

## 1) Analysis of Polyester by a Combination of Curie-Point Heating Techniques and Preparative Liquid Chromatography

Naoki Oguri , Akira Onishi , Sigeki Uchino , Keiji Nakahashi And Xigao Jin *Japan Analytical Industry Co., Ltd., 208, Musashi Mizuho, Nishitama, Tokyo 190-12, Japan*  
*Institute of chemistry, Chinese Academy of Sciences, Beijing, 100080, China*

A Curie-point heating technique has already been introduced to pyrolysis-gas chromatography, which was developed by us. We analyzed the component of a multi-component polyester completely by using a combination of the technique and preparative HPLC. We used Curie-point pyrolysis-GC/MS, direct injection/MS, headspace-GC/MS and preparative HPLC for this study. We could thus determine the composition of the uncured polyester for manufacturing man-made marble consisting of an uncured polyester prepolymer, a crosslinking accelerator, an acrylate copolymer as the modification agent and some additives (Surfactant and plasticizer). This analytical method is an available, convenient way for compositional analysis of complex Polymers materials.

**Keyword** Curie-point pyrolysis, Curie-point direct injection probe, headspace gas chromatography, mass spectrometry, preparative liquid chromatography, polyester

Pyrolysis gas chromatography-mass spectrometry (Py-GC/MS) has recently become popular for polymer analysis owing to its simplicity and capacity for providing important compositional and structural information, especially regarding multi-component materials. One of the advantages of this method is that all compositions of the polymer(s), and additive(s) employed in the material can be investigated without any pretreatment.<sup>1,2</sup> On the other hand, headspace-GC/MS is a powerful measurement technique for volatile compounds in solids.<sup>3</sup> Moreover, it is suggested that that data be compared with the Py-GC results for a distinction of volatile components from pyrolyzates on a pyrogram of a multi-component polymer material. An on-line direct injection/MS (DI/MS) technique could separate the pyrolyzates and volatile components of a polymer sample according to the mass on a linear scale with very high sensitivity, it thus enables a rapid analysis with a throughput of up to one sample per minutes.<sup>4,5</sup> For the most complex material system, fractional separation by preparative liquid chromatography is helpful, and sometime necessary, to obtain pure fractions and then identify them individually by Py-GC or pyrolysis-DI/MS in order to determine definite mass data.<sup>6</sup> Due to the high heating speed (less than 0.2s of the temperature raise time), accurate temperature reproducibility ( $\pm 1$  ) and a wide temperature range (160 – 1040 ), the Curie-point heating technique has successfully been applied to Py-GC/MS, DI/MS and headspace-GC/MS.<sup>2,3,7,8</sup> In this work, all of the

measurements mentioned above were used to characterize a multi-component thermosetting polymer system composed by the uncured unsaturated polyester resin, curing agent modification agent and additives.

### Experimental

#### Sample

A set of uncured unsaturated polyester resin (BX-923, Synthetic Resin Co. of Beijing, China) comprised two parts (coded as part A and B), including a prepolymer, reactive monomer, curing accelerator, modification material and additives in the sample. This polymer was mixed with marble powder, and used for manufacturing man-made marble.

#### Apparatus

Pyrolysis or headspace sampling was carried out using a Model JHP-3 Curie-point Pyrolyzer or a Model JHS-100 Curie-point Headspace Sampler (Japan Analytical Industry Co., Ltd.), which was combined with an on-line Model QP-2000A GC/MS system (Shimadzu Co., Japan). The GC/MS was equipped with a high-resolution, fused-silica capillary column (J&W Sci., DB-1, 0.25mm i.d. X 30m) coated with immobilized poly(dimethyl silicone) of 0.25  $\mu$ m thickness, and a quadrupole mass spectrometer with an EI ionization source (70eV). A JD1 800 Curie-point DI Probe (Japan Analytical Industry Co., Ltd.) was inserted in a QP

2000A mass system up to the position where the sample cell (9 mmX2mmi.d.) at the tip of the probe could be connected to the ion source.<sup>8</sup> The sample was wrapped in Pyrofoil with tight contact. The amounts of samples to be injected were less than 2 µg, 0.1 mg and 0.4mg for DI/MS, Py-GC/MS and headspace-GC/MS, respectively. The GC column temperature was initially maintained at 35 °C for 5 min, and then programmed to 300 °C at 8 °C/min. From the carrier gas of helium, 50ml/min was split at a ratio of 50:1. The volatile fractions of the headspace samples extracted at 220 °C for 10 min were transferred to an adsorbent, (Tenax) at -40 °C, and then desorbed at 255 °C for 10s by Pyrofoil with Curie-point heating. A Model LC-908, preparative liquid chromatograph (HPLC) was equipped with the series of columns(GPC) of Model Jaigel-IH and Jaigel-2H and a refractive index detector (Japan Analytical Industry Co., Ltd.). Chloroform was used as the solvent (40kg/cm<sup>2</sup>, 3.8ml/min). The sample size injected was 50 mg in 3 ml of the chloroform.

#### Results and Discussion

##### Resin and its additives

A total ion current (TIC) pyrogram obtained from Py-GC/MS of the uncured resin (part A) pyrolyzed at 500 °C, as shown in Fig.1. The structures assigned to the mass signals of the pyrolyzates are listed in Table 1; the identification was carried out mainly on basis of mass spectral fragmentation patterns. The code numbers of

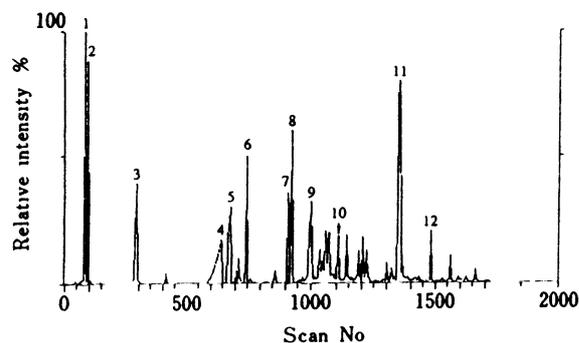
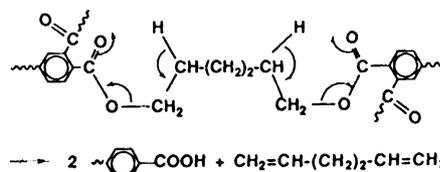


Fig 1 TIC pyrogram of part A obtained by Py GC/MS  
The peak notations correspond to those in Table 1

