Thermochimica Acta, 188 (1991) 265–272
Elsevier Science Publishers B.V., Amsterdam

Thermal analysis of polyaniline tosylate

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(Received 18 January 1991)

Abstract

The thermal-conductivity stability of polyaniline tosylate has been studied using thermogravimetry, infrared spectroscopy and heat-ageing. Its thermal decomposition in nitrogen is a two-step process. The mechanism of the thermal decomposition in air is rather complicated. Oxidation and possible structural rearrangement seem to be the primary causes for loss in conductivity on heat-ageing in air at temperatures below the thermal decomposition.

INTRODUCTION

Polyaniline has been known for a long time [1]. However, owing to its high electrical conductivity, it has recently become the subject of intense research [2–5]. It offers several advantages over other electrically conductive polymers: straightforward processing; ease of transformation between insulating and conducting forms; and thermal stability.

While the synthesis, structure and redox properties of the polymer have been studied extensively, its thermal stability has received little attention. In an earlier paper [6] we reported that neutral (non-conductive) polyaniline is a thermally stable polymer, its stability being in excess of 450 °C in nitrogen. Doped (conductive) polymers are significantly less stable, the thermal stability being dependant on the counter anion. The doped polymers (dry) show a two-step decomposition in nitrogen atmosphere. The first step, at around 200 °C, corresponds to the loss of the dopant; the second step, at around 500 °C, corresponds to the decomposition of the backbone. In samples containing moisture, a loss occurs around 100 °C. Hagiwara et al. [7] in an interesting study have shown that the loss in conductivity of polyaniline hydrochloride on heat aging at 150 °C in air is not accompanied by loss of dopant. The fate of the dopant presumably culminates in chlorination of the aromatic ring. Recently, Chan et al. [8] reported on the thermogravimetric decomposition of halide-doped and mixed-halide-doped polyanilines in dynamic air. They observed the loss of halide dopant between 130 and 290 °C with simultaneous loss in conductivity, followed by the destruction of the skeletal backbone.

0040-6031/91/$03.50

In the present paper we report results on the thermal decomposition of polyaniline doped with *p*-toluene sulfonic acid that provide a better understanding of the decomposition of polyaniline in nitrogen and air atmosphere. The results also provide information on the processing temperature limits for different applications.

EXPERIMENTAL

Polyaniline tosylate was prepared by the reaction of aniline with ammonium persulfate in toluene sulfonic acid medium. Neutral polyaniline was prepared by treatment with excess 1 M ammonium hydroxide.Thermogravimetric curves were recorded in air and nitrogen atmosphere using a Mettler TA 3000 system with a TG 50 measuring module. The heating rate was 10 °C min^{-1}. The purge rate was 100 ml min^{-1}. The samples were dried at 110 °C for 15 minutes under nitrogen prior to recording the thermal curves using a linked program.

Electrical conductivity was determined on pressed pellets using conventional 4-probe and 2-probe techniques. Infrared spectra were obtained using the KBr pellet technique with a Mattson Galaxy 2020 spectrophotometer. Heat-ageing in air was carried out in a conventional air-circulated oven. Heat-ageing in nitrogen was carried out in a round-bottomed flask immersed in a heated oil bath and fitted with a stopper to allow flow of nitrogen.

RESULTS

Figure 1 shows the TG thermograms for the neutral polymer in nitrogen and air atmospheres. The polymer is significantly less stable in air. Further-

