A kinetic study of polypyrrole degradation

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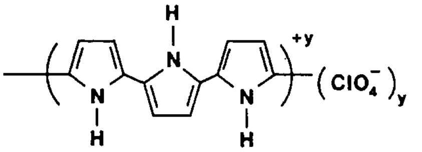
Conducting polypyrrole films with *p*-toluenesulphonate, perchlorate and tetrafluoroborate dopants were aged at elevated temperatures in oxidizing and inert environments. Their decline in electrical conductivity was analysed using a first-order decay model. Films were also examined by X-ray photoelectron spectroscopy, differential scanning calorimetry, thermogravimetric analysis and scanning electron microscopy. Changes in polymer morphology, degree of oxidation and dopant integrity were determined.

(Keywords: conducting polypyrroles; time-dependent degradation; conductivity measurements; activation energies; kinetics; surface analysis)

INTRODUCTION

Polypyrroles conduct low levels of electricity due to modification of the electronic conduction band structure, this mechanism differing from polyolefins with metal or carbon fillers. The polymer exists as a charged complex of 1,4-linked pyrrole units in the backbone, and an electrolyte dopant, e.g.



Preparation involves simultaneous polymerization of the monomer, through chain oxidation and incorporation of the anion, to balance the net positive charge of the polymer backbone[1,2].

Few kinetic studies of the degeneration of electrical and structural properties of polypyrroles have appeared. Typically only initial and final conductivity values are stated. However those papers contain a considerable amount of information. Samuelson and Druy[3] proposed two kinetic models for thermal oxidation of polypyrroles having different dopant types. The conductivity loss of polypyrrole *p*-toluenesulphonate followed a first-order decay function with an activation energy of 62.7 kJ mol^{-1} being obtained. They proposed that the polymer degrades by reaction with oxygen or water. Polymers with tetrafluoroborate and perchlorate dopants did not give first-order decay functions, due to backbone oxidation being accompanied by polymer–dopant reactions. The method of polypyrrole preparation was also said to influence the type of degradation mechanism[3].

The oxidation of polyacetylene and poly(1,6-heptadiyne) shows first-order degradation rates at elevated temperatures in air[4–6]. Although reaction rates for the two polymers were different, the activation energies were found to be identical (58 kJ mol^{-1}). This is despite the allylic hydrogens being more easily extracted in poly(1,6-heptadiyne). This activation energy is assigned to an oxygen insertion barrier in each conjugated backbone.

The conductivity of polypyrrole arises from long chains of conjugated or alternating double bonds within the polymer matrix. The effect of the dopants is to change the configuration of the existing molecular orbitals, to create a 'polaron', or radical cation, free to move under the influence of an electric field. Charge travels along conducting segments of the chain until a conjugation block is found, whereupon the charge hops to another adjacent chain, to continue on[7,8]. Degradation of film conductivity can be caused by any process that changes or hinders the chain hopping conduction mechanism. Reaction of the main polymer chain with oxygen, water or damaging radiation (e.g. u.v.), can lead to an irreversible loss of conjugation and conductivity. The formation of carbonyl, ester and hydroxyl groups primarily at the β-position of the pyrrole group will occur, possibly by a free radical process[8,9]. Chain scission of the five-membered ring, by attack at the α-position, will also disrupt conjugation[10]. Decomposition of the dopant into volatile or reactive fragments will lead to irreversible dedoping reactions of the conjugated system[11,12]. Reaction with oxygen or counterions at the pyrrole nitrogen can occur without loss of conjugation, but with modification of the electronic structure of the polymer, for example by the formation of nitrogen oxide groups[9].

X-ray photoelectron spectroscopy (X.p.s.) relates the chemical environment of an atom to the measure of the binding energy of core electrons ejected by interactions of a molecule with a beam of soft X-rays. Erlandsson *et al.*[13] performed stability experiments on polypyrroles in order to correlate changes in resistivity and composition during storage under various conditions. The only direct evidence for chemical modification due to air or oxygen was the appearance of a high binding energy shoulder on the C(1s) subshell peak after storage in oxygen and air. The splitting from the main carbon peak corresponds well with the shift observed for carbonyl carbon. Dopant decomposition is less well defined, with a number of

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workers[11,13,14] disagreeing on the resultant products of tetrafluoroborate and perchlorate dopants and their effect on the remaining polymer. Our work concentrates on accelerated ageing at higher temperatures.

Numerous morphological accounts have been provided, with structures ranging from dense and uniform films incorporating *p*-toluenesulphonate to dendritic and open webs of tetrafluoroborate films[15,16]. Polypyrroles are relatively amorphous and branched and thus the surface area and porosity will be substantial. Changes in the morphology of these materials with ageing needs to be monitored, as the ingress of oxygen and leaching of dopants is an important factor in polymer degradation. Further, any gross changes including cracks, ablative effects, etc. will affect conductivity. Our present study examines the effects of air and nitrogen ageing at elevated temperatures upon polypyrrole *p*-toluenesulphonate, tetrafluoroborate and perchlorate.

