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Technical Report

Compositional and Structural Analysis of Polymer Materials Using a Size-Exclusion Chromatography Fractionation System for Pyrolysis-GC/MS and MALDI-MS

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Abstract:

Detailed analyses of compositions and structures are often performed to improve the quality control and performance of polymer materials. Pyrolysis-gas chromatography mass spectrometry (Py-GC/MS) and matrix-assisted laser desorption ionization mass spectrometry (MALDI-MS) are used as effective means for such purposes. The analysis of polymer materials with complex compositions are performed on a mixture of components analyzed together, which makes obtaining accurate information for individual components difficult.
This technical report describes a method using the aforementioned equipment to analyze fractions derived by the AccuSpot spotting equipment, which performs automatic fractionation of elute separated by size-exclusion chromatography. This new method, which fractionates and analyzes a mixture of components without requiring any complicated operation, was used to analyze the composition and structure of the paint raw material. This resulted in a successful detailed analysis of the corresponding sample, which was composed of a complex mixture of components.

Keywords: SEC, AccuSpot, Py-GC/MS, MALDI-MS, paint, polymer, structural analysis

1. Introduction

Analyses of compositions and structures in resin components are often performed to improve quality control and performance of polymer materials. Pyrolysis-gas chromatography mass spectrometry (Py-GC/MS) and matrix-assisted laser desorption ionization mass spectrometry (MALDI-MS) are frequently used as effective analysis methods for these purposes. The Py-GC/MS method analyzes compounds generated by the pyrolysis of resins using GC/MS, and is primarily used to measure low-molecular-weight products (molecular weights of 1,000 or less). Analyses of the structures in resin portions, as well as additives, are made possible by analyzing pyrolysates [1, 2]. In contrast, MALDI-MS is primarily used for polymer samples with molecular weights of about 500 to 10,000. The method allows molecular weight measurements to be taken with the components remaining intact, as well as analyses to be performed on repeated structures and end structures of resin polymers [3].

Some polymer materials currently in use have complex compositions. These include blended polymers prepared by mixing multiple resins and others made by blending a variety of additives to enhance functionality. There have been instances where detailed information could not be derived using the above methods due to these compositions, as analysis of the resultant mass spectra comprising multiple components proved difficult.

Separating complex compositions into individual components as much as possible and then taking measurements using Py-GC/MS or MALDI-MS has been considered an effective means to resolve this issue. Size-exclusion chromatography (SEC), which separates constituent components according to molecular size (larger molecules are eluted earlier), is effective for separating samples consisting of a mixture containing a broad range of components varying from low to high molecular weights. For this reason, we developed AccuSpot, equipment which automatically spots fractionated samples separated by SEC into a sample cup or a sample plate. The SEC-AccuSpot system is capable of fractionating samples so that individual fractions separated from complex samples can be easily analyzed using Py-GC/MS or MALDI-MS without requiring complicated operations. The system was built by combining SEC and AccuSpot (Fig. 1). When performing MALDI-MS analysis, the eluate is mixed with the matrix solution and dropped onto the MALDI-MS plate. A sample cup for the pyrolyzer (Py) is set on a dedicated plate for the AccuSpot and the eluate is fractionated directly when performing Py-GC/MS analysis. This equipment was used to perform detailed compositional analysis on raw materials in a blend of paint, which are difficult to analyze directly.

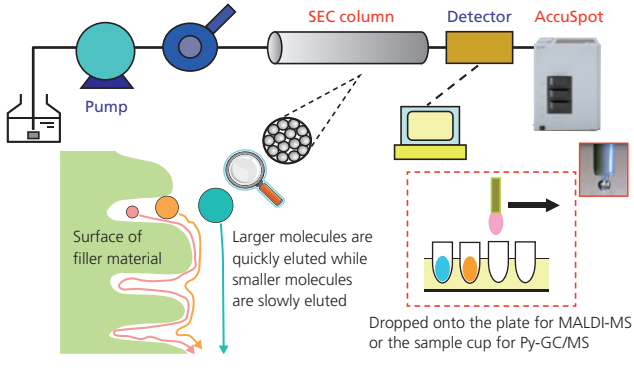

Fig. 1 Composition and Function of SEC-AccuSpot

1 Nagoya Institute of Technology
2 Shimadzu Corporation

2. Experimental

2-1. Sample Preparation

The raw ingredient resin material for paint, comprising primarily of aliphatic urethane acrylate, was used as the measurement sample. This sample is used as a coating agent in practical implementations, having characteristics such as low viscosity, fast drying, colorless, transparent, and non-yellowing. This sample was dissolved in chloroform to prepare a 20 mg/mL solution, 100 µL of which was collected for SEC fractionation.

2-2. Notes on SEC-AccuSpot

SEC-AccuSpot was developed by Shimadzu Corporation and Nissan Chemical Industries, Ltd. for the purpose of automating SEC-MALDI-MS analysis. Much time and effort are required using ordinary SEC fractionation procedures, since individually fractionated samples must be dropped onto a MALDI plate and the process of matrix addition must be performed for each fractionated samples.

