Effect of thermal treatment on the electrochemical properties of conducting polypyrrole polymers

R. Ansari and G. G. Wallace*
Intelligent Polymer Research Laboratory, Chemistry Department, University of Wollongong, Northfields Avenue, Wollongong, NSW 2522, Australia
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The effect of exposing conducting polypyrroles to elevated temperatures on the electroactivity of the polymer has been considered. In all cases the redox properties were improved with mild heating but were degraded at higher temperatures. Thermal gravimetric analysis and dry state conductivity measurements have been used to obtain an understanding of the results observed.

(Keywords: thermal treatment; electrochemical properties; conducting polymers)

INTRODUCTION

Exposure of conducting polymers to elevated temperatures is known to induce changes in the molecular structure of these materials[1-3]. In general it is accepted that at higher temperatures dedoping or at least dopant degradation occurs. However, the mechanism of dedoping is not universally accepted and is most likely dependent on the polymer and counterion employed as well as the method of polymer preparation used. Granstrom and Inganas[4] suggest that with polyalkylthiophenes dedoping occurs due to a loss of polymer planarity and/or thermal excitation of the alkyl side chain causing molecular vibrations (that occupy extra space and hence displace the counterion). These workers also point out the danger in using conductivity decreases alone to interpret the chemical changes induced after exposure to elevated temperatures; they suggest that spectroscopic techniques are much more valuable in this regard. Wang and Rubner[5] obtained spectroscopic evidence which suggests that in the case of polyaniline thermal dedoping occurs due to disordering of the polymer backbone through chemical modifications (substitution of aromatic rings/crosslinking) or changes in molecular reorganization (thermal disruption of crystalline or paracrystalline regions). They also point out, however, that even spectroscopic studies are limited in that minor structural changes would not be detected and yet these could have a major impact on physical properties. In addition, they emphasize the importance of film thickness on thermal properties and yet spectroscopy can only be carried out on thin films. Using Fourier transform infra-red spectroscopy, previous workers[6] have shown that gas evolution (CO_2, SO_2) from conducting films can occur at elevated temperatures and this would obviously disrupt the polymer. SO_2 has been shown to be evolved at temperatures as low as 100°C. A most interesting technique which probes changes at the molecular level during thermal treatment is inverse gas chromatography. Preliminary studies in our laboratories[7] indicated that polypyrrole dodecylsulfate (PP/DS) becomes a more polar stationary phase when treated at higher temperatures. Chehimi *et al.*[8,9] have shown that using appropriate molecular probes changes in acid–base and dispersion properties can be detected at elevated temperatures, and that perhaps even glass transition temperatures (T_gs) can be monitored. Other workers have shown that thermal treatment results in the formation of carbonyl functional groups on the polymer surface[10].

Obviously, these changes in conductivity and molecular structure could have dramatic effects on the electroactive properties of conducting polymers. However, the effect of thermal treatment on the well known oxidation/reduction processes observed with conducting polymers is to our knowledge yet to be considered. This is of particular importance since many applications involve the redox properties of conducting polymers. These applications include battery technologies and electrochromics[11], sensors[12] and chemical separation devices[13,14]. The effect of exposure to elevated temperatures on this property of conducting polymers is therefore important.

In the course of this work we have chosen four commonly investigated conducting polymers to investigate the effect of thermal treatment on their redox activity. The polymers chosen were polypyrrole chloride (PP/Cl), PP/DS, polypyrrole *p*-toluene sulfonate (PP/PTS) and polypyrrole ferricyanide [PP/$Fe(CN)_6$]. The effect of exposure to elevated temperatures has been considered.

EXPERIMENTAL

Reagents

All chemicals were analytical reagent grade purity unless otherwise stated. Pyrrole (Sigma) was distilled before use. The monomer solutions used for electropolymerization contained sodium dodecylsulfonate (Sigma), NaCl

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* To whom correspondence should be addressed

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(BDH), $K_4Fe(CN)_6$ (BDH) or sodium *p*-toluene sulfonate (Merck).

The supporting electrolyte used for all cyclic voltammetry experiments was 0.5 M $NaNO_3$ (BDH).