EXPERIMENTAL

Polypyrrole polymer films were prepared by electrochemical polymerization in a conventional single compartment cell equipped with either platinum or titanium anodes (polished with 6 μm diamond paste) and carbon cathodes[17]. Polymerization solutions consisted of monomer pyrrole (Sigma Chemical Co., doubly distilled prior to use) and tetraethylammonium *p*-toluenesulphonate, tetraethylammonium tetrafluoroborate or lithium perchlorate (Aldrich Chemical Co., dried prior to use). The solvent system used was either anhydrous propylene carbonate (Sigma Chemical Co.) or anhydrous acetonitrile (Waters Assoc.) with 1% v/v water added for the cathodic reaction, the latter yielding more flexible and ductile films[1]. Electrodeposition was carried out galvanostatically at low current densities with respect to the anode area (0.7–1.0 mA cm^{-2}), resulting in low growth rates. The free standing films (20 μm thick) were removed from the electrode with a scalpel, and washed in water and alcohol and dried.

To monitor film conductivity during ageing, the four-in-line technique was employed, four conducting silver epoxy fingers being arranged laterally across a 30 mm × 5 mm strip of polypyrrole[18]. The inner electrode spacing was 10 mm, and sample thickness was measured to within 1 μm. The dependent variable, conductivity was measured on line to determine decay kinetics. All experiments were in the dark to ensure only triplet oxygen interactions. U.v. radiation ageing was performed using a Phillips HPR 125 W u.v. lamp in air.

X.p.s. data were obtained using a Vacuum Generators Scientific (VGS) HB-100 electron spectrometer. X-Rays (Al Kα 1486.6 eV) were produced by an aluminium anode operating at 15 kV. The photoelectrons emitted were analysed by a VG CLAM-100 150° spherical section electrostatic analyser, in constant energy analyser mode and pass energy of 20 eV. Data collection and processing were performed by a DEC 11/23 minicomputer. Scanning electron micrographs were obtained on a Cambridge-360 Stereoscan SEM, operating at 15 kV, with gold-coated samples. Thermogravimetric analysis (t.g.a.) was performed using a Du Pont Instruments 951 system with air and nitrogen purge gases (20 cm^3 min^{-1}), sample sizes of 30–50 mg and heating ramped at 20°C min^{-1}. Differential scanning calorimetry (d.s.c.) was performed with a Du Pont 910 DSC unit using 1–5 mg samples heated at 20°C min^{-1} in nitrogen.

RESULTS AND DISCUSSION

Conductivity values are calculated from the voltage output using the four-probe technique. For the process to follow first-order decay rates[3,4,6], equation (1) must be obeyed.

$$\sigma_t = \sigma_0 e^{-kt} \tag{1}$$

where k is the rate constant.

Conductivity decay plots are produced when the logarithm of the normalized conductivity is plotted against time:

$$\ln(\sigma_t/\sigma_0) = -kt \tag{2}$$

The apparent rate constant may be correlated to changes in temperature by fitting the data to an Arrhenius model:

$$\ln(k) = \ln(A) - E/RT \tag{3}$$

Films of *p*-toluenesulphonate doped polypyrrole (nominally 20 μm thick), were aged for 1000 min at temperatures from 65 to 170°C in air, to produce conductivity decay traces as shown in *Figure 1*. This process can be seen to be thermally activated, with higher temperatures producing much higher decay rates and loss ratios. The conductivity decay is linear after 200–400 min at the higher temperatures and linear after 100 min at the lower temperatures. During the initial stages of ageing a higher loss of conductivity occurs making extrapolations to zero time for higher temperatures suspect.

Above 160°C, decay trace shapes are non-linear at short ageing times differing slightly from results by Samuelson and Druy[3]. However, poly(3-alkylthiophenes) show similarly shaped decay traces[19]. Rate constants from slopes at 1000 min (consistent with the method of Wang and Rubner[19]) give the Arrhenius plot shown in *Figure 2* and an activation energy of 56 kJ mol^{-1}, in close agreement with the 58 kJ mol^{-1} attributed to oxygen insertion of the conjugated chain[4].

The ageing characteristics of thick laboratory prepared films made using extended polymerizations were compared with 'Lutamer' a commercial BASF polypyrrole doped with *p*-toluenesulphonate (66 μm thick). When aged in air over the temperature range 65–140°C, a linear

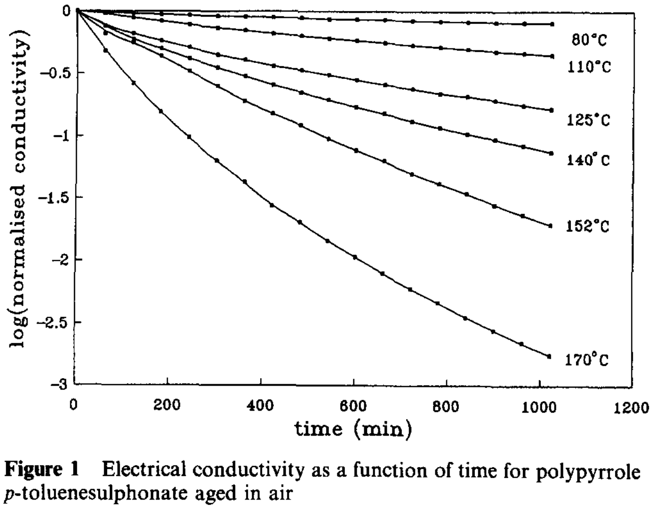

Figure 1 Electrical conductivity as a function of time for polypyrrole *p*-toluenesulphonate aged in air

