

Molecular characterization of oligomeric pyrolysis compounds of ethyl acrylate-butyl acrylate copolymer using thermal desorption/pyrolysis DART-MS

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Introduction

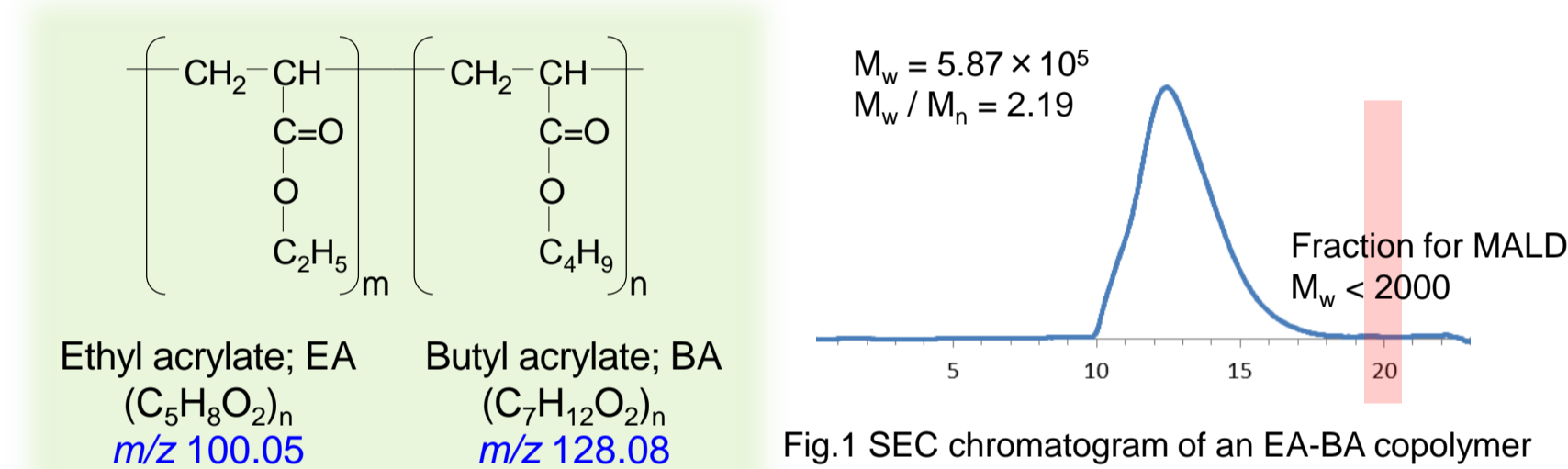
Industrial acrylic polymers are often synthesized with various comonomers to realize desired functions and physical properties. Since physical properties are affected by not only the average comonomer composition but also its distribution, molecular characterization of polymers is important from the viewpoint of controlling physical properties.

In this study, we investigated an ethyl acrylate (EA)-butyl acrylate (BA) copolymer by thermal desorption/pyrolysis (TDP)/DART-MS which can rapidly detect both thermally desorbed intact oligomers and oligomeric pyrolysis products of polymers. The observed results were compared with those by pyrolysis (Py-)GC/MS and MALDI-MS.