Instrumentation

Thermal gravimetric analyses (t.g.a.) were carried out using a Rigaku thermogravimetric analyser.

Cyclic voltammetry was carried out using a Bio-Analytical Systems 100A electrochemical analyser. Scanning electron microscopy was performed using a Hitachi S-450 SEM.

Electropolymerization was carried out using a home-made galvanostat and a CV-27. Alternatively, a Princeton Applied Research potentiostat (model 363) was employed.

Thermal treatment was carried out using the above gas chromatography oven or a homemade tubular furnace equipped with a temperature programmer and N_2 gas flow.

Procedures

Electropolymerization was carried out in a single compartment cell equipped with glassy carbon as a working electrode, a platinum gauze auxiliary electrode and a Ag/AgCl reference electrode.

For synthesis of PP/Cl, PP/DS or PP/PTS constant current (1–2 mA cm^{-2}) polymerization was used and for preparation of PP/$Fe(CN)_6$ polymerization was achieved by applying a constant potential of 0.72 V *versus* Ag/AgCl.

Free standing films of PP/DS, PP/PTS or PP/$Fe(CN)_6$ were prepared electrochemically using a stainless plate as the working electrode, RVC as the auxiliary electrode and a Ag/AgCl reference electrode. Platinum plate was used to prepare PP/Cl and PP/$Fe(CN)_6$ for t.g.a.

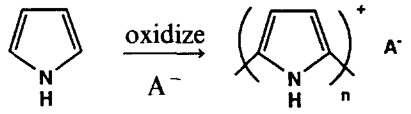
For conductivity and t.g.a. experiments the polymer films were peeled from the substrate, washed and then dried at room temperature for 72 h before characterization. The range of temperatures considered was between 100°C and 300°C, in either air or N_2. A special tubular furnace equipped with a temperature programmer and a N_2 flow through system was used for thermal treatment. The rate of heating employed was 10°C min^{-1}. The samples were heated at the maximum temperature for 1 h. The N_2 gas flow during heating was 80 ml min^{-1}.

Cyclic voltammetric experiments were carried out after cooling the sample to room temperature.

RESULTS AND DISCUSSION

Polypyrroles containing Cl, PTS, DS or $Fe(CN)_6$ were prepared using the procedures outlined in the Experimental section. All polymers were prepared at room temperature.

The polymerization process occurs according to:



where A$^-$ is the counterion incorporated during polymerization.

It has been shown previously[11] that the value of *n* is usually between 2 and 4. The conductivity of the polymer samples grown in this work was determined using the four-point probe technique (*Table 1*). The mechanical properties (tensile strength) of the samples as grown were then determined using a Universal testing machine. Only the PP/PTS samples had adequate strength to allow quantitative data to be obtained on the free standing films (*Table 2*).

Table 1 Conductivity (S cm^{-1}) of samples as grown and after exposure[a] to different temperatures

Counterion	As grown	100°C	150°C	200°C
Cl$^-$	–[b]	–[b]	–[b]	–[b]
$Fe(CN)_6^{3-}$	22	8	1	–[b]
DS	30	40	24	–[b]
PTS	90	110	130	136

[a] Samples were exposed to the temperature stated for 1 h. Samples were maintained under N_2

[b] Mechanical properties were not adequate to allow conductivity to be determined

Table 2 Effect of thermal treatment on mechanical properties of PP/PTS

Temperature (°C)[a]	Tensile strength (MPa)
As grown	60
100	60
150	55
200	27
250	–[b]

[a] Polymer samples (3 cm × 0.5 cm × 10 μm) were treated at different temperatures for 1 h under N_2

