

Electroactive Poly(amino acids). Part 5.1 Poly(*N*^ε-4-nitrobenzoyl-L-ornithine) Coated on Platinum: Activity Corrections Applied to the Behaviour of Thin Films

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Poly(*N*^ε-4-nitrobenzoyl-L-ornithine) was obtained with average molecular weight 8.0×10^4 by reaction between the monomer *N*-carboxyanhydride and sodium hydride. The material was dip-coated onto platinum from dimethylacetamide solution and the behaviour of the coating examined in acetonitrile by cyclic voltammetry. Surface coverages in the range of 13.8 to 1.4 mmol cm⁻² 4-nitrobenzoyl residues were obtained by dipping from 0.6–0.07% solution, corresponding to from 20 to 2 layers of close-packed α -helices. The coated electrodes showed i_{pc} proportional to scan rate. They do not show the severe ageing phenomena on repeated cyclic voltammetry that was associated with poly(*N*^ε-4-nitrobenzoyl-L-lysine). Expressions are developed which simulate the voltammograms by introducing activity coefficients for reduced and oxidised species within these multilayer films.

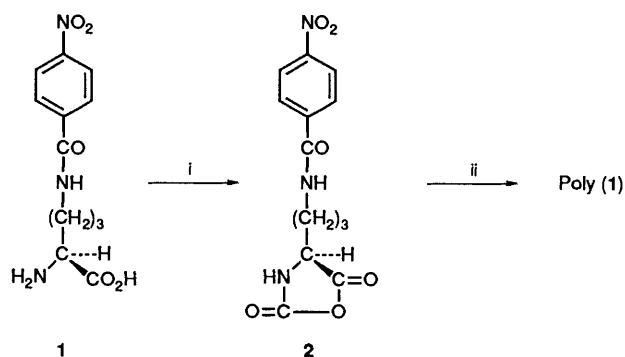
The basic amino acids L-lysine and L-ornithine are readily available. They offer possibilities for the generation of electroactive polymers through covalent attachment of an electroactive group by amide formation with the terminal amino function, followed by polymerisation through the α -amino acid functions. We have proposed the use of the resulting poly(amino acids) along with derivatives of glutamic acid, as electroactive coatings for solid electrodes.² So far examined have been poly(*N*^ε-4-nitrobenzoyl-L-lysine), (Poly-NBL), and copolymers of *N*^ε-4-nitrobenzoyl-L-lysine with electroinactive amino acids.^{2,3} We also modified poly(L-lysine) by amide formation with ferrocenecarboxylic acid² and poly(γ -ethyl L-glutamate) by reaction with ferrocenylmethylamine.¹ Surface coatings formed from these materials showed redox activity in acetonitrile and the ferrocene derivative was also electroactive in water.

Electrodes modified with a poly(amino acid) film are an attractive possibility for the mediation of electron transfer between the electrode and the active site of a redox enzyme. Other workers have realised this mediation using different approaches to the problem.⁴ Poly(amino acids) have the advantage that they allow a range of electroactive groups to be attached and they allow for the introduction of either free amino or free carboxylate groups to interact with the enzyme. The ideal coated electrode should be stable and have a redox centre stable in water. However, the films based on *N*^ε-4-nitrobenzoyl-L-lysine deteriorated on continuous charging, due to electrostatic repulsion between the nitrobenzoyl radical-anions.^{2,3} An α -helix to random coil transition was triggered over regions of the charged polymer and this caused separation between the film and the metal support.

In this paper we examine the properties of films from poly(*N*^ε-4-nitrobenzoyl-L-ornithine) in order to compare the relative stability of films from ornithine with those from lysine.

