ELSEVIER

Thermochimica Acta 267 (1995) 209–221

thermochimica
acta

A combined thermogravimetric-gas chromatographic/mass spectrometric analysis (TG-GC/MS) using a high resolution TG technique[1]

Tadashi Arii[a,*], Tetsuya Senda[a], Nobuyuki Fujii[b]

[a]*Thermal Analysis Division, Rigaku Corporation, 3-9-12 Matubara-cho, Akishima-shi, Tokyo 196, Japan*
[b]*Department of Chemistry, Nagaoka University of Technology, 1603-1 Kamitomioka, Nagaoka 940-21, Japan*

Received 5 December 1994; accepted 15 February 1995

Abstract

A new combination system of TG-GC/MS using high resolution TG technique is reported. The present high resolution TG technique is a dynamic rate control (DRC) method that belongs to the controlled rate thermal analysis (CRTA). In this technique, the heating rate of the sample is dynamically and continuously varied in response to changes in the sample's decomposition rate. In the present study, the performance and applicability of this system is illustrated by using the thermal decomposition of polyimide/polytetrafluoroethylene/graphite (PI/PTFE/GR) resin. The presented data demonstrate that this novel feature improves resolution and enhances the accuracy of identification and quantification. It is concluded that the present method gives more detailed information than that obtained from the conventional method, even for materials decomposing through consecutive and close-lying reactions.

Keywords: TG-GC/MS; High resolution TG

1. Introduction

Thermogravimetry (TG) is a well established tool which gives information about the relation between the weight change and the temperature of materials heated under various atmospheric conditions. Most thermoanalytical studies were performed with a well designed combination of instruments, composing a versatile thermoanalytical tool. Since the major thermal analysis techniques provide physical information, ancillary data are

---

[*] Corresponding author.

[1] Presented at the 30th Anniversary Conference of the Japan Society of Calorimetry and Thermal Analysis, Osaka, Japan, 31 October–2 November 1994.

SSDI 0040-6031 (95) 02479-4

required for chemical interpretation of the observed thermal events. Evolved gas analysis (EGA) is particularly valuable and it provides direct chemical information about the processes caused by the physical techniques of TG, DTA and others. The simultaneous technique of coupling between TG and mass spectrometry (MS) or Fourier-transform infrared absorption spectroscopy (FTIR) offers the possibility of identification of the volatile products formed during the thermal events. Recently, studies of the thermal decomposition of materials by these hyphenated techniques have been noticed, and EGA is most effectively performed by TG-MS [1,2]. The successful design of a coupled TG-MS apparatus has been realized in a multitude of ways.

In the present paper the application of the TG-MS method to the analysis of materials of interest in quality assurance is described together with available instrumentation. The advantages of this method in the analysis of samples such as polymers, lubricants and their additives is demonstrated.

High-resolution TG using controlled rate thermal analysis (CRTA) has been actively studied and gives a significant improvement to TG results. Historically, the better known techniques are quasi-isothermal and the quasi-isobaric analysis by J. and F. Pauliks [3], stepwise isothermal analysis (SIA) by Sorensen [4], and constant rate thermal analysis by Rouquerol [5]. The CRTA is a thermoanalytical method in which the controlled parameter is not the temperature but any parameter linked to the thermally activated transformation. This technique is especially useful in studies of thermal decomposition and it is believed that the dehydration temperatures for hydrate compounds will be measured under conditions at which the influence of released water molecules is negligible, i.e. where the water molecules are removed from the sample as soon as they are released from solid. We devised a dynamic rate control (DRC) method that belongs to the CRTA, and reported that it was an especially effective technique in the detection of intermediate products for the dehydration of inorganic salts [6].

The resolution of successive TG weight loss is important for obtaining accurate and reproducible weight change, as well as accurate component identification of the component in the evolved decomposition gases by MS.

In this study, the applicability of a new combination system of TG-GC/MS using the high resolution TG technique for the analysis of the thermal decomposition process of polymer resin is discussed.

2. Principle of the high resolution TG technique

The basis for the algorithm for dynamic rate control is described below. The heating rate in the present DRC method is controlled in such a way that the absolute value of a sample's temperature decrease rate is expressed as a monotonous function of the sample's weight decrease. In this manner, the rate of a sample's temperature increase is so slow that the rate of the sample's weight decrease becomes high. (The heating rate is controlled to be decreased as the weight loss occurs promptly.)

