

Influence of pH on the Electropolymerisation of 2-Aminophenol and 2-Aminobenzyl Alcohol

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Abstract: The electrochemical oxidation and polymerisation of 2-aminophenol and 2-aminobenzyl alcohol in aqueous solutions of different pH values has been studied. Polymer films of the studied monomers on gold electrodes were synthesized. The behaviour of both monomers is quite different, illustrating the resonance effect of the hydroxyl group being bound directly to the benzene ring for 2-aminophenol. For each compound it is shown that oxidation in acidic solutions is most difficult due to the protonation of the amine group. These polymer films can be used for applications such as corrosion protection and as structures from which textured electrodes, microelectrode arrays for example, can be generated.

Keywords: electrochemical polymerisation; oxidation; resonance; voltammetry.

1. INTRODUCTION

The published work on the polymerisation of 2-aminobenzyl alcohol is quite limited [1-3]. Lei et al.[3] have prepared a novel conducting copolymer with different compositions based on aniline and 2-aminobenzyl alcohol using a chemical oxidative polymerization method. The authors demonstrated that 2-aminobenzyl alcohol copolymerizes with aniline using this method [3] It was shown that the conductivities decreased with increasing molar ratio of 2-aminobenzyl alcohol in the copolymer [3].

Rivas and Sanchez [4] studied the polymerisation of 2-aminobenzyl alcohol and aniline derivatives by using ammonium persulphate as oxidizing reagent in hydrochloric acid and hydrochloric acid/acetonitrile in the presence and absence of Cu(II), Ni(II), and Co(II) ions. It was found that the metal cations act as oxidizing agents, increasing the electrical conductivity and thermal stability [4]. Hua and Ruckenstein[5] showed that poly(2-aminobenzyl alcohol) can be grafted with poly(ethylene oxide). Reduced poly(2-aminobenzyl alcohol) was prepared through the acid-mediated polymerization of 2-aminobenzyl alcohol, followed by neutralization with an aqueous ammonium hydroxide solution and reduction with hydrazine [5].

The polymerisation of 2-aminophenol has received widespread attention. Ohsaka et al.[6] have looked at the heterogeneous electron-transfer process at electrode-poly(2-aminophenol) interface and the homogeneous charge-transport process within the poly(2-aminophenol) films. Barbero et al. [7] reported on the formation of electroactive films from acidic solutions of 2-aminophenol and the cyclic dimer 3-aminophenoxazone. It was noted in studying 3 and 4 aminophenol that ortho substitution was required for the formation of ring chain films. The polymerisation is described as a sequential event and the radicals formed upon electrochemical oxidation react chemically to form the polymer.

Barbero et al.[8] has published extensively in the area, studying for example the characteristics of poly (2-aminophenol) films at various pHs.[8] Jackowska et al.[9] propose that the polymerisation pathway is pH dependant. At high and neutral pH they claim that nitrogen-nitrogen coupling of 2-aminophenol radical cation dominates to form a linear 2,2-dihydroxyazobenzene. At low pHs nitrogen to carbon coupling predominates and 3-aminophenoxazone is formed in the main. This is supported by Genies et al.[10] who states that whilst polymerisation over a broad pH range is possible only those polymers formed under acidic conditions are electro-active. Mu[11, 12] has published two related papers on the co-polymerisation of aniline and 2-aminophenol.

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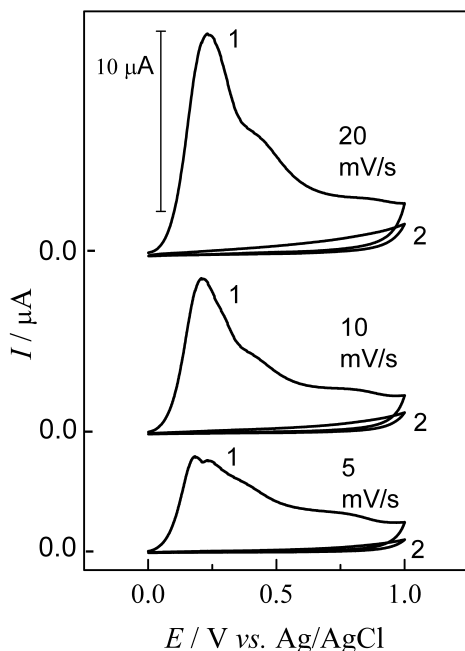


Figure 1. Cyclic voltammograms for the oxidation and polymerisation of 100 mmol L⁻¹ of 2-aminophenol in neutral, aqueous solutions using a gold working electrode with a diameter of 1.6 mm at various sweep rates (first two CV's shown at each sweep rate).

