TGA/APCI/MS/MS, A New Technique for the Study of Pyrolysis and Combustion Products

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ABSTRACT

The Fire Research Section, Division of Building Research, National Research Council of Canada has acquired a SCIEX TAGA 6000 APCI (atmospheric pressure chemical ionization)/MS/MS, an analytical instrument unique for its high sensitivity and high speed in analysis. The instrument is capable of monitoring simultaneously many types of gases generated in pyrolysis/combustion. Coupled with a Dupont 951 thermogravimetric analyser (TGA), it has been used for studying the pyrolysis products of polyacrylonitrile (PAN) at different stages of the pyrolysis process.

A 1 mg specimen was pyrolyzed in the TGA in a stream of nitrogen or air and the products were introduced to the APCI/MS/MS through a short glass capillary. The molecules of the product were ionized under atmospheric pressure, and analyzed in real time with three serial quadrupole mass filters. The main products were HCN, acetic acid, and a series of nitriles. The generation of each product is discussed in the light of the thermogravimetric analysis.

KEYWORDS

APCI/MS/MS, TGA/MS, polyacrylonitrile, combustion products, nitriles, HCN.

INTRODUCTION

A combination of thermogravimetric analysis (TGA) and mass spectrometry (MS) is a powerful tool for studying thermal degradation of materials. With a TGA, a specimen of the material can be thermally degraded at accurately controlled temperatures in a desired atmosphere. The effluent degradation products from the TGA can be analyzed by a highly sensitive MS. It is not surprising that many applications of TGA/MS, using various types of instrumentation, have been reported in the past 15 years, as shown in Table 1 (1-15), although the table is not intended to present a complete list.

The conventional MS, used in most of the earlier studies, had some limitations. The electron impact (EI) ionization extensively fragmented the molecules of the degradation products at the ion source, making the mass spectra complicated and restricting the use of the technique to the analysis of relatively simple degradation products. Chemical ionization (CI) has simplified the spectra, but the information on molecular weights supplied with

TABLE 1 TGA/MS Studies in Literature

Author	Year	TGA	MS	EI/CI	mL/min	°C/min	Material
Zitomer	1968	Dupont 950	Bendix T-O-F	EI	100	15	Polyethylsulfide
Chang	1971	Dupont 900/PE 881 GC	Dupont CEC 21-110B		60-80	10-15	Ethyl vinylacetate
Gibson	1972	Mettler	Finnigan 1015	EI		2,4,6	Geochemical samples
Mol	1974	Mettler I	UTI 100C	EI	Vacuum	2,4,6	PVC, ABS, PU, Polyester
Tsur	1974	PE TGS1	Finnigan 1015	EI	A, Air 18	16	Polybenzimidazole
Kleinberg	1974	Cahn RH	Dupont 21-491 DF	EI	Oxid.	5-25	PVC, PMM, PU
Baumgartner	1977	Mettler TAC	Finnigan 3200	EI-CI	60-80	4	Ca oxalate
Muller	1977	Mettler	Balzers Quad MS	EI		10	Ca oxalate
Morisaki	1978	IR ray thermobalance	Quad MS Analyzer	EI	He, Air 150		PTFE
Shimizu	1979	Dir. insert. probe	Dupont 21-110B DF	CI			PVC, PMM
Chiu	1980	Dupont 990	Dupont 21-104	EI	He 60	5-10	Ca acet. Polyacetal
Yuen	1982	Mettler TA1	HP 5992	EI	He, O_2/He	15	Ca oxalate, SB etc.
Chan	1982	Temp. prog. fraction.	Hitachi RMS-4	EI	50		PS, peanut oil
Dyszel	1983	PE TGS 2	SCIEX TAGA 3000	APCI	N_2 80		Guar gums
Whiting	1984	Dupont 951/HP 5710 GC	LKB 9000	EI	He 100	10	Coal
NRC Fire	1984	Dupont 951	SCIEX TAGA 6000	APCI	N_2, Air 110	2-10	PAN

the use of CI is often not sufficient to identify the degradation products. In studying oxidative degradation, which is of particular interest to fire researchers, there is also a technical difficulty: an oxidative atmosphere causes drastic reduction in the life of the ion source.

In the present study an APCI/MS/MS (tandem) was used for the analysis of effluent degradation products of polyacrylonitrile (PAN) from the TGA. This MS is compatible with TGA, since the products can be analyzed in air under atmospheric pressure.

EXPERIMENTAL

Materials

An Orlon cloth that contained more than 85% polyacrylonitrile was used without further treatment. For comparison a 100% pure solid amorphous polyacrylonitrile (Cellomer Assoc. Inc. Cat# 134c) was also used.

