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A study of the effects of acid on the polymerisation of pyrrole, on the oxidative polymerisation of pyrrole and on polypyrrole

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The polymer products arising from the hydrochloric acid treatment of aqueous pyrrole were shown to have spectroscopic data consistent with alternating pyrrole and pyrrolidine units with varying degrees of ring opening of the pyrrole units. The acid catalysed polymerisation of pyrrole offers a facile route to polymers with amine and carbonyl functional groups, which could be further derivatised. The products were polydisperse spheres; however the use of steric stabilisers induced monodisperse sphere formation and a concomitant ten fold decrease in size. Dilute nitric acid treatment of aqueous pyrrole gave polydisperse spheres (and ovoid shapes) in lower yield, plus a small proportion of curious particles which resembled pitted olives. The presence of acid in the reaction mixture of pyrrole and ferric ions was shown to have a relatively small effect on the conductivity of the resultant polypyrrole. The ability of polypyrrole to withstand harsh acidic conditions was assessed. Polypyrrole was shown to possess significant conductivity even after treatment with boiling concentrated hydrochloric acid.

Introduction

There have been many reports[1–3] of the oxidation of pyrrole to produce polypyrrole but the acid promoted polymerisation has been little studied.[4] The control of pH may be an important factor in the synthesis of highly conducting polypyrrole.[5] It has been suggested that low pH lowers the conductivity of polypyrrole, possibly by incorporation of pyrrolidine into the growing polymer giving rise to saturated linkages.[6] This is substantiated by the fact that 2,5-dipyrrol-2-ylpyrrolidine is known[4] to be formed by protonation of pyrrole at low pH. No previous studies have been reported which have investigated the possibility that oxidatively-produced polypyrrole may be contaminated with particles of acid-produced polypyrrole, nor have there been any previous reports published of the morphology of the polypyrrole produced by acid means. However "pyrrole red" was first synthesised in the nineteenth century,[7] Potts and Smith[8] analysed an oligomer (a trimer) product from the action of acid on pyrrole in 1957, and a re-investigation by Lamb and Kovacic[4] (1980) confirmed the structure of the trimer and undertook a limited analysis of the polymer produced by the action of trifluoroacetic acid on pyrrole.

Many synthetic procedures for preparing conducting polypyrrole involve highly acidic conditions and extensive reaction times (24 hours is not uncommon). Hydrogen ions are created as an inevitable part of the pyrrole polymerisation (approximately 2 moles of acid per mole of pyrrole polymerised). Furthermore ferric ions are commonly used in an aqueous environment for the oxidative polymerisation of pyrrole and under these circumstances the reaction conditions are made significantly more acidic due to extensive hydrolysis of the ferric ions. For example the initial pH of a solution of 0.1 mol dm^{-3} ferric nitrate is 1.5.[9]

For a similar π-conjugated system, Naarman *et al.*[10] have shown that polyacetylene exhibits an increase in conductivity of two orders of magnitude when improved synthetic techniques reduced the percentage of sp^3 carbons from 1% to an undetectable amount. This may also be the situation for polypyrrole syntheses: a decrease in the number of sp^3 carbon centres arising from H^+ attack on pyrrole units may enhance the conductivity.

Hence a study was undertaken of the effects of acid on the polymerisation process involving pyrrole and ferric ions and on the polymer products. A further reason for a study of the products of acid polymerised pyrrole is justified to aid the understanding of significant electrorheological effects recently reported[11] for polypyrroles prepared in acidic conditions. Concentrated dispersions of these types of materials have produced large viscosity changes which are reversible and reproducible, under ac and dc applied electric fields.

Experimental

Materials

Reagents were purchased from the Aldrich Chemical Company (Dorset, UK). Pyrrole was distilled before use. Aqueous solutions of pyrrole (0.75 mol dm^{-3}) were prepared with doubly distilled water and filtered through a 0.22 μm filter before use. The polyvinyl alcohol (PVA, 88% hydrolysed, $\bar{M}_w$ 115 000) was used as received, as was polyvinylpyrrolidone (PVP, $\bar{M}_w$ 350 000). Acetonitrile was dried with calcium hydride and distilled prior to use.

Analyses

Scanning electron microscopy was carried out using an Hitachi S-450 scanning electron microscope; the accelerating voltages used were in the range 9.9–11.0 kV, and the values are as described on the figures. Samples were prepared for microscopy by sputter coating with gold, using an Emscope SC500 sputter coating unit. Infrared spectra were obtained using a Perkin Elmer 1760 FTIR spectrometer, with a resolution of 2 cm^{-1}. Samples were ground and KBr discs prepared of the polymers at 10 tons pressure for 30 seconds. The ^{13}C NMR measurements were undertaken at 298 K and at a spin rate of 4035 Hz and a frequency of 75.43 MHz using a Varian VXR300 at Durham University Industrial Research Laboratories. An external standard was used, adamantane, using the 38.4 ppm peak. X-Ray photoelectron spectroscopy (XPS) studies were

