

## Electroactive Poly(amino acids). Part 2.<sup>1</sup> Copolymers of *N*<sup>ε</sup>-4-Nitrobenzoyl-L-lysine with Inactive Amino Acids: Modified Electrodes with these Polymers and Poly(pyrrole) and with Poly{1-[2-(4-nitrobenzoyl)aminoethyl]pyrrole}

James Grimshaw\* and Sarath D. Perera

Department of Chemistry, Queen's University, Belfast BT9 5AG, Northern Ireland

Co-polymerization of the *N*-carboxyanhydrides derived from *N*<sup>ε</sup>-4-nitrobenzoyl-L-lysine (NBL) and one of the amino acids, *N*<sup>ε</sup>-4-benzoyl-L-lysine, L-leucine, and glycine afforded electroactive materials. These can be adsorbed onto platinum from dimethylacetamide solution. The electrochemical response of the adsorbed layers quickly deteriorates to give broad peaks on continuous cyclic voltammetry. Deterioration of the response is thought to be due to a combination of poor adhesion and conformational changes which accompany charging and discharging of the film. Poly{1-[2-(4-nitrobenzoyl)aminoethyl]pyrrole} forms a coherent film on platinum. It shows a good response due to the nitro group on continuous cyclic voltammetry. The height of this response falls with time due to loss of electroactive material. Poly(NBL) also forms a film by adsorption onto a 20–60 nm thick layer of poly(pyrrole) and the composite gives a response on continuous cyclic voltammetry that is much more stable than any of the previous cases. Coating platinum with poly(NBL) and then with poly(pyrrole) also gives a stable composite.

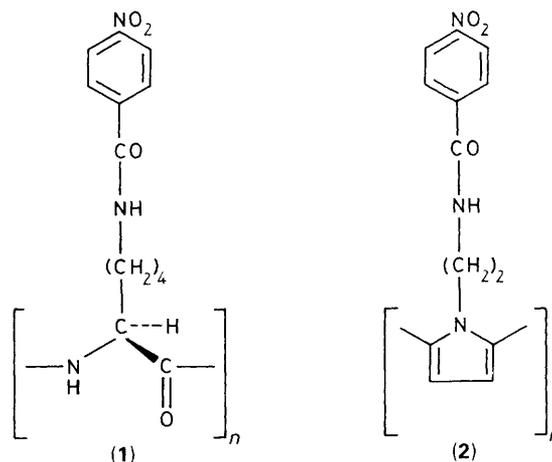
We have shown<sup>1</sup> that a multilayer coating of poly(*N*<sup>ε</sup>-4-nitrobenzoyl-L-lysine) (1), poly(NBL), average molecular weight  $2 \times 10^5$ , is adsorbed onto platinum from dimethylacetamide solution. This adsorbed material shows the expected electrochemical behaviour for the 4-nitrobenzoyl group, but after a short period of stress in continuous cyclic voltammetry, the original smooth cyclic voltammogram shows aging phenomena. Aging manifests itself first by the splitting of the cathodic and anodic branches into overlapping waves and finally by a deterioration to give broad peaks. The anodic branch in particular becomes very broad and ill-defined.

The aging process under electrical stress was interpreted as due to buckling of the charged film and local separation of the film from the metal surface. The repulsive force between negatively charged nitrobenzoyl radical anions causes this buckling. An analogous electrostatic force causes poly(L-lysine) to adopt a random coil in acid solution but the  $\alpha$ -helix form results in alkaline solution where the terminal amino groups are not charged.<sup>2</sup>

### Results and Discussion

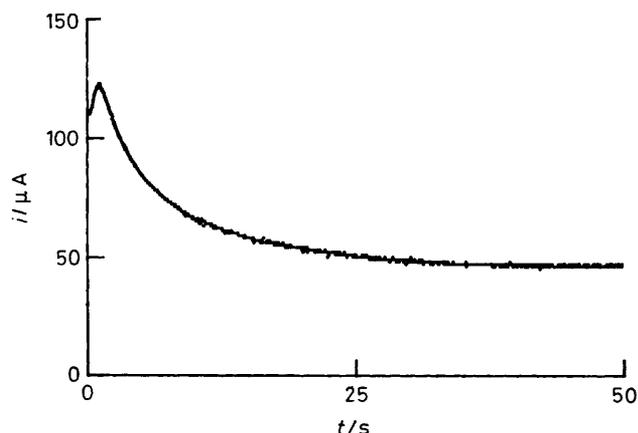
**Poly(pyrrole) with Attached 4-Nitrobenzoyl Groups.**—The electrochemical properties of other poly(pyrroles) with either reducible or oxidizable substituents on the side chain have been explored in the recent literature.<sup>3</sup> We have examined the behaviour of poly{1-[2-(4-nitrobenzoyl)aminoethyl]pyrrole} (2), poly(NBA), as an electroactive coating and the results provide good support for our explanation of the behaviour of (1) under electrical stress. During the preparation stage of our coatings, the pyrrole ring is oxidized but at the potentials where nitrobenzoyl groups are active, the polypyrrole backbone is in the uncharged and electrically non-conducting form.

The required monomeric pyrrole, NBA, was obtained by reaction between *N*-(2-aminoethyl)pyrrole<sup>4</sup> and 4-nitrobenzoyl chloride. Oxidation of the monomer at a platinum sphere anode in 1.5 mmol dm<sup>-3</sup> solution in acetonitrile containing 0.1 mol dm<sup>-3</sup> tetrapropyl- or tetramethyl-ammonium fluoroborate led to the formation of a coherent dark-coloured coating of poly(NBA) on platinum. An oxidation potential of 1.2 V *vs.*

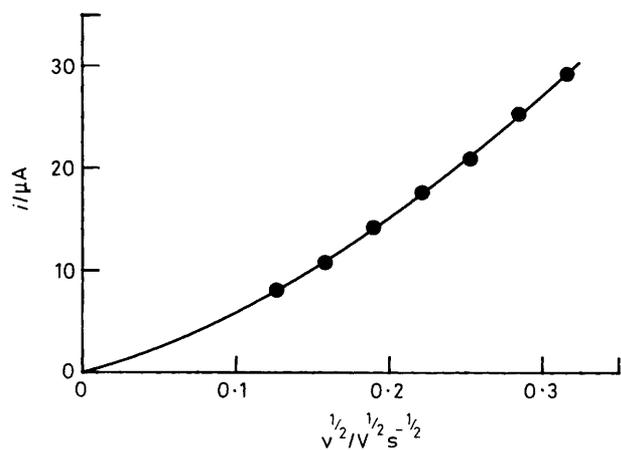


SCE was used. This polymerization is expected to proceed by reaction between pyrrole rings as for pyrrole<sup>5</sup> and other *N*-substituted pyrroles.<sup>3,6</sup> The current passed during this oxidation reached a plateau value (Figure 1) and the thickness of the film formed could be regulated by controlling the time of oxidation. The plateau current density was 0.31 mA cm<sup>-2</sup> with tetrapropylammonium fluoroborate and 0.59 mA cm<sup>-2</sup> with tetramethylammonium fluoroborate as electrolyte. No dark-coloured soluble products were formed during the oxidation so we believe that all the oxidised monomer is converted into polymer. The polymer layer formed a coherent coat firmly attached to the metal support.

