THERMAL STABILITY AND DEGRADATION OF SOME CHEMICALLY SYNTHESIZED POLYPYRROLE COMPLEXES

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ABSTRACT

The thermal degradation processes in some chemically synthesized polypyrrole(PPY)/ acceptor complexes and uncomplexed PPY of some specific intrinsic oxidation states have been studied by thermogravimetric (TG) analysis and X-ray photoelectron spectroscopy (XPS). In general, the PPY/acceptor complex, such as the PPY/perchlorate, PPY/halide and PPY/halobenzoquinone complexes, exhibit greater thermal stability over the deprotonated PPY (DP-PPY, consisting of 20–25% =N– structure) and the fully reduced PPY (PPY^0, consisting of 100% –NH– structure). The temperatures for the onset of major weight loss in the PPY/organic acceptor complexes, such as the PPY/o-chloranil, PPY/p-chloranil and PPY/DDQ complexes, coincide approximately with the decomposition temperatures of the respective acceptors. All the PPY/acceptor complexes studied degrade initially via the loss or decomposition of the "dopants". The subsequent deprotonation process or the further loss of the dopant at high temperature is always accompanied by the appearance of the imine-like pyrrolylium nitrogens (=N– structure).

INTRODUCTION

The synthesis and characterization of electroactive polymers have become one of the most important areas of research in polymer science (see for example ref. 1). Among these electroactive polymers, polypyrrole (PPY) and its derivatives have received a good deal of attention because of their high electrical conductivity, environmental stability and interesting redox properties associated with the chain nitrogens [2–5]. Most of the studies on PPY involve materials synthesized by electrochemical methods. PPY can also be synthesized by chemical polymerization and oxidation [6–12] and by the chemical vapour deposition technique [13,14]. Chemical polymerization and

oxidation offer a relatively simple route for obtaining highly conductive PPY complexes in high yield. Accordingly it should be interesting to compare some of the physicochemical properties of the highly conductive PPY complexes synthesized chemically in the presence of various chemical oxidants. This report deals mainly with the comparison of the thermal stability and degradation behaviour of the various chemically synthesized PPY/acceptor complexes, using thermogravimetric (TG) analysis and X-ray photoelectron spectroscopy (XPS) as primary tools.

Pyrrole has been known to undergo chemical polymerization in the presence of a large number of oxidants. Among these oxidants, iron(III) salts, such as $FeCl_3$ and $Fe(ClO_4)_3$, are by far the most commonly used oxidants for the preparation of highly conductive PPY complexes [5–9]. The use of other oxidants such as acids [15], halogens [11] and organic electron acceptors [16] has also been reported. The PPY samples studied in this work include the various PPY/halide, PPY/perchlorate and PPY/organic acceptor complexes, as well as the "undoped" or "compensated" [17] PPY corresponding to some specific intrinsic oxidation states.

EXPERIMENTAL

Polymer samples

Pyrrole monomer (Merck) was vacuum distilled before use. The polymerization and oxidation of pyrrole by ferric chloride hexahydrate ($FeCl_3 \cdot 6H_2O$) were carried out in methanol at $0-5\,^{\circ}C$ under a nitrogen atmosphere [7]. The polymerization and oxidation by hydrated ferric perchlorate ($Fe(ClO_4)_3 \cdot 9H_2O$) and cupric perchlorate ($Cu(ClO_4)_2 \cdot 6H_2O$) were carried out in acetonitrile under similar conditions [10]. Other PPY/halide complexes, such as the PPY/iodide and PPY/bromide, were prepared by the simultaneous polymerization and oxidation of pyrrole by iodine and bromine, respectively [11]. Similarly, the PPY/organic acceptor complexes were prepared by the oxidative polymerization of pyrrole by the respective organic acceptors [16,18]. The organic acceptors used include tetrachloro-*o*-benzoquinone (*o*-chloranil), tetrachloro-*p*-benzoquinone (*p*-chloranil) and 2,3-dichloro-5,6-dicyano-*p*-benzoquinone (DDQ). The PPY complexes prepared in the presence of various transition metal and halogen oxidants were also "compensated" or deprotonated by 0.5 M NaOH [17]. The deprotonated PPY (DP-PPY) can readily undergo reprotonation in the presence of protonic acids or formation of PPY/organic acceptor complexes in the presence of the organic acceptors in acetonitrile [19]. It can also undergo rehydrogenation in the presence of phenylhydrazine to give rise to the fully reduced PPY (PPY^0). The various PPY/acceptor complexes studied in this work are summarized in Table 1.