carried out using a VG Scientific ESCALAB Mk 11 instrument. Lineshape analysis was performed on each peak in an attempt to resolve the broad signals. Al-Kα radiation was used as the X-ray source. Bonding energies were adjusted so that the main C1s peak occurred at 285.00 eV and atomic percentages were calculated from the peak areas using standard atomic sensitivity factors. Differential scanning calorimetry (DSC) work was undertaken on a Perkin Elmer 7 Thermal Analysis system. A heating rate of 10 K min^{-1} was used, in air under static conditions, using sealed stainless steel pans. Conductivity measurements were determined using a 4 point probe method at 15 °C, on disks of material (10 mm diameter).

Preparation of the polymers

Reactions were undertaken under nitrogen and at room temperature unless otherwise specified. All the recovered material was dried at 70 °C *in vacuo* (2 mmHg) for 4 hours. Material was collected by vacuum filtration unless otherwise stated.

Product 1. An aqueous solution of pyrrole (20 cm^3, 0.75 mol dm^{-3}) was rapidly added to hydrochloric acid (80 cm^3, 7.5 mol dm^{-3}) at 100 °C. The precipitate was filtered after 10 minutes, washed with water (100 cm^3) and then dried. The yield of **1** was 1.07 g (yield 76%).

Products 2 and 3. An aqueous solution of pyrrole (20 cm^3, 0.75 mol dm^{-3}) was rapidly added to hydrochloric acid (80 cm^3, 7.5 mol dm^{-3}). The product was collected by filtration after 80 minutes, washed with water (100 cm^3) and dried. The yield of **2** was 0.08 g. The experiment was repeated by the addition of the pyrrole solution to the acid containing 0.5 g of dissolved PVA. After 80 minutes the product was obtained by the use of high speed centrifugation (10 000 rpm, 10 min), washed with water, re-centrifuged and dried. The yield of **3** was 0.19 g.

Products 4, 5 and 6. An aqueous solution of pyrrole (20 cm^3, 0.75 mol dm^{-3}) was rapidly added to hydrochloric acid (80 cm^3, 2.5 mol dm^{-3}). The product was collected by filtration after 24 hours, washed with water (100 cm^3) and dried. The yield of **4** was 0.13 g. The experiment was repeated with PVA (0.5 g) dissolved in the acid (product **5**) and a sample taken for electron microscopy investigations after 24 hours. The same experiment was repeated with PVP replacing PVA (product **6**), and a sample taken for electron microscopy investigations.

Product 7. An aqueous solution of pyrrole (20 cm^3, 0.75 mol dm^{-3}) was rapidly added to nitric acid (80 cm^3, 2.5 mol dm^{-3}). The product was collected by filtration after 24 hours, washed with water (100 cm^3) and dried. The yield of **7** was 0.35 g.

Product 8. An aqueous solution of pyrrole (20 cm^3, 0.75 mol dm^{-3}) was rapidly added to nitric acid (80 cm^3, 7.5 mol dm^{-3}). The product was collected by filtration after 80 minutes, washed with water (100 cm^3) and dried. The yield of **8** was 0.10 g.

Product 9. Product **2**, 0.50 g, was heated in an oven at 180 °C for 3 days to produce **9**.

Product 10. Ferric chloride hexahydrate (33.75 g, 0.125 mol) was dissolved in water (100 cm^3) and nitrogen bubbled through the solution for 5 minutes. Pyrrole (2.20 g, 0.02 mol) was added with stirring and the reaction continued under nitrogen, with stirring, for 10 minutes. The black precipitate was collected by filtration, washed with water (300 cm^3) and dried. The yield of **10** was 2.19 g.

Products 11 and 12. Anhydrous cupric bromide (4.47 g, 0.020 mol) was dissolved in dry acetonitrile (100 cm^3) and pyrrole (1.34 g, 0.02 mol) added with vigorous stirring. The black precipitate was collected by filtration, washed with acetonitrile (50 cm^3) and dried. This reaction was undertaken for 60 minutes **11** and 2.5 minutes **12**. The yields of products **11** and **12** were 1.18 g and 0.58 g respectively.

Products 13, 14 and 15. Batches of ferric chloride hexahydrate (33.75 g, 0.125 mol) were dissolved in hydrochloric acid (100 cm^3) of three concentrations (0.375 mol dm^{-3}, 0.75 mol dm^{-3} and 1.5 mol dm^{-3}) and deoxygenated with nitrogen for 5 minutes. Pyrrole (2.20 g, 0.033 mol) was added to each of the ferric chloride–acid solutions with stirring and the reaction continued for 10 minutes. The black precipitates were collected by filtration, washed with water (300 cm^3) and dried to give products **13**, **14** and **15** from 0.375 mol dm^{-3}, 0.75 mol dm^{-3} and 1.5 mol dm^{-3} hydrochloric acid respectively. The yields of **13**, **14** and **15** were 2.27 g, 2.15 g, and 1.79 g respectively.