Consequently, the weight decrease rate (first derivative of TG signal) and the derivative of the weight decrease rate (second derivative of TG signal) are successively computed, and the heating control is carried out according to the following equation:

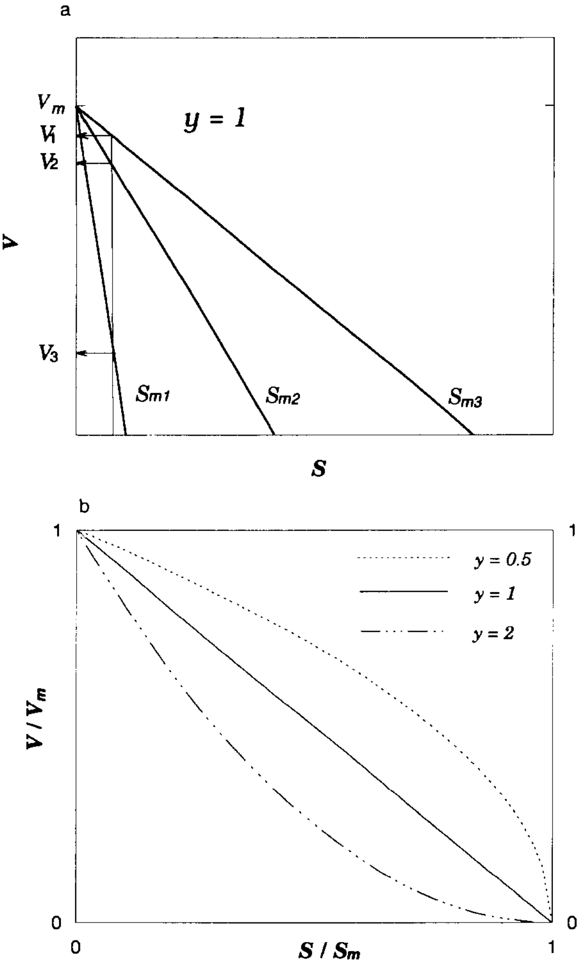

Fig. 1. (a) The influence of S_m value on heating rate at $y = 1$ in Eq. (1) $S_{m1} < S_{m2} < S_{m3}$. (b) The influence of y on the heating rate under identical V_m and S_m in Eq. (1).

$$V = V_m[(S_m - S)/S_m]^y \tag{1}$$

Here, V is the heating rate dT/dt, V_m is the maximum heating rate, S is the weight change rate dw/dt. Also S_m is the set value of the weight decrease rate which decides the relative derivation with S.

The graphic representations of Eq. (1) are shown in Fig. 1a,b. The influence of the S_m on the heating rate at exponent $y = 1$, is shown in Fig. 1a. The value of V becomes small with increasing amount of S when the S_m is set at a small value under an identical V_m. Therefore, the S_m acts as a sensitivity coefficient of V against the value of S. The influence of exponent y on the heating rate under the V_m and S_m values is also shown in Fig. 1b, where the vertical and the horizontal axis are expressed with the normalized V/V_m and the S/S_m, respectively. The relation is a linear curve at $y = 1$. The relation shows a convex quadratic curve at $y = 2$ and a concave curve at $y = 0.5$. Thus, when y is larger than 1.0, the slope of the curve grows large as the weight decrease rate becomes small. In the reverse, when y is smaller than 1.0, the slope of the curve grows large as the weight decrease rate becomes large.

The exponent y acts as a local sensitivity coefficient of V against S. On the other hand, for the physical meaning of Eq. (1), when S is zero (i.e. sample weight does not change), V is exactly equal to V_m. The value of V becomes small with increasing value of S, and when S equals S_m, V becomes zero, and whereupon the heating control changes to isothermal.

Generally, S_m is set to a value which S must not exceed. If $S > S_m$, formally V leads to negative, the actual control is maintained isothermally.

This temperature control equation is only available for weight loss rate in the decreasing direction and moreover in the condition of $S < S_m$.

The each physical quantities used in this method were the optimum values for $S_m = 2 \times 10^{-6}$–4×10^{-3}% min^{-1}, and $y = 0.1$–3.0.

3. Experimental

3.1. Sample

The sample of polyimide/polytetrafluoroethylene/graphite resin (PI/PTFE/GR, Vespel SP-211) used in this study was supplied from DuPont Co., Ltd. as commercial grade material. The sample of about 20 mg was heated in a platinum pan from ambient temperature to 700°C in an inert helium atmosphere with a dry flow rate of 100 ml min^{-1}.

