

# Application News

MALDI-TOF Mass Spectrometry

No.B02

## Analysis of Minor Components in Synthetic Polymers Using SEC-AccuSpot-AXIMA System (1)

MALDI-TOF mass spectrometry is widely used as a technique for the characterization of synthetic polymers. However, when multiple components are present in samples, major components may suppress ionization of the trace components present, preventing their detection.

Size exclusion chromatography, (SEC) is a chromatographic method that can be used to prevent this adverse result by separating the components into fractions beforehand. However, off-line SEC/MALDI MS involves fraction collection, evaporation, pipetting, etc. and is laborious and time consuming, so direct deposition methods in which SEC fractions and MALDI matrix are directly deposited onto the MALDI target are preferred.

Shimadzu has developed the AccuSpot automated spotter to mix the eluate from the LC with the various

reagents and directly load them onto the MALDI sample plate. As a result, an automated analytical SEC-MALDI analysis system was constructed that can rapidly simplify all the processing from LC separation to MALDI-TOFMS measurement.

Here, using a copolymer - poly (methylmethacrylate-*b*-*n*-butylmethacrylate) (poly (MMA-*b*-*n*-BMA)) - a sample with a complicated composition, we present an example of detection of a homopolymer present at trace levels in the sample. The size exclusion chromatography (SEC) mode was used for the separation, and a micro-scale separation column was used to load all of the components onto the MALDI sample plate without any waste. The AccuSpot body is constructed with enhanced resistance to many organic solvents used in the field of synthetic polymers.

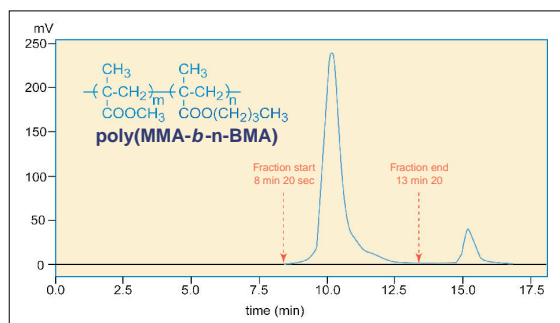


Fig.1 SEC Chromatogram of Poly (MMA-*b*-*n*-BMA)

Table 1 Analytical Conditions

• SEC	Column	: Shodex GF310A-1E (1.0 mmI.D. × 250 mm)
	Flow Rate	: 10 $\mu$ L/min, Eluent : THF
	Detector	: UV ( $\lambda$ =220 nm), Injection volume : 1 $\mu$ L
• AccuSpot	Spot Interval	: 6 sec, Loadage : 1 $\mu$ L/well
	Loadage (mixture of matrix and cationizing reagent)	: 0.2 $\mu$ L/well
• MALDI - TOFMS	Matrix	: Dithranol-20 mg/mL- THF
	Cationizing Reagent	: Na-TFA-10 mg/mL -THF