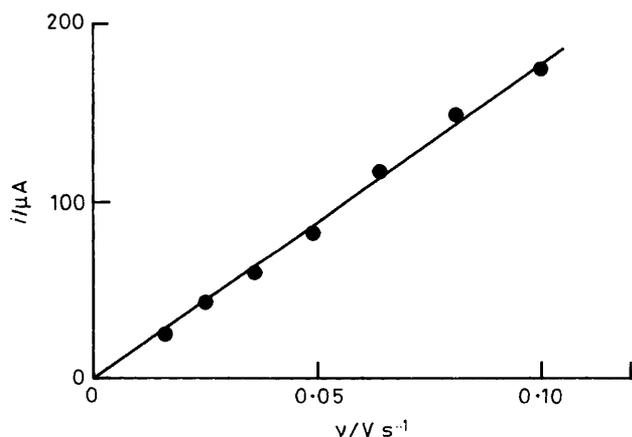
The behaviour of electrodes coated with poly(NBA) was first examined using tetrapropylammonium fluoroborate in acetonitrile as the supporting electrolyte. Cyclic voltammetry was run between 0 and -1.5 V *vs.* SCE. The first cyclic voltammogram shows a wave due to reduction of the oxidized pyrrole. Subsequent cyclic voltammetry curves show reversible redox behaviour due to the 4-nitrobenzoyl groups and continuous cyclic voltammetry did not appreciably change the shape of the response with time. The only change noted was a slow decrease in peak height of about 2.8% per cycle, probably due to loss of



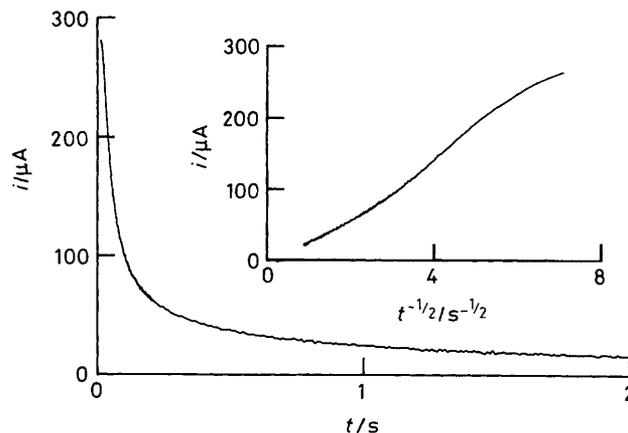
**Figure 1.** Current passed during the oxidation of NBA (2 mg) in acetonitrile (5 cm<sup>3</sup>), 0.1 mol dm<sup>-3</sup> tetrapropylammonium fluoroborate, at a Pt sphere electrode; potential +1.2 V *vs.* SCE, area 0.155 cm<sup>2</sup>.



**Figure 2.** Cyclic voltammetry experiments with a film of poly(NBA), (2), on Pt sphere electrode (area 0.126 cm<sup>2</sup>). Variation of cathodic peak current with sweep rate, *v*. Solvent acetonitrile, 0.1 mol dm<sup>-3</sup> tetrapropylammonium fluoroborate, sweep between 0 and -1.5 V *vs.* SCE. A charge of 10.3 mA s cm<sup>-2</sup> was passed during polymerization of the monomer at +1.2 V *vs.* SCE.



**Figure 3.** Cyclic voltammetry experiments with a film of poly(NBA), (2), on Pt sphere electrode (area 0.182 cm<sup>2</sup>). Variation of cathodic peak potential with sweep rate, *v*. Solvent acetonitrile, 0.1 mol dm<sup>-3</sup> tetramethylammonium fluoroborate, sweep between 0 and -1.5 V *vs.* SCE. A charge of 9.9 mA s cm<sup>-2</sup> was passed during polymerization of the monomer at +1.2 V *vs.* SCE.



**Figure 4.** Chronoamperometry on a film of poly(NBA), (2), on Pt sphere electrode (area 0.123 cm<sup>2</sup>). Solvent acetonitrile, 0.1 mol dm<sup>-3</sup> tetrapropylammonium fluoroborate. Potential step 0 to -1.5 V *vs.* SCE. Inset shows the Cottrell plot. A charge of 12.8 mA s cm<sup>-2</sup> was passed during polymerization of the monomer at +1.2 V *vs.* SCE.

the radical anion through slow protonation, either by NH groups within the film or by extraneous moisture. Surface coverage of accessible 4-nitrobenzoyl groups was determined by cyclic voltammetry and by chronoamperometry. Even after the chronoamperometry experiment, the cyclic voltammetry response of the film retained a normal reversible behaviour.

These observations support the conclusion that aging of the poly(amino acid) film, (1), is due to flexing of the charged polymer molecule with separation of the film from the surface support. The poly(pyrrole) residue in poly(NBA), (2), is expected to be more firmly anchored to the metal support and to be more rigid.

Cyclic voltammetry curves for poly(NBA) films with tetrapropylammonium fluoroborate electrolyte show  $i_{pc}$  proportional to  $v^{1/2}$ . This relationship (Figure 2) is not exact because of the gradual loss of electroactive material. The behaviour of films of similar thickness with tetramethylammonium fluoroborate in acetonitrile shows marked contrasts. On cyclic voltammetry, the film shows  $i_{pc}$  proportional to  $v$  (Figure 3). This result must be brought about by a much faster rate of diffusion of charge through the film in the presence of the smaller tetramethylammonium cation. Thus on the time scale used here, there is an even distribution of electrons across the thickness of the film<sup>7</sup> when tetramethylammonium counter-ions are used. Diffusion of the counter-ion must be the rate-limiting step in electron transfer through these films at negative potentials where electrons are carried by the 4-nitrobenzoyl groups and the poly(pyrrole) backbone is non-conducting.

The amount of charge passed during oxidation of the monomer pyrrole is a measure of the number of monomer units attached to the film. In the formation of poly(pyrrole) itself, 2.25 electrons are removed for the addition of one pyrrole unit to the polymer.<sup>5</sup> Poly(pyrrole) so formed is the black electrically conducting material carrying positive charges on the backbone. Poly(*N*-alkylpyrrole) consumed 2.1–2.2 electrons per pyrrole unit oxidized.<sup>6</sup> We can determine the surface coverage of accessible nitrobenzoyl groups in poly(NBA) by either chronoamperometry in the case of tetrapropylammonium counter-ion or by integration of the cathodic branch of the cyclic voltammogram in the case of the tetramethylammonium counter-ion. The chronoamperometry current (Figure 4) was integrated over 4 s to give the total coverage of accessible sites. After this time the current had fallen to a low value. Treatment of the chronoamperometry data according to the Cottrell equation, as discussed in the next section, gives a value for  $D^{1/2}c_0$  where  $D$  is the diffusion coefficient for charge

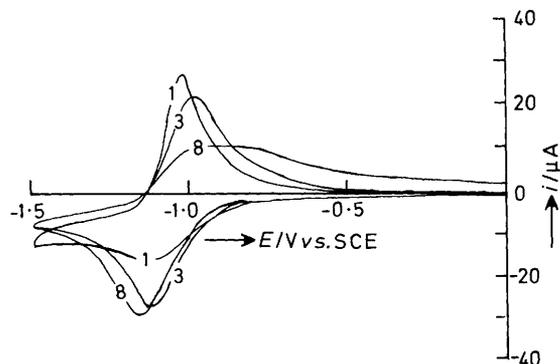
**Table 1.** Surface coverage by films of (2) in acetonitrile polymerized on Pt at +1.2 V vs. SCE for the times given.  $\chi$  is the charge passed during oxidation.  $\Gamma$  is the coverage of accessible 4-nitrobenzoyl groups. The poly(pyrrole) forms an inert matrix for the electron acceptor.

| Electrode area/cm <sup>2</sup> | Oxidation time/s | $\chi$ /mA s cm <sup>-2</sup> | $\Gamma$ /nmol cm <sup>-2</sup> | $\chi/\Gamma F$ | $D^{1/2}c_0^c$ /nmol cm <sup>-2</sup> s <sup>-1/2</sup> | Electrolyte <sup>d</sup>         |
|--------------------------------|------------------|-------------------------------|---------------------------------|-----------------|---|----------------------------------|
| 0.182                          | 15               | 9.9                           | 17.5 <sup>a</sup>               | 5.9             | —   | Me <sub>4</sub> NBF <sub>4</sub> |
| 0.123                          | 20               | 12.8                          | 8.4 <sup>b</sup>                | 15.8            | 5.9   | Pr <sub>4</sub> NBF <sub>4</sub> |
| 0.126                          | 50               | 18.8                          | 9.0 <sup>b</sup>                | 23.2            | 6.1   | Pr <sub>4</sub> NBF <sub>4</sub> |
| 0.155                          | 80               | 34.1                          | 28.2 <sup>b</sup>               | 12.5            | 18.8  | Pr <sub>4</sub> NBF <sub>4</sub> |

<sup>a</sup> From integration of the cathodic branch of cyclic voltammetry at slow scan rates. <sup>b</sup> From chronoamperometry at -1.5 V vs. SCE. <sup>c</sup> From the limiting slope of the Cottrell plot. <sup>d</sup> 0.1 mol dm<sup>-3</sup>.

