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Thermochimica Acta 352–353 (2000) 177–180

thermochimica
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Thermogravimetry and evolved gas analysis of polyimide[☆]

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Received 2 June 1999; received in revised form 7 August 1999; accepted 23 August 1999

Abstract

TG–DTA–EGA simultaneous measurements were made for polyimide isothermally at 498 and 541°C in simulated air, in order to confirm the previously found facts by TG–DTA that below 520°C the mass loss is a single step process but above 550°C it proceeds by a two step process. All detected volatile products are carbon dioxide, carbon monoxide, water, nitrogen and nitrogen monoxide at the both temperatures, but the volatilization behavior at 541°C is different from that at 498°C, as was expected from the previous results. Thus the previous postulate was confirmed. However, because volatilization of water at 498°C differs from that of nitrogen monoxide, the process in the lower temperature range really proceeds by a two step process. On the other hand, at 541°C the volatilization rates of all products change similarly to each other and also to the mass loss curve and the DTA curve. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: Thermogravimetry; Evolved gas analysis; Mass spectrometry; Polyimide; Thermo-oxidative decomposition

1. Introduction

Previously one of the present authors applied controlled rate thermogravimetry (CRTG) and conventional linear heating TG (LHTG) at a constant rate to thermo-oxidative decomposition of polyimide in air [1]. By applying a kinetic method (Friedman–Ozawa method) to the data of the both types of TG, it was concluded that the mass loss of polyimide proceeds as a single step process below 520°C, but it proceeds by a two step process above 550°C. These results were made sure by isothermal TG (iso-TG) runs below 520°C and above 550°C.

Although a number of papers were published on thermal and thermo-oxidative decompositions of many varieties of polyimide, results relating to the above facts have not yet been obtained [2–13]. To confirm the above finding and to investigate the processes in more detail, simultaneous measurements of TG–DTA and evolved gas analysis (EGA) with a mass spectrometer (MS) was applied to thermo-oxidative decomposition of polyimide in simulated air. These results are reported in this paper.

2. Experimental

A TG–DTA (Rigaku TG–DTA 8120D) was coupled to a quadrupole mass spectrometer (Q-MS, Rigaku ThermoMass) through a gas interface system with a 110 cm long fussed silica capillary of 0.07 mm inner

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[☆] A paper presented at the Second International and the Fourth Japan–China Joint Symposium on Calorimetry and Thermal Analysis, 1–3 June 1999, Tsukuba, Japan (CATS 99).

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PII: S0040-6031(99)00464-5

diameter. The capillary was heated at 250°C to prevent condensation. The acceleration voltage of the ionization was fixed at potential of 70 eV. Here, in the MS ion source, a thoria-coated iridium filament was employed instead of tungsten or rhenium one in order to prevent the filament from oxidation-deterioration under oxidative atmosphere.

The atmosphere for TG–DTA–EGA measurements was simulated air, i.e., mixture of helium and oxygen (20%). The temperature was raised at 20°C/min and kept at a constant temperature (498 or 541°C). The sample is polyimide film kindly supplied by Toray du Pont (Kapton 500H) and it was used as received.

3. Results and discussion

An iso-TG curve and a total ion chromatograph (TIC) at 541°C obtained by TG–DTA–EGA are shown in Fig. 1 together with a DTA curve. As reported in the previous paper [1], a two step mass loss is observed in the TG curve and two sharp exothermic peaks are seen in the DTA curve. In the TIC showing sum of ion currents of all detected species, two peaks are exactly corresponding to the two DTA peaks. The mass spectrum at the first peak is reproduced in Fig. 2. All the products we can find are carbon dioxide (*m*/*z* 44, 28 and 12), carbon monoxide (*m*/*z* 28 and 12), nitrogen (*m*/*z* 28), water (*m*/*z* 18) and nitrogen monoxide (*m*/*z* 30). By using the NIST database for MS spectra [14], ion of *m*/*z* 28 is ascribed to carbon dioxide, carbon monoxide and nitrogen, and existence of nitrogen is ascertained. Since no organic substance is detected in this experiment, the products seem to be combustion products of volatilized organic compounds due to high temperature and oxidative atmosphere. A quite similar mass spectrum was observed at the second peak (Fig. 2). Changes of their ion currents are shown in Fig. 3. Relative formation rates of carbon dioxide, nitrogen and water are the same with each other and similar to the TIC and the DTA curve, but that of nitrogen monoxide is somewhat different from the others. As seen in the figure, tailing of the curve for nitrogen monoxide is somewhat longer than the others.