TABLE 1

Summary of the PPY/acceptor complexes studied

Complex	Synthesis conditions		Conductivity σ (S cm^{-1})	References
	Oxidant	Medium		
PPY/iodide	I_2	H_2O	5	11
PPY/bromide	Br_2	Acetonitrile	20	11
PPY/chloride	$FeCl_3 \cdot 6H_2O$	Methanol	30	5–8
PPY/perchlorate	$Fe(ClO_4)_3 \cdot 9H_2O$	Acetonitrile	13	6
PPY/perchlorate	$Cu(ClO_4)_2 \cdot 6H_2O$	Acetonitrile	15	10
PPY/o-chloranil	o-Chloranil	Bulk	10^{-3}	16
PPY/o-chloranil	o-Chloranil	Toluene	10^{-4}	–
PPY/DDQ	DDQ	Bulk	10^{-1}	16
PPY/DDQ	DDQ	Toluene	1	–
PPY/p-chloranil [a]	p-Chloranil	DP-PPY in acetonitrile	10^{-2}	19

[a] Obtained by charge-transfer interaction between DP-PPY and p-chloranil in acetonitrile. PPY/o-chloranil and PPY/DDQ complexes obtained by a similar method were also studied.

Stability and degradation studies

Thermogravimetric (TG) analysis was carried out using a Netzsch simultaneous TG–DTA apparatus, Model STA409, at a heating rate of $10\,^{\circ}$C min^{-1} in nitrogen. For thermal stability studies, all samples were heated to the desired temperatures in nitrogen in the TG apparatus. They were allowed to return to room temperature before being removed for analysis. Differential scanning calorimetry (DSC) was performed on a Perkin–Elmer DSC-2C calorimeter with a heating/cooling rate of $10\,^{\circ}$C min^{-1} under a constant flow of nitrogen. The electrical conductivities of the complexes were measured using both the standard collinear four-probe and two-probe techniques on compressed pellets. The X-ray photoelectron spectroscopy (XPS) measurements were carried out on a VG ESCALAB MkII spectrometer with an Mg $K\alpha$ X-ray source (1253.6 eV photons). The X-ray source was run at a reduced power of 120 W (12 kV and 10 mA). The polymer samples were analysed in powder form. Pressure in the analysis chamber was maintained at or below 10^{-8} mbar. All core-level spectra were referenced to the C1s neutral carbon peak at 284.6 eV. The peak area ratios for the various elements were corrected by the experimentally determined instrumental sensitivity factors and might be liable to a maximum of $\pm 10\%$ error. In all cases, the chemical compositions at the surface agree well with those of the bulk. The IR absorption spectra were measured on a Perkin–Elmer Model 682 spectrophotometer with the polymer samples dispersed in KBr.