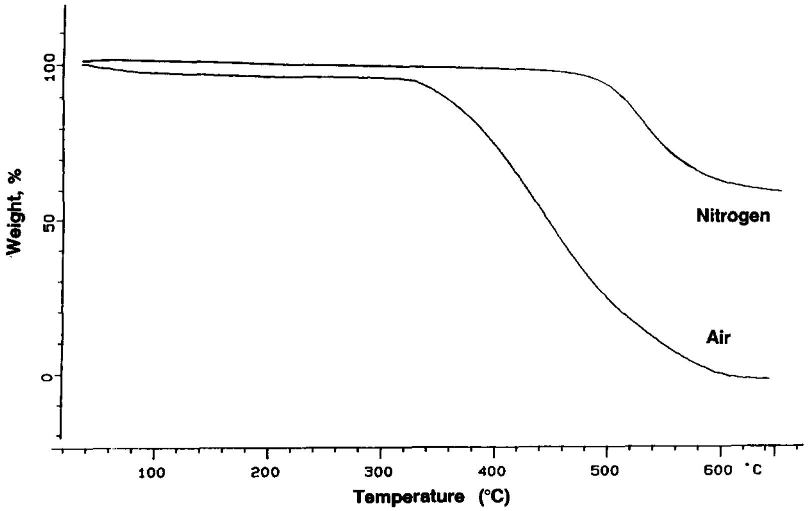

Fig. 1. TG thermogram of neutral polyaniline in air and nitrogen atmospheres.

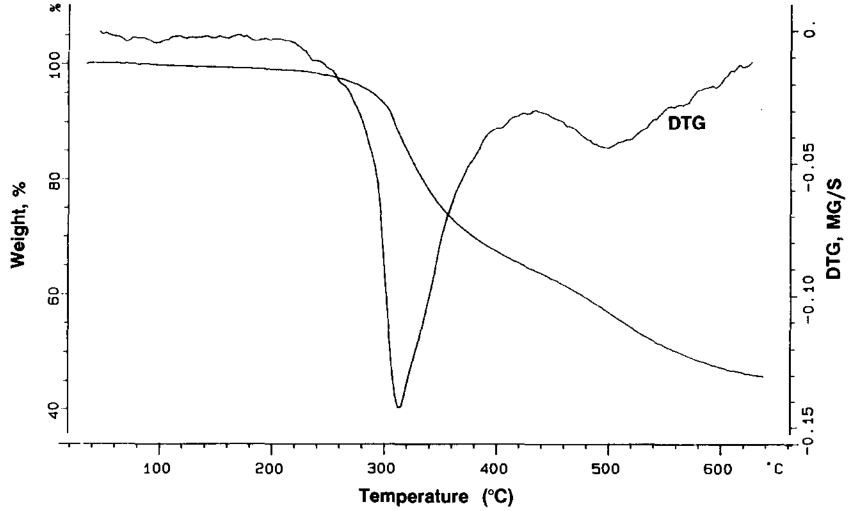

Fig. 2. TG thermogram of polyaniline doped with toluene sulfonic acid in nitrogen atmosphere.

more, the degradation mechanisms are different. In nitrogen atmosphere, the polymer has lost only 45% of its original weight at 650 °C. At this temperature in air, the polymer has completely decomposed. The activation energies of thermal degradation of neutral polyaniline in air and nitrogen are 76 and 311 kJmol^{-1} respectively. The low activation energy in air indicates the relative ease with which the decomposition occurs.

Figures 2 and 3 show the thermograms of polyaniline tosylate in nitrogen and air atmospheres, respectively. As indicated earlier [6], polyaniline tosy-

