

Electroactive Poly(amino acids). Part 4.¹ Poly(γ -ethyl L-glutamate) Modified by Side Chain Reaction with Ferrocenylmethylamine

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Poly(γ -ethyl L-glutamate) was treated with ferrocenylmethylamine to replace 0.21 side chain esters by ferrocenylmethylamide. The modified polymer could be coated onto platinum as a film which showed the redox behaviour of the ferrocene units. Reversible redox behaviour was found in acetonitrile and in water. In water the apparent diffusion coefficient of charge through the film depends markedly on the supporting electrolyte and increases in the sequence LiClO₄, NaClO₄, KClO₄, which is the sequence of increasing limiting molar conductance for these salts. This suggests that the rate determining step for charge diffusion is electrolyte migration within the film.

In a search for polymers with a relatively rigid spine and possessing flexible side chains to which electroactive groups can be attached, we have investigated materials derived from poly(L-lysine) by modification of the side chain amine functions.¹⁻³ A second group of materials is derivable from poly(γ -alkyl L-glutamates) by modification of the side chains through ester exchange or amide formation so as to introduce the desired electroactive centres. Electroactive polymers have recently been the subject of much research aimed at producing coatings which will modify the properties of a solid electrode.^{4,5} Of particular interest for incorporations into polymers are groups that will carry out an inner sphere oxidation-reduction process on some substrate in solution and subsequently be regenerated by outer sphere electron transfer from the electrode surface. Examples have been given recently where the catalyst can oxidise alcohols to aldehydes or ketones, reduce carbon dioxide, ketones and alkyl halides and catalyse the reaction between alkenes and oxygen to give alkoxides.⁵ As yet these systems cannot achieve large turnover numbers before the catalyst is destroyed. The poly(γ -alkyl L-glutamate) groups are well suited to side chain modification for the introduction of electroactive catalytic centres and we present the results of some experiments on the modification of poly(γ -ethyl L-glutamate). Part of our work in this area has been the subject of a brief communication.⁶

Poly(γ -methyl glutamate) has been modified by the introduction of electroactive groups for other purposes. Japanese workers⁷ have used ester exchange with ferrocenylmethanol to generate a ferrocene-loaded polymer that can function as an ion gate. Here, oxidation of the ferrocene centres to the iron(III) state opens the gate. Another group⁸ has attached viologen groups by ester exchange and used a membrane prepared from the material to transport electrons between solutions of two different redox couples separated by the membrane. An alternative method⁹ for modifying the ester side chains by reaction with a substituted amine to form a substituted amide, offers much greater flexibility for our purposes in that both the amide group and the ester group can be varied. A range of poly(γ -alkyl glutamate)s is readily prepared from the appropriate *N*-carboxyanhydride by reaction with a variety of nucleophilic catalysts.¹⁰ In this first series of experiments using a polyglutamate, ferrocenylmethylamine was used to insert the electroactive sites (see Scheme 1).

Preparation and Examination of the Polymers.—Poly(γ -ethyl glutamate) was prepared with a degree of polymerization of 350. The material was freely soluble in a mixture of dimethylacetamide and ferrocenylmethylamine. Reaction between the ester groups and the primary amine occurred at 70 °C and, after

some time, the doped polymer was precipitated by the addition of ether. The extent of ferrocene doping was determined by analysis of the product for iron. The degree of polymerization is assumed from the molecular weight of the parent poly(γ -ethyl glutamate).

The work described here was carried out using polymer loaded with 0.21 mole fraction of ferrocene side chains. The doping process, of course, offers possibilities for the preparation of electroactive polymers with a wide range of physical properties by beginning with a different poly(γ -alkyl glutamate), and also by regulating the number of ferrocene groups attached.

This doped polymer was dip-coated onto platinum from dimethyl sulphoxide solution. After being dried *in vacuo* the coated electrode was examined by cyclic voltammetry and chronoamperometry in acetonitrile containing 0.1 mol dm⁻³ tetrapropylammonium perchlorate.