AccuSpot automatically mixes with matrix solution and drops a few µL of each elute that has been fractionated using SEC onto the MALDI plate, thereby significantly reducing the time and effort required. This automatic fractionation system can be adapted to procedures using Py-GC/MS by arranging sample cups for Py on a dedicated plate (Fig. 2).

The tip that is brought in proximity with the plate in SEC-AccuSpot is comprised of a dual layer structure (Fig. 3), with the center releasing the eluted component and the second layer releasing the matrix solution. These are mixed at the tip of the nozzle before being dropping onto the plate. The pipe is made of solvent resistant material because organic solvents are used, and is also equipped with a ventilation feature for discharging volatilized solvent [4]. As no matrix is required for Py-GC/MS, no matrix solution is used and only the eluate is fractionated into sample cups for Py.

2-3. Fractionation Operation Using SEC-AccuSpot

The setup was comprised of a pump model LC-20AD (Shimadzu Corp.), a model CTO-20AC (Shimadzu Corp.) column oven, serially connected organic SEC (GPC) columns GPC-K803 and GPCK-860M (Showa Denko), and a guard column GPC K-G (Showa Denko). A model RID-10A differential refractometer (Shimadzu Corp.) was used for the detector. Chloroform was used as the mobile phase, with the flow rate set to 1.0 mL/min. A portion of the fractions, which included the sample components fractionated by SEC, was dropped directly into the sample cup to be measured by Py-GC/MC at a rate of 20 µL every 30 s for a duration of 20–26 min from the start of the measurement, using automatic fractionation equipment AccuSpot NSM-1 (Shimadzu Corp.). The sample was dropped onto a sample plate for MALDI-MS measurements. The drops were 0.55 µL after mixing the sample with matrix solution using AccuSpot, ensuring that the ratio of column elute to matrix solution (described later) was 10:1 for MALDI-MS measurements. The operation was repeated up to ten times for the purpose of Py-GC/MS measurements with fractions containing low component concentrations, while five repeated spotting were performed at the same position for all fractions for the purpose of MALDI-MS measurements.

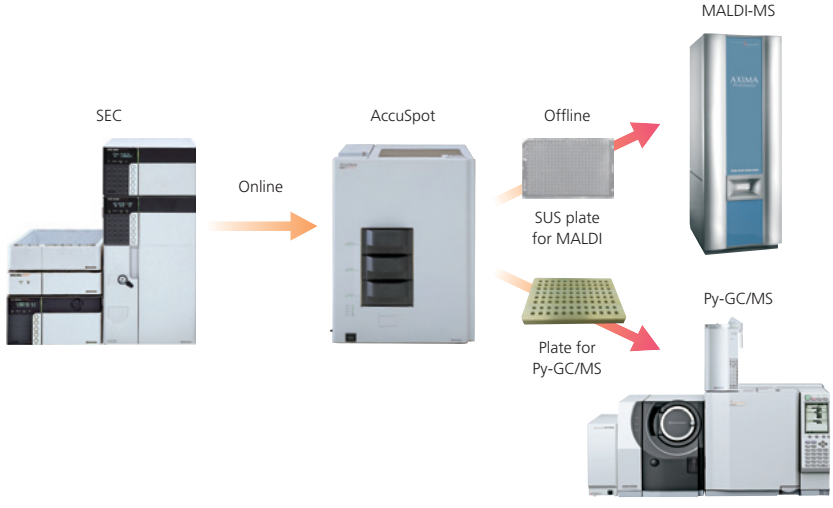

Fig. 2 System Configuration for SEC-AccuSpot/MALDI-MS or Py-GC/MS

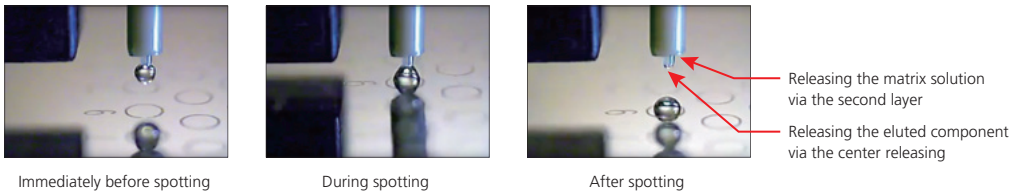

Fig. 3 Tip of Pipe on AccuSpot

2-4. Analysis Conditions for Py-GC/MS

Py-GC/MS analysis was performed on fractions that were fractionated in sample cups by AccuSpot. The system consisted of a furnace type pyrolyzer PY-2020iD (Frontier Laboratories Ltd.) fitted on the GCMS-QP2010 Plus (Shimadzu Corp.) of the GC-MS, which was used as the pyrolyzer for taking measurements. The metallic capillary column, Ultra ALLOY-5 (30 m length, 0.25 mm I.D., and 0.25 μm film thickness; Frontier Laboratories Ltd.) was used as the separation column.

2-5. Analysis Conditions for MALDI-MS

A mixture of 1 mL matrix (22.6 mg/mL dithranol in THF solution), 1 mL cationization reagent (1 mg/mL sodium trifluoroacetate in THF solution), and 100 μL standard substance for mass calibration (1 mg/mL Chimassorb 119 FL (primary isotope ion peak with *m/z* value of 2285.61) in THF solution) was used as the matrix solution for MALDI-MS. MALDI-MS measurements were taken using an AXIMA-CFR Plus time-of-flight mass spectrometer (Shimadzu Corp.), with analysis performed in linear positive mode.

