3. Coupled Techniques in Thermal Analysis

- Coupled Techniques in Thermal Analysis as Evolved Gas Analysis (EGA)
  - TG/FT-IR
    - Technique for analyzing gas evolved from TG with FT-IR
  - TG/MS
    - Technique for analyzing gas evolved from TG with MS
  - TG/GC/MS
    - Technique in which gas evolved from TG is trapped and analyzed with GC/MS

We introduce here the third new Thermal Analysis technique, Coupled Technique.

In Coupled Techniques, an EGA device connected to a TG analysis device is commonly used. Three types of evolved gas analysis used are FR-IR (Fourier Transformation-Infrared Spectrometry), MS (Mass Spectrometry) and GC/MS (Gas Chromatography/Mass Spectrometry).

TG Coupled System Comparison

		FTIR	MS	GC/MS
Real-time Measurement		Yes	Yes	No
Detection Sensitivity		Normal	High	Extremely high
Measurement Object		All evolved gasses	Partial (Split gasses)	Partial (Trapped gasses)
Identification of evolved gas	Mixed gas with low molecular mass	Yes (except IR inert gasses)	Yes	Sometime difficult (Requires gas collector)
	Mixed gas with high molecular mass	Yes (Identification at peak position)	Difficult (Complicated by secondary resolution by ionization)	Yes (Suited for separation detection, high accuracy)
Carrier gas		No restrictions	He	No restrictions
Interface		Gas line and gas cell	Gas line maintains vacuum in ionization chamber	Gas trap mechanism and injection mechanism to GC/MS
Overall Assessment		Easily connects and good for screening all evolved gas during heat decomposition	Fit for tracing specific evolved gas when evolved gas is known	Best for identifying mixed evolved gas during heat decomposition. Good for identifying micro-analysis for evolved gas (i.e. additives) during heating

The above table shows comparison of TG coupled system by evolved gas analysis techniques.
Real time measurements of evolved gas analysis in TG/FT-IR and TG/MS are possible, but it is not possible with TG/GC/MS as evolved gas is trapped.
There are few measurement restrictions for TG/FT-IR can be used relatively easily. Also, if the evolved gas is a mixed gas, identifications can be made with functional groups. However, detection sensitivity is generally low compared to MS and GC/MS.
In TG/MS, interface between the atmospheric TG and the high vacuum MS is necessary. He is good as carrier gas but depending on the MS, measurement in air is possible. Detection sensitivity of evolved gas is relatively high but if the evolved gas has a complex compound then analysis is difficult.
TG/GC/MS traps evolved gas and detects separately with GC/MS, so mixed gasses can be detected separately and sensitivity is high. However, detection gas sensitivity depends on the evolved gas trapping, GC/MS injection method. As the information amount is high, analysis takes time as well.

2. New Thermal Analysis Techniques

TG Coupled System's Application Fields

	Microscopic evolved gas analysis during heating of various materials	Evolved gas analysis during heat decomposition of various materials
Environmental Fields	Analysis of odors and poisonous gas that evolve from products and parts, analysis of odor and poisonous gas in parts assembly.	Evolved poisonous gas during combustion
Material Development	Small additives, non-reacting material analysis, competitor product composition analysis	Decomposition mechanism and structure analysis
Quality Control (Claims)	Added impurity between lots, check at shipping time.	

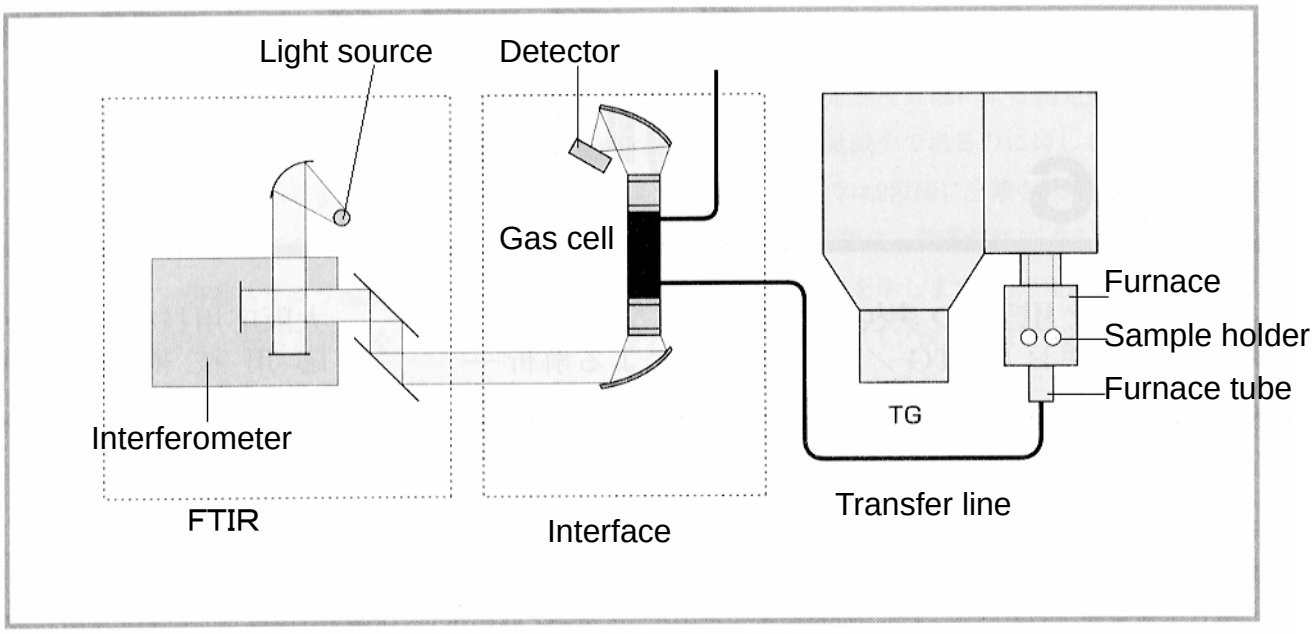
The above table provides an overview of TG Coupled Systems' application fields.