3.2. High resolution TG system

A Rigaku dynamic TG-DTA 8110D thermogravimetry (main body of differential thermobalance)/differential thermal analysis module was used to measure the weight loss profile. A schematic diagram of the dynamic TG-DTA installation is shown in Fig. 2. The dynamic TG-DTA 8110D can use both standard (constant heating rate) and high-resolution modes, in which the heating rate of the sample is dependent on the rate of sample weight loss. The furnace responsiveness is quite important to give the precise temperature measurement and to rise the separation ability. For the purpose of a very fast heating response, an infrared image furnace unit was used instead of a conventional type which utilizes relatively high heat capacity and resistivity heater. In the present unit, one sensor only attached directly to the sample controls the heating and cooling rates, and measures the temperature. Also this furnace can be heated (and cooled) at a precise heating rate from the conventional values of 0.5–20°C min^{-1} to a much higher speed up to 100°C min^{-1}. This combined ability of measuring the sample temperature directly and using the same sensor for precise control of the furnace heating and cooling rates allows thermoanalytical studies to be undertaken in the high-resolution mode as well as normal standard mode. The weight change signal detected at the TG control circuit is fed back to

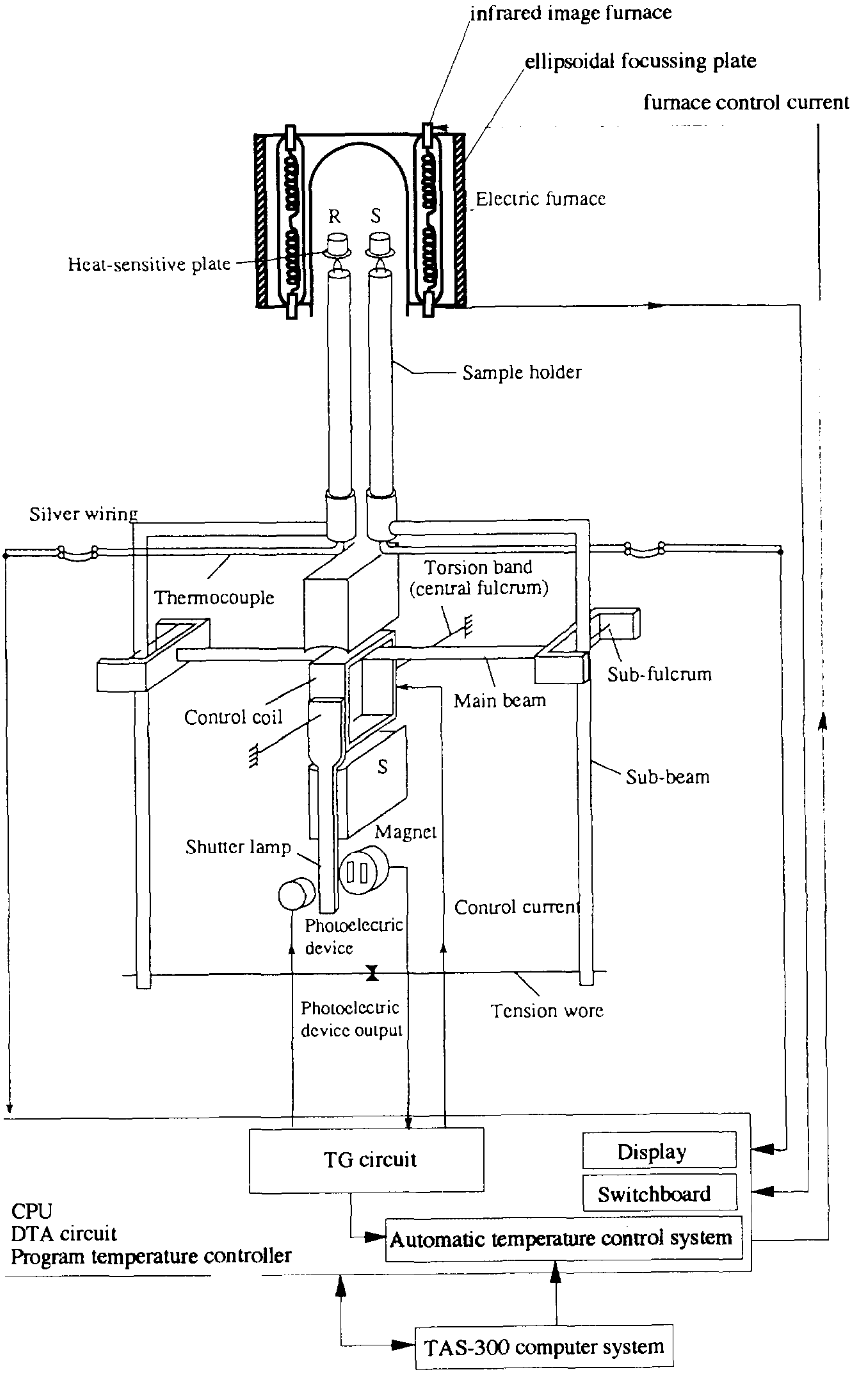

Fig. 2. Schematic diagram of dynamic TG-DTA system.

an automatic temperature control system. Here, the heating rate signal according to the control parameters from the CPU is calculated in succession, and is supplied as a control current to the infrared image furnace.