RESULTS AND DISCUSSION

The N1s XPS core-level spectrum of oxidized PPY complexes shows, in general, a major component at a binding energy (BE) of about 399.7 eV, attributable to the neutral pyrrolylium nitrogen (–NH– structure) and a high BE tail above 401 eV, attributable to the positively charged pyrrolylium nitrogen (–N$^+$H– structure) [20–27]. For complexes prepared in a less oxidative environment [22,25] or for complexes 'compensated' with a base [17], a low BE shoulder which is shifted by about −2 eV from the neutral pyrrolylium nitrogen peak is also discernible. This low BE component has been associated with the formation of an imine-like structure (=N– structure), as a result of dehydrogenation of a certain fraction of the pyrrolylium nitrogens. Our recent study [28] on the chemically synthesized PPY has suggested that, as in the case of nitrogens in polyaniline [29], proton modifications of pyrrolylium nitrogens can give rise to a number of intrinsic oxidation states, ranging from that consisting of about 20–25% oxidized imine-like (=N–) structure (DP-PPY) to the fully reduced all amine-like (–NH–) structure (PPY^0). The former is obtained via deprotonation of the oxidized and positively charged pyrrolylium nitrogens with 0.5 M NaOH and is susceptible to re-protonation by protonic acids, while the latter is obtained from the reduction of DP-PPY with phenylhydrazine and is susceptible to re-oxidation by electron acceptors. Figures 1(a)–(d) show the N1s XPS core-level spectra for the PPY/chloride complex, DP-PPY, DP-PPY reprotonated by 1 M H$_2$SO$_4$ and PPY^0 respectively. The persistence of a high BE tail in the N1s spectra of DP-PPY and PPY^0 is partially
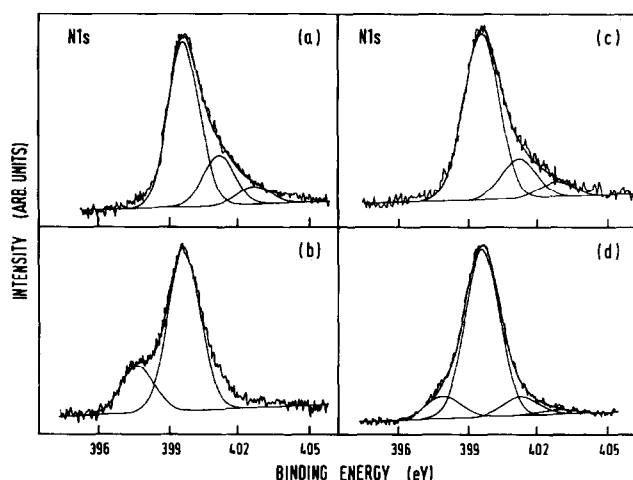

Fig. 1. N1s XPS core-level spectra of (a) PPY/chloride complex, (b) deprotonated PPY (DP-PPY), (c) DP-PPY reprotonated by 1 M H$_2$SO$_4$ and (d) reduced PPY (PPY^0).
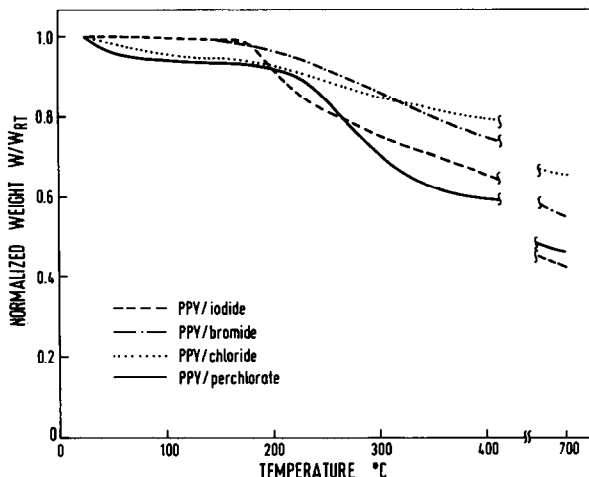
Fig. 2. TG scans of the PPY/halide and PPY/perchlorate complexes in N_2.

attributable to the surface oxidation products, as uncomplexed PPY has a relatively low oxidation potential [30,31].

Figure 2 shows the TG scans of the PPY/halide and PPY/perchlorate complexes in N_2. In this case, the PPY/perchlorate complex was synthesized with $Fe(ClO_4)_3$. Similar weight-loss behaviour is observed for the PPY/perchlorate complex synthesized in the presence of $Cu(ClO_4)_2$. On the basis of the initial weight-loss behaviour, the thermal stability of the PPY complexes can be arranged in the following descending order: PPY/iodide, PPY/bromide, PPY/chloride and PPY/perchlorate complex. However, it is appropriate to point out that although the PPY/perchlorate complex suffers a gradual weight loss immediately upon heating above room temperature, it has the highest temperature for the onset of major weight loss among the four complexes. Furthermore, the initial weight loss observed in the PPY/chloride and PPY/perchlorate complexes is at least partially attributable to the loss of water incorporated in the complexes. This is supported by the fact that the minute loss of the dopants, as revealed by XPS, at low temperature cannot account for the amount of weight loss observed in both complexes. Moreover, the incorporation of water molecules in the PPY/perchlorate complexes has been suggested in an earlier study [10].