It appears that polymer films formed from the anodic oxidation of 2-aminophenol are quite permeable.[2, 13, 14] Bonfranceschi et al.[13] studied the response of a poly(2-aminophenol) covered gold electrode to a variety of redox couples including ferricyanide/ferrocyanide and 1,4-dihydroxybenzene/benzoquinone. A rotating disc study was performed and linear Koutecky Levich plots were obtained, demonstrating that the films are permeable to certain mediators. Ortega[2] and Hernandez et al.[14] studied the deposition of both copper and silver at poly(2-aminophenol) covered platinum electrodes. Two different models were proposed to explain the observed results. The first was that of metal deposition at conducting strands on the polymer surface. The second was that of metal deposition on the underlying platinum through pinhole defects in the polymer. Their conclusion was that the second model was the more valid for porous films. This provides a useful reference system for the work of this paper. In the present study, the electrochemical behaviour of 2-aminophenol will be compared to that of 2-aminobenzyl alcohol.

2. EXPERIMENTAL

2.1. Chemicals

All chemicals were analytical grade and used without further purification. 2-aminophenol (99%), 2-aminobenzyl alcohol (98%), potassium chloride (99%), potassium ferrocyanide trihydrate (>98%), potassium ferricyanide (>98%) were all procured from Alfa Aesar GmbH & Co KG, Karlsruhe, Germany. Sodium hydroxide (98%) and sulfuric acid (95-98%) were purchased from PRS, Panreac, Spain.

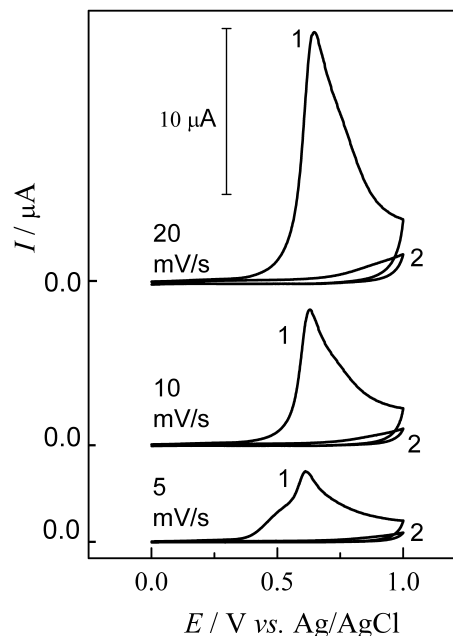


Figure 2. Cyclic voltammograms for the oxidation and polymerisation of 100 mmol L⁻¹ of 2-aminobenzyl alcohol in neutral, aqueous solutions using a gold working electrode with a diameter of 1.6 mm at various sweep rates (first two CV's shown at each sweep rate).

2.2. Film Preparation

All electrochemical experiments were carried out in a three-electrode glass cell. An EZstat Pro potentiostat (NuVant Systems Inc., IN, USA) equipped with an EZware 2013 V7 was used throughout the course of the work. Before each cyclic voltammetry (CV) experiment, the gold working electrode was polished mechanically for 2 min using 0.05 μm alumina on polishing pads (PK-4 polishing kit, BASi, IN, USA). This was followed by flushing the electrode surface with deionised water for a few minutes, in order to remove any residual alumina. The polished electrode was then electrochemically tested using a solution of 5 mmol L⁻¹ ferricyanide/ferrocyanide containing 100 mmol L⁻¹ potassium chloride between -0.2 V and 0.6 V vs. Ag/AgCl, 3.0 mol L⁻¹ KCl at a sweep rate of 20 mV s⁻¹ for 2 sweeps of potential.