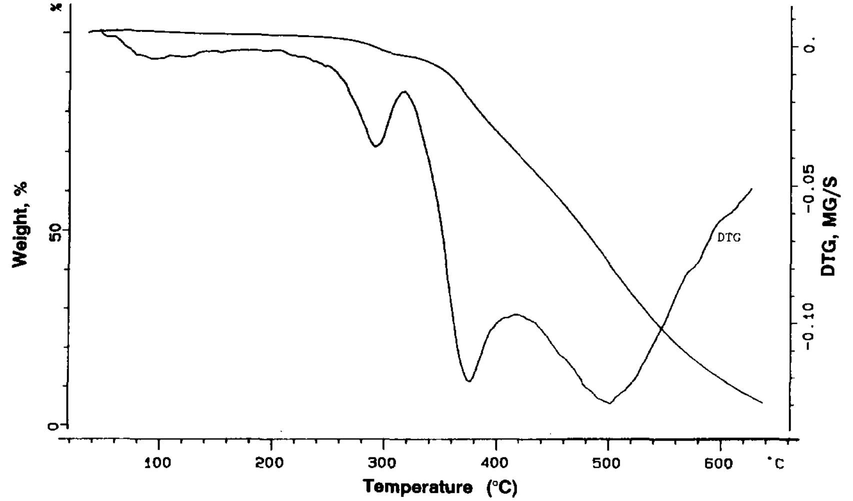

Fig. 3. TG thermogram of polyaniline doped with toluene sulfonic acid in air atmosphere.

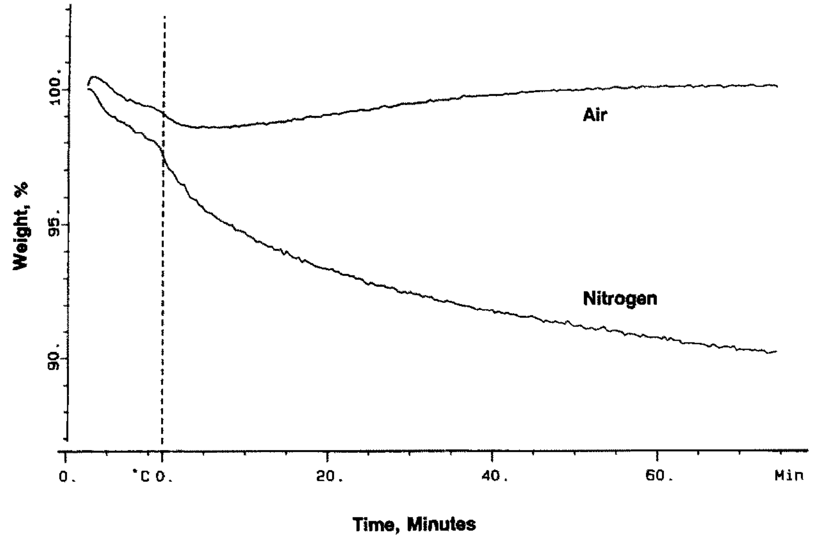

Fig. 4. Isothermal TG curves for polyaniline doped with toluene sulfonic acid in air and nitrogen atmospheres at 250 ° C.

late also shows a two-step decomposition in nitrogen. The polymer has lost only 55% of its original weight at 650 ° C. In contrast, the polymer has completely decomposed in air. This is quite understandable as the neutral polymer behaves in the same way. Of particular interest is the weight loss in the 250–420 ° C region and the mechanism of the decomposition in air. It shows a three-step decomposition. The initial decomposition seems to follow the same pattern as in nitrogen. However, other side reactions are evident from the second decomposition step at around 370 ° C, which is not observed in nitrogen atmosphere. The lower loss in the first step and the apparent higher thermal stability suggest a competing reaction between loss of dopant and weight gain due to oxidation (the net result is a lower loss in weight). At still higher temperatures, oxidative degradation is more predominant and results in decomposition of the dopant and complete destruction of the backbone. The DTG thermogram shows the process clearly. Figure 4 illustrates the isothermal TG curves for polyaniline tosylate in nitrogen and air at 250 ° C. The thermogram in nitrogen shows a steady weight loss, leveling off at 10%. In contrast, the thermogram in air shows an initial weight loss similar to the curve in nitrogen, but it soon levels off with a slight gain in weight (100.2%). This corroborates the lower loss in weight (1st step) observed in the dynamic thermogravimetric analysis.

In order to understand the nature of the decomposition and the decomposition products, polyaniline tosylate was heated to 415 and 650 ° C in nitrogen atmosphere in the TGA furnace, corresponding approximately to the first- and second-step TG losses. Table 1 shows the elemental composition of these samples compared to unheated sample and neutral polyaniline.