Results and Discussion

Polymer Preparation.—Preparation of the monomer, *N*^ε-4-nitrobenzoyl-L-ornithine (**1**) followed the route we have devised for the corresponding lysine derivative. The copper(II) complex of ornithine was acylated using 4-nitrobenzoyl chloride after which copper ions were removed as the very insoluble complex with salicylaldehyde.² Removal of copper ions by the usual route of precipitation using hydrogen sulfide causes partial reduction of the nitro-groups. The amino acid



Reagents: i, COCl₂; ii, NaH

monomer was converted to the cyclic anhydride **2** by reaction with phosgene. The anhydride was then polymerised using sodium hydride as catalyst since this process is known to give high molecular weight products.⁵ Experience with poly(*N*^ε-4-nitrobenzoyl-L-lysine) had shown that high molecular weight materials are required to form a stable electrode film. Progress of the polymerisation step is conveniently followed by withdrawing a sample of the reaction mixture and examining its IR spectrum for disappearance of the characteristic bands due to the carbonyl groups of the cyclic anhydride. The polymer was obtained purified by swelling into dichloroacetic acid and then precipitation with water. It showed an intrinsic viscosity $[\eta]$ of 3.15 dm³ g⁻¹ in dichloroacetic acid from which a molecular weight of 8.0×10^4 was derived. For calibration we used a survey of the literature results for poly(*N*^ε-benzoyloxy-carbonyl-L-lysine).² The molecular weight should be compared with the value of 2.0×10^5 obtained for the specimen of poly(*N*^ε-4-nitrobenzoyl-L-lysine) used previously.

Preparation and Behaviour of Electrodes.—Following our experience with poly(NBL),² poly(*N*^ε-4-nitrobenzoyl-L-ornithine), [Poly(NBO)], was swollen into dimethylacetamide to give a viscous solution. Platinum spheres (diameter *ca.* 2 mm) supported on glass were dip-coated from solutions (0.07–0.6% w/v) by immersing the sphere undisturbed in the solution for 20 min and then withdrawing slowly. By analogy with other *N*-acyl derivatives of poly(ornithine) and poly(lysine),⁶ we assume that poly(NBO) is present in dimethylacetamide solution as the α -helix and is absorbed as such onto platinum.

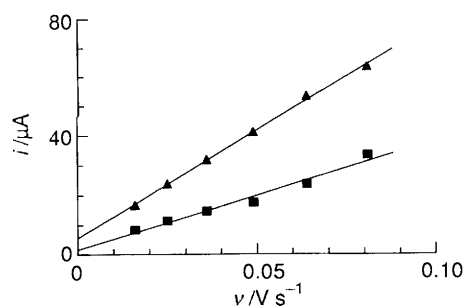


Fig. 1 Cyclic voltammetry experiments with films of poly(NBO) on Pt sphere electrode (area 0.135 cm^2). Variation of cathodic peak current with sweep rate, v . Solvent acetonitrile; 0.1 mol dm^{-3} tetrapropylammonium fluoroborate; sweep between 0 and -1.5 V vs. SSCE . ▲, Dip-coated from 0.6% solution, experimental sequence JTG1; ■, dip-coated from 0.3% solution, experimental sequence JTG2.

Table 1 Dip-coated layers of poly(NBO) on a platinum sphere (area 0.135 cm^2). Summary of data from cyclic voltammetry in acetonitrile containing $0.1 \text{ mol dm}^{-3} \text{ Et}_4\text{NBF}_4$ and showing thin film behaviour

Experiment	Dip solution % polymer	$\Delta i_p/\Delta v$ $\mu\text{A s V}^{-1}$	$\Gamma_T/10^{-10} \text{ mol}^a$	$-E_{pc}^b$ V vs. SSCE
JTG4A	0.07	65.4	1.87	1.08
JTG3	0.15	99.8	2.69	1.09
JTG2	0.30	368	9.84	1.14
JTG1	0.60	726	18.7	1.22

^a Γ_T is derived by integration of the cathodic branch of the cyclic voltammogram. ^b Measured at 0.025 V s^{-1} .