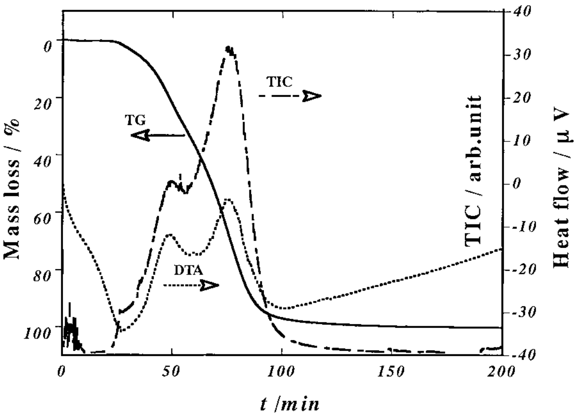

Fig. 1. TG–DTA–EGA (TIC) curves of polyimide in simulated air isothermally observed at 541°C.

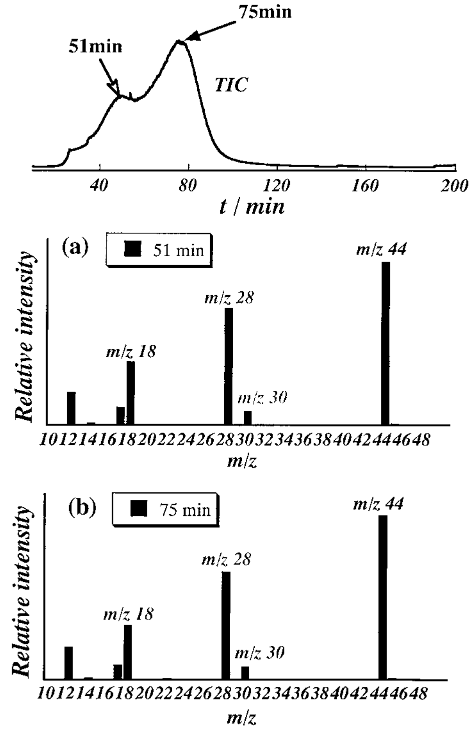

Fig. 2. Mass spectra obtained at two peaks in TIC curve during isothermal decomposition at 541°C. The peaks are indicated with arrows in the upper part of the TIC curve shown above.

The TG–DTA–EGA results at 498°C are reproduced in Fig. 4 and the TG–DTA curves are quite the same as reported in the previous paper [1]. The mass loss seems to be a single step process. A TIC curve at 498°C shown in Fig. 4 looks like a broad peak. In contrast to the results at 541°C (Fig. 1), the TIC curve at 498°C does not correspond to the DTA curve. The mass spectra at the two points of TIC (indicated with arrows) are seen in Fig. 5. The spectrum at the

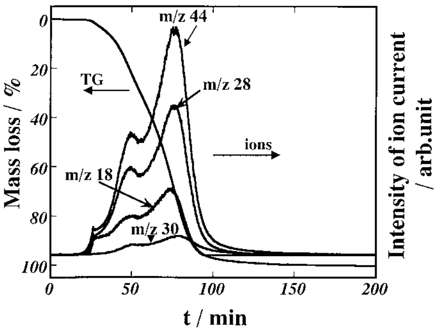

Fig. 3. Change of ion currents during isothermal decomposition at 541°C.

first point (120 min) is quite the same as in Fig. 2. However, the mass spectrum at the second point (190 min) is different from the other three in the fact that water is not detected. The volatilized products at 498°C are the same as those at 541°C, and organic products are not detected also at this temperature. The changes of production rates of these species are shown in Fig. 6. We can learn that water production occurs in the beginning of the mass loss and water is not detected in the higher conversion, while production of nitrogen monoxide shifts to the higher conversion.

Thus the mass loss in the lower temperature range looks a single step process, but it is really a two step process. In the first step water is formed by extracting hydrogen in the sample and in the second step residual compounds, rich of nitrogen, decomposes to form nitrogen monoxide (m/z 30) without forming water. Because the activation energy estimated is almost constant during the process below 520°C and the

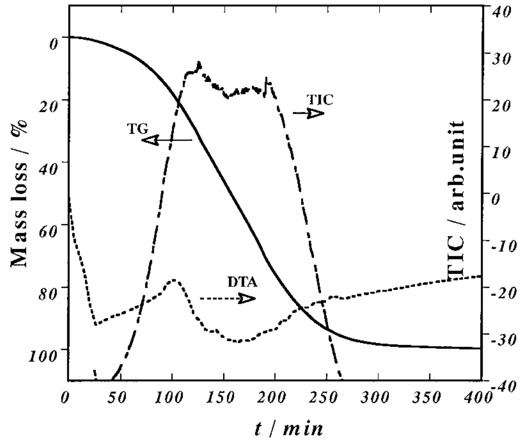

Fig. 4. TG–DTA–EGA (TIC) curves of polyimide in simulated air isothermally observed at 498°C.

