

Thermal analysis of conducting polymers. Part 3. Isothermal thermogravimetry of doped and pristine polyaniline

H.S.O. Chan *, L.M. Gan, T.S.A. Hor, S.H. Seow and L.H. Zhang

*Department of Chemistry, National University of Singapore, Kent Ridge, Singapore 0511
(Singapore)*

(Received 18 December 1992; accepted 24 February 1993)

Abstract

A study of the thermooxidative decomposition of electroactive polyanilines (PANI) has been carried out using isothermal thermogravimetry (TG). At low decomposition temperatures the process is governed by first-order kinetics, while at higher temperatures the decomposition is controlled by a one-dimensional diffusion mechanism. This has been attributed to changes in sample geometry, viscosity, and secondary cross-linking reactions and structural rearrangement at high temperatures which make it more difficult for the volatile fragments to diffuse to the surface of the polymer matrix. The activation energy ΔE values for the expulsion of free water/HCl and dopant HCl have been determined from the Arrhenius plots and are in good agreement with those obtained previously by differential scanning calorimetry (DSC).

INTRODUCTION

Electrically conducting organic polymers are a novel class of synthetic metals that combine the chemical and mechanical attributes of polymers with the electronic properties of metals and semiconductors. They breach the traditional view of mutual exclusion between plastics and electrical conductivity, and their development has spurred intense interdisciplinary research in the last fifteen years [1–4].

A wide variety of polyenes, polyaromatics and polyheterocyclics have been investigated in the search for conducting polymers. Among those attracting considerable interest are polyacetylene [5], polythiophene [6], polypyrrole [7] and PANI [8]. PANI offers several advantages over the other conducting polymers, namely straightforward synthesis, ease of transformation between conducting and insulating forms, and thermal stability.

* Corresponding author.

Recently, the thermal stability of PANI has been reported by a number of workers [9–13]. The degradation can be roughly divided into three major steps: the loss of moisture, free HCl and unreacted monomer; the elimination of dopant; and the destruction of the skeletal backbone at increasing temperatures. While the loss of dopant is mainly responsible for the drop in conductivity at high temperatures, Kulkarni [14] suggested that for polyaniline tosylate, oxidation and possible structural rearrangement may also play an important part. Hagiwara et al. [9] reported that the deterioration of conductivity in air was based on the chemical change involving the elimination of hydrochloric acid from the amino group and the simultaneous chlorination of the aromatic ring. Most of the papers reported on the overall decomposition of the polymer and dopant without investigating the kinetics of the thermal reactions.

Kinetic studies of the thermal decomposition of polymers have been published by many workers [15–18]. The main problem is that the decomposition kinetics in a solid state differ in many ways from that found in a homogeneous fluid phase. For this reason, the results must be interpreted with care when comparisons are being made, especially when the TG data have been obtained under different conditions, e.g. isothermal or non-isothermal. The isothermal approach is preferred in the present work because of its simpler interpretation of the complex solid-state decomposition reactions and its direct access to the determination of ΔE . In this paper, we report the isothermal TG results of the decomposition of electroactive polyanilines in an attempt to study the kinetics and enthalpic changes of the deprotonation step of the doped polymer, as well as the overall decomposition of the pristine polymer.

EXPERIMENTAL

Chemicals

Aniline (Aldrich) was distilled and stored under nitrogen in the dark prior to polymerization. Reagent grade sodium persulphate ($\text{Na}_2\text{S}_2\text{O}_8$) and HCl (BDH) were used without further purification.

Preparation of PANI–HCl

A 50 cm³ aqueous solution of $\text{Na}_2\text{S}_2\text{O}_8$ (3.8 g, 16 mmol) was added dropwise with constant stirring to a 100 cm³ aqueous solution containing fresh aniline (1.5 cm³, 16 mmol) and about 1.0 M of HCl to maintain a pH of about 1.0. Polymerization was carried out at a room temperature for 24 h,

after which the powder obtained was filtered, washed with a small amount of HCl and dried in a desiccator.

