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Effect of thermal treatment on the electroactivity of polyaniline

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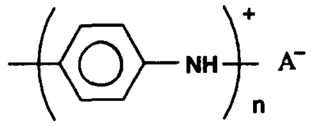
A series of polyaniline films have been coated on electrodes by chemical and electrochemical means in order to investigate the thermal stability of the electroactivity in air and nitrogen atmospheres. Polyaniline was also synthesized chemically and cast as a membrane (thick film). It was found that the electroactivity and conductivity of the films was stable up to 150°C. Exposure to higher temperatures leads to a decrease in electroactivity and conductivity, although use of a nitrogen atmosphere had less effect on the properties. Thermogravimetric analysis profiles confirmed that the polymer was stable to above 350°C. The changes in the electroactivity may be attributed to morphological (annealing) effects in the polymer and to loss of moisture and dopant ions.

(Keywords: thermal treatment; electroactivity; polyaniline)

INTRODUCTION

The environmental stability of polyaniline (**I**) appears to be extremely good compared with a number of other conducting polymer materials. (In the structure shown (where $n = 1$), A is a counterion incorporated during electrolysis.) For this reason it is one of the most potentially useful conducting polymers at present[1–3] and there is much interest in exploiting its unique properties in a number of application areas.



(I)

Consequently, polyaniline has received considerable attention in recent years, and amongst the properties investigated are those related to thermal stability[4–6]. La Croix and Diaz proposed that the thermal decomposition of the material occurs in *two* stages[4]. The first was attributed to the loss of moisture and the second to breakdown of the polymer backbone. However, Patil and coworkers[5] as well as Chan[6] have subsequently reported a *three*-step decomposition process for the HCl-protonated conducting form. They suggest that the initial stages of weight loss are due to the volatilization of water molecules (at about 100°C). At temperatures of around 200°C the protonic acid component of the polymer is lost, and finally at more extreme temperatures (approximately 500°C) the degradation of the polymer can lead to the production of gases such as acetylene and ammonia[7]. By contrast, Neoh and coworkers[8] have shown that the emeraldine base (EB) form of this material is stable up to approximately 500°C. These results suggest that the deprotonated form of polyaniline is also quite hydrophobic since no moisture loss was reported. Other workers[9] have reported an increase in the crystallinity as the temperature is increased to 150°C. At more extreme temperatures, crystallinity decreases and the polymer becomes more amorphous.

In the course of this work the effect of thermal treatment on the electroactive properties of polyaniline has been considered. Given the technological importance of this material, it is surprising that such a study has not appeared previously. Many of the applications of polyanilines, e.g. in batteries[10,11], sensors[12,13], membranes[14] and electrochemical devices[15,16], rely on the electroactive switching properties of polyanilines. In a number of these application areas, exposure to elevated temperatures is quite possible or indeed likely. In addition, the effect of thermal treatment on dry-state conductivity and mechanical strength of films (two important properties for membrane use) are investigated.

EXPERIMENTAL

Reagents and standard solutions

All chemicals used were analytical reagents (AR). Ammonium persulfate $(NH_4)_2S_2O_8$, aniline, NH_3 and HCl were purchased from BDH. 1-Methyl-2-pyrrolidone (NMP) was purchased from Aldrich.

Instrumentation

A conventional three-electrode cell (*Figure 1*) was used for synthesis and cyclic voltammetric (c.v.) analyses. All c.v. experiments before and after thermal treatment were carried out in 1 M HCl using an Electrolab (DI Instruments). A temperature-controlled bath (Julabo F20) was

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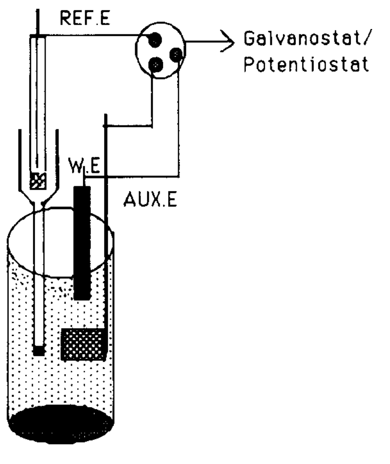


Figure 1 The three-electrode cell used in this study

used for maintaining the temperature during synthesis of the polymer. Electrical conductivity was measured using the four-point probe technique at room temperature in air. Thermal gravimetric analyses (t.g.a.) of samples were carried out using a Rigaku thermal analyser, under both nitrogen and oxygenated conditions. The Rigaku thermal analyser also enabled simultaneous differential thermal calorimetric analysis (d.t.a.) of the samples to indicate any enthalpic reactions occurring. It should be noted that in the graphs no scale for the d.t.a. is given; however, positive changes indicate that an exothermic reaction is occurring and negative changes endothermic ones.

