High performance HPLC / GPC-FTIR interface system by ST Japan

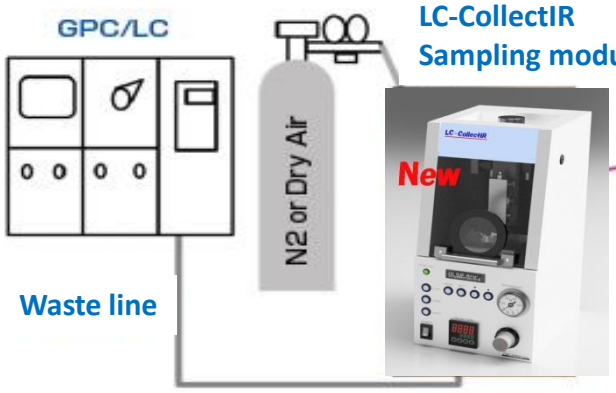
New LC-CollectIR®

The new LC-CollectIR system developed by S.T. Japan Inc. is an interface system for evaporating the mobile phase solvent from HPLC and GPC with high efficiency, depositing solute components on a germanium (Ge) disc, and FTIR (or Raman) can be easily measured. The LC-CollectIR system is optimal for studying the change in the composition of the copolymer in simple , rapid molecular weight distribution and structural analysis by spectroscopic measurements such as FT-IR for each component of the mixture separated by chromatography. Compared to conventional preparative methods, it is possible to reduce time and cost dramatically.

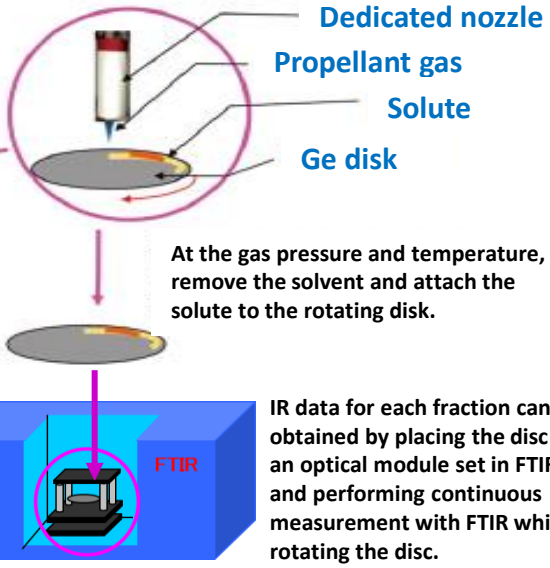
Application example

- Separation of mixture and simple and rapid structural analysis of each component
- Change in composition of copolymer in molecular weight distribution
- Microstructure analysis and discrimination of mixture system of resin
- Estimation of terminal end and internal structure of resin
- Interface of pyrolysis GC/MS

Flow of LC-CollectIR measurement

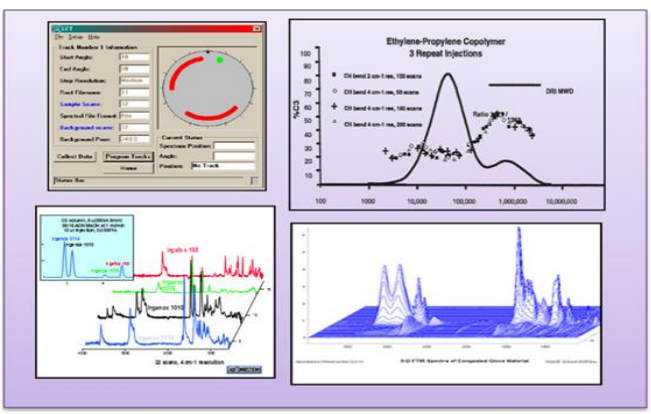


Attach the waste line from GPC / LC to the sampling module

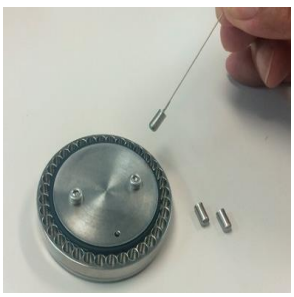


At the gas pressure and temperature, remove the solvent and attach the solute to the rotating disk.

IR data for each fraction can be obtained by placing the disc in an optical module set in FTIR and performing continuous measurement with FTIR while rotating the disc.