3.3. TG-DTA/GC-MS system

The dynamic TG-DTA was connected with a Hewlett Packard GC-MSHP5890-5971A gas chromatography/quadrupole mass spectrometer using a Rigaku TG-MS interface to create an integrated simultaneous TG-DTA/GC-MS system. The simultaneous TG-DTA/GC-MS configuration is shown schematically in Fig. 3. The purge gas/product mixture is drawn into the alumina tube and passes to the GC-MS via a stainless steel tube whose internal surface is inactivated. This alumina tube extends from the vicinity of the sample pan into the top of the protection tube and is connected to the "T" piece which is sealed with graphite ferrule at the one end. The stainless steel transfer tube is maintained at 250°C to prevent condensation, and the inactivating minimizes adsorption, corrosion, or catalytic degradation of sensitive organic species. Introduction of carrier gas from the upper part of the protection tube around the measuring sample and a gas sampling system with a small inner diameter tube minimizes the dilution of the products with the purge gas and increases the sensitivity of detection. The amount of TG effluent allowed into the splitter is controlled by a micro-metering needle valve in the purge gas line.

Our original TG-MS system can be used for two kinds of interface modes. They are distinguished between continuous sampling (direct coupling mode) and intermittent sampling (trap coupling mode). In a direct coupling mode, the evolved degradation products are immediately carried off with a helium flow gas from the thermobalance into the MS unit for "on-line" analysis. The signal representing the concentration of products in the purge gas stream are continuously recorded with the TG-DTA signal as a function of

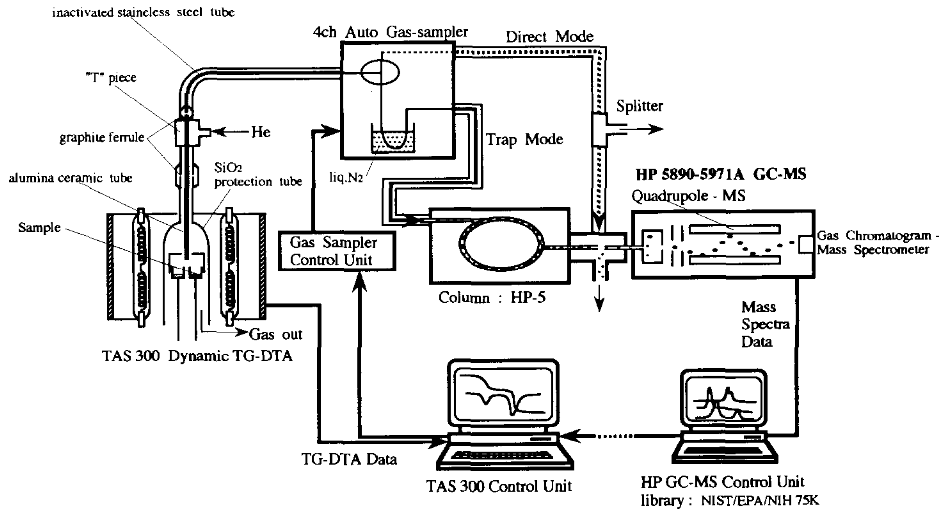

Fig. 3. Schematic diagram of a simultaneous TG-DTA/GC-MS installation.

time or temperature. Depending on the regulated split amount and length of the transfer line between the thermobalance and the ionization chamber of the MS, the transfer time was estimated to be typically less than 1 s. In the trap coupling mode, a portion of the analysis is "off-line". In this case, more frequent sampling is realized with an autosampler controlled at arbitrary temperatures, and this is possible by switching a series of four trap tubes cooled at liquid nitrogen temperature. Each evolved gas component in the trap tubes is rapidly heated from liquid nitrogen temperature to 250°C and then introduced to GC/MS. The use of the GC separation technique was required to evolve the complex products at several stages. Separation of the degradation products was achieved using a fused silica capillary column (25 m × 0.2 mm i.d.) coated with immobilized methylphenylsilicone (5% phenyl) supplied from Hewlett-Packard, temperature programmed from 50 to 280°C at a rate of 10°C min^{-1}. Peak identification was primarily carried out by the GC-MS system in electron ionization (EI) mode. A library search compared the spectrum of an unknown compound against a library of reference spectra using the NIST/EPA/NIH chemical structures database.

4. Application

PI/PTFE/GR resin has the most excellent thermostable and abrasion-resistance among the high-functional resins, and the resin is widely used for spacecraft, aircraft, motorcar, electrical and electronic materials.