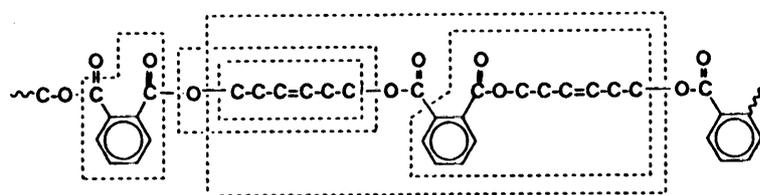
the pyrolyzate peaks in Fig. 1 corresponded to the numbers in Table 1. Peaks 2 and 3 (with shorter retention times) indicate unsaturated hydrocarbon and alcohol derived from the hexylene sequences in the polymer chains. In particular, the *cis*-, *w*-diens are most likely formed through the predominant pyrolysis mechanism involving a cyclic transition state at two neighboring ester linkages for the polyester (Scheme 1<sup>9</sup>). The 1, 5, and 7 peaks correspond to benzene, phthalic anhydride, and cyclohexenyl phthalate, respectively, which were also the main peaks on the pyrogram of the polyester synthesized by phthalic acid and hexenediol.<sup>10</sup> A mostly characteristic pyrolyzate, dihexenyl phthalate as the monomer (peak 11), was reflected on the repeat units of poly(dihexenyl phthalate). The relationship between the polymer structure and the pyrolyzates is summarized in Scheme 2. The presence of phenyl benzoate (peak 8) and polycyclic aromatic pyrolyzates (peak 6, 9 and 10) on the pyrogram of the resin would be caused either by the secondary and tertiary thermal processes of the polyester, or by a thermal decomposition of other aromatic component mixed with the polyester. To distinguish the different conclusions, part A of the sample was separated and collected into two fractions (F-I and F-2), as shown in Fig. 2, by preparative HPLC with high-performance columns; F-I and F-2 were then identified by Py-GC individually. The pyrogram of F-I also showed all of the characteristic pyrolyzates of

Table 1 Pyrolyzates assignments of part A of the sample

1. Benzene	7. Cyclohexenyl phthalate
2. Hexadiene	8. Phenyl benzoate
3. Hexenol	9. Methoxydibenzofuran
4. Benzoic acid	10. Dihydronaphthacene
5. Phthalic acid	11. Dihexenyl phthalate
6. Acenaphthene	12. C <sub>16</sub> aliphatic alcohol



Scheme 1



Scheme 2

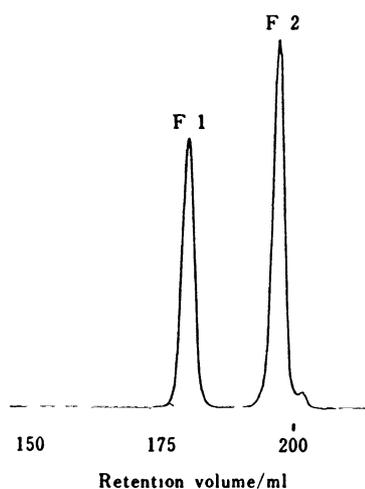


Fig 2 HPLC chromatogram of part A

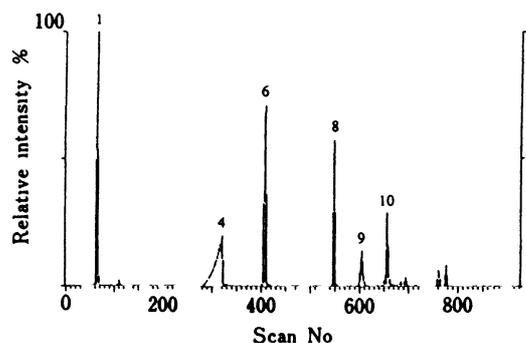
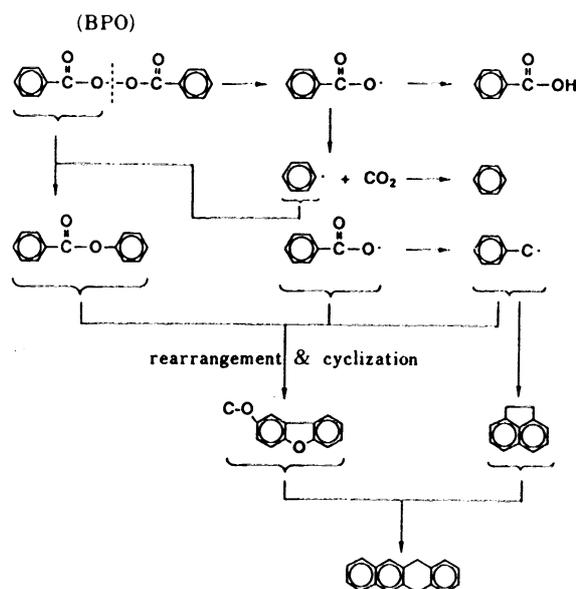


Fig 3 TIC pyrogram of F 2 obtained by Py GC/MS The peak notations correspond to those in Table I

poly(dihexenyl phthalate) and reconfirmed the same results mentioned above. The pyrogram of F-2, performed at a relatively lower temperature of 220 for 3 s, is shown in Fig. 3. The sufficient decomposition of F-2 in a weaker thermal environment indicated that it could be a thermally labile compound. Some of the assigned pyrolyzates of F-1 (see Table I) corresponded to benzoic acid (peak 4) and phenyl benzoate (peak 8) and implied the scission, elimination, and recombination of an aromatic peroxide. A rearrangement of the peroxide with subsequent cyclization to polycyclic compounds (acenaphthene, methoxydibenzofuran and dihydronaphthalene, as peak 6, 9, and 10 on the pyrograms) has also been considered to a significant extent. Summarizing all of this information, F-2 was identified as benzoyl peroxide (BPO), a crosslinking accelerator for the unsaturated polyester. The decomposition mechanism of BPO is shown in Scheme 3. In addition, a broadly exothermic peak with a maximum temperature



Scheme 3

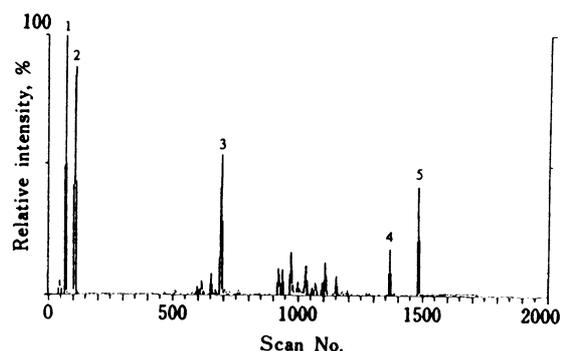


Fig. 4 TIC pyrogram of part B obtained by Py-GC/MS: 1, methacrylate; 2, methyl methacrylate; 3, isohexyl methacrylate; 4, dioctyl phthalate; 5, C<sub>16</sub> aliphatic alcohol.

of 133 was observed in the differential scanning calorimetry (DSC) profile of F-2, which was identical with the thermal decomposition behavior of BPO. Finally, a weaker mass signal (peak 12) with a longer retention time in Fig. 1 indicated the presence of a high aliphatic alcohol in the resin, implying that component as a kind of additives (a surfactant, perhaps).

#### Curing agent and modification agent

Figure 4 shows a TIC pyrogram of part a carried out by Py-GC/MS, pyrolyzed at 500 for 5s, on which some acrylate monomer peaks, methyl acrylate (MA, peak 1), methyl methacrylate (MMA, peak 2) and isohexyl methacrylate (HMA, peak 3), were identified.

