Structure Analysis of Polymer Pyrolyzate by Pyrolysis GC-TOFMS and AI -A Case Study of AI Library Containing *in silico* Pyrolyzate

Product: Mass spectrometer (MS)

Introduction

We have developed msFineAnalysis AI which has an automated structural analysis method [1] (hereafter referred to as AI structural analysis) that combines data from a time-of-flight mass spectrometer (TOFMS), a high mass resolution GC-MS, and mass spectrum prediction by deep learning, as a solution for unknown compound analysis. This software contains a database (DB) of structural formulas and predicted EI mass spectra of approximately 100 million compounds obtained from the PubChem DB (hereinafter referred to as the AI library). By utilizing the molecular formula information determined by integrated analysis [2], it is possible to quickly estimate the structural formula of an unknown compound.

The pyrolysis GC-MS method is a widely utilized technique for the analysis of solid polymer samples, such as resins. A significant number of the pyrolyzates observed in pyrolysis GC-MS have not been registered in commercially available electron ionization (EI) mass spectrum databases. We attempted an analysis using the AI library and confirmed that the structural analysis of unknown compounds in acrylic resin can be performed with high accuracy (MSTips No.389). However, some oligomer components, such as trimers, lacked a correct structural formula in the AI library. This may be attributed to the limited number of structural formulas registered in the PubChem DB for polymer pyrolyzates.

Consequently, a novel AI library was developed, encompassing predicted EI mass spectra of approximately 25 million pyrolyzates. This library was derived from the exhaustive generation of pyrolyzate structure formulas by in silico. In 2024, we have released msFineAnalysis AI ver. 2 with a new AI library for 120 million compounds, including polymer pyrolyzates.

In this MSTips, we report a case study of analysis using the AI library including *in silico* pyrolyzates equipped with msFineAnalysis AI ver. 2.

Experiment

Commercially available acrylic resin was used as the test sample. The sample pretreatment system was an EGA/PY-3030D pyrolyzer (Frontier Labs Inc.), GC-MS was performed using a JMS-T2000GC (JEOL Ltd.), and an EI/FI combination ion source was used. The obtained data were analyzed using msFineAnalysis AI ver. 2 (JEOL Ltd.). For details of the measurement conditions, refer to MSTips No. 389.

in silico Pyrolyzate

The structural formulas for the *in silico* pyrolyzates were prepared by the following procedure. The homopolymer and copolymer species prepared for the AI library are shown in Table 1.

(1) 49 monomer compounds are selected [3].

(2) Generate hexamer linear chain structural formulas of 49 homopolymers and 18 copolymers.

(3) Generate the structural formula by randomly cleaving 1 to 5 single bonds in the structural formula of (2).

(4) Hydrogen addition or double bond substitution at the cleavage position in the structural formula of (3).

(5) Perform the processes described in (2) and (3) for all patterns to create the pyrolyzates structural formula.

After all the steps, we got structure formulas for about 25 million pyrolyzates. These were put into the developed deep learning model, and the EI mass spectra of about 25 million compounds were predicted.

Table 1 Polymer list of the predicted EI mass spectrum DB for 25 million *in silico* pyrolyzates