Thermal treatment

Thermal treatment of polymer-coated electrodes for electroactivity experiments was carried out using a glass chamber (*Figure 2*) connected to a gas chromatography oven, allowing the control of temperature and nitrogen gas flow ($80\,\mathrm{ml\,min^{-1}}$). The samples were heated at $10^{\circ}\mathrm{C\,min^{-1}}$ and then held for 1 h at the maximum temperature. Thermal treatment was also carried out under air using similar procedures.

Chemical preparation of polyaniline powder

Polyaniline–HCl was prepared chemically using a modified technique from the literature[17,18]. Freshly distilled aniline (4 ml) was dissolved in 200 ml of 1.2 M HCl and cooled to 0°C. Then 10 g of $(NH_4)_2S_2O_8$ was dissolved separately in 100 ml of 1 M HCl. The oxidant solution was added dropwise into a well stirred monomer solution at 0°C. The reaction solution was deoxygenated during polymerization by continuous purging with N_2 gas. Polymerization was initiated only when the concentration of oxidant was high enough. The reaction was allowed to continue for 1 h after complete addition of the oxidant solution. The polymer powder produced was filtered and washed with 0.1 M HCl and then with copious water. After this it was dried at room temperature.

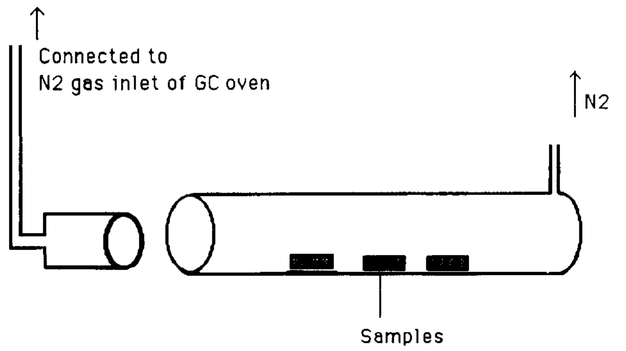


Figure 2 Glass chamber used for thermal treatment in electroactivity experiments

Preparation of polyaniline membranes

First, 2 g of chemically prepared polyaniline powder (EB form) was poured into 500 ml of 1 M NH_4OH and mixed for 1 h. Then it was filtered and washed completely with water and dried at room temperature. The filtered particles were further washed with methanol and ether. The polymer powder was collected and dried at 60°C for 1 h under N_2.

The finely powdered particles (1 g) of the emeraldine base salt (EB) were poured slowly into vigorously stirred NMP (80 ml). The colour of the solution changed very quickly to deep blue. Mixing was continued for 2 h, after which the solution was filtered. After filtration no insoluble material was observed.

Casting membranes of polyaniline

A suitable amount of the solution of polyaniline (PAn) in NMP was poured into a very clean glass Petri dish. This solution was first dried in an oven (24 h) at 60°C to evaporate the solvent. When the majority of solvent had evaporated, the polymer film was peeled off by soaking the polymer-coated dish in water.

The polymer film was dried at 70°C under vacuum for another 12 h. It was then treated for 2 h at 90°C under nitrogen in order to remove the solvent. The copper-coloured membrane was washed again with water and methanol to enable further purification. It was then dried at room temperature before doping. PAn membranes after casting were left in 1 M HCl for 24–36 h for doping.

Electrochemical preparation of polyaniline

Polyaniline was prepared electrochemically using 0.4 M of freshly distilled aniline in a solution of 1.4 M HCl. A constant-potential (0.80 V vs. Ag/AgCl) method was used for the deposition of the polymer. Glassy carbon, polished with diamond paste and alumina powder ($0.3\,\mu\mathrm{m}$), was used as the working electrode. Pt (gauze) was used as the counter-electrode and Ag/AgCl (3 M NaCl) was used as the reference.