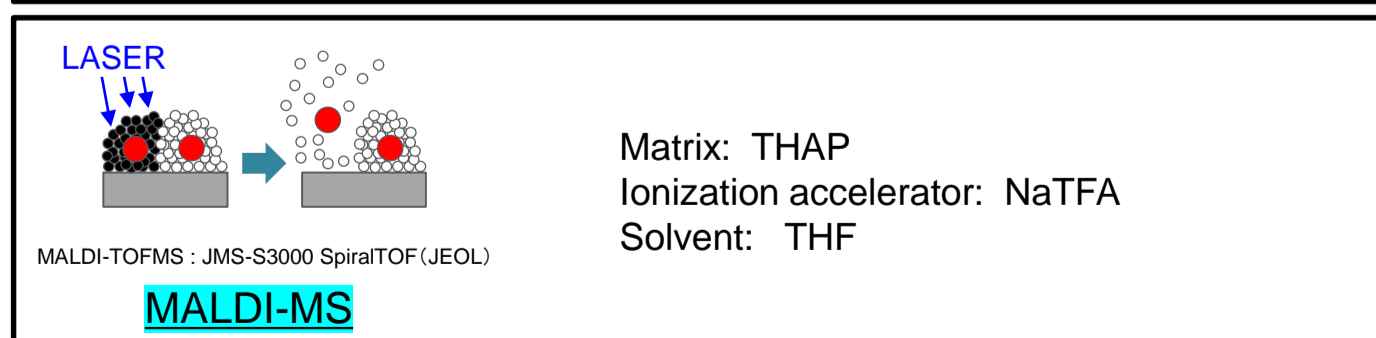
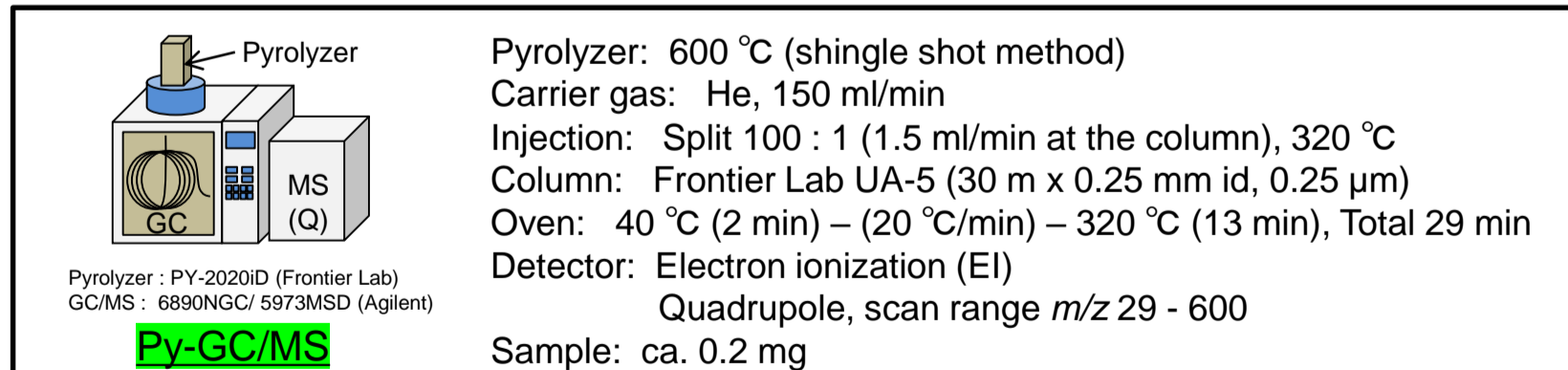
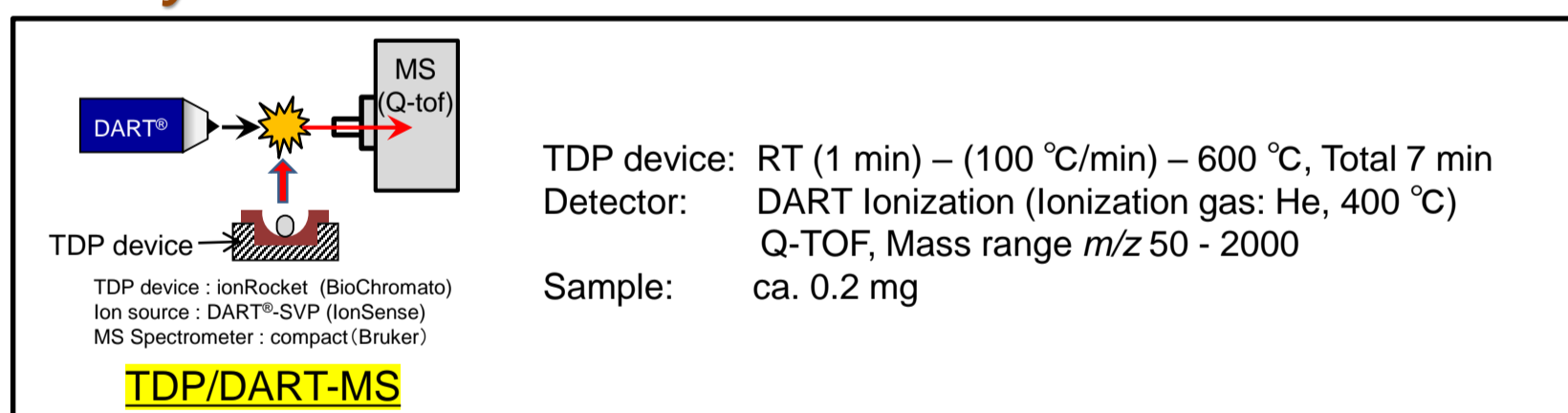
Experimental

Sample: EA-BA copolymer

- produced through random-copolymerization
- the feed monomer ratio of EA:BA = ca. 1:1



Analytical methods:

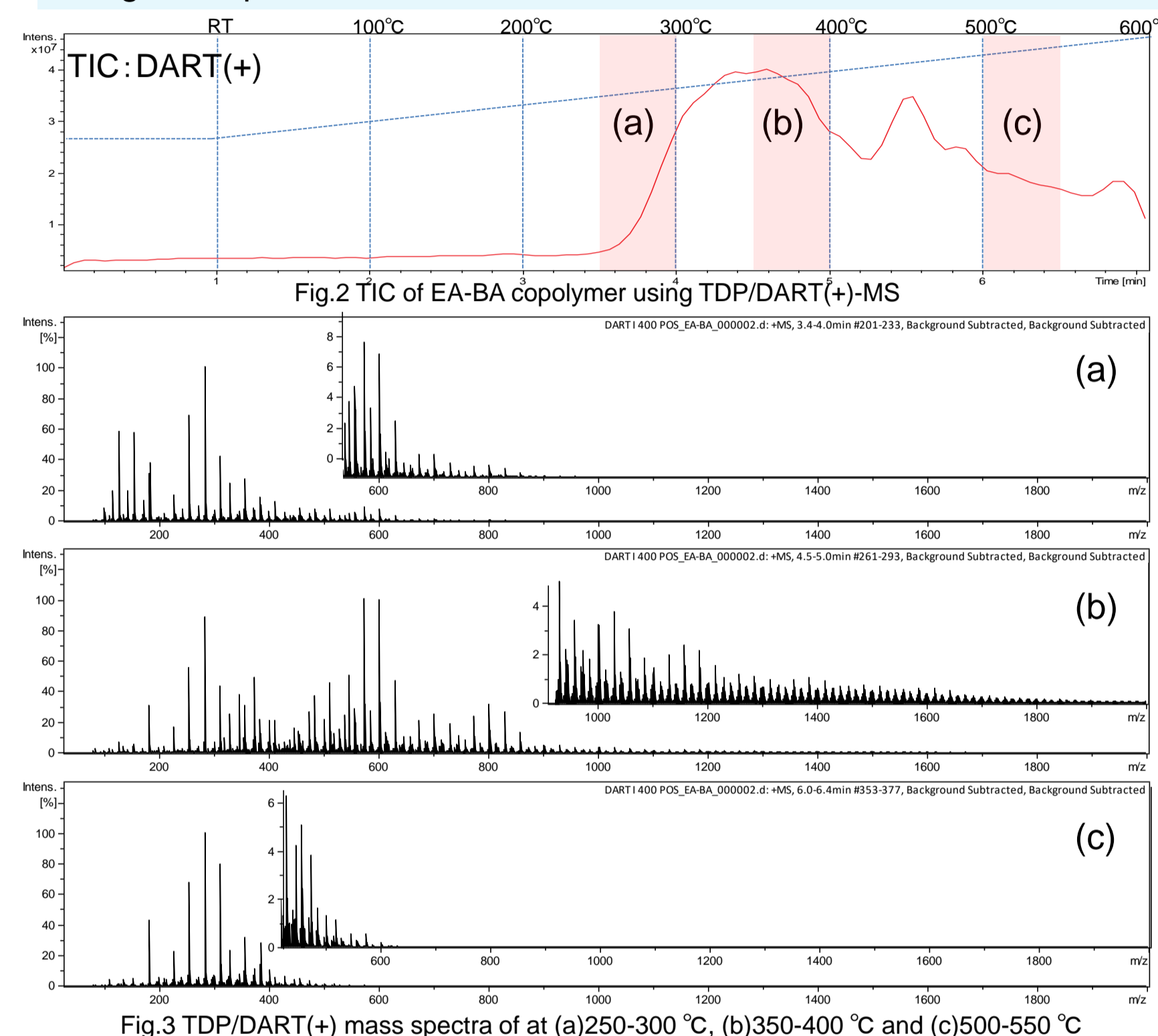


References

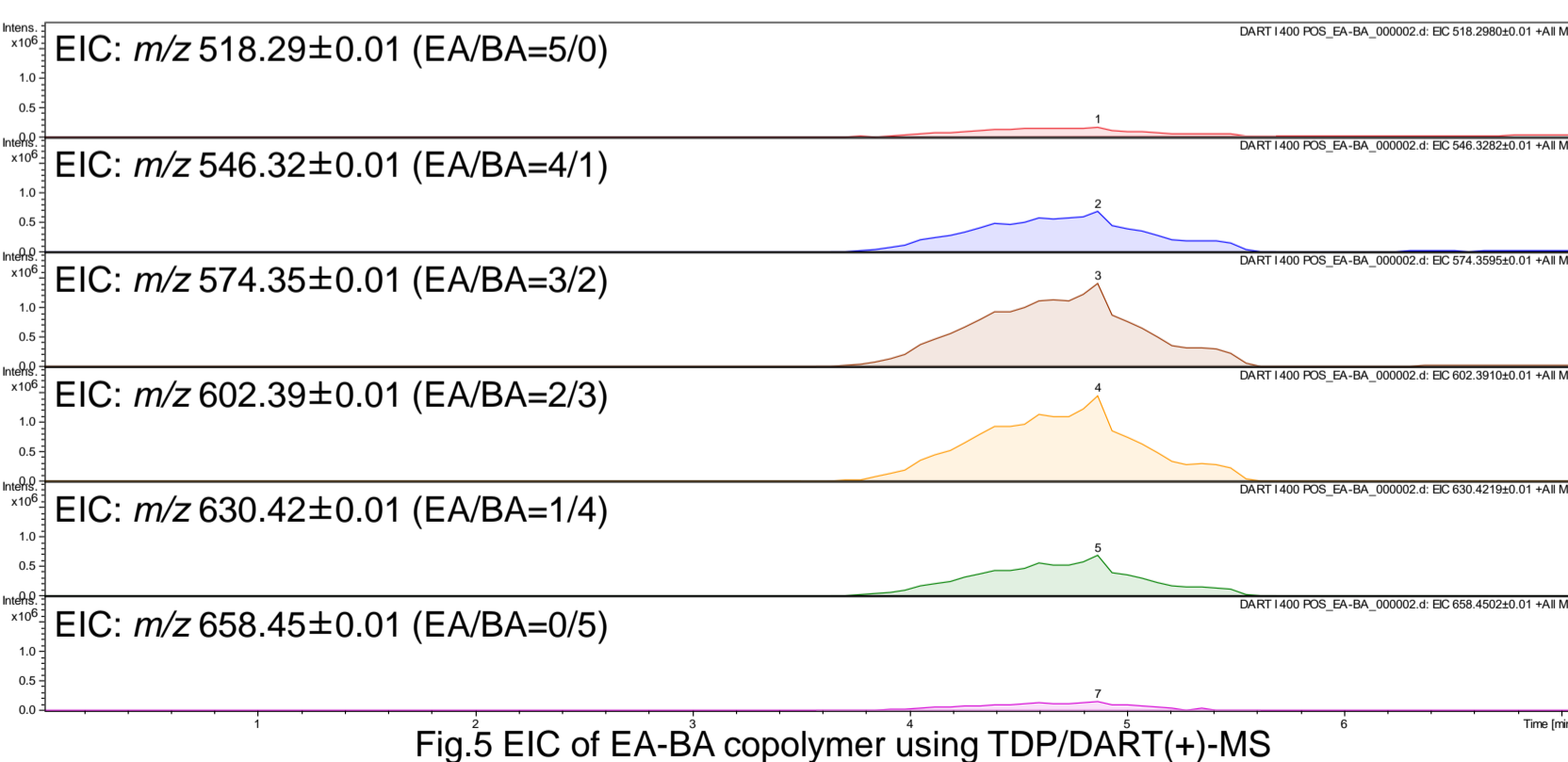
- H.Sato, S.Nakamura, K.Teramoto, T.Sato; JASMS, 2014, 25(8), 1346-1355
- S.Tsuge, H.Ohtani, and C.Watanabe; Pyrolysis-GC/MS Data Book of Synthetic Polymers, Elsevier (2011) p. 90-93

Results and Discussions

TDP/DART-MS can show evolution profiles of volatilized compounds and/or pyrolysis products during the heating process (Fig. 2). In the lower temperature (Fig. 3(a)), the observed compounds were mainly low molecular weight components. In the middle temperature (Fig. 3(b)), several series of thermal desorbed oligomers (up to m/z 1800) were observed. In the higher temperature (Fig. 3(c)), the observed compounds were mainly low molecular weight pyrolysis products of higher molecular weight components.



Compositional distribution of 5-mer showed normal distribution with the maximum around EA/BA = 3/2 and 2/3 (Fig.5 and Table 1). This result suggest that this sample should be a random copolymer having a monomer composition estimated as EA/BA = 50/50 (Fig. 6).



Conclusion

TDP/DART-MS can individually provide mass spectral information of volatile low molecular weight compounds and oligomeric pyrolysis products of higher polymeric compounds evolved during the heating process. The observed distributions suggest that the EA-BA copolymer should be a random copolymer having a monomer composition estimated as EA:BA = ca. 1:1. And, it was confirmed that these results were supported by Py-GC/MS and SEC-MALDI-MS. The distributions of oligomeric products up to 8-mer observed by TDP/DART-MS were more informative than those by Py-GC/MS. Thus, TDP/DART-MS can be a useful analytical technique to characterize polymers together with Py-GC/MS and MALDI-MS complementarily.

