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Poly(pyrrole) as a Support for Electrocatalytic Materials

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1 Introduction

Pyrrole undergoes oxidative polymerization from acetonitrile solution at a metallic anode to form a dark coloured skin that adheres firmly to the metal surface. This simple electropolymerization step, when applied to pyrrole monomers with covalently attached redox centres, offers a method for fixing these redox centres to an electrode. The very large range of modified electrodes prepared by this method is discussed here. A main aim of this area of research is the construction of electrodes on which a catalytic centre is present, and which can be activated by placing the electrode at the required redox potential.

A number of important oxidation and reduction processes involve the transfer of atoms or groups of atoms and the making or breaking of bonds which involve a pair of electrons. These reactions do not occur readily at a normal electrode surface which promotes the transfer of single electrons only. Hence, there is a need to develop an electrode surface coating containing an electrocatalyst. If we consider an oxidation process, the catalyst is so designed that it reacts with the substrate and is itself reduced to an inactive form. This inactive form is in turn oxidized at the electrode surface by a sequence of single electron transfer steps. The advantage of such a system lies in constraining the catalyst to the electrode surface where it can be regenerated. The rate of the catalysed oxidation or reduction is limited by the diffusion of substrate to the coated electrode surface. Examples will be given where electrocatalytic processes have been achieved on a small scale.

2 Poly(pyrrole)

The first electrochemical polymerization of pyrrole was reported in 1968 and involved the anodic polymerization of pyrrole in aqueous sulphuric acid to give a laminar electrically conducting polymer containing oxygen (oxypyrrole black).[1] Diaz[2,3] in 1979 reported the formation of highly stable and continuous films of poly(pyrrole) by the oxidation of the monomer at a platinum anode in acetonitrile or, better, acetonitrile–water (99:1) using tetraethylammonium tetrafluoroborate as background electrolyte. Oxidation occurs at about 1.2 V *vs.* saturated calomel electrode. Monomer concentration is in the range 2—20 mM.

[1] A. Dall'Olio, G. Dascola, V. Varacca, and V. Bocchi, *Compt. Rend. C*, 1968, **267**, 433.
[2] A. F. Diaz, K. Kanazawa, and G. P. Gardini, *J. Chem. Soc., Chem. Commun.*, 1979, 635.
[3] K. K. Kanazawa, A. F. Diaz, R. H. Geiss, W. D. Gill, J. F. Kwak, J. A. Logan, J. F. Robolt, and G. B. Street, *J. Chem. Soc., Chem. Commun.*, 1979, 854.

Films have been grown either by maintaining the anode at a suitable potential or by cycling the anode potential over a range.

Poly(pyrrole) is insoluble in all solvents. Films of the polymer have a high electrical conductivity around 10–100 Ω^{-1} cm^{-1} and are black in colour. The polymer consists of chains of pyrrole units where one in four units has been oxidized to a radical-cation. Positive charges are balanced by anions from the solution (*e.g.* BF_4^-).[2] Raman and IR reflectance spectroscopy have confirmed the presence of pyrrole rings in the structure.[3] Solid state ^{13}C-NMR studies indicate α,α^1-coupling.[4] Evidence for the α,α^1-coupling was also provided by Diaz who examined the polymerization of substituted pyrroles.[5] 2,5-Disubstituted pyrroles did not polymerize and 2-substituted pyrroles formed only soluble dimers. Further, the destructive oxidation of pyrrole blacks yields pyrrole-2,5-dicarboxylic acid.

The initial step in this anodic polymerization of pyrrole involves oxidation to pyrrole radical-cation which then reacts with a second molecule of pyrrole leading to dipyrrole. The oxidation potentials for pyrrole oligomers become less positive[6] with increasing chain length. Thus, this dimer is converted preferentially into the radical-cation which reacts with monomer leading to pyrrole trimer. The continuing preferential reaction is a lengthening of polymer chains already started, and this leads ultimately to the precipitation of polypyrrole with a negligible loss of material as soluble oligomers. Polymer films are formed in this way by a nucleation and growth mechanism.[7] Scanning electron micrographs reveal that the films are very poorly crystalline and are space filling rather than fibrillar.[8] The forming film is itself electrically conducting, so that thickening of the film does not inhibit growth.

The apparent stoicheiometry for the reaction is 2.2—2.4 electrons per pyrrole ring.[9] Two electrons per pyrrole ring are involved in the polymerization process and the remaining charge is used up in partial oxidation of the pyrrole rings. Cyclic voltammetry studies show that the polymer can be cycled between the conducting (oxidized, doped) form which is black in colour and the insulating (reduced, neutral, undoped) form which is pale yellow.