Product 16. Polypyrrole (1.01 g, **10**) was stirred with deoxygenated hydrochloric acid (100 cm^3, 4.4 mol dm^{-3}), under nitrogen, for 10 minutes. The product was filtered, washed with water (300 cm^3) and dried. The yield of **16** was 0.99 g.

Products 17 and 18. Ferric chloride (33.75 g, 0.125 mol) was dissolved in deionised water and cooled to 0 °C. Pyrrole (2.79 g, 0.042 mol) was added rapidly to the well stirred solution. Two reaction times were employed, 180 minutes and 10 minutes, giving products **17** and **18** respectively. The method, including the work up, has been reported by S. Rapi *et al.*[6]

Products 19 and 20. Polypyrrole (**10**, 150 mg) was boiled with concentrated hydrochloric acid (20 cm^3) for 5 minutes and the black product collected by filtration, washed with water (100 cm^3) and dried. The yield of **19** was 135 mg. The experiment was repeated with a reaction time of 60 minutes to give **20** with a yield of 137 mg.

Results and discussion

Experiments were undertaken by rapidly mixing either 2.5 mol dm^{-3} or 7.5 mol dm^{-3} hydrochloric acid to aqueous pyrrole solutions, giving final acid strengths of 2.0 mol dm^{-3} and 6.0 mol dm^{-3} respectively. The use of hot (100 °C) 6.0 mol dm^{-3} hydrochloric acid resulted in a precipitate of **1** in less than a second and scanning electron microscopy showed that a structureless particle morphology was obtained. In contrast, at room temperature, 6.0 mol dm^{-3} and 2.0 mol dm^{-3} hydrochloric acid conditions resulted in induction times of *ca.* 5 minutes and 4 hours respectively, and the products were composed of polydisperse spheres with little difference in the particle size ranges of the two products: 0.4–5 μm **2** and 1–5 μm **4**. Fig. 1 shows the type of particle morphology obtained with the use of 6.0 mol dm^{-3} hydrochloric acid at 20 °C. The morphology of product **4** is similar. All the above products were brown: this is in contrast to oxidatively produced polypyrrole which is black. However, there are similarities on a microscopic scale[12] since both methods yield material composed of agglomerated polydisperse spheres. Addition of steric stabilisers such as polyvinyl alcohol (PVA) to pyrrole, followed by oxidative polymerisation, has been shown to produce monodisperse spheres.[12,13] For comparison we undertook a similar methodology and found that PVA also induced monodispersity in the polypyrrole when present in the reaction mixture of pyrrole and 6.0 mol dm^{-3} hydrochloric acid at room temperature (**3**,

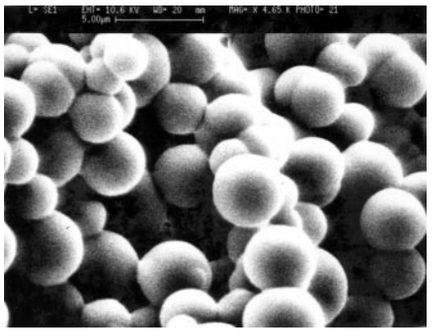


Fig. 1 Scanning electron micrograph of polypyrrole, produced by the reaction of 6.0 mol dm^{-3} hydrochloric acid with pyrrole at room temperature. Magnification $\times 4650$.

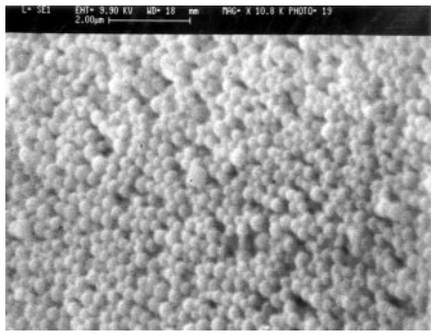


Fig. 2 Scanning electron micrograph of polypyrrole produced by the reaction of 6.0 mol dm^{-3} hydrochloric acid with pyrrole at room temperature, in the presence of polyvinyl alcohol. Magnification $\times 10\,800$.

Fig. 2). PVA also induced a concomitant 10-fold reduction in the diameter of the spheres to *ca.* 0.2 μm. There was a similar change in particle size when 2.0 mol dm^{-3} hydrochloric acid and PVA was utilised for the polymerisation (**5**). The ferric chloride–PVA system has been reported[13] to similarly cause a reduction in the diameter of polypyrrole particles, but in this case the reported percentage change was considerably less, only *ca.* 5%. The presence of polyvinylpyrrolidone in the polymerisation of pyrrole with 2.0 mol dm^{-3} hydrochloric acid did not result in monodispersity—particle sizes ranged from 0.13–0.26 μm (**6**).