For t.g.a., PAn/Cl was electrochemically deposited on a Pt plate (0.80 V vs. Ag/AgCl). An RVC sheet was used as the auxiliary electrode.

Preparation of the reduced form of polyaniline was also achieved by using a scanning deposition method onto a platinum plate (potential sweep from -0.2 to $+0.9\,\mathrm{V}$ and scan rate of $20\,\mathrm{mV\,s^{-1}}$). Then a negative potential ($-0.2\,\mathrm{V}$ vs. Ag/AgCl) was applied to the polymer-coated electrode for 1 h in a monomer-free deoxygenated solution of 1 M HCl. This method produced more adherent deposition than the potentiostatic one.

RESULTS AND DISCUSSION

The electroactivity of polyaniline is easily monitored by cyclic voltammetry. *Figure 3* shows the response of

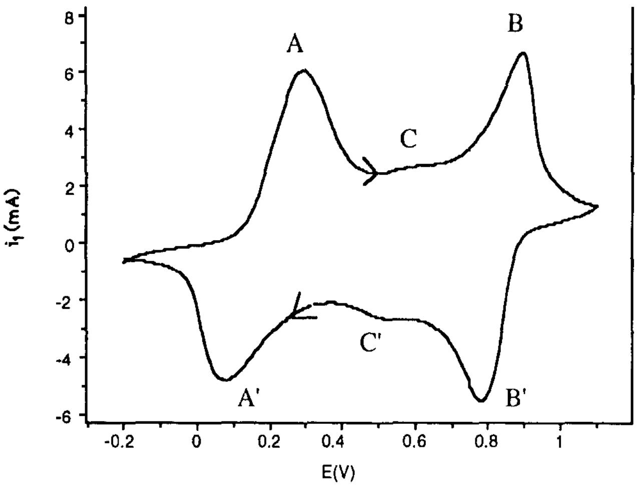
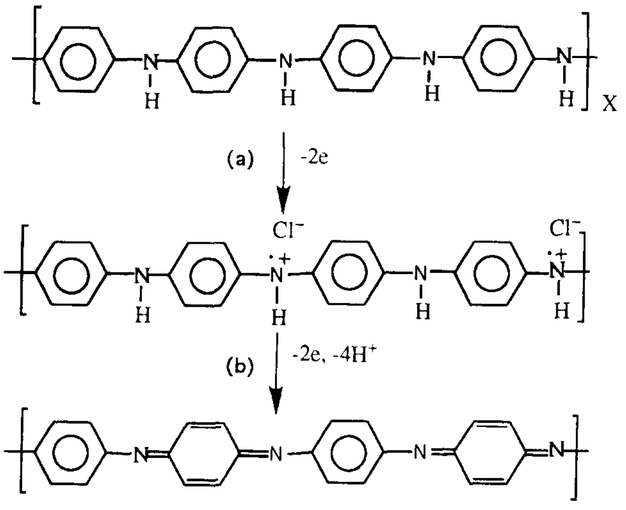


Figure 3 C.v. of electrodeposited polyaniline on glassy carbon

polyaniline electrodeposited onto a glassy carbon electrode. The responses observed (A/A′) and (B/B′) are due to:



Peaks labelled A/A′ are pH-independent and only electrons are transferred. Peaks labelled B/B′ are pH-dependent[19]. PAn is an insulator in both the fully reduced (leucoemeraldine) and the fully oxidized (pernigraniline) states. It is conductive when it is partially oxidized, and the most conductive state is half-reduced and half-oxidized.

The middle peak (C/C′) ($\sim$0.5 V in the cathodic scan) can be related to the formation of quinones (mostly benzoquinone) as a consequence of a hydrolysis reaction induced at more positive potentials[20,21]. Bhandani and coworkers[22] have attributed the middle peak to degradation of PAn chains during polymerization.

In this work c.v. experiments before and after thermal treatment were carried out in 1 M HCl. Samples were soaked in 1 M HCl for 20 min before starting the experiment and the second scan of each c.v. was recorded. The first scan was not used as it is known to yield non-representative or irreproducible results due to such effects as charging currents.

