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THERMAL ANALYSIS OF CONDUCTING POLYMERS PART I

Thermogravimetry of acid-doped polyanilines

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Thermogravimetry (TG) has been conducted on a series of electroconducting acid-doped polyanilines. The weight loss results suggest that the majority of dopants are eliminated between 230 °C to 350 °C leaving behind the skeletal non-conducting polyaniline. The doped polyaniline are thermally more stable than the pristine polyaniline in air at high temperatures. This suggests that despite the early elimination observed, the presence of dopant at the begining has a stabilizing effect on the skeletal polyaniline. By comparison the acid-doped polyanilines are more thermally stable than many other electroconductive polymers, such as polypyrroles and polyacetylenes.

The demand for electrically conductive polymers used in the electronic industry have in the past been met by adding high loading of conductive metal powders (sometimes as high as 80% by weight) such as silver, gold and graphite to render the plastics conducting. There are, however, a number of serious drawbacks to this approach in terms of high cost and deterioration in other properties of the polymer. Recently, the promise of new intrinsically conductive polymers which combine high conductivity with such properties as light weight, low cost, flexibility, and processability has generated considerable interest among the industrial and academic researchers. Experts envisage such diverse applications as light weight batteries, polymer electronic devices, microwave absorbers, electromagnetic shield, photoconductors, chemical sensors and switches. It is not surprising therefore that the search for these new polymers is one of the most active areas in polymer science and engineering at this moment.

The most promising candidates at present are polyacetylene, polyheterocycles such as polypyrrole and polythiophenes and polyanilines. Conductivities in the range of 10^0 to 10^3 S cm^{-1} are possible for these polymers when doped with either

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an electron acceptor or an electron donor. Characterisation of these polymers by IR spectroscopy [1], UV spectroscopy [2], X-ray photoelectron spectroscopy (XPS) and other techniques have been reported [3–6]. The use of thermal analysis, however, has been cited only in parts for polypyrrole [7] and polyaniline [8] and no attempts have been made to make a systematic studies of the thermal behaviour of these conductive polymers.

In this laboratory we have focused our attention on polyanilines due to the following reasons; (i) low cost of the monomer compared to pyrrole, thiophene and acetylene, (ii) the ability of the polymer to undergo both redox and protonic exchange and (iii) their inherent thermal stability. We like to report in this paper some preliminary thermogravimetric results of a number of acid-doped polyanilines to determine the effect of dopants on thermal stability, the upper temperature limits for these polymers and to compare them with other electroconducting polymers.

Chemistry of polyaniline

It has been reported [9] that polyaniline can be prepared in four limiting forms as depicted below:

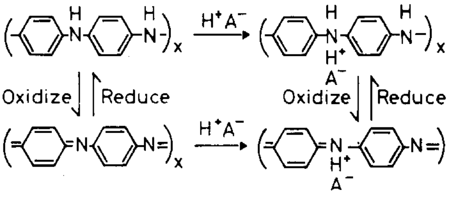

Fig. 1 Four limiting reduced/oxidised forms of polyanilines

These forms are interconvertible by means of chemical or electrochemical redox reactions. Emeraldine, which is a specific base form of polyaniline, and consists of equal repeating units of the reduced and oxidised forms, is of particular interest. It exists as a resonance hybrid of contributing structures in a degenerate ground state:

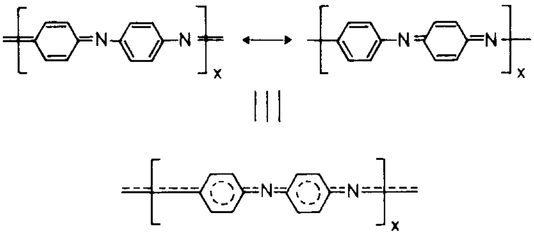

Fig. 2 Resonance hybrid structures of polyanilines

Such resonance effects may enable it to exhibit defect states in the form of solitons which are believed to be responsible for the conducting ability of the polymer.