THF : Tetrahydrofuran, TFA : Trifluoroacetic acid

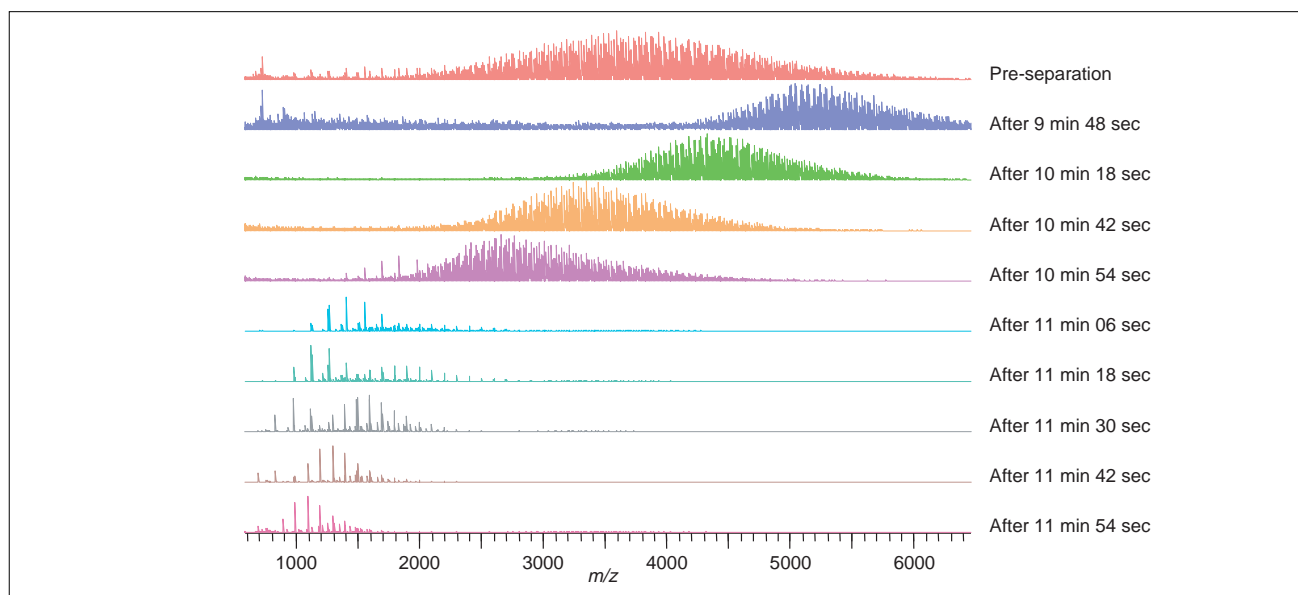


Fig.2 MS Spectra of SEC-Separated Fractions

Fig.1 shows the SEC chromatogram of poly (MMA-*b*-n-BMA). The main peak was collected every 6 seconds from the start to the end of elution (8 min 20 sec to 13 min 20 sec) using the AccuSpot, and 50 sample spots were created on the MALDI sample plate. Each spot was measured using the MALDI-TOFMS instrument, and the mass spectra corresponding to the elution times were obtained (Fig.2). The mass spectra obtained from the fractions each show a different molecular weight distribution. Focusing on the fraction after 11 min 18 sec, two different types of molecular weight distribution were detected that had not been seen before separation (Fig.3). The peaks indicated by ● in the molecular weight distribution with  $m/z$  1200 at the top show an interval

of 142 between adjacent peaks, a distribution indicating the existence of the PnBMA homopolymer. On the other hand, the peaks indicated by ■ in the molecular weight distribution with  $m/z$  1800 at the top show an interval of 100 between adjacent peaks, indicating the existence of the PMMA homopolymer. The above results clearly show that the PnBMA and PMMA homopolymers are present as minor constituents in the poly (MMA-*b*-n-BMA) sample used here. The detection of these minor components included in the synthetic polymer demonstrates that this SEC-AccuSpot-AXIMA System achieves higher time resolution of eluted constituents than the manual SEC/MALDI-TOFMS technique previously (Fig.4).