Preparation of PANI–base

The PANI–HCl powder was converted to the base by stirring the powder in excess NaOH for 4 h. The product was filtered and dried in vacuo at 60°C for 24 h.

Thermogravimetry

TG experiments were conducted on a Du Pont 2100 thermal analyser with a TGA 2950 thermogravimetric analyser. Very finely divided samples of about 3–5 mg were heated in air at a constant flow rate of 60 cm³ min⁻¹. A temperature range of 175–250°C was employed to monitor the evolution of both free and doped HCl as well as trapped water in the polyaniline. A higher temperature range of 350–450°C was used to study the decomposition of the polymer backbone.

RESULTS AND DISCUSSION

Isothermal analysis of the expulsion of water and HCl

Isothermal analysis of the evolution of trapped water and HCl in PANI, either as proton donor or as free acid (unreacted), was carried out in the temperature range 175–250°C. A typical isothermal weight loss curve at 225°C (Fig. 1) shows two consecutive weight loss steps, the first of which can be attributed to the expulsion of water and free HCl, and the second to the loss of protonating HCl. The rates of weight loss (r) at 6% and 12% at four different temperatures (175, 200, 225 and 250°C) were determined. The apparent activation energies for the two processes were hence determined by plotting r against the reciprocal of the temperature in K. The results are listed in Table 1 and the plots are shown in Fig. 2. The overall activation energy (18.6 kJ mol⁻¹) calculated in this work for the expulsion of free and dopant HCl, agrees quite well with that determined previously by DSC (≈ 20 kJ mol⁻¹) [19].

Isothermal analysis of the thermal decomposition of pristine PANI

Isothermal weight loss curves for the pristine polyaniline in the main degradation temperature range of 350–450°C are shown in Fig. 3. The rate of decomposition was determined at different times, and the kinetics of the

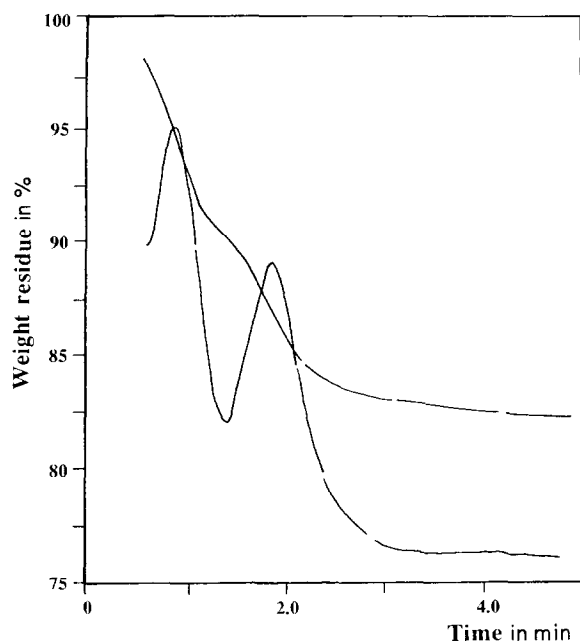


Fig. 1. Isothermal TG and DTG curves of PANI-HCl at 225°C.

main decomposition step was analysed by fitting the experimental data into the most frequently used equations for solid state decomposition, given in Table 2 [20], where α is the fraction of solid decomposed in time t , and k is the rate constant which is related to temperature by the Arrhenius equation $k = A e^{-\Delta E/RT}$, and $g(\alpha)$ is a function depending on the decomposition mechanism. It can be seen from Fig. 4 that a straight line plot was obtained based on the weight loss data at 350°C using the first-order rate equation. The same model, when applied to data for 375°C, provided a curve which suggests that a different decomposition mechanism was in operation. Of the various equations shown in Table 2, the one-dimensional diffusion model was found to be the most accurate in monitoring the decomposition at higher temperatures (see Figs. 5 and 6).

TABLE 1

Summary of ΔE values calculated for elimination of free water and HCl and expulsion of the bound dopant HCl

$r^a/$ (% min ⁻¹)	Temperature/K				$E/(\text{J mol}^{-1})$ $\times 10^{-3}$
	448	473	498	523	
r_6	13.49	14.53	18.03	18.57	7.8
r_{12}	8.95	9.47	11.56	12.94	10.8

^a Subscript refers to the percentage weight loss.

