

Simultaneous measurement system of thermogravimetry-differential thermal analysis and photoionization mass spectroscopy equipped with a skimmer-type interface

—TG-DTA-PIMS—

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1. Introduction

Although thermal analysis has wide range of applications, to understand thermophysical and chemical changes at a macro-molecular level, it is necessary to perform complex measurements, such as hyphenated methodology combined with other spectroscopic methods to obtain specific micro-molecular information on reaction products^{(1)–(4)}. An example of a complex measurement is the thermogravimetry-differential thermal analysis-mass spectrometry (TG-DTA-MS), which is a simultaneous measurement technique composed of thermogravimetry-differential thermal analysis (TG-DTA) combined with mass spectrometry (MS) through an interface system. This process has garnered attention as a major thermoanalytical technique^{(5)–(7)}. It is suitable for the qualitative analysis of the different gases evolved in response to heating a sample in the TG-DTA process.

This article aims to propose a novel thermoanalytical method that integrates a “skimmer-type interface” and a “photoionization method” in order to overcome the serious disadvantages of the conventional TG-DTA-MS. A simultaneous thermogravimetry-differential thermal analysis and photoionization mass spectrometry (TG-DTA-PIMS) system equipped with a unique skimmer-type interface has been thus successfully developed.

The principles and the instrumental composition of the TG-DTA-PIMS are described in detail and compared with those of the conventional TG-DTA-MS. To demonstrate the effectiveness of the technique, the results of its application to the evolved gas analysis of typical polymeric materials are presented.

2. Principle

2.1. From Capillary-type interface to Skimmer-type interface

A photograph and the structural diagram of the skimmer-type TG-DTA-PIMS are illustrated in Fig. 1. An interface is necessary for gaseous transport to accurately inject the gaseous compounds evolved from the TG-DTA sample chamber into the mass spectrometer. Various devices are necessary in this

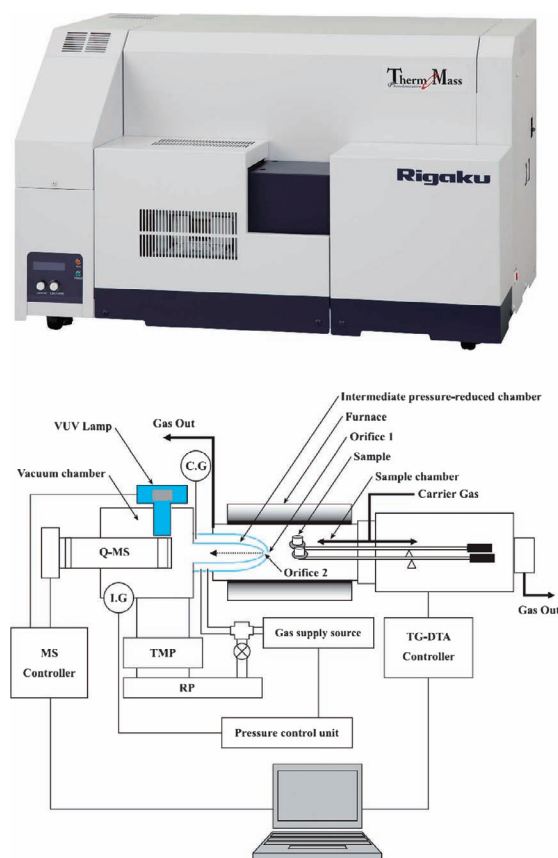


Fig. 1. Photograph and schematic diagram of TG-DTA-EI/PIMS system using a skimmer type interface. Ion gauge, I.G; Crystal gauge, C.G; Turbo molecular pump, TMP; Rotary pump, RP.

interface to prevent condensation, side reactions, and delay in evolution of gases. This complex composition of the interface results in limitations of the analysis, which governs the sensitivity and analytical accuracy.

In general mass spectrometry, the interface is a structure that creates a difference in pressure between the TG-DTA sample chamber at atmospheric pressure and the MS vacuum chamber in order to operate in a vacuum. The conventional TG-DTA-MS employs a capillary-type interface. The capillary-type interface is a relatively long narrow tube connecting both modules, and it adopts the principle that the injection tube is

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maintained at a constant temperature. Usually, the inner diameter and path length of the interface are selected on the basis of the retention value of the vacuum pressure in the MS chamber for the mass spectrometer to perform at a pressure under 10^{-3} Pa. In the capillary-type interface system, transformation of the gas in the inner injection tube becomes uncertain if the interface path length is too long. Furthermore, shortening the capillary decreases the tube diameter resulting in easy occurrence of gas selectivity. Therefore, these factors must be optimized. Considering ease of use and maintenance of a general-purpose instrument, the interface is often constructed with a length of 1–2 m. The holding temperature of the interface is determined by considering re-condensation and transformation of the injected gas as well as the user's safety; therefore, the upper limit is usually set below 300°C. However, if the boiling point of the gasification products exceeds this interface temperature, the gases re-condense within the interface and are trapped internally. On the other hand, increasing the interface temperature to more than 300°C will lead to problems such as gas transformation due to secondary reactions. This may be due to surface activation caused by the degradation of the inner wall of the interface tube and the acceleration of secondary reactions between the activated pyrolysates. In case of unknown samples where the prediction of the boiling points of the gases is impossible, the evolved gases may condense and/or be transformed within the interface, which often interferes with the measurement results.

