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Application News

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MALDI-TOF Mass Spectrometry

Thermal Deterioration Analysis of Polymers using a Linear Benchtop MALDI-TOF MS

In recent years, MALDI-TOF mass spectrometers are being utilized more and more for simple molecular weight measurement and profiling of synthesized products and high-molecular compounds. This is because instruments of this type have several advantageous features: singly-charged ions are generated so molecular weights can be recognized easily, the mass range is wide, and there are many solvent options because the sample is dried before measurement.

On the other hand, due to changes in social conditions over the last several years, government offices, universities and private enterprises strongly request the reduction of costs for both the introduction and running of instruments used for such applications. The benchtop "MALDI-8020" MALDI-TOF mass spectrometer is a new instrument that can adequately meet these market needs. The noteworthy point about this instrument is that it has a shorter flight tube, which is the key feature of its small size, while retaining performance equal to or higher than that of a conventional model.

In the process of the recent development and quality control of materials and chemical products, there is an increasing need to simply and quickly examine the degradation of synthesized polymer products based on chemical changes at a molecular level in association with durability tests. This article introduces an example of analyzing the thermal degradation of polymers using the MALDI-8020 mass spectrometer.

Y. Yamazaki

Benchtop MALDI-TOF Mass Spectrometer, MALDI-8020

The MALDI-8020 (Fig. 1) is a compact-design, minimal-space linear mode-only MALDI-TOF mass spectrometer. Its performance in linear mode (positive ion) is comparable to the same mode of a conventional MALDI-TOF mass spectrometer. Equipped with a 200 Hz solid laser and a load lock chamber mechanism that enables a target plate change in a few minutes while maintaining the degree of vacuum at the measuring position, the instrument ensures rapid measurements.

The flight tube of this instrument is shortened to 0.85 m long; however, the mass resolving power is as good as that of a conventional model. The instrument has a practical resolving power that enables isotope separation even near *m/z* 4000.

Degradation Model Creation and Measurement Conditions

We prepared degradation model samples by repeating the process of heating and molding polymers 0, 1, 4 and 10 times. We dissolved these polymers without treatment and used the solution for MALDI measurement. In addition, we introduced these polymers, after dissolving in a good solvent, into a poor solvent, then collected supernatants containing oligomers with no precipitates (dissolution/reprecipitation method), and used this solution for MALDI measurement. We used dithranol (20 mg/mL, chloroform) for the matrix, and Na-TFA (10 mg/mL, THF) as a cationization agent.

Statistical Analysis

Statistical analyses including multivariate analysis are effective tools to detect defective products by comparison with normal products; however, some commercially available software requires advanced knowledge of statistical analysis, which may give the impression of a barrier to the use of such software. The newly developed eMSTAT Solution™ provides an intuitive and prompt statistical analysis. We used this software for analysis.

Fig. 1 MALDI-8020 Benchtop MALDI-TOF MS

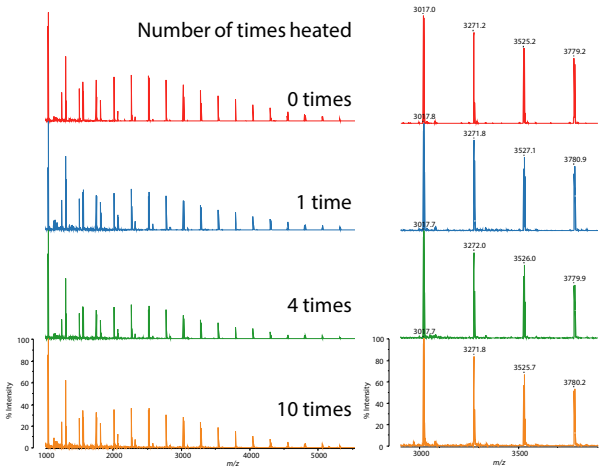

Fig. 2 Mass Spectrum of General-purpose Polyester
*** Polymers dissolved to 10 mg/mL were measured without treatment.**

Measurement and Analysis Results of Oligomer Domains

First we dissolved polymers in chloroform and carried out measurements on the MALDI-8020 (Fig. 2). There were no significant differences among the samples. Then, we used chloroform as a good solvent and acetonitrile as a poor solvent, separated relatively low molecular oligomer components using the dissolution/reprecipitation method, and carried out measurement. The results are shown in Fig. 3. From the figure, minor molecular weight components, clearly different from the main component signals, were observed. These components showed an increasing tendency as the number of times heated increased. All data were converted into text form, and analyzed on eMSTAT Solution (Fig. 4). At the instant when eMSTAT Solution reads the data, statistical analysis results are displayed at the default settings, and by intuitively changing the minimally required parameters, the optimal results can be obtained. As shown in the score plot in Fig. 4, these components were clearly grouped into four components.