Nitric acid treatment of aqueous pyrrole also resulted in particulate formation. Induction times were of the same order as hydrochloric acid: 11 minutes for 6.0 mol dm^{-3} nitric acid in comparison with 5 minutes for 6.0 mol dm^{-3} hydrochloric acid. The yield of precipitate collected was a little higher for 2.0 mol dm^{-3} nitric acid and for 6.0 mol dm^{-3} nitric acid conditions in comparison with hydrochloric acid under similar conditions . The reaction mixtures involving nitric acid were green in contrast to the yellow solutions arising from hydrochloric acid mediated polymerisations. The solid material obtained from nitric acid treatment of pyrrole was found to have a curious morphology when studied by electron microscopy. In contrast to the polydisperse spheres produced by the action of hydrochloric acid on pyrrole, the reaction of pyrrole and 6.0 mol dm^{-3} nitric acid at 20 °C resulted in particles which were spherical or ovoid in shape (**8**, Fig. 3). Curiously, some of these particles appeared to be hollow, with the appearance of pitted olives.

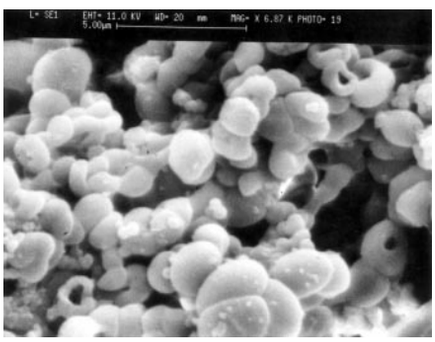


Fig. 3 Scanning electron micrograph of polypyrrole produced by reaction of 2.0 mol dm^{-3} nitric acid with pyrrole at room temperature. Magnification $\times 6870$.

Chemical analyses

The intractable nature of the products of the acid polymerisation of pyrrole prevents complete analyses of the products. However, the following discussion of the hydrochloric acid polymerisation of pyrrole reveals the major building blocks and their approximate ratios.

The first step of the polymerisation of pyrrole is considered[4] to be protonation of the carbon at position 3 on the pyrrole ring giving **21** (Fig. 4) which dimerises by reaction with an unprotonated pyrrole. This step has previously been reported[4] to explain the formation of the trimer **22** (Fig. 4).

The second step in the polymerisation process is likely to be the formation of this trimer. Compound **22** has been isolated in 40% yield (after purification) by the action of 6.0 mol dm^{-3} hydrochloric acid on pyrrole, followed by quenching 30 seconds after mixing.[8]

The third step is likely to be the formation of polymer with an alternating pyrrole–pyrrolidine polymer structure (**23**) (Fig. 4). A similar type of mechanism for explaining the formation of the trimer **22** can be used to explain the more extensive polymer structure. Analogous alternating saturated–unsaturated ring systems have been postulated for the structure of the polymer derived from acid treatment of thiophene.[4]

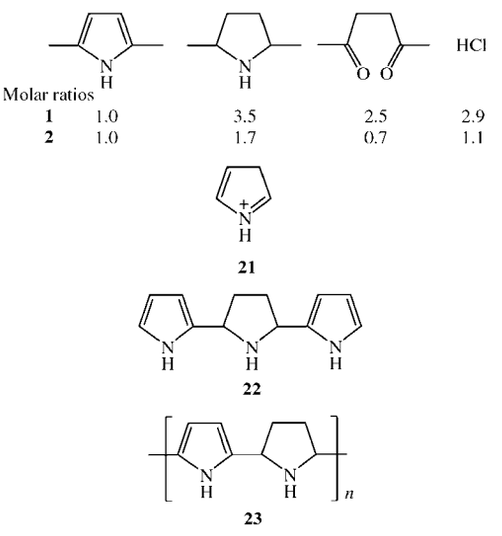


Fig. 4 Structures of compounds implicated in the acid polymerisation of pyrrole.

The fourth step is likely to be partial hydrolysis of **23** to give polymer structures akin to **1** in the case of 6.0 mol dm^{-3} hydrochloric acid at 100 °C. Milder conditions resulted in less loss of nitrogen and structures akin to polymer **2** (Fig. 4) were consistent with the microanalytical data in the case of 6.0 mol dm^{-3} hydrochloric acid at room temperature. The molar ratios of the polymer units for polymers **1** and **2** were derived by finding the best fit to the microanalysis data. Small discrepancies in the hydrogen elemental ratios, which occur between the theoretical and observed values for **1** and **2**, could be due to the presence of small amounts of chemical moieties produced by non-specific aerobic oxidative dehydrogenation.

