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THERMAL DEGRADATION OF LEUCOEMERALDINE, EMERALDINE BASE AND THEIR COMPLEXES

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ABSTRACT

Thermogravimetric scans of leucoemeraldine in N_2 revealed minimal weight changes below 400 °C. The initial stages in the degradation of leucoemeraldine involved the loss of some hydrogen, resulting in the formation of imine-like structures. The presence of these structures was confirmed by IR absorption spectroscopy and X-ray photoelectron spectroscopy. The presence of high O_2 concentration and elevated temperatures accelerated the formation of the imine structures. Emeraldine base showed slightly higher thermal stability in N_2 than leucoemeraldine. In air, volatile oxidation products were formed from both leucoemeraldine and emeraldine base above 350 °C. The thermal stability of acid protonated emeraldine depended to a large extent on the protonating acid. With HCl and H_2SO_4 as protonating acids, absorbed moisture accounted for an initial weight loss of ca. 10% upon heating to 100 °C, and the loss of the protonating acid species commenced above 250 °C. The degradation of the halobenzoquinone complexes of leucoemeraldine and emeraldine was initiated by the decomposition of the incorporated organic acceptor.

INTRODUCTION

Recent interest in electroactive polymers [1] has resulted in a great deal of research on the aniline family of polymers. These polymers are basically poly(*p*-phenylenaminimine)s in which the oxidation state can be varied from the fully reduced poly(*p*-phenylenamine), or leucoemeraldine (Fig. 1a), to the fully oxidized poly(*p*-phenylenimine) or pernigraniline. The 50% oxidized polymer has been termed emeraldine base (Fig. 1b). Each oxidation state can exist as the 'doped' or 'undoped' form [2]. The electrical conductivity of the polymers can be varied from about 10^{-11} S cm^{-1} to over 1 S cm^{-1} by acid protonation [3] or by electrochemical doping [4,5]. Most of the studies on the chemical doping of polyaniline have been centered on the

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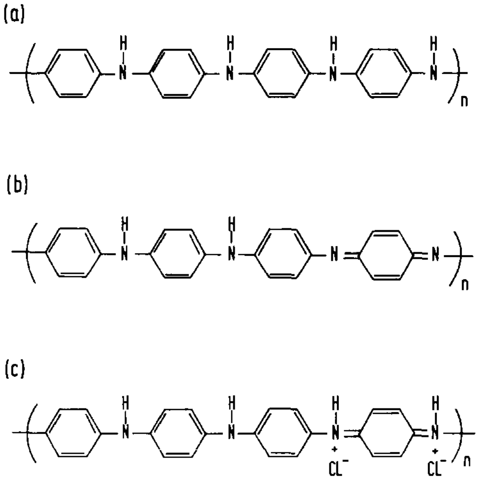

Fig. 1. Chemical structure of (a) leucoemeraldine, (b) emeraldine base, and (c) emeraldine hydrochloride.

protonation of emeraldine base by acids such as HCl. It has been postulated that the protonation occurs preferentially at the imine repeating units of the emeraldine base (Fig. 1c) [3]. Recently, we have also carried out studies on the structural changes associated with the interaction of proton-free halogen and organic electron acceptors [6,7] with emeraldine base. A number of studies on the fully reduced leucoemeraldine and its oxidized complexes has also been reported [8–10]. With the exception of leucoemeraldine and emeraldine, the other oxidation states have not been well studied.

This work reports on the thermal degradation of leucoemeraldine and emeraldine and how the degradation process is affected by the oxidation state and the dopants used. A thermogravimetric analyzer is used to monitor the degradation process. Infrared (IR) absorption spectroscopy and X-ray photoelectron spectroscopy (XPS) are used to characterize the polyanilines and to study the structural changes associated with the degradation process.