Fig. 4 illustrates a comparison of weight loss curves for PI/PTFE/GR resin using conventional TG at 20°C min^{-1} with high resolution TG (DRC method). The sample is

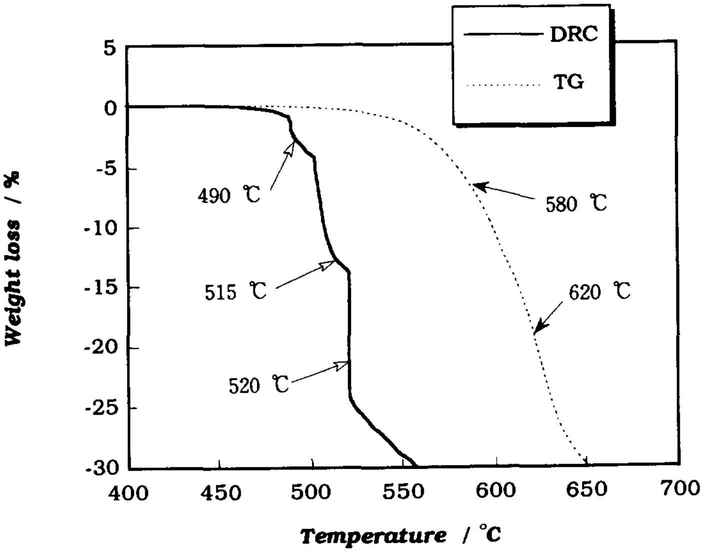

Fig. 4. Comparison of weight loss curves for PI/PTFE/GR resin using conventional TG of 20°C min^{-1} with the DRC method.

Table 1

Comparison of temperatures between the conventional TG and DRC method on the same weight loss values for PI/PTFE/GR resin

Weight loss /%	Temperature T_c /°C conventional mode (20°C min^{-1})	Temperature T_d /°C DRC mode	Temperature difference $T_c - T_d$/°C
5	577.4	502.9	74.5
10	597.4	507.6	89.8
15	611.5	521.1	90.4
20	622.5	521.1	101.4
25	631.4	523.6	107.8
30	648.0	556.2	91.8

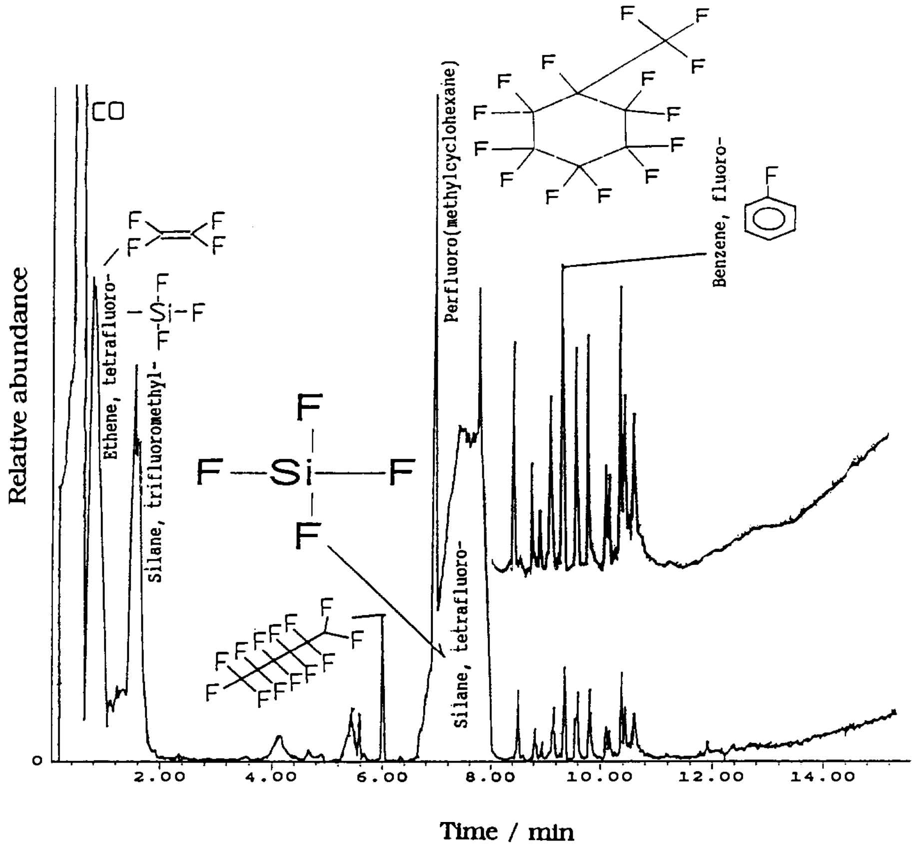

Fig. 5. Conventional TG/GC/MS pyrogram of decomposition components at 580°C on a heating rate of 20°C min^{-1}