Though the emeraldine salt form of polyaniline has been known to be a very stable electronic conducting polymer; the mechanism of its charge generation has yet to be consolidated. Typically, *p*-doping (oxidising) of an organic polymer involves the removal of π electrons from the polymer by chemical or electrochemical oxidation:

$$(\text{polymer}) \rightarrow (\text{polymer})^{+x} + xe^{-}$$

Conversely, it should be possible to *p*-dope a conducting polymer by adding a proton, which interacts with and hence partially depopulate the π system with a concomittant increase in its conductivity:

$$\underset{\text{base}}{(\text{polymer})} + \underset{\text{acid}}{x\text{H}^{+}} \rightarrow \underset{\text{salt}}{(\text{polymer})\ \text{H})^{x} + x}$$

Such novel *p*-doping to the metallic regime involves a simple acid/base interaction in which no formal oxidation of the polymer occurs. Similarly, the base form of emeraldine, an insulator, when doped by dilute aqueous protonic acids, conducts in the metallic regime to give the corresponding minimum salt (rather than a carbocation as is the case with conventional *p*-doping) [10].

Experimental

Chemicals

The chemicals used for the synthesis of the polyanilines were: aniline purchased form BDH Laboratory Chemicals which was distilled before polymerisation and solid ammonium peroxysulphate from Reachim. The three minerals acids used for doping were HCl, HBr and HF.

Synthesis of polyaniline

In the present investigation, the method employed for the chemical synthesis of polyaniline was based, in part, on previously described procedure [11]. The acid-doped polyanilines are dark green powder. The pristine polyaniline was obtained by stirring the doped polyaniline with copious 1 M ammonium hydroxide solution and then with deionised water. The product was filtered and dried in vacuum oven at 80° for 48 hrs. The pristine polyaniline powder is black in colour with a copper glint.

Elemental analysis

The composition of the various samples were determined using the Perkin–Elmer C, H. N, elemental analyser model 240. The % halogen was determined by the oxygen-flask method.

Conductivity measurement

The doped and pristine polyanilines were pressed into a disk-shaped pellet 7 mm in diameter using KBr die. The conductivity was measured using a four-in-line probe with 1 mm spacings. The two outer probes were connected to a Keithley model 228 constant voltage/current source. The inner two probes were connected to a Keithley model 195A digital multimeter for voltage measurement.

Thermogravimetry (TG)

The sample in powder form (10–20 mg) was analysed using the 951 thermogravimetric analyser in a DuPont 9900 System at a heating rate of 10 deg min^{-1}. A flow rate of 75 cc min^{-1} was selected for both air and nitrogen atmospheres.

Results and discussion

a) In nitrogen

The TG results are summarised in Table 1 and the thermograms are illustrated in Figs 3 to 10. In general, all the conductive polymers exhibit similar weight loss

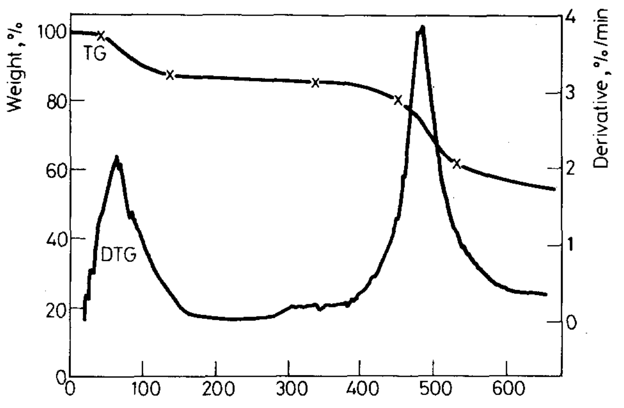

Fig. 3 TG and DTG curves of pristine PAn in nitrogen

Table 1 Summary of TG results

		Evolution of water and free acid		Elimination of dopant		% Wt. loss at 400 °C	% Wt. loss at 500 °C	% Wt. loss at 600 °C	% halogen	Conductivity, S cm^{-1}
		temp., °C	%	temp., °C	%					
PAn–Base	Air	35–140	10.0			32.3	95.4	100.0		$<10^{-6}$
	N_2	35–140	10.0			17.0	36.3	47.7		$<10^{-6}$
PAn–HCl	Air	35–180	10.0	220–360	10.6	22.5	60.8	100.0	13.0	5.0
	N_2	35–190	13.0	240–360	10.2	26.0	41.4	48.0		
PAn–HBr	Air	30–200	8.0	260–375	16.0	23.8	49.2	100.0	27.3	14.0
	N_2	30–180	11.0	250–380	18.2	32.4	40.7	48.0		
PAn–HF	Air	35–150	11.5	270–360	9.6	27.7	76.0	98.0	9.84	3.7
	N_2	30–170	12.3	250–370	9.3	26.9	42.3	50.2		

characteristics when subjected to similar heating regimes in the same atmospheric environment. Based on the TG thermograms (Figs 3–6), we suggest that in an inert atmosphere, the initial weight change corresponds to the loss of water and free hydrohalide and halogen trapped in the polymer matrix. The second weight loss step indicates mostly the loss of the hydrohalides "bound" to the polymer chain as protonating dopant interacting with the positively charged nitrogen as well as a small amount of ring-substituted halogens which has been identified by X-ray photoelectron spectroscopy [12]. The % loss of halogens observed in this step is lower than that determined by microanalysis which is not unexpected because the microanalysis examines the total halogen content which includes the free halide and halogen that would have been lost in the first step.