Consequently, because of the limitations of the capillary-type interface, the conventional TG-DTA-MS was mainly used initially for inorganic materials and ceramics. However, in recent years, TG-DTA-MS analysis has been applied to organic compounds such as polymer resins, highly functional polymers, and pharmaceuticals. In particular, polymer characterization is often performed by a traditional method called pyrolysis gas chromatography⁽⁸⁾, which may be influenced by the restrictions of the capillary-type interface. For this reason, the skimmer-type interface was introduced. This interface solves the potential problems and limitations of the capillary-type interface as described below in detail.

As shown in Fig. 2, the skimmer-type interface consists of two concentric ceramic tubes with orifices in which the orifice diameter of the outer tube is smaller than that of the inner tube. The interface connects the two devices, one at atmospheric pressure and the other at vacuum. The inner tube is directly connected to the high vacuum MS chamber, and the space between the two tubes exists as a differential vacuum structure evacuated by the vacuum pump. As shown in Fig. 1, the sample position and two orifices of the skimmer-type interface as well as the MS ion source are arranged in a straight line. Through heating, the evolved gases from the sample together with the carrier gas are transmitted toward the skimmer-type interface and efficiently injected into the MS chamber by the effect of the jet

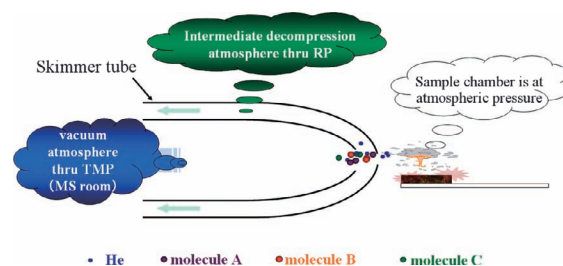


Fig. 2. Operation principle of skimmer-type interface.

separator principle. In this way, high-precision gas analysis becomes fundamentally possible because the interface length connecting the sample chamber under atmospheric gas flow and the MS high vacuum chamber is minimized and, therefore, negligible.

Because the differential vacuum source of the skimmer-type interface is located in the furnace in close proximity to the sample, the temperature of the gas injection chamber and the sample temperature are thermally programmed under the same environment. Consequently, problems such as re-condensation and transformation of evolved gases or gas leaks in the interface path can be avoided.

As a result, because the skimmer-type interface and the sample can be heated to the maximum operating temperature of the module, components with boiling points higher than the interface maintenance temperature can be measured; lack of this feature inevitably restricts the high-temperature utility of the capillary-type interface. These are the advantages offered by the skimmer-type interface compared with the conventional capillary-type interface^{(9)–(13)}.

With the abovementioned advantages, use of the skimmer-type interface for the analysis of evolved gases greatly enhances instrument adaptability to broader classes of organic compounds, including polymer resins. However, because many organic compound gases will be simultaneously measured, the gas detection mass spectra may be more complicated, and therefore, data interpretation becomes more difficult.

2.2. From Electro impact ionization method to Photoionization (soft ionization) method

Traditionally, the gaseous species introduced into the MS by evolved gas analysis-mass spectrometry (EGA-MS) have been elucidated by the electron ionization (EI) method of 70 eV. Although a gaseous molecule is ionized by colliding with an accelerated electron by the EI method, a part of the generated molecular ion further decomposes, and consequently, the molecular ion is observed simultaneously with the fragment ions. When multiple gases are ionized simultaneously, and the resulting fragment ions mutually overlap, although the fragment ions give significant information about the structure of the molecule, the apparent mass spectrum may be too complicated.

As mentioned above, qualitative analyses of complex organic species formed by the pyrolysis of polymeric

materials using conventional EGA-MS with EI become substantially more difficult because many kinds of pyrolysates may evolve simultaneously or continuously by heating. This means that the fragment ions generated as a result of the higher ionization potential of EI often obstruct the identification of the gaseous species formed by heating.