Instrumentation

A Dupont 951 TGA and the SCIEX TAGA 6000 APCI/MS/MS were the two main instruments used in this study. The SCIEX TAGA 6000 APCI/MS/MS has been described elsewhere (16). Unlike other MS instruments, it employs a large volume of sample gas continuously introduced into the instrument (typically 2 L/min). Components of the gas are ionized by a corona discharge under atmospheric pressure using oxygen or water in the sample gas as the chemical reagent. A nitrogen flow forms a gaseous membrane between APCI source and the high vacuum analyzer section to prevent un-ionized molecules from going into the analyzer. The ionized molecules (parent ions) penetrate the membrane and are separated according to their mass/charge ratio (M/Z) at the first quadrupole mass filter. Argon gas flows perpendicular to the path of parent ions at the second mass filter. Parent ions colliding against argon atoms fragment with a pattern characteristic of the ion. The pattern is analyzed by the third mass filter.

The MS/MS and the TGA were coupled with a short glass capillary (0.5 mm dia., 20 mm long). The flow of effluent from the TGA to the MS/MS through the capillary was measured from the pressure difference across the capillary and controlled by a 'dump' valve fitted with a micrometer. The whole interface assembly was heated to prevent the condensation of degradation products. To the effluent flow, a make-up flow of 2 L/min of zero air (purified air with practically no organic gases) was added. The schematic diagram of the interface is shown in Fig. 1. A Hewlett Packard 5996 GC/MS/Data system with a CDS 100 pyrolysis unit was used separately to analyze the pyrolysis products and the results were compared with those from the APCI/MS/MS.

RESULTS AND DISCUSSION

The pyrolysis products of PAN analyzed by the pyrolysis GC/MS are shown in Fig. 2. The pyrolysis occurred in 3.6 atms of helium. The main products were HCN, a series of nitriles and acetic acid. The last was not generated when the experiment was repeated with 100% pure solid polyacrylonitrile. In Fig. 3, the results of TGA of PAN in atmospheric nitrogen are shown; they may be compared with the total ion vs time from MS/MS analysis of the effluent (Fig. 4). The total current varied in a manner similar to the first derivative of TGA curve. The total ion is the sum of each of the parent ions; the latter are shown in Fig. 5.
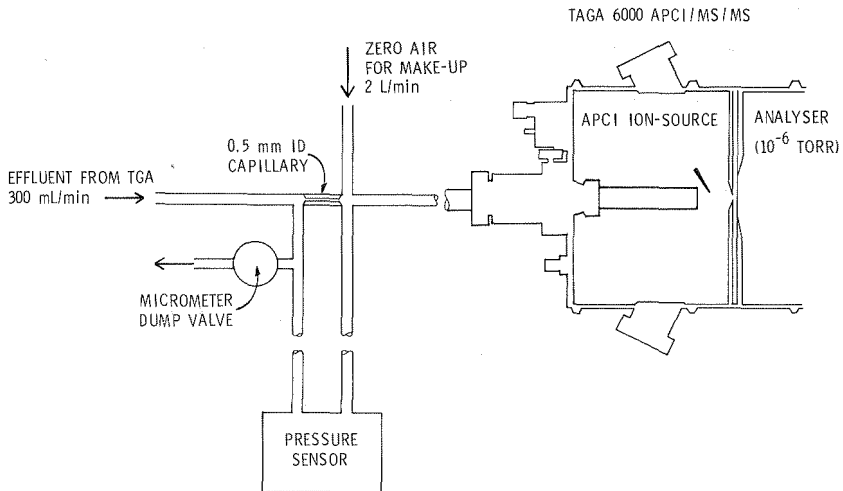
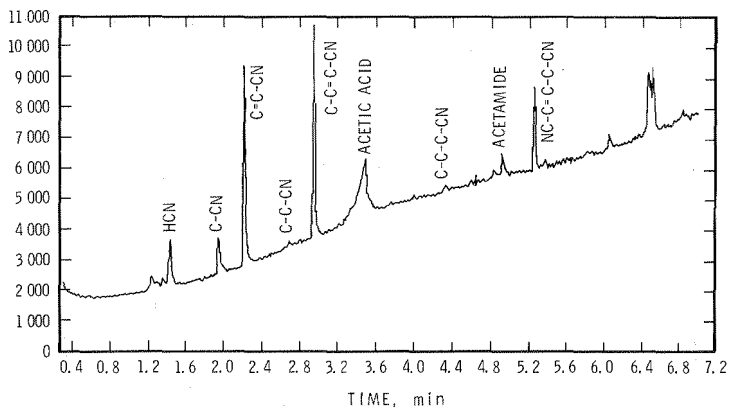413

FIGURE 1. TGA/MS/MS interface.