EXPERIMENTAL

Polymer samples

Emeraldine hydrochloride (EM–HCl) was prepared by the oxidative polymerization of aniline by ammonium persulfate in 1 M HCl according to the method reported in the literature [2,3]. Sulfuric acid and hydrobromic acid were also used in place of HCl to synthesize EM–H_2SO_4 and EM–HBr samples respectively. The product was rinsed with deionized water before drying under a dynamic vacuum. Emeraldine (EM) base was obtained by treating EM–HCl with excess 0.5 M aqueous NH_4OH. The emeraldine–organic acceptor complexes were prepared by suspending the finely ground EM base in acetonitrile solutions of the acceptor. Each complex mixture was vigorously agitated under a nitrogen atmosphere. The solvent in the sample was removed by suction. The organic acceptors used were tetrachloro-*o*-benzoquinone (*o*-chloranil) and tetrabromo-*o*-benzoquinone (*o*-bromanil). Leucoemeraldine (LM) was obtained by the treatment of EM base with excess phenylhydrazine according to the method of Green and Woodhead [11]. The LM–organic acceptor complexes were prepared in a similar manner to the EM–organic acceptor complexes.

Degradation and characterization studies

A Netzsch STA 409 simultaneous thermogravimetric–differential thermal analyzer unit was used to monitor the degradation of the polyaniline samples under heating. Gaseous N_2–O_2 mixtures at a flowrate of 100 ml min^{-1} were used, and the oxygen concentration of these mixtures ranged from 0 to 50%. Two different types of thermogravimetric experiments were conducted. In the first series of experiments, a heating rate of 10 °C min^{-1} was used to raise the sample temperature from ambient to 700 °C. In the second series of experiments, the samples were rapidly brought to a desired temperature and isothermal conditions were maintained for extended periods of time. The treated samples were then analyzed. The following analytical techniques were used to characterize the samples: elemental analysis with a Perkin–Elmer 2400 CHN Elemental Analyzer, IR absorption spectroscopy on a Perkin–Elmer model 682 spectrophotometer with the samples dispersed in KBr pellets, and XPS on a VG ESCALAB MkII spectrometer with a Mg $K\alpha$ X-ray source (1253.6 eV photons). In the XPS measurements, the polymer samples in powder form were mounted on standard sample studs using double-sided adhesive tape. All core-level spectra were referenced to the C 1s neutral carbon peak at 284.6 eV.

RESULTS AND DISCUSSION

Leucoemeraldine

The thermogravimetric (TG) scans of LM being heated from 25–700 °C in N_2, air and a 50% O_2–50% N_2 mixture are shown in Fig. 2. In N_2, there is minimal weight loss below 400 °C. Although the increase in O_2 content of the gas mixture causes the onset of weight loss to be shifted to lower temperatures, the polymer does not appear to undergo any significant weight changes below 300 °C. However, the absence of significant weight changes may not indicate that the polymer has not undergone some struct-

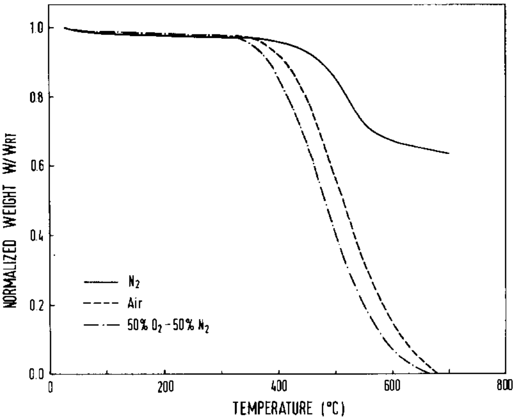

Fig. 2. TG scans of leucoemeraldine in N_2, air and 50% O_2–50% N_2. W_{RT} is the weight at room temperature.

ural changes, since, although the oxidation of some of the amine units to imine units would involve the loss of hydrogen, the associated weight loss would be slight. Hence samples were collected from isothermal TG runs which were carried out either in N_2 or in a 50% O_2–50% N_2 mixture and the structures of the heated samples were compared with that of the pristine LM.