The electrode was then dried under vacuum and examined for electroactivity in acetonitrile containing tetraethylammonium fluoroborate (0.1 mol dm^{-3}). Electrodes were first 'broken-in' by a few cyclic voltammetry sweeps at 0.1 V s^{-1} through the electroactive region until the response became stable. During 'breaking-in' the film is swollen by solvent and ions.^{7,8}

Cyclic voltammograms were run on prepared films sweeping from 0 to -1.5 V vs. SSCE and showed the reversible redox behaviour of a couple with a formal redox potential around -1.09 V vs. SSCE . All films prepared from solutions in the concentration range stated showed a linear relationship between cathodic peak current (i_{pc}) due to one-electron reduction of the nitrobenzoyl groups, and scan rate (v). Two examples of this relationship for the highest coverages of electroactive groups are given in Fig. 1. Such behaviour is characteristic for the situation where migration of charge through the film is sufficiently fast that no concentration gradient in reduced or oxidised species exists across the thickness of the film.⁷ Results from cyclic voltammetry are collected in Table 1. Surface coverages of electroactive sites were estimated by integrating the current which passed during the cathodic sweep at slow sweep speeds.

Films were also subjected to chronoamperometry by stepping the potential from 0 to -1.5 V vs. SSCE and collecting the current transient. These films of poly(NBO) did not show the pronounced ageing phenomena associated² with poly(NBL). The three thinnest films could be subjected to chronoamperometry and cyclic voltammetry in sequence without deterioration of the cyclic voltammetry response. The thickest film showed gradual deterioration of the response and ageing as described for poly(NBL), but on a longer time scale. In a previous paper,² we concluded that the ageing phenomenon associated with poly(NBL) is due to α -helix to random coil transformation within the reduced and therefore negatively charged form which causes the film to buckle away from the electrode surface and give rise to electrical resistance. The α -helix of poly(NBO) is much more robust when in the charged form.

Pertinent to these observations, comparisons have been made in the literature⁶ of the relative stability of the helical structures of poly(N^ϵ -benzyloxycarbonyl-L-lysine), poly(N^δ -4-benzyloxycarbonyl-L-ornithine) and poly(N^γ -benzyloxycarbonyl-L-2,4-diaminobutyric acid) in chloroform towards disruption by the addition of dichloroacetic acid. The helical structure of the ornithine derivative is found to be more stable than that of the lysine derivative, while that of the diamino-butyric acid derivative is substantially more stable. Increased stability is attributed to hydrogen bonding between the side chain amido functions.

In order to obtain an estimate for the dimensions of the α -helix in poly(NBO) we can look at the X-ray diffraction data from oriented films of poly(N^δ -benzyloxycarbonyl-L-ornithine)⁹ and of poly(N^ϵ -benzyloxycarbonyl-L-lysine).¹⁰ The ornithine derivative gave only poorly oriented films so we can draw conclusions with the help of data for the lysine derivative. From this data it can be shown that a close packed monolayer of α -helices has $\Gamma = 0.663 \text{ nmol cm}^{-2}$. Taking this figure as an estimate for the monolayer of poly(NBO), the thinnest film of poly(NBO) listed in Table 1 has *ca.* 2 layers of adsorbed helices and the thickest film has *ca.* 20 layers.

Activity Coefficients of Species Confined to Films.—We have been able to prepare films from poly(NBO) with different thickness. On cyclic voltammetry these films show behaviour characteristic of the situation where the Nernstian equilibrium between potential and concentrations of reduced and oxidised species is maintained across the film thickness. The relationship between E and i during cyclic voltammetry at a scan rate v for films of this type can be expressed analytically.¹¹ When activity effects are neglected the peak potential, i_p varies in a linear fashion with v according to eqn. (1) where Γ_T is the total surface

$$i_p = F^2 \Gamma_T v / \epsilon RT \quad (1)$$

coverage of electroactive sites, $\epsilon = 4$ and is a pure number, while the other terms have their usual significance.

Data collected in Table 2 indicate that in the real situation ϵ is not equal to 4. Some data is included from our papers on lysine derivatives in which this divergence from the ideal value of ϵ was also noted.

In the real situation we have to consider the thermodynamic activity of the oxidised and reduced species confined within the film and incorporate these activities in the Nernst equation. Studies of Langmuir films formed from fatty acids at the air-water interface have shown that the activity coefficient of an adsorbed species is exponentially dependent on the surface coverage.¹² These studies led to derivation of the Frumkin isotherm for adsorbed monolayers.¹³ The exponential relationship between activity coefficient and surface concentration coverage, deduced in this early work, has been used in descriptions of the reversible adsorption of molecules on charged electrodes,¹⁴ and in description of the voltammetric behaviour of redox species irreversibly attached as a surface monolayer.¹⁵

Our films have multilayer coverage. The treatment below follows that applied to monolayers and is developed for the cathodic branch in the cyclic voltammetry of a one-electron reduction process. We assume an exponential relationship between activity coefficient and the mean surface concentration of a species.