**Table 2.** Copolymers of *N*<sup>ε</sup>-4-nitrobenzoyl-L-lysine (NBL) with other amino acids. Determination of mole fraction of NBL in the polymer chain by u.v. spectroscopy.

| Co-amino acid residue | Mole fraction NBL taken | [Polymer]/g dm <sup>-3</sup> | U.v. absorbance 300 nm | Mole fraction NBL from u.v. data |
|-----------------------|-------------------------|------------------------------|------------------------|----------------------------------|
| Gly                   | 0.67                    | 3.102 × 10 <sup>-2</sup>     | 0.440                  | 0.66                             |
| Leu                   | 0.67                    | 3.832 × 10 <sup>-2</sup>     | 0.428                  | 0.50                             |
| BZL                   | 0.67                    | 3.67 × 10 <sup>-2</sup>      | 0.457                  | 0.76                             |
| BZL                   | 0.33                    | 4.11 × 10 <sup>-2</sup>      | 0.200                  | 0.27                             |

**Figure 5.** Continuous cyclic voltammetry of an NBL-BZL (2:1) polymer modified Pt sphere electrode (area 0.116 cm<sup>2</sup>) in acetonitrile, 0.1 mol dm<sup>-3</sup> tetraethylammonium fluoroborate,  $\nu = 0.100$  V s<sup>-1</sup>. Only the 1st, 3rd, and 8th scans are shown.

transfer through the film and  $c_0$  is the concentration of active sites per unit volume of the film. This data is collected in Table 1.

The surface coverage of accessible 4-nitrobenzoyl groups ( $\Gamma$ ) is smaller than expected relative to the charge passed on oxidation ( $\chi$ ) of the monomer. If every nitrobenzoyl group is accessible, the ratio  $\chi/\Gamma F$  should have the value 2.25. Clearly a large proportion of the nitrobenzoyl sites are blocked and cannot accept an electron during reduction. The blocked sites must be surrounded by a matrix of poly(pyrrole). More sites are opened to accept an electron in the presence of the smaller tetramethylammonium counter-ion. For the thickest polymer also, more sites are available and the value of  $D^{1/2}c_0$  is larger.

*Copolymers of N<sup>ε</sup>-4-Nitrobenzoyl-lysine and Inert Amino Acids.*—Any modification to the poly(amino acid) which decreases the density of electroactive sites on the  $\alpha$ -helix could be expected to lower the tendency of films of these materials to buckle when the electroactive groups are charged. Accordingly, amino acid copolymers were prepared by reacting solutions of the *N*-carboxyanhydride of *N*<sup>ε</sup>-4-nitrobenzoyl-L-lysine (NBL) with one of the *N*-carboxyanhydrides from *N*<sup>ε</sup>-4-benzoyl-L-lysine (BZL), L-leucine (Leu), and glycine (Gly). Sodium hydride was used as the polymerisation catalyst in all cases since this gives the highest molecular-weight products.<sup>8</sup>

Loading of 4-nitrobenzoyl groups in the polymer samples can be assumed from the ratio of monomers taken. This loading was checked by u.v. absorption in dimethylacetamide solution at 300 nm. The solvent is not sufficiently transparent below 270 nm for quantitative work. At the wavelength used, poly(NBL) has  $\epsilon = 4\,341$  dm<sup>3</sup> mol<sup>-1</sup> cm<sup>-1</sup> and the other amino acids used do not absorb. (The term mole here refers to the repeat unit of the polymer). Thus the fraction,  $n$ , of 4-nitrobenzoyl-lysine sections in a copolymer can be found from the expression

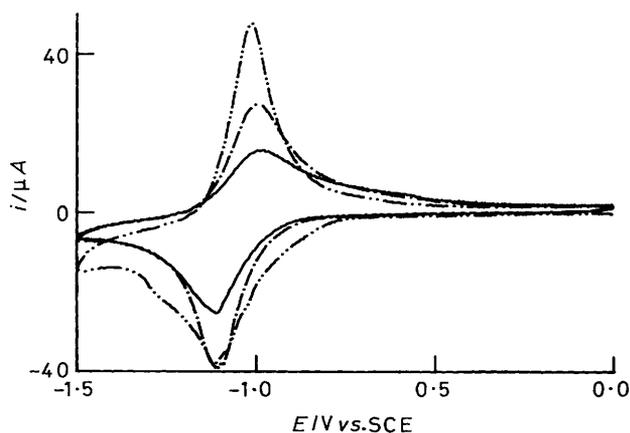
$$\text{Absorbance} = \frac{4\,341nW}{277n + (1-n)B}$$

where  $B$  is the relative formula mass of the other repeat unit of a copolymer and  $W$  is the weight concentration of copolymer in g dm<sup>-3</sup>. The results (Table 2) are in fair agreement with the values expected assuming total conversion of the two *N*-carboxyanhydrides used in the synthesis.

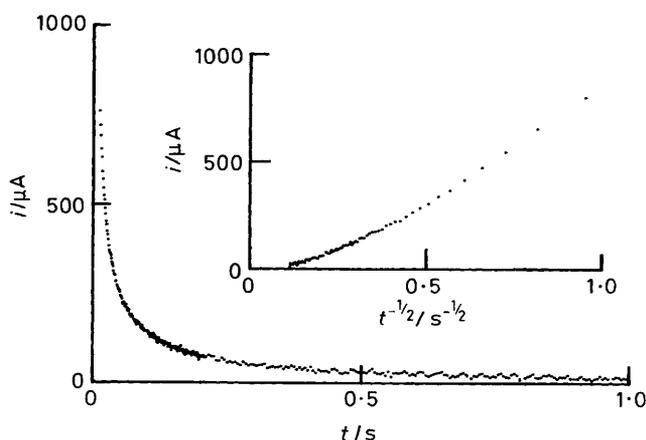
These electroactive polymers were readily dip-coated onto platinum from their solutions in dimethylacetamide. The films were dried in vacuum and their behaviour on repetitive cyclic voltammetry under acetonitrile was observed using tetrapropyl-, tetraethyl-, and tetramethyl-ammonium fluoroborate as the supporting electrolyte. The behaviour of the copolymer NBL-BZL (2:1) in the presence of 0.1 mol dm<sup>-3</sup> tetraethylammonium fluoroborate is illustrated in Figure 5. The copolymer NBL-Leu (2:1) showed a similar behaviour. On repetitive cyclic voltammetry, the cathodic peak moves slowly to more negative potentials while the anodic peak rapidly flattens and broadens towards more positive potentials.

This aging pattern is almost identical with that of the homopolymer of poly(NBL), discussed in Part 1.<sup>1</sup> We ascribe aging to the same cause as before: flexing of the charged polymer with consequent separation of the polymer from the metal support.