New product preparative attachment for pyrolysis GC/MS



Preparative attachment for pyrolysis GC/MS

Instead of the Ge plate for FTIR, we have developed an optional disk that can mount a sample cup for pyrolysis GC/MS and software that can rotate the disk in steps.
This makes it possible to collect GPC fractions efficiently in sample cups for pyrolysis equipment and to use them as GPC – PGC/MS systems.

S.T.JAPAN INC.

Pyrolysis GC/MS Attachment for LC-CollectIR

In order to confirm the effectiveness of preparative attachment for pyrolysis GC/MS (see catalog), LC-CollectIR / FT-IR analysis and LC-CollectIR / pyrolysis GC/MS preparative analysis on a mixture of two kinds of polymers and additives GC/MS analysis of each fraction by attachment was carried out.

Composition analysis and characterization of polymer materials are very important for product performance improvement and quality control. The pyrolysis GC/MS method analyzes compounds generated by instantaneous thermal decomposition of polymers by the GC/MS method, so it is very effective to analyze the composition of polymers, detailed structures and additive components.

Polymer materials are mixed with plural resins for high functionality and additives are blended, so it is necessary to separate each component as much as possible for detailed analysis. Generally, preparative GPC and preparative HPLC are used, but the preparative work is complicated and it takes a long time.

Therefore, we added the development of a preparative attachment for pyrolysis GC/MS that can efficiently collect GPC and HPLC preparations into a sample cup for pyrolyzer and the function to set disk rotation in steps. This enables simple and efficient separation of HPLC and GPC and pyrolysis GC/MS of its fractions. In this application note, a mixture of two kinds of polymers and additives is fractionated by GPC by LC-CollectIR and the results of FT-IR analysis and pyrolysis GC/MS of each fraction are reported.

GPC measurement and LC-CollectIR preparative conditions

GPC device ：Prominence HPLC system(DGU-20A3/LC-20AD/SIL-20AHT/CTO-20A/SPD-20A/RID-10A/CBM-20A) (Shimadzu Corporation)

- Detector ： RI detector / UV detector (detection wavelength: 254 nm)
- Prep equipment ： LC-CollectIR 700 (ST Japan)
- Nebulizer ： 80℃． N_2 = 15psi
- Split ratio ： RI detector / LCT = 6/4
- Column ： TSKgel GMHHR-H ×2本 (7.8mmID × 30cm, Tosoh Corporation)
- Eluent ： Chloroform (Wako Pure Chemical Industries, HPLC grade)
- Flow rate ： 1.0mL/min.
- Concentration ： 2mg/mL
- Injection volume ： 200µL
- Column temperature ： 40℃
- Preparative conditions ： 90sec / 1 fraction, 6 fractions (see FIG. 1)
- Sample pretreatment ： Samples were weighed, eluent was added and allowed to stand dissolving overnight. The mixture was gently shaken and filtered through a 0.5 µm PTFE cartridge filter.

Sample ： Blend of (1) / (2) / (3) = 90/5/5 (wt%)

(1) Polydisperse polystyrene SRM 706 (NIST)
(2) Monodispersed PMMA No. 0006158374 (Mp = 617500) (Agilent)
(3) Irganox1010

Figure 1 shows the chromatogram by the RI detector (dotted line shows the preparative fraction interval).

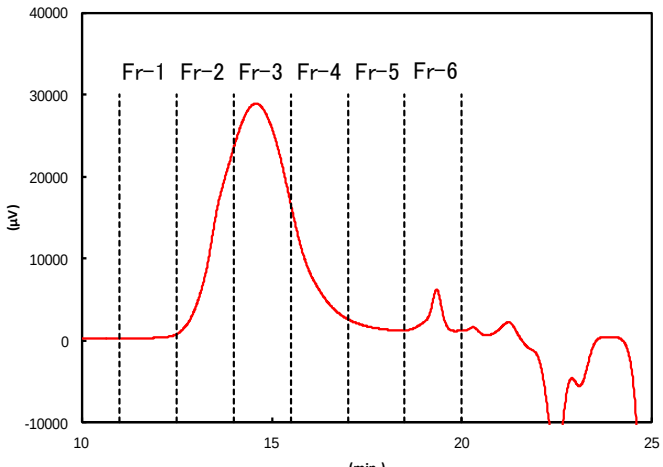


Fig. 1 Chromatogram by RI detector

Analysis results of each fraction by FT-IR

Figure 2 shows the spectrum of each fraction obtained by FT-IR measurement of deposits by adhering GPC eluted components to germanium (Ge) disc by LC-Transform under the above conditions.