As can be seen from Figs 4 to 6, dehydrohalogenation process ranges from approximately 230° to 370° for all three doped polymers. This indicates that the

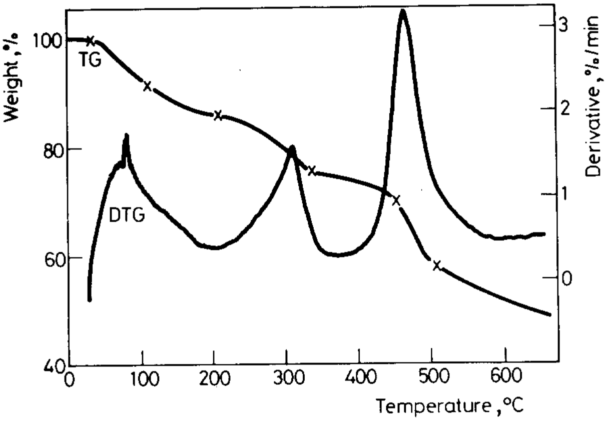

Fig. 4 TG and DTG curves of PAn–HCl in nitrogen

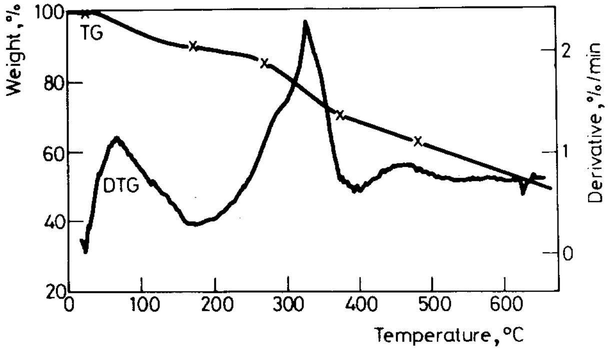

Fig. 5 TG and DTG curves of PAn–HBr in nitrogen

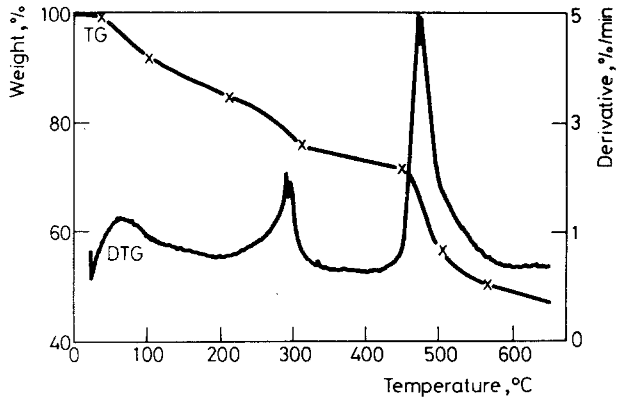

Fig. 6 TG and DTG curves of PAn–HF in nitrogen

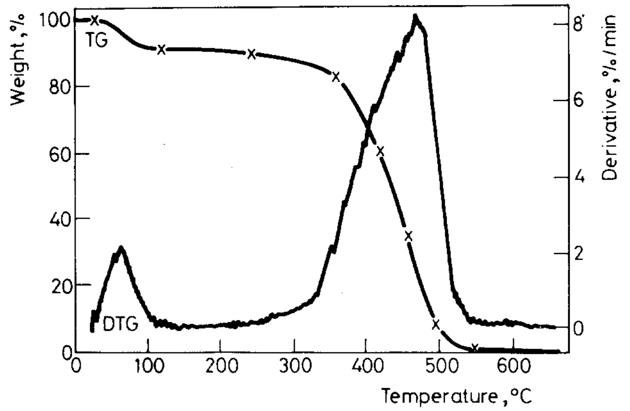

Fig. 7 TG and DTG curves of pristine PAn in air

conductive doped form of all these polymers have the same stability as well as setting the upper temperature limits for application of their conductive properties. The basic polyaniline polymer skeleton is retained after the elimination of the dopant, though it may start to lose electrical conductivity beyond 230°. Thermal degradation of the pristine polyaniline commences at approximately 380° as shown by the onset of the major DTG peak and at 650°, approximately 50% of the polymer remains as residue (see Fig. 3). The doped polyanilines are slightly less stable at 400° (see Table 1) than the pristine polymer but they have almost the same amount of residue at 600° to 650°. It is interesting to note that in nitrogen, the HBr dopant seems to slow down the degradation of the skeletal polyaniline as indicated by the very low rate of weight loss (see Fig. 5).