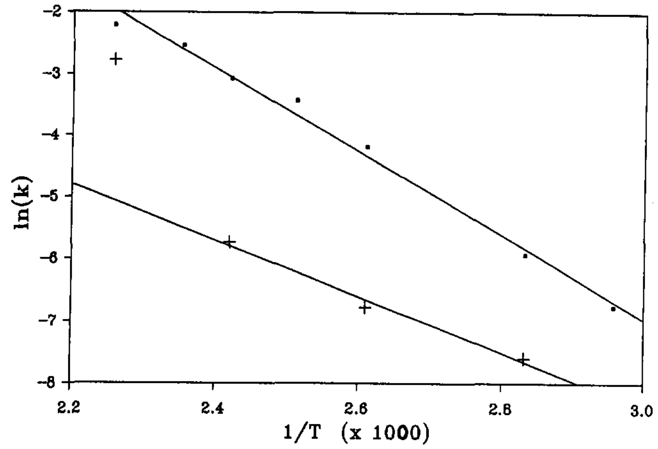

Figure 2 Rate constants as a function of temperature for polypyrrole *p*-toluenesulphonate aged in air (■) and nitrogen (+)

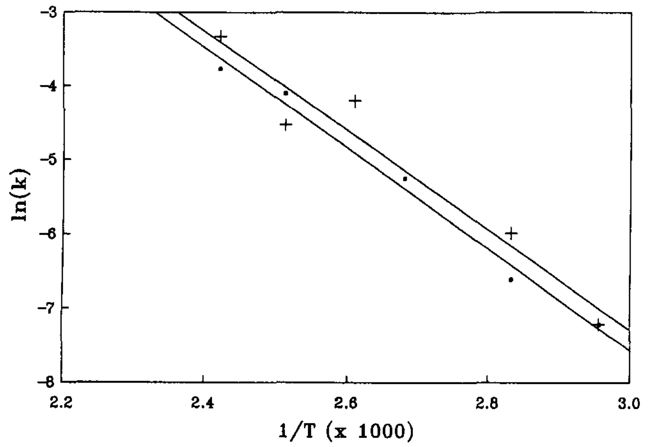

Figure 3 Comparison of rate constants as a function of temperature for BASF Lutamer (■) and as-prepared polypyrrole *p*-toluenesulphonate (+)

Arrhenius plot (*Figure 3*) was obtained for each film to give almost identical activation energies of 55 kJ mol^{-1}.

In the absence of u.v. light, oxidation should only involve triplet (ground state) oxygen interactions, reaction occurring only at existing free radical sites. Assuming that absorption of oxygen onto the polymer surface is much faster than the degradation reaction, the oxidation is most likely a pseudo-first-order process[5]. Polypyrroles have a large population of free radical sites in order to act as charge carriers in the conduction process, which are very vulnerable to triplet oxygen insertion. The formation of hydroperoxy radicals at these sites [equations (4a) and (4b)] will not only lead to oxidation of the carbon backbone, but also the loss of the free radicals and hence conductivity will be reduced. Decomposition of the polymer hydroperoxides [equation (4c)] will lead to the formation of hydroxide, carbonyl and aldehyde groups through a number of intermediates and stages[5,20,21].

$$\mathrm{P^{\bullet} + O_2 \rightarrow POO^{\bullet}} \qquad (4a)$$

$$\mathrm{POO^{\bullet} + PH \rightarrow POOH + P^{\bullet}} \qquad (4b)$$

$$\mathrm{POOH \rightarrow {>}C{=}O + {>}CH(OH)} \qquad (4c)$$

Polypyrrole samples doped with *p*-toluenesulphonate were exposed to air at 110°C for up to 28 days. The carbon region of the X.p.s. spectrum shows a subtle increase in shoulder intensity of the main carbon peak at 285 eV, corresponding to the carbonyl linkage at 288 eV and carboxyl linkage at 289–290 eV. Examination of the sulphur peak of the anion dopant showed no appreciable difference in peak shape or height over time, indicating negligible dopant degradation at this temperature. At higher ageing temperatures (up to 200°C) the peak height of sulphur is reduced by half, showing moderate levels of surface dopant removal.

We conclude on the basis of the combined work of Samuelson and Druy[3], Pochan *et al.*[4,5,8] and present information (with more information given elsewhere[22]), that a direct reaction of oxygen with polypyrrole *p*-toluenesulphonate backbone occurs at the indicated temperatures. At higher temperatures, conductivity loss may be attributed to dopant decomposition.

When experiments were repeated with a nitrogen atmosphere (*Figure 4*), lower rates of conductivity loss are observed, with for example no decrease in conductivity being observed for 200 min at 80°C. The normalized conductivity for air ageing at 110°C for 1000 min is 0.71, or 71% initial conductivity, as seen in *Figure 1*, while in a nitrogen atmosphere the loss ratio is 0.99. The rate of loss, as shown in the Arrhenius plot (*Figure 2*), is also much lower at low temperatures 80–140°C, but comparable to air ageing at higher temperatures. This suggests that at this temperature (170°C) an Arrhenius law prediction is not adequate. The extra contribution may be thermally induced dedoping of the polymer or thermal breakdown of the polymer backbone.