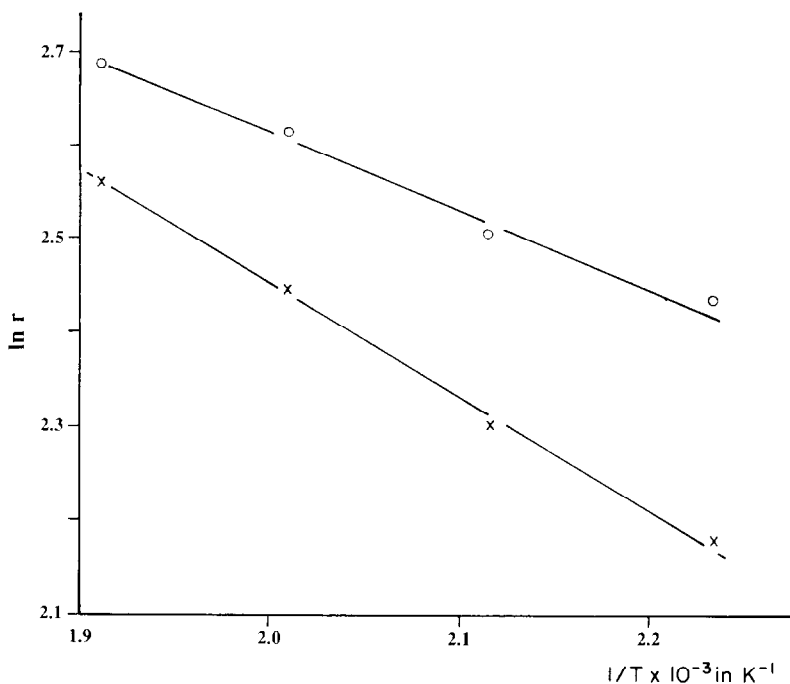


Fig. 2. Plot of the rate of decomposition ($\ln r$) vs. $1/T$: ○, 6% wt. loss; ×, 12% wt. loss.

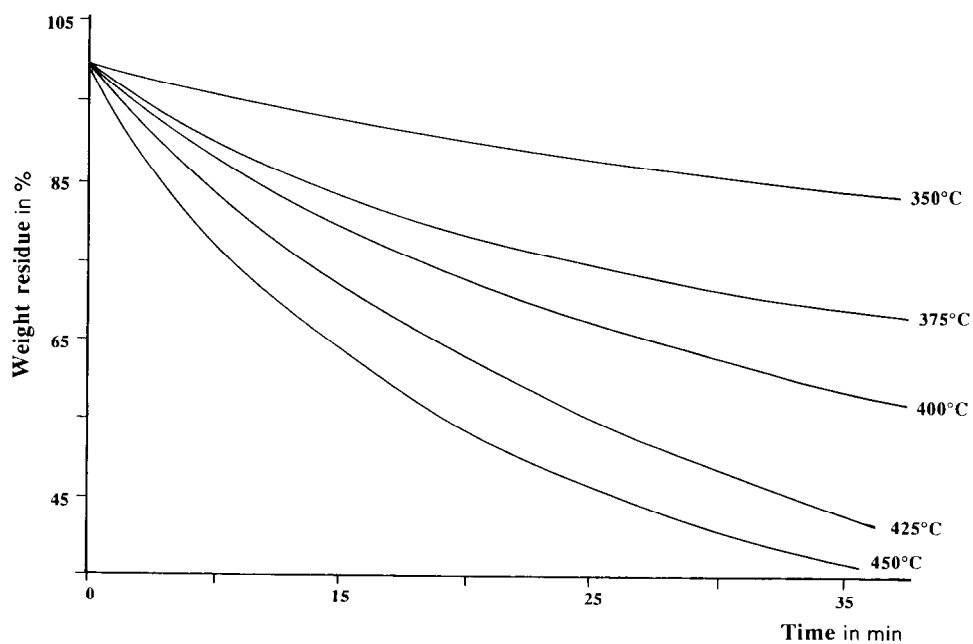


Fig. 3. Isothermal TG curves of PANI at various temperatures.