In order to differentiate the mixed multiple evolution gases, use of separation and quantitative techniques such as gas chromatography-mass spectrometry (GC-MS) can be effective⁽¹⁴⁾. However, this prevents real-time monitoring and measurement of the amount of evolved gases as a function of temperature. In addition, because the thermal hysteresis of the evolved gases may change, it is difficult to confidently state that the gaseous components evolved from the sample are traced directly and accurately without modification.

The essential problem of differentiation of multiple organic gaseous species evolved simultaneously from the sample by conventional EGA-MS using EI still remains. In order to solve this issue, one feasible approach is the use of MS with a selective and soft (fragment-free) ionization method, such as chemical ionization, laser desorption ionization, ion attachment⁽¹⁵⁾, and photoionization (PI), all of which control fragmentation during the ionization process.

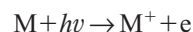
Single-photon ionization with a vacuum ultraviolet (VUV) light source is a particularly soft and selective ionization method^{(16)–(18)}, suited well for the detection of both aromatic and aliphatic species. The PI process that is used to distinguish mixed gases evolved simultaneously in real-time, is described in the following paragraphs.

The PI process is the simplest electron transfer reaction induced by photoabsorption. In this process, ionization occurs when a photon of sufficient energy is absorbed by a molecule, resulting in the formation of a positively charged ion and an electron. The associated energy is described by the equation

$$E = h\nu$$

where h is Planck's constant and ν is the frequency of the incident photon.

It is a process whereby a molecule at the ground state (M) is irradiated with a photon of sufficient energy resulting in molecular excitation to an ion level. Therefore, ionization occurs as follows:



where M is an ionizable species and $h\nu$ is a photon with sufficient energy to ionize M.

In general, although a gaseous molecule is ionizable when the energy of the supplied photon is at the same level as the ionization energy of the molecule, the molecular ion thus formed dissociates if the energy of the photon is relatively higher than that, and ionization cannot occur if it is too low. The ionization potentials of typical components are listed in Table 1⁽¹⁹⁾. The ionization potentials of many organic compounds are generally 8–11 eV and are lower than those of inorganic compounds such as water vapor, nitrogen, oxygen, carbon monoxide, and carbon dioxide. When the energy of the irradiated photon is larger than the ionization energy and smaller than the dissociation energy, ionization of almost all organic compounds becomes possible by the VUV lamp source of approximately 10 eV. Thus, because only the parent ions of the gas molecules are observed in the resulting fragment-free mass spectrum, it is possible to directly differentiate multiple gases evolved by using the discrete information on their molecular ions. Furthermore, this fragment-free ionization information is also useful when observing individual organic species in the presence of ionizing components such as oxygen, nitrogen, and water vapor in the atmosphere being measured. This is especially valuable for TG-DTA-MS conducted in various heated atmospheres, including oxidative and experimental humidity conditions^{(20),(21)}.

Table 1. Ionization potentials of typical organic

Compound	E(eV)	Compound	E(eV)
Argon	15.76	Benzene	9.25
Oxygen	12.07	Toluene	8.82
Nitrogen	15.57	Naphthalene	8.12
Carbone dioxide	13.78	Anthracene	7.40
Water	12.61	Phenanthrene	7.86
Methane	12.60	Biphenyl	8.27
Ethane	11.52	Biphenylene	7.53
Propane	10.97	Xylene	8.44
Butane	10.57	1-Methylnaphthalene	7.95
Acetone	9.71	Phenol	8.50
Hexane	10.18	Fluorobenzene	9.20
Ethylene	10.51	Chlorobenzene	9.07
Acetylene	11.40	Nitrobenzene	9.85
Methanol	10.80	Thiophene	8.87
Ethanol	10.49	Methylamine	8.90
Formaldehyde	10.90	Ethylamine	8.86
Tetrachloromethane	11.47	<i>n</i> -Butylamine	8.71
Tetrabromomethane	10.31	Aniline	7.72

3. Construction Details

Figure 3 shows the schematic diagram of a quadrupole mass spectrometer equipped with a 30 W VUV photoionization source for PIMS. The VUV lamp

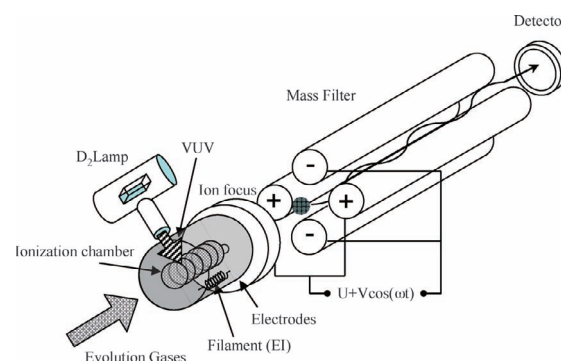


Fig. 3. Schematic drawing of the quadrupole mass spectrometer equipped with VUV photoionization source.

directly irradiates through the MgF_2 window toward the MS ionization chamber, where the emission line is $\lambda = 112.6 \text{ nm}$, and the maximum photoionization energy is $10.2 \text{ eV}^{(22)}$. Moreover, the EI source is also attached in the MS ion source chamber making it possible to arbitrarily select EI or PI ionization mode. Nevertheless, because the PI source is installed within the MS vacuum chamber, regardless of the interface type, it can be used for TG-DTA-PIMS.

