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Preliminary communication

REVERSIBLE DIOXYGEN BINDING TO PORPHYRINIRON(II) COMPOUNDS COVALENTLY LINKED TO POLYSTYRENE

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Summary

Porphyriniron(II) compounds covalently linked to polystyrene were prepared using copolymers from styrene, 4-aminostyrene and divinylbenzene. In the solid state, reversible dioxygen binding was observed only in the case of highly cross-linked polymer.

There is increasing interest in the synthesis of stable dioxygen complexes of porphyrinirons which could mimic or give insights into the function of dioxygen binding hemoproteins. However, at room temperature, solutions of simple porphyriniron(II) compounds are rapidly and irreversibly oxidized to the μ-oxodimer:

$$\mathrm{Fe^{II} + O_2 \rightarrow FeO_2 \xrightarrow{Fe^{II}} Fe^{III}{-}O{-}O{-}Fe^{III} \rightarrow \quad \rightarrow Fe^{III}{-}O{-}Fe^{III}}$$

Much work has been directed towards avoiding this bimolecular reaction between the dioxygen complex and the excess of porphyriniron(II) by using sterically hindered porphyrins [1—3] or by lowering the temperature [4]. A third approach, initiated by the work of Wang [5] was to incorporate porphyriniron(II) compounds into a polymer [6—10] or to bind them at the surface of a solid support [11].

In this communication we report the reversible oxygenation of a porphyriniron(II) covalently linked to polystyrene and the effects of the rigidity of the polymer.

Macroporous aminopolystyrenes were prepared by copolymerisation of a mixture of styrene, 4-aminostyrene and divinylbenzene [12] and treated with 5,10,15,20-tetrakis(p-chlorocarbonylphenyl)porphyrin in dry pyridine and then with methanol. Table 1 indicates the composition of the two aminopolystyrenes which were used in this study. Insertion of the iron was achieved by treating the polymer-bound porphyrin with an excess of $FeCl_2$ in hot

TABLE 1

PERCENTAGE COMPOSITION OF THE MONOMER MIXTURE USED FOR THE PREPARATION OF THE POLYMERS

Monomer	Polymers	
	P_{20}	P_{30}
4-Aminostyrene	5	5
Styrene	75	65
Divinylbenzene	20	30

dimethyl formamide. Elemental analysis showed that the concentration of the porphyrin bound to the polymer was only about 20% of that of the amino groups in the starting material. Thus, there is probably more than one amide linkage per porphyrin and this is consistent with the relative intensities observed in IR spectroscopy for ν(CO)(ester) at 1725 cm^{-1} and ν(CO)(amide) at 1670 cm^{-1}. In both cases the insertion of iron was complete and the concentration of the porphyriniron was found to be about 9×10^{-5} mol/g. The polymers were treated with an excess of dry piperidine to reduce the iron, and dried overnight under vacuo.

The effect of exposure to the air was monitored in the solid state by diffuse reflectance visible spectroscopy on the whole beads. Only poorly resolved spectra have been obtained, as illustrated in Fig. 1, after equilibration with air. However, polymer P_{30} gave a broad absorption near 535 nm which is clearly different from that obtained with polymer P_{20} at 570 nm.

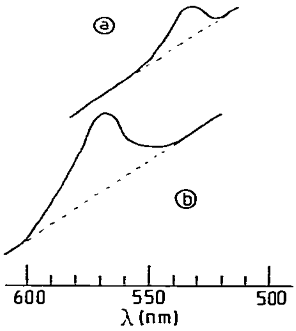

Fig.1. Diffuse reflectance visible spectra of porphyriniron(II) compounds linked to polystyrene, after exposure to air. (a) polymer P_{30}, (b) polymer P_{20}.

IR difference spectra were obtained by Fourier Transform techniques on a Digilab FTS 14 spectrometer. The adduct obtained with oxygen and P_{20} exhibited a broad absorption in the 860 cm^{-1} region which did not appear with the P_{30} adduct. This band was attributed to the μ-oxo vibration which was observed at 868 cm^{-1} in the case of 5,10,15,20-tetrakis(*p*-methoxycarbonylphenyl)porphyrin. More than 10 oxygenation—deoxygenation cycles were performed without any significant alteration of the absorption at 535 nm for the polymer P_{30} and this compound was stable in the air over a period of more than 2 months. This behavior was found to be reproducible with 3 different batches of each polymer.

Exposure of the oxygen-polymer P_{30} adduct to carbon monoxide caused no noticeable change in the visible spectrum. However, in the IR spectrum a new band appeared at 1985 cm^{-1} ; this was attributed to an iron(II)—CO complex, which is in agreement with ν(CO) reported for 5,10,15,20-tetrakis-(*p*-methoxyphenyl)porphinato(piperidine)(carbonyl)iron at 1981 cm^{-1} [13].

These experiments strongly suggest the formation of a stable dioxygen complex with polymer P_{30}. In order to check that the "reversible oxygenation" was not due to the presence of an excess of reducing agent (free amino groups or piperidine), the following experiments were carried out:

(a) 5,10,15,20-Tetraphenylporphyriniron(II) was adsorbed on the amino-polystyrene used for the synthesis of polymer P_{20}, by slow evaporation of a suspension of the polymer in a dichloromethane solution of the porphyrin. Introduction of air gave an absorption at 540 nm in the visible spectrum and this shifted to 575 nm, within 1 hour. This new spectrum was not modified by exposure to piperidine.

(b) The same experiment was performed with "picket fence porphyrin" [14]. Exposure to air gave a similar spectrum at 535 nm, but this was stable for more than 20 hours.

We conclude that stable dioxygen complexes can be easily obtained by use of low concentrations of porphyriniron(II) covalently linked compounds to highly cross-linked polystyrenes. Dramatic effects are observed on changing the ratio of the cross-linking agent in the polymer. These results are consistent with the failure to observe a reversible dioxygen binding in an analogous system [15] and with recent reports of site separation in synthetic polymers [16—18].

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