Table 1 Elemental ratios, derived from microanalytical data, for a range of polypyrrole compounds. Oxygen values were obtained by difference

Elemental ratios						Conductivity[a]/S cm^{-1}
Compound	C	H	N	O	Cl	
1 calc.	4.00	5.83	0.64	0.71	0.42	
1 obs.	4.00	5.60	0.64	0.74	0.42	$<10^{-6}$
2 calc.	4.00	5.97	0.86	0.44	0.33	
2 obs.	4.00	5.76	0.81	0.41	0.22	$<10^{-6}$
9	4.00	3.20	0.69	0.56	0.23	$<10^{-6}$
10	4.00	2.97	1.01	0.38	0.36	1.5
15	4.00	2.78	1.00	0.37	0.32	0.4
20	4.00	2.80	0.96	0.61	0.23	0.2

[a]Conductivities were measured by a four point probe method at 15 °C.

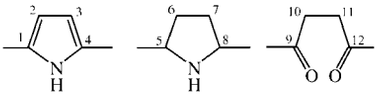
The microanalysis and conductivity results are presented in Table 1. The products of acid polymerised pyrrole (**1**, **2** and **9**) were insulating, whilst polypyrrole prepared by oxidative polymerisation (**10**, **15** and **20**) showed significant conductivities. This implies that the acid polymerised pyrrole does not possess a conjugated π system with mobile charge carriers. Consideration of the microanalyses of the polymer products of hydrochloric acid treatment of pyrrole showed that the material isolated was not solely composed of polymer **23** since the expected ratio of 4 carbons to 1 nitrogen was not found. There were varying degrees of nitrogen deficiency relative to the number of carbons, which implied ring opening and concomitant nitrogen loss. The ring opening of pyrroles by chemical reagents is a known phenomenon and these rings would be expected to hydrolyse in preference to the saturated pyrrolidine rings. Hydrochloric acid (6.0 mol dm^{-3}) at room temperature acting on pyrrole produced a polymer (**2**) with a C : N ratio experimentally determined as 4 : 0.81 and not 4 : 1 as expected assuming product **23** to be the principal product. Also **23** clearly possesses no oxygen yet the product **2** has a C : O ratio of 4 : 0.41. A comparison of the C : N ratio of 4 : 0.81 and a C : O ratio of 4 : 0.41 strongly suggests incorporation of about 2 oxygens for every nitrogen lost. Interpretation of the microanalyses results for **1** and **2** suggest that a standard reaction for producing pyrrole (ammonium species acting on open chain 1,4-dicarbonyl compounds) is occurring in reverse *i.e.* hydrolyses of the pyrrole rings to produce 1,4-dicarbonyl groups within the polymer. Total hydrolysis of all the pyrrole rings in structure **23** to dicarbonyl moieties cannot be occurring since this would satisfy neither the microanalytical nor the spectral data: for instance a C : N ratio of 4 : 0.50 would then have been expected. Partial hydrolysis is compatible with the spectral analyses (Table 2) and the elemental ratios deduced from the microanalysis data (Table 1). Hydrochloric acid (6.0 mol dm^{-3}) at 100 °C gave a product (**1**) with less nitrogen than the room temperature product (**2**) *i.e.* the extent of hydrolysis was greater at the higher temperature (see Fig. 4).

The peak data from the magic angle spinning cross polarised ^{13}C proton decoupled NMR spectrum of **2** is also consistent with the structure described (Table 2). Carbonyl groups feature in the spectrum and there are prominent peaks which are consistent with pyrrolidine and aromatic pyrrole carbons.[14,15] There is a prominent peak at 122 ppm which is likely to represent carbons 1 and 4 on the pyrrole nucleus. Non-quaternary suppression caused significant enhancement of the 122 ppm resonance and quaternary suppression virtually eliminated this peak, whilst clearly preserving the resonance at 107 ppm. These peaks are therefore assigned to carbons 1 and 4, and carbon 2 respectively on the pyrrole part of the polymer. Carbons 1 and 4 would be expected to possess a range of chemical shifts due to the effects of the carbonyl moieties occurring at variable positions in the polymer and this is the reason for the unresolved broad peak at 122 ppm. Carbons 2 and 3 in trimer **22** would also be expected to have differences in chemical shift as they are clearly in different environments and in the polymer case differences again would be expected due to carbonyl moieties present, and inhomogeneity of the polymer in the solid state. The broad peak centred at 176 ppm, coupled with the infrared spectral data, clearly revealed the presence of carbonyl groups. The peaks at 32 ppm and 56 ppm support the presence of pyrrolidine units: these chemical shift values are consistent with spectral evidence published[4] for the trimer **22**; a peak at 75 ppm is probably due to α-pyrrolidine carbons, with the nitrogen in the protonated form. The infrared spectrum of **2** (KBr disk) supported the presence of the following functional groups: 3374, 3250, 1624 cm^{-1}(all due to N–H bonding), 1690 cm^{-1} (typical for 1,4-di-ketone groups) and 1587 cm^{-1} (unsaturated carbon–hydrogen bonds). The infrared spectrum of **1** supported the presence of the following functional groups: 3110 and 1620 cm^{-1} (due to N–H stretch and bend respectively), 3090 cm^{-1} (aromatic C–H stretch), 1700 cm^{-1} (C=O stretch, typical for 1,4-diketone groups), 1588 cm^{-1} (unsaturated C–H). It would appear likely that this product originated from further hydrolysis of **2**.