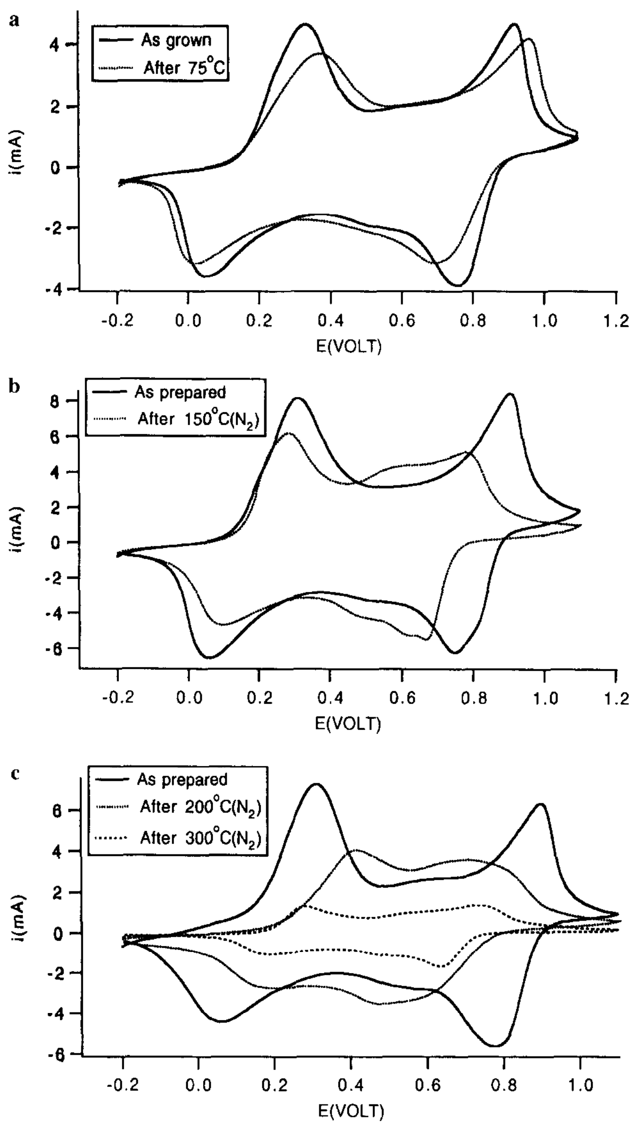


Figure 4 C.v. of electrochemically prepared polyaniline after heat treatment at (a) 75°C, (b) 150°C, (c) 200°C and (d) 300°C under a N_2 atmosphere for 1 h

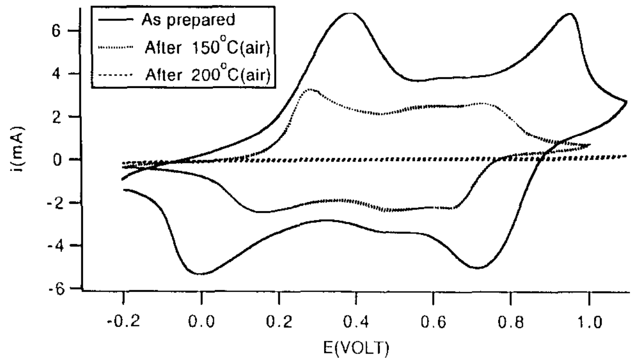


Figure 5 C.v. of electrochemically prepared polyaniline after heat treatment at 150 and 200°C in an oxygenated environment

Effect of thermal treatment on the electroactivity of electrochemically prepared polyaniline

Figure 4 shows c.v. data obtained after thermal treatment (under a nitrogen atmosphere up to 300°C) of electrochemically prepared polyaniline. Some decrease in peak currents was observed after exposure to temperatures ≥70°C. Exposure to temperatures greater than 150°C had an obvious detrimental effect and a significant loss in electroactivity was observed after treatment at 300°C. By contrast, *Figure 5* shows the effect of exposure to an oxygenated environment at elevated temperatures. After treatment at 150°C there was much greater loss of electroactivity compared with treatment in a N_2 atmosphere, and exposure to 200°C resulted in a total loss in electroactivity. It may be concluded that the rate of decay of electroactivity was much faster when samples were heated in air at $T > 150°C$. This is probably due to chemical reaction of O_2 with the highly conjugated PAn system. It should be noted that the samples exposed to 300°C, under nitrogen, still had some stable electroactivity, although the currents recorded were much less than for the original sample. This was not observed when the polymer was exposed to this temperature in an air atmosphere.

