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STUDY ON THERMAL DECOMPOSITION OF POLYMERS BY EVOLVED GAS ANALYSIS USING PHOTOIONIZATION MASS SPECTROMETRY (EGA-PIMS)

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Photoionization mass spectrometry (PIMS) with vacuum ultraviolet (VUV) light source provides an efficient and fragmentation-free method for the soft ionization of gaseous compounds, in order to facilitate an understanding of thermal decomposition behavior and chemical composition of polymeric materials. The PIMS was applied to the evolved gas analysis (EGA) system equipped with a skimmer interface which is constituted based upon a jet separator principle between a vacuum MS chamber and an atmospheric sample chamber in a furnace. A photoionization source with a deuterium (D_2) lamp was closely installed to the vacuum ionization chamber of a mass spectrometer to improve the ionization efficiency.

The thermal decomposition of typical polymers in inert gas atmosphere was investigated by the EGA-PIMS and the resulting PI mass spectrum was characterized satisfactorily by only the parent ions with no contribution as a result of fragmentation during the ionization. The results suggested that the EGA-PIMS was an especially powerful and desirable in situ thermal analysis method for polymeric materials which evolve organic gases simultaneously and concurrently. The combination of EGA equipped with skimmer interface with no change of evolved gaseous species and PIMS with fragmentation-free during the ionization is described briefly, and the effective results are presented by comparing with EGA using conventional electron impact ionization mass spectrometry.

Keywords: *EGA-MS, fragmentation-free, photoionization, polymer decomposition, soft ionization, VUV*

Introduction

Determination of the mass loss for the thermal decomposition of polymeric materials as function of temperature, i.e. thermogravimetry (TG), provides information on thermal events related to the structure and thermal behavior of the materials. However, TG provides no information on the chemistry of these thermal events or on the nature of the evolved gases. Typically, this can be achieved by the combination of TG and other techniques capable of providing both qualitative and quantitative information [1–5]. For instance, by coupling to gas analysis methods such as Fourier transform infrared spectroscopy (FTIR) and mass spectrometry (MS), the evolved molecular fragments can be detected and identified. Nowadays, these combinations are well-established thermal analytical techniques, and TG-FTIR and TG-MS interfaces are commercially available. In practice, the most popular EGA technique is combined with MS because of its sensitivity, versatility, and fast analysis time.

In general, with these interfaces the evolved gases are led by a carrier gas flow *via* a heated transfer line to the EGA. A great variety of EGA-MS systems has been presented in literatures during the past decade and reviews [6–8] have been written on the advantages, disadvantages, and applications. EGA-MS type is roughly classified into two kinds of gas interface systems from the difference in interface structure which connects between a sample chamber and a vacuum chamber : capillary type and skimmer type interface systems. Especially, because the gaseous species evolved by pyrolysis are not only stable species but also unstable species are existed, skimmer interface system based upon jet-separator principle offers principally significant advantages over capillary interface system [9–11].

In traditional, the gaseous species introduced into MS by EGA-MS are ionized by electron impact ionization (EI) technique of 70 eV. Although a gaseous molecule is ionized by colliding with an accelerated electron by EI method, a part of the generated molecular ion is further decomposed, and observed simultaneously as the fragmentation ions. When the multiple gases generate simultaneously and the resulting fragmentation ions overlap mutually, while the fragmentation ion gives the significant information about the structure of molecule, the apparent mass spectrum may be complicated.

As mentioned above, the qualitative analysis of complex organic species formed by thermal decomposition of polymeric materials by conventional EGA using

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EI (EGA-EIMS) is made substantially more difficult because so many kinds of gaseous species may evolve simultaneously or continuously by heating. This means that the fragmentation due to higher ionization potential by EI often prevents the identification of the gaseous species formed by heating in a furnace.

In order to differentiate such mixed multiple evolution gases, the use of separation and quantitative techniques such as gas chromatography (GC)/MS become effective [12]. However, this prevents the real-time monitoring and measuring the amount of evolved gases as a function of temperature. In addition, the thermal history of evolution gaseous species may change, which makes it difficult to confidently state that the gaseous components evolved from the sample are traced directly and correctly without any changes.

The essential problem of differentiation of multiple organic gaseous species evolved simultaneously from the sample by conventional EGA-EIMS still remains. In order to solve this issue, one feasible approach is the use of MS with a selective and soft (fragment-free) ionization technique such as chemical ionization (CI), laser desorption ionization (LDI), ion attachment (IA) [13] or photoionization (PI) which controls fragmentation during the ionization.