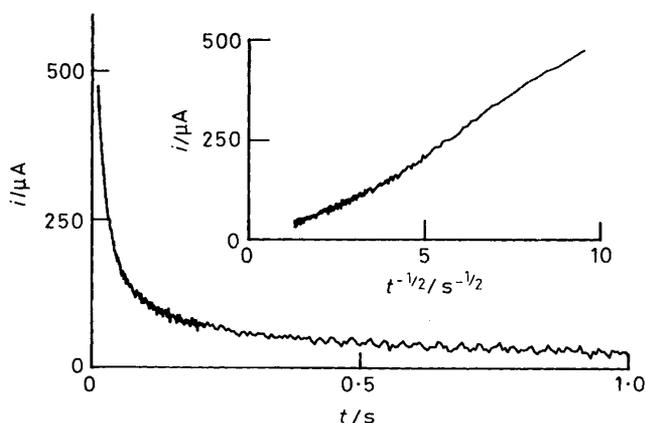
Aging of the two copolymers on repetitive cyclic voltammetry in the presence of 0.1 mol dm<sup>-3</sup> tetrapropylammonium fluoroborate proceeded more slowly but followed the same pattern. Thus, after 12 scans, the cathodic and anodic peaks had moved and broadened only very little. In contrast, the aging process proceeded rapidly when using 0.1 mol dm<sup>-3</sup> tetramethylammonium fluoroborate as the electrolyte. With this supporting electrolyte the anodic peak had broadened extensively after



**Figure 6.** Continuous cyclic voltammograms of an NBL-Gly (2:1) polymer modified Pt sphere electrode (area  $0.116 \text{ cm}^2$ ) in acetonitrile  $0.1 \text{ mol dm}^{-3}$  tetraethylammonium fluoroborate,  $\nu = 0.100 \text{ V s}^{-1}$ ,  $\Gamma = 8.82 \text{ n mol cm}^{-2}$ . --- 1st scan, — 5th scan, - - - 11th scan.



**Figure 7.** Chronoamperometry of an NBL-Leu polymer modified Pt electrode (area  $0.118 \text{ cm}^2$ ),  $\Gamma = 7.61 \text{ n mol cm}^{-2}$ . Solvent acetonitrile,  $1.0 \text{ mol dm}^{-3}$  tetraethylammonium fluoroborate. Potential step 0 to  $-1.5 \text{ V vs. SCE}$ . Inset shows Cottrell plot.



**Figure 8.** Chronoamperometry of an NBL-Gly polymer modified Pt electrode (area  $0.106 \text{ cm}^2$ ),  $\Gamma = 8.82 \text{ n mol cm}^{-2}$ . Solvent acetonitrile containing  $1.0 \text{ mol dm}^{-3}$  tetraethylammonium fluoroborate. Potential step 0 to  $-1.5 \text{ V vs. SCE}$ . Inset shows Cottrell plot.

only 6 scans, the whole aging pattern being similar to those previously described but on a shorter time scale.

The behaviour of copolymer NBL-Gly (2:1) on continuous cyclic voltammograms is different (Figure 6). After the initial

'break-in' sweep, the anodic and cathodic peaks remain with almost the same half widths and peak potentials. However, the peak heights slowly decrease with time which suggests that electroactive material is slowly being lost from the coating.

Poly(glycine) is unique among the homopolymers of the amino acids used here in that it is precipitated from solution as the  $\beta$ -form [poly(glycine)-I].<sup>9</sup> Under carefully defined conditions, another form, poly(glycine)-II, is obtained which contains an unusual helical conformation.<sup>10</sup> Poly(glycine)-I has i.r. bands due to the amide groups<sup>11</sup> at  $1636$  and  $1517 \text{ cm}^{-1}$ . The i.r. spectrum of the copolymer of NBL-Gly shows a shoulder at  $1630 \text{ cm}^{-1}$  indicating the presence of the  $\beta$ -form along sections of the amino acid chain. Unfortunately, the nitro group also shows a band at  $1517 \text{ cm}^{-1}$  which masks the second amide band.

Thus the copolymer NBL-Gly is unlikely to adopt the  $\alpha$ -helix conformation along its whole length. In contrast, the copolymers NBL-BZL and NBL-Leu can be expected to adopt the  $\alpha$ -helix conformation since the related homopolymers themselves adopt the  $\alpha$ -helix.<sup>12</sup> This fundamental difference in the conformation of NBL-Gly with respect to the other copolymers studied must account for the greater stability of the copolymer on repetitive cyclic voltammograms.

A series of electrodes were prepared by coating with poly(NBL) and by coating with the copolymers discussed above, then examined by chronoamperometry with a potential step from 0 to  $-1.5 \text{ V vs. SCE}$ , carried out after two cyclic voltammograms experiments. The current transients so obtained on chronoamperometry are related to the diffusion coefficient,  $D$ , associated with charge migration and the surface concentration,  $c_0$ , of active sites per unit volume according to the Cottrell equation

$$i = (nFA D^{1/2} c_0 / \pi^{1/2} t^{3/2}) \left[ 1 + 2 \sum_{k=1}^{\infty} (-1)^k \exp(-k^2 d^2 / Dt) \right]$$

where  $n$  is the number of electrons per active site,  $A$  is surface area,  $d$  is the film thickness and  $k$  is an integer.<sup>7,13</sup> Thus the value of  $D^{1/2} c_0$  can be obtained from the plot of  $i$  vs.  $t^{-1/2}$  at short times.

Figures 7 and 8 illustrate the chronoamperometry of copolymer NBL-Leu and copolymer NBL-Gly respectively. The data obtained from a number of films is collected in Table 3. The redox potential of the films  $[= \frac{1}{2}(E_{pc} + E_{pa})]$  is in the region expected for the 4-nitrobenzoyl group. Surprisingly the value of  $D^{1/2} c_0$  is larger for the copolymers with Leu than for poly(NBL). This indicates that the structure of the copolymer is more open so allowing freer access of counter-ions. In this way the diffusion coefficient associated with charge migration becomes larger to compensate for the smaller bulk concentration of electroactive sites. There is a parallel to this observation in results on the electrical conductivity of poly(thiophene). The oxidized polymers from 3-alkylthiophenes show much higher conductivity than oxidized poly(thiophene). It is assumed that the side chains make the polymer more open and allow freer migration of counter-ions through the structure.

Freshly prepared films of NBL-Leu and NBL-Gly were examined by cyclic voltammograms at different scan rates. At scan rates less than  $0.08 \text{ V s}^{-1}$  these showed the response expected when  $d^2/D$  is small so that the concentration of radical ions and electrolyte remains uniform across the film during the experiment.<sup>7,13,15</sup> The linear relationship found between  $i_{pc}$  and  $\nu$ , at scan rates less than  $0.08 \text{ V s}^{-1}$ , is illustrated in Figure 9. The ideal behaviour of such thin films has been well established in the literature and is shown by the relation

$$i_p / \nu = n^2 F^2 \Gamma_{tot} / 4RT$$

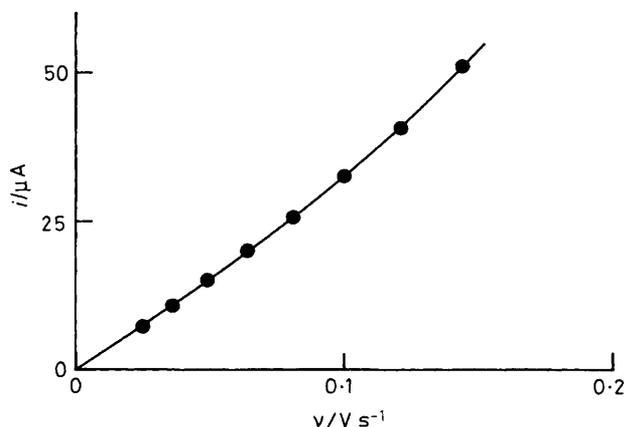
**Table 3.** Cyclic voltammetry and chronoamperometry experiments with NBL-polymer films on Pt. The solvent is acetonitrile containing  $1.0 \text{ mol dm}^{-3}$   $\text{Et}_4\text{NBF}_4$ . Charging potential for chronoamperometry  $-1.5 \text{ V vs. SCE}$ , is derived from the charge passed during 2 s. Coatings obtained by adsorption over 20 min from a solution of the polymer in dimethylacetamide.