In the case of the PPY/iodide complex, the temperature for the onset of major weight loss occurs at about 180°C, which coincides approximately with the boiling point of iodine at 184°C. Thus the initial weight loss observed in the iodide complex is associated with the physical vaporization or removal of iodine from the complex. This is supported by the presence of an endothermic peak at about 183°C in the DSC scan and a substantial reduction in the $I3d_{5/2}$ core-level signal intensity. Figures 3(a) and 3(b) show the N1s and $I3d_{5/2}$ core-level spectra, respectively, for the pristine
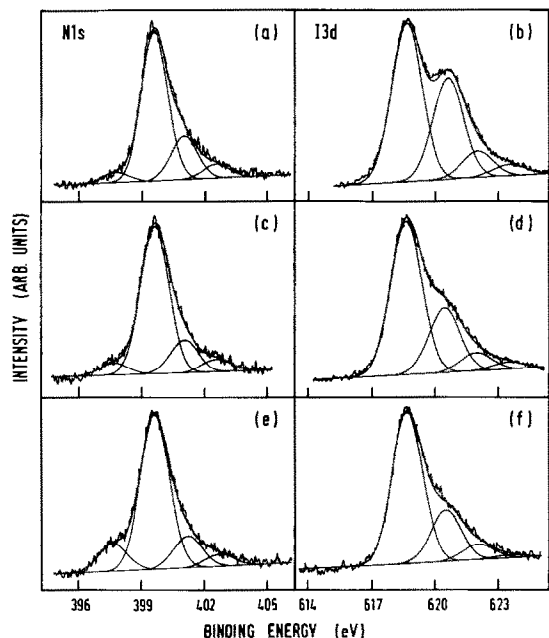
Fig. 3. N1s and I3d$_{5/2}$ core-level spectra of (a) and (b) pristine PPY/iodide complex (I/N = 0.44), (c) and (d) PPY/iodide complex after heating to 190 °C (I/N = 0.25), and (e) and (f) PPY/iodide complex after heating to 300 °C (I/N = 0.15).

PPY/iodide complex, while Figs. 3(c) and 3(d) show the corresponding core-level spectra after the complex has been heated to 190°C in N_2. Deconvolution of the I3d$_{5/2}$ core-level spectra gives two major peak components with BEs of about 618.6 and 620.5 eV and attributable to the I_3^- and $I_2 + I_3^- = I_5^-$ species respectively [26,32]. A significant decrease in the proportion of the I3d high BE component for the sample heated to 190°C is consistent with the proposed mechanism of iodine removal. Upon further increasing the temperature, the decomposition of the complex is shifted towards a deprotonation process which gives rise to the oxidized imine-like pyrrolylium nitrogens. This is suggested by the appearance of a low BE =N– component in the N1s core-level spectrum and a further decrease in the overall I3d$_{5/2}$ core-level signal intensity, as shown in Figs. 3(e) and 3(f) respectively.

The presence of two distinct weight-loss processes is also observed in other PPY/halide complexes. Figures 4(a)–(f) show the respective N1s and Br3d XPS core-level spectra of three PPY/bromide samples: the pristine PPY/bromide complex, the PPY/bromide complex heated to just above the temperature for the commencement of weight loss and the PPY/bromide complex heated to well above this temperature. The XPS data again suggest that at a temperature just above the temperature for the onset of weight loss, the complex suffers a loss of the bromine dopant and the pyrrolylium
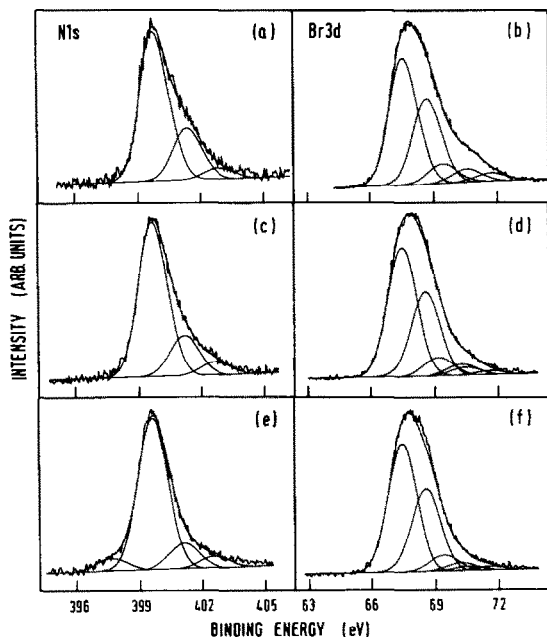
Fig. 4. N1s and Br3d core-level spectra of (a) and (b) pristine PPY/bromide complex (Br/N = 0.46), (c) and (d) PPY/bromide complex heated to 155°C (Br/N = 0.31) and (e) and (f) PPY/bromide complex heated to 275°C (Br/N = 0.20).