Single photon ionization with vacuum ultraviolet (VUV) light is a particularly soft and selective ionization method [14–16], well-suited for detection of both aromatic and aliphatic species. Traditionally, PI technology has been used in the elucidation of atmospheric chemical reaction processes and in monitoring for special toxic substances as part of research in the direct detection of free radicals and ion-molecule reaction clusters.

In the present work, we have focused attention to the validity of a combination of skimmer interface with no change of evolved gaseous species and PIMS with fragmentation-free during the ionization. The instrumentation and experimental set-up are presented together with the representative results in polymer research. It is proposed that the skimmer interface type of EGA equipped with PIMS is powerful thermal analytical tool to differentiate real-timely the activated pyrolyzates formed during the complex decomposition process of polymers.

Table 1 Ionization potentials of typical organic components

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	*n*-Butylamine	8.71
Tetrabromomethane	10.31	Aniline	7.72

Photoionization technology

Photoionization process is the simplest electron transfer reaction induced by photoabsorption. The process of ionization occurs when a photon of sufficient energy is adsorbed by a molecule and results in the formation of an ion plus and electron.

$$R+h\nu\rightarrow R^{+}+e^{-}$$

where R=an ionizable species, $h\nu$=a photon with sufficient energy to ionize species R.

In general, although a gaseous molecule is ionizable when the supplied photon energy is in the same levels as the ionization energy of the molecule, the molecule ion is dissociated if too larger than that, and if too small, it can not be ionized at all. The ionization potentials of typical components are listed in Table 1 [17]. As shown in the table, the ionization potentials of many organic compounds are in 8 to 11 eV and are smaller than those of inorganic compounds such as water vapor, nitrogen, oxygen, carbon monoxide and carbon dioxide. Therefore, when the energy of the irradiated photon is larger than ionization energy and is smaller than dissociation energy, ionization of almost all organic compounds becomes possible enough by the VUV lamp source of about 10 eV. Thereby, since only the parent ions of the gas molecule can be observed by the fragment-free mass spectrum, it is enabled to differentiate easily the multiple evolution gases, using the information of molecular ion. Additionally, these specific ionization characteristics are useful when observing selectively organic species even when ionizing components such as oxygen, nitrogen and water vapor, etc. are present in the measurement atmosphere. This is especially valuable for EGA carried out in various heating atmospheres including oxidative and humidity experimental conditions [18, 19].

Experimental

Materials

Two different types of the pellet samples for polymethylmethacrylate (PMMA) of depolymerization type and polycaproamide (Nylon-6) of random scission type were supplied by Kanto Chemical Co. Inc. and Mitsubishi Chemical Co. Inc., respectively, as the commercially available reagent grade without any further purification.

The samples were weighed into a crucible, and were heated in high-purity dry helium gas (99.999%), at a flow rate of 300 mL min^{-1}.

Apparatus

A part of the vacuum chamber of quadrupole - mass spectrometer (Q-MS) for a commercialized EGA-MS equipment (Model TPD type R, Rigaku Co.) [11, 20] was modified in order to adapt photoionization function. This EGA-MS is equipped with the unique gas sampling system called skimmer interface structure, and it consists of two concentric quartz tubes with orifices which connected the two devices at atmospheric and vacuum pressures, for continuous and immediate sampling of the gaseous species without any changes from the sample. The gas generated in the sample chamber is controlled through these two orifices, and is introduced into the MS ionization chamber. Since the carrier gas used was also high-purity helium, the evolved gaseous species with higher masses were enriched after the second orifice, in consequence of the principle of a jet separator, i.e., the second orifice ensures that the composition of the molecular beam is identical to that of the gas presented in the sample chamber.

Single photon ionization mass spectrometry is performed using a VUV deuterium discharge lamp supplied by Hamamatsu Photonics K.K as photon source. The VUV spectrum consists of a weak broad-bond continuum: the Werner and Lyman molecular bonds around 130 and 160 nm, respectively; the narrow intense Lyman α atomic line at 121.567 nm [21]. Ionization was accomplished by photoionization at 10.2 eV.

