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Conducting polyaniline salts: thermogravimetric and differential thermal analysis

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Abstract

Five different polyaniline salts have been prepared by chemical polymerization. The thermal stabilities and energies of activation for all the salts under oxygen and nitrogen atmospheres have been determined from thermogravimetric analysis. Polyaniline salts undergo a three step weight loss process in the heating cycle. In the first step, a water molecule escapes from the polymer matrix; in the second step, it is possible that a phase transition occurs, along with evolution of a small percentage ($\approx 2-3\%$) of adsorbed acid present on the polymer chain; and finally, thermal degradation occurs. It was found that the thermal stability of polyaniline depends on the counter anion used, and the polymer is apparently stable up to 250°C. The energy of activation for the degradation process has been calculated using five different methods and the results are compared.

INTRODUCTION

Recent advances in the field of electrically conducting polymers have led to a variety of materials with considerable potential for commercial application. Among them, polyaniline (PANI) is one of the most interesting materials because of its moderately high conductivity ($10\ \mathrm{S\ cm^{-1}}$) upon doping with acids [1, 2], its well behaved electrochemistry [3, 4] and its processibility [5].

It is of interest to compare the thermal stability of polyaniline in its conducting and insulating forms. Several methods have been developed to allow kinetic analysis of thermogravimetric data but few attempts have been made to compare them critically. In the present work, a critical comparison is made of five methods [6–10] which have been proposed for analyzing TGA curves.

In the present work, conducting polyaniline salts were synthesized by chemical polymerization of aniline using different acids such as hydrochloric acid (HCl), sulfuric acid (H_2SO_4), phosphoric acid (H_3PO_4), formic acid

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(HCOOH) and *p*-toluenesulfonic acid (TSA), and the thermal behavior of the products was studied by thermogravimetric analysis (TGA) and differential thermal analysis (DTA). A critical comparison is made of five methods which have been proposed for analyzing TGA curves.

EXPERIMENTAL

Reagent grade aniline (Merck) was vacuum distilled under nitrogen prior to use. All other reagents were used as received. The polyaniline salts were synthesized as reported earlier [11].

The TGA and DTA thermograms of the polymer samples were recorded using a thermogravimetric analyzer DT-40 (Shimadzu) in the presence of an oxygen/nitrogen atmosphere up to 700°C and at a heating rate of 5 K min^{-1}.

RESULTS AND DISCUSSION

Two forms of thermal behavior of polyaniline salts are reported in the literature [8, 12–15]. One of these indicates a two step weight loss process in which, initially, water escapes from the polymer chain, followed by thermal degradation of the polymer salt [13–15]. The other form shows a three step weight loss process wherein water escapes first, followed by acid dopant present in the polymer salt, and finally complete degradation of the polymer results [8,12]. In the present study, a three step weight loss process was observed, and the analysis of the results is described here.

TGA and DTA thermograms

Generally similar TGA and DTA thermograms were observed for all the polymer salts when recorded under both oxygen and nitrogen atmospheres. The polymer salts are slightly more stable under a nitrogen atmosphere than under an oxygen atmosphere. The stability of a polyaniline salt depends on the acid used (Table 1).

The TGA and DTA thermograms of a PANI-HCOOH sample recorded under an oxygen and a nitrogen atmosphere are shown in Figs. 1 and 2 respectively. The DTA thermogram of PANI-HCOOH sample recorded under oxygen shows one endotherm (peak maximum at 55°C; this endotherm is complete at 105°C), one exotherm hump around 200°C and another broad exotherm around 325°C. The data for all the systems, corresponding to one endothermic and two exothermic peak maxima, are reported in Table 1.