On the basis of measurable activation energies, the conductivity of a 20 μm film after exposure for 1 year at 30°C could be 49% of its initial value. Although this seems quite high, the difference on a logarithmic conductivity scale is not that great. In nitrogen or in sealed conditions, the degree of oxygen intrusion into the film and subsequent oxidation of the polymer chain would be minimized, resulting in a reduction in conductivity loss, and an extension of material lifetime.

Perchlorate doped films aged in nitrogen showed similar results to those of *p*-toluenesulphonate, with considerably higher conductivity loss rates (*Figure 5*) whilst at temperatures less than 100°C in air a linear relationship is found but a discontinuity is observed above 170°C. We attribute this increased rate to dopant

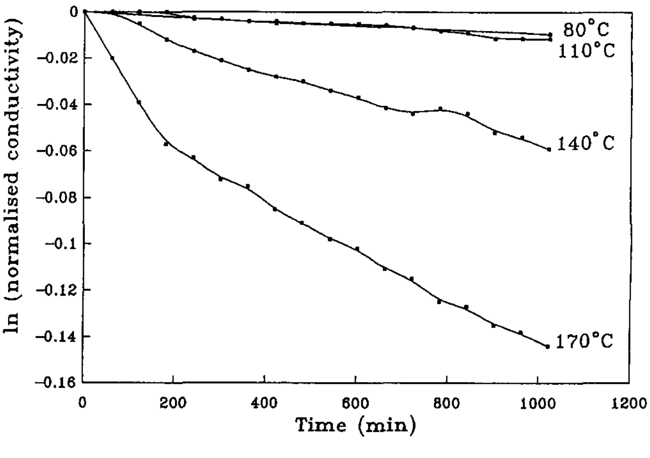

Figure 4 Electrical conductivity as a function of time for polypyrrole *p*-toluenesulphonate aged in nitrogen

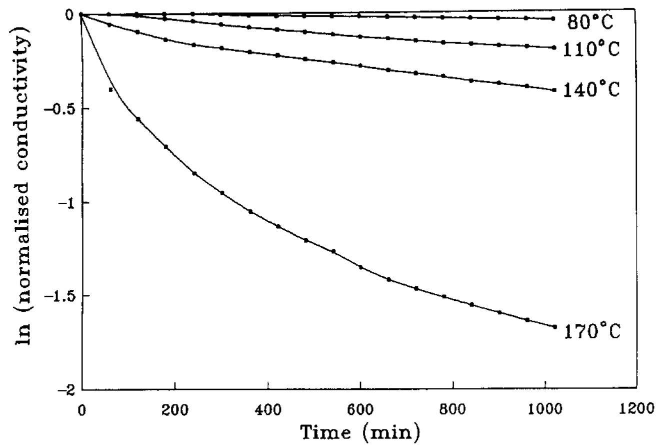

Figure 5 Electrical conductivity as a function of time for polypyrrole perchlorate aged in nitrogen

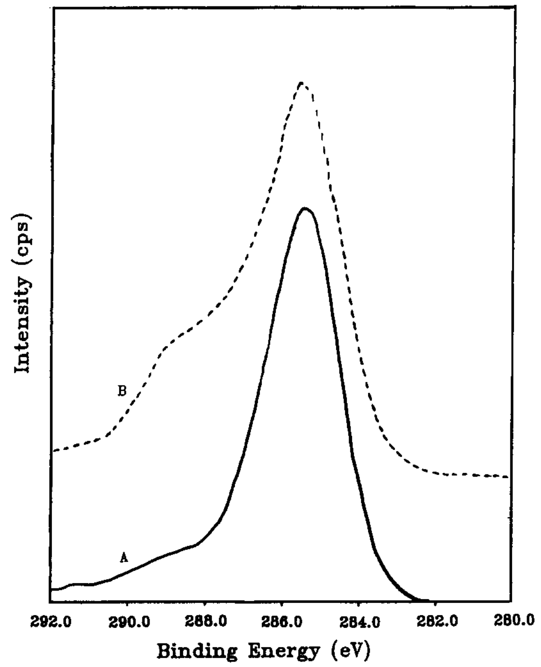

Figure 6 X.p.s. scans of the carbon (1s) peak for polypyrrole perchlorate control (A) and film aged at 110°C for 14 days (B), showing increase in shoulder intensity

decomposition and greater polymer breakdown. The activation energy in air is ~26 kJ mol^{-1}, much lower than that for polypyrrole *p*-toluenesulphonate, and correlates activation energy with observed electrical stability.

The results for polypyrrole tetrafluoroborate exhibit curious trends. The Arrhenius plot shows the rate constant to be independent of temperature, contrasting with the previous two cases. The conductivity decay proceeds at a constant yet high rate. The normalized conductivity ratio for tetrafluoroborate doped polypyrrole after 1000 min is 0.38, while for perchlorate doped polymers is 0.14, considerably less than that shown for *p*-toluenesulphonate films.