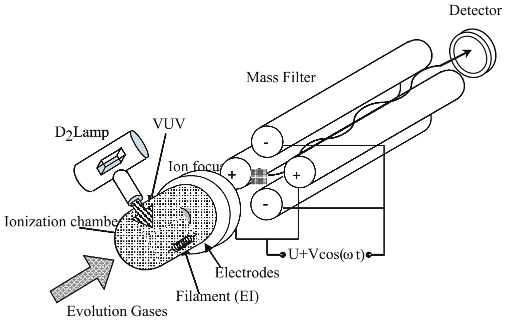

Fig. 1 Schematic drawing of D_2-lamp-Quadropole Mass spectrometer system equipped with VUV photoionization source

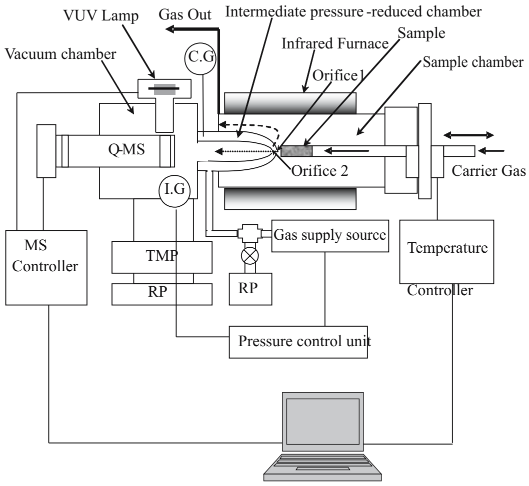

Fig. 2 Schematic diagram of EGA-PI/EIMS using skimmer interface system. Ion gauge, I.G; Crystal gauge, C.G; Turbo molecular pump, TMP; Rotary pump, RP

The VUV lamp-QMS constitution was built and the EGA-PI/EIMS system is schematically shown in Figs 1 and 2. In this system, the Q-MS supplied by Canon Anelva Technix (Model, M-400QA-MU) with a few modifications was used. The VUV photoionization source was installed as close as possible to the EI ion source. The MgF_2 window was used to seal the rare gas volume against the vacuum in the ion source. Direct VUV light is focused through the MgF_2 window on the centre of the ion source of the Q-MS. A sequence of experiments was carried out with full automated and computerized EGA system, and the ionization mode of EI and PI could be selectable arbitrarily. The acceleration voltage of EI was fixed at potential of 70 eV. In the present experiments, a change in the ionization mode was performed by changing the EI filament and acceleration voltage without switching the VUV photoionization source.

TG-GC/MS system used was manufactured by Rigaku using a GC/MS made by Shimadzu, QP-5050A [22]. GC separation of the decomposition components was achieved by using a 30 m×0.25 mm i.d.×0.25 μm film thickness DB-5 fused silica capillary column (supplied by J&W Scientific) and the GC was temperature programmed from 30 to 280°C at a rate of 10°C min^{-1}. Peak identification was primarily carried out by the GC/MS system in the EI mode, using the NIST/EPA/NIH chemical structures database.

Results and discussions

Thermal decomposition of polymethylmethacrylate(PMMA) in inert atmosphere

The thermal decomposition of polymer is a typical example that simultaneously generates multiple organic gaseous species. In order to precisely measure the activated pyrolyzates, the EGA equipped with the skimmer interface based upon a jet separator principle is useful, and is very effective in enhancing the detection sensitivity in a higher mass range and a wide temperature range [11].

When degraded alone in the pure state, PMMA breaks down in a very simple manner. It has been established that homolysis occurs at some points in the polymer backbone and is followed by depolymerization to monomer. The depropagation reaction has a long zip length. The initial homolysis occurs preferentially at unsaturated chain ends which are normally present in a sample prepared by a free radical route; the concentration of ends varies inversely with molecular mass [23].

Figure 3 illustrates the typical conventional EGA-EIMS for the PMMA sample, at a heating rate of 20°C min^{-1} in dry helium flow, and the mass spectra obtained at the main peaks in the total ion current (TIC) chromatogram at 176, 266, 288 and 362°C. The mass loss was characterized through four decomposition stages in which the mass spectra obtained at the peaks in the TIC chromatogram were identified as methylmethacrylate (MMA) ($C_5H_8O_2$: *m*/*z* 39, 41, 69, 99 and 100) [24] in agreement with NIST database data, except for the weak ions of *m*/*z* 77 and *m*/*z* 105 in the mass spectrum of the first stage at 176°C. As the results, it can interpret simply that the thermal decomposition of PMMA proceeded via four steps which were mainly controlled by depolymerization to form a monomer.