| Experiment no. | Area/cm <sup>2</sup> | Cyclic voltammetry   |                             | Chronoamperometry            |   | Polymer composition | Dipping solution (%) |
|----------------|----------------------|----------------------|-----------------------------|------------------------------|---|---------------------|----------------------|
|                |                      | $\Delta E/\text{mV}$ | $-E^\circ/\text{V vs. SCE}$ | $\Gamma/\text{nmol cm}^{-2}$ | $D^{1/2}c_0/\text{nmol cm}^{-2} \text{ s}^{-1/2}$ |                     |                      |
| 180            | 0.106                | 42                   | 1.030                       | 2.5                          | 2.5   | NBL                 | 0.05                 |
| 182            | 0.106                | 34                   | 1.021                       | 2.4                          | 2.8   | NBL                 | 0.05                 |
| 176            | 0.119                | 64                   | 1.030                       | 6.2                          | 5.9   | NBL                 | 0.3                  |
| 179            | 0.119                | 67                   | 1.031                       | 6.9                          | 7.3   | NBL                 | 0.3                  |
| 181            | 0.118                | 46                   | 1.013                       | 3.3                          | 3.2   | NBL-BZL (2:1)       | 0.3                  |
| 178            | 0.118                | 49                   | 1.035                       | 7.3                          | 12.8  | NBL-Leu (2:1)       | 0.3                  |
| 175            | 0.118                | 55                   | 1.044                       | 7.8                          | 12.9  | NBL-Leu (2:1)       | 0.3                  |
| 174            | 0.106                | 57                   | 1.024                       | 8.8                          | 8.6   | NBL-Gly (2:1)       | 0.3                  |
| 177            | 0.106                | 47                   | 1.028                       | 6.2                          | 7.5   | NBL-Gly (2:1)       | 0.3                  |

**Table 4.** Cyclic voltammetry experiments with thin films of copolymers of NBL on Pt. The solvent is acetonitrile containing  $0.1 \text{ mol dm}^{-3}$  tetraethylammonium fluoroborate. For these films  $i_{pc} \propto v$ .

| Experiment no. | Area/cm <sup>2</sup> | Polymer composition | $\partial i_{pc}/\partial v$<br>$\mu\text{A s V}^{-1}$ | Calc. <sup>b</sup> / $\text{nmol cm}^{-2}$ | $\Gamma$ by integration <sup>c</sup> /<br>$\text{nmol cm}^{-2}$ |
|----------------|----------------------|---------------------|--|--|---|
| 167            | 0.106                | NBL-Gly (2:1)       | 255  | 2.6  | 4.9   |
| 168            | 0.119                | NBL-Leu (2:1)       | 301  | 2.7  | 5.1   |
| a              | 0.106                | NBL                 | 229  | 2.3  | 5.4   |

<sup>a</sup> Taken from Figure 3 of ref. 1. <sup>b</sup> From relationship  $i_{pc}/v = n^2 F^2 \Gamma_{\text{total}}/4RT$ . <sup>c</sup> From integration over the cathodic branch of the cyclic voltammetry curve.



**Figure 9.** Cyclic voltammetry of an NBL-Leu polymer modified Pt electrode (area  $0.119 \text{ cm}^2$ ),  $\Gamma = 5.1 \text{ nmol cm}^{-2}$  (by integration where  $v = 0.036 \text{ V s}^{-1}$ ). Variation of cathodic peak current with sweep rate,  $v$ . Solvent acetonitrile,  $0.1 \text{ mol dm}^{-3}$  tetraethylammonium fluoroborate. At slow scan rates,  $\partial i/\partial v = 301 \mu\text{A s V}^{-1}$ .

A comparison of surface coverage calculated in this way with surface coverage obtained from integration of the cathodic branch of the cyclic voltammetry curve is given in Table 4. Clearly the two results diverge and these films depart considerably from ideal behaviour. The non-ideal behaviour may be due to activity effects within the film which decrease the value of  $i_{pc}$  and broaden the cyclic voltammetry curve.<sup>16</sup>

The object of preparing these copolymers was to find a way to improve the stability of the charged films and to halt the aging process of these films. In this objective we did not succeed with the NBL-BZL and NBL-Leu copolymers that are expected to adopt predominantly the  $\alpha$ -helix conformation. The development of multiple peaks on continuous cyclic voltammetry is prevented but a gradual deterioration of the response is seen. A greater dilution of active sites along the polymer chain may have been effective in improving stability. A polymer was prepared

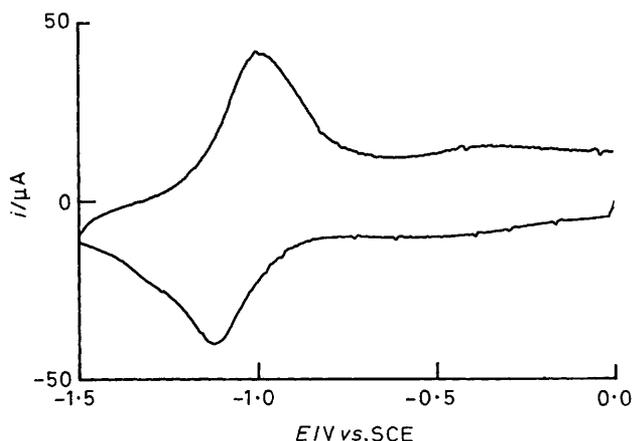
with an NBL to BZL ratio of 1:2. This, on cyclic voltammetry showed a weak response due to the 4-nitrobenzoyl groups superimposed on an equally large charging current. Further experiments in this direction were abandoned because the method for preparing these materials by copolymerization of two monomers may not give a random distribution of units along the polymer chain. The presence of NBL residues as blocks in the copolymer structure would defeat the object of the investigation.

The copolymer NBL-Gly shows greater stability under electrical stress and useful results may be obtained by developing copolymers with glycine and an electroactive amino acid.

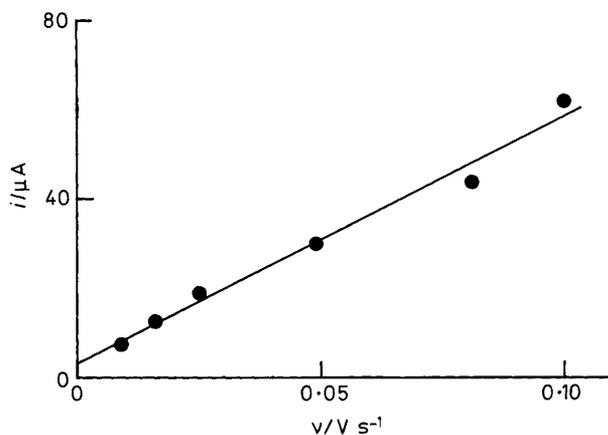
**Bilayers from Poly(pyrrole) and Poly(NBL).**—In Part 1 of this series,<sup>1</sup> we noted that the 'clean' platinum used as a support for the polymer films is covered with a thin layer of hydrocarbon material. Such a layer assists in adsorption of the polypeptide, so it is worthwhile to experiment with platinum that has been deliberately coated with organic carbon compounds. Poly(pyrrole) forms a tough coating on platinum so the advantages of bilayers using this material were examined. Other workers have examined a bilayer of poly(pyrrole) and a Ru<sup>II</sup>-containing poly(vinylpyridine).<sup>17</sup> Poly(pyrrole) has also been used to immobilize redox enzymes on platinum.<sup>18</sup>