The activity coefficients for the two redox species in the electrode film are represented by eqns. (2) and (3).

$$\text{Oxidised species: } \gamma_o = \exp[-(r_{oo}\Gamma_o + r_{or}\Gamma_r)/\Gamma_T] \quad (2)$$

$$\text{Reduced species: } \gamma_r = \exp[-(r_{rr}\Gamma_r + r_{ro}\Gamma_o)/\Gamma_T] \quad (3)$$

Table 2 Data from cyclic voltammetry of thin films of poly(NBO) and poly(NBL) in acetonitrile containing 0.1 mol dm⁻³ Et₄NBF₄

Experiment	$\Delta i_p/\Delta v$ $\mu\text{A s V}^{-1}$	$\Gamma_T/10^{-10}$ mol	ε^d	$-(r_o + r_r)^e$
JTG4A	65.4	1.87	10.74	6.74
JTG3	99.8	2.69	10.12	6.12
JTG2	368	9.84	10.04	6.04
JTG1	726	18.7	9.68	5.68
a	229	5.50	9.03	5.03
168 ^b	301	6.07	7.58	3.58
167 ^c	255	5.19	7.65	3.65

^a Homopolymer of NBL from ref. 2. ^b Random copolymer NBL–Leu (2:1) from ref. 3. ^c Random copolymer NBL–L–Gly(2:1) from ref. 3. ^d A dimensionless quantity defined in eqn. (1). ^e Defined through eqns. (1) and (7).

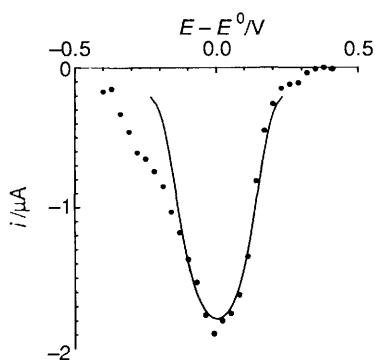


Fig. 2 Cathodic sweep during cyclic voltammetry of poly(B=NBO) on Pt sphere electrode (area 0.135 cm²), v 0.025 V s⁻¹. Solvent acetonitrile; 0.1 mol dm⁻³ tetrapropylammonium fluoroborate. ●, Experimental points, corrected for charging current; —, simulated response with Γ_T 1.87 × 10⁻¹⁰ mol, $-(r_o + r_r)$ 6.74.

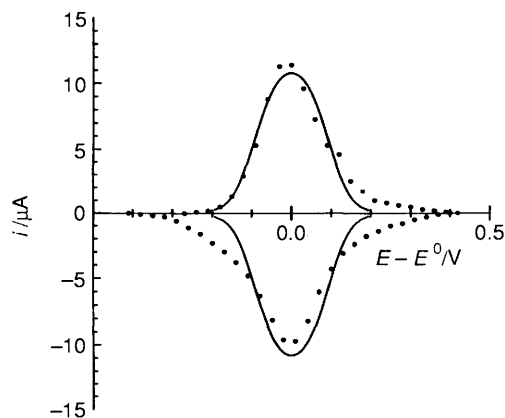


Fig. 3 Cyclic voltammetry of copolymer NBL–Gly(2:1), from ref. 3, on Pt sphere electrode (area 0.106 cm²), v 0.049 V s⁻¹. Solvent acetonitrile; 0.1 mol dm⁻³ tetrapropylammonium fluoroborate. ●, Experimental points, corrected for charging current; —, simulated response with Γ_T 5.19 × 10⁻¹⁰ mol, $-(r_o + r_r)$ 3.65.

The numbers r_{oo} and r_{or} are dimensionless parameters which describe the perturbing influence experienced by a given molecule of the attached oxidant due to the presence of the other attached oxidant and reductant molecules, respectively. The symbol Γ represents the total surface coverage by the species indicated according to the subscript. The numbers Γ_o/Γ_T and Γ_r/Γ_T are proportional to the concentrations of oxidised and reduces species, respectively, in films of differing thickness comprised of the same polymer.