As is well known, acrylate polymers and copolymers thermally degrade mainly to the correlative monomers in the absence of oxygen.<sup>12,13</sup> Based on that information, a solid sample of part B was reasonably deduced as being a copolymer of MA, MMA and HMA. Otherwise, peak 4 and 5 on the pyrogram assigned to a high aliphatic alcohol and dioctyl phthalate (DOP) would reflect the thermal volatilization of some additives, which are considered to be a surfactant and a plasticizer in the material, respectively.

Pyrolysis-DI/MS is a simple, rapid analytical pyrolysis measurement technique without any chromatographic separation process. Since the mass profiles of all pyrolyzates are labeled on a linear mass scale, it is suitable for fingerprint identification purposes.<sup>7,8</sup> Figure 5 is the TIC pyrogram of part A pyrolyzed at 500 °C for 3 s by

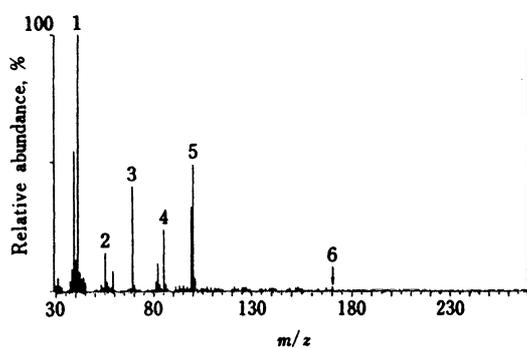


Fig. 5 Mass spectrum of part B obtained by pyrolysis-DI/MS: 1, propylene; 2, acrolein; 3, 2-methyl acrolein; 4, methacrylate; 5, methyl methacrylate; 6, isohexyl methacrylate.

DI/MS. The corresponding mass spectrum indicated that the observed species was a co(MA-MMA-HMA)polymer identified by the related monomer fragments with  $m/z$  values of 86(MA), 100(MMA), and 170(HMA), respectively. Though the conclusion is the same as that by Py-GC, since the throughput of up to one sample was within a few minutes, the analysis is more effective.

An important point remained regarding the previous discussion, i.e. the monomer peaks of MA, MMA and HMA on both of Py-GC and DI/MS pyrograms of the part B must have originated from two considerable ways; thermal pyrolysis of the copolymer to the corresponding monomers or/and thermal volatilization of free monomers dissolved in the copolymer.<sup>14</sup> To confirm that, headspace GC/MS was carried out at a purging temperature of 220°C within 1 min for both part B and a

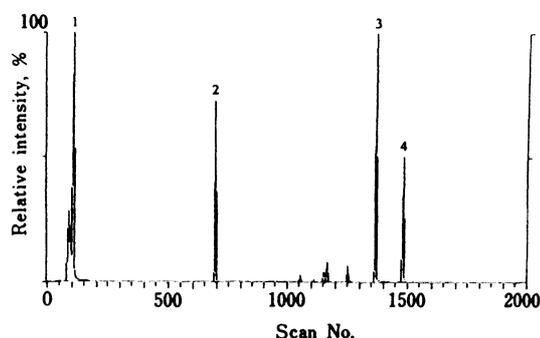


Fig. 6 TIC chromatogram of part B by headspace GC/MS: 1, methyl methacrylate; 2, isohexyl methacrylate; 3, dioctyl phthalate; 4, C<sub>16</sub> aliphatic alcohol.

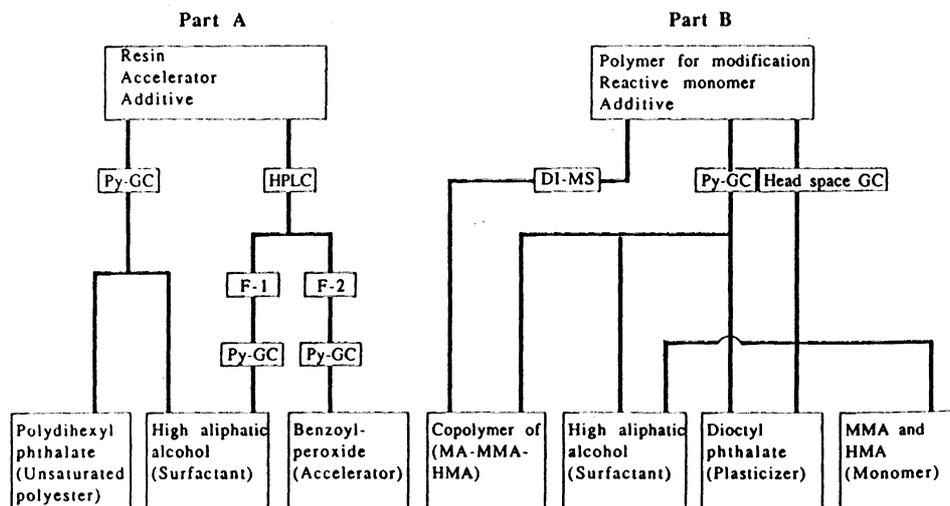


Fig. 7 Flowchart diagram of the analytical measurements in this work.

monomer-free co(MA-MMA)polymer for the same sample size and condition. Since no significant peak showed on the headspace chromatogram of the monomer-free copolymer, this indicated that no detectable pyrolyzate formed at that temperature for the purified co(MA-MMA)polymer. A headspace TIC chromatogram of part a at 225 °C is shown in Fig. 6, in which the monomer peaks of MMA and HMA presented with the obvious intensities are compared to the standard copolymer. The results show that there were some reactive monomers (MMA and HMA) dissolved in the copolymer as the crosslinking agents of the unsaturated polyester. Therefore, it could be deduced that the copolymer in part a acted as a modification material and an adsorbent for the reactive monomers.

In conclusion, all of the components in a set of uncured unsaturated polyester system, including an unsaturated polyester prepolymer, a crosslinking accelerator, an acrylate copolymer as the modification agent and some additives (surfactant and plasticizer) were well identified by a combination of Curie-point Py-GC/MS, DI/MS, headspace-GC/MS and preparative HPLC. A flowchart diagram of the analytical measurements used in this work is illustrated in Fig. 7. The results showed that the Curie-point heating technique combined to multi-chromatographic and mass spectroscopic methods is an available and convenient way for the compositional analysis of complex polymer materials.

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## 2) Multichannel Autosampler for Curie-Point Pyrolysis Capillary Gas Chromatography

Naoki Oguri and Akira Onishi

Japan Analytical Industry Co. Ltd. 208 Musashi. Mizuho. Nishitama. Tokyo 190-12. Japan

Toshihiko Hanai

Int. Inst. of Technol. Anal. Health Res. Fond., Inst. Pasteur de Kyoto 5F. Sakyo-ku. Kyoto 60, Japan

Xigao Jin

Institute of Chemistry. Chinese Academy of Sciences. Peking. 100080 China

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Curie-point pyrolysis  
GC-MS  
Multichannel autosampler

### Summary

A multichannel autosampler which can automatically analyze up to 20 samples in sequence has been developed for on-line Curie-point pyrolysis - capillary GC. The results obtained from the system show that the analysis of thermally labile samples could be performed without either thermal degradation or reaction during the waiting time before the final pyrolysis. The reproducibilities of the relative peak areas and retention times of the characteristic pyrolysates of a tricomponent copolymer were significantly better than those obtained by manual sample manipulation.