Figure 4 illustrates the EGA-PIMS for the PMMA sample, at a heating rate of 20°C min^{-1} in dry helium flow and the mass spectra obtained at the TIC peak temperatures of 173, 263, 288 and 361°C. The thermal behavior of TIC agreed satisfactorily with that of the EGA-EIMS as shown in Fig. 3: the four decomposition steps were observed. However, the mass spectra observed were completely different to those by the EGA-EIMS and all showed the simple mass spectrum. The mass spectra were easily characterized by appearance of only *m*/*z* 100 ion assigned to the parent ion of MMA as controlled by depolymerization to monomer. Furthermore, we can clearly observe the additional significant ions of *m*/*z* 105, 198 and weak ion of *m*/*z* 154 in the mass spectrum of the first decomposition stage at 173°C. The result suggested that since the apparent ions observed by the PIMS belong to each independent component, the intense ions of *m*/*z* 198, 154 and 105 may result presumably in the impurity components. In radical polymerization, the fragments of polymerization initiators often remain in the chain end-groups in the final polymeric products. The weak ions of *m*/*z* 105, 154 and 198 may be due to impurities such as the fragment residue of polymerization initiators evolved due to heating.

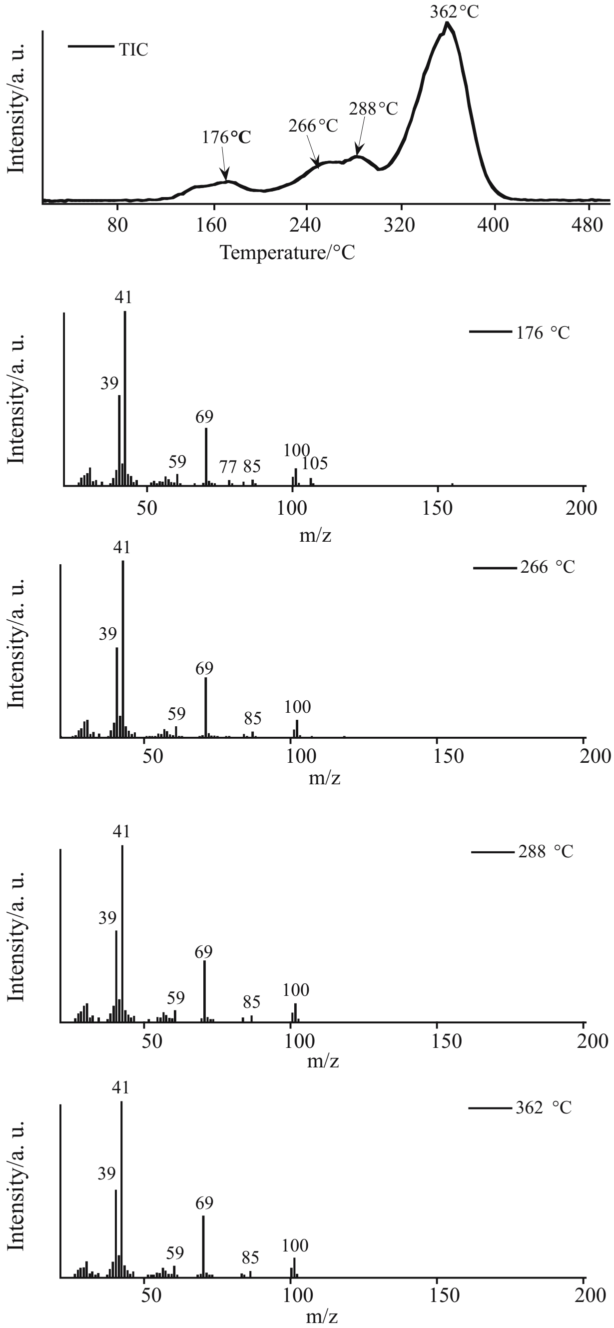

Fig. 3 Typical EGA-EIMS results at 20°C min^{-1} for PMMA in helium atmosphere and mass spectrum obtained at TIC peak temperatures of 176, 266, 288 and 362°C

In order to elucidate the small amount of the impurity components detected by PIMS, TG-GC/MS measurement was made for the PMMA sample in the first decomposition stage. The results of the GC/MS measurement for the decomposition components collected at 100~250°C which are decided by the TIC curve in the first stage are shown in Fig. 5; three intense TIC peaks including MMA component are ob-