The IR absorption spectra of freshly prepared LM, a LM sample after exposure to dry air at 25 °C for two months and samples after being heated at 270 °C for 2 h in either N_2 or 50% O_2–50% N_2 are compared in Fig. 3. Earlier studies [10,12] have suggested that the absorption bands at ca. 1500 cm^{-1} and 1600 cm^{-1} are associated with the aromatic ring stretching. Tang et al. [13] have associated the band at ca. 1500 cm^{-1} with the benzenoid (B) ring and the band at 1600 cm^{-1} with the quinonoid (Q) ring. When this peak assignment is applied to the IR spectrum of freshly prepared LM (Fig. 3a), the very low 1600 cm^{-1}/1500 cm^{-1} intensity ratio is consistent with a structure rich in B units. The 1600 cm^{-1}/ 1500 cm^{-1} intensity ratio increases upon aging of LM in air and upon heating, and this suggests the conversion of some amine units to imine units. This process appears to proceed very slowly under ambient conditions and, although it can also proceed in the absence of O_2 at elevated temperatures (Fig. 3c), it is accelerated by the presence of O_2 (Fig. 3d). The weight loss of the sample heated at 270 °C for 2 h in 50% O_2–50% N_2 is ca. 4%, while the weight loss of the corresponding sample heated in N_2 is less than 1%. The weight loss is not due solely to the loss of amine hydrogens, which amount to only 1.1% of the weight of LM (see below). When LM is heated in the 50% O_2–50% N_2 mixture, oxygen containing groups are also formed, as indicated by the absorption shoulder at 1700 cm^{-1} attributable to C=O groups and the broad band centered at 3440 cm^{-1} attributable to O–H type species [14]. Due to

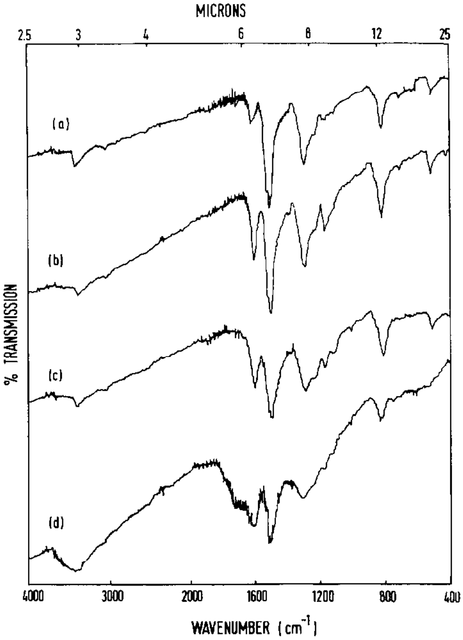

Fig. 3. IR absorption spectra of (a) freshly prepared LM, (b) LM after two months' exposure to dry air at 25 ° C, (c) LM after heating in N_2 at 270 ° C for 2 h, and (d) LM after heating in 50% O_2–50% N_2 at 270 ° C for 2 h.

the intensity of this latter band, the N–H stretching band at 3400 cm^{-1} is no longer discernible.

The N 1s XPS core-level spectra of the four samples described above are compared in Fig. 4. As expected, the freshly prepared LM sample (Fig. 4a) exhibits only a single nitrogen environment at a binding energy (B.E.) of 399.3 eV, which is characteristic of the amine structure [15]. The spectrum of the sample after exposure to dry air for two months (Fig. 4b) is skewed slightly towards the low B.E. side, and a new peak component at B.E. of 398.1 eV, characteristic of the imine repeating units [15], is resolvable. The possibility of some amine units undergoing oxidation to imine units in air has been postulated in an earlier study [8]. Our results confirm this possibility, although the process appears to be rather slow under ambient conditions. The LM samples after heat treatment at 270 ° C in both N_2 and 50% O_2–50% N_2 have also undergone transformation, resulting in some imine-type species (Figs. 4c and 4d). The fraction of nitrogen existing as such species is much higher in the latter sample. Thus the increase in imine-type structures upon aging and heat treatment, as indicated by the N 1s XPS core-level spectra in Fig. 4, is consistent with the increase in the 1600 cm^{-1}/1500 cm^{-1} intensity ratio of the IR absorption bands in Fig. 3. However, it should be noted that, in both heated samples, a large fraction of the nitrogen still has the amine structure. In Fig. 4, the high binding energy