The TGA thermograms of polyaniline salts show typical three step weight loss behavior. In a representative thermogram of a PANI-HCOOH sample recorded under an oxygen atmosphere, the first step indicates a 5–6%

TABLE 1

Second step of the thermograms of polyaniline salts under an oxygen and nitrogen atmosphere

Salt	Oxygen		Nitrogen	
	Temperature range/°C	Weight loss/%	Temperature range/°C	Weight loss/%
PANI-HCl	110–310	4	100–315	3
PANI-H_2SO_4	110–250	2	105–280	2
PANI-H_3PO_4	100–250	3	90–285	3
PANI-HCOOH	100–285	3	100–300	2
PANI-TSA	100–285	<1	95–295	1

weight loss at temperatures up to 110°C (whereas the DTA curve shows an endotherm at ≈55°C which is complete at 105°C). This step can be attributed to the loss of a water molecule from the polymer matrix, as reported by others [12–16]. In the second step, there is a small weight loss (3%) which takes place continuously from 110 to 250°C (the DTA curve shows a hump shaped exotherm at 200°C). This may possibly be attributable to the coevolution of water, evolution of acid or phase transition (one or more of these). The data for all the systems corresponding to the second step weight loss process are reported in Table 2. The third step starts at 250°C onward and involves complete weight loss (the DTA curve shows a broad exotherm around 325°C). This step can be logically attributed to the thermal degradation of the polyaniline salt.

In order to understand the second step process, the TGA and DTA thermograms were recorded up to 250°C for PANI-HCOOH and PANI

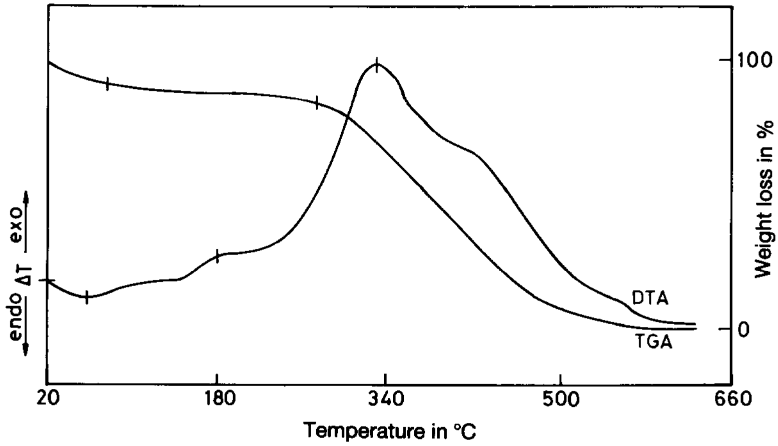

Fig. 1. TGA and DTA thermograms of PANI-HCOOH recorded under an oxygen atmosphere.

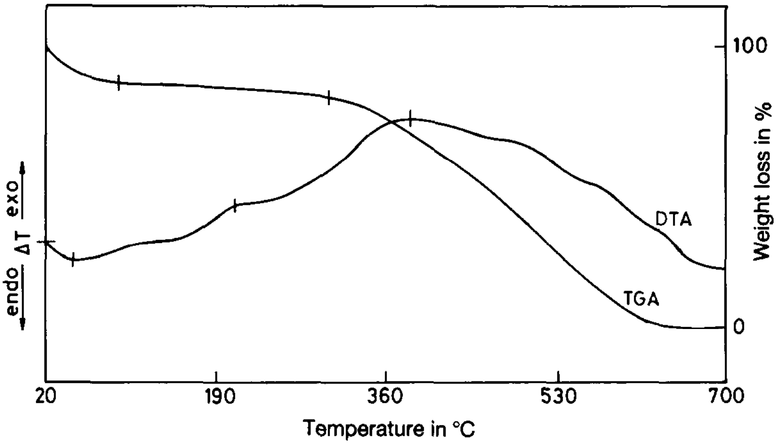

Fig. 2. TGA and DTA thermograms of PANI-HCOOH recorded under a nitrogen atmosphere.