[b] Mechanical properties were inadequate for tests

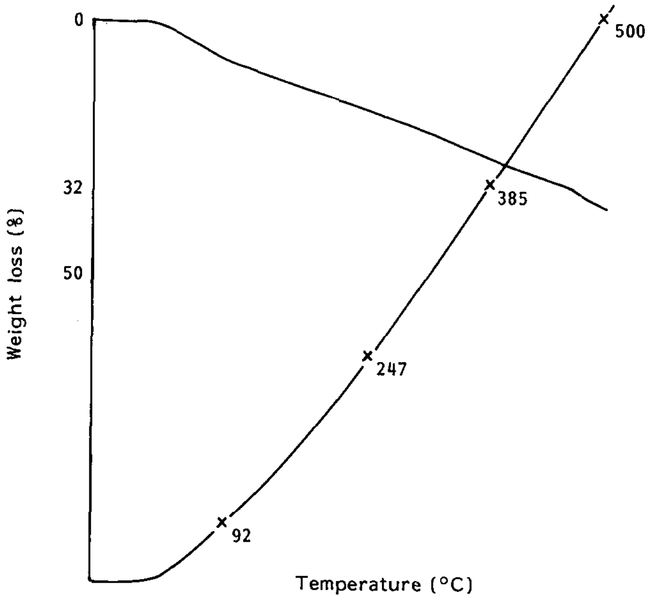


Figure 1 T.g.a. of PP/Cl. Samples prepared as in the Experimental section. Sample weight = 10 mg; rate of temperature increase = 10°C min^{-1}; N_2 gas flow rate = 75–80 ml min^{-1}

Thermal treatment

T.g.a. was carried out on polymers containing different counterions (*Figures 1–4*). Polymers were prepared electrochemically and then removed from the substrate prior to t.g.a. The samples were heated from 20 to 500°C at a rate of 10°C min^{-1} in air and N_2. With all counterions some weight loss was observed even at temperatures less than 100°C. This was attributed to a loss of moisture. The difference in percentage weight loss for each of the polymers up to 100°C presumably reflects the different amounts of moisture incorporated during

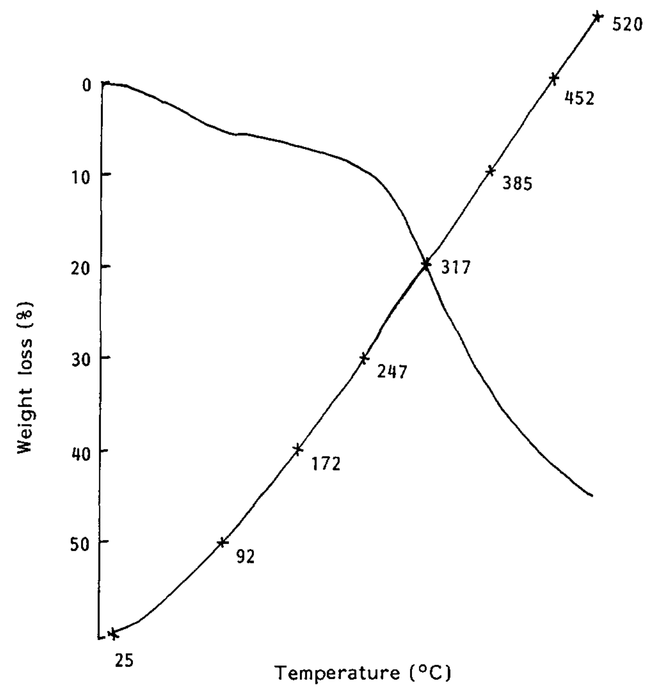


Figure 2 T.g.a. of PP/PTS. Samples prepared as in the Experimental section. Sample weight = 10 mg; rate of temperature increase = 10°C min^{-1}; N_2 gas flow rate = 75–80 ml min^{-1}