Conclusion

We performed degradation analysis of polymers using the benchtop MALDI-8020 MALDI-TOF mass spectrometer and eMSTAT Solution statistical analysis software, and rapidly obtained useful results. Degradation or anomalous components even in trace amounts may exert a significant effect on the properties of polymers. The minimal pretreatment and MALDI-8020 performance can be an effective means of catching small changes in a molecular level. In addition, for the purpose of detecting specific anomalous components to check a process for example, eMSTAT Solution can be useful software that is simple and smooth to operate.

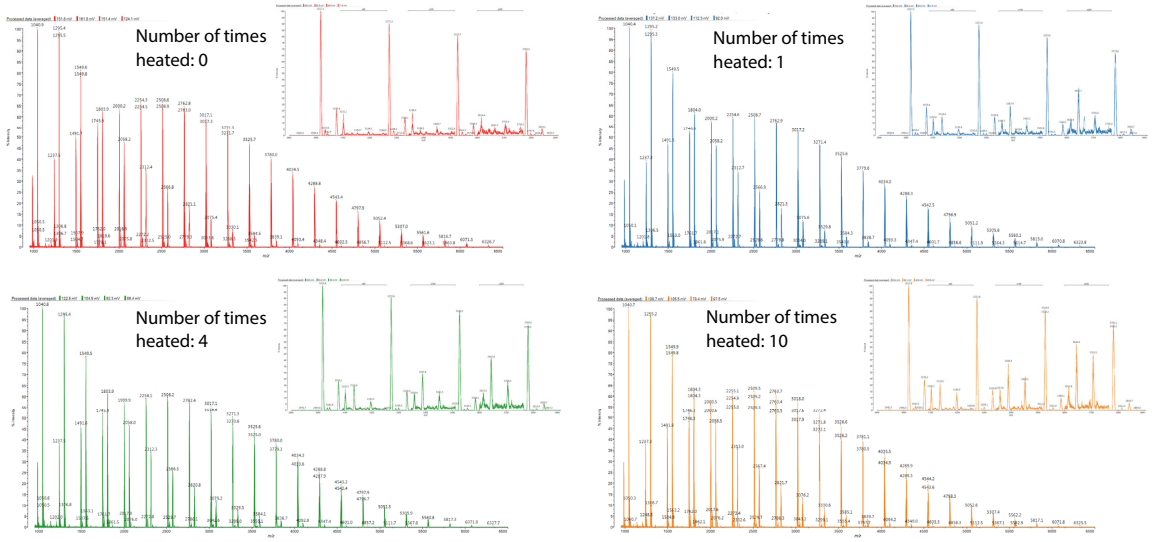

Fig. 3 Mass Spectrum of General-purpose Polyester after Dissolution/Reprecipitation Treatment

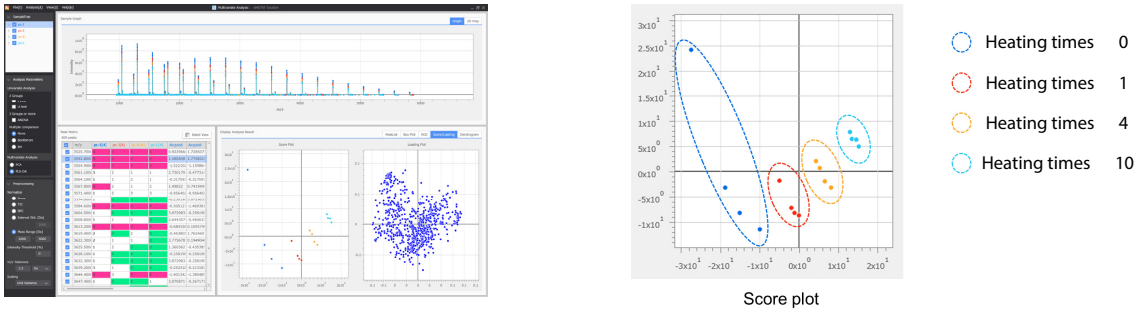

Fig. 4 Statistical Analysis Software Screen (Left) and Enlarged Score Plot (Right)

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