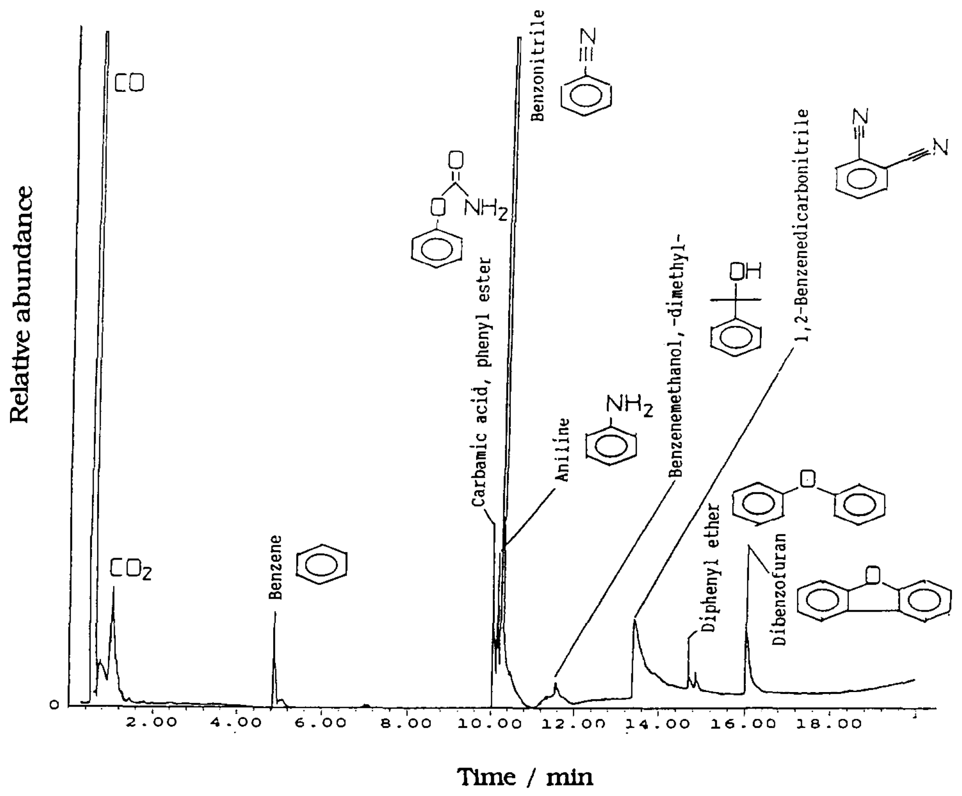

Fig. 6. Conventional TG-GC/MS pyrogram of decomposition components at 620°C on a heating rate of 20°C min^{-1}.

gradually and continuously decomposing between 450 and 650°C under conventional conditions. It is suggested that the analysis of this sample with conventional TG does not have clearly resolved decomposition processes. On the other hand, the resolution of weight loss is improved with the DRC method. Here it is worth noting how greater resolution and detail is achieved in the decomposition profile with the DRC method compared with the conventional method. Particularly, between 450 and 520°C, clear decomposition steps are evident in the DRC curve. Also, the effect of applying the DRC method is significant in the DRC curve and the effect of applying the DRC method is to cause significant decomposition steps at lower temperatures and over narrower temperature ranges than conventional TG. For these reasons, the ability of DRC to resolve clearly the different steps in multi-step processes is generally much better than conventional methods.

The results show that the sample begins to lose weight from around 450°C, however, when the temperature presented at identical weight loss values are compared between both measurements, a big difference was obtained between two experimental results. Table 1 shows the comparison of temperatures between conventional TG and the DRC