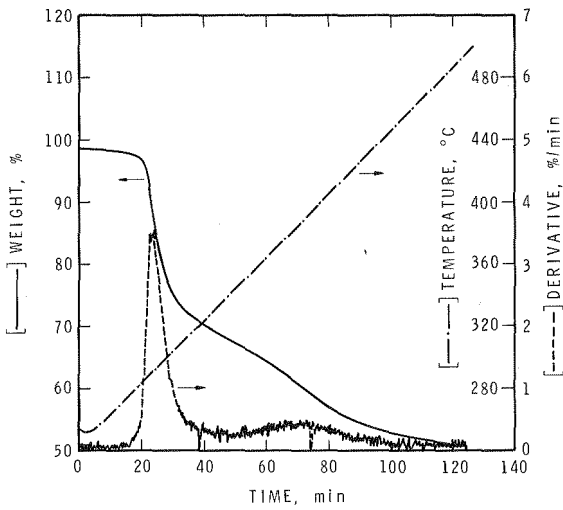FIGURE 2. Pyrolysis products of PAN, pyrolysis/GC/MS.

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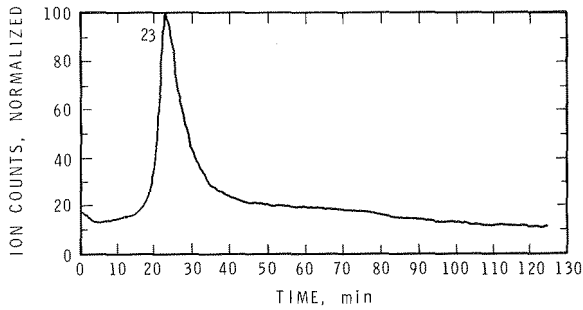FIGURE 3. Thermogravimetric analysis of PAN in nitrogen.

FIGURE 4. Pyrolysis of PAN in nitrogen, total ion in MS/MS analysis, positive mode.
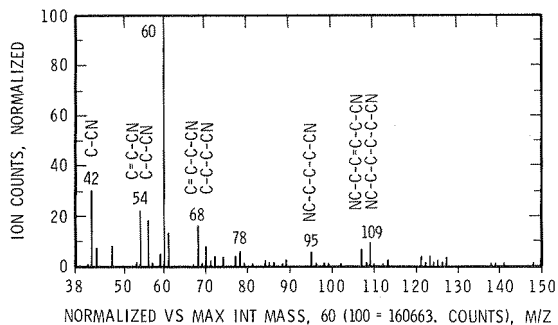
FIGURE 5. Pyrolysis of PAN in nitrogen, MS/MS analysis, parent scan, positive mode.
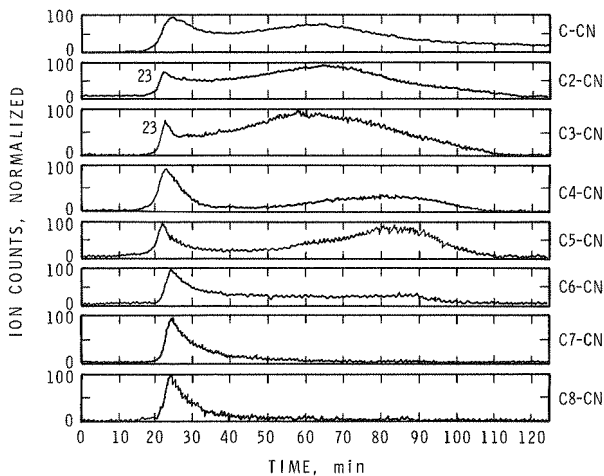

FIGURE 6. Pyrolysis of PAN in nitrogen, MS/MS analysis, single ion monitoring.

From both the GC/MS and the MS/MS experiments, it was clear that a series of nitriles were formed. M/Z = 60 was acetamide, which was very easily ionized and was dominating in the parent scan, but its actual concentration was smaller than that of the nitriles. In Fig. 6, generation of each nitrile

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is shown against time. Some nitriles were generated in two steps; the first step occurs at the same temperature (290°C) for all the nitriles; the second step at increasingly higher temperatures for higher nitriles. This phenomenon is not simply explained by the difference in their boiling points. For example, butane nitrile (shown as C3-CN in Fig. 6) and pentane nitrile (C4-CN) have boiling points of 117.6 and 140.7°C, respectively, while the recorded temperatures in the TGA at the peak of generation were 372 and 410°C, respectively. The elucidation of the mechanism is left for future studies.