b) In air

Results in Table 1 indicate that the evolution of free acid and water and the elimination of dopants are little affected by the atmosphere. Infact the doped polyanilines are more stable in air than in nitrogen up to 400° after which we observe the beginning of the major weight loss step due to the breakdown of the polyaniline polymer. Attention should be drawn to the very different decomposition pattern for the skeletal polyaniline observed for the doped polyanilines in air compared to that in nitrogen. In the case of PAn–HCl (Fig. 8) and PAn–HF (Fig. 10) the decomposition comprises two consecutive steps as shown by the two DTG peaks. The PAn–HBr has three DTG peaks between 450° and 600° (Fig. 9). In

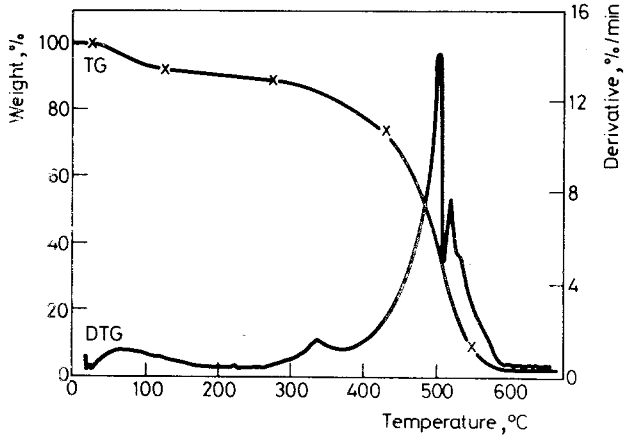

Fig. 8 TG and DTG curves of PAn–HCl in air

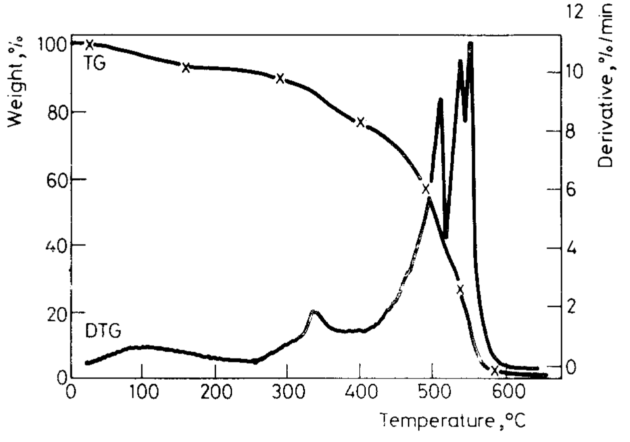

Fig. 9 TG and DTG curves of PAn–HBr in air

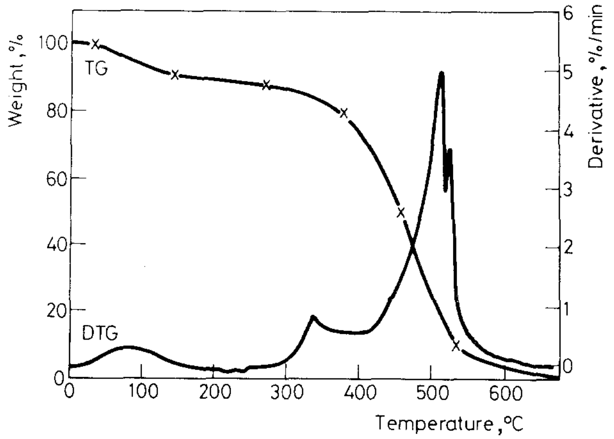

Fig. 10 TG and DTG curves of PAn–HF in air

addition, weight loss data at 500° (see Table 1) indicate the skeletal polyanilines are thermally more stable than the pristine polyaniline. This suggests that despite their elimination at about 350°, the presence of dopants at the lower temperatures has an influence on the eventual decomposition pattern of the polyaniline polymer in air. It is also possible that the products of the first step (between ≈ 420° to 510°) act as catalysts for the decomposition of subsequent step(s).