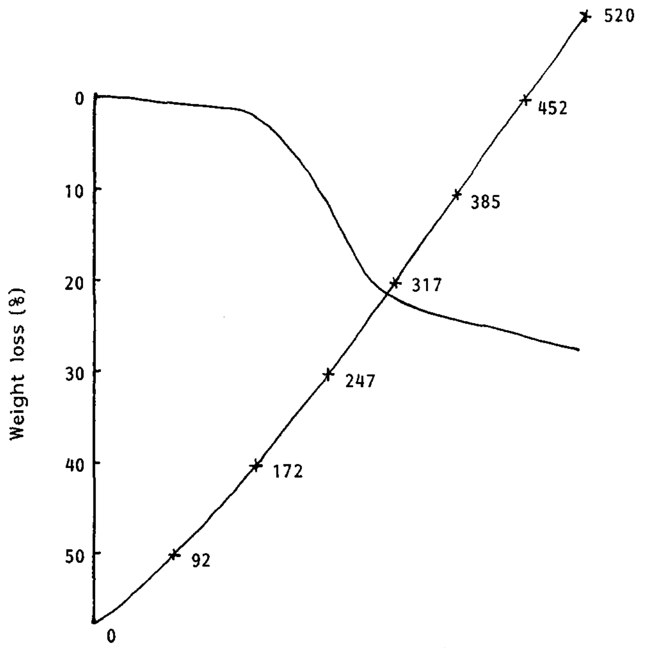


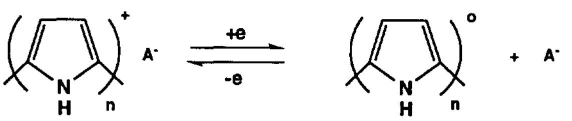
Figure 3 T.g.a. of PP/DS. Samples prepared as in the Experimental section. Sample weight = 10 mg; rate of temperature increase = 10°C min^{-1}; N_2 gas flow rate = 75–80 ml min^{-1}

synthesis. For example, it has been shown previously that the incorporation of the DS counterion produces a more hydrophobic polymer[15]. The weight loss behaviour at higher temperatures was extremely dependent on the counterion employed. The rate of weight loss and the final percentage of weight lost was found to be counterion dependent. A particularly interesting result in this regard was the extraordinary stability of PP/Cl.

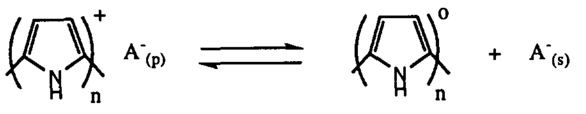
The effect of thermal treatment at different temperatures on the dry state conductivity of the polymer materials was considered. The results are summarized in *Tables 1* and *2*, respectively. In the case of PP/$Fe(CN)_6$ it was found that the conductivity decreased when the polymer was exposed to elevated temperatures. This correlates with the significant mass losses observed when this polymer was heated to even moderate temperatures with t.g.a. For DS and PTS conducting polymers there was a slight increase when the polymers were heated to 100°C. This is presumably due to the fact that loss of moisture improves conductivity. As the temperature was increased further the conductivity of the DS containing polymer decreased while that containing PTS continued to increase. This is presumably due to differences in moisture content since neither polymer exhibits large mass loss at these temperatures using the t.g.a. method.

The effect of thermal treatment on the electroactivity of the polymer was then considered.

In all cases cyclic voltammograms revealed the normal oxidation/reduction process which occurs according to:

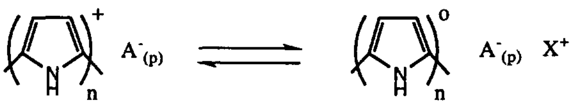


As an example, the cyclic voltammogram for PP/PTS is shown in *Figure 5*. This electrochemical reaction involves the transport of ions in and out of the polymer. The processes labelled A/A[1] and B/B[1] are attributed[16] to anion and cation movement, respectively, and may be described as:



[couple A/A[1]]

and



[couple B/B[1]]

where $A^-_{(p)}$ is the counterion bound in the polymer, $A^-_{(s)}$ is the counterion in solution and X^+ is the cation from the electrolyte solution.

Of particular interest in this work was the effect of thermal treatment on these properties as determined using cyclic voltammetry. For example, using PP/Cl, heat treatment up to 100°C altered the ion exchange capabilities of the polymer as determined using cyclic voltammetry. It was found that after exposure to higher temperatures the more positive oxidation peak usually associated with anion insertion was only induced at more positive potentials while the less positive couple, usually associated with cation insertion, became better defined (*Figure 6*). This may be due to annealing or crosslinking of the polymer making anion movement from the bulk more difficult. Heating above 100°C caused a loss in electroactivity, which was interesting given the very small (*Figure 6*) decrease in mass loss observed with this polymer. This may be due to changes in conductivity that could not be studied with this polymer due to the weak mechanical properties.