XPS data expressed as binding energy (BE), in eV, followed by peak component for **1** is as follows: 284.40, C (1s); 285.00, C (1s); 286.95, C (1s); 288.45, C (1s); 399.85, N (1s); 401.35, N (1s); 531.80, O (1s); 197.45, Cl (2p). The oxygen BE of 531.80 eV is similar to a previously reported[16] value of 531.53 eV for C=O in conducting polypyrrole. The nitrogen BEs of 399.85 eV and 401.35 eV are likely to be due to the species *N*–H and N^+–C respectively (literature values[16] are 399.60 eV and 401.10 eV respectively for conducting polypyrrole). The carbon values are consistent with the structures described in Fig. 4, with four different carbon types due to α-carbons and β-carbons on the five membered rings, a protonated pyrrolidine and carbonyl groups. XPS is not particularly effective at resolving saturated and unsaturated carbons, therefore this method alone could not differentiate between pyrrole and pyrroline rings (a mechanistically plausible although unlikely possibility in the polymer). However, NMR data preclude this, except possibly as a minor contribution to the polymer structure.

Microanalyses of **1** and **2** showed the presence of chlorine. The X-ray photo electron spectrum of **1** revealed a single signal

Table 2 Magic angle spinning ^{13}C NMR data for polypyrrole **2** prepared by the action of 6.0 mol dm^{-3} hydrochloric acid acting on pyrrole at room temperature



Chemical shift (ppm)	31 br[a]	37	56	107	115	122 br	176
Lit. value (ppm)	26[b], 32[e]	35[14]	47[b], 56[e]	108[c,d], 104[d]	118[d]	134[e], 118[d]	175[15]
Carbon No. (likely assignation)	6, 7	10, 11	5, 8	2	3	1, 4	9, 12

[a]Abbreviation: br = broad. [b]Pyrrolidine (in solution). [c]Pyrrole. [d]Trimer (in solution) but not assigned in the literature.[4] [e]Trimer (in solution).[4]

for chlorine (with a binding energy of 197.45 eV) which correlated with chlorine solely present in the anion form.[17] We have therefore assumed that the hydrochloric acid has protonated the nitrogens of the pyrrolidine rings. The interpretation of the microanalytical data was made assuming that the chlorine is present as the hydrochloride.

Product **9** was obtained by heating **1** in air for 3 days at 180 °C: **1** slowly changed from brown to black during the heating process. The microanalyses showed little change in the C : N ratio but there was a large decrease in the hydrogen and chlorine component (Table 1). A similar colour change with concomitant loss of hydrogen has been previously reported[18] to occur with acid-produced polypyrrole standing in air at room temperature over long periods. The authors[18] suggested aromatisation of the pyrrolidine rings was occurring. However, **1** lost oxygen on heat treatment as shown by interpretation of the microanalytical results. This may be due to the 1,4-dicarbonyl groups of **1** reacting intramolecularly, with water elimination, to give furan rings. There is a precedent for such a statement since classical methods exist for the preparation of furans by the dehydration of 1,4-dicarbonyl compounds with dehydrating agents. Differential scanning calorimetry showed **1** is relatively thermally stable at room temperature, and indicates that significant thermal decomposition does not occur until after 150 °C (Fig. 5). The material retained its insulating properties after thermal treatment.

The acid catalysed polymerisation of pyrrole produces moderate yields of polymer products, especially at elevated temperatures, and the acid catalysed hydrolysis offers a facile route to polymers with amine and carbonyl groups, which could then be further derivatised.

The effect of acid on the oxidative polymerisation of polypyrrole

The result of the action of 2.0 mol dm^{-3} hydrochloric acid on pyrrole showed that the acid polymerisation gives insoluble material in 4 hours, the same reaction time used in some oxidative polymerisation methods. The acid strengths in the ferric chloride mediated polymerisation might be much higher than this; there are no reports of the rate of hydrolysis of ferric chloride at high concentrations, although equilibrium studies concerning the influence of acid concentration on $Fe(ClO_4)_3$ hydrolysis have recently been reported.[19] Therefore, it would be likely that oxidatively prepared polypyrrole would be contaminated by small amounts of acid produced polymer, whether as polymer chains or as part of a block co-polymer. This contamination would be expected to adversely affect the electrical conductivity.