TABLE 2

Kinetic equations examined in this work

Reaction model	$g(\alpha) = kt^a$
First-order kinetics	$-\ln(1 - \alpha)$
One-dimensional diffusion	α^2
Two-dimensional diffusion	$\alpha + (1 - \alpha) \ln(1 - \alpha)$
Three-dimensional diffusion (Jander equation)	$[1 - (1 - \alpha)1/3]^2$
Three-dimensional diffusion (Ginstling– Brounshtein equation)	$(1 - 2/3\alpha) - (1 - \alpha)^{2/3}$
Two-dimensional phase boundary reaction	$[1 - (1 - \alpha)^{1/2}]$
Avrami equation (random nucleation)	$[-\ln(1 - \alpha)]^{1/2}$
Erfeev equation (random nucleation)	$[-\ln(1 - \alpha)]^{1/3}$

^a α is the fraction of solid decomposed at time t .

Although the decomposition of solid PANI is a complicated process and its mechanism may be influenced by such factors as procedural conditions, viscosity, thermal history, sample geometry and size, the overall process should still follow one of the many kinetic laws proposed for the decomposition in the solid state. At low temperatures, the decomposition proceeds relatively slowly, both at the surface and in the bulk of the material. Under these circumstances, the concentration of the reactant at the surface is very near to the concentration in the bulk: the diffusion resistance of the reactant is far less than the chemical resistance. In this circumstance, the observed reaction rate will depend on the concentration of the reactants in some complex manner appropriate to the mechanism of

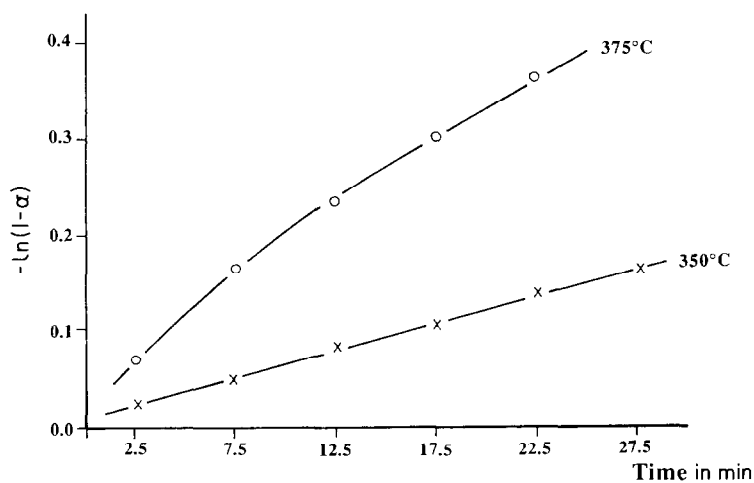


Fig. 4. Plot of $-\ln(1 - \alpha)$ vs. time at 350 and 375°C.

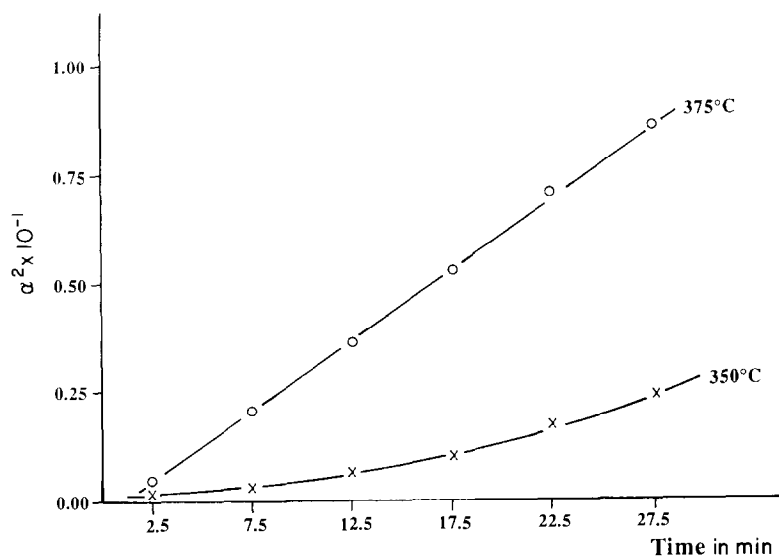


Fig. 5. Plot of α^2 vs. time at 350 and 375°C.