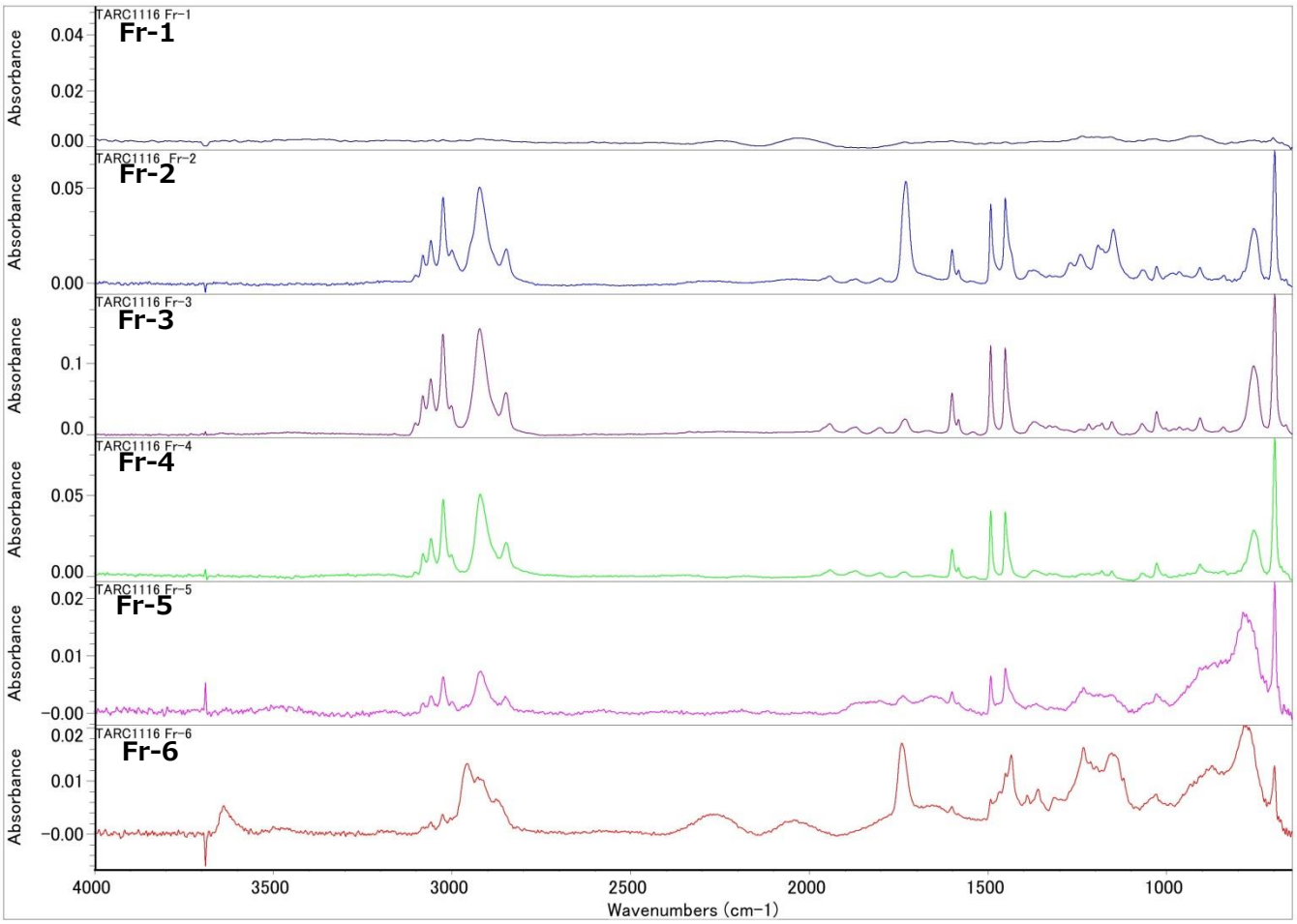


Fig. 2 FT-IR measurement result of each fraction

As a result of analyzing each spectrum, it is expected that Fr - 2 is PMMA and polystyrene (PSt), Fr - 3 is trace amounts of PMMA and PSt, Fr - 4 and Fr - 5 are PSt and Fr - 6 is Irganox 1010. However, the presence of acrylic resin can be expected, but it is difficult to identify it as PMMA from the IR spectrum of Fr - 2, so analysis by pyrolysis GC/MS method is necessary.