(the polyaniline base, which was prepared from PANI-HCOOH by dedoping with 0.5 M aqueous ammonium hydroxide solution) and the samples were then cooled to room temperature under a nitrogen atmosphere. The DTA thermogram of PANI-HCOOH showed a clear exotherm with 3% weight loss (measured by TGA) during heating and a clear endotherm during cooling back to room temperature (TGA showed no increase in weight during cooling from 250 to 120°C and the weight then increased owing due to absorption of water). However, the DTA thermogram of PANI showed a very broad exothermic hump during heating, and no endotherm was observed while cooling down to room temperature. This result suggests that a phase transition occurs along with the evolution of the acid moiety.

All five polyaniline samples were subjected to heat treatment at four different temperatures: 150, 200, 275 and 375°C. The infrared and electronic absorption spectra were recorded for the samples as prepared and also after

TABLE 2

Peak maxima for endotherm and two exotherms (in °C) under an oxygen and a nitrogen atmosphere for polyaniline salts

System	Oxygen			Nitrogen		
	endo	exo	exo	endo	exo	exo
PANI-HCl	60	200	325	60	215	345
PANI-H_2SO_4	60	185	330	55	185	375
PANI-H_3PO_4	45	190	320	55	280	410
PANI-HCOOH	55	185	330	50	210	390
PANI-TSA	50	260	340	60	260	350

TABLE 3

Method		Y axis	X axis	Slope [a]
I	Horowitz and Metzger [6]	$\ln\left\{\ln\left[\frac{(w_0 - w_f)}{(w_t - w_f)}\right]\right\}$	θ	$\frac{E \times 10^3}{RT_s^2}$
II	Coats and Redfern [7]	$\log\left[\frac{-\log(1-\alpha)}{T^2}\right]$	$\frac{10^3}{T}$	$-\frac{E}{2.303R}$
III	Chan et al. [8]	$\ln\frac{k}{w_t}$	$\frac{10^3}{T}$	$-\frac{E}{R}$
IV	Freeman and Carroll [9]	$\frac{\Delta \log(\mathrm{d}w/\mathrm{d}t)}{\Delta \log(w_a - w_b)}$	$\frac{10^3(\Delta T)^{-1}}{\log(w_a - w_b)}$	$-\frac{E}{2.303R}$
V	Ingraham and Marier [10]	$\log(\mathrm{d}w/\mathrm{d}t) - \log T + \log a$	$\frac{10^3}{T}$	$-\frac{E}{2.303R}$

[a] From the slope, the energy of activation can be calculated.

heat treatment. The infrared and electronic absorption spectra of the salts that had been heated to 200°C indicated no changes by comparison with the spectra of the salts as prepared. The polymer salts heat treated at 275 and 375°C revealed the initiation and completion, respectively, of structural changes [17]. Such changes are due to the thermal degradation of the polymer salt, which is in accordance with the TGA results.

Calculation of energy of activation

The energy of activation for the polymer degradation process was calculated using five different methods, each assuming first order kinetics. Details of the methods used here are given in Table 3.

The parameters in the expressions are: E = energy of activation; R = gas constant; T = temperature; t = time; a = heating rate; α = fraction of the sample decomposed at time t; w_0 = initial weight of the sample; w_f = final weight of the sample; w_t = weight of the sample at time t; w_a = total mass loss; w_b = total mass loss up to time t; $\theta = T - T_s$; T_s = reference temperature, where $(w - w_t)/(w_0 - w_t) = 1/e$.

Methods I and II give a perfect straight line, but in method III the points deviate slightly from a straight line. Methods IV and V do not give a straight line. The energy of activation of polymer degradation for all five salts under an oxygen and a nitrogen atmosphere has therefore been calculated using only the first three methods, and the results are reported in Table 4.