### 1 Introduction

Pyrolysis is used as a means of sample introduction for the gas chromatographic analysis of high molecular weight compounds. The technique uses high temperatures to degrade the compounds to a characteristic mixture of volatile monomers, oligomers and other pyrolysates. Curie-Point Pyrolysis - Capillary GC is a powerful method for analysis of the composition and structure of such non-volatile compounds as synthetic plastics [1], Rubbers [2], and paints [3].

In previous work, liquid, solid, and powder samples have been handled by wrapping in 50  $\mu\text{m}$  thick Pyrofoil. Placed in a specially developed, magnetic metal foil holder, and inserted into the pyrolyzer [4, 5]. Because pyrolysis can be effected by a number of experimental parameters, it should be performed as reproducibly as possible, especially for quantitative analysis. For this reason we have developed a multichannel autosampler which can handle up to 20 samples without causing any degradation and/or further polymerization inside the sample holder during the waiting time before final pyrolysis. This has solved a problem observed with another autosampler [6] in which thermally labile compounds could be degraded or polymerized before pyrolysis [7, 8]. The results from quantitative analysis of multi-component polymers has shown that as a result of the standardization of experimental conditions the reproducibility obtained using the autosampler is much improved in comparison with manual sample manipulation.

### 2 Experimental

#### 2.1 Instrumentation

A schematic diagram of the model JPS-220 multichannel autosampler and JHP-22 pyrolyzer is shown in **Figure 1**. Samples are weighed and individually wrapped in Pyrofoil in a manner ensuring good contact. The Pyrofoil-wrapped samples (A) are placed on a magazine (a), the purge valve (C) opened to replace the air inside the equipment with carrier gas, and, after 1 min, the six-port valve (D) turned to the sampling position. The first sample is pushed by the injector (E) down to a pyrolysis chamber (F) where it is instantaneously pyrolyzed. The pyrolysates are transferred, through (D), to an on-line GC column to chromatograph.

A magnet (G) is then lowered to retrieve the spent sample and returned to the upper position. A slide-way (I) is placed below the magnet and when the electricity supply to the magnet is switched off the used sample (H) slides into the trap (J). The slide is then returned to its initial position. The instrument is controlled by unit (K).

When gas chromatographic analysis of the first sample is complete, the foil magazine is moved forward, the second sample dispensed into the pyrolysis chamber by the plunger, and the second processing begins automatically. This sample introduction method is repeated up to 20 times from one magazine.

In order to keep the carrier gas flow rate constant, during operation the inlet gas pressure is controlled by a pressure balancer (L). Without this pressure controller, it took more than 30 min to obtain the stable gas pressure which is important for production of reproducible pyrograms.

#### 2.2 Condition for Pyrolysis GC

About 0.2 mg of a sample, wrapped in Pyrofoil<sup>®</sup>, was heated at 590 °C for 3 s. The sample introduction and pyrolysis system were coupled directly to a model HP 5890A gas chromatograph (Hewlett-Packard) equipped with a model D-2520 integrator (Hitachi). The GC system was equipped with flame ionization detection and fitted with a 30 m  $\times$  0.25 mm i.d. fused silica

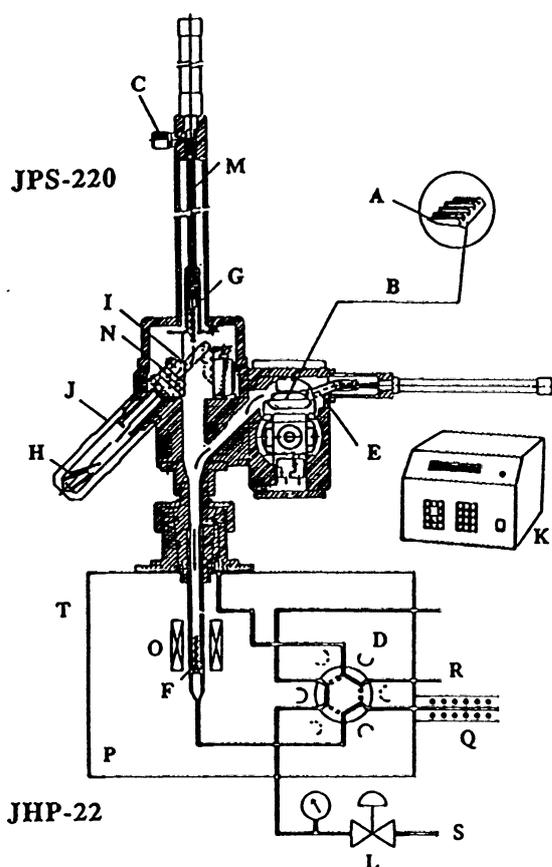


Figure 1

The JPS-220 multichannel autosampler coupled with the JHP-22 Curie-point pyrolyzer: A, Pyrofoil<sup>®</sup>-wrapped sample; B, magazine; C, purge valve; D, six port valve; E, injector; F, pyrolysis chamber; G, foil collection magnet; H, used samples; I, slide way; J, trap for used samples; K, controller; L, pressure balancer; M, foil collection shaft; N, photosensor; O, radio frequency coil; P, sample tube; Q, transfer pipe coupled to GC; R, carrier gas inlet; S, gas inlet for pressure balancing; T, oven.

capillary column coated with a 0.25  $\mu\text{m}$  film or immobilized polydimethylsiloxane (DB1: J&W, Folsom, CA, USA). Following pyrolysis, the column temperature was maintained at 50  $^{\circ}\text{C}$  for 3 min and then programmed at 10  $^{\circ}\text{C}/\text{min}$  to 250  $^{\circ}\text{C}$  which was held for 10 min. Helium was used as carrier gas; a total flow rate of 50 ml/min was split in the ratio 50:1. The identification of the pyrolysates was performed with a directly coupled model QP 2000 A quadrupole mass spectrometer (Shimadzu); ionization was by EI at 70eV.

### 2.3 Samples

A commercial bisphenol A type epoxy prepolymer and modified polyamide hardener were obtained from Konishi. A Toyolac 700 ABS resin, a copolymer of acrylonitrile (23%), butadiene (13%), and styrene (64%) was obtained from Toray industries.