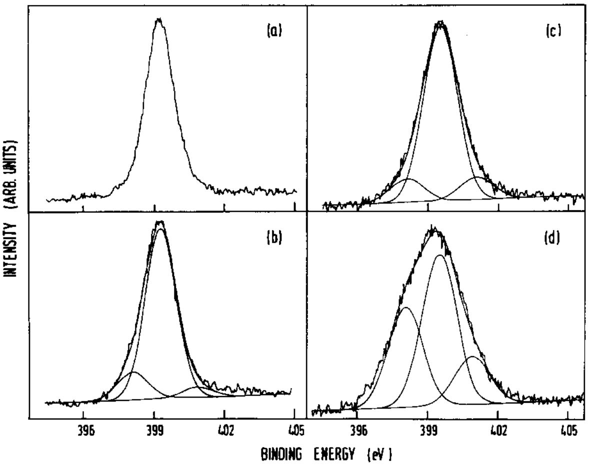

Fig. 4. XPS N 1s core-level spectra of (a) freshly prepared LM, (b) LM after two months' exposure to dry air at 25° C, (c) LM after heating in N_2 at 270° C for 2 h, and (d) LM after heating in 50% O_2–50% N_2 at 270° C for 2 h.

component at ca. 401 eV is characteristic of positively charged nitrogen [15,16] which may be attributable to surface oxidation products. The significant amount of positively charged nitrogen in the LM sample heated in N_2 suggests that this sample readily reacts with O_2 in the air during sample handling after the heat treatment process.

The elemental analysis of the freshly prepared LM sample yields a C : H : N ratio of 6 : 5.0 : 0.98, which is consistent with the structure depicted in Fig. 1a. The C, H and N account for 97% of the total mass. The LM sample after heat treatment in N_2 at 270°C has a C:H:N ratio of 6:4.4:1.05, and these three elements account for 96% of the material. In contrast, the corresponding C:H:N ratio of the sample heated in 50% O_2–50% N_2 is 6 : 3.8 : 1.18, and only 82% by weight of the sample consists of C, H and N. The lack of complete closure in the mass balance may be due to the presence of oxygen. This would be consistent with the IR absorption spectrum (Fig. 3d) which indicates the formation of oxygen containing groups such as C=O and O–H in the sample heated in 50% O_2–50% N_2. In both heated samples, a decrease in the H : C ratio is expected, since some hydrogen is lost from the amine groups to form imine-type structures. However, a large fraction of the nitrogen still possesses the amine structure, and the amount of hydrogen lost in the formation of the imine structures would not completely account for the decrease in H : C ratio. Therefore hydrogen must also be lost from the aromatic rings. Finally, the N : C ratio in the sample heated in 50% O_2–50% N_2 is substantially higher than the 1 : 6 value for pristine LM. This suggests ring opening, with loss of some carbon as volatile oxidation products.

Emeraldine base and protonated emeraldine

The TG scans of EM base and EM–HCl samples in N_2 and in air are shown in Fig. 5. In N_2, the onset of weight loss for EM base is at a slightly higher temperature than the corresponding temperature for LM, and the rate of weight loss of the former is also slower. In air, the weight loss behavior of EM base is similar to that of LM. However, for EM base in both N_2 and air, there is an initial weight loss of about 4% upon heating from room temperature to 100 ° C. This weight loss is attributed to the loss of moisture from the EM base. The higher moisture content of EM base as compared to LM is due to the different synthesis conditions for the two samples. EM base is exposed to NH_4OH solution and deionized water during its conversion from EM–HCl, while LM is obtained from EM base by treating it with phenylhydrazine and then rinsing with anhydrous ether.

The initial weight loss (between 25 ° C and 100 ° C) of EM–HCl, which is also attributable to the loss of water, is substantially higher than that of EM base. This larger amount of absorbed water in EM–HCl is consistent with the findings in an earlier NMR study of polyaniline, which suggests that the amount of absorbed water is almost proportional to the protonation level and the water molecules are bound by hydrogen bonds to the acidic protons [17]. It has been reported too, that electrochemically prepared EM–H_2SO_4 films also show an initial weight loss upon heating to 100 ° C, and this process is endothermic in nature [18]. The amount of absorbed water in protonated emeraldine has been found to affect the conductivity of the sample significantly [19,20].