The most facile method for ascertaining that acid-produced material is contaminating oxidatively produced polymer would be a study of microanalyses of polypyrrole. The presence of pyrrolidine units (formed by the reaction of H^+ with pyrrole) would be expected to increase the hydrogen : carbon ratio of 3 : 4 expected for oxidatively prepared polypyrrole. However, the use of ferric chloride in aqueous conditions produced polypyrrole with a hydrogen : carbon ratio of 2.97 : 4 (**10**, Table 1), slightly less than the expected 3 : 4 ratio. This latter result is complicated by the presence of relatively large amounts of oxygen incorporated into the polymer. The use of ferric chloride in methanol has been reported to produce a polymer with much less oxygen incorporation and high hydrogen : carbon ratios of 3.25 : 4 were reported.[20] It has been hypothesised that high ratios of hydrogen : carbon in conducting polymers correlate with low conductivities.[10] Despite the high hydrogen content of the polymer produced using ferric chloride in methanol its conductivity was higher than that of **10** which had a lower hydrogen content (Table 1). We have prepared polypyrrole under nitrogen with copper bromide in acetonitrile and a high hydrogen : carbon ratio of 3.32 : 4 was also found (**11**). Again, despite the extra hydrogens present in **11** relative to the idealised polypyrrole structure, the conductivity was also higher than for **10** (7.5 S cm^{-1} for **11** *cf.* 1.5 S cm^{-1} for **10**). These examples do not substantiate the hypothesis that high polymer hydrogen : carbon ratios correlate with lower conductivities of polymers. Workers attempting to prove that the presence of acid produces lower conducting material have utilised additives in the polymerisation reaction to reduce acidity. For instance an increase of 4 to 30 S cm^{-1} has been reported on the addition of urea to a ferric chloride mediated reaction;[6] however the authors also decreased the reaction time from 180 minutes to 120 minutes which might also be expected to affect the results. The only result which was directly comparable, using potassium ferricyanide as oxidant in the presence of urea[6] gave less of an improvement in conductivity from 15 to 21 S cm^{-1} and there was also a large drop in yield.

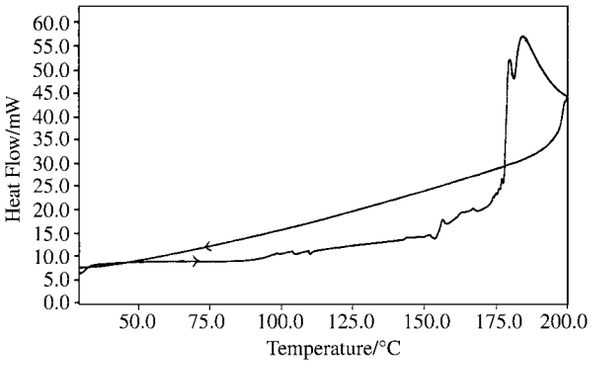


Fig. 5 Differential thermal analysis of **2**, heating rate 10 K min^{-1}, sample weight 8.670 mg.

The effect of the addition of hydrochloric acid at the commencement of oxidative polymerisation was investigated as follows. Products **13**, **14** and **15** were prepared by dissolving ferric chloride in 0.375, 0.75 and 1.5 mol dm^{-3} hydrochloric acid respectively, followed by the addition of pyrrole. The respective conductivities of **13**, **14** and **15** were 99%, 62% and 25% of the conductivity of the conventionally prepared material **10**. Clearly in this study higher acid concentrations have a significant adverse effect on the conductivity of the polypyrrole produced.

Various authors have investigated the effect of added acid on the conductivity of the resulting polypyrrole. For example, van den Schoor[5] has investigated the effect of perchloric acid (0–1 mol dm^{-3}) on the conductivity of polypyrrole film formed in the presence of ferric perchlorate (0.1–0.6 mol dm^{-3}). For $Fe(ClO_4)_3$ concentrations above 0.4 mol dm^{-3} the conductivity of the film was independent of the $HClO_4$ concentration, whilst at lower $Fe(ClO_4)_3$ concentrations the film conductivity increased to a moderate extent with increasing $HClO_4$ concentration.

At a fixed $Fe(ClO_4)_3$ concentration of 0.20 mol dm^{-3} and various $HClO_4$ concentrations between 0 and 2.5 mol dm^{-3}, there was a maximum in film conductivity at 1.5 mol dm^{-3} $HClO_4$. In a subsequent experiment, $HClO_4$ was replaced by $LiClO_4$ and the film conductivity was similar for either reagent up to 2.0 m mol dm^{-3}. It was proposed that the perchlorate ions screened the charge between the radical cations involved in the oxidative polymerisation process. Thus this process occurs faster than the proton-catalysed polymerisation of pyrrole which leads to non-conducting oligomers and polymers. Ayad[21] investigated the effect of added HCl on the conductivity of polypyrrole prepared at low concentrations. The author found that, with an initial $FeCl_3$ concentration of 0.0322 mol dm^{-3} and a pyrrole concentration of 0.0138 mol dm^{-3}, there was a maximum in conductivity at 0.3 mol dm^{-3} HCl. The increase in conductivity at added HCl concentrations up to 0.3 mol dm^{-3} was attributed to the

possibility of increased doping by Cl^- or $FeCl_4^-$. At higher acid concentrations, there was a decrease in conductivity.