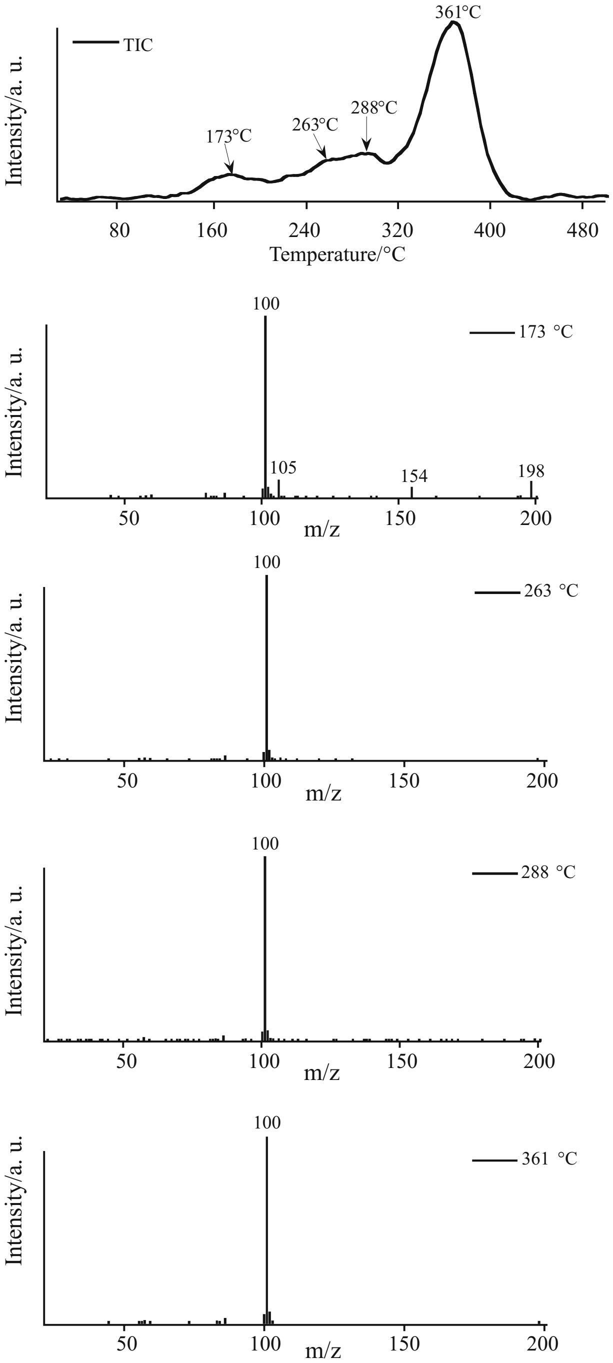

Fig. 4 Typical EGA-PIMS results at 20°C min^{-1} for PMMA in helium atmosphere and mass spectrum obtained at TIC peak temperatures of 173, 263, 288 and 361°C

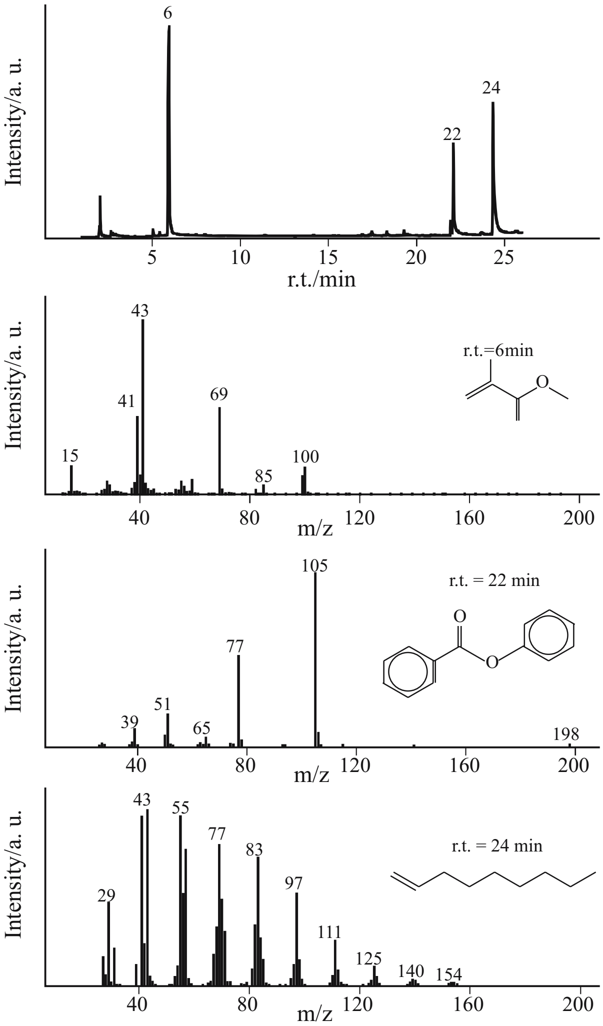

Fig. 5 TG-GC/MS pyrogram for evolved gases collected in first decomposition stage of PMMA, and mass spectra obtained at TIC peak times of 6, 22 and 24 min with chemical structures assigned by NIST-MS database