The following different types of commercially available reagent grade polymers were used without further purification: polymethylacrylate (PMMA) (Kanto Chemical Co., Inc.), polystyrene (PS), high-density polyethylene (HDPE) and Nylons (Scientific Polymer Products, Inc.), including polycapromide (Nylon6), polyhexamethyleneadipamide (Nylon6/6), polydodecamethyleneadipamide (Nylon6/12), polyundecanoamide (Nylon11), polylauroamide (Nylon12), and poly(*m*-xylene adipamide) (NylonMXD6). Commercially available Nylon resins, including cable ties (INSULOK), tubes, and edge guards, were used to characterize the original materials of the polymers.

The samples were weighed into a platinum crucible, and then heated in high-purity helium gas (99.999%) at a flow rate of $200 \text{ mL} \cdot \text{min}^{-1}$.

4. Results and Discussion

4.1. Thermal degradation of polymer resins

The thermal degradation of polymers is a typical example where several complex organic gases simultaneously evolve upon heating. The application of thermal degradation to commercially available reagents is described below.

When degraded alone in the pure state, PMMA breaks down in a very simple manner. It has been established

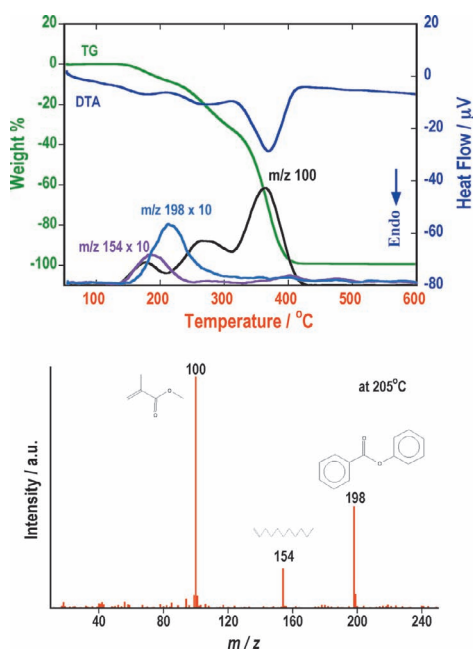


Fig. 4. Results of TG-DTA-PIMS at $20^\circ\text{C} \cdot \text{min}^{-1}$ for PMMA in helium atmosphere and mass spectrum obtained at TIC curve of 205°C .

that homolysis occurs at some points in the polymer backbone and is followed by depolymerization to monomers. Figure 4 shows the TG-DTA-PIMS results for PMMA at $20^\circ\text{C} \cdot \text{min}^{-1}$ in a helium atmosphere. PMMA breaks down in a very simple manner in which homolysis occurs at some points in the polymer backbone followed by depolymerization to the corresponding monomers. Through the soft-ionization effect of PI, the molecular ion of the monomer ($m/z = 100$) can be clearly seen. In addition, the existence of molecular ions from some minor impurities, such as undecene ($m/z = 154$) and phenyl benzoate ($m/z = 198$), are directly detected at high sensitivity near 200°C .

On the other hand, PS, when degraded alone at temperatures exceeding 300°C , it undergoes chain scission, depolymerization and both intra- and intermolecular transfer. A styrene unit, when present in copolymers, does not become involved in inter-unit reactions. When pyrolysis was carried out using PMMA in the presence of an equal weight of PS, no evidence of any interactions were found.

Figure 5 shows conventional TG-DTA-EIMS data for a mixture of PMMA and PS, at a heating rate of $20^\circ\text{C} \cdot \text{min}^{-1}$ in a flow of dry helium. The pyrolysis of the sample proceeds via a single step with the appearance of an inflection point in the course of the reaction. A

