Electrode materials derived from poly(amino acids). Synthesis and application of porphyrin doped materials

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Abstract

Reaction of poly(γ -ethyl L-glutamate) with N-(3-aminopropyl)imidazole gives an imidazole doped polymer which forms 6-coordinate complexes with iron(III) porphyrins. Modified electrodes are prepared using these porphyrin containing polymers. The new materials are characterised by cyclic voltammetry, UV-visible spectroscopy and by surface enhanced resonance Raman spectroscopy. The techniques allow complete characterization of the oxidation state and ligation state of the iron centre. The modified electrodes will catalyse the reduction of dioxygen.

Introduction

Homopolymers of amino acids are prepared by the action of a base on the cyclic carboxy anhydride formed from the monomer amino acid using phosgene. The polymers derived from lysine and ornithine as well as glutamic acid and aspartic acid possess either an amine function or a carbonyl function on each side chain that can be chemically modified so as to incorporate electroactive groups. Thus, this group of homopolymers possesses intriguing possibilities for the development of a new series of electroactive polymers. The solubility properties of these modified poly(amino acids) allow them to be applied to an electrode surface from solution in dimethylacetamine or hexafluoroisopropanol. The electrochemical properties of the coated surface can then be examined in acetonitrile or water which are poor solvents for the polymers described here.

Poly(N^ε-4-nitrobenzoyl-L-lysine) was the first example of this class of electro-active polymer we prepared. The material could be coated onto platinum and showed the expected reversible redox behaviour for the 4-nitrobenzoyl group in acetonitrile (1).

Porphyrin Doped Polymers

Poly(γ -ethyl L-glutamate) proved a much more versatile material from which to develop electroactive polymers. The ester side chains can be derived from a reaction with N-(3-aminopropyl) imidazole where the degree of loading of imidazole groups is governed by the reaction time. The imidazole loaded arms are now available for coordination to a transition metal and a redox centre is attached to the polymer in this way (see Scheme).

Scheme. Imidazole loaded poly(amino acid) and the redox centres deuterioporphyrin (IX) dimethyl ester and tetraphenylporphyrin, both as the iron(III) complex.

We have concentrated our work on the properties of coordinatively attached iron porphyrins. Imidazole forms either one or both of the axially coordinated ligands. Iron porphyrins are the active site in a variety of electron transfer enzymes. Their electron transfer properties can be altered by a change in axial coordination. The combination of poly(amino acid) and iron porphyrin is a crude enzyme model which we hope will display interesting electrochemical properties.

The composition of imidazole doped poly(γ -ethyl-L-glutamate) can be determined from the ^1H -nmr spectrum of the polymer in trifluoroacetic acid. The absence of glutamic acid residues is established and the ratio of ethyl ester to imidazole doped side arms can be calculated. Spectra also demonstrate that the purified polymer contains no excess of free N-(3-aminopropyl)imidazole. The porphyrin doped material is prepared by mixing appropriate amounts of polymer and porphyrin so as to obtain the bisimidazole ligated porphyrin. Suitable solvents are either dimethylsulphoxide or a hexafluoroisopropanol-dichloromethane mixture. Electrodes are dip-coated from the first solvent or spray-coated from the second solvent. Porphyrins used in this work are haem, deuterioporphyrin(IX) dimethyl ester and tetraphenylporphyrin, all as the iron(III) complex.

Cyclic Voltammetry

Polymer films deposited on platinum or indium doped tin oxide coated glass (ITO) show cyclic voltammetric behaviour expected for the Fe(III) (Fe(II) couple. After an initial break-in period the couple is very stable in both water and acetonitrile. Film containing the very hydrophobic tetraphenyl porphyrin give an excellent CV response in water.

Spray coating of the electrode is a very convenient technique but because of the rapid precipitation of the polymer onto a pre-heated electrode, annealing of the film is necessary before the CV response becomes stable. Spray coated electrodes were conditioned by allowing them to soak in water for a short time and then drying slowly in air. This gives a dramatic improvement in the CV response from the electrode.

The apparent redox potential of these porphyrin doped films is strongly dependent on the nature and concentration of the anion in the supporting electrolyte (2). Perchlorate stabilises the Fe(III) state for the deuterioporphyrin doped material by 130 mV relative to chloride ion. This could be due to differences in solvation within the micro environment of the film, influenced by the anion.

UV-VIS Spectra

The films deposited on ITO show characteristic spectra for six coordinate Fe(III) or Fe(II) porphyrins as they are electrochemically cycled between the oxidised and reduced forms. Immersion in aqueous electrolyte does however cause a decrease in intensity and a broadening of the Soret band in a process which eventually reaches a steady state. The effect is most predominant in the case of

tetraphenylporphyrin containing films and is attributed to hydrophobic effects which cause the porphyrins to cluster together so as to reduce the surface area exposed to water.