A new platinum sphere was coated<sup>5</sup> with poly(pyrrole) (PP) by oxidation at  $+0.81 \text{ V vs. SCE}$  in a solution of pyrrole in acetonitrile,  $0.1 \text{ mol dm}^{-3}$  tetraethylammonium fluoroborate, for a fixed period. The thickness of the poly(pyrrole) coating was regulated by the time period used. Film thicknesses are calculated assuming that  $24 \text{ mA s cm}^{-2}$  of charge produce a film  $0.1 \mu\text{m}$  thick.<sup>5</sup> This coated electrode was then dipped into a  $0.3\%$  solution of poly(NBL) in dimethylacetamide for 20 min, withdrawn and dried under vacuum. Finally, the properties of this Pt/PP/Poly(NBL) electrode were examined in acetonitrile,  $0.1 \text{ mol dm}^{-3}$  tetraethylfluoroborate.

On cyclic voltammetry, the electrode showed a slow 'breaking-in' period. The first scan caused reduction of the



**Figure 10.** Cyclic voltammogram of a Pt/PP/Poly(NBL) modified electrode (area  $0.148 \text{ cm}^2$ ). Fully swelled film in acetonitrile,  $0.1 \text{ mol dm}^{-3}$  tetraethylammonium fluoroborate,  $\nu = 0.049 \text{ V s}^{-1}$ . Charge passed to make PP =  $14.1 \text{ mA s cm}^{-2}$  (corresponding to  $60 \text{ nm}$  thickness); surface coverage of accessible nitro groups =  $11.9 \text{ nmol cm}^{-2}$ .

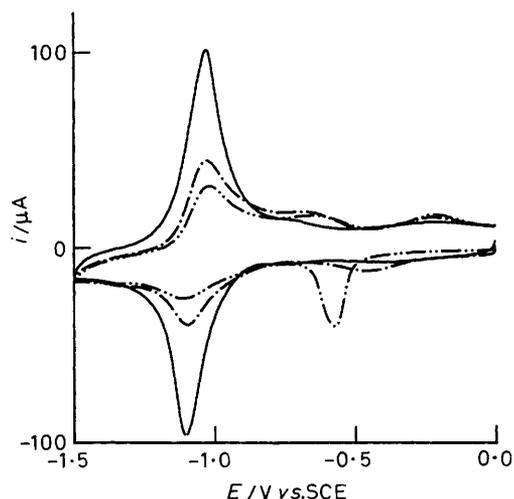


**Figure 11.** Cyclic voltammetry of a Pt/PP/Poly(NBL) modified electrode (area  $0.148 \text{ cm}^2$ ). Relationship between cathodic peak current and scan rate,  $\nu$ . Solvent acetonitrile,  $0.1 \text{ mol dm}^{-3}$  tetraethylammonium fluoroborate. One cyclic voltammogram of this film is shown in Figure 10.

poly(pyrrole) to the pale non-conducting form and a redox response for the 4-nitrobenzoyl groups that was much distorted from the ideal. On subsequent scans the response of the 4-nitrobenzoyl groups increased in height reaching a maximum after about 8 scans (see Figure 10), and obtained a normal shape. Repetitive cyclic voltammetry caused a slow decrease in peak height but the anodic and cathodic peaks showed no shifts and deterioration in shape associated with the aging of plain poly(NBL) films.

Experiments with various thicknesses of poly(pyrrole) indicated that thin films of this material give the most satisfactory results and we used those formed by passing  $5\text{--}14 \text{ mA s cm}^{-2}$  during the oxidation step giving thicknesses of  $20\text{--}60 \text{ nm}$ . The response of the 4-nitrobenzoyl group on cyclic voltammetry showed  $i_{pc}$  proportional to  $\nu$  (Figure 11). A Pt/PP/Poly(NBL) electrode formed where  $22 \text{ mA s cm}^{-2}$ , thickness *ca.*  $100 \text{ nm}$ , had been used during the oxidation of pyrrole showed a large charging current on cyclic voltammetry, a very slow 'breaking-in' of the poly(NBL) coating. This was inferior in performance to the films with a thinner poly(pyrrole) layer.

We experimented also with the alternative of fixing an



**Figure 12.** Cyclic voltammogram of a Pt/Poly(NBL)/PP modified electrode (area  $0.148 \text{ cm}^2$ ,  $\nu = 0.100 \text{ V s}^{-1}$ . Solvent acetonitrile,  $0.1 \text{ mol dm}^{-3}$  tetraethylammonium fluoroborate. — · · 1st scan; — · — 2nd scan; — · — · — 8th scan. Surface coverage of accessible nitro groups =  $9.0 \times 10^{-9} \text{ mol cm}^{-2}$ ; charge passed to make PP =  $5.11 \text{ mA s cm}^{-2}$  (corresponding to  $20 \text{ nm}$  thickness).

adsorbed layer of poly(NBL) on 'clean' platinum with an over coating of poly(pyrrole). Poly(NBL) was dip-coated from dimethylacetamide solution onto platinum and then dried under vacuum. Two cyclic voltammograms were then run in acetonitrile containing  $0.1 \text{ mol dm}^{-3}$  tetramethylammonium fluoroborate, on this film between 0 and  $-1.5 \text{ V vs. SCE}$  in order to swell the film. Pyrrole was then oxidatively polymerized from acetonitrile onto the poly(NBL) electrode at  $+0.81 \text{ V vs. SCE}$  for 100 s. The charge passed would give a normal film of  $20 \text{ nm}$  thickness.

The composite electrode was then subjected to cyclic voltammetry between 0 and  $-1.5 \text{ V vs. SCE}$ . After reduction of the oxidized poly(pyrrole), the wave due to the 4-nitrobenzoyl group gradually increased in height. The electrode became fully 'broken-in' after 8 scans (Figure 12). At this point the electrode behaved well during continuous cyclic voltammetry showing only a slow decrease in peak height with time. Again there was none of the deterioration in peak shape associated with the aging of plain poly(NBL) films.

Composite electrode coatings from poly(pyrrole) and an electroactive poly(amino acid) appear to offer an excellent way forward towards the goal of a stable coated electrode based on the electroactive poly(amino acid).

## Experimental

All solvents used for the preparation and polymerization of oxazolidine-2,5-diones 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.

I.r. 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 dry air. Viscosity measurements were made in dichloroacetic acid. The relationship between intrinsic viscosity and molecular weight for poly( $\gamma$ -benzyl-L-glutamate) given in Part 1<sup>1</sup> was used here. <sup>1</sup>H N.m.r. spectra were recorded at 250 MHz in  $\text{CDCl}_3$  relative to  $\text{SiMe}_4$ .

Non-SI units of surface concentration ( $\text{mol cm}^{-3}$ ), surface coverage ( $\text{mol cm}^{-2}$ ) and diffusion content ( $\text{cm}^2 \text{ s}^{-1}$ ) are common in the literature and have been retained here. In this

context 1 mol of electroactive species refers to  $6.02 \times 10^{23}$  electroactive units that are attached to the polymer chains.