Details of analysis conditions for respective operating processes are shown in Table 1.

Table 1 Analysis Conditions for SEC, AccuSpot, Py-GC/MS, and MALDI-MS

SEC

[Instrument]

Pump	: LC-20AD
Column Oven	: CTO-20AC
Detector	: RID-10A
Degassing Unit	: DGU-20A$_3$

[SEC]

Column	: Shodex GPC-K803 (8.0 mm I.D. × 300 mm, 6 mm, Showa Denko) + Shodex GPC K-806M (8.0 mm I.D. × 300 mm, 10 mm, Showa Denko) + Shodex GPC K-G (Showa Denko)
Mobile Phase	: Chloroform
Flow Rate	: 1.0 mL/min
Split Ratio	: 1:1000
Injection Vol.	: 100 μL (20 mg/mL in Chloroform)
Oven Temp	: 40 °C

AccuSpot

Instrument	: AccuSpot NSM-1
Fraction Collection Time	: 20–26 min
Spot Interval	: 30 s
Matrix Flow Rate (MALDI-MS)	: 0.1 μL/min
Loadage (Py-GC/MS)	: 20 μL/cup
Loadage (MALDI-MS)	: 0.55 μL/well (Fraction:Matrix=10:1)

Py-GC/MS

[Instrument]

Pyrolyzer	: PY-2020iD (Frontier Laboratories Ltd.)
GC/MS	: GCMS-QP2010 Plus

[Pyrolyzer]

Furnace Temp.	: 600 °C
Interface Temp.	: Manual (300 °C)

[GC]

Column	: Ultra ALLOY-5 (30 m × 0.25 mm I.D., df = 0.25 μm, Frontier Laboratories Ltd.)
Injection Temp.	: 320 °C
Column Oven Temp.	: 50 °C (10 min) → (5 °C /min) → 300 °C (20 min)
Injection Mode	: Split
Carrier Gas	: He
Flow Control Mode	: Pressure (84.4 kPa)
Purge Flow	: 3.0 mL/min
Split Ratio	: 30

[MS]

Interface Temp.	: 250 °C
Ion Source Temp.	: 250 °C
Measurement Mode	: Scan
Scan Mass Range	: *m/z* 40–600
Scan Event Time	: 0.5 sec
Scan Speed	: 1250 u/sec

MALDI-MS

Instrument	: AXIMA-CFR plus
Analysis Mode	: Linear Positive
Laser Strength	: 40–80
Mass Range	: *m/z* 0–5000
Shots	: 10
Profiles	: 100

[Mixture of matrix, cationizing reagent and mass calibration standard]

Matrix	: 22.6 mg/mL Dithranol in THF 1mL
Cationization Reagent	: 1 mg/mL Na-TFA in THF 1 mL
Mass Calibration Standard	: 1 mg/mL Chimassorb 119FL in THF 100 μL

THF: Tetrahydrofuran, TFA: Trifluoroacetic acid

3. Results and Discussion

SEC chromatogram for the entire paint raw material, as well as the pyrogram and MALDI mass spectra for respective fractions, is shown in Fig. 4. Two significant peaks were observed in the SEC chromatogram for the entire sample. Pyrograms derived from Py-GC/MS analyses of respective fractions roughly corresponded to the two peaks in the SEC chromatogram, with each indicating different patterns. The peak appearing in the pyrogram at around 35 min was the main component in the high-molecular weight fraction, but was observed as a minor peak in the low-molecular weight fraction. Furthermore, the peak at around 45 min was observed only in the low-molecular weight fraction. Meanwhile, in the MALDI mass spectrum it was evident that the *m/z* value of the observed peak group has gradually shifted in a manner corresponding to the molecular weight of the fractions.

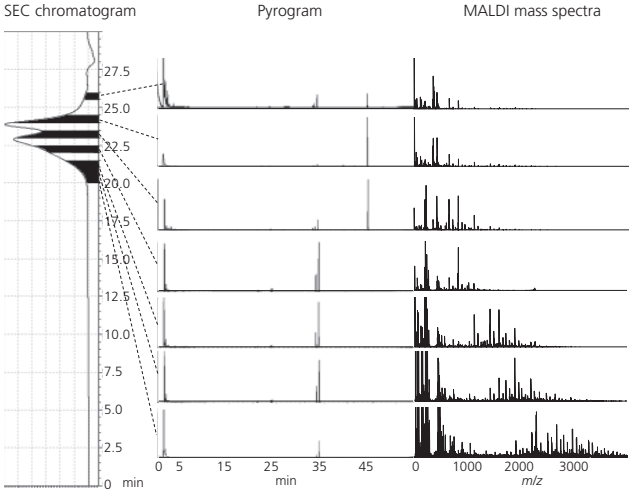

Fig. 4 SEC Chromatogram for Entire Sample, and Pyrograms and MALDI Mass Spectra of Respective Fractions

