End group analysis of poly(methyl methacrylate) using MALDI-TOFMS and GC-TOFMS

Product used: Mass Spectrometer (MS)

Mass spectrometry can be used to analyze synthetic polymers, providing a variety of information, such as the main chain structure, end group structure, and molecular weight distribution (average molecular weight, polydispersity). Analysis of end group structure is particularly important for the following reasons.

- The physical properties of polymer materials can change depending on the end groups, even though they are relatively small part of the whole polymer molecules.
- End group structure might change (or degrade) due to environmental exposures.
- End group structure can provide insight into the polymerization mechanism.

MALDI is a soft ionization method that allows the observation of polymer molecules as singly charged ions. Using high-resolution MALDI-TOFMS, it is possible to elucidate the elemental compositions of end groups from the accurate masses. On the other hand, pyrolysis GC-TOFMS analyzes the pyrolysis products produced by instantaneous heating of a polymer. Mainly monomers and dimers are observed, but if pyrolysis products containing end groups are observed, structural information on the end groups can be obtained. In this report, we performed structural analysis of the end groups of poly(methyl methacrylate) by using MALDI-TOFMS and pyrolysis GC-TOFMS in a complementary manner.

Experiments

Two types of commercially available PMMA (Mw 7 kDa and 10 kDa) were used as samples. Each was dissolved in THF at the concentration of 10 mg/mL. For MALDI-TOFMS measurements, DCTB was used as the matrix and sodium trifluoroacetate was used as the cationization agent. Mass spectra were acquired using JMS-S3000 (JEOL Ltd.) in Spiral positive ion mode. For the pyrolysis GC-TOFMS measurements, a gas chromatograph time-of-flight mass spectrometer JMS-T2000GC (JEOL Ltd.) equipped with a pyrolyzer EGA/PY-3030D (Frontier Labs) was used. 10 uL of the sample solution was placed in an eco cup and allowed to dry. The obtained data was subjected to differential analysis using msFineAnalysis AI (JEOL Ltd.).

JMS-S3000

JMS-T2000GC

Table 1 Py-GC-TOFMS measurement and analysis conditions

Pyrolysis conditions	
Pyrolyzer	EGA/PY-3030D (Frontier Lab)
Pyrolysis Temperature	600°C
GC conditions	
Column	DB-5MS UI (Agilent Technologies)
	30 m x 0.25 mm, 0.25 µm
Oven Temperature	40°C (2 min) - 20°C / min
	- 320°C (10 min)
Injection Mode	Split mode (100:1)
Carrier flow	He: 1.0 mL / min

MS conditions	
Spectrometer	JMS-T2000GC (JEOL Ltd.)
Ion Source	EI/FI combination ion source
Ionization	EI+:70 eV, 300 µA
	FI+:-10 kV
Mass Range	*m/z* 29 - 800

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MALDI-TOFMS measurement results

Figure 1 shows the mass spectrum of a mixture of PMMA 7 kDa and 10 kDa. In the mass spectrum, two distributions were observed in the molecular weight range of 2,000 to 13,000. Zooming in on the *m/z* range of 7350 to 7850 reveals that both distributions (Mw 7 kDa ▼ , Mw 10 kDa ▼) have peaks with the $C_5H_8O_2$ interval, which is the PMMA monomer, but there is a mass difference between two distributions due to the different end groups. Since the degree of polymerization of each peak cannot be determined from the mass spectrum, the mass difference due to the difference in the end groups of the two components has an uncertainty of the number of repeating units ($C_5H_8O_2$). Therefore, possible candidates for the total mass of both end groups include 136.110, 236.156, and 336.206u. The elemental compositions elucidated from these mass differences are shown in Table 2. Since the end groups of PMMA 7 kDa are known to be H/H based on the elemental composition elucidation for the low molecular weight region, the elemental composition of the combined end groups of PMMA 10 kDa is elucidated to be those in Table 2 plus +2H.