Effect of thermal treatment on electroactivity of polyaniline prepared chemically

The c.v. obtained from the chemically synthesized PAn deposited film exhibited the same well defined redox peaks observed with electrochemically synthesized PAn (*Figure 6*). However, it was found that the stability of these responses for polyaniline prepared in this manner was lower than for electrochemically prepared PAn. A major irreversible loss in electroactivity was observed at $T > 150°C$ in air and $T > 200°C$ in nitrogen as depicted in *Figures 6* and *7*.

Both electrochemically and chemically prepared polyaniline show similar responses to temperature exposure in that electroactivity is retained more substantially in a heated inert atmosphere compared to an oxygenated one. Electrochemically prepared polymer appears to be slightly superior in its stability in a nitrogen atmosphere.

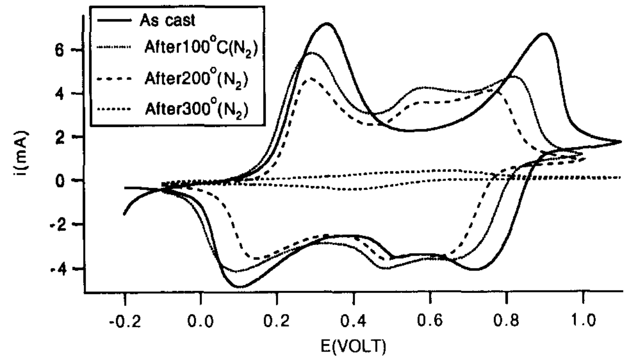


Figure 6 Effect of heat treatment under nitrogen on c.v. of chemically prepared polyaniline

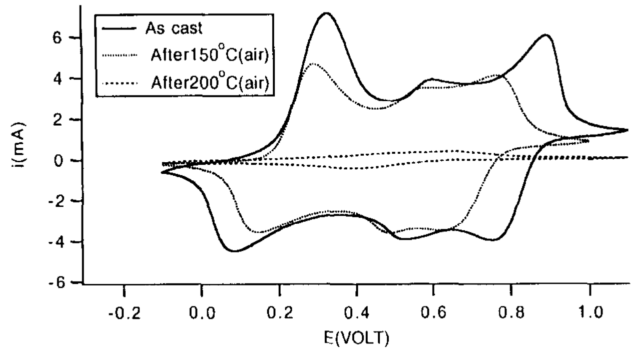


Figure 7 Effect of heat treatment in an oxygenated atmosphere on c.v. of chemically prepared polyaniline

Whether this is due to a difference in molecular weight, degree of crystallinity or morphology is unclear.

Dry-state conductivity

Using chemically prepared films having adequate mechanical strength, it was found that the dry-state conductivity decreased after even mild heat treatment (*Table 1*). However, as reported previously, this is most likely due[10,11] to simple dehydration of the polymer and evaporation of free dopant, HCl. There was little difference between thermal treatment in air or nitrogen for these samples, which is consistent with this. In the present work it was found that at least 80% of the loss in dry-state conductivity observed up to 150°C could be restored by soaking in acid media (1 M HCl). However, thermal treatment at temperatures higher than 150°C caused an irreversible loss in dry-state conductivity. This may be due to some irreversible structural changes or chemical interactions between dopant or solvent with the polymer chain as reported previously[18], perhaps involving chlorination of the benzene ring at high temperatures by the dopant HCl. Thermal ageing might also involve the reactions of amine and imine groups[11,16,17] resulting in fewer N atoms being available or accessible for reprotonation (or redoping).

Electrochemically prepared polyaniline samples showed quite different dry-state conductivity behaviour. Although having much smaller absolute conductivities initially, mild thermal treatment (100°C for 1 h under N_2) enhanced the conductivity by over 30%. Exposure to higher temperatures led to a major irreversible loss in conductivity (*Table 2*).