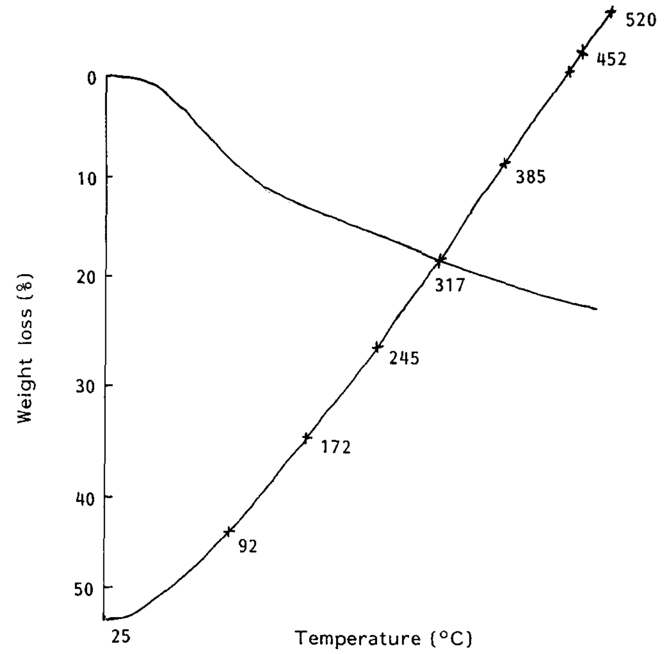


Figure 4 T.g.a. of PP/Fe(CN)$_6^{2-}$ prepared electrochemically. Samples prepared as in the Experimental section. Sample weight = 10 mg; rate of temperature increase = 10°C min^{-1}; N_2 gas flow rate = 75–80 ml min^{-1}

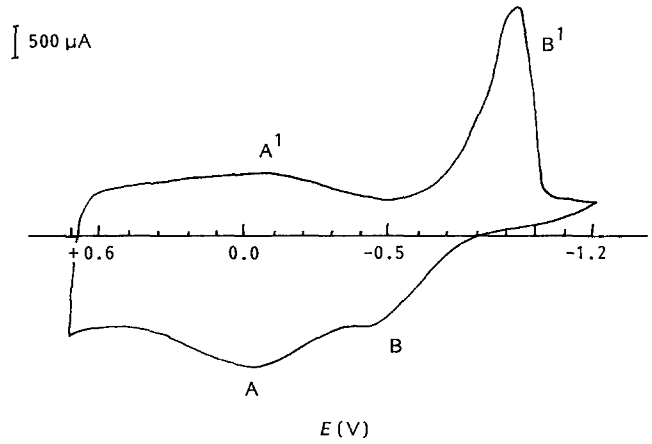


Figure 5 Cyclic voltammogram obtained using PP/PTS. Supporting electrolyte was 0.5 M $NaNO_3$. Scan rate = 100 mV s^{-1}

For PP/PTS, cyclic voltammetry revealed that cation exchange character was enhanced after thermal treatment while the anion exchange process was diminished at least up to 100°C (*Figure 7*). Interestingly, with thermal treatment above 100°C the anion exchange capacity appears to increase again although between 100°C and 200°C only small mass losses are recorded. Presumably exposure to higher temperatures again inhibits anion movement and encourages cation exchange. PP/PTS polymers were still electroactive even after exposure to 200°C. This is in agreement with dry state conductivity data (*Table 1*) which show that conductivity of the PP/PTS sample increases upon exposure to higher temperatures.