Perchlorate and tetrafluoroborate polymer complexes, at least at low temperatures, closely follow first-order Arrhenius laws, differing from the results of Samuelson and Druy[3] where the decay process showed possible fractional order kinetics. In both air and nitrogen, we find first-order decay, but activation energies are considerably lower than that for our polypyrrole *p*-toluenesulphonate and those published by other workers[3–7].

Whilst tetrafluoroborate doped polypyrrole showed an increased shoulder on the main carbon X.p.s. peak, polypyrrole perchlorate showed the largest change (*Figure 6*) indicating the highest amount of carbon oxidation. This correlates with the conductivity results for air ageing at 110°C, where polypyrrole perchlorate showed the largest conductivity loss, attributed to polymer oxidation. The broad shape of the carbon peak indicates a number of carbon–oxygen bonded species existing on the surface of the polymer. Further X.p.s. work curve fitting and peak shape analysis may produce semiquantitative information into the nature of the oxidized carbon species.

In addition to previous degradation mechanisms, the latter two polymer complexes are also susceptible to dopant decomposition. Perchlorate ions thermally degrade to chloride ions and free oxygen, while tetrafluoroborate ions degrade to fluoride ions and boron trifluoride gas[11–14]:

$$ClO_4^- \rightarrow Cl^- + 2O_2 \qquad (5a)$$

$$BF_4^- \rightarrow BF_3 + F^- \qquad (5b)$$

Changes in dopant X.p.s. spectra will reflect this degradation, with the chlorine spectrum for perchlorate doped polypyrrole exhibiting changes in position and intensity over time. The chlorine peak for perchlorate occurring at 208–209 eV (*Figure 7*) decreases in thermally

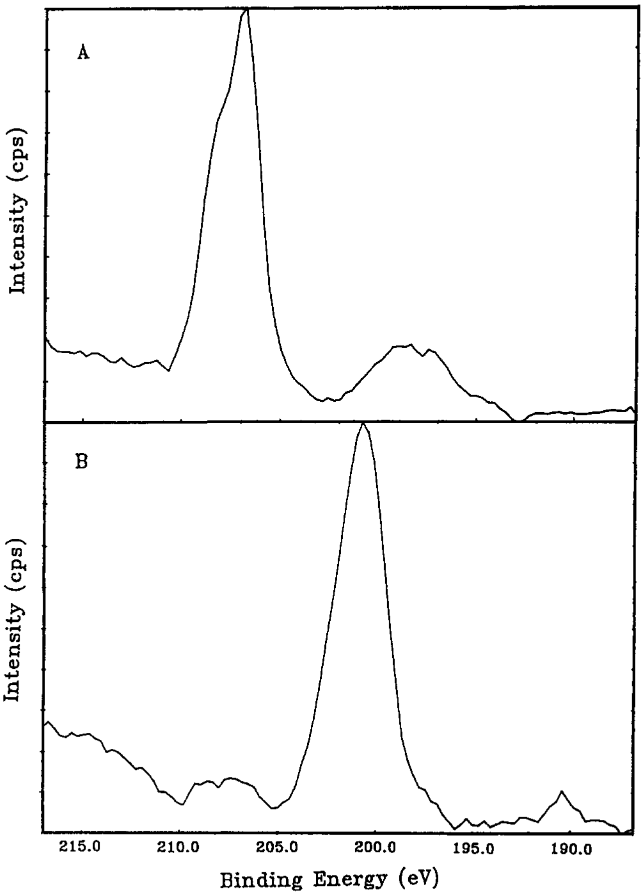

Figure 7 X.p.s. scans of the chlorine (2p) peak for polypyrrole perchlorate control (A) and film aged at 110°C for 14 days (B), showing changes in perchlorate and chloride species

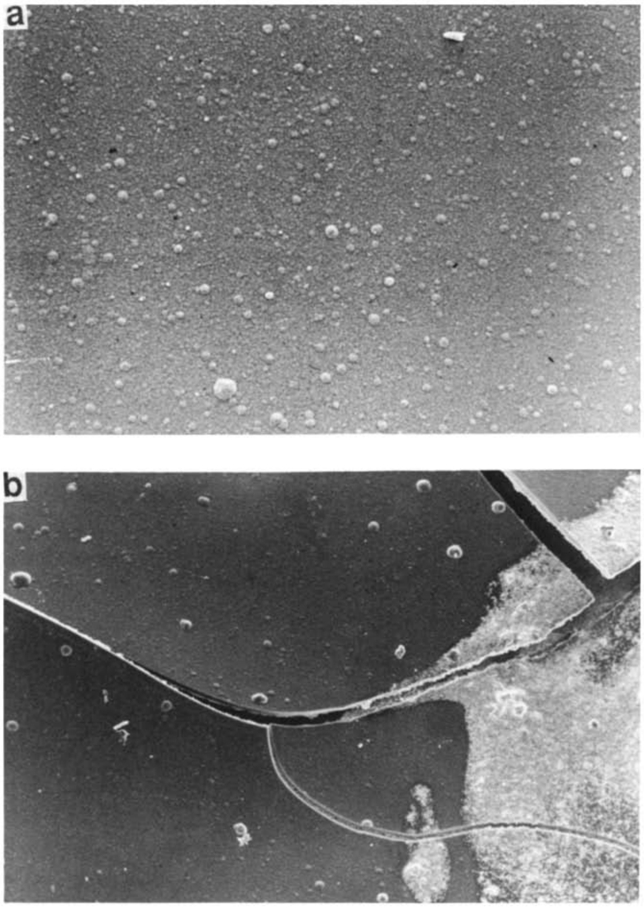

Figure 8 Scanning electron micrographs of polypyrrole *p*-toluenesulphonate control (a) and sample aged at 300°C for 1 day (b). Magnification ×210