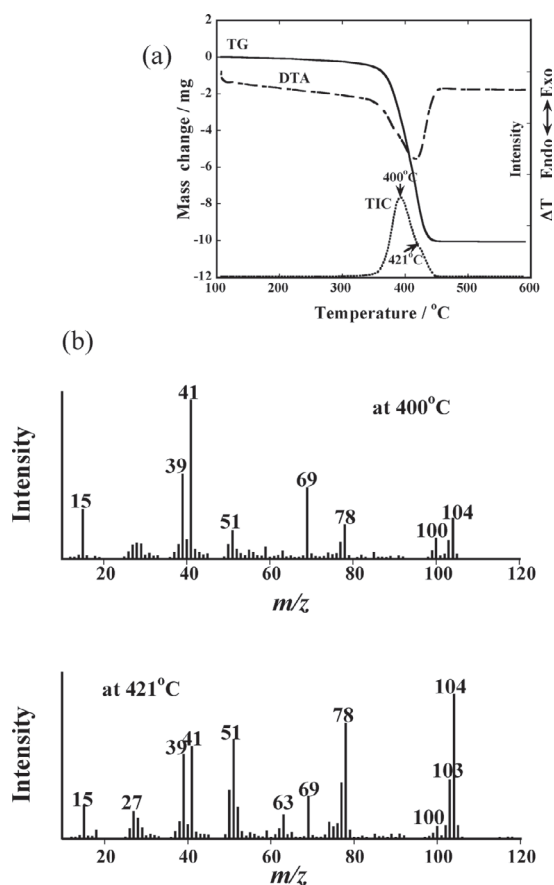


Fig. 5. Typical TG-DTA-EIMS results at $20^\circ\text{C} \cdot \text{min}^{-1}$ for blended sample of PMMA and PS in a helium atmosphere and mass spectra obtained at TIC curves of 400°C and 412°C .

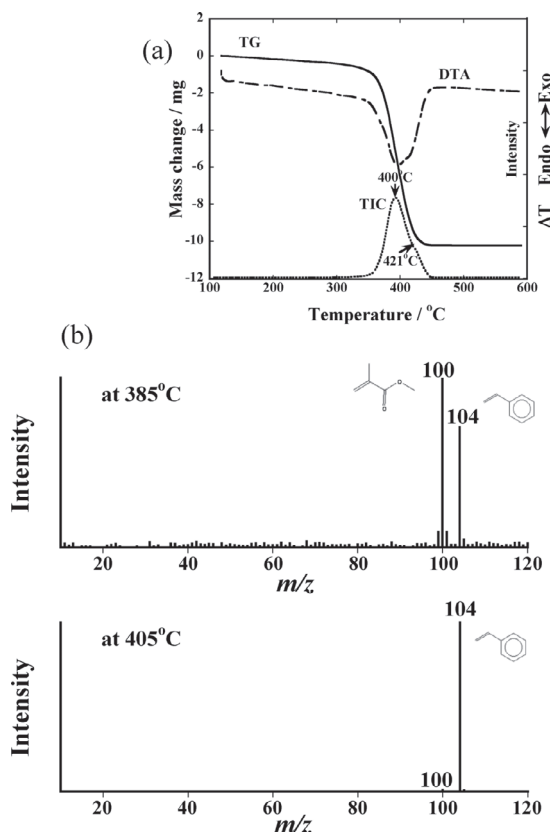


Fig. 6. Typical TG-DTA-PIMS results at $20^{\circ}\text{C}\cdot\text{min}^{-1}$ for blended sample of PMMA and PS in a helium atmosphere and mass spectra obtained at TIC curves at 385°C and 405°C .

comparison of the mass spectra obtained at 400°C and 412°C in the total ion current (TIC) chromatogram are shown in Fig. 5(b). The apparent mass spectra are completely different from each other, and suggest that different gaseous species were evolved in each temperature region. However, both of the mass spectra consisted of molecular ions along with numerous fragment ions formed by the high ionization energy of the EI. Since the detected fragmentation and molecular ions were mutually mixed, the identification of the evolved gas species was complicated and difficult.

Figure 6(a) illustrates the TG-DTA-PIMS of a PMMA and PS mixture, measured at a heating rate of $20^{\circ}\text{C}\cdot\text{min}^{-1}$ in a flow of dry helium, while Figure 6(b) shows the mass spectra obtained for the TIC chromatogram of 385°C and 405°C , respectively. The thermal behavior appears to be similar to that of the TG-DTA-EIMS in Fig. 5(a), in which a single decomposition step accompanied by an inflection point was observed. However, the observed mass spectra were completely different from those obtained using TG-DTA-EIMS and a simple mass spectrum was obtained. The mass spectra were easily characterized by the appearance of only m/z 100 and 104 ions assigned to molecular ions of methylmethacrylate (MMA) and styrene, produced by depolymerization to monomers.