cations. At higher temperatures, the deprotonation process again results in the formation of the imine-like pyrrolylium nitrogens. The Br3d core-level spectrum of each sample suggests that the bromine dopant exists predominantly as bromide anion with a characteristic $Br3d_{5/2}$ BE at about 67.4 eV [26]. The two minor species in the high BE tail of the spectrum with $Br3d_{5/2}$ BEs at about 70.5 and 69.4 eV are attributable, respectively, to the covalent bromine and the bromide species absorbed or charge-transfer complexed with the polymer (see PPY/chloride complex below).

In the case of the PPY/chloride complex, the weight loss of the complex commences immediately upon heating to above room temperature. Figures 5(a)–(f) show the respective N1s and Cl2p core-level spectra for the pristine PPY/chloride complex and PPY/chloride complex heated to various temperatures. The XPS data again suggest that the initial loss of the chlorine dopant does not cause a corresponding increase in the amount of the deprotonated pyrrolylium nitrogens. The Cl2p core-level spectrum of each PPY/chloride complex is best fitted with three spin-orbit split doublets ($Cl2p_{3/2}$ and $Cl2p_{1/2}$), with the BE for the $Cl2p_{3/2}$ peaks lying at about 197.1, 198.6 and 200.1 eV. Thus the chlorine dopant in the PPY/chloride complex can exist in three distinct chemical states. The components with BE of 197.1 eV and 200.1 eV can be assigned to the ionic (Cl^-) and covalent (−Cl) chlorine species respectively [33]. The Cl2p species (Cl^*) with BE
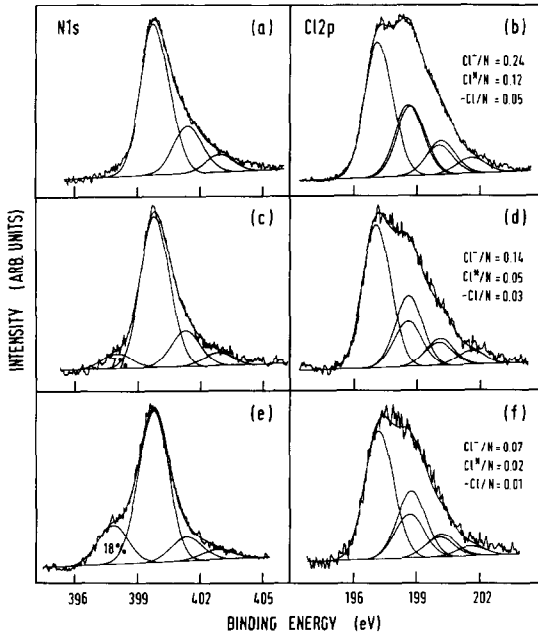
Fig. 5. N1s and Cl2p core-level spectra of (a) and (b) pristine PPY/chloride complex (Cl/N = 0.41), (c) and (d) PPY/chloride complex heated to 230°C (Cl/N = 0.22) and (e) and (f) PPY/chloride complex heated to 350°C (Cl/N = 0.10).

intermediate between those of the covalent and ionic species is probably attributable to the chloride anion arising from the charge transfer interaction between the chlorine dopant and the highly conducting polymer chain. Similar intermediate chloride species have also been observed in the Cl2p core-level spectrum of the HCl-protonated imine nitrogens in the emeraldine oxidation state of polyaniline [34].

On exposure to elevated temperature, both the Cl^- and Cl^* species are removed from the complex, with the initial rate of removal of the latter being somewhat higher. The initial loss of all the chlorine species is not accompanied by a corresponding increase in the amount of the =N– component, as revealed by the N1s core-level spectrum of Fig. 5(c). Furthermore, comparison of the Cl2p core-level spectra in Figs. 5(d) and 5(f) reveals that only the loss of the chlorine species at high temperature is accompanied by the corresponding appearance of the deprotonated pyrrolylium nitrogens or the =N– structure. Thus the thermal decomposition behaviour of the three PPY/halide complexes is largely similar.