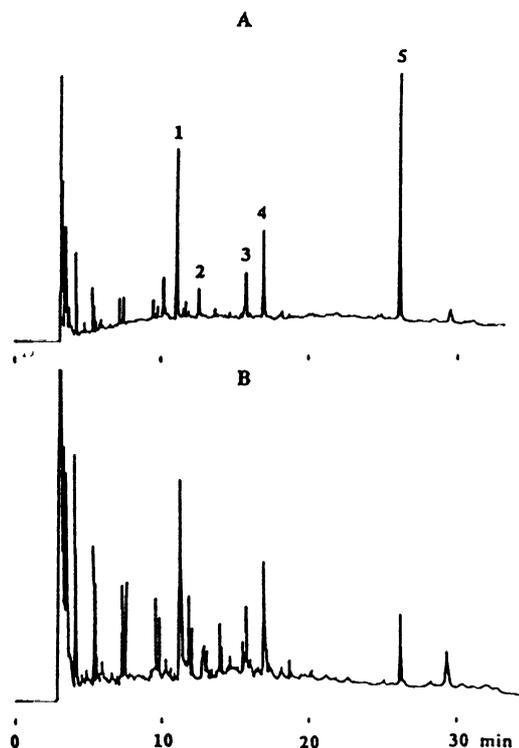


Figure 2

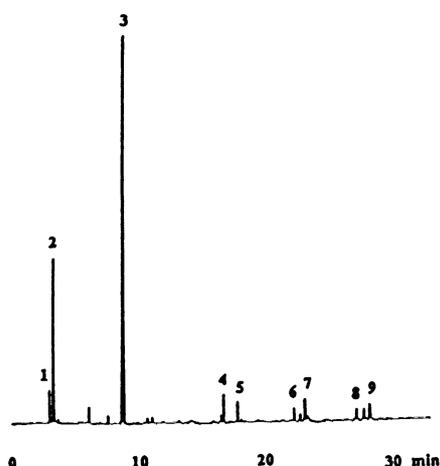
Pyrograms of (A) uncured epoxy resin mixed with amide hardener at room temperature and stored in the sample magazine for 1 to 60 min, and (B) the epoxy resin cured at 150  $^{\circ}\text{C}$  for 1 h: 1, phenol; 2, cresol; 3, *p*-isopropylphenol; 4, *p*-isopropenylphenol; 5, bisphenol A.

## 3 Results and Discussion

The multichannel autosampler coupled on-line with the Curie-point pyrolyzer and the capillary GC system may be used not only for time-saving automatic measurements on a large number of samples, but also for the highly accurate quantitative analysis of thermally labile samples.

### 3.1 Analysis of a Thermally Labile Sample

Conventional autosamplers for pyrolysis GC are usually provided with auxiliary heating in order to maintain the sample holder at a temperature sufficient to prevent condensation of pyrolysates on its inner wall [6]. Because uncured epoxy resins are susceptible to further curing, even at low temperatures. When such samples are mounted in a conventional pyrolyzer they are often exposed to temperatures which cause further curing during the waiting period before final pyrolysis; the degree of reaction depends on the temperature, the waiting time, and the size of the sample, etc.; these are, in turn, reflected in the specificity and the reproducibility of the resulting pyrograms [8]. Since the sample magazine of JPS-220 is designed to be located far from the pyrolysis chamber, such heating is not necessary. This enables thermally labile samples to be analyzed reproducibly.



**Figure 3**  
**Pyrogram of ABS (acrylonitrile - butadiene - styrene) copolymer**  
**1 B 2, A 2 S 4 AS 5 SA 6 SS 7 ASA 8 ASS 9 SAS.**

bly. Figure 2 A Shows the pyrogram obtained from a sample of the epoxy resin mixed with 4mlde hardener[ (1:1) at room temperture. No changes were observed in the pyrograms when smpls were stored in the sample magazine from 1 to 60 min. which indicates that the JIPS-220 is suitable for the analysis of thermally labile samples.

The pyrogram of the epoxy resin cured at 150 for 60 min is shown in Figure 2 B : compared with the

pyrogram from the uncured resine some of the monophenol pyrolysate peaks had increased in size whereas that of bisphenol A had, in contrast, decreased. These differences obviously reflected the curing reactions of epoxy resin with amide-hardener.

### 3.2 Reproducibility

The reproducibility of Py.GC analysts is Influenced by each of a series of steps: One of the most critical is the sample handling technique [9]. As already mentioned, the use of an autosampler enables reproducible Sampling handling; because of this an enhancement of the reproducibility and standadization of quantitative analysis would be expected.

A tricomponent copolymer: an ABS resin, was analyzed quantitatively using both automated and manual sample introduction systems. figure 3 shows the pyrogram of the ASS resin: the intensities of the monomer (A, B, and S), dimer (AS, SA, and SS) end trimer (ASA, ASS, and SAS) peaks represent the structural specificity and composition of the copolymer.

The relative peak areas and retention times of the specific pyrolysates are Summarized in Tables 1 and 2, respectively. The relative standard deviations (CV%) of the peak areas and retention times (t) are listed in the tables and (in part) presented schematically Figure 4. The CV% and ti data show that the experimental reproducibilities obtained using Ike autosampler were as much as 1.3 and 2.3 times better, respectively, than those obtained by manual sample introduction under the Same conditions.

We consider that in addition to the completely uniform sample introduction, pyrolysis, and chromatographic processing effected by the autosampler control, there is another reason for this Improvement: the removal of air by purging the pyrolyzer with carrier gas. During manual sample introduction, air enters the

**Table 1**  
**Reproducibility of relative peak areas of the characteristic pyrolysates of an ABS coploymer**

No	Relative peak areas Monomer			Dimer			Trimer		
	B	A	S	AS	SA	SS	ASA	ASS	SAS
<i>JPS 220 multichannel autosampler</i>									
1	2 11	12 54	65 16	3 32	2 89	2 37	4 79	2 67	4 10
2	2 03	12 10	66 25	3 41	2 75	2 29	4 60	2 54	3 85
3	2 17	12 36	66 46	3 28	2 70	2 02	4 46	2 58	3 93
4	2 02	12 06	66 31	3 43	2 78	2 27	4 50	2 51	3 90
5	1 81	11 47	67 22	3 72	2 72	2 45	4 54	2 32	3 71
Average	2 03	12 10	66 28	3 43	2 77	2 28	4 58	2 52	3 90
CV%	6 7	3 4	1 1	5 0	2 7	7 1	2 8	5 1	3 6
<i>Manual sample handling</i>									
1	2 17	12 46	65 30	3 22	2 80	2 43	4 33	2 43	4 81
2	2 11	12 70	69 41	3 16	2 70	2 25	2 99	1 71	2 88
3	2 05	12 00	71 14	2 80	2 42	2 02	2 61	2 30	2 53
4	1 45	10 96	65 34	3 30	2 80	2 69	3 91	3 32	6 19
5	1 73	11 62	70 28	2 91	2 13	1 78	2 35	1 82	5 32
Average	1 90	11 95	68 29	3 08	2 57	2 23	3 24	2 32	4 35
CV%	16	5 8	4 1	6 9	11	16	26	28	36

Table 2

Reproducibility on retention times of the characteristic pyrolysates of an ABS copolymer