For the EM–HCl sample heated in N_2, there is essentially no further weight change between 100 ° C and ca. 250 ° C. The onset of the second weight loss step at 250 ° C is probably due to the loss of the acid species as

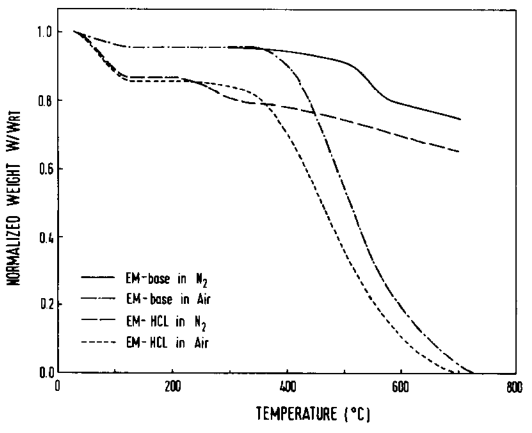

Fig. 5. TG scans of EM base and EM–HCl in N_2 and air.

TABLE 1

Surface stoichiometries of EM–HCl, EM–HBr and EM–HBr after $CHCl_3$ and HCl treatment [a]

	$Cl^-:N$	$-Cl:N$	$Cl:N$	$Br^-:N$	$-Br:N$	$Br:N$
Pristine EM–HCl	0.36	0.15	0.51	–	–	–
Pristine EM–HBr	–	–	–	0.32	0.57	0.89
EM–HBr after $CHCl_3$ treatment	–	–	–	0.30	0.27	0.57
EM–HBr after HCl treatment	0.22	0.06	0.28	≈ 0	0.49	0.49

[a] Based on the corrected N 1*s* and respective species spectral areas. X^-, $-X$ and X represent the ionic, covalent and total halogen (X being Cl or Br) components in the sample respectively.

HCl, since EM base in N_2 shows no substantial weight loss below 500 °C. The XPS Cl 2p core-level spectrum of pristine EM–HCl suggests the presence of two major components which can be attributed to chloride anion and covalent chlorine. The ratios of these two species to N in pristine EM–HCl, as determined from the XPS data, are given in Table 1. The XPS analysis of the EM–HCl sample after being heated to 300 °C in N_2 reveals a significant decrease in the chlorine to nitrogen ratio. This decrease in the chlorine content of the polymer is due predominantly to the decrease in the ionic chlorine component. Thus the chlorine that is lost as volatile species in the initial stages must be predominantly from the chloride anions.

In air, the weight loss behavior of EM–HCl from room temperature to about 250 °C is similar to that in N_2. Between 250 °C and 350 °C, the rate of weight loss of EM–HCl is slightly lower than when N_2 is used. It has been postulated that, when EM–HCl is heated in air at 150 °C, the reaction of the polymer with O_2 results in deprotonation accompanied by chlorine substitution at the aromatic ring, although the total chlorine content changes little [12]. XPS analysis of the EM–HCl sample after being heated to 150 °C in air in the present work confirms that there is no significant change in the Cl : N ratio, although the covalent chlorine to ionic chlorine ratio has increased by a factor of 1.4 over the pristine value. The XPS data, together with a comparison of the TG scans of EM–HCl in N_2 and air between 250 °C and 350 °C, suggest that the covalent chlorine is more stable to heat than the mainly ionically bonded chlorine present in the pristine protonated structure. This is consistent with the above mentioned difference in the rates of decrease of the ionic and covalent chlorine components in EM–HCl above 250 °C in N_2.

Above 350 °C, the weight loss of EM–HCl in air becomes much more rapid than that in N_2. This is mainly due to the formation of volatile products resulting from the attack of O_2 on the polymer. When LM or EM base is heated in air, the onset of rapid weight loss also occurs at this temperature.

The degradation of the electrical conductivity of EM–HCl does not follow the weight loss behavior exactly. The loss of absorbed water upon heating to 100 °C results in a decrease in conductivity. However, this decrease in conductivity is reversible when the heated sample is cooled and allowed to reabsorb water from the atmosphere. In air, although there is minimal weight change of EM–HCl between 100 °C and ca. 300 °C, the conversion of chloride anions to covalently bonded species above 150 °C results in the irreversible loss of conductivity. Thus, the upper temperature limit for the application of EM–HCl as a conducting polymer would be determined more by the degradation in conductivity than by its weight loss behavior.