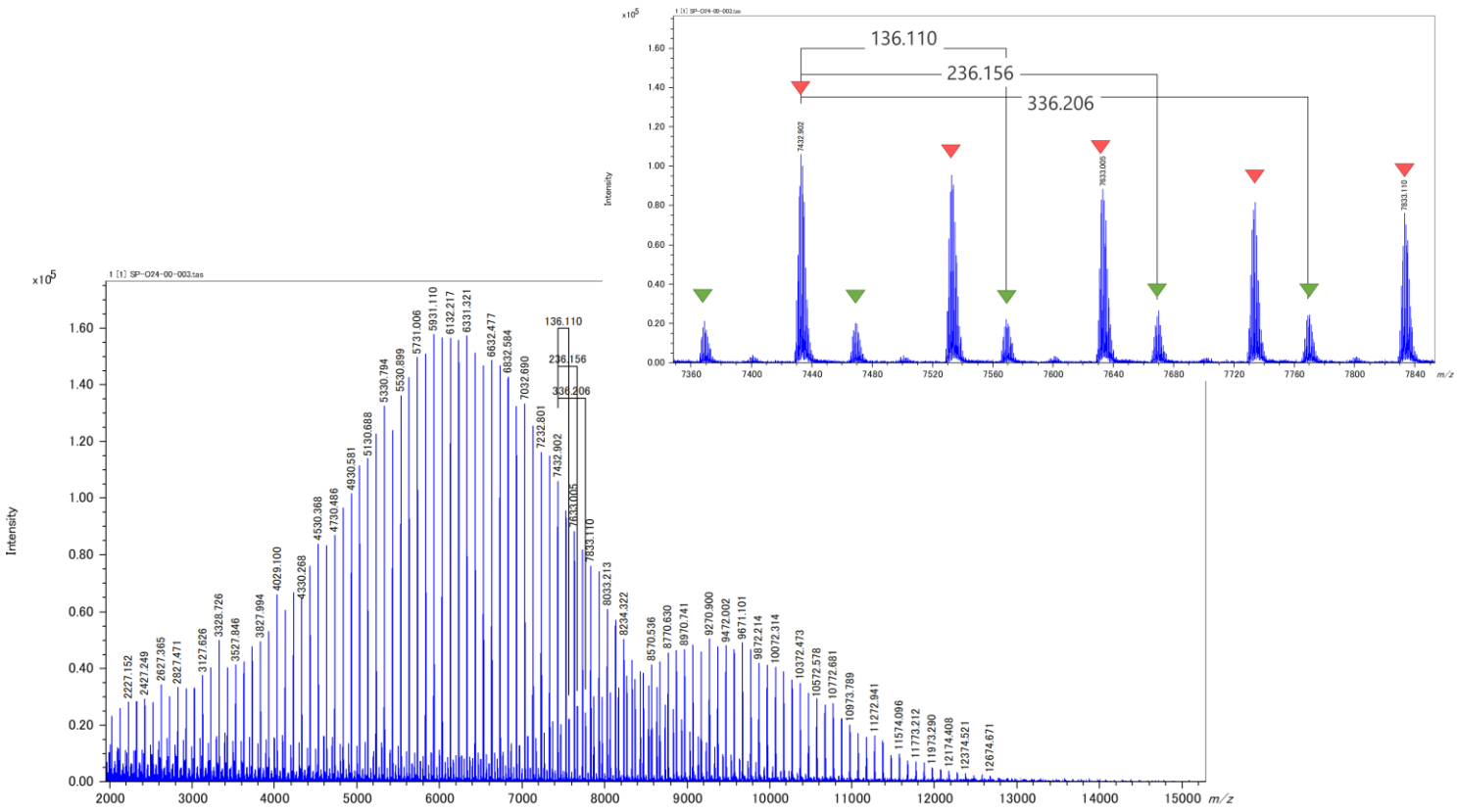

Figure 1. Mass spectrum of sample mixture of PMMA 7 kDa and 10 kDa

Table 2. Elemental composition analysis of mass difference of PMMA 7 kDa and 10 kDa

136u

#	Formula	Mass	Error (mDa)	Error (ppm)
1	C10 H16	136.1247	-14.7	-107.65

236u

#	Formula	Mass	Error (mDa)	Error (ppm)
1	C18 H20	236.156	0	0.2
2	C11 H24 O5	236.1618	-5.8	-24.67
3	C14 H20 O3	236.1407	15.3	64.8

336u

#	Formula	Mass	Error (mDa)	Error (ppm)
1	C23 H28 O2	336.2084	-2.4	-7.08
2	C16 H32 O7	336.2143	-8.3	-24.55
3	C19 H28 O5	336.1931	12.9	38.29
4	C26 H24	336.1873	18.7	55.76

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Pyrolysis GC-TOFMS measurement results

Next, the results of differential analysis between PMMA 7 kDa and 10 kDa are shown. Figure 2 (a) shows the TICC of EI, in which monomers are observed as the main component. Next, Figure 2(b) shows an enlarged view of 10-12.5 min. The red peaks are characteristic of PMMA 10 kDa, and three components, ID: 050, 056, and 057, were observed. The results of the integrated analysis of these three components are shown in Table 3, and their structural formulas are shown in Figure 3. Assuming that the end group structure of PMMA 10 kDa is C18H21/H, the structure of ID:056 (and ID:057) and the result of 236u difference #1 in Table 2 (MALDI-TOFMS results) show good agreement. Since ID:050 is a partial structure of ID:056, there is no contradiction here either. Therefore, PMMA 10 kDa is considered to be produced by anionic polymerization using 1,1-diphenylhexyllithium as an initiator.