Figure 1. UV-VIS spectra from an iron tetraphenylporphyrin doped film at equilibrium under an applied potential. Potential is changed between each spectrum so as to convert Fe(III) sites to the Fe(II) state.

A series of spectra (Figure 1) were obtained from the tetraphenylporphyrin films at equilibrium under an imposed potential arranged to pass from the Fe(III) to the Fe(II) state. These spectra yield the proportions of Fe(III) and Fe(II) porphyrin as the potential used. A Nernstian plot constructed from this data gives a slope of many times the expected value for thermodynamic reversible behaviour. This arises as a consequence of interactions within the film. As further evidence of these interactions, the isosbestic point from this series of spectra is not sharp, as expected for a simple reaction involving two species. Two distinct regions of thermodynamic behaviour are found and arise because the degree of association of the porphyrins is dependent on the oxidation state. After 40% reduction to the non-ionic Fe(II) state, a more hydrophobic porphyrin region is formed. Related behaviour can be found in the literature for another polymer system (3).

At very low concentrations of porphyrin centres within the film, no electroactivity is observed which precludes any extrapolation of behaviour to infinite dilution of centres within the film. Electroactive groups are held rigidly within the film and at low dilution this causes the electron transfer rate to be very slow or non-existent (4).

A parallel series of polymers have been prepared by reaction of poly(γ -ethyl glutamate) with N-(3-aminopropyl)-2-methylimidazole and then coordinated to tetraphenylporphyrin. The system leads to a 5-coordinate Fe(III) porphyrin centre, as expected from solution studies with substituted imidazoles. The resulting porphyrin doped film deposited on ITO showed no electrochemical behaviour. Spectroscopy established that in this case association of the 5-coordinate porphyrin centres leads to the eventual formation of an oxo-bridged dimer which is not electroactive. A similar reaction is observed for 5-coordinate porphyrins in aqueous solution.

Surface enhanced resonance Raman spectra (SERRS)

Figure 2. SERRS spectra from iron tetraphenylporphyrin doped films. Upper spectrum with Fe(III) state, lower spectrum with Fe(II) state. The band shifts observed correspond to 6-coordinate low spin iron centres.

SERRS is a powerful vibrational spectroscopic technique that gives detailed information on molecules directly adjacent to the electrode surface where the initial charge injection to the polymer film takes place. Films are prepared on roughened silver electrodes. By choosing the wavelength of the laser probe to fall within an absorption band of the iron porphyrin, resonance enhancement of the scattered Raman signal is obtained. This allows us to probe the iron porphyrin centre with no interference from the remainder of the complex system. SERRS obtained from these films are dominated by porphyrin skeletal vibrations. The frequencies of these vibrations act as markers for the oxidation state, the spin state and the ligation state (5). The SERRS for the bis-imidazole ligated iron porphyrin loaded polymer system in water indicate that the integrity of the electroactive unit is maintained at the electrode-polymer interface. There is no direct action between the electrode and the iron porphyrin, surface iron porphyrins exist in the same state as the other porphyrin units in the bulk of the polymer film.

This spectral information confirms the observations made from the UV-VIS studies of both 6-coordinate and 5-coordinate complexes. The N-(3-aminopropyl)imidazole porphyrin polymer system shows spectral bands (Figure 2) indicative of bis-imidazole coordination to iron in both the Fe(III) and Fe(II) oxidation states (6). The N-(3-aminopropyl)-2-methylimidazole ligand attached to the polymer induced 5-coordination to the Fe(II) porphyrin centre.

Interaction with Dioxygen

CV indicates that the 6-coordinate polymer bound Fe(II) porphyrins interact directly with dioxygen. The reduction wave for the Fe(III) state is greatly enhanced in the presence of dioxygen and no reoxidation wave is observed. Such behaviour is expected if the Fe(II) state reduces dioxygen to hydrogen peroxide. After several cycles the electroactivity of the polymer shuts down.

On CV in acetonitrile solution, the reduction wave for polymer bound 6-coordinate Fe(III) porphyrin is only weakly enhanced in the presence of dioxygen and a reoxidation wave is present at a sweep rate of 25 mVs^{-1} . The addition of benzoic anhydride results in a massive enhancement of the reduction wave and the absence of a reoxidation wave. This behaviour is expected if benzoic anhydride acylates an intermediate and allows to cleave dioxygen bound so as to form a high valent iron-oxygen intermediate which will be reducible at the potentials used. Attempts to use the high valent iron-oxygen intermediate as an oxygen atom transfer agent towards cyclohexene have so far not succeeded due to a low number of turnovers of the system. We are presently examining the use of porphyrins more stable towards oxidative degradation.

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