TDP/DART mass spectrum of the copolymer observed at around 350 °C (b) were informatively interpreted using the KMD¹⁾ plot (Fig. 4). The plot showed a parallelogram-like dot distribution, which is the typical pattern of random copolymers. The plot revealed that the largest oligomer detected in this region was 8-mer composed of EA/BA = 4/4.

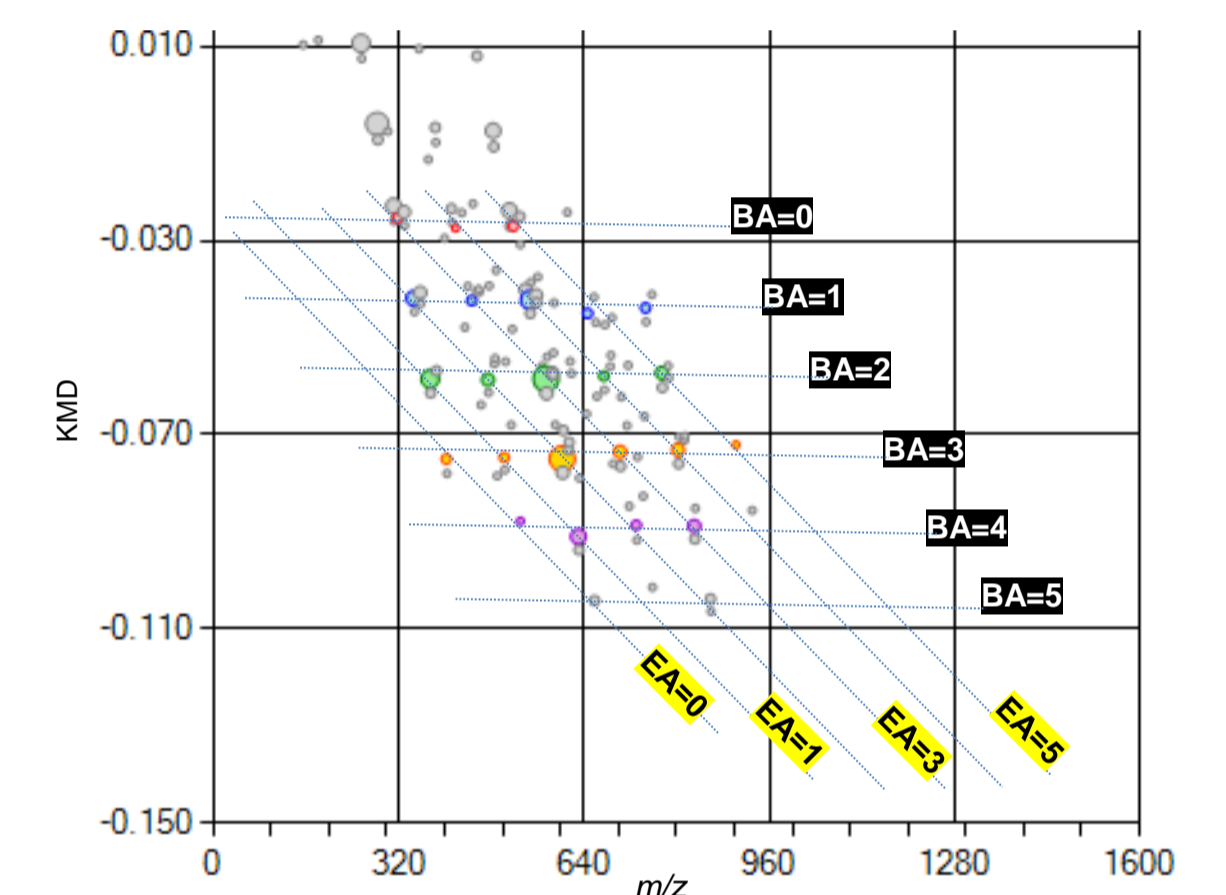


Fig.4 KMD plot of mass spectrum of Fig.3(b) with base unit EA (C₅H₈O₂)

m/z	Chemical formula *	Error (mDa)	Comonomer ratio EA/BA	Relative peak area
518.2980	C ₂₅ H ₄₄ NO ₁₀	2.1	5 / 0	2.9
546.3282	C ₂₇ H ₄₈ NO ₁₀	-1.0	4 / 1	16.1
574.3595	C ₂₉ H ₅₂ NO ₁₀	-0.9	3 / 2	31.5
602.3910	C ₃₁ H ₅₆ NO ₁₀	-1.1	2 / 3	31.7
630.4219	C ₃₃ H ₆₀ NO ₁₀	0.8	1 / 4	14.8
658.4501	C ₃₅ H ₆₄ NO ₁₀	2.3	0 / 5	3.0