The monomers 2-aminophenol and 2-aminobenzyl alcohol were electrochemically oxidised at 1.6 mm diameter gold electrodes. Acidic, basic and neutral solutions of 100 mmol L⁻¹ of 2-aminophenol and 100 mmol L⁻¹ of 2-aminobenzyl alcohol were prepared using either potassium chloride (100 mmol L⁻¹), sulphuric acid (100 mmol L⁻¹) or sodium hydroxide (100 mmol L⁻¹) as the supporting electrolyte. The electrochemistry of said solutions was studied by sweeping the potential of the working electrode between 0 V and 1 V vs. Ag/AgCl, 3.0 mol L⁻¹ KCl at various sweep rates (5, 10 and 20 mV s⁻¹) for 5 sweeps of potential. The counter electrode was a 230 mm coiled platinum wire mounted in a CTFE cylinder. All electrodes were manufactured by BASi Preclinical Services, IN, USA. After the polymerisation stage, a cyclic voltammetry run was conducted in ferricyanide/ferrocyanide solution to insure that the film formation was achieved and this was done at the same settings as mentioned previously.

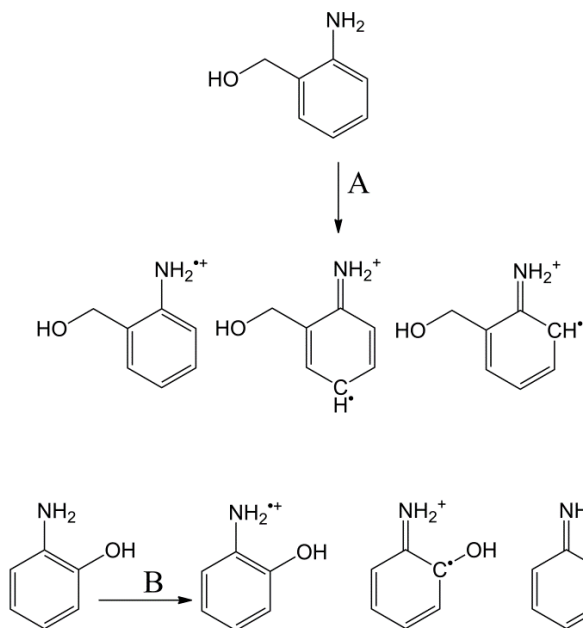


Figure 3. A. Oxidation of 2-aminobenzyl alcohol and B. oxidation of 2-aminophenol in neutral solutions.

3. RESULTS AND DISCUSSION

There are two measured pKa values, 4.78 and 9.97, associated with 2-aminophenol [15]. These pKa values indicate that 2-aminophenol is amphoteric and will exist primarily as the neutral species at pH values of 5 to 9. At the first pKa of 4.78 the neutral molecule and monovalent cation co-exist at equal concentration. The neutral species and monovalent anion have equal concentrations at the second pKa of 9.97. Consequently the species that may be electrochemically oxidised is dependent on the pH of the solution. In contrast 2-aminobenzyl alcohol has only one pKa value of 3.5[16] related to the ionisation of the amino group on the benzene ring. The hydroxyl group which is not bonded directly to the benzene ring behaves similarly to benzyl alcohol, an aromatic compound with a pKa in excess of 15.

Figures 1 and 2 present the cyclic voltammograms for the oxidation and polymerisation of 2-aminophenol and 2-aminobenzyl alcohol in neutral solutions at which pH the uncharged species predominate. The onset and peak potentials for oxidation and polymerisation are different for both compounds, being 0 and 0.25 V vs. Ag/AgCl, 3.0 mol L⁻¹ KCl for 2-aminophenol and 0.4 and 0.6 V vs. Ag/AgCl, 3.0 mol L⁻¹ KCl for 2-aminobenzyl alcohol. For both compounds scans subsequent to the first exhibit much lower currents demonstrating that an insulating polymer film is formed by the electropolymerisation reactions.

The oxidation of 2-aminophenol at neutral pH first proceeds by the loss of an electron from the lone pair on the nitrogen atom in a similar manner to the oxidation of 3-aminophenol as shown by Kennedy et al.[17] The oxidation of 2-aminobenzyl alcohol, as shown in Figure 3(A), must proceed in a similar fashion as the aliphatic alcohol group does not participate in electrochemical oxidation reactions. The radical cation formed upon the oxidation of 2-aminophenol is stabilized by resonance structures that results in redistribution of electron density onto the oxygen atom, as shown in Figure 3(B). This lowers the oxidation potential relative to what