Figure 7 exhibits the characteristic ion intensities of m/z 100 and 104 as a function of temperature. The

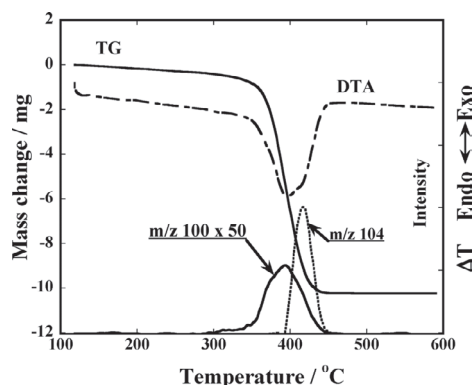


Fig. 7. TG-DTA curve and Mass chromatograms of characteristic ions of m/z 100 and 104 as a function of temperature obtained by TG-DTA-PIMS for blended sample of PMMA and PS.

thermal behavior of both ions differed and was not synchronized to each other. The pyrolysis of the blended sample proceeded via PMMA followed by PS without any interaction. Based on these results, it can be concluded that the pyrolysis of the blended sample of PMMA and PS progressed via two independent reactions which were respectively controlled by depolymerization to form a monomer.

By the introduction of the PI fragment-free ionization method to TG-DTA, the elucidation of the pyrolysis mechanism of blend of polymers became very clear because only molecular ions of the pyrolyzates, produced by degradation of the sample were observed.

Thermal degradation of PE progresses through intramolecular radical transfer and/or transfer hydrogenation, and the thermal degradation products consist of n -paraffins, which are saturated hydrocarbons, and the principal components, n -1-olefins, which are derived from unsaturated hydrocarbons with a large carbon number distribution. The thermal degradation analyses of HDPE measured by TG-DTA-PIMS are shown in Fig. 8. By the skimmer-type interface effect, the apparent mass spectra clearly illustrate the detection of ion clusters of $m/z > 200$, indicating the presence of high boiling point compounds. In the EI spectra, it is difficult to directly distinguish the evolved gas components because of overlapping signals resulting from fragmentation during ionization. On the other hand, by controlling fragmentation using the PI method, the presumption that each component is associated with an unfragmented molecular ion becomes possible in real-time because the high boiling point components, having more than 20 carbons, can be directly detected in the molecular ion state.

4.2. Characterizing thermal degradation of polymers

Nylon is a polyamide consisting of several amide-linked aliphatic monomers. A comparison between the results from EIMS and PIMS for pyrolysates of Nylon6 obtained by TG-DTA-EI/PIMS is shown in Figs. 9 and 10. It is difficult to individually characterize each

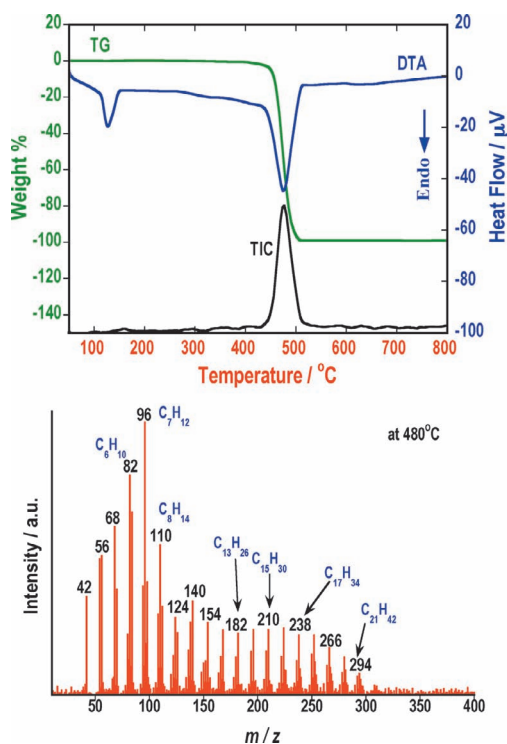


Fig. 8. Results of TG-DTA-PIMS at $20^{\circ}\text{C}\cdot\text{min}^{-1}$ for HDPE in helium atmosphere and mass spectrum obtained at TIC peak temperature of 480°C .

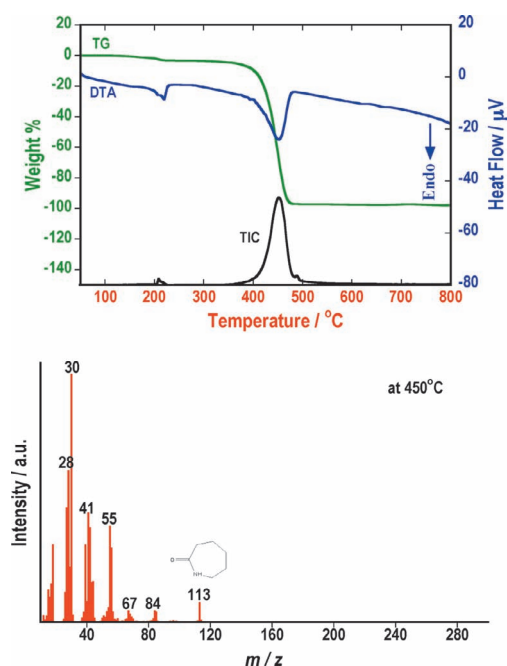


Fig. 9. Results of TG-DTA-EIMS at $20^{\circ}\text{C}\cdot\text{min}^{-1}$ for Nylon6 in helium atmosphere and EI mass spectrum obtained at TIC peak temperature of 450°C .