3-1. Analysis of Fractions in Low-Molecular Weight Regions

The peak at 45 min in the Py-GC/MS pyrogram was identified as pentaerythritol tetraacrylate (PETTA) in the lowest molecular weight fraction, at 25.5–26.0 min. Acrylic acid and 2-methyl-2-propenal, which are derived from pyrolysates, were also detected. The peak at *m/z* 375, which corresponds with the molecular weight of [PETTA+Na], was also detected as the primary peak in the MALDI mass spectrum of the same fraction. Furthermore, a series of peak groups (●) were observed at intervals between *m/z* 375 and 298. This mass interval matched the molecular weight of PETTA (*m/z* 298), revealing the existence a component resulting from the polymerization of pentaerythritol triacrylate (PETA) on PETTA (Figs. 5 and 6).

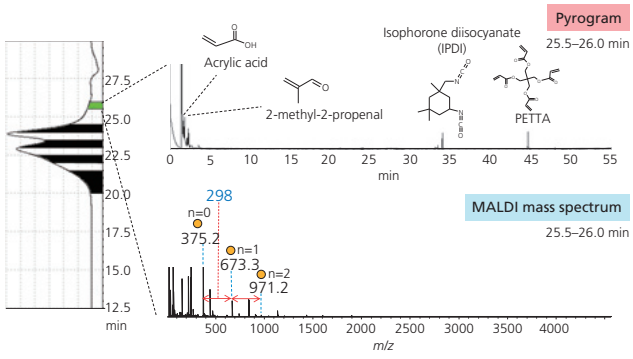

Fig. 5 Analysis Results for Fractions in the Interval 25.5–26.0 min: Detection of ● Peaks

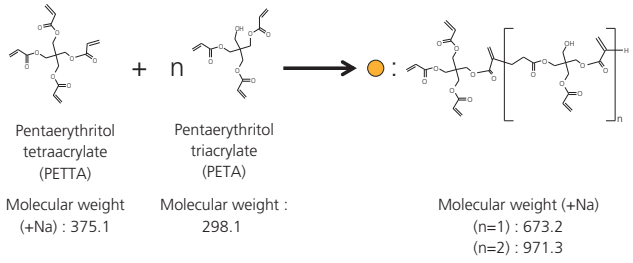

Fig. 6 An Example of the Molecular Structure Proposed for Peak ●

Furthermore, the peak at 35 min in the pyrogram was identified as isophorone diisocyanate (IPDI). This was estimated to be a urethane acrylate component derived from the formation of urethane bonds between hydroxyl groups in two molecules of PETA and isocyanate groups in IPDE, since *m/z* 841 was detected in the MALDI mass spectrum. Furthermore, as a series of peak groups (■) was detected at an interval of *m/z* 298, starting from *m/z* 841, this revealed the existence of a series of urethane acrylate components polymerized with PETA (Figs. 7 and 8).

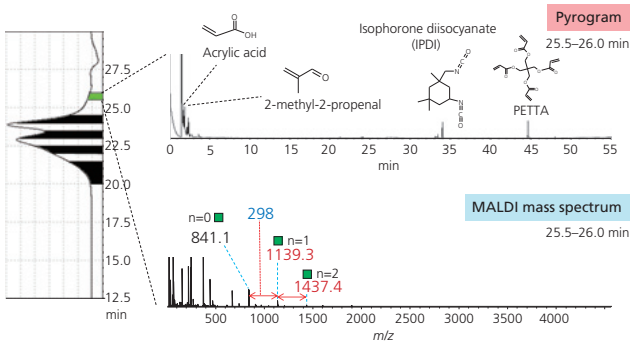

Fig. 7 Analysis Results for Fractions in the Interval 25.5–26.0 min: Detection of ■ Peak

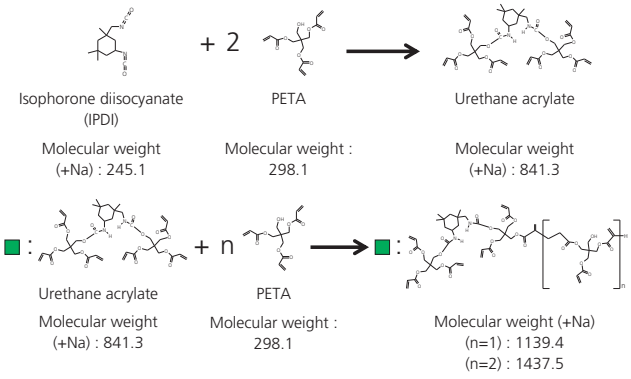

Fig. 8 An Example of the Molecular Structure Proposed for Peak ■

The peak intensity of PETTA in the pyrogram of Py-GC/MS had increased corresponding to the peak in the SEC chromatogram of the fraction at 24.0 to 24.5 minutes in comparison to the fraction at 25.5 to 26.0 minutes. This led to greater proportion in the overall pyrogram. Peak groups of ● and ■ emerged (n = 0, 1, and 2 in all cases) in the MALDI mass spectra of the same fraction, as well as the 25.5–26.0 min interval. In addition, peaks at *m/z* 447 and 913 had also emerged (Fig. 9).