Polymerization to form a coherent film on a platinum anode is tolerant of a wide range of substituents attached to the pyrrole nitrogen atom. The reaction fails when the substituent has a basic function attached such as pyridine,[10,11]

[4] G B Street, T C Clarke, M Krounbi, K Kanazawa, V Lee, P Pfluger, J C Scott, and G Weiser, *Mol Cryst Liq Cryst*, 1982, **83**, 253

[5] A F Diaz, A Martinez, K K Kanazawa, and M Salmon, *J Electroanal Chem*, 1981, **130**, 181

[6] A F Diaz, J Crowley, J Bargon, G P Gardini, and J B Torrance, *J Electroanal Chem*, 1981, **121**, 355

[7] A J Downard and D Pletcher, *J Electroanal Chem*, 1986, **206**, 139

[8] K K Kanazawa, A F Diaz, W D Gill, P M Grant, G B Street, and G P Gardini, *Synth Met*, 1979/80, **1**,329

[9] R J Waltman and J Bargon, *Can J Chem*, 1986, **64**, 76, A F Diaz, *Chem Scr*, 1981, **17**, 145

[10] G Bidan, A Deronzier, and J -C Moutet, *Nouv J Chim*, 1984, **8**, 501

[11] S Panaro, P Prosperi, F Bonino, and B Scrosati, *Electrochim Acta*, 1987, **32**, 1007, T Osaka, K Nari, and S Ogano, *J Electrochem Soc*, 1988, **135**, 1071, T Sata and K Saeki, *J Chem Soc, Chem Commun*, 1989, 230

bipyridyl,[12,13] or dialkylamino.[14] These groups act as nucleophiles towards the pyrrole radical-cation centres and stop interaction of these radical-cations with a pyrrole monomer. Addition of a trace of acid to protonate the basic centres usually allows polymerization to proceed.

3 Electrochemical Characterization of Substituted Poly(pyrroles)

Substituted poly(pyrroles) considered here show electrochemical behaviour due to two functions. First, the polypyrrole chain itself can be oxidized and reduced: it exists in the oxidized form at potentials greater than 0.6 V *vs.* SCE. Secondly, the electroactive group in the side chain shows its own characteristic electrochemistry which may be in the same potential range as that shown by related monomeric compounds in solution. Occasionally groups show unusual electrochemical behaviour when immobilized within a polypyrrole.

The most widely used electrochemical techniques for characterizing these polymers are cyclic voltammetry (CV) and chronoamperometry (CA).[15] Spectroscopic techniques such as multiple reflection infra-red spectroscopy, Raman scattering, and transmission spectroscopy at optically transparent electrodes have also been used to characterize the species involved in the electrochemistry.

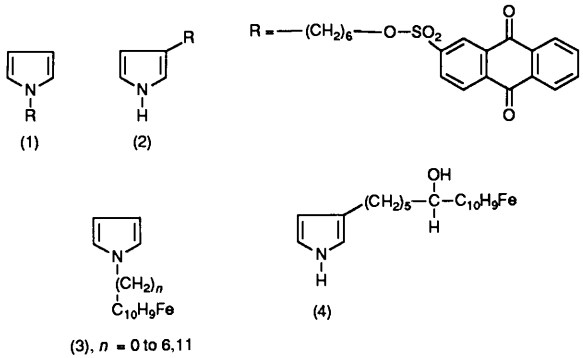
CV is a technique in which the potential of the working electrode can be scanned in one direction, anodic or cathodic, at a predetermined rate, whilst the current due to oxidation or reduction of the electroactive group is observed. The electrode is then immediately scanned in the opposite direction to observe the peaks due to reduction or oxidation of the intermediates formed during the forward scan. During the process, cell current is recorded as a function of the applied potential. Continuous CV is a convenient means of recording the gradual deterioration of a film under electrical stress.

In CA the film potential is stepped up to a region where the electroactive group must change its redox level. Potential is maintained constant and the current required to charge the film is recorded. Integration of this current gives the number of redox sites available in the film. During the initial phase of charging, the film current is proportional to $t^{-\frac{1}{2}}$ and the constant of proportionality is a measure of the diffusion coefficient for charge through the film.[16] After this initial phase and when charge has migrated to the outer surface of the film, the current becomes less than that expected from extrapolating the region where $i \propto t^{-\frac{1}{2}}$.

4 1- and 3-Substituted Poly(pyrroles)

3-Substituted pyrroles are relatively difficult to prepare, with the consequence

[12] M. Salmon, M. E. Carbajal, M. Aguiler, M. Saloma, and J. C. Jaurez, *J. Chem. Soc., Chem. Commun.*, 1983, 1532.
[13] F. Daire, F. Bedioni, J. Devynck, and C. Bied-Charreton, *J. Electroanal. Chem.*, 1986, **205**, 309.
[14] J. Grimshaw and S. D. Perera, *J. Electroanal. Chem.*, 1989, **265**, 335.
[15] For a discussion see A. J. Bard and L. R. Faulkner, *Electrochemical Methods. Fundamentals and Applications*, J. Wiley and Sons, New York, 1980.
[16] P. Daum, J. R. Leonard, and R. W. Murray, *J. Am. Chem. Soc.*, 1980, **102**, 4649.



