SHIMADZU

Application News

MALDI-TOF Mass Spectrometry No.B15

Analysis of Polymer Additives in Synthetic Polymers using a SEC-MALDI System

Synthetic polymers may deteriorate as a result of various factors such as light, heat, mechanical stress, electrical stress, radiation, chemicals and moisture. Various additives such as antioxidants, UV absorbent, HALS (Hindered Amine Light Stabilizers) and thermal stabilizers have been developed to maintain the properties of polymers and prevent degradation. The amount of additive depends on the intended use of the polymer but, typically, it is less than 1% (w/w). The additive also depends on the grade or the manufacturer of the polymer, even if the type of polymer is the same.

Analysis of additives in synthetic polymers is therefore important for the evaluation or improvement of polymer properties. Recently, MALDI-TOF MS has been used for the analysis of polymer additives. However, minor components such as additives may not be detected as a result of ion suppression by major components present in the sample. SEC (Size Exclusion Chromatography)-MALDI is an effective tool for detecting these minor components. In SEC-MALDI, a mixture of components is first separated by SEC and the resulting fractions are analyzed by MALDI-TOF MS. We have developed a spotting/fraction collection robot (AccuSpot) which can be used for the automatic collection and preparation of fractions for MALDI analysis. Eluent from the SEC column is mixed with MALDI matrix and automatically deposited onto a MALDI target as discrete fractions. The AccuSpot used for this application has been modified so it is tolerant to the organic solvents typically used for SEC separation of synthetic polymers.

Here, we present an example demonstrating the detection of an additive present in a commercial acrylic resin plate.

■ Method

Approximately 1g of acrylic resin plate was immersed in 1mL of THF (tetrahydrofuran) and sonicated for 1min. An aliquot of the supernatant was used for subsequent SEC-MALDI analysis (Fig.1). Dithranol (20 mg/mL) was used as MALDI matrix and sodium trifluoroacetate (10 mg/mL) was used as a cationizing reagent. The dithranol and sodium trifluoroacetate solutions were mixed and the resulting matrix/salt solution was added using the matrix delivery pump of the AccuSpot (Table 1). The SEC chromatogram (UV detection) following separation of the extraction liquid of the acrylic resin plate is shown in Fig.2. Fractions were collected every 6 sec (RT = 7 to 17.5 min) using the AccuSpot, resulting in 105 fractions.

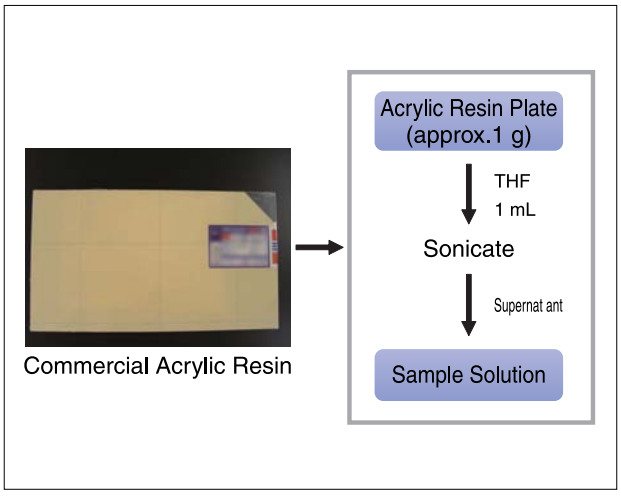

Fig.1 Sample Preparation

Table 1 Analytical Conditions

• SEC	
Column	: Shodex GF310A-1E (1.0 mmID × 250 mm)
Mobile Phase	: THF(*)
Flow Rate	: 10 µL/min
Injection Volume	: 1 µL
Detector	: UV (λ = 220 nm)
Column Temp.	: 40 °C
• AccuSpot	
Spot Interval	: 6 sec
Fraction Volume (SEC)	: 1 µL/well
Fraction Volume (mixture of matrix and cationizing reagent)	: 0.2 µL/well
• MALDI - TOFMS	
Instrument	: AXIMA *Performance*™ (SHIMADZU KRATOS)
Mode	: Linear, Positive
Matrix	: Dithranol-20 mg/mL-THF
Cationizing Reagent	: Na-TFA(**)-10 mg/mL-THF