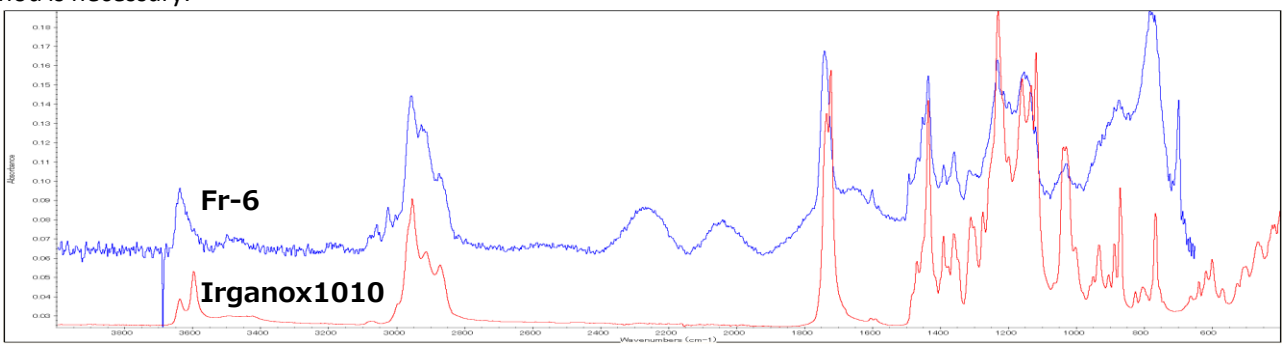


Fig. 3 FT-IR spectrum of Fr-6 and Irganox 1010

Figure 3 shows the spectra of Fr-6 and Irganox 1010. It was found that about 5% of the additive Irganox 1010 in the sample can be qualitated by FT-IR analysis of fraction.

Analysis results of each fraction by pyrolysis GC/MS

The model mixture (polydisperse polystyrene / monodisperse PMMA / Irganox 1010 = 90/5/5 (wt%)) was fractionated into 6 fractions in the pyrolysis measurement sample cup using LC-CollectIR preparative attachment for pyrolysis and pyrolysis GC/MS analysis of each preparation was carried out.

Conditions for pyrolysis GCMS measurement

GC/MS	GC：Agilent6890N （ Agilen ）
	MS：Jms-Q1000GC K9(JEOL)
Pyrolyzer	PY-2020iD(Frontier Lab)
Column	UA+-5 30 m x 0.25 mm i.d., film thickness 0.25 mm(No.313)
Pyrolysis temp.	600ºC
Interface temp.	320ºC
MS ion source temp.	200ºC
MS GC Interface temp.	250ºC
Ionization current	200 μA
Ionization energy	70 eV
Voltage	-900 volt
Injection temp.	320ºC
Oven temp.	50ºC(10 min)-<10ºC/min>-320ºC(10 min)

Figure 4 shows the structure estimated from pyrolysis GC/MS measurement results and mass spectrum of each fraction. The peak at 3.3 min is the MMA monomer, the peak at 23.6 to 26.0 min is the peak derived from Irganox 1010, and the other peak is derived from polystyrene. From Fig. 3, polystyrene was detected as a whole with Fr-3 as the peak top, PMMA was detected as Fr-1 to 3 on the peak top with Fr-2, and Irganox 1010 was found only in Fr-6. The LC-CollectIR disk was a continuous rotation at a constant speed, but we added a function that allows you to set the rotation angle in step for preparing. Since it is possible to fractionate multiple times in the same pyrolyzer sample cup, it is also possible to analyze small amounts of samples, especially low concentration samples and additives.
The relative quantitative was evaluated by the difference of the number of fractionating (1 to 3 times). PMMA had a peak of 3.3 minutes, Irganox 1010 had 3 peaks, polystyrene measured the intensity (TIC) of 8 other peaks. As a result, the relative value of PMMA was 2.6 times and 3.2 times, and the relative value of polystyrene was 2.4 and 2.7 times, which is not the theoretical value, but the relative value of 2 times and 3 times for the number of sorting, The result was obtained according to the theoretical value, and it was found that each fraction was fractionated with good reproducibility even in the case of multiple preparation to the same cup.
Qualitative analysis of polystyrene and PMMA and Irganox 1010 with 5% each was possible using pyrolysis GC/MS analysis of one time GPC fractionation by LC-CollectIR. From the above, we confirmed the effectiveness of this LC-CollectIR preparation attachment for pyrolysis GC/MS. Furthermore, since multiple fractions are almost quantitative, analysis of low concentration components in the sample can be performed by multiple fractionation.