In this study an increase in conductivity with added HCl was not observed, although addition of modest amounts of acid, 0.375 mol dm^{-3} hydrochloric acid, had negligible effects on the conductivity of the resultant polypyrrole. Increased amounts of added HCl did produce a decrease in conductivity although there was little evidence of incorporation of acid produced polypyrrole/oligomers *etc.* as the microanalyses of **13**, **14** and **15** were remarkably similar to **10** which was produced in the absence of added acid. As an example the elemental ratios of **15**, produced with 1.5 mol dm^{-3} added acid, are shown in Table 1.

Summarising our results and others regarding the effect of H^+ on polypyrrole syntheses: modest changes in conductivity are produced, sometimes with an improved conductivity on increasing H^+concentration. There is little evidence at present to consider that orders of magnitude of improvement in conductivity would arise by reducing the H^+ concentration in the ferric chloride mediated polymerisation of pyrrole.

The effect of acid on conducting polypyrrole

Electrochemically prepared polypyrrole, treated with sulfuric acid at relatively low concentrations (1 mol dm^{-3}) has been recently reported[22] to give a slight increase in conductivity which has been attributed to protonation of the pyrrole structure, particularly at the imine nitrogens.

Polypyrrole **10** was stirred with higher concentrations of hydrochloric acid (4.4 mol dm^{-3}) for 10 minutes. This treatment resulted in a drop in conductivity of 64% for the polypyrrole product **16**. The maximum acid concentration of a ferric chloride mediated reaction would be expected to be of this order assuming the ferric chloride is fully hydrolysed. These results indicate that a significant reason for the increase in conductivities with a shortening of reaction time of oxidative polymerisations[6] is likely to be due to the reduction of exposure of polypyrrole to the acid present in the reaction vessel. S. Rapi *et al.* reported[6] that 0.75 mol dm^{-3} ferric chloride acting on pyrrole at 0 °C, with reaction times of 180 and 10 minutes, gave materials with conductivities of 4 and 25 S cm^{-1} respectively. We obtained rather lower values on repetition of this work: compounds **17** and **18** possessed conductivities of 4 and 11 S cm^{-1} respectively. However a similar trend of reaction time *versus* conductivity was observed. The conductivity differences between our work and earlier reported work may be due to experimental factors such as differing stirring and addition rates; it cannot be explained by the small differences in the temperature conditions of the conductivity measurements. We further investigated this relationship using the cupric bromide–acetonitrile oxidising system. There was also an increase in conductivity with reduction in reaction time, for instance **12**, prepared with a reaction time of 2.5 minutes, possessed a conductivity of 28.5 S cm^{-1} , whilst **11**, prepared with a reaction time of 60 minutes, possessed a conductivity of 8.7 S cm^{-1}.

The resilience of polypyrrole to higher acid concentrations was tested. Polypyrrole **10**, which had a conductivity of 1.6 S cm^{-1}, was boiled with concentrated hydrochloric acid for 5 minutes and 60 minutes to give products **19** and **20**. These had conductivities of 0.3 S cm^{-1} and 0.1 S cm^{-1} respectively, *i.e.* a reduction in conductivity of 81% in the former case. The only significant change in the microanalysis of the 60 minute treated material (Table 1) was a small decrease in the chloride elemental ratio and an increase in the oxygen ratio.

Conclusion

Hydrochloric acid acting on pyrrole produces a product with spectroscopic data consistent with a polymer possessing alternating pyrrole and pyrrolidine units, with varying degrees of ring opening of the pyrrole units and concomitant nitrogen loss. This has not been previously reported. Syntheses at elevated temperatures resulted in more extensive loss of nitrogen. The acid catalysed polymerisation of pyrrole offers a synthetic route, in modest yield (76% for polymer **1**), to polymers with amine and carbonyl functional groups, which could then be further derivatised.

The action of hydrochloric acid on aqueous pyrrole produced a non-conducting polypyrrole with a polydisperse sphere morphology. Monodisperse, sub-micron diameter spheres could be achieved with the addition of steric stabilisers to the reaction media. Nitric acid acting on aqueous pyrrole produces spheres and ovoids, some of which were hollow and appeared as pitted olives under the SEM.

A study was undertaken of polypyrroles prepared by oxidative polymerisation, using chemical reagents. It was shown that additional acid added to the ferric chloride mediated polymerisation of pyrrole has a relatively small effect on the conductivity of polypyrrole. It would seem likely that further work to reduce the presence of acid in oxidative polymerisations, *e.g.* by the use of additives, would result in only modest improvements in the conductivity. It has been demonstrated that polypyrrole is relatively stable to adverse environmental conditions: concentrated hydrochloric acid at 100 °C only reduced the conductivity of polypyrrole by approximately a factor of 10 after 1 hour. An investigation of the oxidative polymerisation reaction time revealed that a shortening of the reaction period between cupric bromide and pyrrole in acetonitrile gave a superior conducting polypyrrole.

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