Cyclic voltammetry between 0 and +0.8 V *vs.* SCE gave information on the reversible electron transfer reaction of the ferrocene residue. Chronoamperometry was carried out by stepping the electrode potential from 0 to 0.8 V *vs.* SCE and then collecting the resulting current transient due to oxidation of the film.

Current transients recorded on chronoamperometry are ideally described¹² by the Cottrell equation [eqn. (1)] where

$$i = (n F A D^{\frac{1}{2}} C_0 / \pi^{\frac{1}{2}} t^{\frac{1}{2}}) [1 + 2 \sum_{k=1}^{\infty} (-1)^k \exp(-k d^2 / D t)] \quad (1)$$

i is the current at time *t*, *n* is the number of electrons per active site, *A* is the surface area, *d* is the layer thickness, *C*₀ is the surface concentration of active sites per unit volume, *D* is the diffusion coefficient of charge through the film and *k* is an integer. Under conditions of semi-infinite diffusion *d*² > *Dt* and the exponential terms can be neglected. The inset of Fig. 3 shows the plot of *i vs.* *t*^{- $\frac{1}{2}$} . Values for *D* ^{$\frac{1}{2}$} *C*₀ are obtained from the limiting slope at large values of *t*^{- $\frac{1}{2}$} . As charge accumulates on the surface of the film away from the electrode, this plot deviates from the line of limiting slope.

Integration of the current transient also indicates the surface coverage (Γ) of electroactive groups.

Results and Discussion

Reversible redox behaviour of the ferrocene groups with *E*⁰ = 0.384 V *vs.* SCE was found in acetonitrile, with a linear dependence of anodic peak height on the square root of scan rate, Fig. 1, characteristic of a thick film where, on the time scale, *d*² > *Dt*. Ferrocene in acetonitrile solution shows *E*⁰ 0.307 V *vs.*

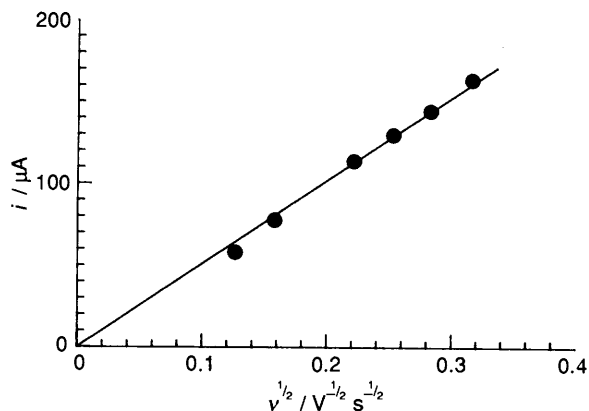


Fig. 1 Data from cyclic voltammetry using a thick film of ferrocene loaded poly(γ -ethyl L-glutamate) on Pt; film area 0.202 cm^2 solvent acetonitrile containing $0.1 \text{ mol dm}^{-3} \text{ Pr}_4\text{NClO}_4$, Γ $15.7 \text{ nmol cm}^{-2}$ measured by CA in acetonitrile, used in experimental sequence 17 of Table 1

Table 1 Chronoamperometry experiments on ferrocene-doped poly(γ -ethyl glutamate) films (0.21 mole fraction ferrocene chains) as film on Pt. Electrode area 0.202 cm^2 ; coatings no. 17, 20 and 30; potential step $0 \rightarrow 0.80 \text{ V vs. SCE}$. Current transient was integrated over 2 s to obtain surface coverage, Γ , and fitted to the Cottrell equation to obtain $D^{\frac{1}{2}}Co$.

Experiment no. ^a	Solvent	Electrolyte/ 0.1 mol dm^{-3}	$\Gamma/\text{nmol cm}^{-2}$	$D^{\frac{1}{2}}Co/\text{nmol cm}^{-2} \text{ s}^{-\frac{1}{2}}$
17-13	AN	Pr_4NClO_4	15.7	21.2
17-30	H_2O	LiClO_4	3.74	2.47
20-11	H_2O	LiClO_4	4.05	2.92
20-22	H_2O	KClO_4	6.16	6.46
20-27	H_2O	KClO_4	5.10	5.27
30-2	H_2O	KClO_4	5.82	4.29
30-4	H_2O	KClO_4	6.40	6.26
30-8	H_2O	NaClO_4	5.46	6.82

^a The first figure, 17, 20 or 30, denotes the film number; the second figure denotes the experiment on that film.

