different preparations are of the same character: an absorption band at 2040 cm$^{-1}$ characteristic for the –SCN group, and a wide band between 1100–1500 cm$^{-1}$ and at 1610–1630 cm$^{-1}$ characteristic for –C=N– conjugated bonds. In the case of polymers containing a small amount of iodine the bands at 1610–1630 and 2040 cm$^{-1}$ are sharper and more intensive than those of iodine-rich samples.

The polythiocyanogens prepared via oxidation by iodine are insoluble in water or dilute acids and bases, and in most of the organic solvents with the exception of acetone, dimethylformamide, and dimethylsulphoxide. In concentrated sulphuric acid or NaOH the polymers are decomposed with evolution of a sharp-smelling gas containing $SO_2$, $H_2S$, $NH_3$, and $I_2$. The fractions of low molecular weights are soluble in DMSO, DMF and acetone. In DMSO a characteristic absorption band is observed at 425 nm. Evolution of small amounts of $CO_2$ was detected in the interaction of aqueous suspensions of polythiocyanogens with Ag(I) and Cu(II) ions, because of the reducing groups on the surface of the polymer particles.

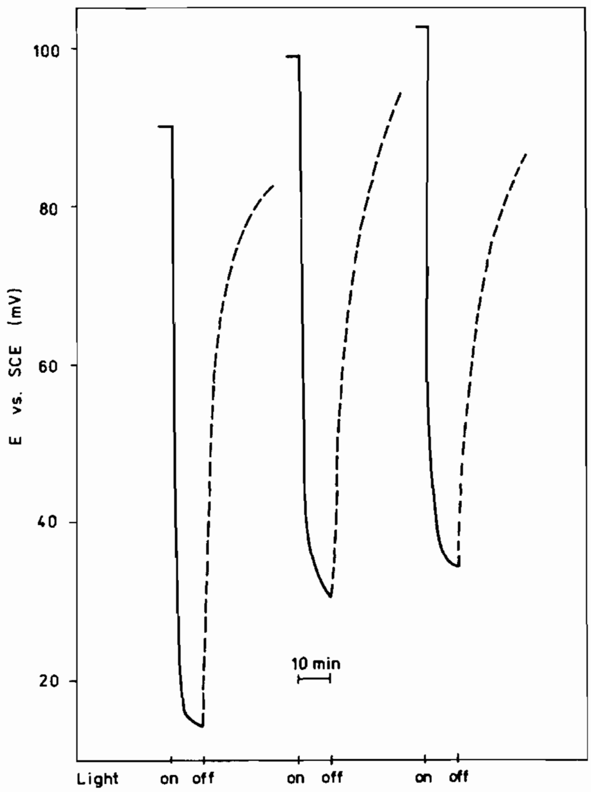

Fig. 1. The potential change of the platinum electrode coated with polythiocyanogen (no. 11) under illumination of visible light ($T$ = 30 °C).

The potential of the platinum electrodes covered with polythiocyanogens decreased by 10–100 mV on the effect of visible light. This potential change was rather reversible, and the electrode potential returned near the original value in 30–70 min after switching off the light (Fig. 1). Since the photoelectrochemical measurements made in air or in a nitrogen atmosphere gave the same results, most of the experiments were made in air.

The photoactivity is influenced by several factors. The photopotential, which was obtained from the difference of the measured dark potential and the steady-state potential of the working electrode under illumination of visible light, increased with an increase in pH, and in light intensity. The photoactivity of the products obtained at higher temperatures is greater than that of the products obtained at lower temperatures. Although the photoactivity of the polymers decreased with their ageing, product no. 10 retained approx. 40% of its original photoactivity standing in water for five months after preparation, contrary to the electrodes prepared by Pucciarelli *et al.* [14].

When a bright platinum electrode was immersed into 80 cm$^3$ phosphate buffer suspension of 10 mg polymer prepared by Method B, and dried at room temperature, the photopotential changed from −30 to −130 mV by adding triethanolamine and methylviologen to the dispersion. This means that the polythiocyanogens sensitize the photoredox reaction between triethanolamine and methylviologen [21].

Detailed investigations of structures, properties, and photoelectochemical behaviour of the polythiocyanogens obtained in the presence of different oxidants (e.g. $Cl_2$, $Br_2$, $I_2$, $S_2O_8^{2-}$) are in progress.

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