The energies of activation calculated using these three methods for all the polymer samples under oxygen and nitrogen atmospheres showed large variations. For example, considering methods I, II and III, the calculated

TABLE 4

Energy of activation (kJ mol^{-1}) under an oxygen and a nitrogen atmosphere for polyaniline salts calculated using three methods (I, II and III)

System	Oxygen			Nitrogen		
	I	II	III	I	II	III
PANI-HCl	46.8	66.5	22.3	37.4	49.5	20.4
PANI-H_2SO_4	50.3	77.6	51.2	40.9	53.0	40.1
PANI-H_3PO_4	49.7	43.7	31.9	36.3	45.8	20.0
PANI-HCOOH	44.5	64.5	39.6	42.7	59.6	46.8
PANI-TSA	68.1	52.0	20.7	61.8	68.6	41.1

energy of activation for PANI-HCl under oxygen is 46.8, 66.5 and 26.3 kJ mol^{-1} respectively. Furthermore, such variability was found for all the polyaniline salts; no uniform trend among the three methods was seen in the values of energy of activation.

The values of energy of activation calculated using method I for all the five polyaniline salts are higher for an oxygen atmosphere than for a nitrogen atmosphere. Also, the energy of activation under an oxygen or a nitrogen atmosphere of the salts PANI-HCl, PANI-H_2SO_4, PANI-H_3PO_4 and PANI-HCOOH is nearly the same, and is lower than that of PANI-TSA. However, no such trend was observed in the value of energy of activation calculated using methods II and III (Table 4).

It is concluded, therefore, that method I can lead to a satisfactory kinetic analysis of the polymer degradation process; however, methods IV and V are considered less satisfactory.

CONCLUSIONS

Polyaniline salts undergo a three step weight loss process in the heating cycle. The first step (up to 110°C) corresponds to the loss of a water molecule from the polymer chain. In the second step, phase transition possibly occurs around 185–265°C (depending upon the acid) along with the evolution of a small amount of the adsorbed acid present on the polymer chain. Finally, above 275°C, the polymer undergoes oxidative thermal degradation in the third step. The polymer is apparently stable up to 250°C. The method of Horowitz and Metzger gives a satisfactory value of energy of activation for the polymer degradation process.

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REFERENCES

1 A.G. MacDiarmid, J.C. Chiang, M. Halpern, W.S. Huang, S.L. Mu, N.L.D. Somasiri, W. Wu and S.I. Yaniger, Mol. Cryst. Liq. Cryst., 121 (1985) 173.
2 J.C. Chiang and A.G. MacDiarmid, Synth. Met., 13 (1986) 193.
3 T. Kobayashi, H. Yoneyama and H. Tamura, J. Electroanal. Chem., 161 (1984) 419.
4 W.S. Huang, B.D. Humphrey and A.G. MacDiarmid, J. Chem. Soc., Faraday Trans. 1, (1986) 82.
5 T. Wessling and H. Volk, Synth. Met., 16 (1986) 127.
6 H. Horowitz and G. Metzger, Anal. Chem., 35 (1963) 1464.
7 A.W. Coats and J.P. Redfern, Nature, 201 (1964) 68.
8 H.S.O. Chan, P.K.H. Ho, E. Khor, M.M. Tan, K.L. Tan, B.T.G. Tan and Y.K. Lim, Synth. Met., 31 (1989) 95.
9 E.S. Freeman and B. Carroll, J. Phys. Chem., 62 (1958) 394.
10 T.R. Ingraham and P. Marier, Can. J. Chem. Eng., (1964) 161.
11 S. Palaniappan and B.H. Narayana, Polym. Adv. Technol., in press.
12 V.G. Kulkarni, L.D. Campbell and W.R. Mathew, Synth. Met., 30 (1989) 321.
13 M.C. Gupta and S.S. Umare, Macromolecules, 25 (1992) 138.
14 S.H. Khor, K.G. Neoh and E.T. Kang, J. App. Polym. Sci., 40 (1990) 2015.
15 A.D. Borkar and M.C. Gupta, Indian J. Chem., Sect. A, 29 (1990) 631.
16 J. Yue, A.J. Epstein, Z. Zhong, P.K. Gallagher and A.G. MacDiarmid, Synth. Met., 41 (1991) 765.
17 S. Palaniappan and B.H. Narayana, J. Polym. Sci., Polym. Chem., in press.