Measurement objects for TG Coupled System can be divided largely into evolved gas analysis with heat decomposition in materials and small evolved gas analysis during material heating.

In environment-related fields, analysis of small evolved gas during material heating can be applied to analysis of odors from products and parts, poisonous gasses, and odors and poisonous gasses during parts building. In material development, it can be applied to small additives, non-reactive material analysis and competitor product composition analysis. And in quality control, it can be used to identify added impurities between lots, and to determine whether products can be shipped.

Thermal decomposition analysis can be applied to evolved poisonous gas in combustion and analysis of thermal decomposition structure and construction.

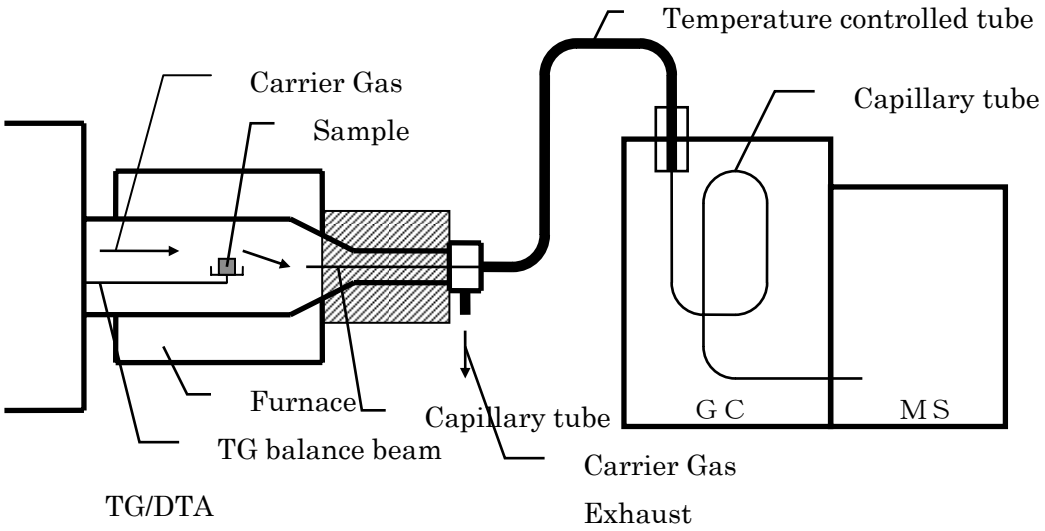
TG/FT-IR Structure



The above diagram shows an example of a TG/FT-IR system structure.
Heated gas cell is installed in the light path of the FT-IR as the connection interface, and the evolved gas from TG is sent to the gas cell through the heat controlled transfer line. Carrier gas, which is blown into TG, is used for the evolved gas flow.
FTIR measures IR spectrum of the gas content simultaneously as TG measurement.[*1] [*2]
For the gas cell and transfer line does not condense during the process, and temperature is set where heat decomposition does not occur. Generally, 200ºC to 300ºC is selected.

[*1] R. Kinoshita, Y. Teramoto, T. Nakano and H. Yoshida, J. Thermal Anal., 38, 1891 (1992)
[*2] R. Kinoshita, Y. Teramoto, H. Yoshida, Netsusokutei, 19 (2), 64 (1992)

TG/MS Structure



The above shows an example of a TG/MS system structure.

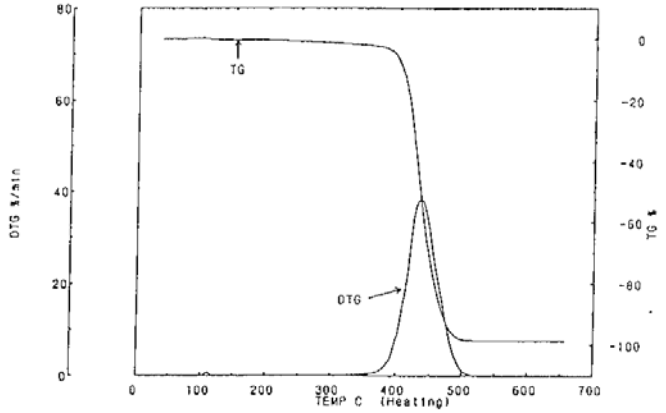
While MS measures in high vacuum, evolved gas from TG occur in the atmosphere. In the above example, a capillary tube of appropriate length and inside diameter is used as the interface that connects to this system.