When H_2SO_4 is used instead of HCl for the synthesis of protonated EM, the TG scan of the resulting EM–H_2SO_4 in N_2 is very similar, to that of EM–HCl, i.e. there is an initial weight loss upon heating from room temperature to 100 °C, followed by a plateau region up to 250 °C. Thus, the mechanisms of degradation of these two protonated EM samples are similar, with an initial loss of absorbed water followed by the loss of the protonating acid species commencing at 250 °C. When protonated EM samples (EM–HCl and EM–H_2SO_4) are rinsed with the corresponding acid rather than deionized water in the preparation stage, these samples undergo an even greater weight loss during heating as compared to their water washed counterparts, suggesting a greater retention of the acid species in the former samples.

The TG scan of EM protonated by HBr (EM–HBr) in N_2 differs markedly from those of EM–HCl and EM–H_2SO_4 (Fig. 6). In the case of EM–HBr, after the initial weight loss step, there is a sharp decline in weight

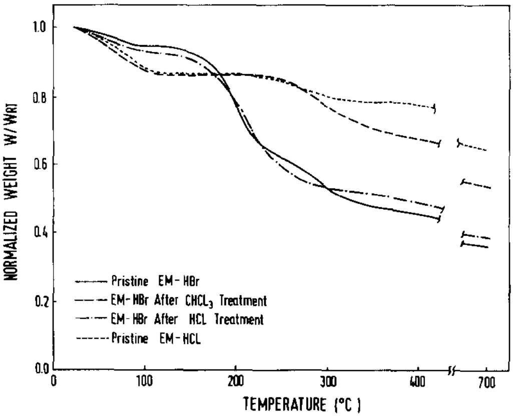

Fig. 6. TG scans of EM–HCl, EM–HBr and EM–HBr after $CHCl_3$ and HCl treatment.

between 150 °C and 225 °C followed by a more gradual weight loss. When EM–HBr is treated with $CHCl_3$, it loses over 40% of its original weight. In contrast, there is no significant weight change when EM–HCl is treated with $CHCl_3$. However, the $CHCl_3$-insoluble fraction of EM–HBr shows greater thermal stability than the pristine sample. The TG scan of this sample shows the same trend as that of EM–HCl (Fig. 6). The XPS results for pristine and $CHCl_3$ treated EM–HBr are shown in Table 1. In this table, the total halogen to nitrogen ratio (X : N) and the ratios of the ionic and covalent halogen to nitrogen (X^- : N and –X : N respectively) are compared. The XPS results indicate that, during $CHCl_3$ treatment, the covalent bromine is preferentially removed, whereas the Br^- : N ratio is not significantly affected. The similarities between the TG scan of the $CHCl_3$-insoluble fraction and those of EM–HCl and EM–H_2SO_4 suggest that in the former sample the onset of weight loss at 250 °C is also due to the loss of the protonating acid species. In pristine EM–HBr, the material lost over the lower temperature range of 150–225 °C constitutes the $CHCl_3$-soluble fraction, which has a higher fraction of covalent bromine than the $CHCl_3$-insoluble fraction. In addition, the former fraction may consist of shorter polymer chains, as evidenced by its solubility in $CHCl_3$.

The treatment of EM–HBr with HCl results in almost complete removal of the Br^- anions, and Cl^- anions are incorporated (Table 1). However, the covalent bromine content is not substantially affected by HCl treatment. The Cl^- : N and –Cl : N ratios in the HCl treated EM–HBr sample are somewhat lower than the corresponding ratios in pristine EM–HCl. As discussed earlier, a larger fraction of the covalent bromine is associated with the material that decomposes between 150 °C and 225 °C. Hence the small decrease in covalent Br content as a result of HCl treatment indicates that the thermal stability of the HCl treated sample would not be substantially improved over the pristine EM–HBr. The TG scans in Fig. 6 confirm that the HCl treated sample is much less stable than EM–HCl, and its degradation behavior is almost identical to that of the pristine EM–HBr.