* [M + NH₄]⁺

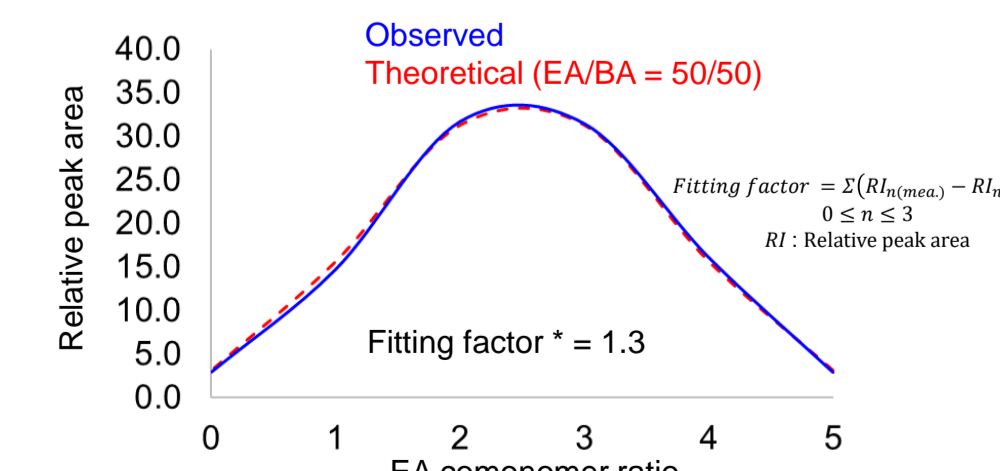


Fig.6 Curve fitting of relative peak area for 5-mer between observed and theoretical.

Py-GC/MS

The largest pyrolysis products were trimers. The relative peak intensities among the trimers correspond to a random distribution with EA/BA = 46/54 (Table 2, Fig. 8), which is close to the feed monomer ratio.

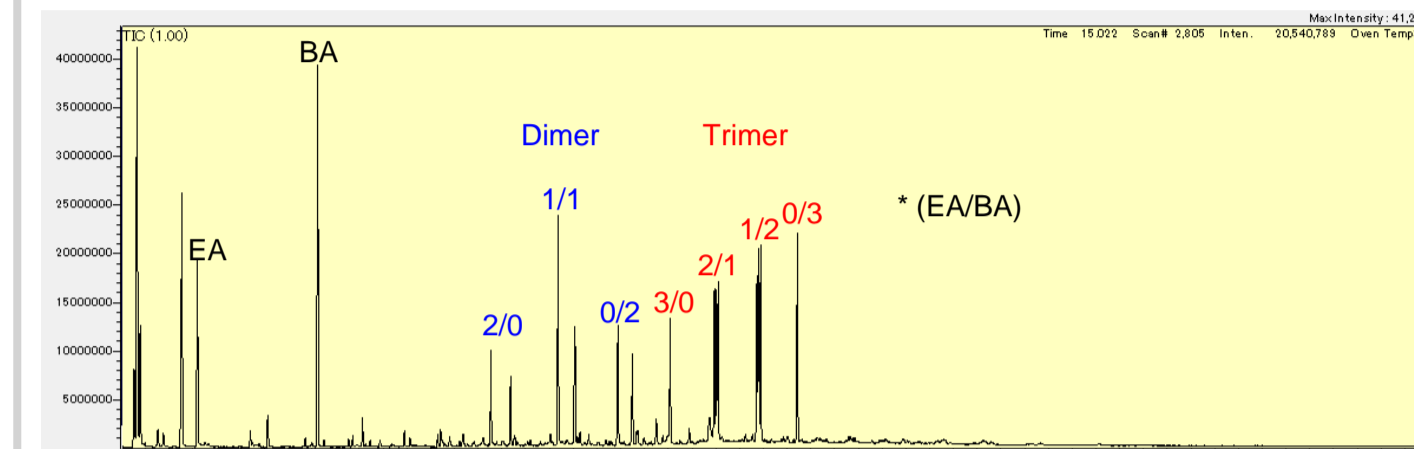


Fig.7 Pyrogram of EA-BA copolymer using Py-GC/MS²⁾

Retention time	Comonomer ratio EA/BA	Relative peak intensity
12.54	3 / 0	8.7
13.47 ~ 13.55	2 / 1	35.0
14.36 ~ 14.44	1 / 2	40.9
15.21	0 / 3	15.4