One end of the capillary tube connects to the ionization chamber of the MS and the other end is placed around the sample inside the TG. The vacuum emission sends the evolved gas is directly into the MS ionization chamber. [*1]

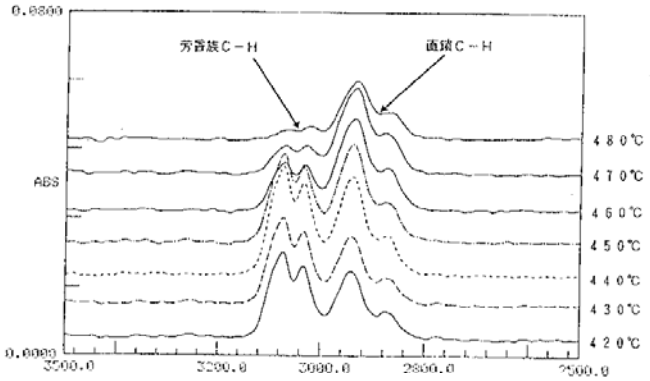
Capillary tube protects the evolved gas from condensation and goes through the transfer tube that is kept warm.

[*1] R. Kinoshita et al., J. Mass Spectrom. Soc. Jpn., 46 (4), 365 (1998)

Measurement Data of TG/FT-IR



TG/DTA curve of ABS



FTIR spectrum of ABS decomposition gas

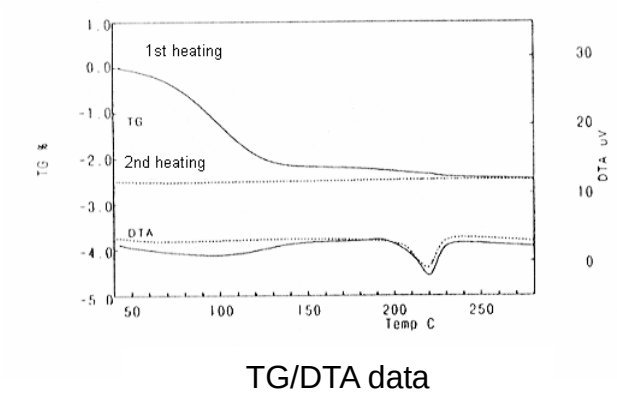
The above figures show a measurement data of TG/FT-IR.

The sample is ABS (acrylonitrile butadiene styrene) resin, commonly used in home appliances, and measures heat decomposition in nitrogen. The top is the TG curve and you can see that decomposition starts at around 400ºC and completes at around 500ºC. The bottom shows the IR spectrum of the evolved gas at each temperature during decomposition. The peak from 2800cm^{-1} to 3000cm^{-1} occurs due to linear C-H, and peak above 3000cm^{-1} occurs due to aromatic series C-H. The first half of the decomposition, up to about 460ºC, absorption of aromatic series C-H is seen and after that, absorption of only linear C-H is seen. Absorption of aromatic series C-H is thought to be due to styrene, and linear C-H absorption is due to butadiene. This suggests that styrene decomposes in the first half of the thermal decomposition and butadiene decomposition occurs in the second half. [*1]

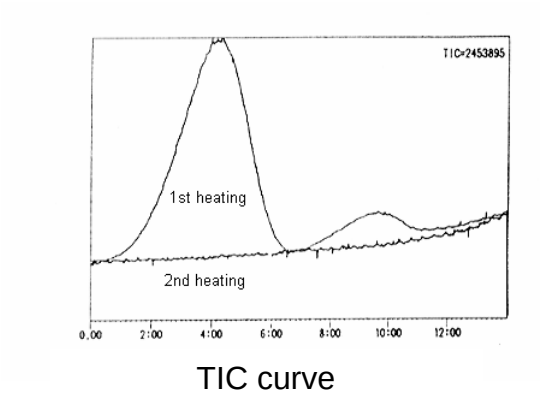
ABS resin is generally made with AS resin graft-polymerized onto butadiene latex, and structurally, butadiene latex is scattered inside AS resin, resulting in the decomposition behavior seen above.

[*1] SII NanoTechnology Application Brief TA-66 (1995)

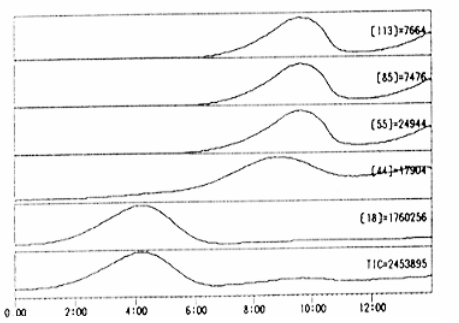
Measurement Data of TG/MS



TG/DTA data



TIC curve



MS curve with time change

The above shows a TG/MS measurement data.