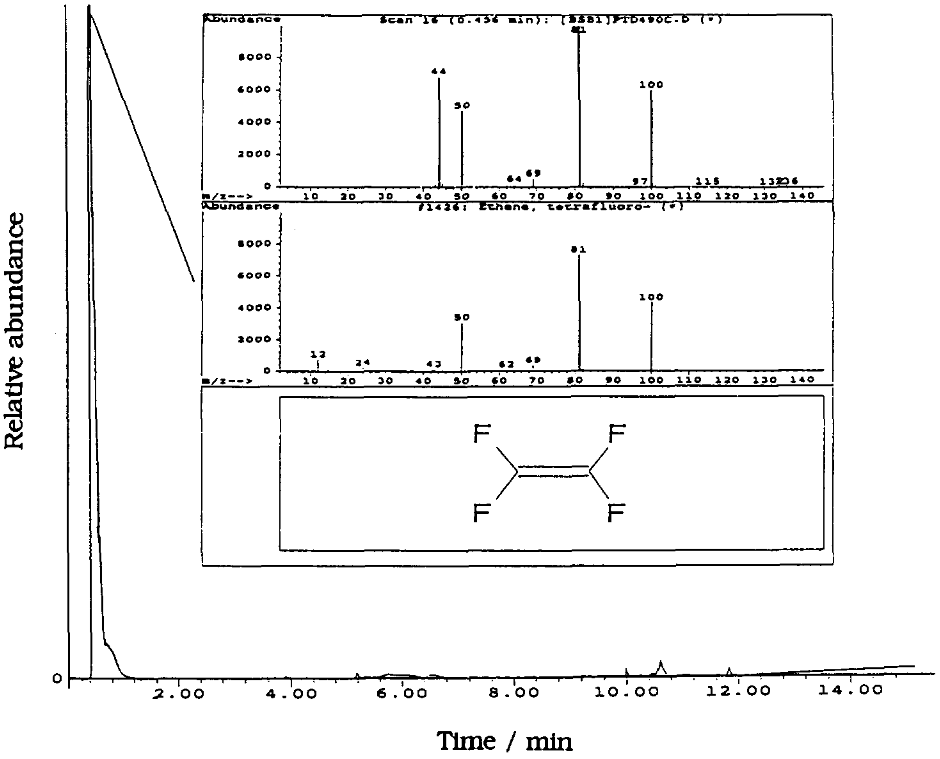

Fig. 7. High resolution TG/GC/MS pyrogram of decomposition components at 490°C.

methods on the same weight loss values. From these results, the temperature difference between two measurements is more than 50°C at 5% weight loss, and reached a maximum of 107.8°C at around 25% weight loss. This result is particularly interesting from the viewpoint of thermal stability which is related to process conditions and the end-use of the material.

On the other hand, it is supposed that the improved resolution of successive weight loss curve is related to a potential effectiveness to quantify and identify the evolved decomposition gases by MS. Figs. 5 and 6 show the conventional TG-GC/MS pyrograms for the decomposition components collected at 580 and 620°C, which are decided by a DTG curve with linear heating rate. As seen in Fig. 5, a number of peaks of the major components such as tetrafluoroethylene, silane compounds and fluorobenzene are observed. These low boiling components before 9 min are expected to be formed mostly from the PTFE group. In the pyrogram in Fig. 6 characteristic aromatic components such as benzene, benzonitrile and aniline are observed and these components are expected to be formed mostly from the PI group. Especially in Fig. 5, numerous peaks of unknown compounds are observed after 9 min.

On the other hand, Figs. 7–9 show high resolution TG-GC/MS pyrograms for decomposition components collected at 490, 515 and 520°C, respectively. These are easily

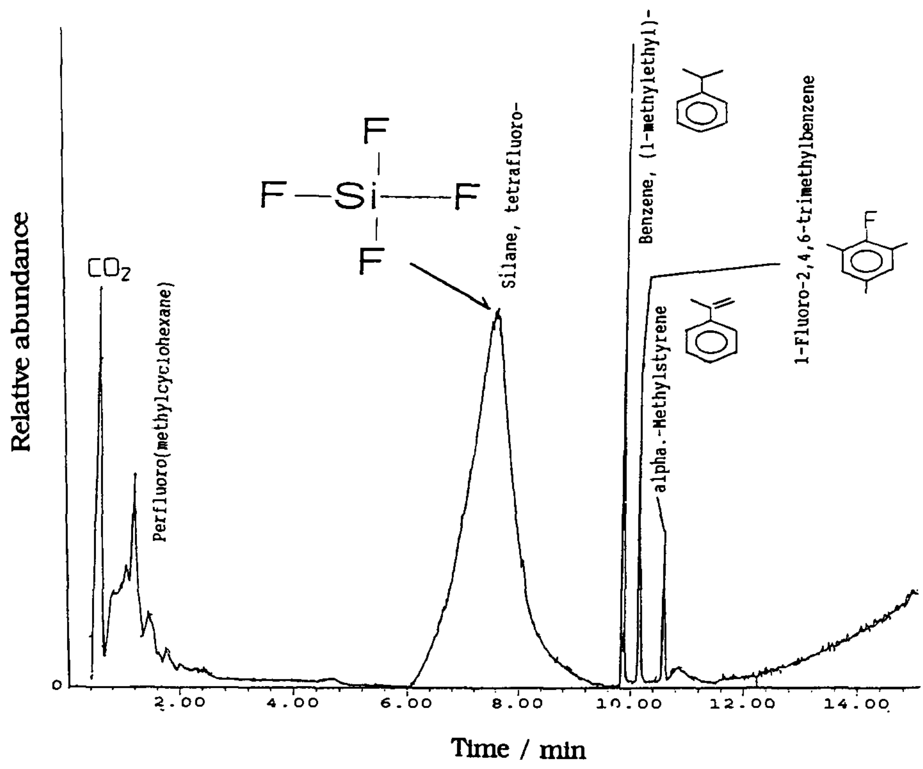

Fig. 8. High resolution TG/GC/MS pyrogram of decomposition components at 515°C.

identified because of the well-defined and simple steps. From these results, only tetrafluoroethylene is observed as the major component at 490°C. Similarly tetrafluorosilane at 515°C and aromatic compounds involving oxygen and nitrogen at 520°C are detected as major components.