SCE.¹¹ The surface coverage of electroactive groups was determined by chronoamperometry, stepping the potential to 0.8 V vs. SCE and then integrating the current transient over 2 s. A surface coverage (Γ) of electroactive groups of $15.7 \text{ mmol cm}^{-2}$ in acetonitrile (see Table 1) is of the same order of magnitude as that obtained for poly(N^{ϵ} -4-nitrobenzoyl-L-lysine) ($12\text{--}28 \text{ mmol cm}^{-2}$).² However, since the mole fraction of ferrocene-doped side chains is 0.21, this film must be thicker than that obtained with PNBL so as to obtain the surface coverage of $15.7 \text{ mmol cm}^{-2}$. The increase in thickness must be $1/0.21$, i.e. approximately five-fold.

The response of this coated electrode in water was markedly dependent on the supporting electrolyte. Thus, peak heights on cyclic voltammetry increased on changing the electrolyte in the order $\text{LiClO}_4 < \text{NaClO}_4 \approx \text{KClO}_4$; at 0.1 V s^{-1} , anodic peak heights were $25.6, 39.3$ and $42.0 \mu\text{A}$, respectively. The measurements were taken using the same coated electrode, number 30, conditioned in each electrolyte by ten prescans. A number of cyclic voltammograms made using the same coated electrode, number 17, are plotted together in Fig. 2 to indicate how peak height depends on supporting electrolyte and solvent.

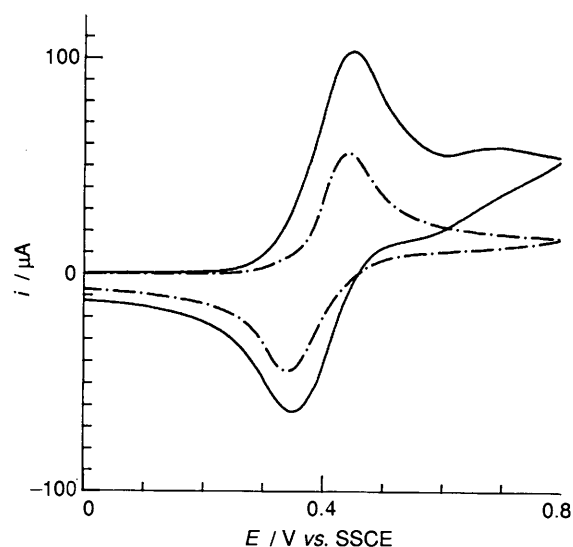


Fig. 2 Cyclic voltammetry of ferrocene-loaded poly(γ -ethyl L-glutamate) on Pt; — solvent: $0.1 \text{ mol dm}^{-3} \text{ Pr}_4\text{NClO}_4$ in acetonitrile. - - - solvent: $0.1 \text{ mol dm}^{-3} \text{ LiClO}_4$ in water; $v = 0.1 \text{ V s}^{-1}$; same film as used to obtain the data for Fig. 1

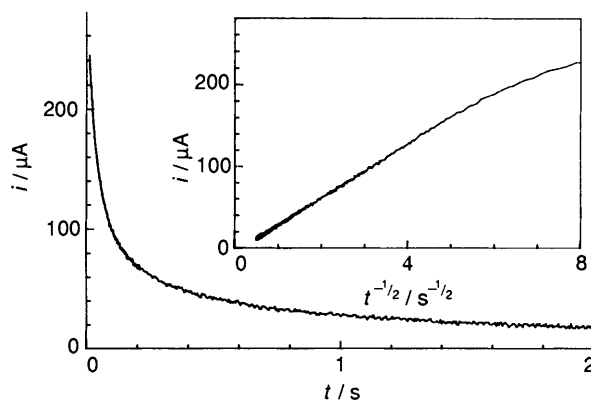
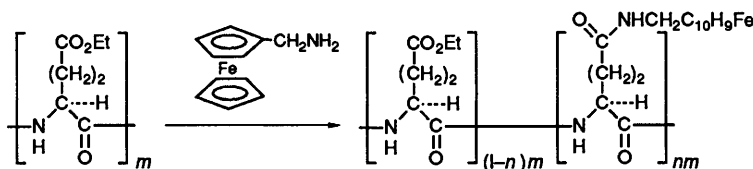