The sample is nylon 6 and the sample shows a measurement of small evolved gas when heated. Nitrogen was blown, and temperature was programmed twice up to 280ºC where nylon dissolution completed.

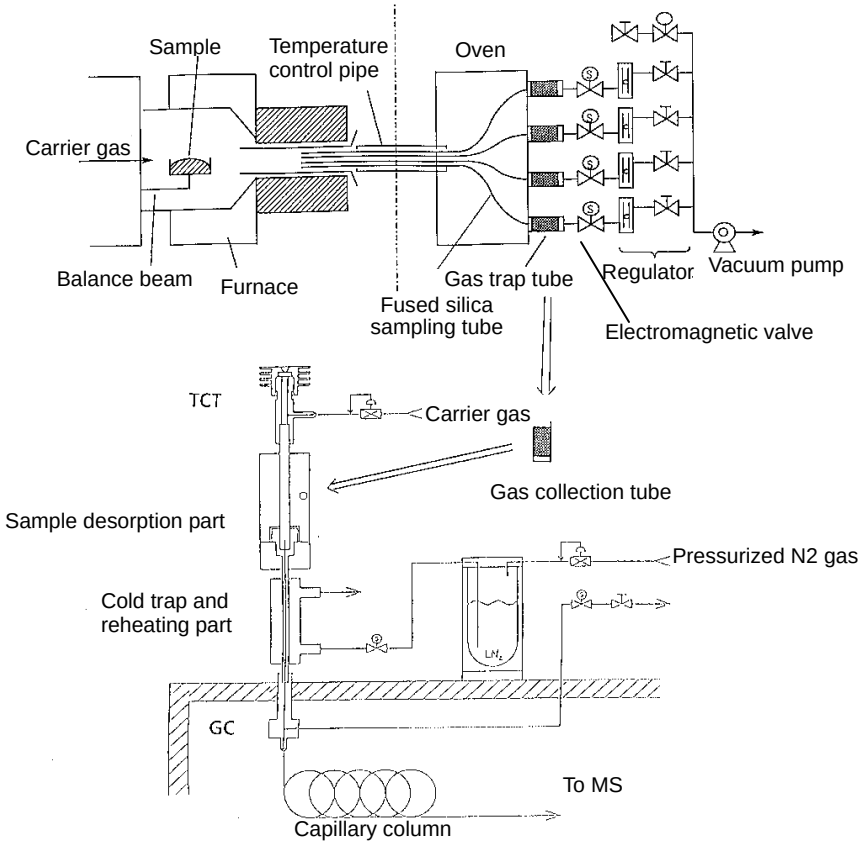
On the left TG/DTA data, the mass reduction that occurs at the first heating at around 100ºC was identified as mass-18 water with MS. The mass reduction that corresponds with melting peak (220ºC) on the DTA data was identified as caprolactam after MS spectrum library search. [*1]On the other hand, in the second heating, neither mass reduction nor gas evolving is observed until melting is complete at 250ºC.

Therefore, the water which was detected in the first heating was the absorption water in the nylon. Caprolactam was residual monomer in the nylon that was ejected with melting.

On the other hand, as gas evolving in caprolactam can be seen at the end of heating, nylon's partial decomposition begins after melting.

[*1] R. Kinoshita et al., J. Mass Spectrom. Soc. Jpn. 46 (4), 365 (1998)

Structure of TG/GC/MS



The above shows a TG/GC/MS system structure.

TG/GC/MS traps the evolved gas from TG, and then induce it into GC/MS to analyze.

The above example shows a gas trapping method that uses a gas trap tube. Analysis is conducted with GC/MS after gas is trapped and the trap tube is placed in the dedicated induction system.