For PP/DS the cation exchange process is known to dominate as the polymer is oxidized/reduced[17,18]. However, after thermal treatment at elevated temperature some anion exchange character appears to be induced (*Figure 8*). This may well be due to the fact that, as shown

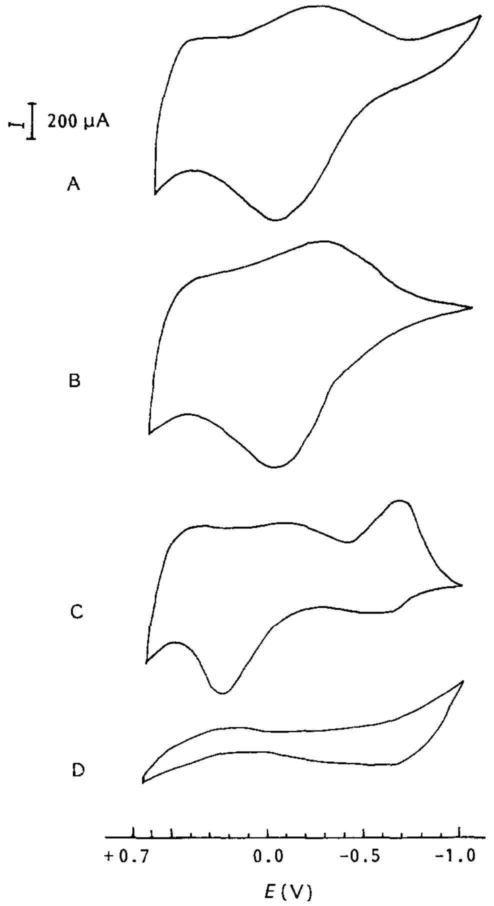


Figure 6 Cyclic voltammograms obtained using PP/Cl: (A) no thermal treatment; (B) heated to 50°C; (C) heated to 100°C; (D) heated to 200°C. Polymers grown on a glassy carbon substrate (surface area 0.2 cm^2) using the procedure described in the Experimental section. Supporting electrolyte was 0.5 M $NaNO_3$. Scan rate = 100 mV s^{-1}