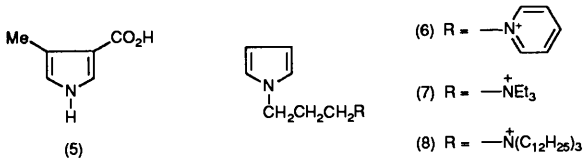
that most of the work on poly(pyrroles) has concentrated on using 1-substituted pyrroles. A direct comparison of properties is available for the polymers prepared from isomers (1)[17] and (2).[18] Both monomers were polymerized in the usual way in acetonitrile and the electrochemistry of the polymers was examined in dimethyl sulphoxide. The films showed two redox processes on CV for the anthraquinone group corresponding to the processes $AQ/AQ^{\cdot -}$ and $AQ^{\cdot -}/AQ^{2-}$ at almost the same potentials found for the monomer. With thicker films of poly(1) however, this ideality disappeared. Side peaks formed on the cyclic voltammogram and the relative size of the dianion response decreased. The decrease was attributed to slow kinetics of dianion formation. Films of poly(2) showed much more nearly ideal behaviour with little evidence for the slow kinetics of dianion formation.[19] The dianion formed in poly(2) was protonated rapidly, presumably by the free pyrrole NH groups. Charge transfer through films of poly(2) is faster than through films of poly(1).

Polymers containing the anthraquinone group are attractive because their electrochemistry in water can be expected to show changes with pH. Unfortunately poly(1) is totally inactive in water, probably because of the hydrophobic nature of the pyrrole backbone. This polymer was electroactive in 70% aqueous acetonitrile, and in this medium its electrochemistry showed changes with pH.[20]

Poly(1) catalysed the reduction of dioxygen at an electrode.[20] This catalysis is brought about by a rapid redox reaction between the reduced anthraquinone and dioxygen. The anthraquinone is regenerated in the process and then re-reduced at the metal electrode. Electron transfer between a bare platinum electrode and dioxygen is much slower at the same electrode potential.

The group of pyrroles (3)[21] and the compound (4)[22] offer a comparison of

[17] P Audebert, G Bidan, and M Lapkowski, *J Electroanal Chem*, 1987, **219**, 165
[18] C P Andrieux and P Audebert, *J Electroanal Chem*, 1989, **261**, 443
[19] C P Andrieux, P Audebert, and J -M Saveant, *Synth Met*, 1990, **35**, 155
[20] P Audebert and G Bidan, *J Electroanal Chem*, 1987, **238**, 183
[21] A Haimerl and A Merz, *Angew Chem, Int Ed Engl*, 1986, **25**, 180
[22] T Inagaki, M Hunter, X Q Yang, T A Skotheim, and Y Okaoto, *J Chem Soc, Chem Commun*, 1988, 126



properties for closely similar 1- and 3-substituted pyrroles. Under the conditions necessary for oxidative polymerization (*E ca.* 1.0 V *vs.* SCE) the ferrocene residues will also be oxidized to ferricinium. For all the examples, homopolymerization resulted in uneven deposits. Satisfactory films could only be obtained by co-polymerization in the presence of pyrrole or *N*-methylpyrrole.

5 Anion Exchange in Oxidized Poly(pyrrole)

The ion exchange properties of the oxidized form of poly(pyrrole) have been used to immobilize anionic species on coated electrode surfaces. Fixation of $[Fe(CN)_6]^{3-}$ in this way can be demonstrated by monitoring the induced redox behaviour. The counterion is released into the solution by pulsing the film at -0.4 V *vs.* SCE, at which potential the pyrrole units are in the neutral state.[23] The much larger anionic species, *meso*-tetrakis(4- sulphonatophenyl)porphyrin-cobalt, is also incorporated into poly(pyrrole). It behaves as a catalyst for oxygen reduction. Thus, the potential for oxygen reduction at a bare gold electrode is -0.2 V *vs.* SCE and this potential is shifted to $+0.2$ V when the gold is coated using poly(pyrrole) doped with the anion. Complexes of tetrasulphonatophthalocyanin with manganese,[24] iron,[25] and cobalt[26] can be incorporated into poly(pyrrole) and these materials also catalyse the reduction of oxygen.

The binding capacity of poly(pyrrole) varies with potential and disappears when the film is reduced. Also, bulky ions cannot be incorporated into a preformed poly(pyrrole) by ion exchange. Rather, they must be the anion present in solution during the polymerization stage. The capability of polypyrroles to bind by an ion exchange mechanism is much improved by linking ionic substituents to the pyrrole monomer.

In one approach to the binding of cations, the monomer (5) was polymerized and the resulting polymer used to bind cobalt ions.[27] In another approach to the binding of anions, the monomers (6)—(8) have been polymerized and the resulting films used to bind ferricyanide or ruthenate ions.[28] Poly(6) incorporates ferricyanide ions when soaked in an acetonitrile solution and these ions are

[23] L. L. Miller, B. Zinger and Q.-N. Zhou, *J. Am. Chem. Soc.*, 1987, **109**, 2267; J. Tietje-Girault, J. M Anderson, I. MacInnes, M. Schroder, G. Tennant, and H. H. Girault, *J. Chem. Soc., Chem. Commun.*, 1987, 1095; G. Lian and S. Dong, *J. Electroanal. Chem.*, 1989, **260**, 127.