No	Retention time of pyrolysate [min]			Dimer			Trimer		
	Monomer B	A	S	AS	SA	SS	ASA	ASS	SAS
<i>JPS 220 multichannel autosampler</i>									
1	3.17	3.43	8.96	16.95	18.09	22.61	23.51	27.60	28.69
2	3.08	3.33	8.81	16.77	17.90	22.40	23.28	27.31	28.36
3	3.08	3.32	8.71	16.66	17.80	22.36	23.23	27.29	28.35
4	3.19	3.45	8.91	16.85	17.99	22.49	23.38	27.44	28.51
5	3.16	3.41	8.83	16.78	17.91	22.42	23.28	27.33	28.38
Average	3.13	3.38	8.84	16.80	17.93	22.45	23.33	27.39	28.45
CV%	1.7	1.8	1.1	0.6	0.6	0.4	0.5	0.5	0.5
<i>Manual sample handling</i>									
1	3.68	3.97	9.71	17.83	18.99	23.65	24.57	29.02	30.23
2	3.58	3.87	9.57	17.64	18.80	23.41	24.33	28.71	29.89
3	3.48	3.76	9.43	17.47	18.62	23.20	24.10	28.41	31.65
4	3.26	3.53	9.15	17.18	18.56	22.87	23.77	27.95	29.08
5	3.24	3.51	9.15	17.15	18.29	22.83	23.73	27.92	29.03
Average	3.44	3.72	9.40	17.45	18.65	23.19	24.10	28.40	29.97
CV%	5.6	5.5	2.7	1.7	1.4	1.5	1.5	1.7	3.6

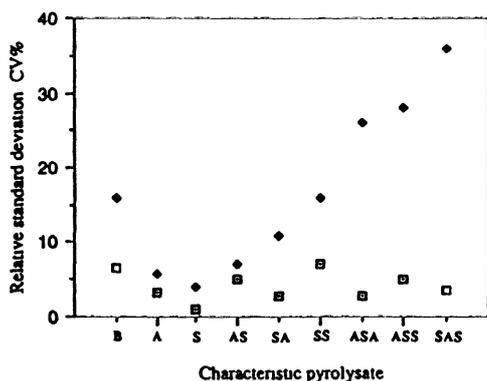


Figure 4

Relative standard deviation of peak areas of characteristic pyrolysates of ABS resin obtained by pyrolysis GC with automated (□) and manual (◆) sample introduction

pyrolyzer to varying degrees and this reduces the quantitative reproducibility of the analysis. This problem is almost eliminated by use of this autosampler.

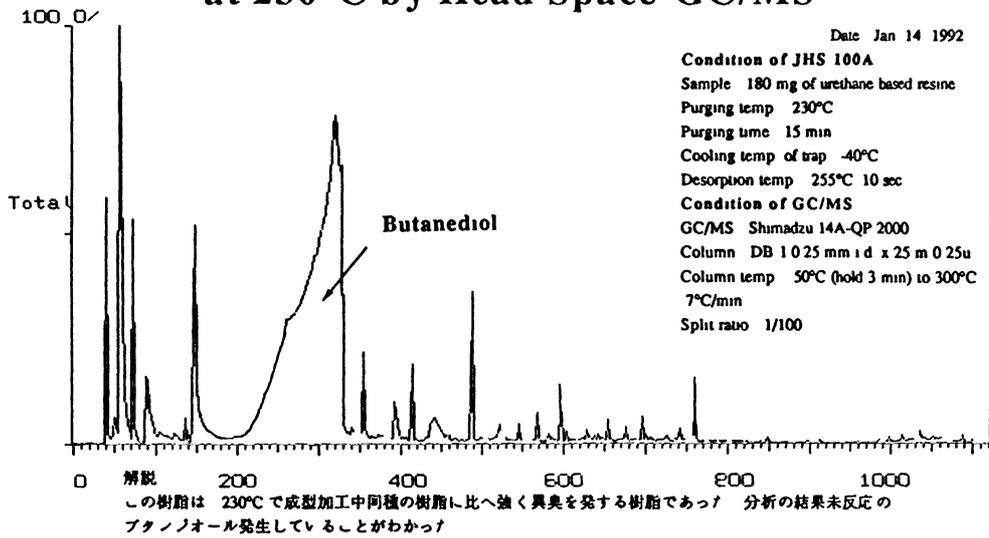
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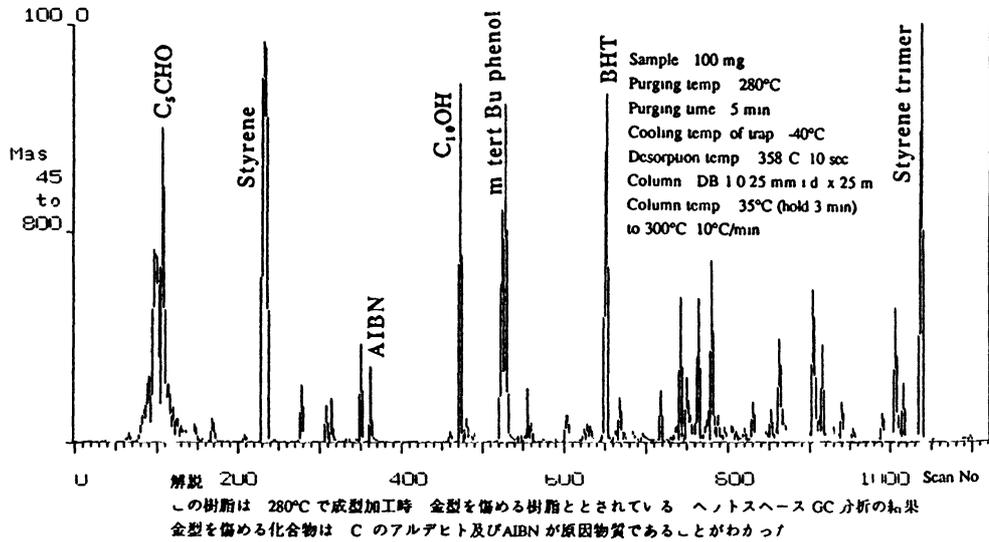
Ms received August 15 1991  
Accepted September 26 1991

3) ヘッドスペース GC/MS 法による高分子中の揮発成分分析

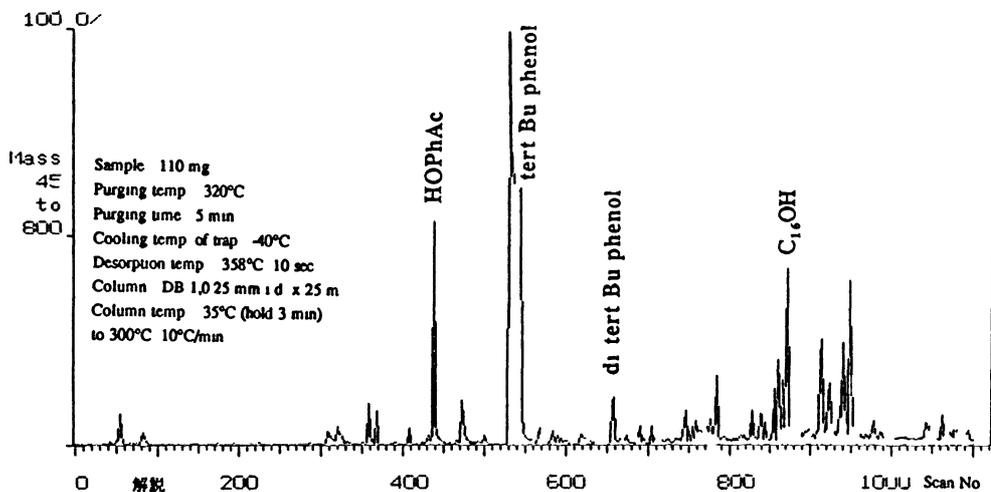
### Odor Analysis from Urethane Resine at 230°C by Head Space-GC/MS