*1-[2-(4'-Nitrobenzoyl)aminoethyl]pyrrole.*—1-(2-Aminoethyl)pyrrole (0.25 g, 2.3 mmol) was added to a stirred solution of 4-nitrobenzoyl chloride (0.38 g, 2.0 mmol) and pyridine (0.35 g, 4.4 mmol) in dichloromethane (20 cm<sup>3</sup>). After 18 h, the precipitate was filtered, washed with water and dried under vacuum. The filtrate was washed with dilute hydrochloric acid and water, dried (Na<sub>2</sub>SO<sub>4</sub>) and the solvent removed. The residue was combined with the previous precipitate and the whole recrystallized from methanol to give brownish yellow crystals (0.38 g, 70%) of 1-[2-(4'-nitrobenzoylamino)ethyl]pyrrole, m.p. 206–207 °C (Found: C, 60.0; H, 5.0; N, 15.8. C<sub>13</sub>H<sub>13</sub>N<sub>3</sub>O<sub>3</sub> requires: C, 60.2; H, 5.1; N, 16.2%); *m/z* 259 (*M*<sup>+</sup>);  $\nu_{\max}$ (KBr) 1 640, 1 596, 1 546, and 1 513 cm<sup>-1</sup>;  $\delta$  3.80 (2 H, m, —CH<sub>2</sub>NH), 4.17 (2 H, m, —CH<sub>2</sub>N), 6.22 (3 H, m, CONH + 2 pyrrole H), 6.69 (2 H, t, *J* 2.1 Hz, pyrrole H), 7.84 (2 H, d, *J* 8.8 Hz, aromatic), 8.28 (2 H, d, *J*, 8.8 Hz, aromatic).

*4-(2-Methylpropyl)oxazolidine-2,5-dione.*—A 12.5% solution of phosgene in toluene (25 cm<sup>3</sup>, 31.6 mmol) was added to a suspension of L-leucine (1.31 g, 10 mmol) in dioxane (30 cm<sup>3</sup>) and ethyl acetate (25 cm<sup>3</sup>) at 40 °C under a static atmosphere of nitrogen. After 4 h, the leucine had dissolved and then the excess of phosgene was removed in a stream of nitrogen. The solvent was removed at 40 °C under vacuum and the residue recrystallized from ether–light petroleum (b.p. 40–60 °C) to yield colourless needles of 4-(2-methylpropyl)oxazolidine-2,5-dione (1.01 g, 69%), m.p. 76–77 °C (lit.,<sup>19</sup> m.p. 76–77 °C) (Found: C, 53.5; H, 6.9; N, 8.8. Calc. for C<sub>7</sub>H<sub>11</sub>NO<sub>3</sub>: C, 53.4; H, 7.1; N, 8.9%);  $\nu_{\text{CO}}$ (CHCl<sub>3</sub>) 1 855 and 1 780 cm<sup>-1</sup>.

*Oxazolidine-2,5-dione.*—A 12.5% solution of phosgene in toluene (120 cm<sup>3</sup>; 0.15 mol) was added to a suspension of glycine (3.75 g, 0.05 mol) in dioxane (125 cm<sup>3</sup>) at 45 °C under a static atmosphere of nitrogen. After 24 h, the excess of phosgene was removed in a stream of nitrogen and unchanged glycine filtered off. Evaporation of the filtrate to dryness left a residue which recrystallized from ethyl acetate–light petroleum (b.p. 40–60 °C) as colourless needles (1.19 g, 22%), m.p. 122–124 °C (decomp.) (lit.,<sup>20</sup> m.p. 100 °C),  $\nu_{\text{CO}}$ (KBr) 1 855 and 1 785 cm<sup>-1</sup>.

*Copolymer of N<sup>ε</sup>-4-Nitrobenzoyl-L-lysine and N<sup>ε</sup>-Benzoyl-L-lysine.*—(a) *NBL:BZL* = 2:1. 4-(4-Nitrobenzoylamino)butyl-oxazolidine-2,5-dione<sup>1</sup> (0.321 g, 1.0 mmol) and 4-(4-benzoylamino)butyl-oxazolidine-2,5-dione<sup>1</sup> (0.138 g, 0.5 mmol) were dissolved in a mixture of dioxane (12 cm<sup>3</sup>) and dimethylacetamide (4 cm<sup>3</sup>). Sodium hydride (5 mg, 0.104 mmol, 50% dispersion in oil) was added (monomer: initiator = 15:1). A drop of the mixture was withdrawn periodically and the i.r. spectrum recorded. After the disappearance of the characteristic bands at 1 855 and 1 785 cm<sup>-1</sup> due to starting materials, in about 20 h, the solution was poured into ether (250 cm<sup>3</sup>) which precipitated a fibrous polymer. The polymer was filtered, washed with ether and dried in vacuum to yield colourless fibres (0.35 g, 89%). This product was purified by being dissolved in dichloroacetic acid and reprecipitated with water. The polymer was filtered, washed with water, ethanol, and ether and dried under vacuum. [Found: C, 59.2; H, 5.6; N, 13.5. Calc. for (C<sub>13</sub>H<sub>15</sub>N<sub>3</sub>O<sub>4</sub>)<sub>2</sub> + (C<sub>13</sub>H<sub>16</sub>N<sub>2</sub>O<sub>2</sub>): C, 59.5; H, 5.9; N, 14.2]. It showed i.r. amide bands at  $\nu$  1 650 and 1 540 cm<sup>-1</sup>. A solution of the polymer in dichloroacetic acid gave intrinsic viscosity  $[\eta] = 0.38 \text{ dl g}^{-1}$  from which the molecular weight was found to be  $5.7 \times 10^4$ .

(b) *NBL:BZL* = 1:2. 4-(4-Nitrobenzoylamino)butyl-oxazol-

idine-2,5-dione (0.167 g, 0.52 mmol) and 4-(4-benzoylamino)butyl-oxazolidine-2,5-dione (0.287 g, 1.04 mmol) were dissolved in a mixture of dioxane (12 cm<sup>3</sup>) and dimethylacetamide (4 cm<sup>3</sup>). Sodium hydride (5 mg, 0.104 mmol; 50% dispersion in oil) was added. After 20 h and work-up as for the first example the polymer (0.36 g, 93%) was formed,  $\nu_{\text{amide}}$  1 650 and 1 540 cm<sup>-1</sup>,  $[\eta] = 1.08 \text{ dl g}^{-1}$  from which molecular weight =  $1.9 \times 10^5$ .

*Copolymer of N<sup>ε</sup>-4-Nitrobenzoyl-L-lysine and L-Leucine.*—4-(4-Nitrobenzoylamino)butyl-oxazolidine-2,5-dione<sup>1</sup> (0.240 g, 0.75 mmol) and 4-(2-methylpropyl)oxazolidine-2,5-dione (0.059 g, 0.375 mmol) were dissolved in a mixture of dioxane (8 cm<sup>3</sup>) and dimethylacetamide (2 cm<sup>3</sup>). Sodium hydride (3 mg, 0.06 mmol; 50% dispersion in oil) was added. After 18 h work-up as usual gave the polymer (0.105 g, 74%) [Found: C, 57.6; H, 6.0; N, 15.0. Calc. for (C<sub>13</sub>H<sub>15</sub>N<sub>3</sub>O<sub>4</sub>)<sub>2</sub> + (C<sub>6</sub>H<sub>11</sub>NO): C, 57.7; H, 6.2; N, 14.7%];  $\nu_{\text{amide}}$  1 648 and 1 542 cm<sup>-1</sup>.