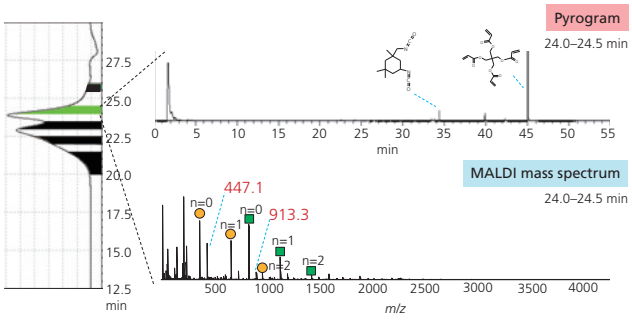

Fig. 9 Analysis Result 1 for Fractions of the Interval Between 24.0–24.5 min: Detection of Peaks ●, ■, and *m/z* 447, as well as 913

The peak at *m/z* 913 was thought to be a component derived from the above-mentioned urethane acrylate ([M+Na] = 841.3) made by two molecules of PETA bonding with IPDI and acrylic acid (molecular weight = 72.0). Furthermore, since peak groups (▲) were also detected at an interval of *m/z* 298, starting from *m/z* 913, it became evident that components of the polymerization of PETA were also included with this component (Figs. 10 and 11).

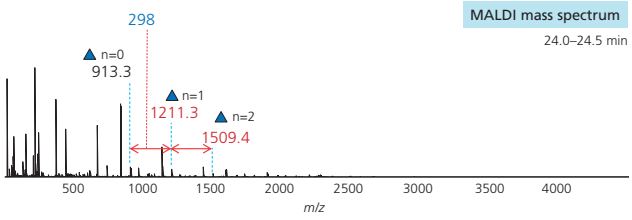

Fig. 10 Analysis Result 2 for Fractions in the Interval Between 24.0–24.5 min: Detection of ▲ Peaks

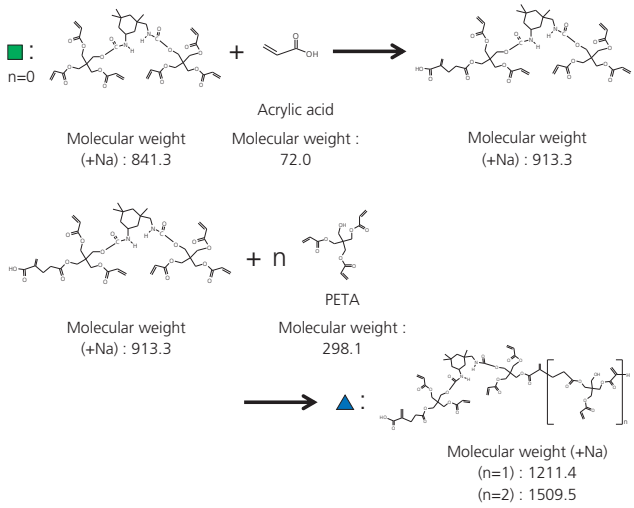

Fig. 11 An Example of Molecular Structure Proposed for Peak ▲

Furthermore, the peak at *m/z* 447 was estimated to be a component derived from acrylic acid (molecular weight = 72.0) bonding with PETTA ([M+Na] = 375.1). Peak groups (☆) were detected at an interval of *m/z* 298, starting from *m/z* 447, suggesting that components in the polymerization of PETA were also included with this component. (Figs. 12 and 13).

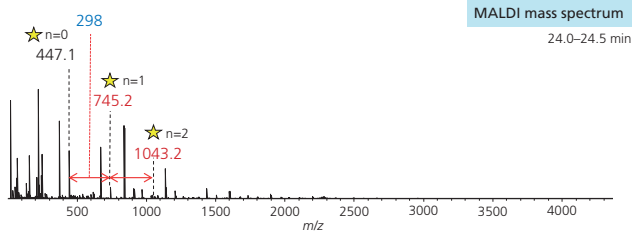

Fig. 12 Analysis Result 3 for Fractions in the Interval Between 24.0–24.5 min: Detection of ☆ Peaks

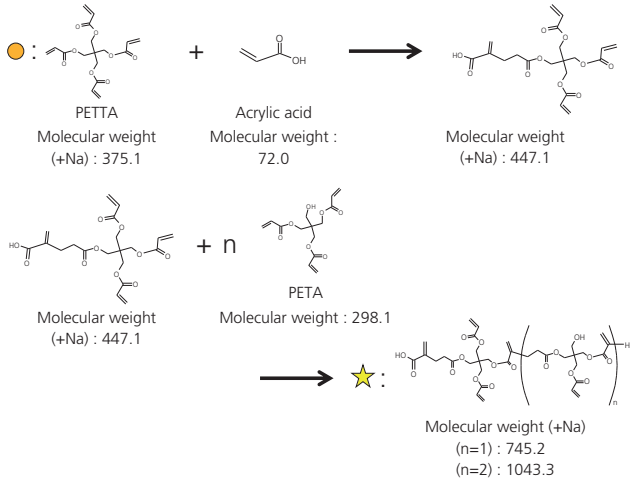

Fig. 13 An Example of the Molecular Structure Proposed for Peak ☆

This revealed that the fractions in the low-molecular weight region included components derived from the polymerization of PETA, with the common structure comprising four types of components, namely "PETTA", "IPDI, and two molecules of PETA", "IPDI, two molecules of PETA, and one molecule of acrylic acid", and "PETTA with one molecule of acrylic acid". The major component was PETTA, while the secondary components were oligomers (trimers and tetramers) comprised of PETTA and PETA, as well as urethane acrylate polymers with a single IPDI unit.