The MS/MS can detect either positive ions or negative ions. In the present study, the positive ion mode was used for nitriles and the negative ion mode for acids. Fig. 7 shows MS/MS analysis in the negative mode. A parent scan at the peak is shown in Fig. 8; major components were HCN and acetic acid.
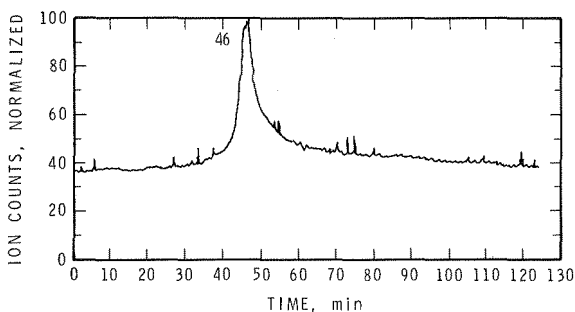

FIGURE 7. Pyrolysis of PAN in nitrogen, total ion in MS/MS analysis, negative mode.
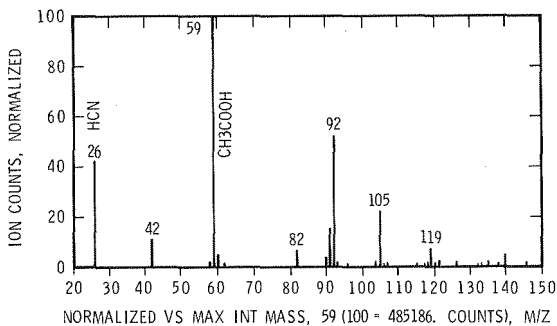

FIGURE 8. Pyrolysis of PAN in nitrogen, MS/MS analysis, parent scan, negative mode.

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The TGA of PAN in air is shown in Fig. 9. PAN degraded in two steps, both in air and in nitrogen; the first step is at 290°C and the second at 400-500°C. In air, the weight loss in the first step was smaller and the second step was larger than the corresponding steps in nitrogen. Generation of HCN, as determined by the MS/MS, is shown in Fig. 10. The curve was similar to the first derivative of the TGA curve. The HCN was also generated in two steps.
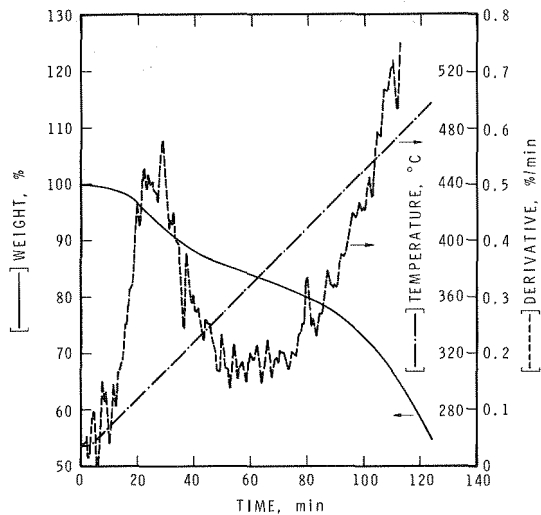
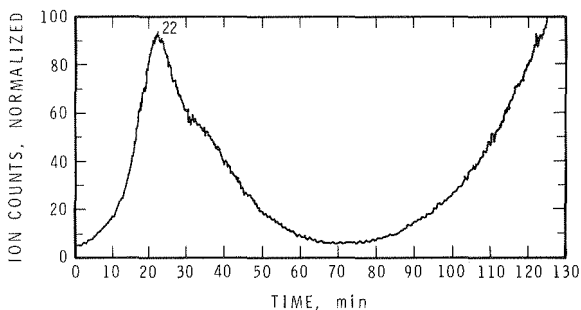FIGURE 9. Thermogravimetric analysis of PAN in air.

FIGURE 10. Pyrolysis of PAN in air, HCN generation, MS/MS analysis.

The first derivative of the TGA curve determined for the solid specimen, and the total ion current determined from the pyrolysis products in the gas phase, were nearly identical in shape in nitrogen and in air. Although this is expected, since the weight loss is a result of gasification (generation of gaseous products) of the solid specimen, the finding underlines the validity of the technique. The two-step generation of HCN may be explained by the unzipping of molecules in the first step and the decomposition of N-containing char in the second step. HCN is the major toxic component in the thermal decomposition products of PAN (17) and other N-containing organic materials (18).

CONCLUSION

The pyrolysis of PAN in nitrogen and in air was studied by TGA/APCI/MS/MS. HCN, a series of nitriles, and acetic acid were identified. The PAN degraded in two steps. Nitriles and HCN were generated in both steps in nitrogen and in air.

The TGA/APCI/MS/MS was found to be an effective tool for studying the pyrolysis of polymers. Pyrolysis products can be identified and their generation at different stages of pyrolysis can be closely observed. Further studies are planned.

ACKNOWLEDGEMENT

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