[24] F. Bedioui, C. Bongas, J. Devynk, C. Bied-Charreton, and C. Hinnen, *J. Electroanal. Chem.*, 1986, **207**, 87

[25] A. Elzing, A. van der Putten, W. Visscher, and E. Barendrecht, *J. Electroanal. Chem.*, 1987, **233**, 113.

[26] T. Skotheim, M. Velazquez-Rosenthal, and C. A. Linkous, *J. Chem. Soc., Chem. Commun.*, 1985, 612. T. Osaka, K. Naoi, T. Hirabayashi, and S. Nakamura, *Bull. Chem. Soc. Jpn.*, 1986, **59**, 2717.

[27] P. G. Pickup, *J. Electroanal. Chem.*, 1987, **225**, 273.

[28] S. Cosnier, A. Deronzier, J.-C. Moutet, and J. F. Roland, *J. Electroanal. Chem.*, 1989, **271**, 69.

retained on rinsing in fresh solution or on cyclic voltammetry. Poly(7) also incorporates ferricyanide ions but these are slowly rinsed out. Incorporation of ferricyanide ions into poly(8) is very small. In general, poly(6) offers the best possibilities of the three materials for the incorporation of electroactive anions. The anions are retained even when the polypyrrole backbone has been destroyed by oxidation at +1.2 V *vs.* SCE.

Poly(6) and poly(7) have been used to adsorb anions from potassium ruthenate. The adsorbed anion was reduced electrochemically to ruthenium dioxide. Such an electrode based on poly(6) prepared on carbon felt has been used to catalyse the oxidation of benzyl alcohol to benzaldehyde at 1.0 V *vs.* SCE on a 10 millimolar scale. The ruthenium is oxidized to the RuO_4^{2-} ion which then oxidizes the alcohol with formation of ruthenium dioxide. The catalyst RuO_4^{2-} is subsequently regenerated electrochemically.[28]

Platinum microparticles have been incorporated into a polypyrrole film by first carrying out an ion-exchange step with chloroplatinate ion followed by the electroprecipitation of platinum. Poly(pyrrole)[29] has been loaded in this way as also has poly(5).[30] The microparticulate platinum electrode incorporated into poly(6) grown on carbon felt was very effective in aqueous ethanol for the electrochemical hydrogenation of the alkene bond in enenones, of benzaldehyde to benzyl alcohol, and of nitrobenzene to aniline.[30]

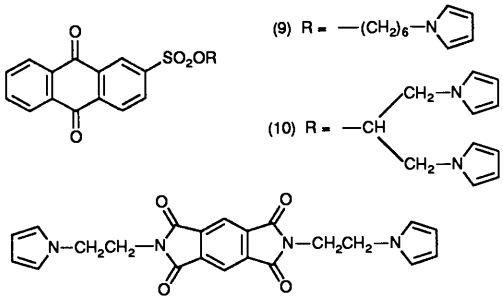
The bulky cluster $[Fe_4S_4(SPh)_4]^{2-}$ can be bound from acetonitrile onto preformed poly(6). Transferring the electrode to an aqueous solution achieves the interfacing of this hydrophobic cluster with an aqueous electrolyte.[31]

6 Poly(pyrrole) with Reducible Substituents

An initial objective for research has been to explore the size and type of substituent that can be attached to pyrrole while still retaining good mechanical and adhesive properties for the corresponding polymer. It is also interesting to see if the crosslinking introduced by polymerization of monomers having two pyrrole units per reducible group will influence the electrochemistry of this group within the polymer matrix. All the pyrroles discussed in this section carry N-substituents.

In the case of polymers derived from monomers (9) and (10) the only indication of an effect of polymer structure was found with poly(9) where the response of the anthraquinone in dimethyl sulphoxide led to slightly broader peaks than usual on cyclic voltammetry. Peak maxima were at the same potential for the two polymers. These polymers were very stable to cycling through the $AQ/AQ^{\bullet -}$ region. However, when cycles included the $AQ^{\bullet -}/AQ^{2-}$ couple, then a decrease in peak height with time was observed on continuous cyclic voltammetry. This decrease is presumably due to protonation of the negative ions. These anthraquinone-containing polymers, coated on platinum, catalysed the reduction of oxygen.[17]

[29] S. Holdcroft and B. C. Funt, *J. Electroanal. Chem.*, 1988, **240**, 89.
[30] L. Coche and J.-C. Moutet, *J. Am. Chem. Soc.*, 1987, **109**, 6887.
[31] C. J. Pickett and J.-C. Moutet, *J. Chem. Soc., Chem. Commun.*, 1989, 188.