TABLE 1

Elemental analysis of neutral polyaniline and polyaniline tosylate—unaged, and heated to 415 and 650 °C in nitrogen atmosphere

Temperature	Atmosphere	%C	%H	%N	%S
Neutral	–	79.30	4.90	15.38	–
Unaged	–	59.84	5.01	7.99	8.32
415 °C	Nitrogen	71.14	4.16	11.29	3.36
650 °C	Nitrogen	80.28	2.86	11.71	0.05

The significant drop in the sulfur content of the sample heated to 415 °C confirms the loss of dopant in the first step of the decomposition. The partial loss of sulfur is attributed to decomposition of the toluene sulfonic acid itself, which leaves behind some sulfur-containing residue (at 415 °C), and to other side reactions. The sample heated to 650 °C contains no sulfur. It is rather surprising to note the elemental composition of the sample heated to 650 °C; it suggests the presence of some organic structure.

Figure 5 shows the infrared spectra of neutral polyaniline and polyaniline doped with *p*-toluene sulfonic acid from 2000 to 500 cm^{-1}. The assignment

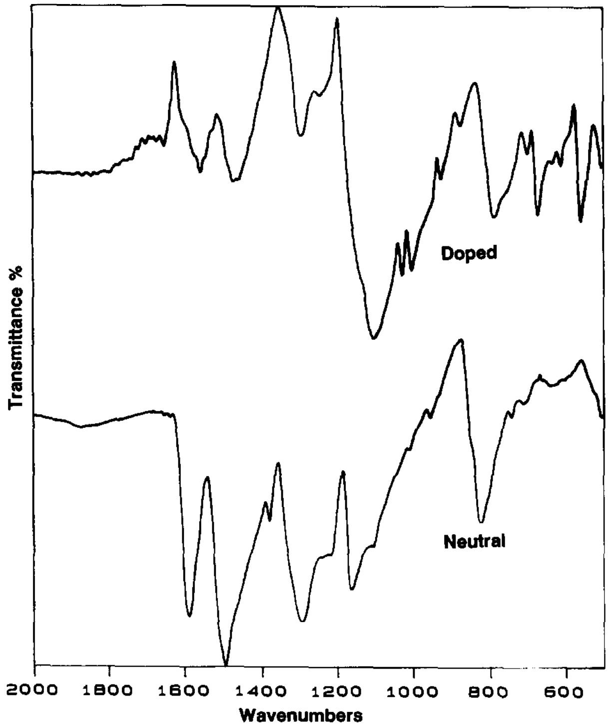

Fig. 5. Infrared spectra of neutral polyaniline and polyaniline doped with toluene sulfonic acid.

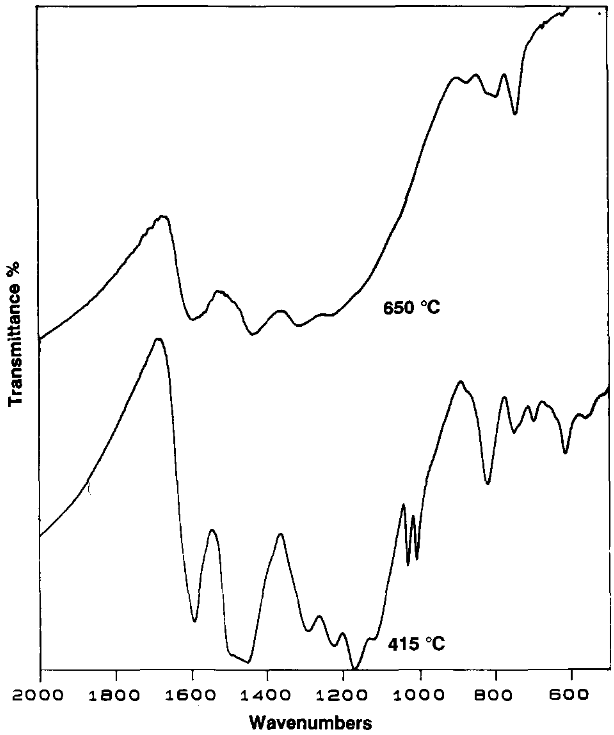

Fig. 6. Infrared spectra of polyaniline doped with toluene sulfonic acid heated to 415 and 650 ° C in flowing nitrogen atmosphere.

of the various bands can be found elsewhere [9]. Of particular interest is the peak at 1110 cm^{-1} in the protonated sample.