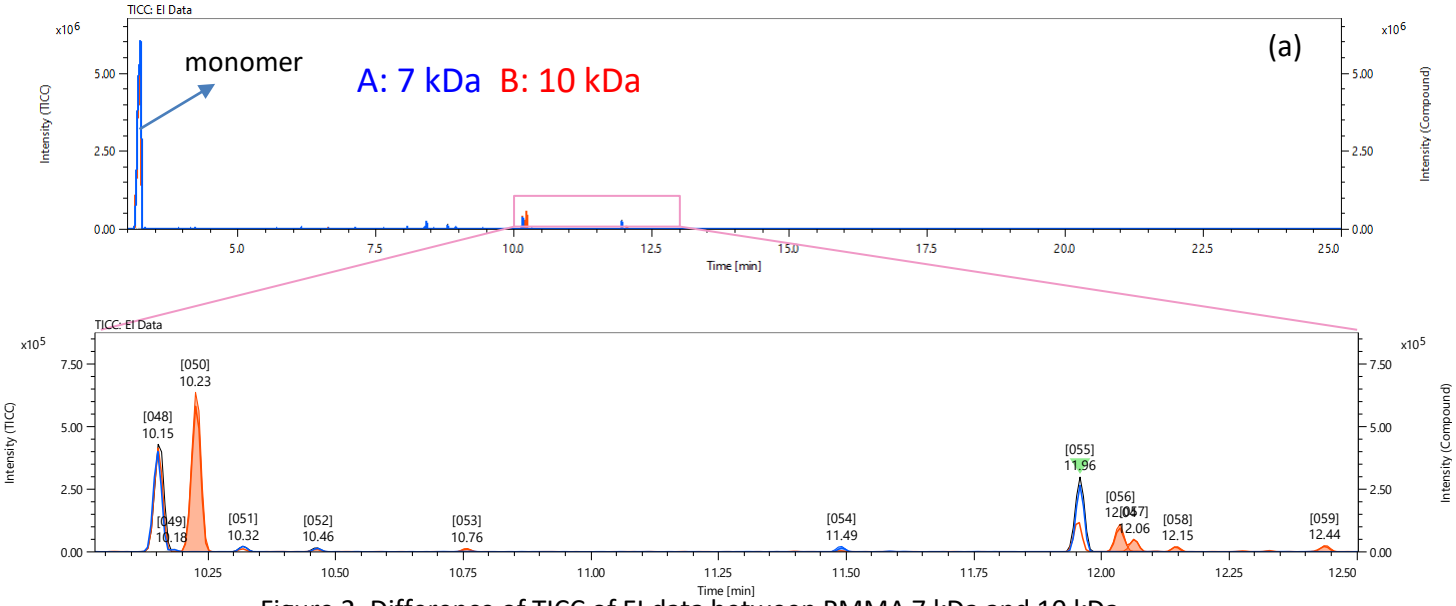
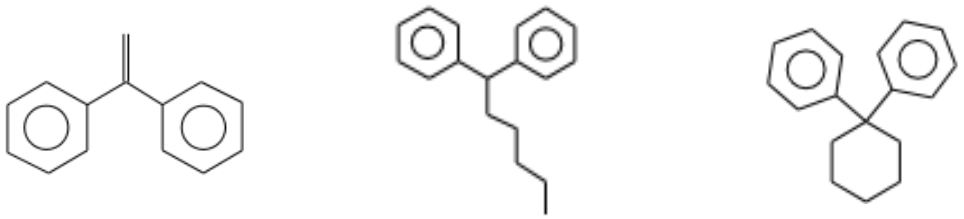


Figure 2. Difference of TICC of EI data between PMMA 7 kDa and 10 kDa

Table 3. Integrated qualitative analysis result of PMMA 7 kDa and 10 kDa

General				Total Result							
ID	RT [min]	Height	IM m/z	Library Name	Lib.	Similarity	Formula	DBE	Calculated m/z	Mass Error [mDa]	EI Fragment Coverage
050	10.23	637882	180.09393	Ethylene, 1,1-diphenyl-	mainlib	901	C14 H12	9.0	180.09335	0.58	100
056	12.04	110741	238.17230	Benzene, 1,1'-hexylidenebis-	mainlib	913	C18 H22	8.0	238.17160	0.70	100
057	12.06	50089	236.15659	Benzene, 1,1'-cyclohexylidenebis-	mainlib	752	C18 H20	9.0	236.15595	0.63	100



ID:050
Formula: C14H12

ID:056
Formula: C18H22

ID:057
Formula: C18H20

Figure 3. Structure of pyrolysis product observed only in PMMA 10 kDa

Conclusion

The end group analysis of PMMA was carried out using complementary techniques of MALDI-TOFMS and pyrolysis GC-TOFMS. MALDI-TOFMS can observe the molecular weight distribution, and the elemental composition of the sum of both end groups can be obtained with high mass accuracy up to a molecular weight of about 10,000. However, uncertainty arises because the degree of polymerization cannot be determined from the exact masses. On the other hand, the results of pyrolysis GC-TOFMS mainly provide information on the main chain structure. Furthermore, by identifying pyrolysis products that contain end group information from among the trace components, it is possible to obtain structural information on the end groups. Thus, the complementary use of MALDI-TOFMS and pyrolysis GC-TOFMS in the analysis of polymer end groups is extremely effective.

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