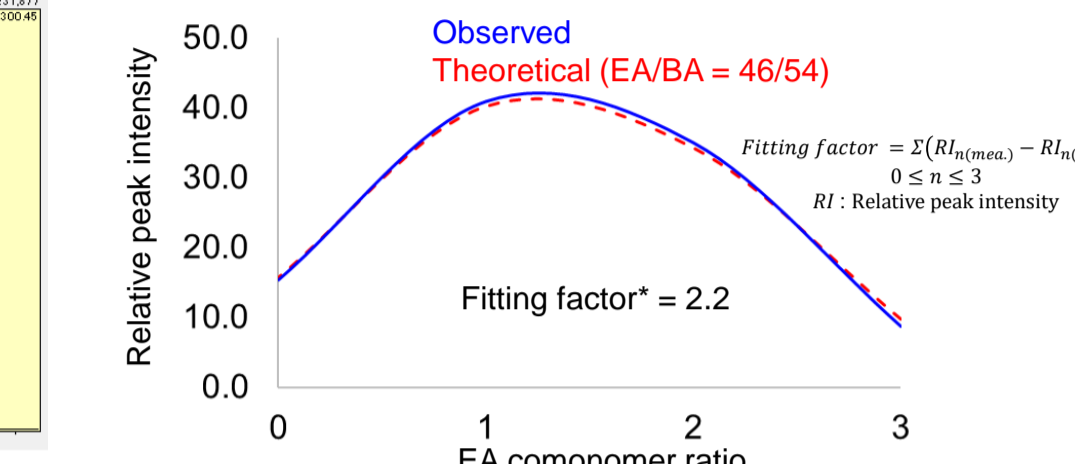


Fig.8 Curve fitting of relative peak intensity for trimer between observed and theoretical.

SEC-MALDI

Intact oligomers of this sample were observed using SEC fractionation. The KMD plot showed a parallelogram-like dot distribution, which is the typical pattern of random copolymers (Fig. 10). Compositional distribution showed normal distribution with the maximum around EA/BA = 4/4 (Fig. 9 and Table 3). From compositional distributions of intact oligomers estimated, it was estimated that this fraction was composed of random oligomers with EA/BA = 46/54 (Fig. 11), also close to the feed monomer ratio.

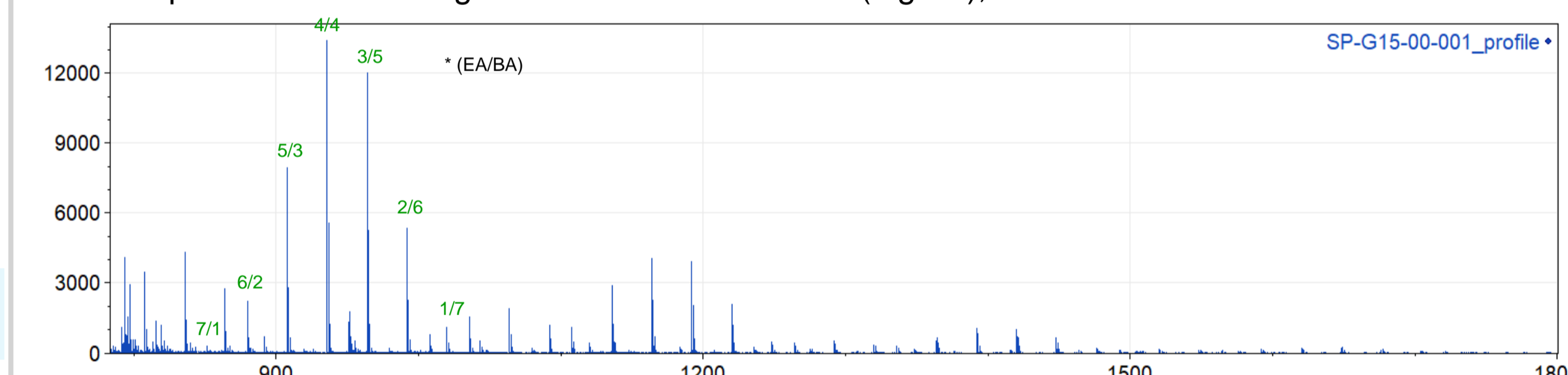


Fig.9 SEC-MALDI mass spectrum of EA-BA copolymer (fraction: 19.5–20.5 min)

m/z	Chemical formula *	Error (mDa)	Comonomer ratio EA/BA	Relative peak intensity
			8 / 0	N.D.
851.4397	C ₄₀ H ₆₄ NaO ₁₆	-0.2	7 / 1	0.7
879.4675	C ₄₂ H ₆₈ NaO ₁₆	-3.7	6 / 2	5.3
907.5049	C ₄₄ H ₇₂ NaO ₁₆	2.4	5 / 3	18.8
935.5313	C ₄₆ H ₇₆ NaO ₁₆	-2.5	4 / 4	31.6
963.5620	C ₄₈ H ₈₀ NaO ₁₆	-3.1	3 / 5	28.4
991.6001	C ₅₀ H ₈₄ NaO ₁₆	3.7	2 / 6	12.6
1019.6284	C ₅₂ H ₈₈ NaO ₁₆	0.7	1 / 7	2.6
			0 / 8	N.D.