Fig. 3 Chronoamperometry of ferrocene-loaded poly(γ -ethyl L-glutamate) on Pt; film area 0.202 cm^2 ; solvent: water containing $0.1 \text{ mol dm}^{-3} \text{ LiClO}_4$; potential step $0 \rightarrow 0.8 \text{ V vs. SCE}$; Γ $4.05 \text{ nmol cm}^{-2}$ from integration of this curve. Inset shows a plot of i vs. $t^{-\frac{1}{2}}$. Experiment no. 20-11.

Peak height increased on changing the solvent from water to acetonitrile.

The results from chronoamperometry experiments with various supporting electrolytes and different films of the same polymer are collected in Table 1. The apparent surface coverage measured for the same electrode is much smaller in water than in acetonitrile. This is probably due to incomplete charging of the film during the time of 2 s allowed for integrating the current because diffusion of charge through the film is slower in water (average $D^{\frac{1}{2}}Co = 4.85 \text{ mmol cm}^{-2} \text{ s}^{-\frac{1}{2}}$) than in acetonitrile ($D^{\frac{1}{2}}Co = 21.2 \text{ mmol cm}^{-2} \text{ s}^{-\frac{1}{2}}$). In water the diffusion rate for charge through the films number 20 and 30 depends on the supporting electrolyte and increases in the order $\text{LiClO}_4 < \text{NaClO}_4 \approx \text{KClO}_4$. Film number 20 on chronoamperometry showed nearly ideal semi-infinite diffusion characteristics in



Scheme 1

$\text{LiClO}_4/\text{H}_2\text{O}$ (Fig. 3) and layer-thickness-limited diffusion in $\text{Pr}_4\text{NClO}_4/\text{AN}$.

The dependence of $D^{\frac{1}{2}}Co$ on the supporting electrolyte in water suggests that the transmission of charge through the film, in this solvent, is limited by the diffusion rate for the ions of the electrolyte. The diffusion coefficient ($D/\text{cm}^2 \text{ s}^{-1}$) for univalent ions in solution is related to ionic mobility ($u/\text{cm}^2 \text{ V}^{-1} \text{ s}^{-1}$) by the Einstein equation¹³ [eqn. (2)] where k_B is the Boltzmann

$$u/D = e/k_B T \quad (2)$$

constant and e the charge on the electron. The migration of charge through a film creates an electrostatic field and the diffusion coefficient for this process is the sum of the migration of both ions in this electrostatic field. The apparent diffusion coefficient for charge migration under these conditions is thus related to the limiting molar conductance ($\Lambda/\text{cm}^2 \Omega^{-1} \text{ mol}^{-1}$) by the expression in eqn. (3).

$$\Lambda/FD = e/k_B T \quad (3)$$

We have available values of molar conductance only in aqueous solution and assume that these are relevant to the environment of the film. The values¹⁴ of Λ in water for LiClO_4 and KClO_4 are 106.1 and 140, respectively, at 25 °C; the corresponding values of D are 2.82×10^{-5} and 3.73×10^{-5} , respectively. In aqueous LiClO_4 and KClO_4 average values of $D^{\frac{1}{2}}Co$ are $2.70 \pm 0.23 \times 10^{-9}$ and $5.57 \pm 0.50 \times 10^{-9} \text{ mol cm}^{-2} \text{ s}^{-\frac{1}{2}}$, respectively. Taking the values calculated for D in water, values for Co of 5.0×10^{-7} and $9.1 \times 10^{-7} \text{ mol dm}^{-3}$ are obtained.