3-2. Analysis of Fractions in Intermediate Regions

In comparison with the low-molecular weight regions at 24.0–24.5 min, fractions in the intermediate regions of 23.0–23.5 min had a lower peak intensity only for the PETTA peak in the MALDI mass spectra, while the Py-GC/MS pyrogram was about the same. The PETTA peak at 45 min in the Py-GC/MS pyrogram had diminished and the peak intensity of IPDI had increased for fractions in the 22.0–22.5 min interval. The peak at *m/z* 375 (●n = 0) for PETTA also diminished with the MALDI mass spectra as well, while the proportion of urethane acrylate (■, ▲) increased (Fig. 14). This revealed that the fraction in the intermediary region contained a larger proportion of polymers of PETA, including urethane acrylate structures, in comparison with those in low-molecular weight regions.

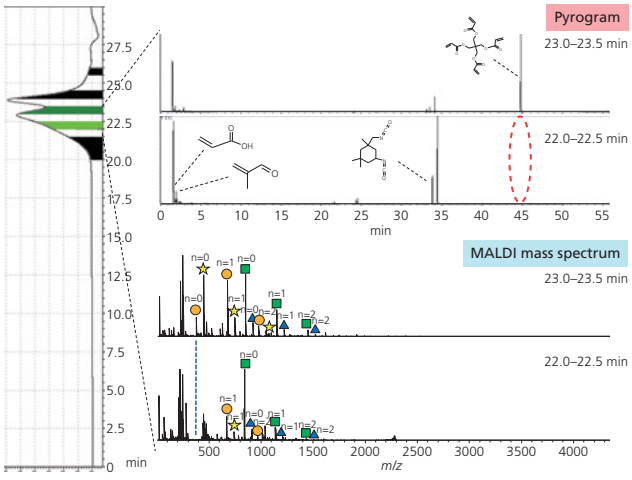

Fig. 14 Analysis Results for Fractions in the Intervals Between 23.0–23.5 min and 22.0–22.5 min

3-3. Analysis of Fractions in High-Molecular Weight Regions

Analysis results for fractions in the high-molecular weight regions are shown in Figs. 15 and 16. The Py-GC/MS pyrogram in this region was essentially identical to that of fractions in the interval 22.0–22.5 min of the intermediate regions, and the PETTA peak had diminished with the significant detection of peak for IPDI, although these are not indicated in the figure. This was thought to be caused by the urethane acrylate containing the IPDI that generated IPDI from pyrolysis, irrespective of the degree of polymerization.

However, in the MALDI mass spectrum, the peak shifted towards a high-molecular weight as the fractions were sampled from higher molecular weight regions. Components formed by the polymerization of up to six PETA units were detected with urethane acrylate (■) made of IPDI and PETA (Fig. 15). Components formed by the polymerization of a maximum of four PETA units were detected with oligomers (●) of PETTA and PETA, and components formed by the polymerization of up to four PETA were detected with urethane acrylate (▲), although these are not indicted in the figure.

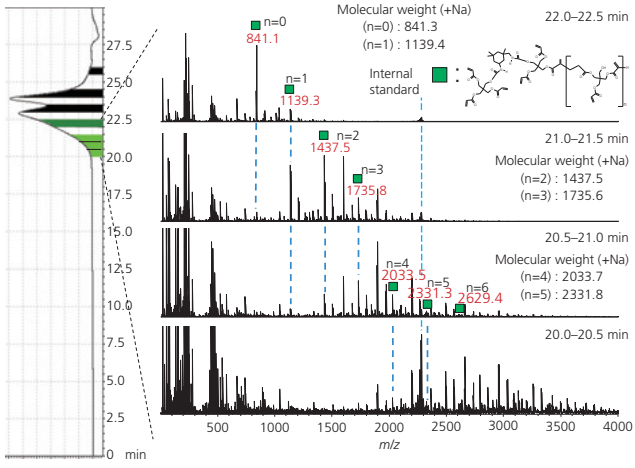

Fig. 15 MALDI Mass Spectra of High-Molecular Weight Fractions 1: Detection of ■ Peaks (Although not indicated in the figure, ● and ▲ peaks have also been detected.)

Peak groups estimated to consist of components comprised of the "one pentaerythritol diacrylate PEDA and two IPDI and two PETA" (✸) or "two PEDA, three IPDI and three PETA" (◆), as well as components from further polymerization, with those and PETA newly detected among fractions on the highest-molecular weight side, particularly from intervals between 21.0–21.5 min, 20.5–21.0 min, as well as 20.0–20.5 min (Fig. 16). This revealed that a substantial amount of urethane acrylate oligomers that include multiple units of IPDI were included in the fractions on the high-molecular weight side (Fig. 17, 18).

