Structural analysis of contaminant in polypropylene product using msFineAnalysis AI

Product used: Mass Spectrometer (MS)

Introduction

Polypropylene has high strength, heat resistance, and excellent workability, so it is used in many industrial products. In the process of productization, material pellets are pulverized, mixed, and molded. Contaminants mixed in these processes causes deterioration in product performance. Pyrolysis-GC-MS method is generally used to identify contaminants, but most of pyrolysis products are not registered in the mass spectra library. So it is difficult to obtain satisfactory results with qualitative analysis relying on library searches. Time-of-flight mass spectrometer JMS-T2000GC and unknown compounds structure analysis software msFineAnalysis AI are effective for qualitative analysis of these unregistered compounds (=unknown compounds). Previous report MSTips No.330 introduced molecular formula derivation by EI/SI integrated analysis for contaminant in polypropylene product. This MSTips introduces structural formula derivation by AI structural analysis.

Experiment

Using (A) normal product and (B) defective products of polypropylene as samples, measurement was performed by the Pyrolysis-GC-MS method. The sample amounts were 0.2 mg for the EI method and 1.0 mg for the FI method. The repeat number of measurements for variance component analysis were n=5 for the EI method and n=1 for the FI method. The peaks specific to (B) defective product were derived by variance component analysis mode of msFineAnalysis AI. And their molecular and structural formulas were derived. Table 1 shows the measurement and analysis conditions.

JMS-T2000GC, msFineAnalysis AI

Table 1 Measurement and analysis conditions

Pyrolysis conditions	
Pyrolyzer	EGA/PY-3030D(Frontier Lab)
Pyrolysis Temperature	600°C
GC conditions	
Gas Chromatograph	8890A GC (Agilent Technologies)
Column	ZB-5MSi (Phenomenex) 30m x 0.25mm, 0.25µm
Oven Temperature	40°C(2min)-10°C/min -340°C(28min)
Injection Mode	Split mode (100:1)
Carrier flow	He:1.0mL/min

MS conditions	
Spectrometer	JMS-T2000GC (JEOL Ltd.)
Ion Source	EI/FI combination ion source
Ionization	EI+:70eV, 300µA
	FI+:-10kV, 40mA/30msec
Mass Range	*m/z* 29-800
Data processing condition	
Software	msFineAnalysis AI (JEOL Ltd.)
Analysis mode	Variance component analysis
	n=5 repeated measurements
Library database	NIST20

TIC chromatograms of EI method

Figure 1 shows the TIC chromatograms of EI method. Chromatograms shapes of (A) normal product and (B) defective product were similar, but a large difference peak was detected around 5 min for the (B) defective product. This peak was derived as styrene by library search.