Homopolymer Name	Abbreviation	Homopolymer Name	Abbreviation	Copolymer Name	Abbreviation
Natural rubber	NR	Poly(p-methyl styrene)	PMS	Ethylene-methyl methacrylate copolymer	P(E-MMA)
Polycaproamide	Nylon-6	Polynorbornene	PNB	Ethylene-acrylic acid copolymer	P(E-AA)
Polyundecanoamide	Nylon-11	Polystyrene	PS	Ethylene-vinyl acetate copolymer	EVA
Poly(tetramethylene adipamide)	Nylon-4,6	Poly(vinyl acetate)	PVAc	Ethylene-ethyl acrylate copolymer	P(E-EA)
Poly(hexamethylene adipamide)	Nylon-6,6	Poly(vinyl butyral)	PVB	Ethylene-vinyl alcohol copolymer	P(E-VA)
Poly(m-xylene adipamide)	Nylon-MXD6	Poly(vinyl chloride)	PVC	Styrene-methyl acrylate copolymer	P(S-MA)
Phenol formaldehyde resin (novolak)	PF	Poly(2-vinylpyridine)	P2VP	Styrene-methyl methacrylate copolymer	P(S-MMA)
Polyacrylamide	PAAm	Poly(4-vinylpyridine)	P4VP	Acrylonitrile-styrene copolymer	AS
Poly(acrylic acid)	PAA	Poly(vinyl pyrrolidone)	PVP	Styrene-maleic anhydride copolymer	P(S-Mah)
Polyacrylonitrile	PAN	Poly(vinylidene chloride)	PVDC	Vinyl chloride-vinylidene chloride copolymer	P(VC-VdC)
Polybutadiene	BR	Poly(vinylidene fluoride)	PVDF	Vinyl chloride-vinyl acetate copolymer	P(VC-VAc)
Poly(butyl acrylate)	PBA	Chloroprene rubber	CR	Acrylonitrile-vinyl chloride copolymer	P(AN-VC)
Poly(butyl methacrylate)	PBMA	Cresol formaldehyde resin (novolak)	CF	Methyl acrylate-vinyl chloride copolymer	P(MA-VC)
Poly(butylene terephthalate)	PBT	Epichlorohydrin rubber	CHR	Styrene-butadiene rubber	SBR
Poly(p-chlorostyrene)	P4ClS	Polycarbonate	PC	Perfluoroethylene propylene copolymer	FEP
Polydimethylsiloxane	PDMS	Polyacetal	POM	Ethylene-tetrafluoroethylene copolymer	ETFE
Poly(ethyl acrylate)	PEA	Modified-polyphenylene ether	m-PPE	Ethylene-chlorotrifluoroethylene copolymer	ECTFE
Poly(ethylene glycol)	PEG	Polytetrafluoroethylene	PTFE	Tetrafluoroethylene-perfluorodimethyldioxole copolymer	TFE/PDD
Poly(ethylene terephthalate)	PET	Polychlorotrifluoroethylene	PCTFE		
Poly(2-hydroxyethyl methacrylate)	PHEMA	Polyvinyl fluoride	PVF		
Poly(lactic acid)	PLA	Polyphenylene sulfide	PPS		
Poly(maleic anhydride)	PMAH	Polysulfone	PSU		
Poly(methyl acrylate)	PMA	Polyether sulfone	PES		
Poly(methyl methacrylate)	PMMA	Polyether ether ketone	PEEK		
Poly(α-methylstyrene)	P-α-MS				

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Result and Discussion

TIC chromatograms obtained from pyrolysis GC-TOFMS measurements are shown in Figure 1. In this study, 48 components of the observed acrylic resin pyrolyzates were analyzed, which were detected in the trimer with a retention time of 14-20 minutes.