Figure 6 shows the infrared spectra of polyaniline tosylate heated to 415 and 650 ° C. The peak at 1110 cm^{-1} is almost unobservable in the spectrum of the sample heated to 415 ° C. Moreover, the spectra indicates structural similarity to neutral polyaniline. This supports the evidence from thermogravimetric data showing that significant amounts of dopant are lost at 415 ° C. The spectrum of the sample heated to 650 ° C indicates that there is significant destruction of the backbone, but shows some residual aromatic character as indicated by the absorbances in the 1600–1200 cm^{-1} range.

Figure 7 shows the infrared spectra of polyaniline tosylate heat-aged in air and nitrogen at 250 ° C for 30 minutes. The spectrum of the sample heated in nitrogen is similar to that of the doped material. In contrast, the spectrum of the sample heat-aged in air shows distinct spectral changes with some similarity to the neutral polymer.

The sample heat-aged in nitrogen at 250 ° C for 30 minutes showed a conductivity of 0.4 S cm^{-1} compared to 6×10^{-5} S cm^{-1} for the sample heat-aged in air at the same temperature. The conductivity of the sample heat-aged in air was not restored on redoping with *p*-toluene sulfonic acid.

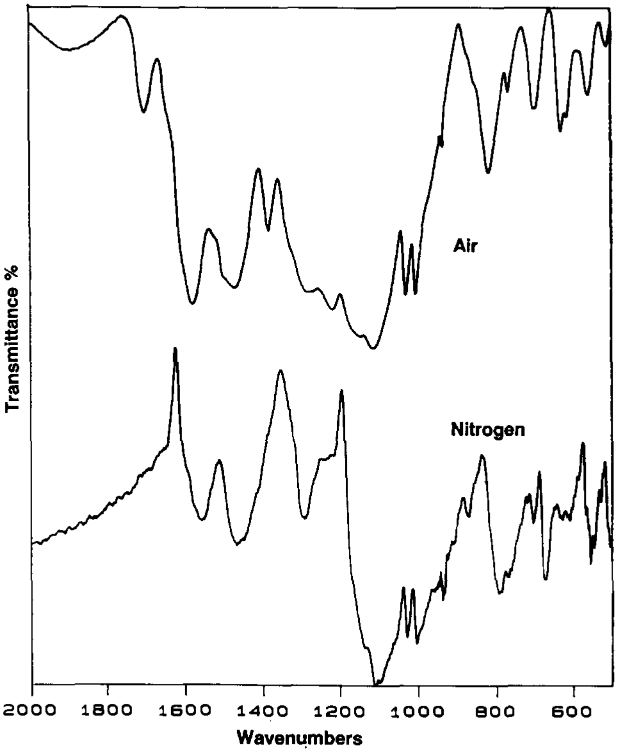

Fig. 7. Infrared spectra of polyaniline doped with toluene sulfoncic acid heat-aged in air and nitrogen at 250 ° C for 30 min.

An extensive report on the effect of heat ageing on the conductivity of polyaniline doped with *p*-toluene sulfonic acid has been reported elsewhere [10].

CONCLUSION

The thermal-conductivity stability of polyaniline doped with *p*-toluene sulfonic acid is a function of time and temperature exposure, and atmosphere. Its conductivity is seriously affected in air atmosphere. The TG and infrared results, together with the conductivity results [10], indicate that oxidation and possible structural rearrangement leading to loss in conjugation may be the primary cause for loss in conductivity on heat-ageing in air. Because its use as a conducting polymer is determined by its degradation in conductivity rather than its weight-loss behaviour, an inert atmosphere should provide better stability at higher processing temperatures.

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