the reaction, and on the temperature according to the Arrhenius equation. The process is dependent only on the fraction of remaining PANI and the reaction rate is related to the size of the free reacting surface. The weight loss results obtained below 375°C supported what has been said so far by providing a straight line plot using the first-order rate equation. With an increase in reaction temperature, however, the change in sample geometry and viscosity, as well as the possibility of secondary cross-linking reaction and structural rearrangement, makes it more difficult for the decomposed

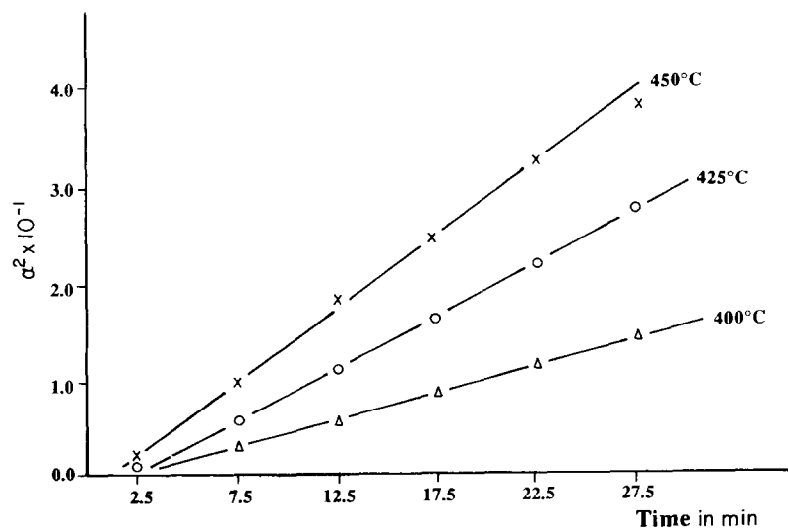


Fig. 6. Plot of α^2 vs. time at 400, 425 and 450°C.

TABLE 3

Summary of ΔE values calculated for the main decomposition of pristine PANI

$r^a/$ (% min ⁻¹)	Temperature/K					$E^\#/(J mol^{-1})$ $\times 10^{-5}$
	623	648	673	698	723	
r_5	0.55	1.94	2.76	3.62	4.67	2.49
r_7	0.51	1.79	2.31	3.46	4.54	2.32
r_9	0.49	1.59	2.15	3.34	4.43	2.32
r_{11}	0.46	1.35	2.01	3.19	4.38	2.24
r_{13}	0.45	1.15	1.88	3.02	4.32	2.08
r_{15}	0.38	1.15	1.71	2.64	3.69	1.83
r_{20}		0.82	1.51	2.42	3.62	1.66

^a Subscript refers to the percentage weight loss.

fragments to diffuse to the surface of the polymer matrix. In this case, the concentration of the reactant in the bulk becomes higher than that at the surface. This, together with the possibility of the sample shrinking during prolonged heating in such a manner as to reduce the reacting area of the surface, would make the diffusion resistance far greater than the chemical resistance. The process is now largely diffusion-controlled, as indicated by the straight line plot obtained using the one-dimensional diffusion equation.

Table 3 summarizes the activation energies calculated by the same method described earlier for the main decomposition region of pristine PANI (375–450°C). The relatively high activation energy at 5% weight loss (249 kJ mol⁻¹) as compared to the lower value at 20% weight loss (166 kJ mol⁻¹) is indicative of the gradual decrease in thermal stability as the extent of degradation increases.