It is interesting to note that Kobayashi[20,24] found large increases in conductivity through mild annealing for chemically prepared polyaniline. Exposure at 150°C for

Table 1 Effect of thermal treatment on dry-state electrical conductivity[a] of polyaniline membranes prepared chemically in air

T (°C)	σ_1	σ_2	σ_1'	σ_2'
R.t.	25 ± 3	25 ± 3	25	25
100	2.1	2	25	25
150	0.21	0.25	20	20
200	0.1–0.2	–[b]	3–4	2.5
300	[b]	–[b]	3–4	–[b]

[a] σ_1 (S cm^{-1}) is the conductivity measured when the polymer was thermally treated under nitrogen; σ_2 is conductivity of polymer after heat treatment in air; σ_1' and σ_2' are conductivity of the polymers after heat treatment and then soaking for 24 h in 1 M HCl solution

[b] The conductivity was too low to be measured by the four-point probe method

Table 2 Effect of thermal treatment on conductivity of electrochemically produced PAn/HCl

Temperature of heat treatment[a] (°C)	Conductivity × 10^3 (S cm^{-1})
As prepared	625
100	830
150	13.5
200	4.5
300	37

[a] 1 h under nitrogen. Polymer samples were then treated in a solution of 1 M HCl for 4 h. The samples were dried at 60°C for 1 h (under N_2). Polymer powder was then compressed into pellets (6 mm diameter × 2 mm thick). The conductivities were then measured by the van der Pauw method[23]

Table 3 Effect of thermal treatment on mechanical properties of PAn/HCl[a]

T (°C)	Tensile strength (MPa)
R.t.	60
100	65
200	70
300	90

[a] Samples for mechanical tests were prepared in 5 μm × 30 μm × 50 μm (width × length × thickness) dimensions. Thermal treatment was carried out under nitrogen for 1 h

about 2 h led to a four-fold increase in conductivity. This was not found in the present work. One reason for this may be that the polymer in Kobayashi's work was prepared in a different manner, as compressed pellets, and was vacuum dried before annealing to remove solvent.

Effect of temperature on mechanical properties of polymer

The effect of thermal treatment upon the tensile strength of the polymer samples was then investigated (*Table 3*). These tests were carried out using the chemically prepared polymer, as the electrochemical preparation produced very fragile samples (indicative of different morphology). The results, showing an increase in tensile strength after heating, confirm that crosslinking reactions occur in the course of thermal treatment at $T > 150$°C. Mechanical tests on polymer samples treated at 300°C also indicate that the polymer structure is stable and does not decompose up to 300°C.

Polyaniline after heating at $T > 300$°C became very rigid and also lost flexibility, becoming brittle and fragile. NMP and water have a plasticizing effect on the polymer. Upon heating to 200°C evaporation of moisture and solvent occurs and the flexibility decreases considerably. Polymer membranes heated at 300°C became insulating materials (see above). However, the mechanical strength was still high even though the material was very brittle even after soaking in water or acid solution.

Previous work by Kobayashi[24] and coworkers has shown that exposure to elevated temperatures (up to about 150–200°C) can have an annealing effect on chemically prepared polyaniline. In an inert atmosphere the regularity of the polymer chains can be increased without any structural changes in the polymer backbone such as ring opening. This is thought to lead to a phase change to a looser-packed ordered system. However, in an oxygenated atmosphere a range of reactions are possible including introduction of substitutions along the polymer chains and subsequent loss of conjugation and conductivity. This is consistent with the present results, as these changes induced by mild heat treatment should be accompanied by increases in conductivity and mechanical strength.

Thermal analysis of polyaniline samples

Thermal analysis of polyaniline samples has been well studied previously, as outlined in the 'Introduction'. The general trends in the weight losses are well understood. However, thermal gravimetric analysis was carried out on both the chemically and electrochemically prepared polyaniline samples used in this work to complement the experiments on the effects of thermal treatment on electroactivity. Thus it is possible to correlate the observed changes in electroactivity with the known physical/chemical changes in polymer structure and morphology that thermal treatment induces.