pyrolysate in the spectrum acquired with the EI method because of mutually overlapping fragment ions in the lower m/z region, as shown in Fig. 9. On the other hand, because the PI method controls the fragmentation of the molecules during ionization, the resulting pyrolysates are detected as the molecular ions that originate directly from the structure of Nylon6, as shown in Fig. 10.

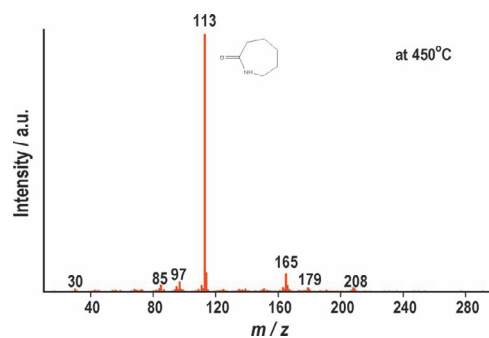


Fig. 10. PI mass spectrum at TIC peak temperature of 450°C obtained by TG-DTA-PIMS at $20^{\circ}\text{C}\cdot\text{min}^{-1}$ for Nylon6 in helium atmosphere.

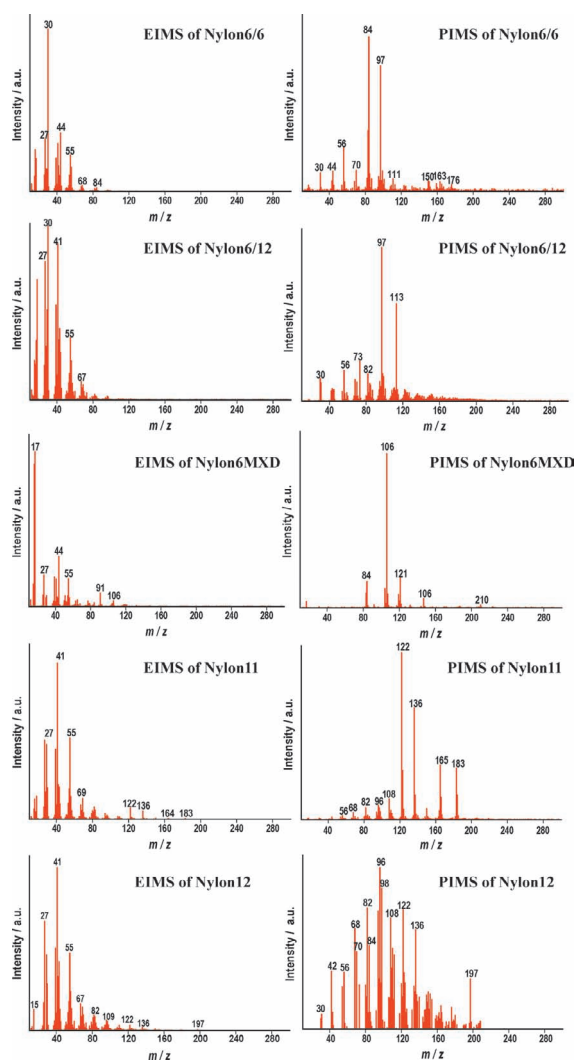


Fig. 11. Comparison of mass spectra obtained by TG-DTA-EIMS and TG-DTA-PIMS for the five different reagent Nylons (Nylon6/6, Nylon6/12, Nylon6MXD, Nylon11 and Nylon12) in helium atmosphere at $20^{\circ}\text{C}\cdot\text{min}^{-1}$.

Therefore, the identification of pyrolysates can be made directly from the apparent mass spectrum. As a result, caprolactam, a monomer generated using the PI method ($m/z=113$), is definitively characterized in the mass spectrum.