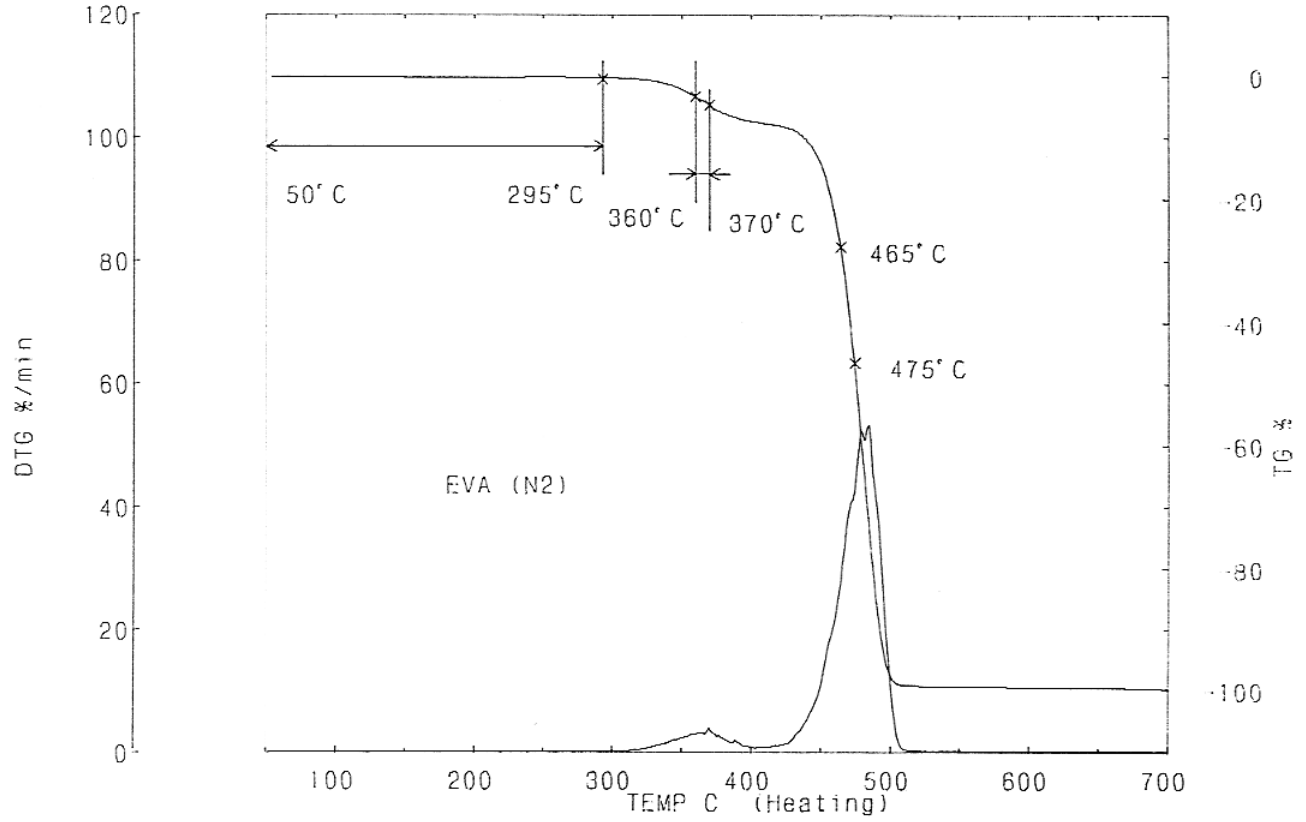
By aspirating gas through the inactive capillary tube to collect evolved gas, adsorption and deterioration of the evolved gas are prevented and the optimal amount of gas for GC/MS analysis is trapped.[*1]

Also with this system, four collection tubes are installed so gas can be trapped separately at multiple temperature regions.

Other trapping methods include simply cooling in the middle of the gas path.

[*1] Japanese Patent #2596882

Measurement Data of TG/GC/MS



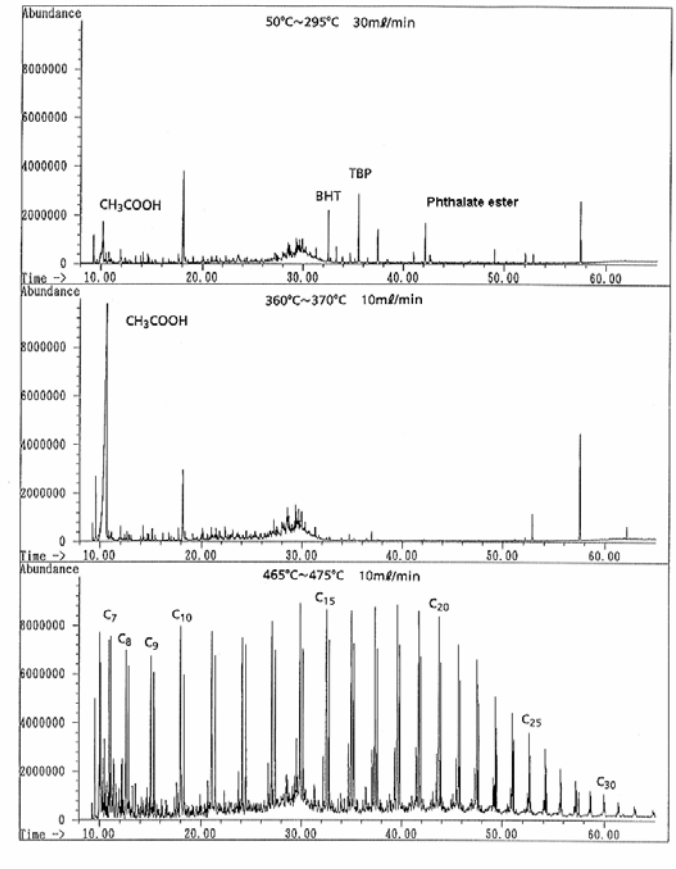
This is data of a TG/GC/MS measurement.

The above shows TG/DTA data from a measurement of commercially available ethylene-vinyl acetate (EVA) copolymer resin in nitrogen.

In TG, mass reduction is observed at two steps, at around 300ºC and over 400ºC.

To analyze with GC/MS, gas trap was conducted at three points, before decomposition started at 295ºC, the first decomposition from 360ºC to 370ºC and the second decomposition from 465ºC to 475ºC.