aged (110°C for 14 days) polypyrrole perchlorate and a lower binding energy chloride peak at 200 eV appears. With tetrafluoroborate doped samples no boron could be resolved after 14 days at 110°C, and only low levels of fluorine occurred as fluoride ions. This provides evidence for dopant degradation additional to polymer oxidation in polymers doped with tetrafluoroborate and perchlorate.

When exposed to u.v. radiation in air, only tetrafluoroborate doped polypyrrole exhibited rapid electrical conductivity deterioration, with a conductivity loss ratio of 0.62 after exposure for 90 h. All exposed samples degraded somewhat faster than control samples, where u.v. light was excluded. The presence of u.v. light complicates the oxidation mechanisms by combining the ground state processes mentioned earlier and reactions with excited state species. U.v. light will produce singlet oxygen at a higher energy state[20]. Polypyrrole tetrafluoroborate may undergo a u.v.-initiated dedoping reaction, where tetrafluoroborate ions decompose to fluoride ions and volatile boron trifluoride gas. This agrees with X.p.s. results where only small levels of carbon oxidation but large levels of dopant decomposition were observed. Polymers doped with *p*-toluenesulphonate and perchlorate showed high resistance to exposure for 90 h.

A factor affecting changes in conductivity and thermal stability is polymer surface morphology. The polypyrrole *p*-toluenesulphonate films employed were homogeneous, flexible and have a relatively featureless surface (*Figure 8a*), and perchlorate-based films showed similar surface textures (*Figure 9a*), but with much larger (50 μm) nodules. The tetrafluoroborate doped films have rough, uneven surfaces (*Figure 10a*). Thus some variation due to surface area effects and porosity are anticipated.

When the polypyrrole *p*-toluenesulphonate samples are aged in air or nitrogen over the temperatures used for the kinetic experiments (i.e. up to 170°C) no evidence for cracking could be found by optical microscopy or scanning electron microscopy. However, at temperatures of 300°C for 24 h, surface and bulk cracks are observed which would reduce conductivity readings and represent gross thermal degradation. Below 300°C, the *p*-toluenesulphonate films showed little cracking in nitrogen. The tetrafluoroborate and perchlorate doped polypyrroles were more unstable, with severe surface and bulk cracking at 200°C in air. The geometry of the cracks is similar in all cases, and for the tetrafluoroborate films follow the 'valleys'. Examples of cracking for each of the films are given in *Figures 8b*, *9b* and *10b*. These cracks are thought to be due to normal oxidative processes involving chain scission of the polymer into lower molecular weight chains and the depletion of the dopant anion resulting in polymer shrinkage and cracking. A cracked polypyrrole perchlorate film after ageing in air at 200°C for 24 h is shown in *Figure 11* at higher magnification. The nodular structure of the upper, exposed surface is now resolvable in the upper left region, and appears largely unaltered. The cross-section is typical of a relatively brittle amorphous polymer, with small peaks indicating limited ductility. There are a few pores,

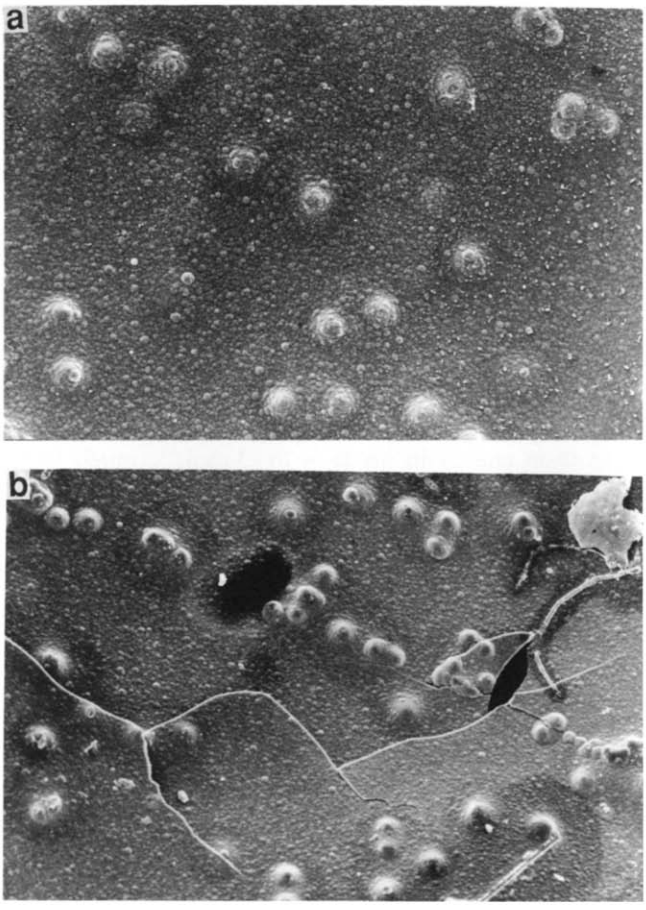

Figure 9 Scanning electron micrographs of polypyrrole perchlorate control (a) and sample aged at 200°C for 1 day (b). Magnification ×210

and a suggestion of 'whitening' at the lower layers although these are not viewed as significant.