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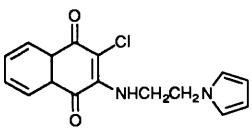

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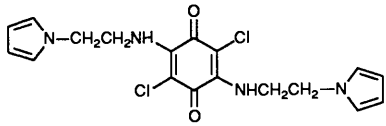

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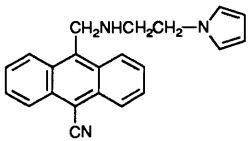
By contrast, the pyrromelitimide group in poly(11) showed a considerably different redox behaviour compared to that for the monomer. In acetonitrile the monomer shows two reversible one-electron transfer steps centred at -0.8 and -1.5 V *vs.* SCE, respectively. The more negative step is not seen in the redox behaviour of the polymer and the first step shows a much broader wave in cyclic voltammetry. A colour change from green to red accompanies the second electron transfer step of the monomer. Since the polymer film becomes red at the negative side of the observed redox peak, here both one-electron transfer steps must be concealed under the one peak. Thus, the second electron transfer step of the pyrromelitimide group in the polymer is moved to substantially less negative potentials compared to its position for the monomer.[32]

Not all attempts to polymerize a substituted pyrrole are successful. Thus, attempts to polymerize (12) oxidatively did not lead to a clean reaction. Substantial amounts of dark coloured soluble products were formed. The polymer film which did form under these conditions showed a redox response due to the $NQ/NQ^{\bullet -}$ couple. This response rapidly decreased on cyclic voltammetry and had disappeared after three cycles.[33]

The benzoquinone (13), was successively polymerized by oxidation of the pyrrole rings. The electrochemistry of the quinone unit in this polymer is modified compared to that shown by the monomer. The anodic and cathodic waves on cyclic voltammetry due to the $BQ/BQ^{\bullet -}$ couple are broader in the polymer and the cathodic wave was moved 0.22 V more negative. Not all the $BQ^{\bullet -}$ units were discharged during the anodic phase of cyclic voltammetry so that, after repeated scanning, the $BQ/BQ^{\bullet -}$ couple response decreased in height.

[32] J. Grimshaw and S. D. Perera, *J. Electroanal. Chem.*, 1990, **278**, 279.
[33] J. Grimshaw and S. D. Perera, *J. Electroanal. Chem.*, 1990, **281**, 125.



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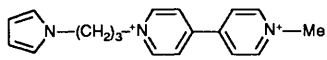

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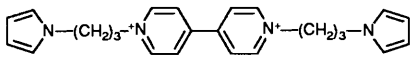


(16)

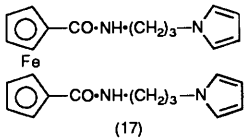
After resting the film to allow complete discharge, the original electrochemical behaviour is restored. It is suggested that the cross-linking within this film limits ion motion and hence the transport of charge through the film.[33]

Films of poly(14) show unusual electrochemical behaviour. When the polymer is placed at a potential where the cyanoanthracene group accepts an electron to form the radical-anion, charging of the film occurs rapidly at approximately constant current density, then in a few milliseconds the current fall to zero.[34] This behaviour strongly suggests that in the film the cyanoanthracene units are stacked in zones which allow rapid transport of charge, and also counter-ions, through the structure. Charging ceases either when the electron acceptor units are all engaged, or when no more counter-ions can be accommodated in the cross-linked structure.

Pyrroles (15) and (16), with attached pyridinium groups, have been successfully polymerized by controlled potential oxidation to give films which show the reversible redox chemistry of the bipyridinium group.[35,36] This group was reduced at the expected potential in two one-electron steps. A film of poly(16) on platinum or on glassy carbon has been used to promote the reduction of aliphatic halogen compounds, dibromostilbene to stilbene[36] and hexachloroacetone to pentachloroacetone.[37] In these reactions the reduced form of the bipyridinium acts as an electron shuttle, transferring an electron to the organic substrate, then being itself re-reduced by reaction with the electrode and adjacent redox centres. When conditions are such that several layers of electrode coating are involved in this way with electron transfer to the substrate, the reaction overall is faster than at a bare metal where only the surface can be involved in electron transfer. There has been a theoretical discussion of the advantages of this mediated, outer-sphere type of electron transfer.[38]

The neutral species from addition of two electrons per bipyridinium group mediate the reduction of dibromostilbene, whereas both the radical-cation and the neutral species mediate the reduction of hexachloroacetone.