Subsequently, related experiments with five different types of Nylons (Nylon6/6, Nylon6/12, NylonMXD6, Nylon11, and Nylon12) that have similar structures were carried out using TG-DTA-EI/PIMS. The spectral differences between EIMS and PIMS are compared as shown in Fig. 11. Because the observed EI mass spectra seem similar to each other, it is difficult to directly characterize them and to differentiate the individual Nylons. On the other hand, because the PI spectra are composed of only the molecular ions from the

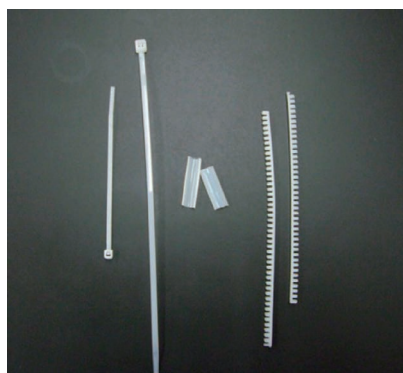


Fig. 12. Photographs of commercial Nylon parts; from left: cable tie, tube and edge guard.

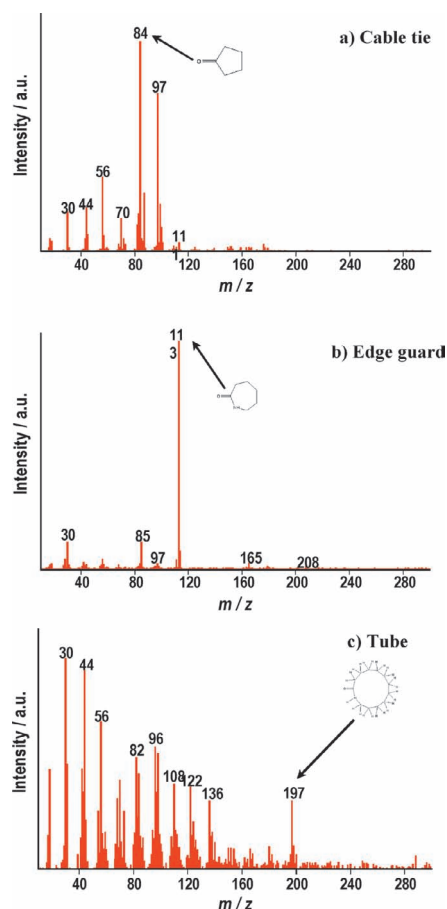


Fig. 13. Comparison of mass spectra obtained by TG-DTA-PIMS for the three different types of commercial Nylon materials at $20^{\circ}\text{C}\cdot\text{min}^{-1}$ in a helium atmosphere.

degradation products that originate from the polymer backbone structure, which are unique to each sample, the individual Nylons can be definitively identified. Nylons are easily assigned by their characteristic molecular ions in the mass spectrum [(Nylon6/6, cyclopentanone ($m/z=84$) and hexanenitrile ($m/z=97$); Nylon 6/12, caprolactam ($m/z=113$) and hexanenitrile ($m/z=97$); Nylon 6MXD, xylene ($m/z=106$); Nylon11, undecanlactam ($m/z=183$); and Nylon12, lauryllactam ($m/z=197$)]. In this way, the fragment-free feature of PIMS enables simplified characterization of the degradation products of polymers because of its sensitivity for the minute structural changes between the samples. Consequently, it is useful for fingerprint analyses owing to its unique PI features.

The following is an illustration of a fingerprint analysis of the components of a commercially available resin. Figure 12 shows a photograph of the three different types of commercially available Nylon resins; namely, cable tie (INSULOK tie), edge guard, and tube. On the other hand, Figure 13 illustrates a comparison of the TG-DTA-PIMS results for their respective evolved gases. The spectral differences are obvious from the PIMS results, although these differences are few in spectra from EIMS, making sample identification difficult with the latter. Comparing the PIMS spectra obtained from the reagent Nylons mentioned above, the cable tie, edge guard, and tube can be easily assigned as Nylon 6/6, Nylon 6, and Nylon 12, respectively.

Thus, as shown in this fingerprint analysis, the unique features of PIMS allows easy differentiation of resins, and its advantages are demonstrated in the rapid identification of organic compounds such as polymers.

7. Conclusions

It is confirmed that the new TG-DTA-MS instrument equipped with a skimmer-type interface and PIMS using a VUV lamp as the photon source has been successfully developed. The application limit of conventional thermoanalytical methods is decreased remarkably and the analytical needs have been greatly increased to mainly polymer resins and organic compounds. Features such as the quality of the evolved gases and the reproducibility of the data are also very important. Furthermore, the prevention of gas condensation throughout the gas injection pathway is remarkably improved by the skimmer-type interface. Significantly, the spectra produced using this system are generally unaffected by interfering ions, such as fragment ions because only the molecular ions of a mixed gas are ionized selectively. Because the fragment-free spectra from PIMS enable direct characterization of polymer degradation products by focusing on the minute structural differences between the samples, the new instrument will be very useful for fingerprint analyses.

In EGA-MS, the combined methodology of the skimmer-type interface and soft-photoionization technique will greatly contribute to quantitative analyses in near future.

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