Finally, for the PPY/perchlorate complex prepared either from $Fe(ClO_4)_3$ or $Cu(ClO_4)_2$, the weight loss commences immediately on heating above room temperature. The TG scan of the complex also indicates the onset of a major weight loss at temperatures above 220°C. Figures 6(a)–(f) show the respective N1s and Cl2p core-level spectra for the pristine PPY/perchlorate
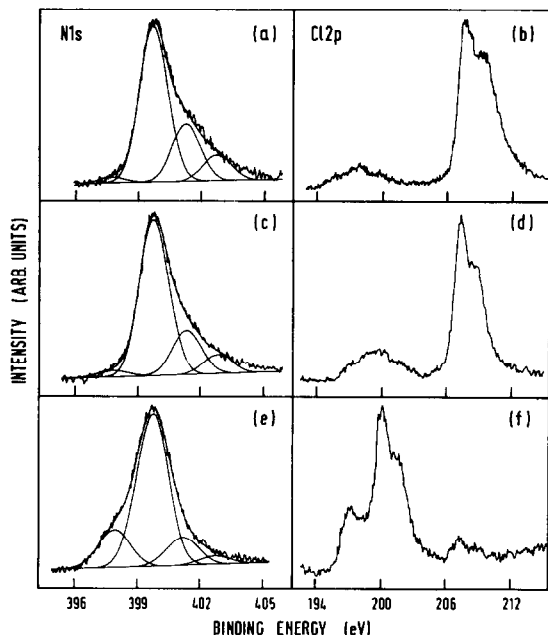
Fig. 6. N1s and Cl2p core-level spectra of (a) and (b) pristine PPY/perchlorate complex (ClO_4^-/N = 0.38, Cl/N = 0.06), (c) and (d) PPY/perchlorate complex heated to 170°C (ClO_4^-/N = 0.30, Cl/N = 0.10 and (e) and (f) PPY/perchlorate complex heated to 280°C (ClO_4^-/N = 0.01, Cl/N = 0.17).

complex (prepared from $Fe(ClO_4)_3$) and the PPY/perchlorate samples that have been heated to 170 and 280°C. Similar changes in the N1s and Cl2p spectral line shapes are observed for the complex prepared from $Cu(ClO_4)_2$. The Cl2p core-level spectrum of the pristine PPY/perchlorate complex suggests that although most of the chlorine incorporated exists as perchlorate species with characteristic $Cl2p_{3/2}$ BEs in the 207 eV region [35], some of the chlorine incorporated also exists as chloride species with characteristic BEs in the 200 eV region. Deconvolution of the Cl2p core-level spectra in both BE regions suggests the presence of chloride and perchlorate species with BEs intermediate between those of the ionic and covalent species, and is probably similar in nature to the intermediate chloride species observed earlier in the PPY/chloride complex.

Upon heating to above room temperature, the PPY/perchlorate complex gradually loses perchlorate species, as suggested by a gradual decrease in the ClO_4^-/N ratio. At sufficiently high temperatures, the rapid decomposition of perchlorate species into chloride species [36] results in the partial "doping" of the polymer by the latter. This is readily supported by the fact that the intensity of the Cl2p core-level signal for the perchlorate species diminishes drastically while that for the chloride species is significantly enhanced at high temperature (see Fig. 6(f)). The loss of perchlorate anions
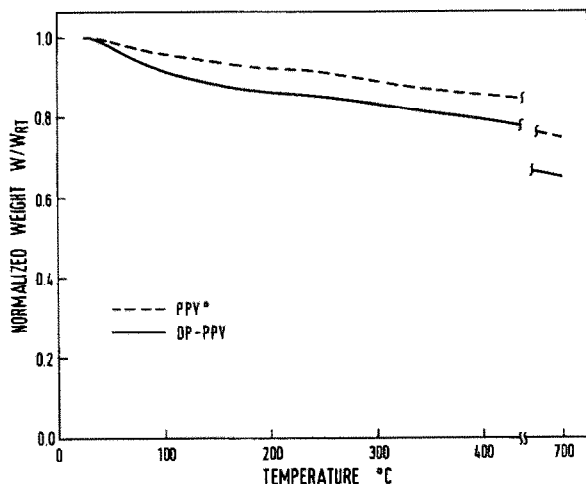
Fig. 7. TG scans of DP-PPY and PPY^0 in N$_2$.

is also accompanied by the deprotonation of the pyrrolylium nitrogens, as indicated by the appearance of a substantial amount of the low BE component in the N1s core-level spectrum (see Fig. 6(e)). Thus with the exception of "redoping" and halogenation of the polymer by the chloride species arising from the decomposition of the perchlorate dopant, the mechanism of thermal decomposition of the PPY/perchlorate complex is not unlike that observed for the PPY/halide complex.