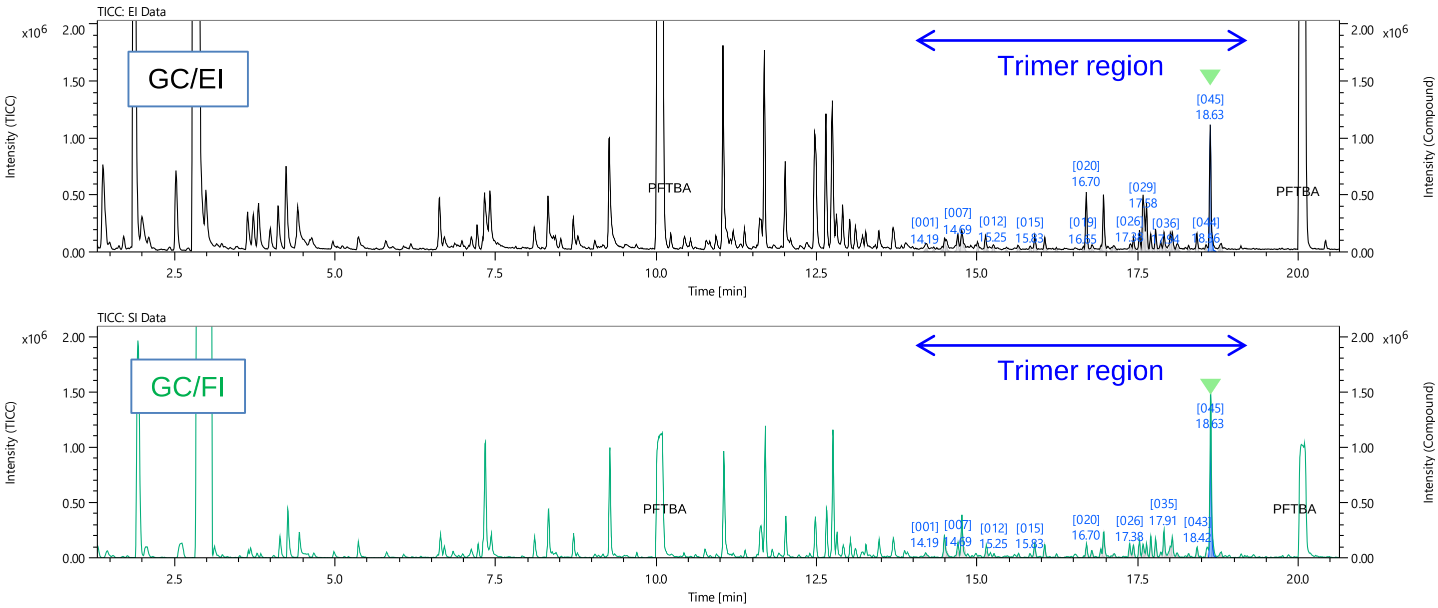

Fig.1 Py-GC-EI and FI TIC chromatograms for an acrylic resin.

A total of 48 compounds were detected in the trimer region. However, only two of these were registered in the NIST23 DB. The remaining 46 compounds were analyzed in the AI library, of which 26 were from the PubChem DB and 20 corresponded to the *in silico* pyrolyzates created in this study. It was possible to deduce the structural formulae of approximately 40% of the trimer region compounds from the *in silico* pyrolyzates information.

The analysis result window in msFineAnalysis AI including the mass spectra and estimated structural formula of ID:045 observed at 18.63 min is shown in Figure 2. This component was hardly observed a molecular ion by the EI method, but by the FI method, *m/z* 300.15728, which is considered to be a molecular ion, was detected as the base peak. The molecular formula was estimated to be C_{15}H24O6 with high mass accuracy. The molecular formula information is used as a filter in AI structure analysis to narrow down the number of candidates. The number of candidate structural formulas was significantly reduced from the AI library of approximately 120 million compounds. The highest scoring structural formula among the 7529 candidates was the *in silico* pyrolyzates that can arise from methyl polyacrylate.

Fig.2 msFineAnalysis AI result window,
ID: 045 mass spectra and estimated structure by *in silico* pyrolyzates

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The estimated structural formulas of the compounds that corresponded to *in silico* pyrolyzates are shown in Figure 3. We were able to confirm the trimer component reflecting the structure of the acrylic resin measured in this study.