Professor Ohtani Hajime of Nagoya Institute of Technology cooperated with this pyrolysis GC/MS analysis. TOSOH Analysis and Research Center Co.,Ltd. cooperated with this GPC preparation by LC-Transform and FT-IR measurement.

a. Fr-1

b. Fr-2

c. Fr-3

d. Fr-4

e. Fr-5

f. Fr-6

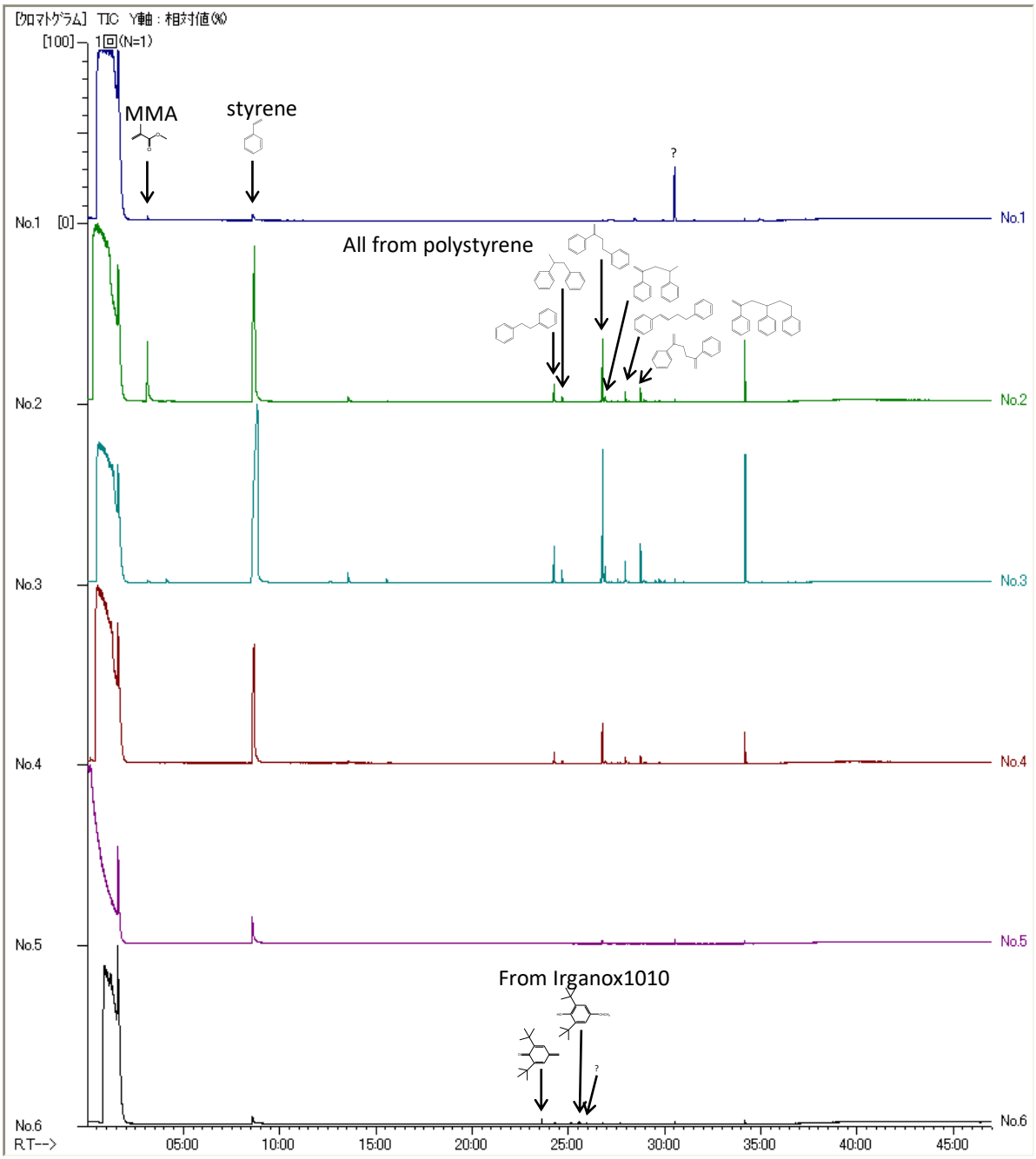


Fig. 4 Results of pyrolysis GC / MS measurement of each fraction at one fractionation