Measurement Data of GC/MS



The above diagram shows the results of GC/MS analysis of collected evolved gas and the gas chromatograph of each collected gas.

The top is the gas chromatograph of the evolved gas before decomposition.

Even before decomposition, antioxidant BHT, plasticizer TBP, phthalate ester and traces of acetic acid are detected as evolved gas. *1

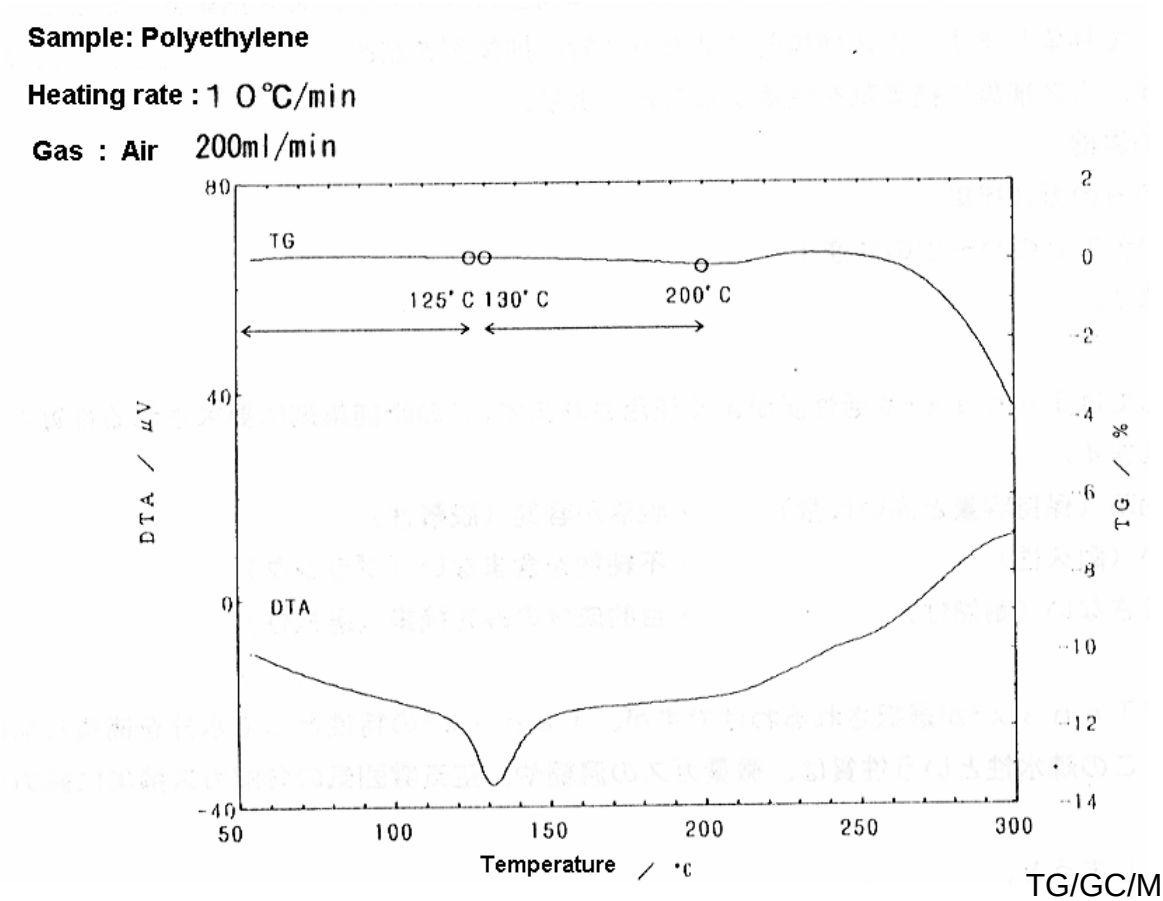
The second and third gas chromatographs represent the evolved gas from the first and second decompositions, respectively. In the first decomposition, mainly acetic acid, and in the second decomposition, carbon hydride of various carbon numbers are detected.

In the first decomposition, acetoxyl from vinyl acetate is severed and acetic acid evolves, while in the second decomposition, the residual structure left by the acetic acid undergoes thermal decomposition and this is thought to result in the evolving of carbon hydride of various carbon numbers.