served at the retention times of 6, 22 and 24 min. Figure 5 shows also a comparison of the mass spectra obtained at these retention times, together with the chemical structures assigned by comparison with NIST-MS library database data. The results suggest that the gases evolved together with MMA were undecene and phenyl benzoate with the molecular ions of *m*/*z* 154 and 198, supporting the ions in the mass spectrum obtained by the EGA-PIMS. However, the characteristic ion of *m*/*z* 105 by the EGA-PIMS could not detect as the molecular ion of the mass spectra in the TIC peaks of the results of TG-GC/MS.

As mentioned above, intermittent sampling (trap coupling) mode in TG-GC/MS, a portion of the evolved gas is collected over a chosen temperature range, and then analyzed by ‘off-line GC/MS’. In this case, the activated unstable pyrolyzates evolved from the sample may be changed to the stable components by both of the cold-trapping and reheating experimental processes. Therefore, it is not appropriate to consider that all of the evolved gases including the unstable states are observable directly and correctly by this method.

From this point of view, a combination of skimmer gas sampling interface with no change of evolved gaseous species and PIMS with no fragmentation during the ionization is very useful. On the principles, skimmer interface has less adsorption and touch of the gaseous species to the wall of the device. Further, PIMS has a potential of detection of the gaseous species even if it is radical species. Thus, there is a possibility of that the present instrument can detect the gaseous species which were disappeared in the TG-GC/MS. Consequently, it seems reasonable to interpret that the original source of *m*/*z* 105 ion may be speculated to the unstable component such as a radical ion of $C_6H_6CO\cdot^+$. Figure 6 exhibits such characteristic ion intensities of *m*/*z* 100, 105, 154 and 198 as function of the temperature. The thermal behavior of *m*/*z* 105, 154 and *m*/*z* 198 ions differed to each other, and moreover did not synchronize with that of the *m*/*z* 100 ion in the first decomposition stage. By introduction of the PI fragment-free mass spectrum to the EGA the elucidation of the thermal decomposition mechanism of PMMA became easily but also a small amount of impurities included in the sample could be detected sensitively, because only the molecular ions of the activated pyrolyzates degraded from PMMA were observed selectively.

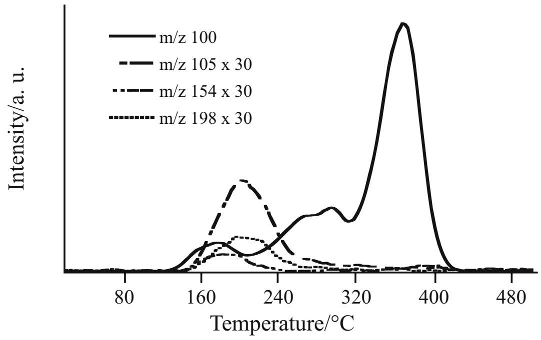

Fig. 6 Mass chromatograms of characteristic ions of *m*/*z* 100, 105, 154 and 198 as a function of temperature obtained by EGA-PIMS for PMMA

Thermal decomposition of polycaproamide (Nylon-6) in inert atmosphere

The significant feature of EGA-PIMS is being able to measure continuously as a function of temperature instead of the measurement which had to be processed in batch by GC/MS until now because the mixed multiple evolution gases can differentiate by each molecular ion.

Figure 7 illustrates a comparison of the mass spectra by typical three-dimensional representation obtained between the PIMS and the EIMS for the thermal decomposition of nylon-6 at a heating rate of 10°C min^{-1} in dry helium flow. We can learn that the *m*/*z* observation region of intense ions detected between the EI and the PI modes is especially different to each other. Figures 8 and 9 show a comparison of mass spectra for the maximum TIC peak temperatures obtained by the EIMS and by the PIMS. Many fragment ions formed by the high ionization potential of the EI were mutually mixed and observed in lower *m*/*z* region, while the parent ions in the mass spectra of the PI were exclusively observed as simple spectrum peaks and observed in the wide *m*/*z* region. In general, an EI mass spectrum of an aliphatic species consists of many fragment ions in which the ionic in-