The Nernst equation for the surface redox couple can be written in the form of eqn. (4), where $\xi = \exp[(F/RT)(E -$

$$\xi = \gamma_o \Gamma_o / \gamma_r \Gamma_r \quad (4)$$

$E^\circ]$. A combination of eqns. (2)–(4) leads to eqn. (5), where $f =$

$$\xi = [(1 - f)/f] \exp[f(r_o + r_r) - r_o] \quad (5)$$

Γ_r/Γ_T , the fraction of redox centres on the surface in their reduced form, $r_o = r_{oo} - r_{or}$ and $r_r = r_{rr} - r_{ro}$.

The use of eqn. (5) as the appropriate form of the Nernst equation in deriving the expected current–potential behaviour leads to eqn. (6) for the current during cyclic voltammetry.

$$i = F^2 \Gamma_T v f (1 - f) / RT [1 - f(1 - f)(r_o + r_r)] \quad (6)$$

Derivation, in parallel with previous work^{11,15} involves differentiation with respect to time and noting that $i = F d\Gamma_o/dt$ and $v = dE/dt$.

The expected cyclic voltammetry response for chosen values of r_o and r_r can then be computed. A range of values of f is chosen and the corresponding values of i and E are obtained using eqns. (6) and (5), respectively. The only adjustable parameters are r_o and r_r . The shape of a computed cyclic voltammogram depends on the values chosen for Γ_T and $(r_o + r_r)$. Adjustment of r_o in eqn. (5) only serves to move the computed cyclic voltammogram along the potential axis.

At the cathodic peak where $f = 0.5$, i_p is given by eqn. (1) and eqn. (7).

$$\varepsilon = [4 - (r_o + r_r)] \quad (7)$$

Thus, a value for $(r_o + r_r)$ is obtained from the linear relationship between i_p and scan rate. Results from films of poly(*N*⁶-4-nitrobenzoylornithine) where Γ_T is varied over one order of magnitude, give closely similar values for $(r_o + r_r)$.

Also, at the cathodic peak, eqn. (8) holds, where E° is the

$$E_p = E^\circ - RT(r_o - r_r)/2F \quad (8)$$

formal potential for the attached couple. Provided E° is known, a value for $(r_o - r_r)$ can be obtained and hence values for both r_o and r_r can be calculated.

Values for the interaction parameter $-(r_o + r_r)$, obtained by application of eqns. (1) and (7), are listed in Table 2. The interaction parameter $-(r_o + r_r)$ becomes smaller for the NBL series as the electroactive sites are diluted through formation of a random copolymer. Such behaviour is expected when the redox centres are moved further apart in the polymer due to the intervening inactive amino acids.

Simulated cyclic voltammograms are compared in Figs. 2 and 3 with the experimental data for a film of poly(NBO) and for a copolymer of NBL and glycine, respectively. The experimental data have been corrected for the background double-layer charging current. Only the typical bell-shaped Faradaic current for a thin film is displayed. Good agreement between the simulated and experimental data can be obtained only in the region of the peak potential. Also, while the areas under the cathodic and anodic branches of a given experimental curve are the same, the widths of half-height are different. For a good fit, the simulation requires different values of the interaction parameter for the anodic and the cathodic sections.

This divergence from the ideal, where it should be possible to simulate the whole curve using one value for the surface coverage and one value for the interaction parameter, arises because the films are not rigid. The films can be expected to swell as they fill with solvent and counter-ions. Swelling and shrinking of the film will cause changes in the density of

Table 3 Interaction parameters (r) for species adsorbed as a monolayer on graphite from ref. 15

	$\Gamma/\text{nmol cm}^{-2}$	$-r/10^9 \text{ cm}^2 \text{ mol}^{-1}$	$-(\frac{3}{2})\Gamma(r)$
1,4-Naphthoquinone	0.51	1.6	1.22
9,10-Phenanthroquinone	0.19	2.7	0.77
9,10-Anthraquinone-2-monosulfonic acid	0.14	5.9	0.95
Iron porphyrin IX	0.11	4.0	0.66
Iron tris(dibenzodithiocarbonate)	0.05	3.4	0.26
Benzo[<i>c</i>]cinnoline	0.12	3.1	0.56

electroactive sites. The Frumkin treatment of activity coefficients used above can only approximate the behaviour of a real flexible film containing electroactive sites.