As we have noted, the diffusion of ions within the film will be restricted so that D is grossly overestimated in the above discussion. This leads to an under-estimation of Co . An estimate for the likely maximum value of Co can be obtained from the dimensions of the crystalline form of the related poly(*N*^ε-benzoyl-L-lysine).¹⁵ For the benzene ring 'concentration' in this polymer $Co = 4.59 \times 10^{-3} \text{ mol cm}^{-3}$. Since, for the glutamate polymer the fraction of side chains substituted by ferrocene is only 0.21, the maximum value for Co becomes $1.25 \times 10^{-4} \text{ mol cm}^{-3}$.

The picture of charge migration limited by ionic mobility qualitatively fits the behaviour of this ferrocene-doped poly(γ -ethyl L-glutamate) in aqueous electrolytes. A value for the concentration of active sites in the film can only be estimated as greater than 9×10^{-7} but less than $1 \times 10^{-4} \text{ mol dm}^{-2}$.

In order to explain the behaviour of this film in acetonitrile, ion conductance values in this solvent are taken from the compilation of Krungalz.¹⁶ The values for Li^+ and ClO_4^- in acetonitrile are not available. Examination of the data for other salts in acetonitrile indicates that it is reasonable to substitute the value of the ion conductance for Na^+ in place of Li^+ and the value of the ion conductance for NO_3^- in place of ClO_4^- . On this basis estimates of the limiting molar conductance of LiClO_4 and Pr_4NClO_4 are 183 and 178, respectively.

The limiting conductance of LiClO_4 and of Pr_4NClO_4 in acetonitrile is greater than that of LiClO_4 in water. Hence, when ion diffusion is the important factor in the transport of charge through a polymer film, we can explain why the same film showed semi-infinite diffusion characteristics (*i.e.* $d^2 > Dt$) in $\text{LiClO}_4/\text{H}_2\text{O}$, but layer-thickness-limited diffusion (*i.e.* $d^2 \leq Dt$) in $\text{Pr}_4\text{NClO}_4/\text{AN}$. It is only in acetonitrile that, on the time scale of the experiment, D is sufficiently large for charge to migrate to the far boundary of the film. Again, the increased rate for ion diffusion explains why, for the same film, peak heights on cyclic voltammetry increase on changing the solvent from water to acetonitrile (Fig. 2). A large value of D allows more electroactive sites to be engaged within the time scale of the experiment.

Conclusions

The method developed in this paper for exchanging polymer side chains through reaction with an amine should be capable of extension so as to introduce other electroactive groups into the side chain. The films which we prepared previously² from the homopolymer poly(*N*^ε-4-nitrobenzyl-L-lysine) were unstable in the charged state. In particular, after chronoamperometry the cyclic voltammetry behaviour of the film was changed. This ageing effect was attributed to repulsion between the charged side chains which destabilised the α -helix adopted by the uncharged form in favour of an irregular coil. The resultant changes in geometry caused the film to separate from the electrode base. We did not encounter this type of instability for the ferrocene-doped polyglutamate films. With the films described here, repeated cyclic voltammetry, chronoamperometry and further cyclic voltammetry could be carried out without the response altering its characteristics. Clearly, in random doping of polyglutamate, we have sacrificed the structural regularity of a homopolymer. However, we have achieved a more stable system which is capable of easy extension to other electroactive groups. This is an advance and the extensions towards the incorporation of other transition metal redox centres should be possible.

Experimental

All solvents used were rigorously purified and dried according to literature methods. Gaseous effluents containing phosgene were passed through scrubbing towers containing aqueous sodium hydroxide before being released.

IR spectra of poly(amino acids) were recorded using skins of material made by evaporating a solution in dimethylacetamide onto a sodium chloride disc, under reduced pressure in a current of air.