### Analysis of Volatile Substances from Blended Polymer (PC+PS) at 280°C by Head Space GC/MS

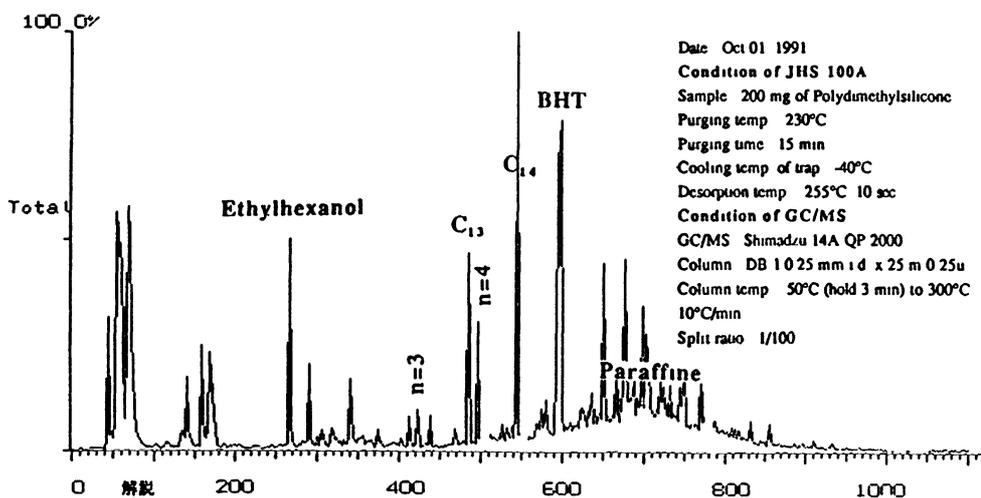


### Analysis of Volatile Substances from Polycarbonate at 320°C by Head Space GC/MS



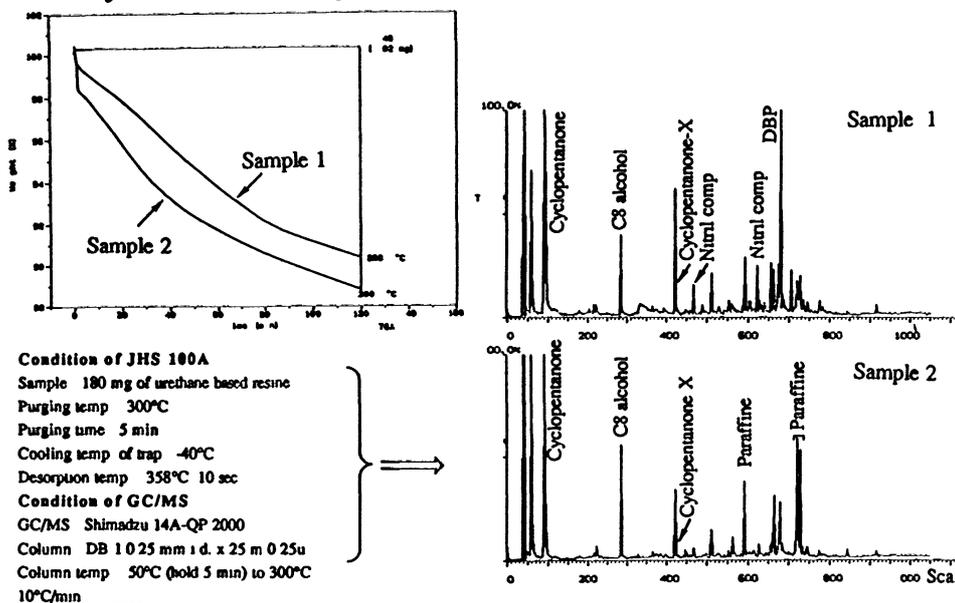
0 解説 200 400 600 800 1000 Scan No  
 この樹脂は 耐熱性に優れ 成型加工時臭気も発生することなく総ての面で優れた樹脂とされている ヘ  
 ットスヘース-GC 分析の結果 分子量の大きいヒンダートフェノール系の安定剤よりの分解生成物と考え  
 られるモノ及びノ-tertブチルフェノール ヒドロキノンアセトフェノール及びシカ 検出されなかつ

### Trace Analysis of Dimethylsilicones from Silicone Rubber at 150°C by Head Space-GC/MS



0 解説 200 400 600 800 1000  
 ノリコン系樹脂とかゴムを電子機器に使用すると絶縁不良を起こすことがある  
 このゴムは 絶縁不良を起こさないよう作成されたものである がしかし 230°C で 15 分間抽出し  
 場合 ノメチルシリコンのオリゴマーとして n=3 及び n=5 を微量ながら検出することができ

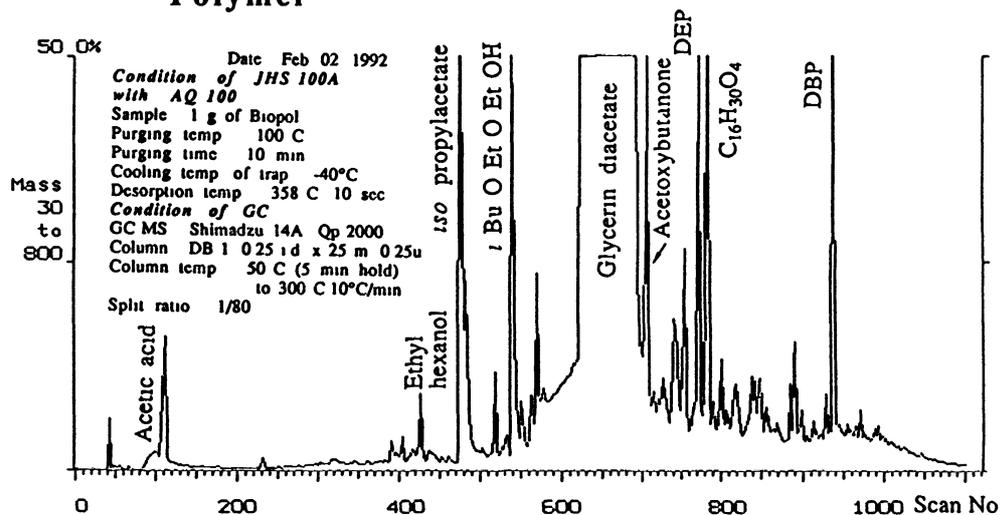
## Analysis of Volatile Substances from Nylon 66 at 300°C by TG and Head Space-GC/MS