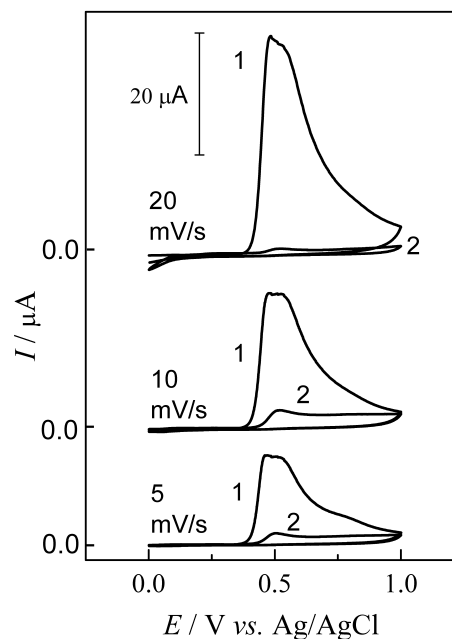


Figure 4. Cyclic voltammograms for the oxidation and polymerisation of 100 mmol L⁻¹ of 2-aminophenol in 100 mmol L⁻¹ of sulphuric acid using a gold working electrode with a diameter of 1.6 mm at various sweep rates (first two CV's shown at each sweep rate).

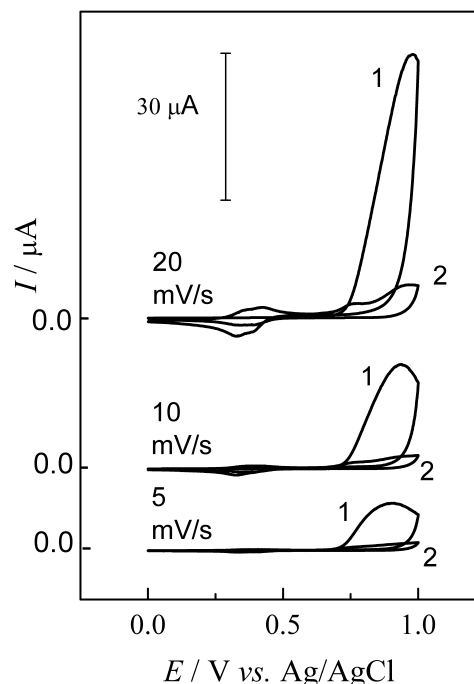


Figure 5. Cyclic voltammograms for the oxidation and polymerisation of 100 mmol L⁻¹ of 2-aminobenzyl alcohol in 100 mmol L⁻¹ of sulphuric acid using a gold working electrode with a diameter of 1.6 mm at various sweep rates (first two CV's shown at each sweep rate).

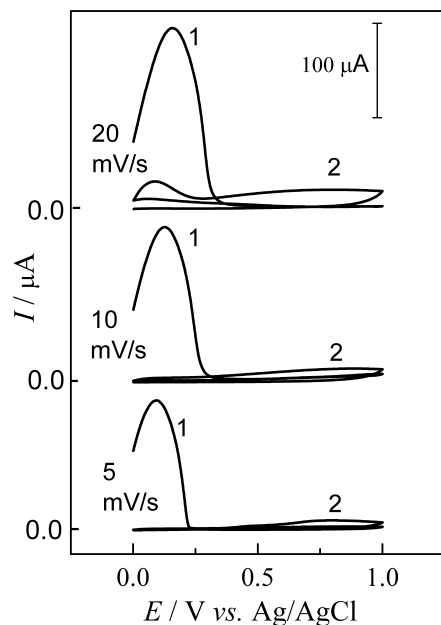


Figure 6. Cyclic voltammograms for the oxidation and polymerisation of 100 mmol L^{-1} of 2-aminophenol in 100 mmol L^{-1} of sodium hydroxide using a gold working electrode with a diameter of 1.6 mm at various sweep rates (first two CV's shown at each sweep rate).