[34] J Grimshaw and S D Perera, *J Electroanal Chem*, 1989, **265**, 335
[35] G Bidan, A Deronzier, and J -C Moutet, *J Chem Soc, Chem Commun*, 1984, 1185
[36] L Coche, A Deronzier, and J -C Moutet, *J Electroanal Chem*, 1986, **198**, 187
[37] L Coche and J -C Moutet, *J Electroanal Chem*, 1988, **245**, 313, L Coche and J -C Moutet, *J Electroanal Chem*, 1987, **224**, 111
[38] W J Albery and A R Hillman, *Annu Rep Progr Chem, Sect C*, 1981, **78**, 414, and references cited therein



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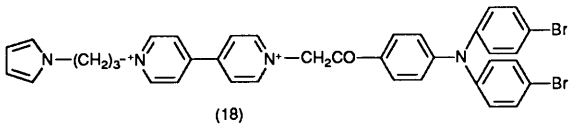

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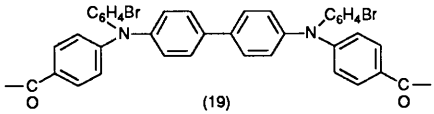

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7 Poly(pyrrole) with Oxidizable Substituents

Polymerization of monomers in this class has the complication that the substituent can be oxidized at a less positive potential than that necessary to polymerize the pyrrole ring. These monomers are usually polymerized successfully by repeated cyclic voltammetry through the electroactive range and farther out to positive potentials where the pyrrole will be polymerized.

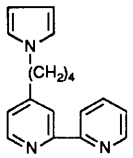
Comment was made previously that the ferrocene-containing polypyrroles derived from (3) and (4) do not give rise to satisfactory films.[21,22] Similar results have been found with poly(17) which can utilize the two pyrrole rings to form a cross-linked film.[39] Copolymerization of these compounds with pyrrole or *N*-methylpyrrole results in much more stable films. All the homopolymer films from (3), (4), and (17) deteriorated rapidly on cyclic voltammetry about the ferrocene response. After about 10 scans the redox behaviour of ferrocene/ferricinium had almost disappeared and could not be restored.

In the polymer derived from (18) there are two electroactive groups on the pyrrole side chain. The triphenylamine residue is reversibly oxidized at 0.92 V *vs.* SCE and the bipyridinium residue is reversibly reduced at −0.71 V *vs.* SCE. The monomer is polymerized by repeated cyclic voltammetry between −0.2 and 1.05 V *vs.* SCE.[40] When this film is placed in a clean solution, repeated cyclic voltammetry at the response of the triphenylamine groups results in a gradual decrease in the current response which is replaced by a new redox couple oxidized at 0.78 V *vs.* SCE while redox behaviour of the bipyridinium group remains unchanged. This new couple is due to the tetraphenylbenzidine residue (19) formed during oxidative coupling of the triphenylamine. Related oxidative coupling reactions have been observed for other triphenylamines in solution. Coupling occurs much more rapidly in the polymer film because of the close proximity of the reacting groups. Dilution of the loading of triphenylamine residues by copolymerization of the monomer with another pyrrole leads to a film that no longer shows the oxidative dimerization.[40]

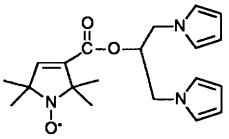
8 Catalysed Oxidation of Alcohols

The oxidation of alcohols to ketones does not proceed in a satisfactory manner

[39] J. G. Eaves, R. Mirrazaei, D. Parker, and H. S. Munro, *J. Chem. Soc., Perkin Trans. 2*, 1989, 373.
[40] A. Deronzier, M. Essakalli, and J.-C. Moutet, *J. Electroanal. Chem.*, 1988, **244**, 163.

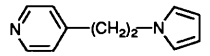


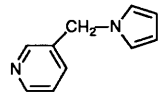
(20)



(21)

$[Ru_3O(CH_3CO_2)_6L_3]^+$

(22) L = 

(23) L = 

at a bare anode. A number of attempts have been made to devise a polypyrrole based electrocatalyst for this process. Mention has already been made of ruthenate based systems[28] where the ruthenate ion is held by ion-pairing with positively charged groups on the polymer side chain.

A more elaborate positively charged ion, poly$[Ru^{II}(20)_3]^{2+}$, has been used in the same way to bind ruthenate ions.[41] In another approach to this problem an electrode has been coated with poly(21).[42] This material shows a reversible redox couple due to the oxidation shown below.

$$>N\text{–}\dot{O} \rightleftharpoons >\overset{+}{N}{=}O + e$$

Addition of an alcohol to the electrolyte solution enhanced the peak in cyclic voltammetry caused by the oxidation $N\dot{O} \longrightarrow N\overset{+}{O}$ and partially suppressed the corresponding cathodic peak. This establishes that the nitroxonium ions oxidize the alcohol to the ketone and are reduced to NOH. Reoxidation of the hydroxylamine so formed to the nitroxonium ion is responsible for the enhanced peak in cyclic voltammetry. Although oxidation of alcohol to ketone could be demonstrated on an analytical scale, on a preparative scale these films were largely destroyed during the process.

More success has been obtained with catalysts derived from ruthenium clusters where the films were obtained by polymerization of monomers (22) and (23).[43] Best results were obtained using a platinum cylinder coated with poly(22). This catalysed the oxidation of benzyl alcohol to benzaldehyde, at 1.62 V *vs.* Ag^+, from dilute solution in acetonitrile. Reduced Ru species generated during this oxidation are re-oxidized electrochemically. This electrode system was stable for several hours.