Eqn. (8) predicts that for our multi-layer films, E_{pc} should be independent of the surface coverage. Experiment with poly(N^{δ} -4-nitrobenzoylornithine) shows a linear relationship between Γ_T and E_{pc} measured at 0.025 V s^{-1} . We believe this indicates an uncompensated resistance which is independent of surface coverage. The consequent potential drop is proportional to i_{pc} which in turn is proportional to Γ_T ; thus a linear relationship between E_{pc} and Γ_T results. Extrapolation of this relationship gives a value for E_{pc} of -1.0 V vs. SSCE at zero surface coverage. Further evidence for the existence of uncompensated resistance in the film can be seen. In the cyclic voltammograms, i_{pc} is negative of i_{pa} , and this is evident at the higher scan rates. Also, i_{pc} moves to more negative potentials at higher scan rates when higher currents pass.

Anson¹⁵ has developed related equations which apply only to less than a monolayer coverage. It is interesting to compare the values for the interaction parameters used in his papers with our values. Anson's interaction parameter ($r_o + r_r$) is not a pure number but has the dimensions of reciprocal surface coverage ($\text{cm}^2 \text{ mol}^{-1}$). A correction must be applied due to this since our parameter is a pure number. Also, in the two-dimensional situation described by Anson, each reduced centre has four nearest neighbours, any one of which may be reduced, whereas in the three-dimensional situation which we use, there are six nearest neighbours. As a consequence, in the three-dimensional situation the forces of interaction between species are increased. Thus, the value of ($r_o + r_r$) used in this paper equates to:

$$(3/2) \times \text{complete monolayer coverage } (/ \text{mol cm}^{-2}) \times [(r_o + r_r) \text{ in ref. 15}]$$

when the same redox sites are employed. Identical redox centres have not been compared in these two situations. Anson's¹⁵ values for the interaction parameter in monolayers on graphite are given in Table 3. The dimensionless parameter which corresponds to our quantity ($r_o + r_r$) is given in the last column. The numerical values of the interaction parameter are significantly smaller than the values for the poly(amino acid) derivatives. Also, the coverage of a monolayer is less than the value of $0.663 \text{ nmol cm}^{-2}$ expected for a monolayer of the poly(amino acid) α -helix. As noted previously, values for the parameter become numerically smaller when the electroactive sites in the poly(amino acid) are diluted by forming a random copolymer. The smaller values found for the monolayers are in accord with this trend.

Experimental

¹H NMR spectra were recorded at 250 MHz in 0.1 mol dm^{-3} DCl/D₂O relative to DSS. All solvents used for the preparation

and purification of oxazolidine-2,5-diones were rigorously purified and dried according to literature methods. Ether refers to diethyl ether throughout. Coupling constant values J are given in Hz.

In the context of polymers, 1 mol of electroactive species refers to 6.02×10^{23} electroactive units that are attached to the polymer chains.