The IR absorption spectra of all the partially deprotonated PPY complexes reported above still exhibit absorption bands, although of somewhat reduced oscillator strength, at about 1550, 1480, 1300, 1180, 1040 and 930 cm^{-1} which are characteristic of PPY [3]. Thus the loss or decomposition of the dopant and the accompanying deprotonation process have probably not yet resulted in a major alteration of the heterocyclic nature of the polymer backbone.

Figure 7 shows the TG scans in N$_2$ of a deprotonated PPY (DP-PPY), obtained via the treatment of PPY/chloride complex with excess 0.5 M NaOH and consisting of about 25% =N− structure, and the fully reduced PPY (PPY^0), obtained via the reduction of DP-PPY by phenylhydrazine. A somewhat better thermal stability is observed for the DP-PPY sample obtained from PPY/perchlorate complex prepared with Cu(ClO$_4$)$_2$. Figure 7 clearly suggests that the thermal stability of DP-PPY is substantially enhanced upon re-hydrogenation of the deprotonated pyrrolylium nitrogens. Furthermore, comparison of Figs. 7 and 2 suggests that the DP-PPY consisting of about 25% =N− units is thermally the least stable. The best thermal stability is observed in oxidized PPY complexes with the heaviest anions, such as the PPY/iodide complex. The thermal stability of DP-PPY is also enhanced substantially upon charge-transfer complexing with organic
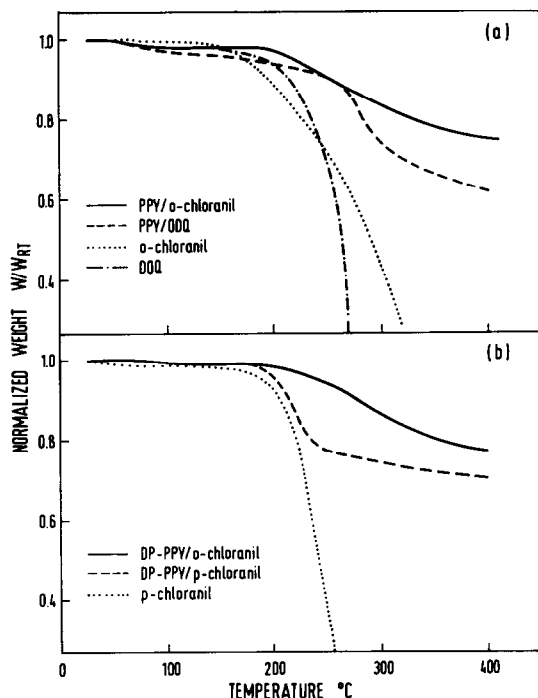
Fig. 8. (a) TG scans of o-chloranil, DDQ and PPY/o-chloranil complex prepared from bulk polymerization, and PPY/DDQ complex prepared in toluene, and (b) TG scans of p-chloranil and PPY/o-chloranil and PPY/p-chloranil complexes prepared via the charge-transfer interaction between DP-PPY with the respective acceptors.

electron acceptors, such as the halobenzoquinones. In this case, the temperature for the onset of major weight loss is elevated to the decomposition temperature of the organic acceptor incorporated (see Fig. 8(b)).

Figure 8(a) shows the TG scans of the PPY/o-chloranil and PPY/DDQ complexes in N_2. For each complex, similar TG curves are observed for samples prepared in the bulk or in organic solvents. Both organic acceptor complexes exhibit similar degradation behaviour, with the temperatures for the commencement of major weight loss coinciding approximately with the decomposition temperatures of the respective acceptors. The TG scans in N_2 of the PPY/o-chloranil and PPY/p-chloranil complexes obtained via the charge-transfer interaction of DP-PPY with the respective acceptors in acetonitrile solutions are shown in Fig. 8(b). Again, good agreement is observed between the temperature of the onset of major weight loss and the decomposition temperature of the acceptor in each complex.