* [M + Na]⁺

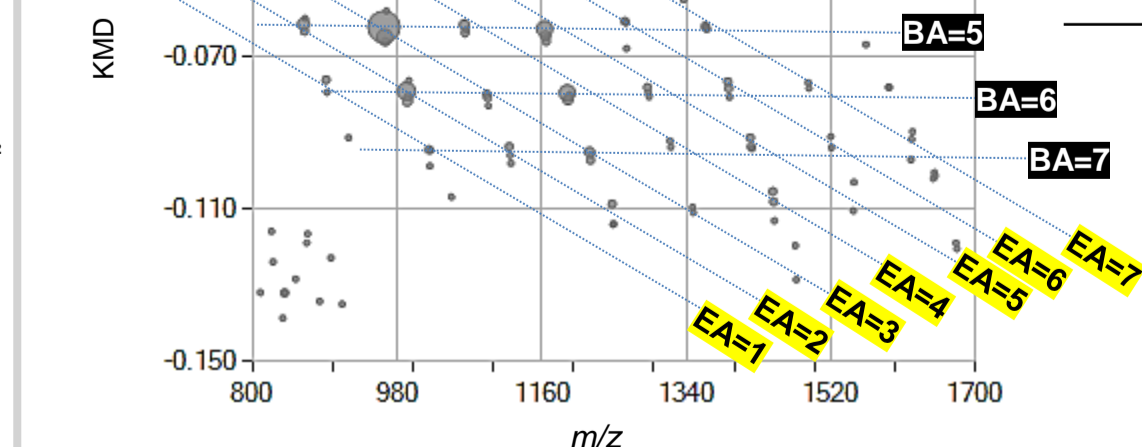


Fig.10 KMD plot of mass spectrum of Fig.9 with base unit EA (C₅H₈O₂)

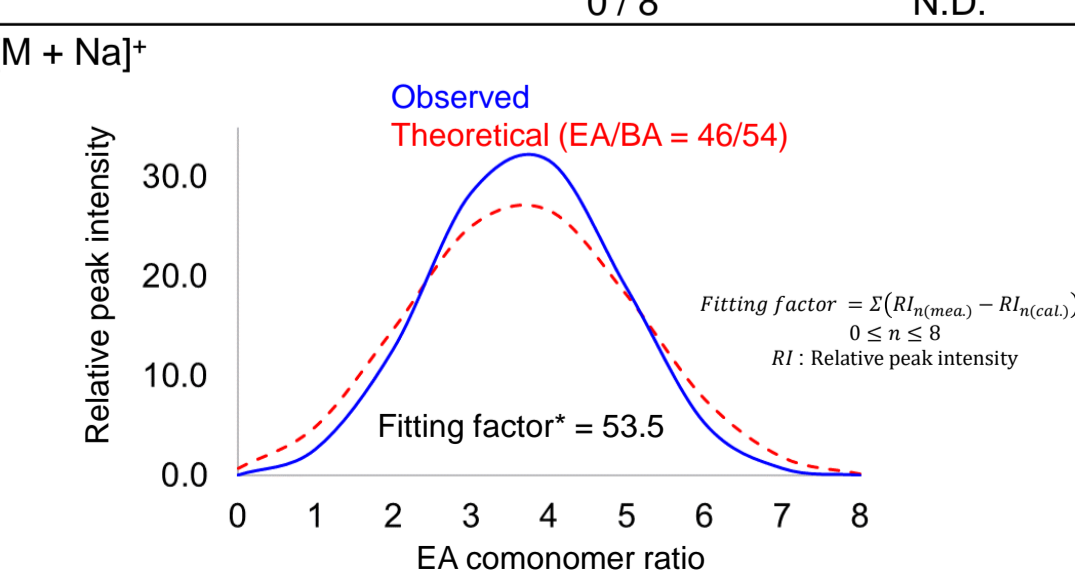


Fig.11 Curve fitting of relative peak intensity for 8-mer between observed and theoretical.