N^{δ} -(4-Nitrobenzoyl)ornithine (**1**).—Ornithine hydrochloride (6.0 g) and basic copper(II) carbonate [$\text{CuCO}_3 \cdot \text{Cu}(\text{OH})_2 \cdot 3\text{H}_2\text{O}$] (2.0 g) were heated in water (100 cm^3) until effervescence ceased and the mixture was boiled for several minutes. The resulting blue solution was cooled to 0°C and filtered from excess copper(II) carbonate. A solution of 4-nitrobenzoyl chloride (8.0 g) in ether (75 cm^3) and a solution of sodium hydroxide (5 mol dm^{-3} ; 20 cm^3) were added simultaneously and dropwise to the blue filtrate with vigorous stirring, which was continued for a further 15 min. The pale blue precipitate of N^{ϵ} -(4-nitrobenzoyl)ornithine copper(II) complex was filtered and washed with water and ether. It was suspended in ethanol (50 cm^3), stirred for 48 h with salicylaldehyde (5.4 g) and filtered. The solid product was suspended in boiling water (50 cm^3) and filtered while hot to leave a residue of the copper(II) complex of salicylaldehyde, together with unchanged N^{ϵ} -(4-nitrobenzoyl)ornithine copper complex. On cooling the filtrate, colourless rods of N^{ϵ} -(4-nitrobenzoyl)ornithine separated. The recovered mixture of copper(II) complexes was treated again with salicylaldehyde. The total yield of amino acid was crystallised from water-ethanol to yield N^{δ} -(4-nitrobenzoyl)ornithine as colourless rods, m.p. $219\text{--}222^\circ \text{C}$ (Found: C, 51.1; H, 5.4; N, 14.6. $\text{C}_{12}\text{H}_{15}\text{N}_3\text{O}_5$ requires C, 51.2; H, 5.4; N, 14.9%); λ_{max} (2 mol dm^{-3} HCl) 272 nm (ϵ 11 500); $[\alpha]_{\text{D}}^{20} +20.4^\circ$ (c 0.5 in 2 mol dm^{-3} HCl); δ_{H} 8.32 (2 H, d, $J = 9$, aromatic), 7.93 (2 H, d, $J = 9$, aromatic), 4.23 (1 H, t, $J = 6$, H_α), 3.50 (2 H, t, $J = 6.5$, H_β), 2.09 (2 H, m, H_β) and 1.86 (2 H, m, H_γ).

Poly[N^{δ} -(4-nitrobenzoyl)ornithine].—A suspension of N^{δ} -(4-nitrobenzoyl)ornithine (1.0 g, 3.4 mmol) in dioxane (30 cm^3) was treated with a solution of phosgene in toluene (10 cm^3), 12%; 12 mmol) and slowly heated to 65°C during 4.5 h. The yellow solid was replaced by a creamy solid. The mixture was allowed to cool, more phosgene in toluene (10 cm^3) was added, together with ethyl acetate (40 cm^3), and the whole was heated to 65°C for 1.5 h. An IR spectrum of the mixture at this stage showed only the N -carboxyanhydride to be present. Nitrogen was then passed through the suspension for 1 h to remove excess phosgene. The suspension was poured into an equal volume of hexane and kept at 0°C for 12 h. The precipitated oxazolidinedione **2** was collected. Recrystallisation was achieved by dissolving the solid in hot ethyl acetate (100 cm^3) with addition of a little dimethylacetamide, filtering from a trace of insoluble material and then adding hexane progressively with cooling. The oxazolidinedione **2** (1.05 g, 96%) obtained showed $\nu_{\text{max}}(\text{KBr})/\text{cm}^{-1}$ 1850 and 1780 due to the heterocyclic carbonyl groups. This N -carboxyanhydride was dissolved in a mixture of dioxane (20 cm^3) and dimethylacetamide (15 cm^3) under nitrogen and stirred with sodium hydride (13 mg, 50% suspension). After 19 h a thin film prepared by evaporating a little of the solution onto a KBr plate no longer showed IR bands due to the N -carboxyanhydride. The solution was then poured into dichloromethane (400 cm^3) when it quickly formed a thick gel. Pouring this gel into methanol gave the polymer as a colourless precipitate that was collected by filtration. Poly[N^{ϵ} -(4-nitrobenzoyl)ornithine] was purified by swelling into dichloroacetic acid and precipitation by pouring into water. It formed a fine colourless powder (0.48 g, 48%). A solution of this polymer in dimethylformamide gave intrinsic viscosity $[\eta] = 3.15 \text{ dm}^3 \text{ g}^{-1}$ from which $M = (8.0 \pm 0.3) \times 10^4$.

Electrochemical Measurements.—Poly(*N*⁶-4-nitrobenzoyl-L-ornithine) was allowed to swell in dimethylacetamide so as to make a solution of known concentration (see Table 1). 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. Using a micromanipulator, the platinum sphere was lowered into the polymer solution so that the sphere and shank of platinum wire were immersed, but not the glass support. After 20 min, the electrode was slowly removed from the solution, then dried at 50 °C/0.1 mm Hg for 20 min. The electrode was then ready for use.