Organic complexes of emeraldine and leucoemeraldine

In our earlier studies [7,22], we have shown that EM and LM interact with halobenzoquinones to give electrically conductive complexes. The charge transfer interactions between the polymer and the halobenzoquinone result in the formation of halogen and benzoquinone anions. The extent of such interactions depends on the type and concentration of the halobenzoquinone, as well as the oxidation state of the polyaniline (i.e. EM or LM). The use of *ortho*-halobenzoquinones, such as *o*-chloranil and *o*-bromanil, results in more conductive complexes than those obtained with *para*-halobenzoquinones. The TG scans of EM–*o*-chloranil and EM–*o*-bromanil complexes having a similar weight fraction of halobenzoquinone (Y) are

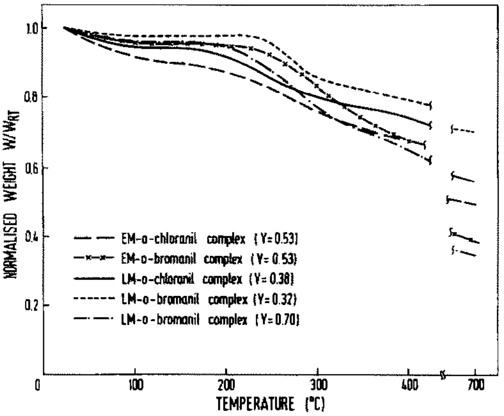

Fig. 7. TG scans of EM–*o*-chloranil, EM–*o*-bromanil, LM–*o*-chloranil and LM–*o*-bromanil complexes. *Y* is the weight fraction of the halobenzoquinone in the complex.

compared in Fig. 7. The EM–*o*-bromanil complex does not undergo any significant weight changes between 100 °C and 225 °C, whereas the EM–*o*-chloranil complex suffers a slow but continuous weight loss upon heating above room temperature. The onset of major weight loss for the latter sample is around 200 °C. Knowing the decomposition behavior of the pristine halobenzoquinones and the EM base, the weight loss of a hypothetical mixture of EM base and halobenzoquinone, in which the two components decompose independently of each other, can be predicted. The predicted weight fractions remaining for such hypothetical mixtures of EM with *o*-chloranil and *o*-bromanil ($Y = 0.53$) at 250 °C are 0.81 and 0.92 respectively. The experimental values obtained for the EM–*o*-chloranil and EM–*o*-bromanil complexes at that temperature are 0.83 and 0.93 respectively. At 300 °C, the ratios of predicted value to experimental value are 0.69 : 0.76 and 0.89 : 0.84 for the EM–*o*-chloranil and EM–*o*-bromanil complexes respectively. These results indicate that the initial weight loss of the complexes is due to the decomposition of the halobenzoquinone molecules, since EM base is thermally stable below 400 °C. However, as the degradation progresses, the initial decomposition products may undergo further reactions with the polymer chain, resulting in a weight loss behavior that cannot be predicted by simply assuming that the two components of the complex decompose independently.

In Fig. 7, the TG scans of a LM–*o*-chloranil complex ($Y = 0.38$) and two LM–*o*-bromanil complexes ($Y = 0.32$ and 0.70) are also shown. Generally, the decomposition behavior of the LM–halobenzoquinone complexes is similar to that of the EM–halobenzoquinone complexes. As expected, a comparison of the TG scans of the three LM complexes reveals that the LM–*o*-chloranil complex decomposes at the lowest temperature, owing to the lower decomposition temperature of *o*-chloranil as compared with *o*-bromanil. In addition, the complex having the higher fraction of halobenzoquinone would show a lower degree of thermal stability, since the pristine halobenzoquinones decompose at lower temperatures than does the polymeric base.

CONCLUSION

The initial stage of the degradation of leucoemeraldine involves the loss of hydrogen to form some imine-like structures. This process proceeds very slowly under ambient conditions but is accelerated by the presence of high O_2 concentration and by elevated temperatures. In N_2, both leucoemeraldine and emeraldine base are thermally stable below 400 °C, whereas in the presence of O_2 volatile oxidation products are formed above 350 °C. In N_2, emeraldine protonated by HCl or H_2SO_4 shows an initial weight loss of ca. 10% due to the loss of absorbed water, and the onset of major weight loss at 250 °C is attributed to the loss of the protonating acid species. The thermal stability of protonated emeraldine is decreased drastically if HBr is used. The thermally less stable component of this polymer is soluble in $CHCl_3$, suggesting the existence of shorter polymer chains. The degradation of the complexes of emeraldine base and leucoemeraldine with *o*-chloranil and *o*-bromanil is initiated by the decomposition of the incorporated acceptor.

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