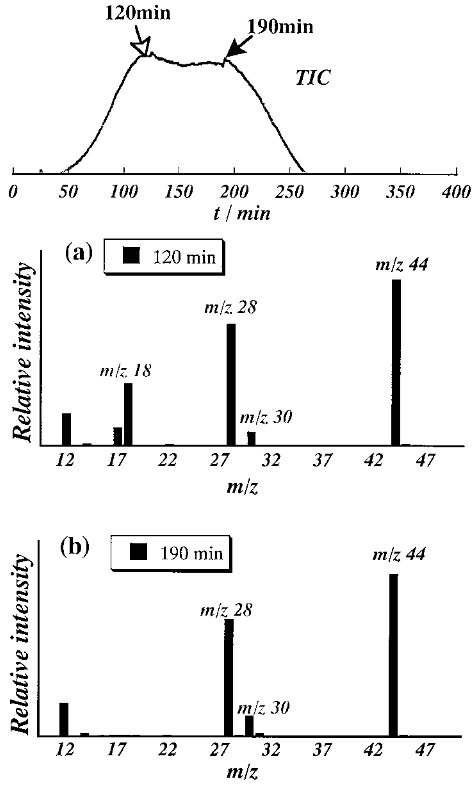

Fig. 5. Mass spectra obtained at two points in TIC curve during isothermal decomposition at 498°C. The points are indicated with arrows in the upper part of the TIC curve shown above.

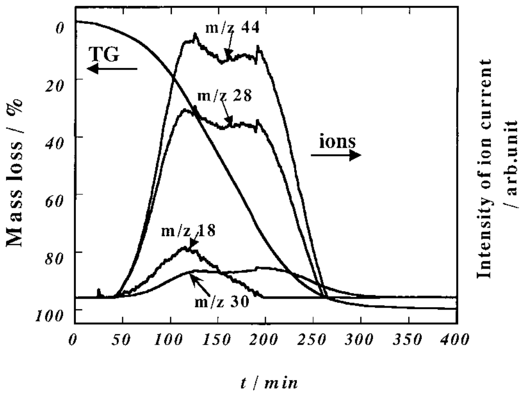

Fig. 6. Change of ion currents during isothermal decomposition at 498°C.

experimental master curve can be drawn as described in the previous paper [1], the activation energies of these two steps are almost equal to each other. The relatively large standard deviation of the reduced rate in the middle of the mass loss, described in the previous paper [1], can be attributed to this fact of the real two step process.

The postulate in the previous paper [1] that the thermal decomposition process below 520°C is different from that above 550°C is confirmed by the TG–DTA–EGA (MS) results described in this paper. It is also found that the volatilized compounds in these processes are combusted into carbon dioxide, carbon monoxide, nitrogen, water and nitrogen monoxide due to the high temperature and oxidative atmosphere.

Similar research on thermal and thermo-oxidative decomposition by mass spectrometry and gas chromatography were done for various types of polyimides and their model compounds, and their results were reported in many papers [2–13]. Irrespective of the varieties of polyimides, reported main volatilized products are the same as in this paper, i.e., carbon dioxide, carbon monoxide and water. The same compounds were also main products even in inert atmosphere and in vacuum [5,7], and it is the case even for model compounds [8]. However, organic substances were also detected [4,7]. For the same type of polyimide, one of the detected organic products is pyromellitimide [4]. These observations were made in a relatively low temperature range than in this paper, and this seems to be the cause for this difference.

Amounts of volatilized carbon dioxide, carbon monoxide and water accumulated for a certain interval were measured for the same type of polyimide in a temperature range from 450 to 500°C [4], but the volatilization behavior of water is not so different from the other two as in our research. The cause for this discrepancy seems to be intermittent sampling of the volatilized gases in this experiment [4]. Advantage of continuous analysis and measurement of volatilized gasses is shown in this fact.

4. Concluding remarks

1. It is confirmed that the low temperature mass loss below 520°C is different from those above 540°C, because the products formations are different from each other (see Fig. 2 vs. Fig. 5 and Fig. 3 vs. Fig. 6, especially for water and nitrogen monoxide).
2. The low temperature mass loss is a two step process, because the products in the beginning are different from those in the latter (see Figs. 5 and 6), though the mass loss was observed to be a single step.
3. The volatilized compounds in these processes seem to be combusted into simple gaseous compounds, such as carbon dioxide, carbon monoxide, water, nitrogen and nitrogen monoxide.

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