Old electrodes were cleaned by burning off the coating in a hydrogen–oxygen flame, then re-coated as above.

A coated electrode was immersed in a solution of 0.1 mol dm⁻³ tetraethylammonium fluoroborate in acetonitrile. A platinum wire formed the counter electrode. The reference electrode was saturated aqueous sodium chloride–calomel (SSCE) dipping into 1.0 mol dm⁻³ sodium nitrate, then connected through a bridge of the supporting electrolyte in acetonitrile. The cell was deoxygenated by a stream of nitrogen.

Cyclic voltammetry was performed by sweeping between 0 and –1.5 V *vs.* SSCE. The potentiostat was a PAR 176 model with 274 digital interface and connected through an Apple IIe computer.

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References

1 Part 4. J. Grimshaw and J. Trocha-Grimshaw, *J. Chem. Soc., Perkin Trans. 2*, 1991, 751.

- 2 A. M. Abeysekera, J. Grimshaw, S. D. Perera and D. Vipond, *J. Chem. Soc., Perkin Trans. 2*, 1989, 43; A. M. Abeysekera, J. Grimshaw and S. D. Perera, *J. Chem. Soc., Perkin Trans. 2*, 1990, 1797.
- 3 J. Grimshaw and S. D. Perera, *J. Chem. Soc., Perkin Trans. 2*, 1989, 1711.
- 4 W. J. Albery, P. N. Bartlett and D. H. Craston, *J. Electroanal. Chem.*, 1985, **194**, 223; A. E. G. Cass, G. Davis, G. D. Francis, H. A. O. Hill, I. J. Higgins, E. V. Plotkin, L. D. L. Scott and A. P. F. Turner, *Anal. Chem.*, 1984, **56**, 677; A. P. F. Turner, S. P. Hendry and M. F. Cardini, EP234938 (1986) (*Chem. Abstr.*, 1987, **108**, P128115); S. Yamaguchi, N. Uchida, T. Shimomura and N. Oyama, EP251915 (1986) (*Chem. Abstr.*, 1988, **109**, P19862).
- 5 M. Goodman, E. Peggion, M. Szwarc and C. H. Bamford, *Macromolecules*, 1977, **10**, 1299.
- 6 M. Hatano and M. Yoneyama, *J. Am. Chem. Soc.*, 1970, **92**, 1392; G. Giacometti, A. Turolla and A. S. Verdini, *Biopolymers*, 1972, **11**, 215; G. Giacometti, A. Turolla and B. Boni, *Biopolymers*, 1970, **9**, 979.
- 7 P. Daum, J. R. Lenhard, D. Rolison and R. W. Murray, *J. Am. Chem. Soc.*, 1980, **102**, 4649; P. Daum and R. W. Murray, *J. Phys. Chem.*, 1981, **85**, 389.
- 8 K. Shigehara, N. Oyama and F. C. Anson, *J. Am. Chem. Soc.*, 1981, **103**, 2552.
- 9 A. Del Pra, P. Spadin and G. Valle, *Biopolymers*, 1973, **12**, 941.
- 10 H. L. Yakel, *Acta Crystallogr.*, 1953, **6**, 724.
- 11 A. T. Hubbard and F. C. Anson, *Anal. Chem.*, 1966, **38**, 58; E. Laviron, *Bull. Soc. Chim. Fr.*, 1967, 3717.
- 12 R. N. Adams, *Proc. R. Soc. London, Ser. A*, 1922, **101**, 526; M. Volmer, *Z. Phys. Chem.*, 1925, **115**, 253.
- 13 A. N. Frumkin, *Z. Phys. Chem.*, 1925, **116**, 466; A. N. Frumkin, *Z. Physik*, 1926, **35**, 792.
- 14 R. Parsons, *J. Electroanal. Chem.*, 1964, **7**, 136; E. Laviron, *J. Electroanal. Chem.*, 1974, **52**, 395.
- 15 A. P. Brown and F. C. Anson, *Anal. Chem.*, 1977, **49**, 1589.

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