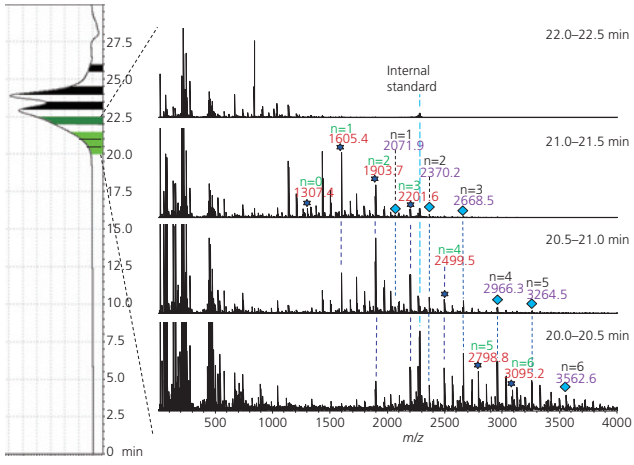

Fig.16 MALDI Mass Spectra of High-Molecular Weight Fractions 2: Detection of ✸ and ◆ Peaks

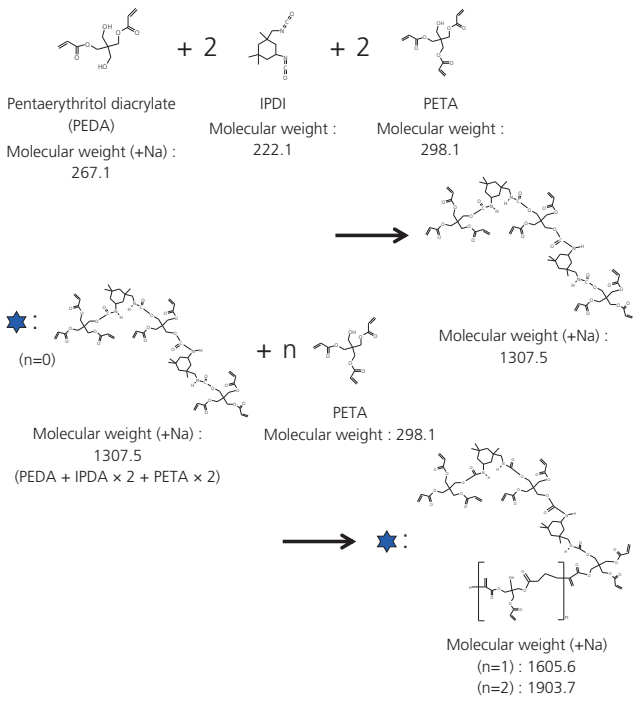

Fig. 17 An Example of Molecular Structure Proposed for Peak ★

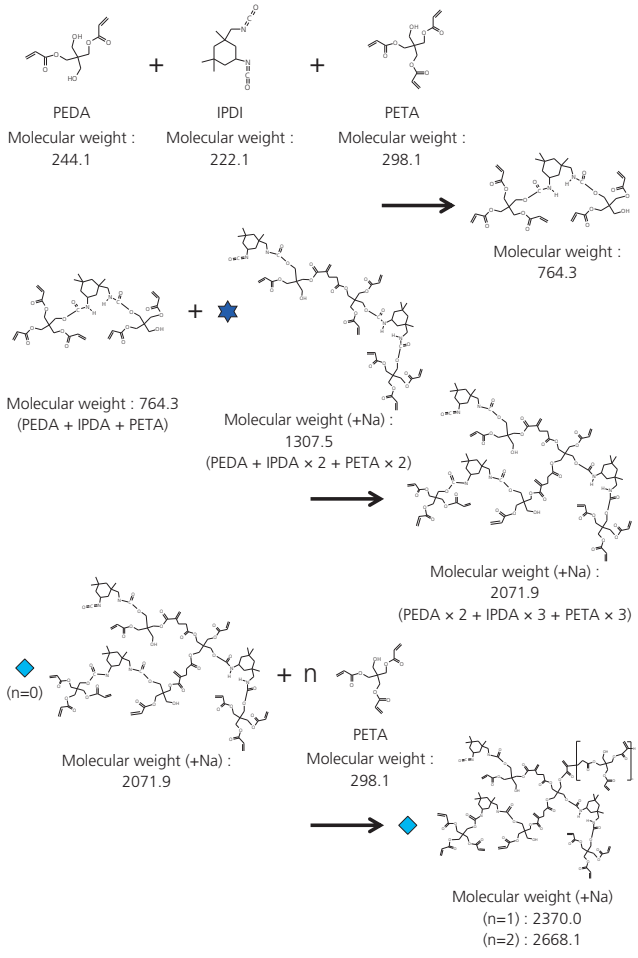

Fig. 18 An Example of Molecular Structure Proposed for Peak ◆

4. Conclusions

Two primary peaks were observed in the chromatogram after SEC of paint raw material samples was subjected to our analyses. Fractionation by AccuSpot, as well as analyses on respective fractions, revealed that the principal components of the peak in the low-molecular weight region near 25 min were PETTA, and polymers formed by PETTA and PETA. Another peak was also shown to form on the high-molecular weight side due to the existence of broad components in high and low-molecular weight regions. Furthermore, urethane acrylate oligomers comprised of PETA and IPDI were confirmed as present in higher ratios in higher-molecular weight regions.