For the pristine polyaniline, only one DTG peak is observed in air and the rate of weight loss is faster than that observed in nitrogen as expected. Further work is required to provide a better understanding of the effect of dopants on thermal stability in air. Comparison in thermal stability can be made between polyanilines prepared in the present work and other conductive polymers. Kang et al. [7] reported that polypyrroles doped with iodine are stable up to 184° in air at which temperature volatilisation of iodine takes place and the bromine-doped polypyrrole is stable only up to 140° with loss of conductivity in both cases. Polyacetylene doped with iodine shows a rather poor thermal stability and suffers a weight loss immediately upon heating above room temperature [13]. The acid-doped polyanilines discussed in the present work are stable up to at least 230° and they offer a substantial increase in working temperature over many other conducting polymers.

Conclusions

Polyanilines doped with strong acids are thermally stable up to about 230° at which point elimination of dopants occurs to give the skeletal non-conducting polyaniline polymer. Based on the thermal analysis data obtained, we suggest that despite early elimination, the dopants can affect the decomposition pattern of the basic polyaniline at higher temperatures, especially in air.

References

1 M. Ohara, T. Sakai, M. Takeuchi, Y. Kobayashi and M. Tsuji, Synthetic Metals, 18 (1987) 365.

2 D. C. Bott, in T. A. Skotheim (Ed.), Handbook of Conducting Polymers, 1987, Chapter 33.

3 W. K. Salaneck, in T. A. Skothiem (Ed.), Handbook of Conducting Polymers, 1987, Chapter 37.

4 Y. Takenaka, T. Koike, T. Oka and M. Tanahashi, Synthetic Metals, 18 (1987) 207.

5 A. F. Diaz and B. Hall, IBM Journal of Research and Development, 27 4 (1983) 342.

6 B. Wang, J. Tang and F. Wang, Synthetic Metals, 13 (1986) 329.

7 E. T. Kang, T. C. Tan, K. G. Neoh and Y. K. Ong, Polymer, 27 (1986) 1958.

8 S. Wang, F. Wang and X. Ge, Synthetic Metals, 16 (1986) 99.

9 A. G. MacDiarmid, J. C. Chiang, M. Halpern, W. S. Huang, S. L. Mu, N. L. D. Somarsiri, W. Wu and S. I. Yaniger, Molecular Crystal Liquid Crystal, 121 (1985) 173.

10 A. G. MacDiarmid, J. C. Chiang and A. F. Richter, Synthetic Metals, 18 (1987) 285.

11 A. G. macDiarmid, S. L. Mu and W. Wu, Molecular Crystal Liquid Crystal, 121 (1985) 187.

12 H. S. O. Chan, H. Munro, C. Davies and E. T. Kang, Synthetic·Metals, 22 (1987) 365.

13 J. E. Osterholm, H. K. Yasuda and L. L. Levenson, Journal of Applied Polymer Science, 28 (1983) 1265.

Zusammenfassung — An einer Reihe von elektrisch leitenden säureversetzten Polyanilinen wurden thermogravimetrische (TG) Untersuchungen durchgeführt. Die Gewichtsverluste zeigen, daß die Mehrzahl der Zusätze bei einer Temperatur zwischen 230 °C und 350 °C eliminiert werden, wobei die nichtleitenden Polyaniline zurückbleiben. Bei hohen Temperaturen ist das versetzte Polyanilin in Luft thermisch stabiler als das ursprüngliche Polyanilin. Das bedeutet, daß eine anfängliche Gegenwart der Zusätze ungeachtet der frühen Eliminierung einen stabilisierenden Effekt auf das Polyanilingerüst ausübt. Im Vergleich erwiesen sich säureversetzte Polyaniline als thermisch stabiler als andere elektrisch leitende Polymere wie z. B. Polypyrrole oder Polyazethylene.

Резюме — Проведены термогравиметрические исследования электропроводящих полианилинов, легированных кислотами. Наблюдаемая потеря веса указывает, что большинство легирующих добавок выделяется в температурном интервале 230–350°, давая скелетный непроводящий полианилин. Легированный полианилин термически более устойчивый в атмосфере воздуха, чем исходный полианилин. Это доказывает, что несмотря на раннее выделение легирующей добавки, наличие ее в самом начале оказывает стабилизирующий эффект на скелетный полианилин. Установлено, что кислотно-легированные полианилины термически более устойчивые, чем многие другие электропроводящие полимеры, как например, полипирролы и полиацетилены.