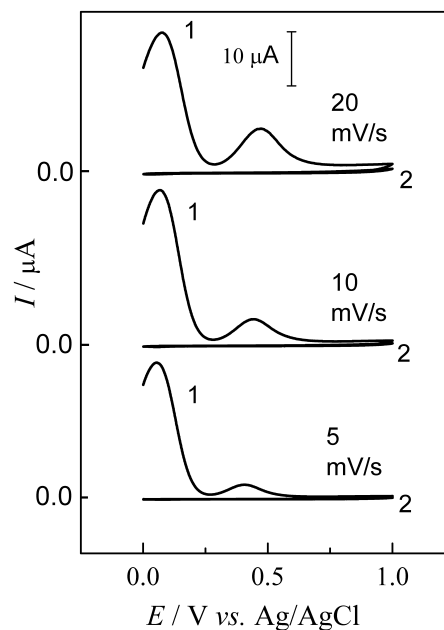


Figure 7. Cyclic voltammograms for the oxidation and polymerisation of 100 mmol L^{-1} of 2-aminobenzyl alcohol in 100 mmol L^{-1} of sodium hydroxide using a gold working electrode with a diameter of 1.6 mm at various sweep rates (first two CV's shown at each sweep rate).

it would be in the absence of this interaction. Such resonance stabilisation is not possible for 2-aminobenzyl alcohol and the potentials that characterize the electrochemical oxidation are more positive.

The pH of solutions of 2-aminophenol and 2-aminobenzyl alcohol in 100 mmol L^{-1} sulphuric acid are 1.5 and 1.6, which is lower than the respective pKa values. Therefore the amine group of both 2-aminophenol and 2-hydroxybenzyl alcohol is protonated in these solutions. This has a significant influence on the oxidation and polymerization of the monomers; the onset and peak potentials being 0.4 and 0.5 V vs. Ag/AgCl for the oxidation of 2-aminophenol and 0.75 V and 0.9 V vs. Ag/AgCl for 2-aminobenzyl alcohol as shown in Figures 4 and 5. The potentials for 2-aminophenol are very similar to those observed for 1,2-dihydroxybenzene in 100 mmol L^{-1} sulphuric acid as determined by Barham et al.[18] This suggests that oxidation, dimerisation and polymerization of 2-aminophenol occurs through the hydroxyl group given that no lone pair of electrons are present on the nitrogen atom. The oxidation of 2-aminobenzyl alcohol is also more difficult than at neutral pH, more difficult even than for 2-hydroxybenzyl alcohol in acid solutions for which the onset and peak potentials are 0.6 V and 0.75 V vs. Ag/AgCl as determined by Barham et al.[18] This illustrates the difficulty of oxidizing aromatic species when there are no atoms bound to the benzene ring with unbonded electron pairs. It is perhaps possible that either oxidation occurs at first for the small proportion of molecules will exist in the unprotonated state or that an electron is stripped from a nitrogen-hydrogen bond.

A solution of 100 mmol L^{-1} 2-aminophenol in 100 mmol L^{-1} sodium hydroxide exhibits a pH of 12.5 as does a solution of 100 mmol L^{-1} 2-aminophenol in 100 mmol L^{-1} sodium hydroxide. At this pH 2-aminophenol is a monovalent anion, a proton having been lost from the hydroxyl group, and 2-aminobenzyl alcohol is

uncharged. The onset and peak oxidation potentials for 2-aminophenol, as shown in Figure 6, are nearly identical to the values at neutral pH despite the predominant form of the compound being different at these different pH values. As described previously the oxidation of 2-aminophenol occurs initially at least through the loss of an electron from the lone pair of electrons on the nitrogen atom, with stabilization of the radical formed occurring through resonance interactions of the ortho orientated amine and hydroxyl groups. The similarity in oxidation potentials can then be understood in the context of the ionization of 2-aminophenol in basic solutions not altering the chemical state of the amine group. However, it has also been demonstrated by Barham et al. [18] that ionisation of the hydroxyl group has a large effect on the energy of the HOMO of similar aromatic molecules making it easier to oxidise the compound so perhaps the electron can be thought of as being removed from the oxygen atom.