In nitrogen, vacuum dried polypyrrole *p*-toluenesulphonate does not lose weight below 300°C, but undergoes a severe irreversible loss in conductivity at 440°C, associated with a 20% weight loss. In air, thermal stability is much less, with significant weight losses at 250°C and a similar irreversible loss in conductivity occurring at 350°C. The first major weight loss for tetrafluoroborate doped polypyrrole occurs at 190–200°C, decomposing at a similar rate to polypyrrole *p*-toluenesulphonate, but at a lower temperature.

Polypyrrole perchlorate retains 95% of its original weight at 250°C in nitrogen but above 280°C detonation of the sample occurs. No corresponding phenomena occur in samples aged for long periods at moderate temperatures, other than a decrease in conductivity. A d.s.c. trace (*Figure 12*) of a small sample (0.6 mg) of this polypyrrole shows a sharp exotherm ($\Delta H = 2.3\ \mathrm{kJ\ g^{-1}}$) at 296°C, indicating the onset of detonation. T.g.a. of a larger sample shows this transition as an instantaneous weight loss (*Figure 13*). The abruptness of the detonation will be affected by sample size and thickness. The intense exotherm is consistent with reaction between a powerful oxidant and the oxidizable polymer backbone. It is known that perchlorate anions when mixed with organometallic ions form potentially explosive compounds,

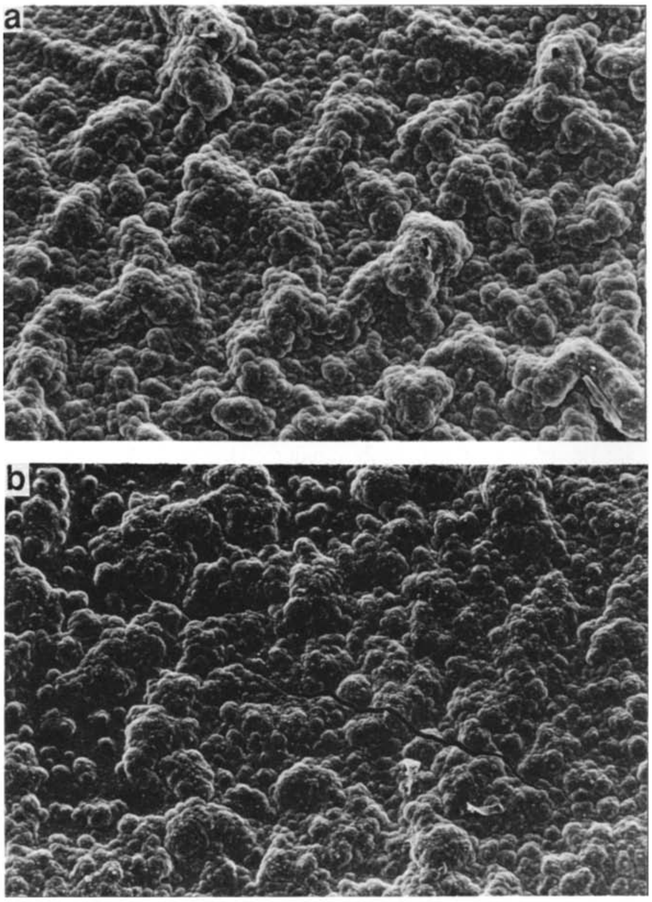

Figure 10 Scanning electron micrographs of polypyrrole tetrafluoroborate control (a) and sample aged at 200°C for 1 day (b). Magnification ×210

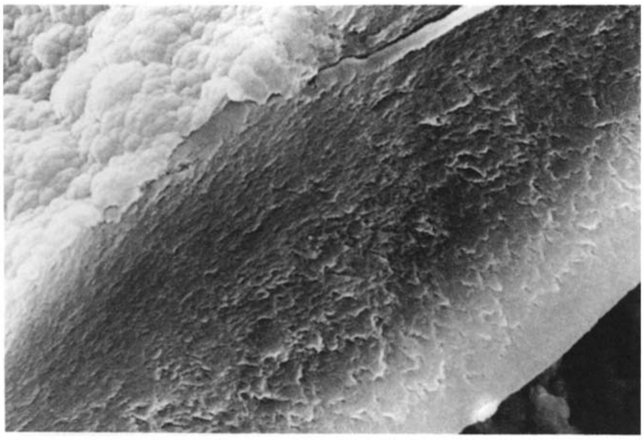

Figure 11 Scanning electron micrograph of crack cross-section of polypyrrole perchlorate aged at 200°C for 1 day. Magnification ×12600