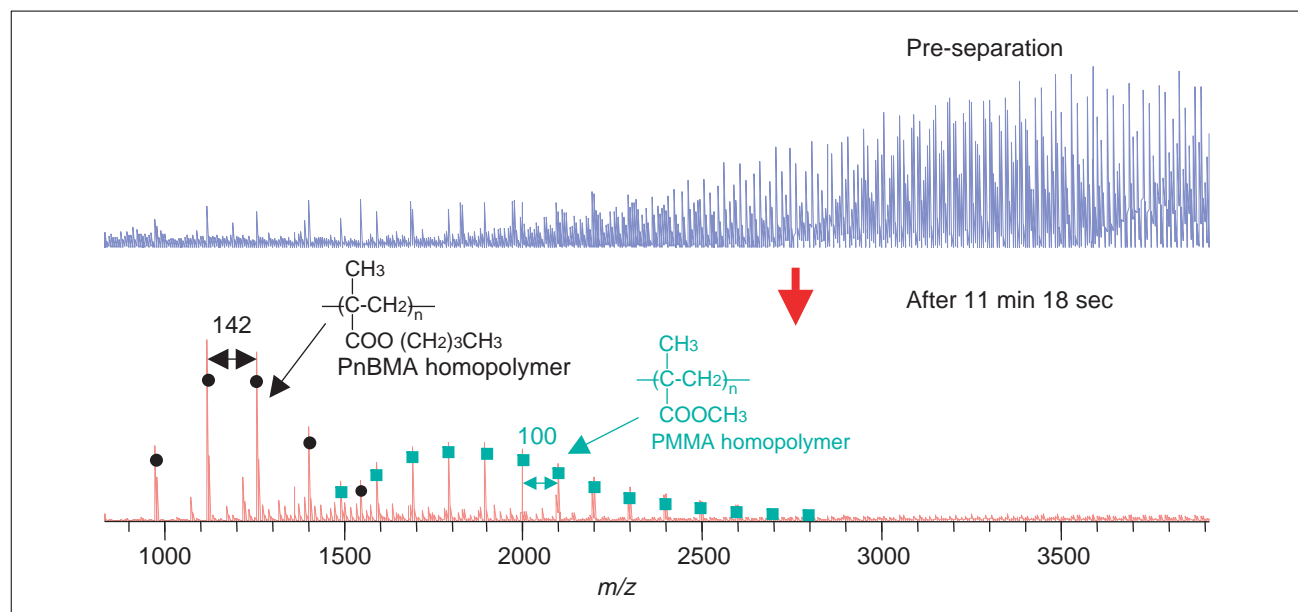


Fig.3 Detection of Homopolymer Components

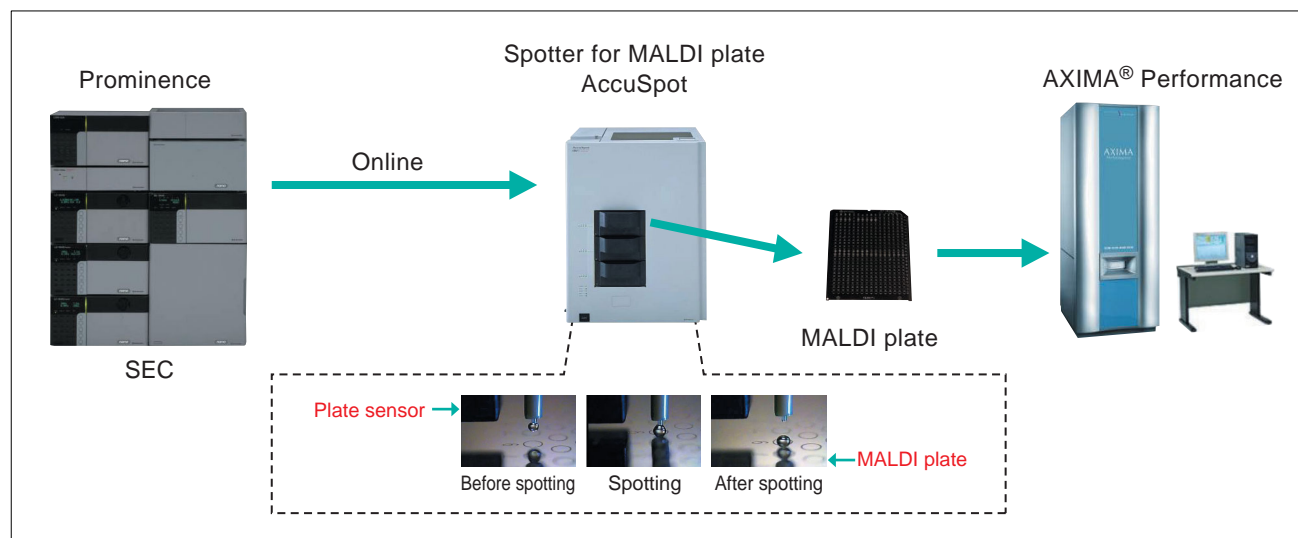


Fig.4 SEC-MALDI System

#### 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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