*Copolymer of N<sup>ε</sup>-4-Nitrobenzoyl-L-lysine and Glycine.*—4-(4-Nitrobenzoylamino)butyl-oxazolidine-2,5-dione<sup>1</sup> (0.240 g, 0.75 mmol) and oxazolidine-2,5-dione (0.038 g, 0.375 mmol) were dissolved in a mixture of dioxane (8 cm<sup>3</sup>) and dimethylacetamide (2 cm<sup>3</sup>). Sodium hydride (4 mg, 0.08 mmol; 50% dispersion in oil) was added. After 42 h work-up as usual gave the polymer (0.180 g, 78%) [Found: C, 54.9; H, 5.9; N, 16.6. Calc. for (C<sub>13</sub>H<sub>15</sub>N<sub>3</sub>O<sub>4</sub>)<sub>2</sub> + (C<sub>2</sub>H<sub>3</sub>NO): C, 55.0; H, 5.4; N, 16.0%];  $\nu_{\text{amide}}$  1 648, 1 630 (shoulder) and 1 540 cm<sup>-1</sup>,  $[\eta] = 0.45 \text{ dl g dm}^{-3}$  from which molecular weight =  $6.9 \times 10^4$ .

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

Cyclic voltammetry on coated electrodes was performed by sweeping between 0 and –1.5 V vs. SCE. Chronoamperometry on coated electrodes was carried out stepping the potential to –1.5 V vs. SCE and collecting the current transient over 4 s. The potentiostat was a PAR 176 model with 274 digital interface and controlled through an Apple IIe computer.

Old electrodes were cleaned by being polished with alumina, with the coat then being burnt off in a hydrogen–oxygen flame. This process could be repeated about five times before the surface of the metal began to deteriorate.

*Coating with Poly(NBA).*—A solution of NBA (2 mg) in acetonitrile (5 cm<sup>3</sup>) containing 0.1 mol dm<sup>-3</sup> tetra-alkylammonium salt to be used in subsequent experiments. Experience showed that oxidation at a Pt sphere anode at 1.2 V vs. SCE gave a coherent dark-coloured coating of oxidized poly(NBA). The oxidation time was varied between 15 and 80 s as noted in Table 1. The current passed during oxidation was recorded digitally and later integrated. During later electrochemical work at negative potentials, the oxidized polypyrrole is reduced to the pale-coloured non-conducting form. All subsequent electrochemical measurements are made with this form and involve redox behaviour of the 4-nitrobenzoyl group.

*Coating with Poly(amino acids).*—The poly(amino acid) was swollen into dimethylacetamide so as to make a 0.3% solution. 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 polymer solution, then dried at 50 °C and 0.1 mmHg for 20 min.

*Pt/PP/Poly(NBL) Electrode.*—A solution of freshly distilled pyrrole (17 mg) in acetonitrile (5 cm<sup>3</sup>) containing 0.1 mol dm<sup>-3</sup> tetraethylammonium fluoroborate was oxidised at a Pt sphere anode at 0.81 V vs. SCE for 100 s. The current passed during oxidation was recorded and later integrated. The black coating of oxidized poly(pyrrole) was rinsed with dimethylacetamide and then dip-coated during 20 min from a 0.3% solution of poly(NBL) in dimethylacetamide. The combined electrode was dried at 50 °C and 0.1 mmHg for 20 min.

*Pt/Poly(NBL)/PP Electrode.*—A platinum sphere was dip-coated for 20 min from a 0.3% solution of poly(NBL) in dimethylacetamide, then dried at 50 °C and 0.1 mm for 20 min. This coated sphere was subjected to two cyclic voltammograms between 0 and -1.5 V vs. SCE in acetonitrile containing 0.1 mol dm<sup>-3</sup> tetraethylammonium fluoroborate. Freshly distilled pyrrole was then added to give a concentration of 0.05 mol dm<sup>-3</sup> and the coated sphere made an anode at 0.81 V vs. SCE for 100 s. The anodic current was recorded and later integrated. The combined electrode was rinsed in acetonitrile before use.

#### Acknowledgements

We thank the SERC and Queen's University for support and Johnson Matthey plc for loan of platinum. S. D. P. is grateful for leave of absence from Sri Jayewardenepura University, Sri Lanka.

#### References

- Part I. A. M. Abeyskera, J. Grimshaw, S. D. Perera, and D. Vipond, *J. Chem. Soc., Perkin Trans. 2*, 1989, 43.
- Y.-W. Tseng and J. T. Yang, *Biopolymers*, 1977, **16**, 921.
- G. Bidan, A. Deronzier, and J.-C. Moutet, *J. Chem. Soc., Chem. Commun.*, 1984, 1185; G. Bidan, A. Deronzier, and J.-C. Moutet, *Nouv. J. Chim.*, 1984, **8**, 501; M. S. Munro and D. Parker, *J. Chem. Soc., Chem. Commun.*, 1985, 684; M. Velazquez Rosenthal, T. A. Skotheim, A. Melo, M. I. Florit, and M. Salmon, *J. Electroanal. Chem.*, 1985, **185**, 297; G. Bidan and M. Lapkowski, *J. Chem. Soc., Chem. Commun.*, 1986, 887; G. Bidan and D. Limosin, *Ann. Phys. (Paris)*, 1986, **11**, 5; A. Haimerl and A. Merz, *Angew. Chem., Int. Ed. Engl.*, 1986, **25**, 180; A. Deronzier, M. Essakalli, and J.-C. Moutet, *J. Chem. Soc., Chem. Commun.*, 1987, 773; J.-P. Collin and J.-P. Sauvage, *ibid.*, 1987, 1075; T. Inagaki, M. Hunter, X. Q. Yang, T. A. Skotheim, and Y. Okamoto, *ibid.*, 1988, 126.
- I. Jirkovsky and R. Bandy, *Synthesis*, 1981, 481.
- A. F. Diaz and J. I. Castillo, *J. Chem. Soc., Chem. Commun.*, 1980, 397.
- A. F. Diaz, J. Castillo, K. K. Kanazawa, J. A. Logan, M. Salmon, and O. Fajardo, *J. Electroanal. Chem.*, 1982, **133**, 233.
- 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.
- M. Goodman, E. Peggion, M. Szwarc, and C. H. Bamford, *Macromolecules*, 1977, **10**, 1299.
- C. H. Bamford, L. Brown, E. M. Cast, A. Elliott, W. E. Hanby, and B. R. Malcolm, *Nature (London)*, 1955, **176**, 396.
- F. H. C. Crick and A. Rich, *Nature (London)*, 1955, **176**, 780.
- S. Suzuki, Y. Iwashita, T. Shimanouchi, and M. Tsuboi, *Biopolymers*, 1966, **4**, 337; Yu. A. Lazarev, B. A. Grishkovorski, and T. B. Khromova, *Biopolymers*, 1985, **24**, 1449.
- H. L. Yakel, *Acta Crystallogr.*, 1953, **6**, 724; P. Dotz and W. B. Gratser in 'Polyamino Acids, Polypeptides and Proteins,' ed. M. A. Stahmann, University of Wisconsin Press, Madison, 1962, p. 111.
- K. Shigehara, N. Oyama, and F. C. Anson, *J. Am. Chem. Soc.*, 1981, **103**, 2552.
- M. Lemaire, R. Garreau, F. Garnier, and J. Roncali, *New. J. Chem.*, 1987, **11**, 703.
- A. T. Hubbard and F. C. Anson, *Anal. Chem.*, 1966, **38**, 38; E. Laviron, *Bull. Soc. Chim. France*, 1967, 3717.
- A. P. Brown and F. C. Anson, *Anal. Chem.*, 1977, **49**, 1589.
- K. Murao and K. Suzuki, *J. Chem. Soc., Chem. Commun.*, 1984, 238.
- N. C. Foulds and C. R. Lowe, *J. Chem. Soc., Faraday Trans. 1*, 1986, **82**, 1259; P. N. Bartlett and R. G. Whitaker, *J. Electroanal. Chem.*, 1987, **224**, 37.
- D. Coleman, *J. Chem. Soc.*, 1950, 3222.
- A. C. Farthing, *J. Chem. Soc.*, 1950, 3213, Y. Go and M. Tani, *Bull. Chem. Soc. Jpn.*, 1939, **14**, 510.

Received 14th March 1989; Paper 8/01096C