

Oligomer pyrolyzates of multicomponent acrylate ester copolymers and monomer composition ratios

Part 1: Identification of oligomers using TOFMS and structural analysis software

[Background] Pyrolysis (Py-)GC/MS is an effective technique for the compositional analysis of polymeric materials. The oligomer pyrolyzates of a multicomponent copolymer reflect the monomer composition, and their structural analysis is essential in the characterization of copolymers. However, elucidating the structures of oligomer pyrolyzates by MS remains challenging. This note describes the identification of oligomer pyrolyzates of a multicomponent acrylate copolymer using a time-of-flight mass spectrometry (TOFMS) together with a structural analysis software program.

[Experimental] Measurements were conducted on a Py-GC/TOFMS system equipped with a Multi-Shot Pyrolyzer (EGA/Py-3030D) directly interfaced to the GC injector. A UA⁺-5 column was used as a GC separation column. The sample was a ternary acrylic copolymer composed of butyl acrylate (BA), 2-ethylhexyl acrylate (2-EHA), and 2-hydroxyethyl acrylate (HEA). The monomer composition of the copolymer is summarized in Table 1. The acrylic copolymer was put in a sample cup and then introduced into the furnace heated at 600 °C. The pyrolyzates were ionized using field ionization (FI), a soft ionization, and electron ionization (EI), a hard ionization, methods, and detected by TOFMS. The chemical structures corresponding to unknown peaks were deduced using msFineAnalysis AI software (JEOL).

[Results] Unidentified polymer Peaks **a**, **b**, and **c** were observed in the pyrogram of an acrylic copolymer obtained by TOFMS using EI (Fig. 1), and peaks **b** and **c** consist of a few peaks. Each peak within Peak **b** or Peak **c** exhibited nearly identical mass spectra when using FI. The structure elucidation workflow for peak **b** is illustrated in Fig. 2. First, the composition formula was deduced from the accurate mass of the molecular ion obtained by FI-TOFMS. Subsequently, the possible structures of the fragment ions obtained by EI-TOFMS were elucidated using msFineAnalysis AI software. Based on the observations, Peak **b** in Fig. 1 was identified as a trimer composed of BA, BA, and 2-EHA, and its possible structure is shown in Fig. 2. Similarly, Peak **a** was identified as a trimer composed of BA, BA, and HEA, and Peak **c** was identified as a trimer composed of BA, 2-EHA, and HEA.

Table 1 Ternary acrylic copolymer

Mass composition ratio (wt%)		
BA ● 	2-EHA ■ 	HEA ▲
45.0	45.0	10.0

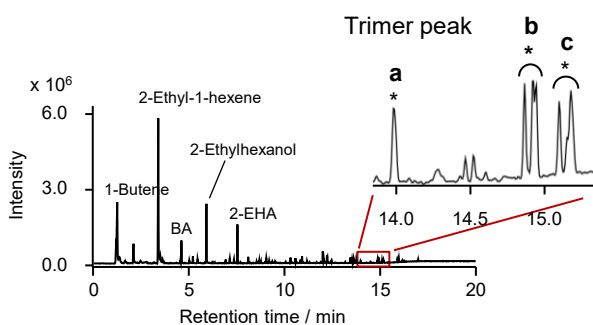


Fig. 1 Pyrogram (EI) of a ternary acrylic copolymer obtained by TOFMS

Pyrolysis temp.: 600 °C, Separation column: UA⁺-5 (5 % diphenyl 95 % dimethylpolysiloxane, L=30 m, i.d.=0.25 mm, df=0.25 μm), GC Injector temp.: 300 °C, Column flow rate: 1.0 mL/min, Split ratio: 1/100, GC oven temp.: 40 °C (2 min hold) - 320 °C(20 °C/min, 14 min hold), Detector: TOFMS, Amount of sample: 0.1 mg

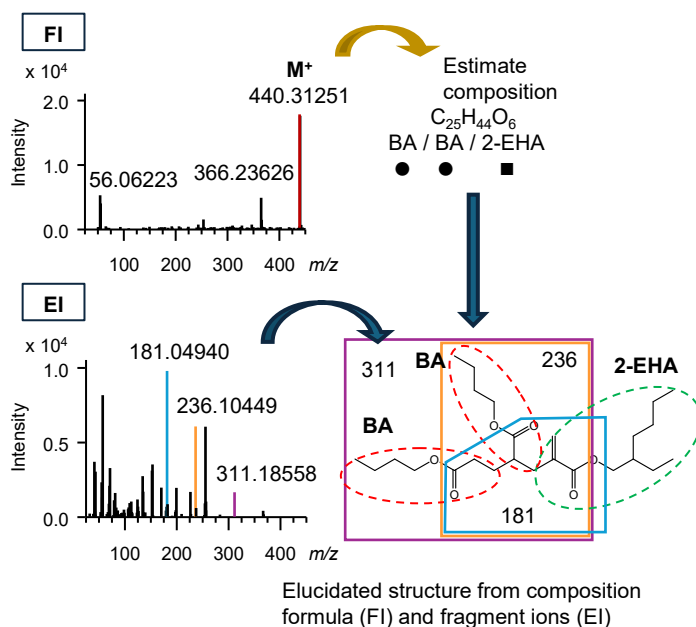


Fig. 2 Structure elucidation workflow for peak **b**

Keywords : Adhesive, Time-of-flight mass spectrometry, Structural analysis

Products used : Multi-Shot Pyrolyzer, Auto-Shot Sampler, UA⁺-5, Vent-free GC/MS adapter, F-Search

Applications : Material analysis, Quality assurance

Related technical notes : [PYA1-180E](#)

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