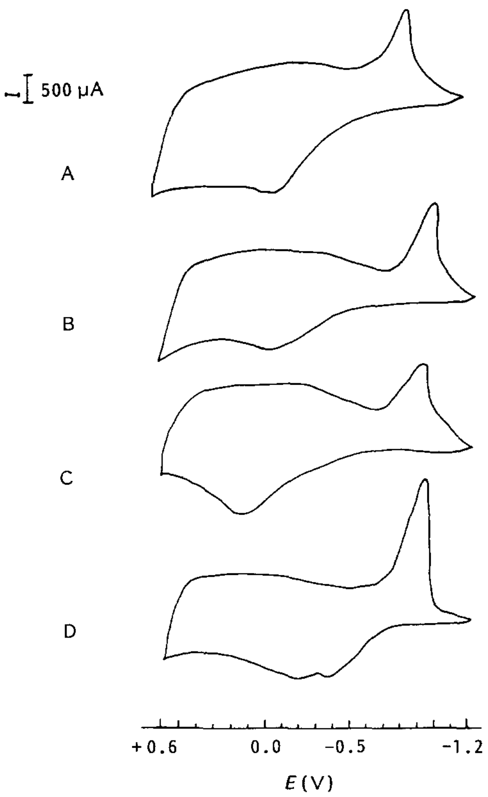


Figure 7 As for *Figure 6* but using PP/PTS

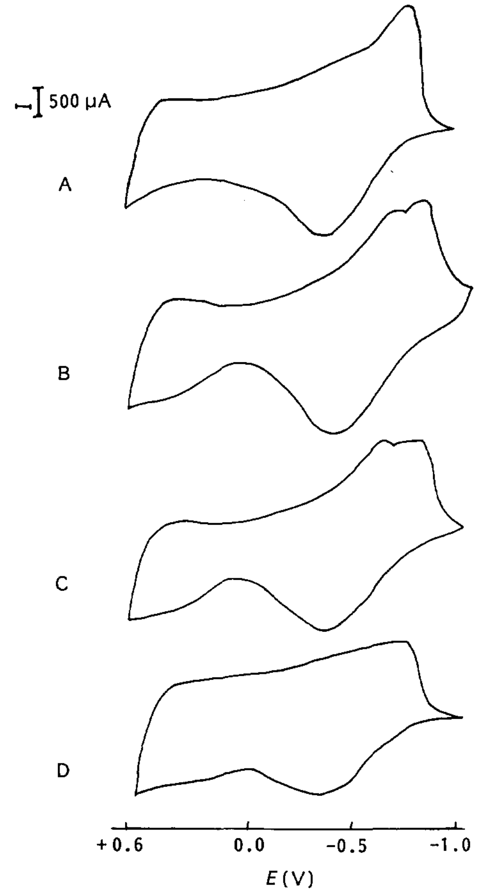


Figure 8 As for *Figure 6* but using PP/DS

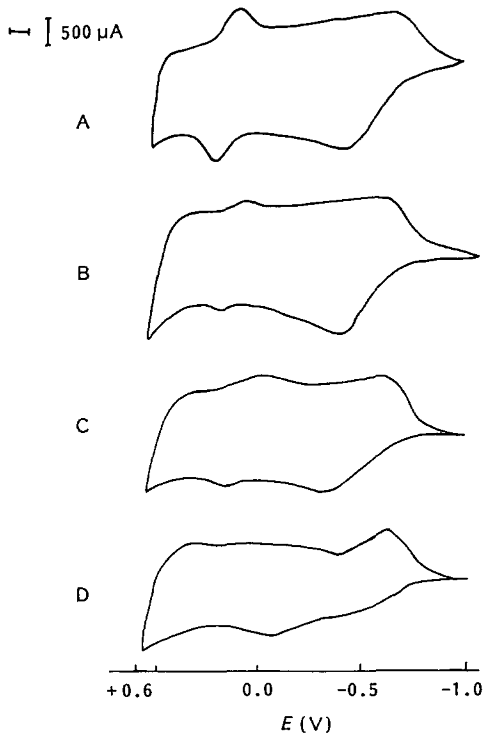


Figure 9 As for *Figure 6* but using PP/Fe(CN)$_6$

previously[7], exposure to elevated temperature is known to break down the large organic DS anion into smaller anionic components. This would enhance the capability of this structure to undergo electrochemically controlled anion exchange processes. Note that this behaviour is not in agreement with the dry state conductivity data which have shown that the PP/DS polymer loses conductivity at temperatures above 100°C. The presence of the substrate in the electroactivity experiments presumably provides some mechanical stability to the polymer.

For Fe(CN)$_6^{4-}$ containing polymers the response of the ferri/ferrocyanide redox couple diminishes even after treatment at 50°C (*Figure 9*). The t.g.a. data suggest that this is not sufficient to break down the Fe(CN)$_6^{4-}$ counterion or the polymer and so the loss in electroactivity is presumably due to some polymer rearrangement. However, the polymer backbone is quite electroactive up to 200°C despite the fact that large mass losses were observed with t.g.a. at this temperature (*Figure 4*). This suggests that the inorganic complex is broken down but as reported for DS previously[7], smaller more stable anionic components are retained in the polymer to facilitate electroactivity. Alternatively the anions from the supporting electrolyte may be incorporated into the polymer during potential cycling and facilitate electroactivity. Note also that there appear to be two polymer redox processes after treatment at 200°C suggesting that cation as well as anion exchange character is induced. These results again appear to contradict the dry state conductivity results confirming that, as suggested previously[4], such measurements are not necessarily an indication of how the polymer properties of interest fluctuate with temperature.

CONCLUSIONS

This work clearly demonstrates that changes in dry state conductivity are observed for polypyrroles exposed to elevated temperatures. These changes can be associated with the mass loss observed during t.g.a. studies and they are markedly affected by the nature of the counterion incorporated during synthesis.

However, in spite of the obvious degradation in these properties with some polymers, this work has shown that exposure to elevated temperatures does not necessarily degrade the electroactive nature of the polymers. It does, however, vary the nature of this electroactivity. In the case of PP/Cl, PP/PTS and PP/Fe(CN)$_6$, the electrochemically induced anion exchange character is diminished while the cation exchange character is enhanced. However, for PP/DS the anion exchange character is enhanced and the cation exchange is diminished after exposure to elevated temperatures. For PP/DS these effects are noticeable even after exposure to temperatures as low as 50°C. These results may have important implications for applications where the electroactivity of the conducting polymer is important.

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