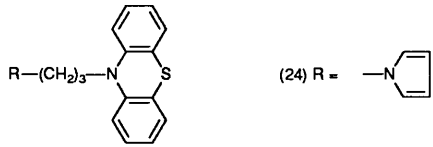
9 Photoassisted Electron Transfer

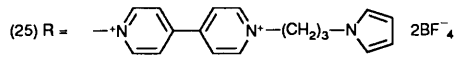
The demonstration of photoassisted electron transfer between a group attached to the polymer and a species in solution has been the object of research. To this end monomers (24) and (25) were polymerized by repeated cycling at positive potentials. Poly(24) showed reversible redox behaviour due to the phenothiazine

[41] L Coche and J-C Moutet, *J Electroanal Chem*, 1988, **245**, 313, S Cosnier, A Deronzier, and J-C Moutet, *Inorg Chem*, 1988, **27**, 2390

[42] A Deronzier, D Limosin, and J-C Moutet, *Electrochim Acta*, 1987, **32**, 1643

[43] S Cosnier, A Deronzier, and A Llobet, *J Electroanal Chem*, 1990, **280**, 213





group.[44] The film was kept at a potential negative of this redox couple and irradiated with visible light while immersed in a solution of tropylium cation. This resulted in a photocurrent. Photoassisted electron transfer between the polymer-based phenothiazine and tropylium cation leads to the phenothiazine radical-cation. Reduction of this radical-cation back to the level of phenothiazine is responsible for the current. The tropylium cation is converted into a radical which undergoes irreversible dimerization.

The polymer prepared from (25) can be expected to undergo photoassisted electron transfer within the polymer because of the two redox units that are present in the side chain.[45] Accounts of experiments in this direction are expected.

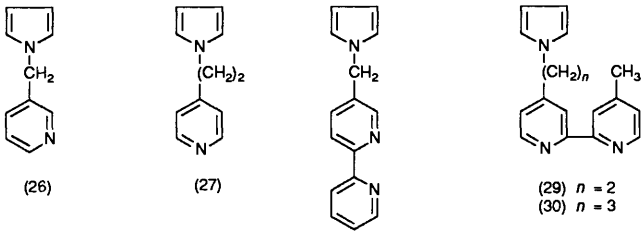
An electrode coated with poly$[Ru^{II}(28)_3]^{2+}$ when kept at a potential where the stable species is Ru^{II} generated a photocurrent in visible light when immersed in a solution containing 4-methylbenzenediazonium fluoroborate as the electron acceptor in acetonitrile.[46] The current results from the reduction of the so formed Ru^{III} complex back to the Ru^{II} state.

10 Polypyrroles with Attached Metal Complexes

A. Pyridine Complexes.—The first reports of the polymerization of pyridine–metal complexes with pyrrole groups attached to the pyridine moiety concluded that $[Ru(byp)_2(26)_2]^{2+}$ and $[Ru(byp)_2(27)_2]^{2+}$ will form films after repeated cyclic voltammetry at a platinum electrode.[10,13] Later, two groups investigated the number of pyrrole units per metal centre that are necessary to allow film formation. They worked with the related ligands (28)[47] and (29),[13] respectively, and reached the same conclusions on the polymer forming ability of this type of ligand–metal complex.

The tris complexes of (28) and (29) with Ru^{II} and the mixed complexes $[Ru(byp)(28)_2]^{2+}$ and $[Ru(byp)(29)_2]^{2+}$ gave stable polymeric films by oxidation on platinum, glassy carbon, or tin oxide. The mixed complexes with only one pyrrole-containing bipyridyl ligand would not form a polymeric film. Thus the film forming ability and the stability of the films obtained from these ruthenium

[44] A. Deronzier, M. Essakalli, and J.-C. Moutet, *J. Chem. Soc., Chem. Commun.*, 1987, 773.
[45] A. Deronzier, M. Essakalli, and J.-C. Moutet, *J. Electroanal. Chem.*, 1988, **244**, 163
[46] S. Cosnier, A. Deronzier, and J.-C. Moutet, *J. Phys. Chem.*, 1985, **89**, 4895.
[47] J. G. Eaves, H. S. Munro, and D. Parker, *Inorg. Chem.*, 1987, **26**, 644.



complexes increases substantially as the number of attached pyrrole groups increases This may be due to cross-linking which makes the resulting polymer less soluble

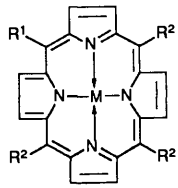
The complexes $[Fe(28)_3]^{2+}$ and $[Cu(28)_2]^{2+}$ have also been polymerized to give stable films on platinum,[47] as has a related bis complex of Cu^{II} [48] Films containing Ru^{II} and Fe^{II} were unstable towards reductive cycling but stable on oxidative cycling between the metal centred redox reactions

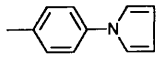
Tris (28) complexes of Co^{II} [49] and Ni^{II} [50] could be oxidatively polymerized on gold but not on platinum or vitreous carbon The cobalt-containing polymer showed a reversible redox couple at $-1\ 09$ V *vs* SCE due to Co^{II}/Co^{I} Reduction of allyl chloride was catalysed by the Co^{I} species formed at potentials more negative than $-1\ 09$ V [49]