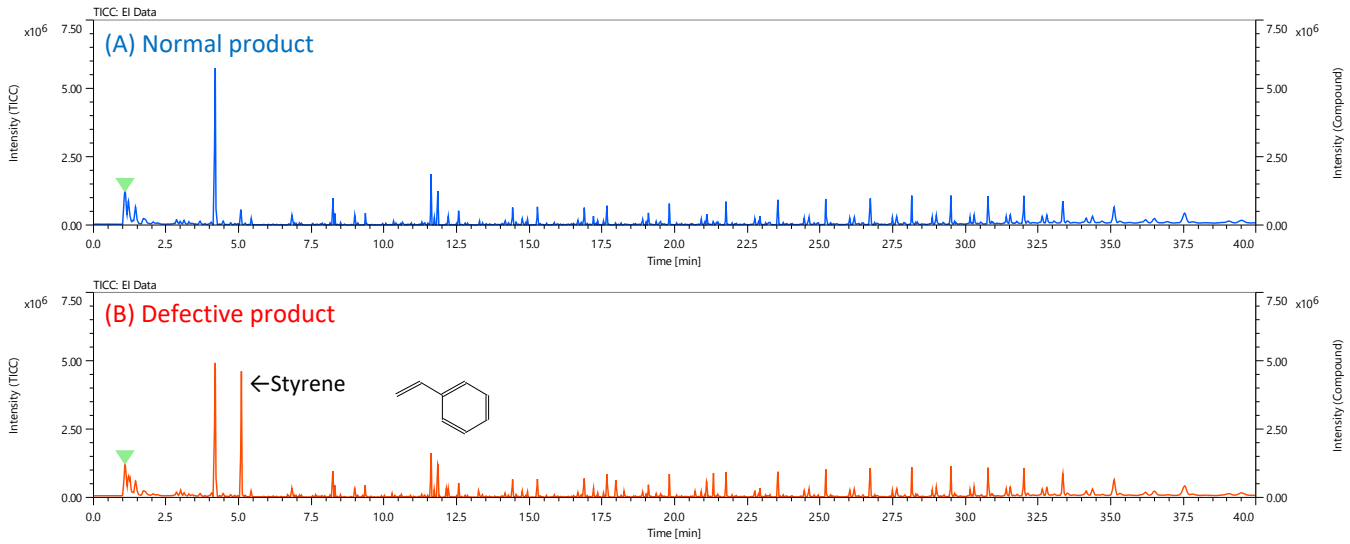
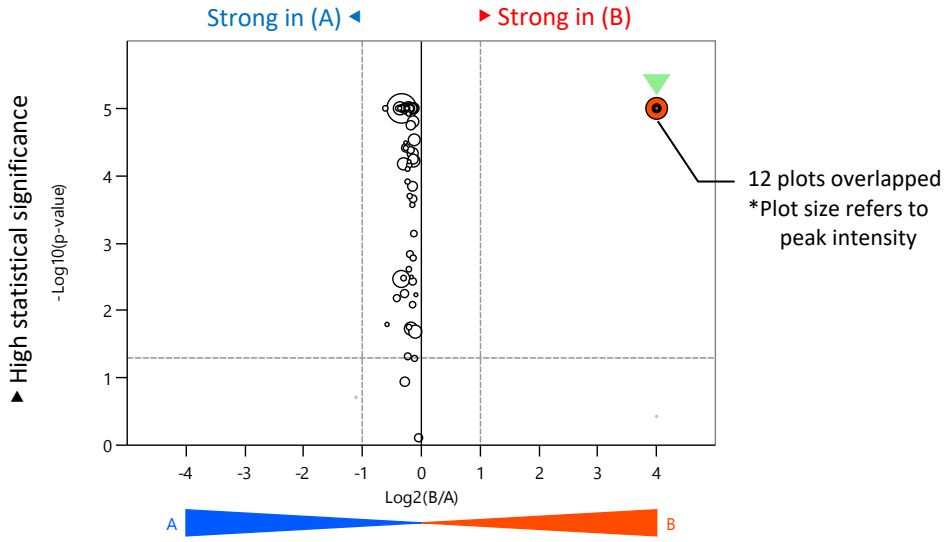


Figure 1 TIC chromatograms of EI method

Volcano plot of variance component analysis

Figure 2 shows the volcano plot of variance component analysis. Each plot corresponds to a peak on the chromatogram, and visually expresses the difference with the intensity ratio on the horizontal axis and the statistical significance (repeatability) on the vertical axis. In this analysis, 82 peaks with an intensity ratio of up to 2% to the maximum peak were targeted, and 12 peaks specific to (B) defective product were extracted.



	A Only	A > B	A = B	A < B	B Only	Others
Total: 82	0	0	68	0	12	2

Figure 2 Volcano plot

Qualitative analysis results of peaks specific to (B) defective product

Table 2 shows the qualitative results of peaks specific to (B) defective product. The compound names and structural formulas of the row which the cell "LIB." is "mainlib" are derived by NIST library search. And these of "AI" are derived by AI structural analysis. Library search derived only for 3 peaks, but AI structure analysis derived for the remaining 9 peaks.

Table 2 Qualitative analysis results of peaks specific to (B) defective product

General				Total Result								
ID	RT [min]	Height [%]	IM m/z	Compound Name	Lib.	Similarity / AI Score	Formula	DBE	Calculated m/z	Mass Error [mDa]	Isotope Matching	EI Fragment Coverage
003	1.27	4.83	53.02651	2-Propenenitrile (= Acrylonitrile)	mainlib	778	C3 H3 N	3.0	53.02600	0.51	0.91	100
007	3.00	2.15	92.06214	Toluene	mainlib	921	C7 H8	4.0	92.06205	0.09	0.89	100
012	5.09	65.31	104.06269	Styrene	mainlib	965	C8 H8	5.0	104.06205	0.64	0.96	100
023	12.14	4.99	157.08970	2-methylidene-4-phenylbutanenitrile	AI	904	C11 H11 N	7.0	157.08860	1.09	0.94	100
026	13.25	3.54	157.08966	4-phenylpent-4-enenitrile	AI	855	C11 H11 N	7.0	157.08860	1.06	0.91	100
034	16.86	2.90	208.12615	3-phenylbut-3-enylbenzene	AI	833	C16 H16	9.0	208.12465	1.50	0.86	100
040	17.68	2.80	210.11566	2-methylidene-4-(2-phenylethyl)pentanedinitrile	AI	729	C14 H14 N2	9.0	210.11515	0.51	0.67	100
041	17.98	8.52	210.11544	2-methylidene-4-phenylheptanedinitrile	AI	622	C14 H14 N2	9.0	210.11515	0.29	0.69	100
042	18.26	3.28	210.11623	2-(2-phenylprop-2-enyl)pentanedinitrile	AI	711	C14 H14 N2	9.0	210.11515	1.08	0.88	92
046	20.70	3.63	261.15184	2-methylidene-4,6-diphenylhexanenitrile	AI	660	C19 H19 N	11.0	261.15120	0.64	0.72	100
048	21.09	3.93	261.15180	3,6-diphenylhept-6-enenitrile	AI	538	C19 H19 N	11.0	261.15120	0.60	0.80	100
050	21.33	9.43	261.15152	4-phenyl-2-(2-phenylethyl)pent-4-enenitrile	AI	597	C19 H19 N	11.0	261.15120	0.32	0.85	100