**解説**

耐熱性のナイロン樹脂を300°Cで加熱減量が異なる二種類の樹脂を顕微鏡的方法で分析を行なった。TGAのデータで加熱開始より5分以後の減量は平行していることから最初の5分間で減量する物質に相違があると考えこの部分の揮発性物質をヘッドスペース-GC法で分析し、減量に關する揮発性物質はパラフィン系化合物であることが判った。

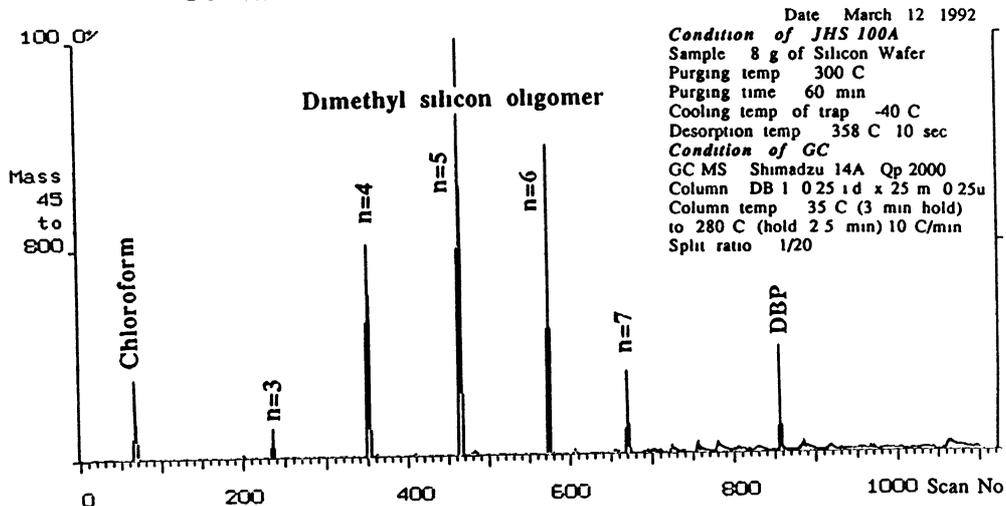
## Head Space-GC/MS analysis of Volatile Substances from Biodegradational Polymer



**生分解性ポリマーの臭気分析の解説**

清涼飲料水などを入れる新しい容器の材料用として開発された生分解性ポリマーの臭気分析を行なった。臭気の強い酢酸、イソプロピルアセテート、グリセリンアセテートおよび可塑剤などが多量に検出された。

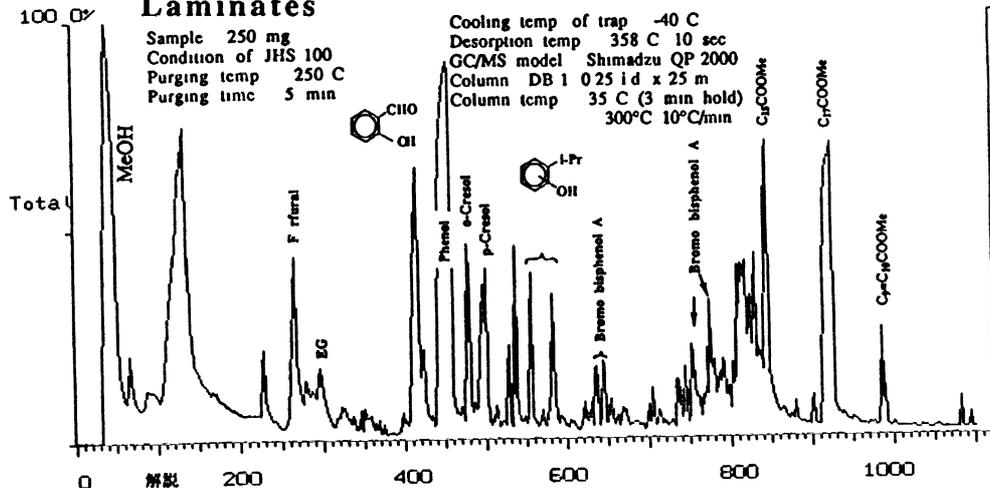
## Head Space-GC-MS Analysis of Organic Contaminants on the Silicon Wafer



シリコンウェーハ上の有機汚染物質の分析

保管中の4インチシリコンウェーハが汚染されるという事故があった。各種の表面分析装置によって汚染物質の究明がなされたが未解決であった。ヘッドスペースGC/MS分析の結果、汚染物質は保管用のキャリヤーボックスに使用されているパッキング材から揮発した物質であることが判明した。

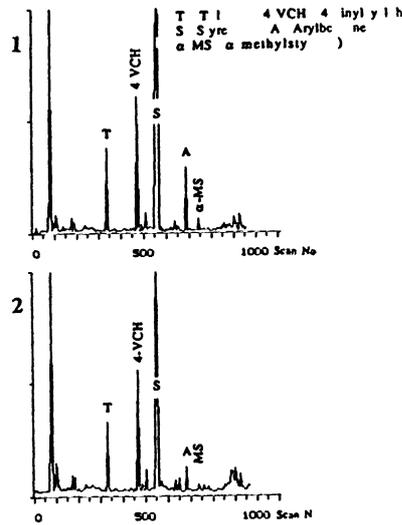
## Head Space-GC/MS Analysis of Volatile Substances from Paper, Phenol-based Laminates



解説  
 250°Cで紙-フェノール積層板より発生するガスを測定した。多量のメタノール、フェノールのほか、クレゾール、臭化ビスフェノールA、高級脂肪酸のメチルエステルが検出された。

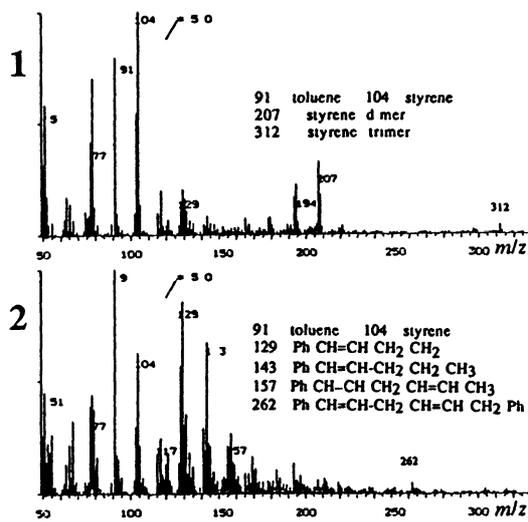
#### 4) Py-MS 法によるブレンド コポリマーの分析

##### Py GC chromatograms of blended polymer (PS + PBu) and SBR



- 1 Blended polymer (polystyrene (43 wt. %) + polybutadiene (57 wt. %))
  - 2 SBR (styrene 43 wt. %)
- Pyrolyzed 590°C 5 sec

##### MS pyrograms of blended polymer (PS + PBu) and SBR



- 1 Blended polymer (polystyrene (43 wt. %) + polybutadiene (57 wt. %))
  - 2 SBR (styrene 43 wt. %)
- Pyrolyzed 590°C 5 sec