Consequently, it is shown that thermal decomposition of PI/PTFE/GR resin occurred from the PTFE portion at first, and subsequently the PI portion. In an intermediate temperature region, both decompositions proceeded simultaneously. With conventional TG-GC/MS, since the sample is exposed to higher temperature than that required for decomposition to each component, analysis of the evolved gases is further complicated. However in high resolution TG-GC/MS, since the decomposition components on clearly separated steps are expressed as a simple profile, analytical treatment becomes easy and improvement of accuracy in identification and quantification is accomplished.

5. Conclusions

Using high resolution TG-GC/MS, we have found interesting effects in the study of

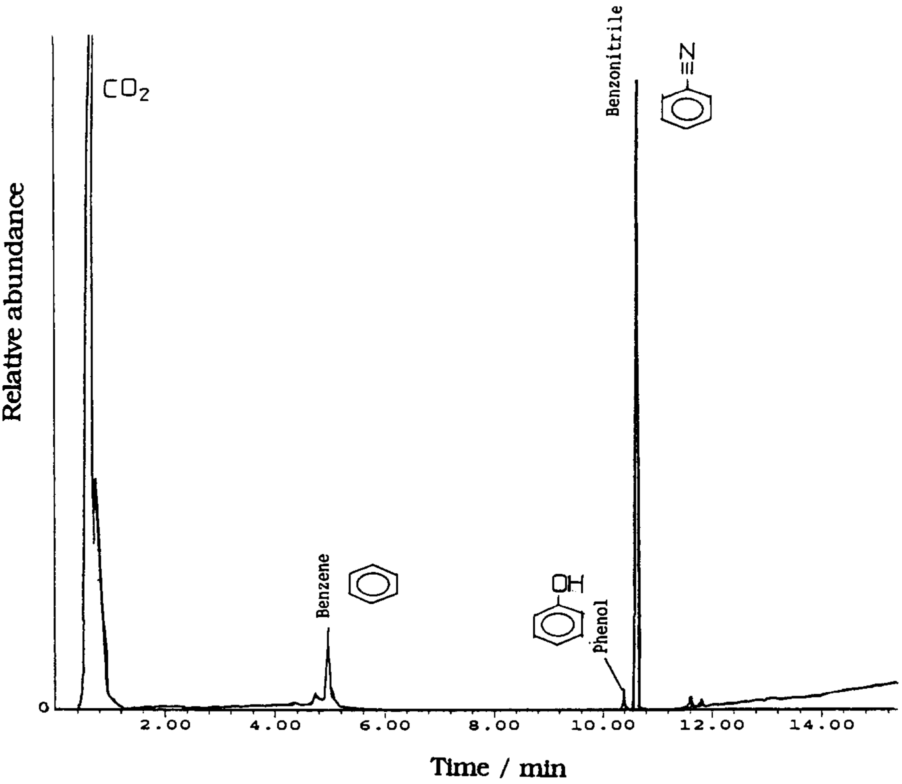

Fig. 9. High resolution TG/GC/MS pyrogram of decomposition components at 520°C.

thermal decomposition of polymeric compounds and this method has yielded more detailed information than that obtained from conventional TG-GC/MS. The information present is accurate regarding composition along with thermal stability. The enhanced resolution aids in characterizing decomposition processes as well as for identification and quantification of complex materials and serves for R&D activities as a thermoanalytical tool.

In summary, the high resolution TG-GC/MS seems to provide a number of advantages. (1) In the present high resolution TG technique, the heating rate of the sample is dynamically and continuously varied in response to changes in the sample's decomposition rate. Additionally, the temperature increase is controlled to stop when the decomposition of a component of the sample is completed. (2) Accordingly, each component of the sample decomposes separately and completely without being affected by the decomposition of other components. (3) Secondary reactions between the decomposed gaseous products become limited. (4) Then, by the effect of reducing the number of peaks in high resolution TG-GC/MS profiles, analytical treatment becomes easy and the decomposition mechanism is clearly elucidated.

Acknowledgements

The authors wish to thank Mr. T. Kanaya, Mr. A. Kishi and Mr. K. Akiyama of Rigaku Co. for direction and suggestions for developing the instrument.

References

[1] J.J. Morelli, J. Anal. Appl. Pyrol., 18 (1990) 1.
[2] C. Dossi, A. Fusi and R. Pasvo, Thermochim. Acta, 236 (1994) 165.
[3] F. Paulik and J. Paulik, Thermochim. Acta, 100 (1986) 23.
[4] O.T. Sorensen, Thermochim. Acta, 138 (1989) 107.
[5] J. Rouquerol, Thermochim. Acta, 144 (1989) 209.
[6] T. Arii, T. Kanaya, A. Kishi and N. Fujii, Netsu Sokutei, 21 (1994) 151.