mainlib=NIST library, AI=AI structural analysis

Figure 3 shows a list of derived structural formulas. Structures of all ID023-050 suggests hybrid dimers and trimers of AS copolymers, and agree with the reference literature with high accuracy [1]. So it was possible to identify that the contaminant mixed in (B) defective product was the AS copolymer.

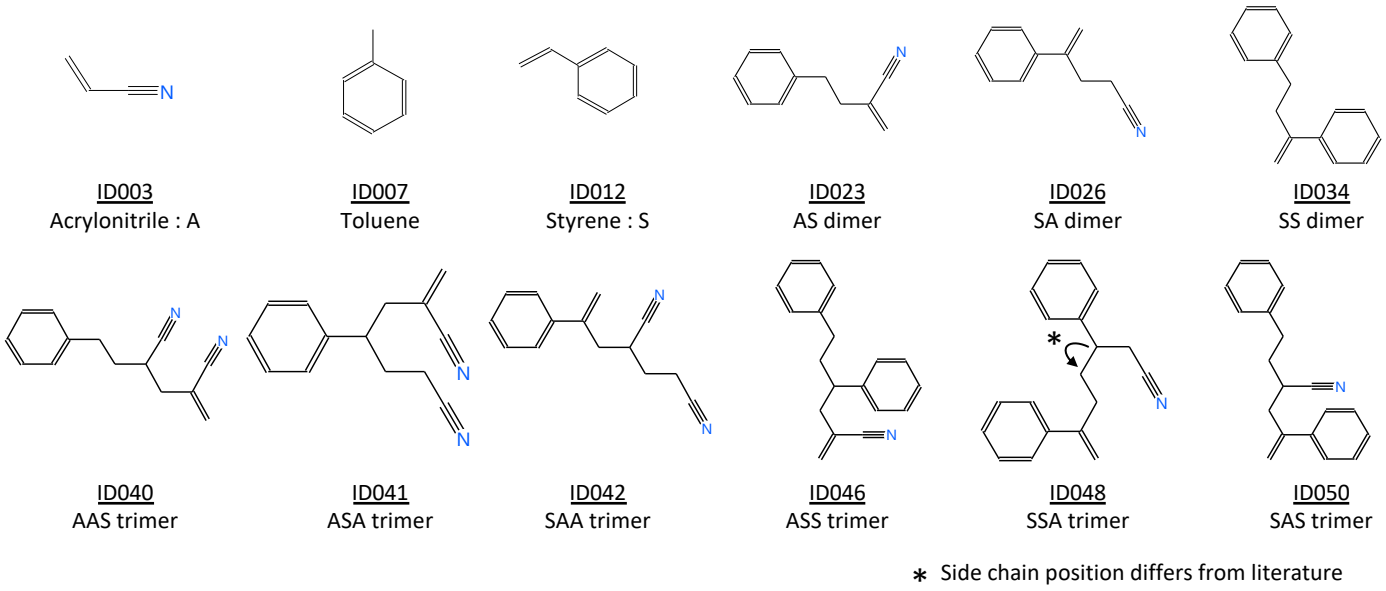


Figure 3 Structural formula of peaks specific to (B) defective product

Conclusion

Using JMS-T2000GC and msFineAnalysis AI, it was possible to identify that the contaminant of (B) defective product of polypropylene was AS copolymer. Many of the pyrolysis products are not registered in the mass spectral library, especially for copolymers such as AS. JMS-T2000GC and msFineAnalysis AI are effective for these analyses.

Reference

1) Shin Tsuge, Hajime Ohtani, Chuichi Watanabe (2011), Pyrolysis - GC/MS Data Book of Synthetic Polymers, Elsevier

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