In this context 1 mole of electroactive species refers to 6.02×10^{23} electroactive units that are attached to the polymer. The mole fraction, n , of ferrocene-doped side-chains in a general polymer of structure shown in Scheme 1 is related to the percentage content of iron, F , by the expression in eqn. (4) where

$$\frac{1}{n} = \frac{100}{F} \cdot \frac{55.85}{A} - \frac{B}{A} + 1 \quad (4)$$

A is the formula mass of the undoped polymer unit and B is the formula mass of the doped polymer unit.

Electrochemical Measurements.—Platinum wire was melted in a hydrogen-oxygen flame to form a sphere 1–2 mm in diameter. The wire was silver soldered to a copper lead and then fused into a glass support so that only platinum was exposed. The sphere was coated with polymer as described below. A coated electrode formed the working electrode together with a platinum wire counter electrode. The reference electrode was saturated aqueous sodium chloride-calomel (SCE) dipping into 1.0 mol dm^{-3} sodium nitrate, then connected through a bridge of the supporting electrolyte. The cell was deoxygenated by a stream of nitrogen.

Poly(γ -ethyl glutamate).—Phosgene was passed into a suspension of γ -ethyl glutamic acid hydrochloride (5.0 g) suspended in dioxane (70 cm^3) at 5 °C for 10 min. The suspension dissolved as the mixture was slowly allowed to warm to room temperature. Finally the solution was warmed on a water bath at 55 °C for 1 h after which unchanged phosgene was removed in a stream of nitrogen. The solvent was removed under reduced pressure and the residue crystallized from dichloroethane and hexane to yield 4-(2-ethoxycarbonyl)oxazolidine-2,5-dione (2.6 g) as large cubes, m.p. 72–73 °C (lit.,¹⁷ m.p. 71–72 °C); $\nu_{\text{CO}}(\text{KBr})/\text{cm}^{-1}$ 1845, 1780 and 1741.

A sample (2.3 g) of the oxazolidine-2,5-dione, when left in a desiccator over silica gel for several days was converted to a powder. This was dissolved in dichloroacetic acid, precipitated by pouring the solution into water, filtered and dried to yield poly(γ -ethyl glutamate) as an amorphous powder (1.2 g); ν_{CO} /cm⁻¹ 1733, 1654 and 1548; intrinsic viscosity, $\eta = 0.0358$ dm³ g⁻¹ from which¹⁸ molecular weight = 5.5×10^4 , degree of polymerization = 350.

Ferrocenylmethylamine.¹⁹—A solution of ferrocenylmethyl azide¹⁹ (10 g) in ether (200 cm³) was stirred at room temperature with triphenylphosphine (10 g) for 24 h in a flask exposed to the moist atmosphere. Water (20 drops) was added and stirring continued for 1 h. The mixture was then filtered from triphenylphosphine oxide, the filtrate dried over potassium hydroxide and the solvent removed. The residue was dissolved in dry benzene and saturated with hydrogen chloride. Ferrocenylmethylamine hydrochloride separated and was collected as a yellow solid, m.p. 220–222 °C (decomp.) (lit.,²⁰ m.p. 233–235 °C). This solid was shaken with potassium hydroxide solution (40%), the liberated amine extracted with ether and distilled, b.p. 108–110 °C/0.3 mmHg (lit.,²⁰ b.p. 108–110 °C/0.3 mmHg).

Ferrocene-doped Poly(γ -ethyl glutamate).—Poly(γ -ethyl glutamate) (0.10 g) was allowed to swell into dimethylacetamide (0.8 cm³) and ferrocenylmethylamine (0.2 g) was added. The viscous orange solution was heated at 75 °C for 18 h, cooled and diluted with ethanol (5 cm³) and ether (20 cm³). This ferrocene-doped polymer (0.10 g) formed a dark orange solid (Found: C, 54.4; H, 6.7; N, 9.2; Fe, 6.0%), mole fraction of ferrocene side chains = 0.21; ν_{CO} (KBr)/cm⁻¹ 1725, 1640 and 1530.

Coated electrodes were prepared by dipping the Pt-sphere into a solution of the polymer (3 mg) in dimethyl sulphoxide (1 cm³) for 1 h, then drying the electrode *in vacuo* at 50 °C for 0.5 h.

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