*1 Ryoichi Kinoshita, Yoshiyuki Takei and others, The 29th Japan Thermal Analysis Conference Summary, 32(1993)

2. New Thermal Analysis Techniques

Analysis of Gas Evolved from PE



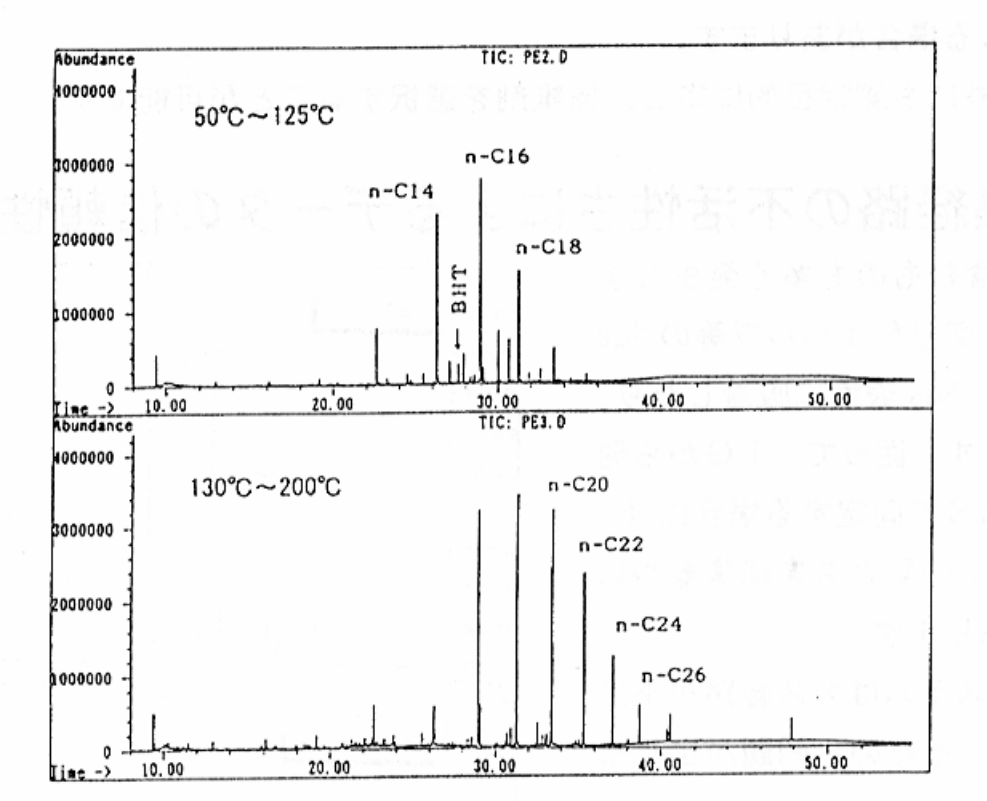
TG/GC/MS

When system with TG/DTA connected to MS or GC/MS is used, evolved gas and thermal decomposition during heating can be observed in various materials.

The above shows the result of commercially available polyethylene wrapping film measured with TG/DTA. A peak due to melting can be observed at 131ºC on the DTA curve, but mass change is not observed on the TG curve until around 200ºC. Above 200ºC, mass increase due to oxidation, followed by mass decrease due to decomposition are observed.

So evolved gas was trapped at temperature range before melting, 50ºC to 125ºC, the temperature range after melting and before oxidation, 130ºC to 200ºC, and the result of GC/MS analysis is shown on the next page.

Analysis of Gas Evolved from PE



TG/GC/MS

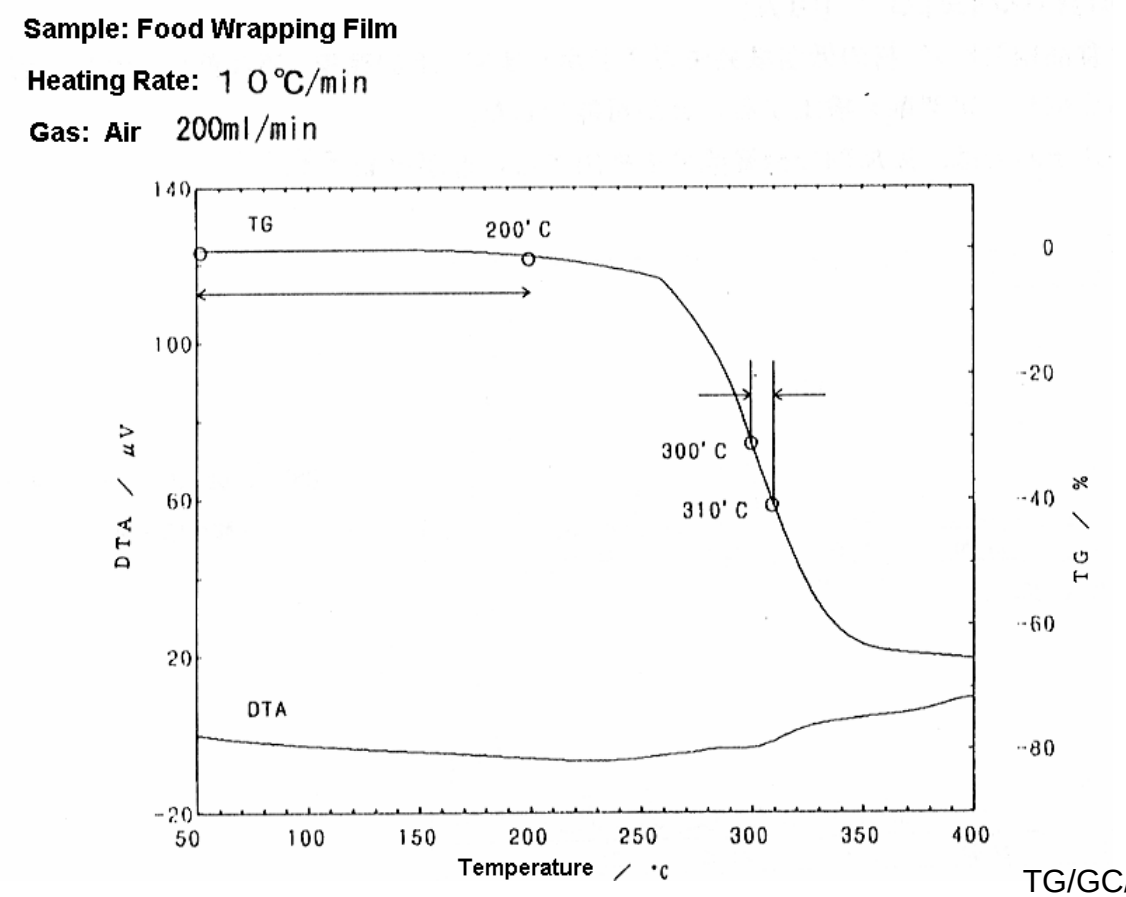
The above shows the result of GC/MS analysis of evolved gas trapped at 50ºC to 125ºC, and at 130ºC to 200ºC. [*1]