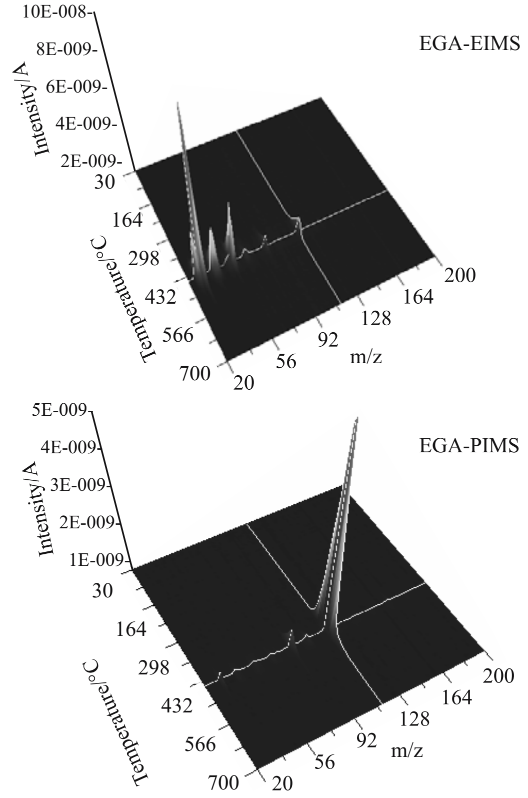

Fig. 7 Comparison of three-dimensional representation between EGA-EIMS and EGA-PIMS for Nylon-6 at 10°C min^{-1} in helium flow

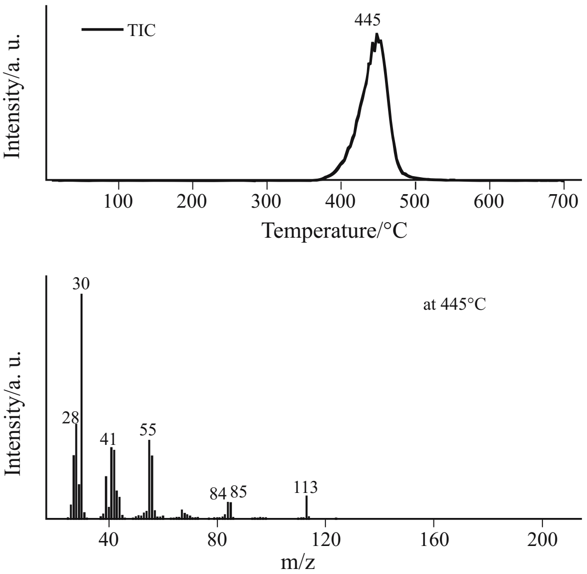

Fig. 8 Mass spectra obtained at maximum TIC peak temperature of 445°C for EGA-EIMS of Nylon-6

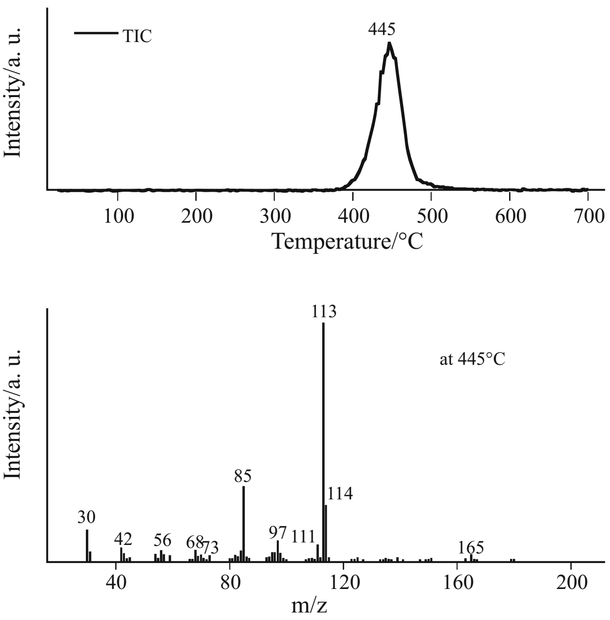

Fig. 9 Mass spectra obtained at maximum TIC peak temperature of 445°C for EGA-PIMS of Nylon-6

tensities are stronger than the parent ion. Sometimes the apparent spectrum profiles seem to be similar to each other because the parent ion may be obscured in the mass spectrum. As the result, it revealed that the EGA-PIMS which depresses the formation of fragment ions and selectively recognizes the parent ion becomes a very effective method to characterize the decomposition components of polymers.