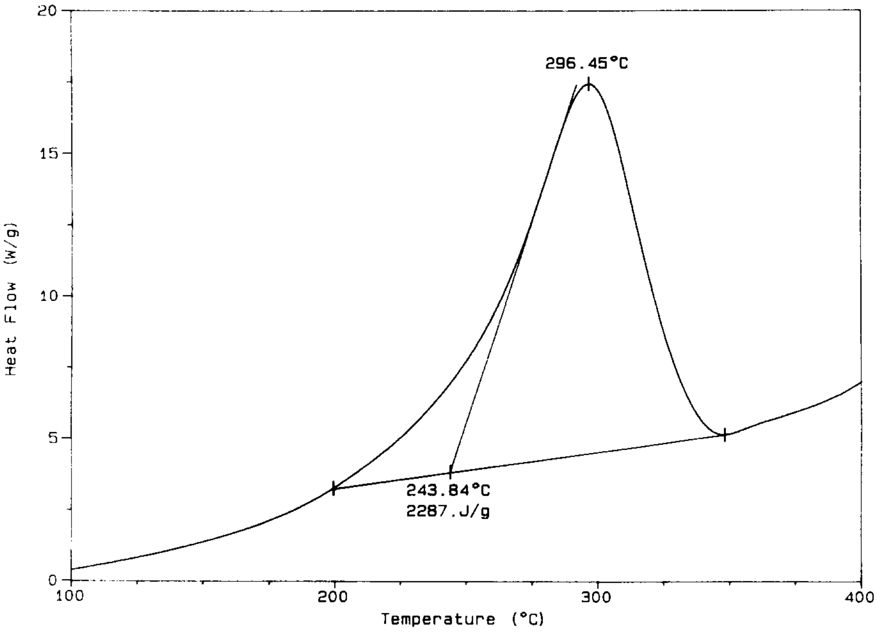

Figure 12 D.s.c. trace of polypyrrole perchlorate heated in nitrogen at 20°C min^{-1}, showing exotherm of detonation

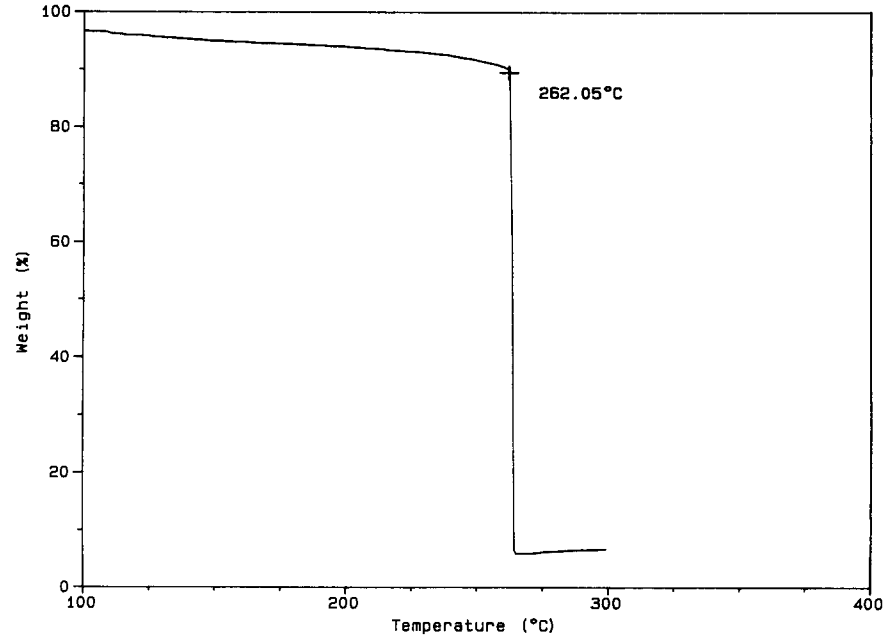

Figure 13 T.g.a. trace of polypyrrole perchlorate heated in nitrogen at 20°C min^{-1}, to spontaneous detonation, showing severe weight loss

through a fast redox reaction[23]. Other workers also have observed detonations with perchlorate doped polyacetylene[24], polythiophene[25,26] and polypyrrole[26]. Further work involving mass spectroscopy of the evolved gases will be undertaken to determine reaction products.

CONCLUSIONS

Polypyrrole *p*-toluenesulphonate aged in air at elevated temperatures exhibits a decline in conductivity, corresponding to first-order decay rates. The activation energy for this process (56 kJ mol^{-1}) is close to the value for triplet oxygen insertion into conjugated chains given by others. X.p.s. studies of oxidized polypyrroles have shown significant amounts of carbon–oxygen species (carbonyl, aldehyde and hydroxyl) on the polymer surface. Ageing in an inert or nitrogen environment produces minimal decline in electrical conductivity and surface oxidation. Polypyrrole perchlorate and tetrafluoroborate films also degrade by a combination of the same mechanism together with dopant decomposition and removal. Morphological studies show severe cracking of the surface at elevated ageing temperatures. Perchlorate doped polymers spontaneously detonate at temperatures above 280°C severely limiting their use in device applications. The dopant type has an important role in the degradation of electrical conductivity and thermal stability.

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