In either case, the main component of the evolved gas is linear carbon hydride, with only even carbon numbers. This suggests that the evolved gas is the occurrence of residual oligomer that did not become polymer at the temperature ranges.

When the evolved gas from before and after melting were compared, there were carbon hydride with higher carbon numbers after melting and they evolved starting with those with the lowest boiling point and evolving in order. Also, in the evolved gas before melting, antioxidant BHT is detected, but not after melting. BHT is thought to be an additive in the film and completes evolving before 125ºC.

*1 Yutaka Ichimura and Yoshiyuki Takei, “Netsubunseki”, 22(3), 193 (1995)

Evolved Gas from Food Wrapping Film



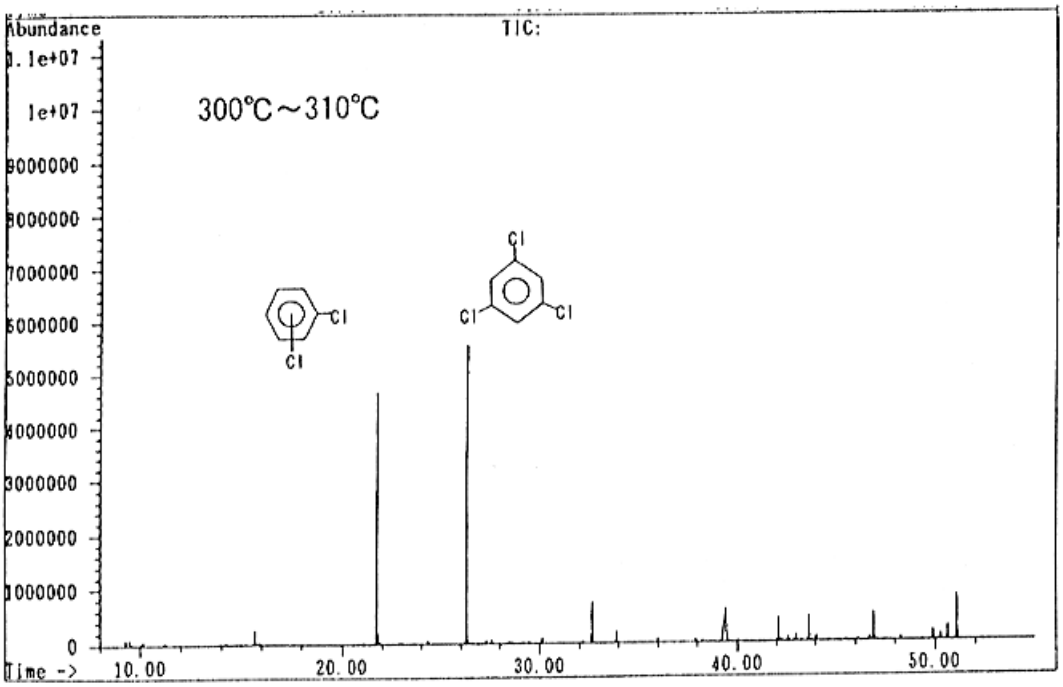
TG/GC/MS

The above data shows the TG/DTA data from a measurement of evolved gas in vinylidene chloride food wrapping film.

No major peak was observed in the DTA curve and very little change is observed in the TG curve until around 200ºC. Weight loss is observed from around 250ºC due to decomposition.

So evolved gas was trapped in the temperature range up to 200ºC and during decomposition from 300ºC to 310ºC, and then analyzed with GC/MS.

Evolved Gas from Food Wrapping Film



TG/GC/MS

The above data is the GC/MS analysis result of evolved gas during decomposition from 300ºC to 310ºC. The evolved gas is a chlorbenzene gas and can be the origin of dioxin, which has recently been spotlighted as a problem.