Polyaniline powder prepared after chemical oxidation and in the doped state with HCl showed poor thermal stability under nitrogen as seen in *Figure 8a*. The t.g.a. trace is consistent with what has been published previously in the literature[25]. Continuous weight loss was observed above room temperature, although this may be broken down into three steps. Up to a temperature of 200°C, 18% of the polymer weight was lost. This may be attributed to evaporation of moisture and HCl and probably some low-molecular-weight polymer segments as well as trapped Cl_2 formed during chemical oxidation. The d.t.a. curve shows a negative change for this weight loss, indicating an endothermic heat associated with it. This is consistent with the attributed physical changes. The loss between 200 and 400°C corresponded with the decrease in electroactivity observed above after such treatment. The major mass loss was observed at 380°C. The total weight loss up to 500°C was 55%, which includes some weight loss due to polymer backbone degradation. Here the d.t.a. curve shows a large exothermic change consistent with a chemical degradation

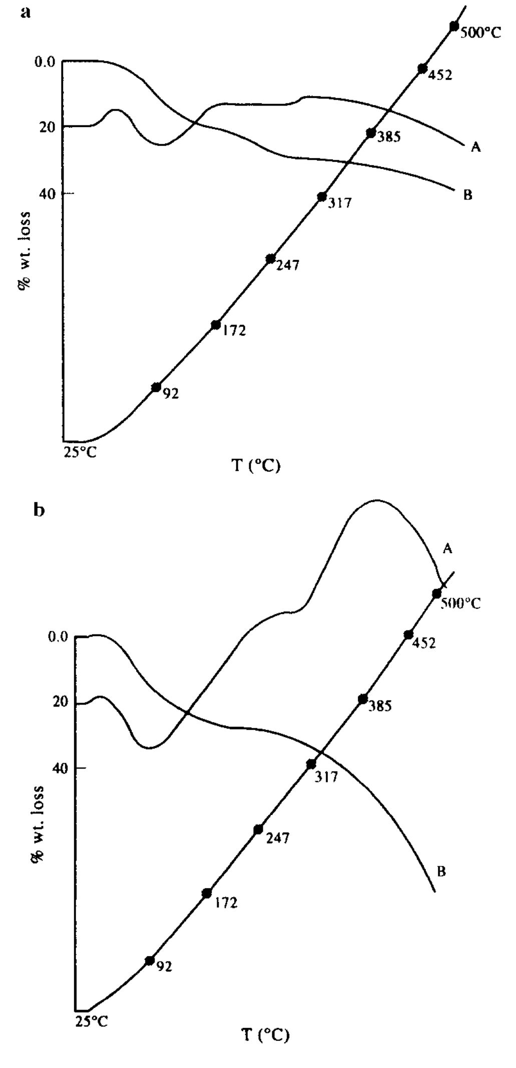


Figure 8 D.t.a. (A) and t.g.a. (B) of HCl-doped emeraldine base form of polyaniline powder prepared by chemical oxidation under (a) N_2 atmosphere and (b) air atmosphere

reaction. The effect under an oxygenated environment (*Figure 8b*) is worse, with an 80% weight loss above 300°C. This confirms previous reportings[26]. It has been shown that under these conditions at temperatures above 150°C elimination of the dopant (HCl) on the amino group occurs simultaneously with chlorination of the polymer's aromatic rings[25,26].

The weight-loss characteristics for an acid-doped polyaniline membrane cast from NMP were then considered. The t.g.a. (*Figure 9*) shows the same characteristic three-stage curve and similar thermal stability. The polymer was stable up to 320°C. Before this the major weight loss was due to evaporation of HCl, moisture and NMP (b.p. 202°C).

T.g.a. on electrochemically prepared polyaniline

Polyaniline was synthesized electrochemically by constant-potential means. Three separate steps of weight loss were observed under N_2 as shown in *Figure 10a*. The first two may be attributed to loss of solvent and dopant (or its degradation) first from easily accessible sites and subsequently from deeper in the material. The d.t.a. curve shows endothermic changes associated with this weight loss, which is consistent with the proposed physical phenomena. The third weight loss is due to degradation of the polymer itself with a large exothermic change associated with it. Similar trends were observed for treatment under an oxygenated atmosphere as shown in *Figure 10b*.