Cyclic voltammograms for the oxidation and subsequent polymerisation of 2-aminobenzyl alcohol in 100 mmol L^{-1} sodium hydroxide are presented in Figure 7. The potentials are very similar to those for 2-aminophenol in sodium hydroxide and significantly less than those for 2-aminobenzyl alcohol at neutral pH. The nature of 2-aminobenzyl alcohol is the same in basic and neutral solutions (i.e. the compound is uncharged) and therefore another cause must be responsible for the lower oxidation potential. It is possible that the oxidation of 2-aminobenzyl alcohol is dependent on pH and the potential of the oxidation reaction varies with pH according to the Nernst equation. However the oxidation of 2-aminophenol does not display this dependence and it would seem unlikely that the oxidation of the amine functional group would be so different. A more likely explanation perhaps is that the dimerization reactions occurring after the initial oxidation (these reactions involving the genera-

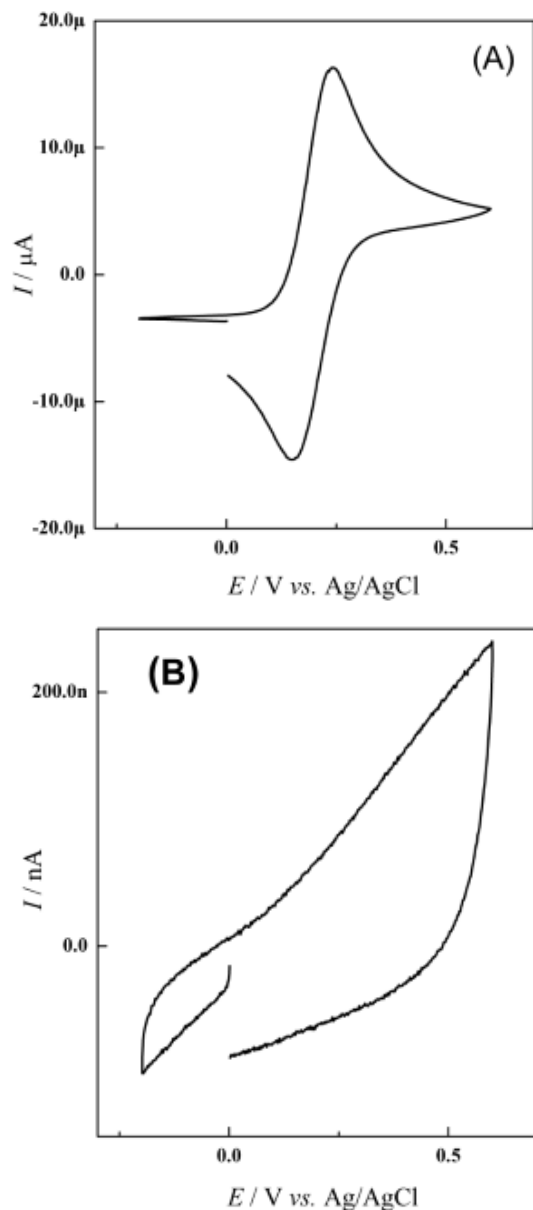


Figure 8. (A) A typical cyclic voltammogram run of polished gold electrode tested in 5mM ferricyanide/ferrocyanide 100 mmol L⁻¹ of KCl solution (before polymerisation), (B) A typical cyclic voltammogram run of the same gold electrode after the polymerisation of 2-aminobenzyl alcohol in 100 mmol L⁻¹ of sodium hydroxide.

tion of protons) are less hindered in basic solutions than in neutral or acidic solutions.

Conclusive proof of the presence of a polymer film on the electrode surface is shown in Figure 8. In Figure 8 (A), a typical cyclic voltammogram run of a gold electrode after mechanical polishing with a slurry of 0.05 μm alumina powder is presented. After the polishing stage the electrode was immediately tested in a 5 mmol L⁻¹ ferricyanide/ferrocyanide solution containing 100 mmol L⁻¹ KCl supporting electrolyte.

In contrast, Figure 8 (B) presents a typical cyclic voltammogram

run of the same gold electrode tested in the same solution after electropolymerisation of 2-aminobenzyl alcohol in 100 mmol L⁻¹ sodium hydroxide. It can be clearly seen that the current is dropped sharply into the nanoamp range and the smooth peaks feature has totally disappeared from the scans.

4. CONCLUSIONS

The compounds 2-aminophenol and 2-aminobenzyl alcohol can both be electrochemically oxidised and polymerised from neutral, acidic and basic aqueous solutions. Oxidation of 2-aminophenol in basic and neutral solutions occurs at very similar potentials, but oxidation in acidic solutions is more difficult. The behaviour of 2-aminobenzyl alcohol is different. Oxidation and polymerisation of this compound become progressively more difficult as pH decreases from basic to acidic conditions. Future papers will focus on applications for these polymer films, including corrosion protection and formation of microelectrode arrays.

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