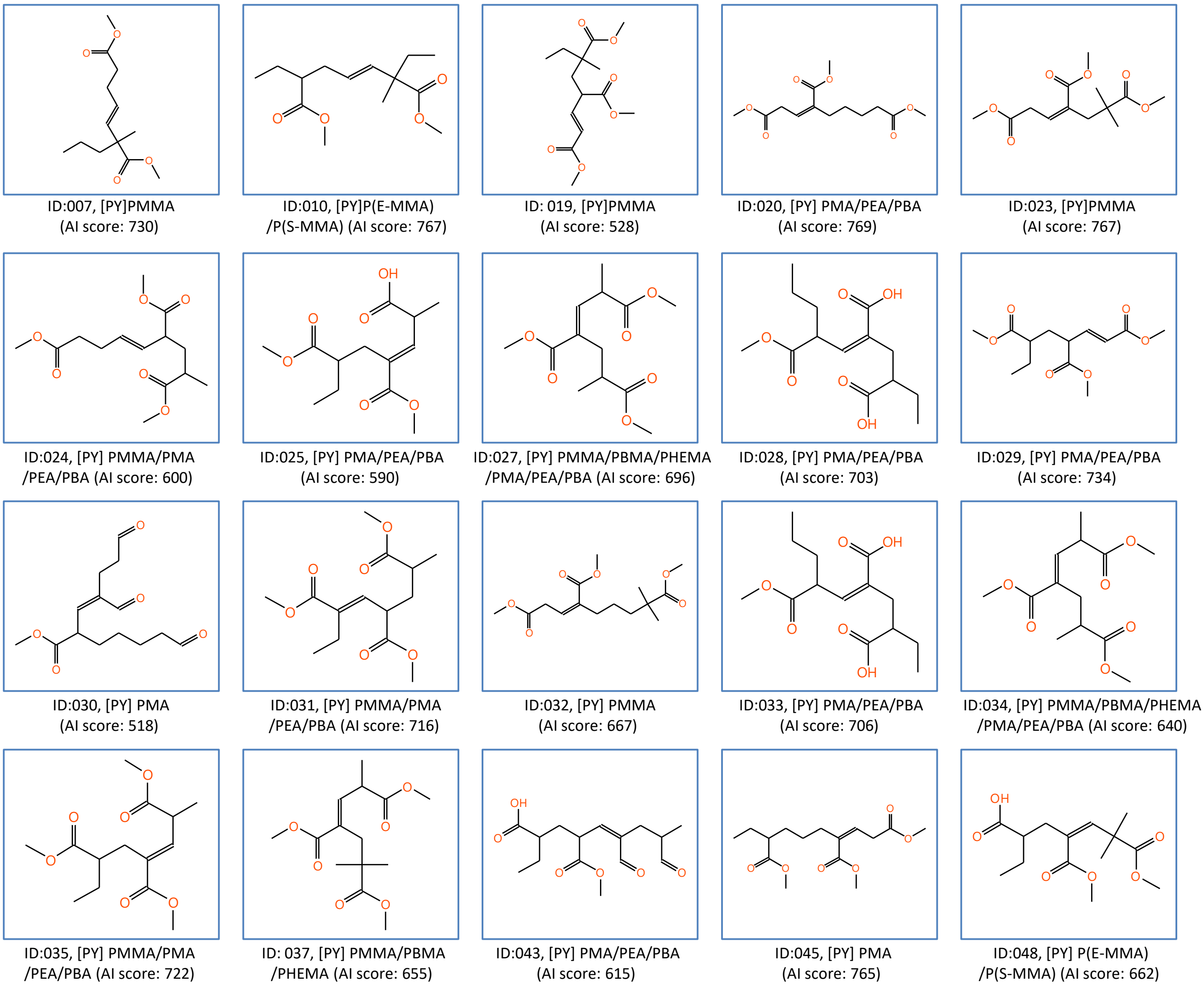

Fig.3 Estimated structures for 20 compounds in the trimer region using AI structure analysis and *in silico* pyrolyzates information

Conclusion

In this MSTips, we introduced a case study of structural analysis in the trimer region of acrylic resin, where most of the detected components are not registered in the NIST DB. msFineAnalysis AI ver.2 newly includes predicted EI mass spectra of 25 million pyrolyzates, enabling more accurate pyrolysis GC -MS qualitative analysis of solid polymer samples. It is expected to be used for various pyrolysis GC-MS qualitative analysis application in the future.

Reference

[1] A. Kubo et al, *Mass Spectrometry*, **2023**, *12*, A0120.
[2] M. Ubukata et al, *Rapid Commun Mass Spectrom., 34 (**2020**). DOI: 10.1002/rcm.8820*
[3] Shin Tsuge, Hajime Ohtani, Chuichi Watanabe (2011), Pyrolysis - GC/MS Data Book of Synthetic Polymers, Elsevier

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