All the polyaniline samples prepared in this work exhibited thermal stability (as shown by thermal analysis) consistent with the proposed three-step degradation[4–9,24–26]. Samples heated in an oxygenated environment showed greater and more rapid weight loss than those in an inert atmosphere. In all samples the polymer backbone was stable beyond 350°C. This implies that the changes in electroactivity (and conductivity) observed between 150 and 250°C were not caused by polymer degradation but may be attributed to morphological changes in the polymer, including cross-linking and loss of dopant and moisture.

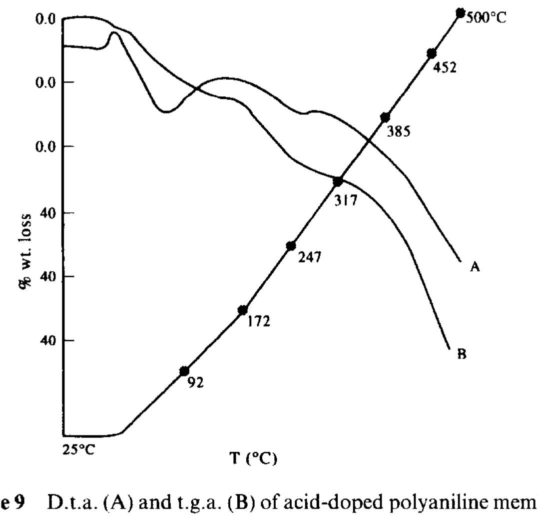


Figure 9 D.t.a. (A) and t.g.a. (B) of acid-doped polyaniline membrane cast from NMP under N_2

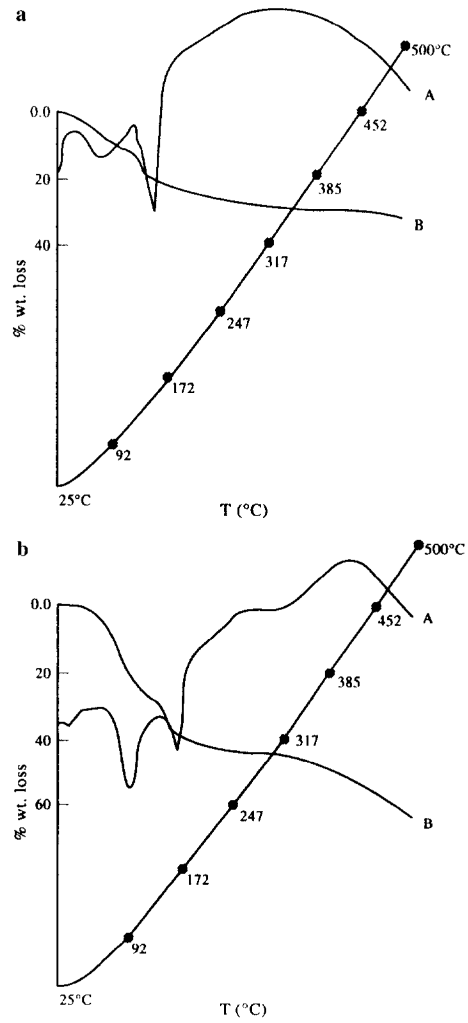


Figure 10 D.t.a. (A) and t.g.a. (B) of electrochemically prepared polyaniline produced by the constant-potential method under (a) N_2 atmosphere and (b) air atmosphere

CONCLUSIONS

It has been shown that the electroactivity of polyaniline starts to decrease after 70°C but then shows little further deterioration until 150°C. This seems to be almost independent of the drying atmosphere, although the inert one is slightly better than air. The electroactivity of polyanilines doped with HCl prepared chemically or electrochemically in both reduced and oxidized and fully oxidized forms are unstable at $T > 150°C$ in air but keep their electroactivity up to 300°C under nitrogen. Thus the results described here of the effect of thermal treatment on electroactivity are significant as electroactivity is a central property to many applications of polyaniline.

Electroactivity changes by thermal treatment are mainly due to morphological changes of polymer that occurs even after mild heating. Previous work, including thermal analysis, has shown that these include cross-linking[19] and chlorination of benzene rings at high temperature ($T > 150°C$) caused by dopant (HCl).

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