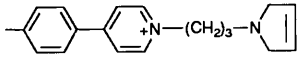
In contrast to the previous example, the complex $[Re(30)(CO)_3Cl]$, which has only one pyrrole ring per metal atom, could be oxidatively polymerized to a stable coating The resulting polymer has been used to effect the catalytic reduction of carbon dioxide to carbon monoxide with good current efficiency However during the experiment about 80% of the electroactivity of the film was destroyed [51]

B. Porphyrin Complexes.—The formation of coherent polypyrrole films containing metalloporphyrin units illustrates the adaptability of this polymer backbone unit Murray[52] first reported the polymerization of tetrakis(*p*-*N*-pyrrolyphenyl)porphyrin and its cobalt complex (31) on platinum or glassy carbon electrodes The monomer was dissolved in dichloromethane containing 0 1 M tetrabutylammonium perchlorate and polymerization was effected by repeated scanning between 0 and 1 1 V *vs* Ag/AgCl The cobalt complex could also be prepared by metallating the porphyrin substituted polypyrrole Other workers[53] reported polymerization of the Ni^{II} porphyrin (32) on platinum by repeated scanning of a solution in dichloromethane This nickel complex showed two

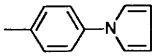
[48] G Bidan B D Blohorn J M Kern and J P Sauvage *J Chem Soc Chem Commun* 1988 723
[49] F Daire F Bedioui J Dveynck and C Bied Charreton *J Electroanal Chem* 1987 **224** 95
[50] F Daire F Bedioui J Devynck and C Bied Charreton *Electrochim Acta* 1988 **33** 567
[51] S Gosnier A Deronzier and J C Moutet *J Electroanal Chem* 1986 **207** 315
[52] A Bettelheim B A White S A Raybuck and R W Murray *Inorg Chem* 1987 **26** 1009
[53] A Deronzier and J M Latour *J Electroanal Chem* 1987 **224** 295



(31) $R^1 = R^2 =$  $M = Co^{2+}$

(32) $R^2 =$ 

$R^2 = p$ tolyl $M = Ni^{2+}$

(33) $R^1 =$ 

$R^2 = p$ tolyl $M = Mn^{3+}$

reversible redox couples at 1 24 V and −0 84 V *vs* SCE respectively The redox couple at positive potential is due to the metal centre, whereas the couple at negative potential is due to the bipyridinium group

The manganese porphyrin (33) has also been successfully polymerized on vitreous carbon [54] This shows a stable and reversible redox couple at −0 3 V *vs* SCE due to Mn^{III}/Mn^{II} The Mn^{II} species formed has been shown to activate molecular oxygen Thus, the system consisting of a polymer coated electrode at −0 5 V *vs* SCE and oxygen effects the oxidation of 2,6-di-t-butylphenol to 2,6-di-t-butylbenzoquinone This same system converts *cis*-cyclooctene into the epoxide During these reactions the active centre of Mn^{II} is converted into Mn^{III} and then reactivated by reduction at the electrode [55]

C. Cyclam Complexes.—Collin and Sauvage [56] reported the polymerization of 3-[4-(pyrrol-1-yl)-butyl]-1,5,8,12-tetraazacyclotetradecane-Ni^{2+} on glassy carbon electrodes Cyclic voltammetry of the monomeric Ni–cyclam complex showed two redox couples due to Ni^{III}/Ni^{II} and Ni^{II}/Ni^{I} at 0 98 V and −1 41 V *vs* SCE, respectively Polymer films were grown by repeated cyclic voltammetry at a vitreous carbon electrode They showed the characteristic Ni^{III}/Ni^{II} redox couple but the Ni^{II}/Ni^{I} couple at negative potentials was not observable

11 Conclusions

The oxidative polymerization of pyrroles with a very wide range of N-substituents has been shown to give stable films on electrodes Substituents with redox centres varying in size and character from small organic groups to bulky metal

[54] F Bedioui A Merino J Devynck C E Mestes and C Bied Charreton *J Electroanal Chem* 1988 **239** 433
[55] F Bedioui P Moisy J Devynck L Salmon and C Bied Charreton *J Mol Catal* 1989 **56** 267
[56] J C Collin and J P Sauvage *J Chem Soc Chem Commun* 1987 1075

complexes are tolerated Redox centres may be active at either positive or negative potentials Attempts to attach catalytic centres to the polypyrrole are continuing, achievements so far have been with catalysts for the oxidation of alcohols and for the activation of molecular oxygen Polypyrrole films with positively charged centres on the N-substituent have been used to immobilize ruthenate ions, which are useful electrocatalysts for the oxidation of alcohols So far only very small scale reactions have been acheived, but the principle of binding catalysts to an electrode in order to achieve an electrocatalytic process has been demonstrated