Detailed analyses of constituent components of polymer materials with complex compositions, which were difficult to analyze in the past, can now be performed on a broad range of molecular weight regions in the manner described, by combining SEC with AccuSpot automatic spotting equipment and mass spectrometry, such as Py-GC/MS and MALDI-MS. Applications in various fields, such as the detailed analysis of compositions for new developments intended for quality control or improving the functionality of polymer materials, and the analysis of impurities in polymers or additives, are expected.

References

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Trace component analysis and polymer structural analysis of synthetic polymers

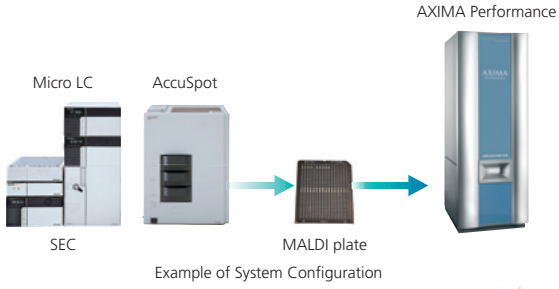
SEC AccuSpot-AXIMA system

Samples eluted separated and fractionated by SEC (size-exclusion chromatography) are automatically spotted by the AccuSpot spotting equipment on the MALDI plate, while simultaneously mixing with the matrix reagents required for MALDI ionization. Plates can be analyzed by the MALDI-TOFMS AXIMA series systems immediately after being spotted.

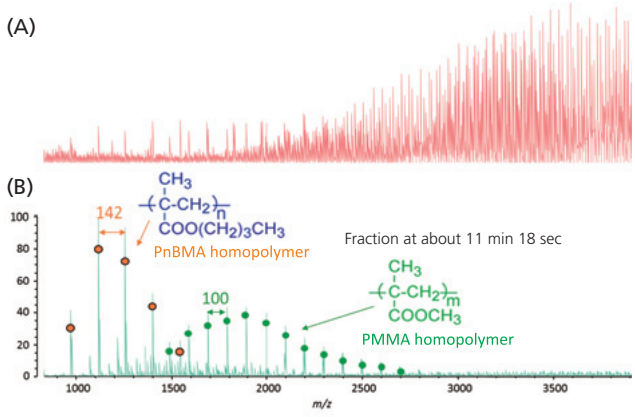
Easy detection and structural analysis of trace components

Inhibition of ionization by principal components occurs less readily in comparison with methods that analyze polymers directly with MALDI-TOF-MS, due to the separation performed by SEC, making detection and structural analysis of trace components, such as byproducts and additives, easier.

Not only molecular mass distribution for samples as a whole, but also detailed structural analysis information, such as the compositions of monomers within polymers, can be derived. The analysis of both simple homopolymer components and complex copolymer components can be performed easily using polymer analysis software (optional).



Example of System Configuration



Comparison of Mass Spectra Before and After Separation
(A) Prior to separation by SEC, (B) After separation by SEC

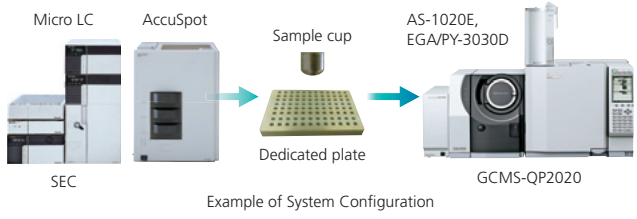
Trace component analysis and polymer structural analysis of synthetic polymers

SEC AccuSpot-Py-GC/MS system

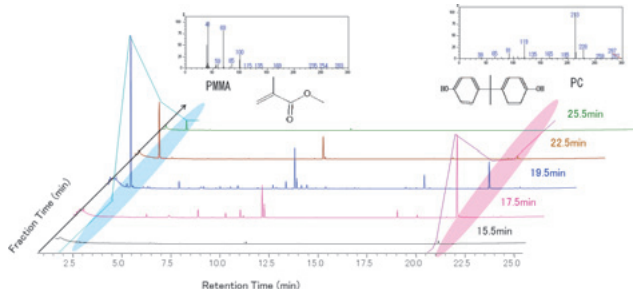
Sample elutes separated and fractionated by SEC are automatically added to sample cups for Py-GC/MS installed on dedicated plates using the AccuSpot equipment. Samples are added into sample cups that can be analyzed immediately with Py-GC/MS.

High separation by combination of SEC and GC, qualitative analysis using mass spectral library

Py-GC/MS is also effective in the structural analysis of polymers by analysis of pyrolysates, as well as for detecting and identifying trace components of impurities and additives. Combining this with separation by SEC makes it possible to analyze blended polymers by reflecting molecular weight distributions, as well as detailed analysis with low-molecular weight components, such as additives, separated from the polymers. Qualitative analysis of various components is possible using mass spectral libraries, such as NIST or Wiley.



Example of System Configuration



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