CONCLUSIONS

Using isothermal TG, we have determined the activation energies for the expulsion of free water/HCl and bound HCl as 6.9 and 10.9 kJ mol⁻¹, respectively. Kinetic analysis suggests that the decomposition of pristine PANI follows a variable mechanism depending on the temperature regime. The first-order rate law is obeyed up to 350°C. In the higher temperature range of 375°C–450°C, a one-dimensional diffusion model describes the process more accurately. This has been attributed to the changes in sample geometry, viscosity and secondary reactions at high temperatures which make it more difficult for the decomposed fragments to diffuse to the shrinking surface. In this case, the reaction rate would be closely related to the mass-transfer condition of the sample which makes it a diffusion-controlled process. The activation energies for the main decomposition step vary from 166 to 249 kJ mol⁻¹.

REFERENCES

- 1 G. Wegner, *Angew. Chem. Int. Ed. Engl.*, 20 (1981) 361.
- 2 A.G. MacDiarmid and M. Maxfield, in R.G. Linford (Ed.), *Electrochemical Science and Technology of Polymers*, Elsevier, London, 1987, pp. 67–101.
- 3 M.G. Kanatzidis, *C&EN*, December 3 (1990) 36.
- 4 T.A. Skotheim (Ed.), *Handbook of Conductive Polymers*, Vols. 1 and 2, Marcel Dekker, New York, 1986.
- 5 H. Shirakawa, E.J. Louis, A.G. MacDiarmid, C.K. Chiang and A.J. Heeger, *J. Chem. Soc. Chem. Comm.*, (1977) 578. C.K. Chiang, C.R. Fincher, Jr., Y.W. Park, A.J. Heeger, H. Shrikawa, E.J. Louis, S.C. Gau and A.G. MacDiarmid, *Phys. Rev. Lett.*, 39 (1977) 1098.
- 6 T.C. Cheung, J.H. Kaufman, A.J. Heeger and F. Wudl, *Phys. Rev. B*, 30 (1984) 702. K. Kaneto, K. Yoshino and Y. Inuishi, *Jpn. J. Appl. Phys.*, 22 (1983) L567, L412.
- 7 A.Z. Diaz, K.K. Kanazawa and G.P. Gardini, *J. Chem. Soc. Chem. Comm.*, (1979) 535. A.F. Diaz and K.K. Kanazawa, in J.S. Miller (Ed.), *Extended Linear Chain Compounds*, Plenum Press, New York, 1982, pp. 417–427.
- 8 A.G. MacDiarmid and A. Epstein, *J. Chem. Soc. Faraday Trans.*, 5 (1989) 1.
- 9 T. Hagiwara, M. Yamaura and K. Iwata, *Synth. Met.*, 25 (1988) 243.
- 10 H.S.O. Chan, M.Y.B. Teo, E. Khor and C.N. Lim, *J. Therm. Anal.*, 35 (1989) 765.
- 11 J.C. LaCroix and A.F. Diaz, *J. Electrochem. Soc.*, 135, (1988) 1457.
- 12 Y. Wei and K. Hsueh, *J. Polym. Sci., Part A*, 27 (1989) 4351.
- 13 V.G. Kulkarni, L.D. Campell and K. Iwata, *Synth. Met.*, 30 (1989) 321.
- 14 V.G. Kulkarni, *Thermochim. Acta*, 188 (1991) 265.
- 15 J.R. MacCallum and J. Turner, *Eur. Polym. J.*, 6 (1970) 907.
- 16 V. Satava and F. Skvara, *J. Am. Ceram. Soc.*, 52(11) (1969) 159.
- 17 C.D. Doyle, *J. Appl. Polym. Sci.*, 5(11) (1961) 285.
- 18 J.H. Flynn and L.A. Wall, *J. Res. Natl. Bur. Stand. Sect. A*, 70 (1966) 487.
- 19 H.S.O. Chan, S.C. Ng and W.S. Sim, *Thermochim. Acta*, 197 (1992) 349.
- 20 A.M. El-Awad and R.M. Mahfouz, *J. Therm. Anal.*, 35 (1989) 1413.