(*) : Tetrahydrofuran, (**) : Trifluoroacetic acid

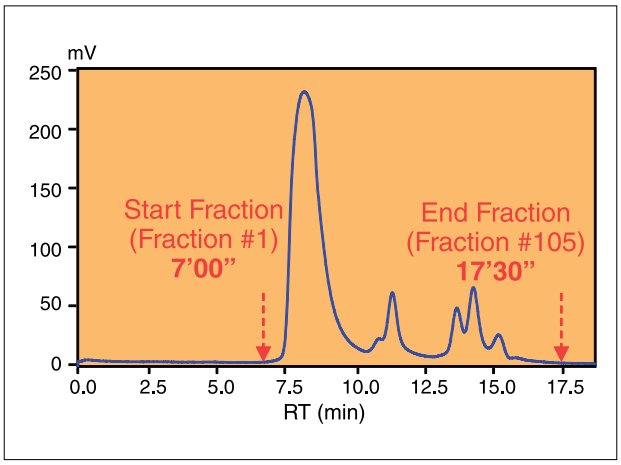

Fig.2 SEC Chromatogram of Extraction Liquid

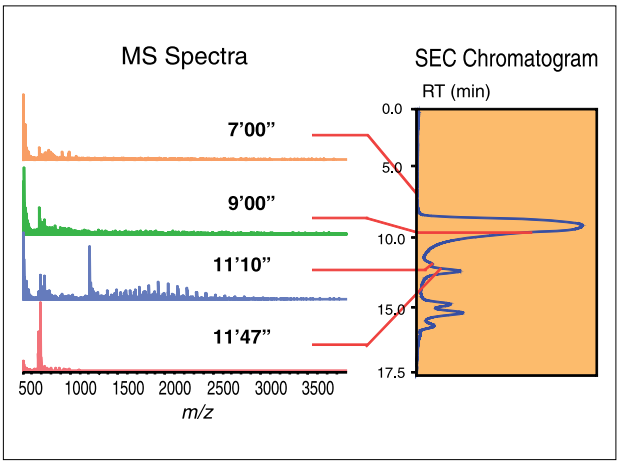

Fig.3 MS Spectra of SEC-Separated Fractions

A mass spectrum was generated for each fraction by MALDI-TOF MS (Fig.3). Each MS spectrum shows a different molecular distribution. The peak corresponding to the additive (IRGANOX 1010 + Na, *m/z* 1200) was detected in the fraction collected at 11 min 10 sec (Fig.4). This peak could not be detected without SEC separation. In addition, distributions corresponding to three different polymer compounds of similar mass (*m/z* 2000) but different molecular distribution were also detected. These peaks can be identified as oligomers of the same monomer, indicated by the mass difference between neighboring peaks of the same series (dM = 100). The molecular distribution differs because of differences in the end groups.

In conclusion, the additive IRGANOX and minor oligomers in a synthetic polymer preparation have been analyzed. The SEC-MALDI system described can be used to analyze various minor compounds present in complex mixtures.

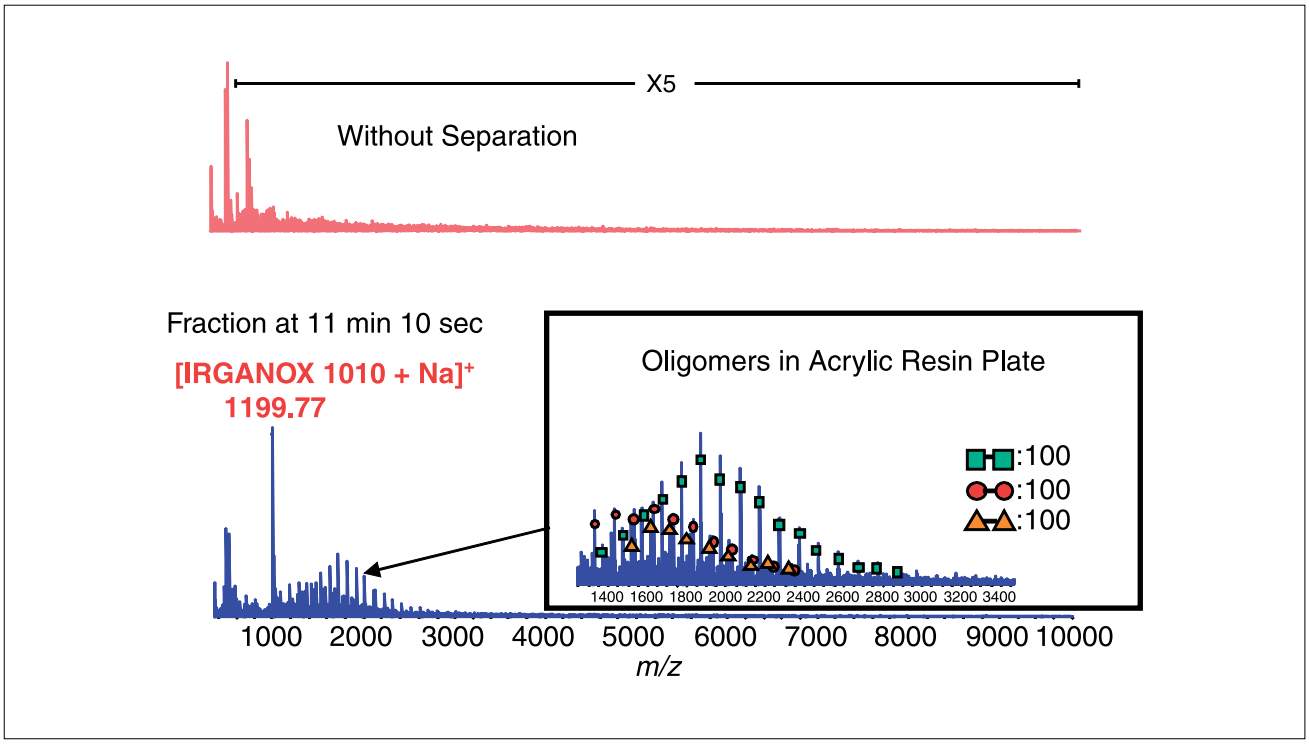

Fig.4 Detection of Additive in Acrylic Board

NOTES:
✻This Application News has been produced and edited using information that was available when the data was acquired for each article. This Application News is subject to revision without prior notice.

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