Figure 10 illustrates the enlarged mass spectrum of EGA-PIMS obtained at a maximum gas evolution temperature (445°C), and the TG-GC/MS pyrogram of the evolution gases collected around same temperature. It suggested that a comparison of these profiles showed a differentiation capability to which the apparent mass spectrum observed by PI was similar with the GC/MS pyrogram. Table 2 summarizes the comparison of the detected major components between the TG-GC/MS and the EGA-PIMS. The evolved gas components which were detected and characterized by TG-GC/MS were detected also by the EGA-PIMS. Although the other components were detected by only the EGA-PIMS, a difference may be attributed to the activated pyrolyzates containing radical and unstable species which are difficult to analyze by GC/MS. These findings proved that the EGA-PIMS conquered the essential drawback of conventional EGA-EIMS and/or TG-GC/MS and has the capability to enable directly differentiation of volatile organic gaseous species evolved simultaneously from the sample in thermal analysis.

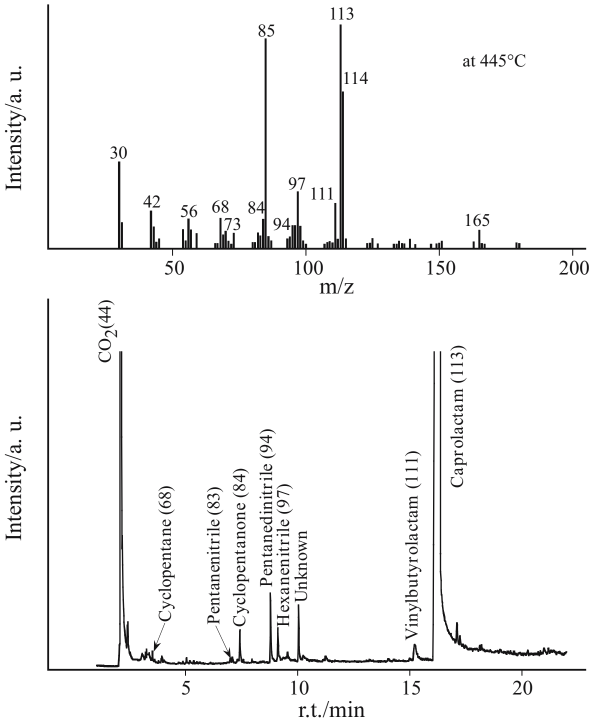

Fig. 10 Enlarged mass spectrum of EGA-PIMS obtained at maximum TIC peak temperature (445°C), and TG-GC/MS pyrogram of evolved gases collected around 445°C

Table 2 Comparison of evolved gaseous species detected by TG-GC/MS and EGA-PIMS for thermal decomposition of Nylon 6

M.W.	TG-GC/MS	Identified compound	Chemical formula	EGA-PIMS
30	N.D.		NO*	◎
42	N.D.			○
56	N.D.			○
68	Δ	Cyclopentane	C_5H_8	○
83	Δ	Pentanenitrile	C_5H_9N	Δ
84	◎	Cyclopentanone	C_5H_8O	○
85	N.D.			◎
94	◎	Pentanedinitrile	C_5H_9N	○
97	◎	Hexanenitrile	$C_6H_{11}N$	◎
111	○	Vinylbutyrolactam	C_6H_9NO	◎
113	◎	Caprolactam	$C_6H_{11}NO$	◎
114	N.D.			◎
165	N.D.			○

*formula speculated by molecular mass
(◎ – Intense clear peak; ○ – Clear peak; Δ – Unclear

Conclusions

It is confirmed that a new EGA instrument equipped with photoionization mass spectrometry using a VUV deuterium discharge lamp as photon source has been developed successfully. This technique could offer unique mass spectra of evolved organic complex gases due to pyrolysis even if it is radical and unstable species. The EGA-PIMS was applied to thermal decomposition of polymethylmethacrylate and polycaproamide. The experimental results clearly indicated that only the parent ions for the activated pyrolyzates were formed by the fragment-free mass spectrum which is characteristic feature of the PI, but also detected sensitively a small amount of residual impurities. By comparing with the results of conventional EGA-EIMS and TG-GC/MS, it is concluded that the more sensitive and precise EGA-PIMS prevented the formation of fragmentation and the change of evolution gas molecules. Furthermore, by combining PIMS and EIMS for the EGA, the analytical accuracy can be significantly improved, and it will be applicable as a useful analytical tool for various fields which simultaneously generate multiple organic gases.

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