The XPS studies of the various PPY/organic acceptor complexes, prepared either by the direct oxidative polymerization of pyrrole by the respective acceptor or through charge-transfer interaction between DP-PPY and the respective acceptor have been reported earlier [19,27]. For the
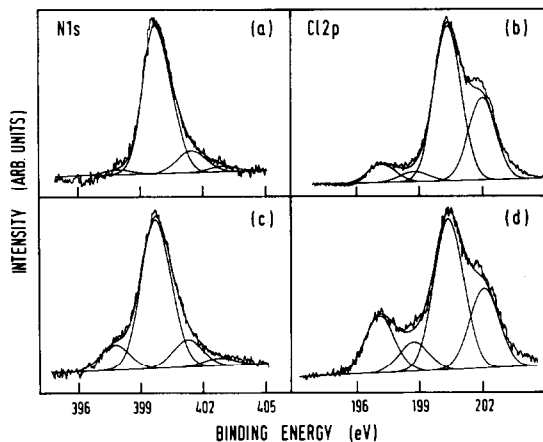
Fig. 9. N1s and Cl2p core-level spectra of (a) and (b) pristine PPY/*o*-chloranil complex prepared in toluene ($Cl_4/N = 0.23$), and (c) and (d) and PPY/*o*-chloranil complex heated to 300 °C ($Cl_4/N = 0.07$).

PPY/halobenzoquinone and PPY/DDQ complexes, the formation of halide and semibenzoquinone anions and pyrrolylium cations strongly suggests the cleavage of some carbon–halogen bonds of the acceptor and the formation of linkages between the pyrrolylium nitrogens and the acceptors through the cleavage sites and the carbonyl oxygens. In the case of the PPY/DDQ complex, the N1s core-level spectrum also reveals the involvement of the cyano anions, as suggested by the presence of a low BE component at about 1.3 eV below the main N1s peak.
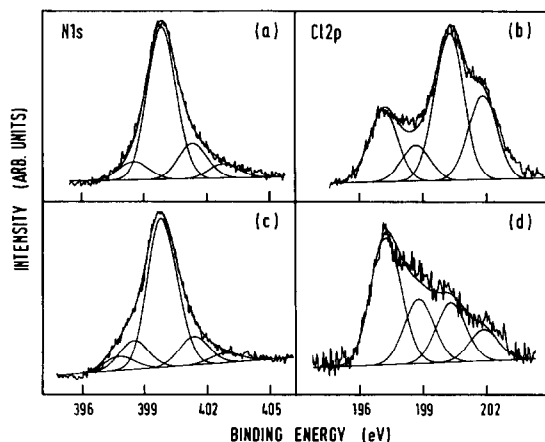

Fig. 10. N1s and Cl2p core-level spectra of (a) and (b) pristine PPY/DDQ complex prepared from bulk polymerization ((Cl_2N_2)/N = 0.20), and (c) and (d) the PPY/DDQ complex heated to 320 °C ((Cl_2N_2)/N = 0.05).

Figures 9(a)–(d) show the respective N1s and Cl2p core-level spectra of the pristine PPY/o-chloranil complex and the PPY/o-chloranil complex after heating to 300 °C. The corresponding core-level spectra for the pristine and heat-treated PPY/DDQ samples are shown in Figs. 10(a)–(d). Thus when heated to above the decomposition temperature of the respective acceptor in each complex, the loss of the acceptor, as suggested by a sharp decrease in the halogen/N ratio, is accompanied by the appearance of the low BE =N– component in the N1s core-level spectrum. Furthermore, the Cl2p core-level spectra of both complexes also indicate a significant increase in the ionic to covalent chlorine ratio upon exposure to high temperature. Thus the decomposition mechanism for the PPY/organic acceptor complexes resembles that of the PPY/perchlorate complex in some aspects.

CONCLUSION

The thermal stability and degradation of pristine PPY of various intrinsic oxidation states and some chemically synthesized PPY/halide, PPY/perchlorate and PPY/organic acceptor complexes have been studied and compared using TG analysis and XPS. The stability of the PPY complexes is governed to a large extent by the stability of the "dopants". The degradation of all the PPY/acceptor complexes studied is initiated by the loss or decomposition of the dopant incorporated. Subsequent deprotonation or further loss of the dopant at high temperature is always accompanied by the formation of the imine-like pyrrolylium nitrogens.

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