JEOL MS Data Sheet

MS Tips

Mass Spectrometry Application Group
Mass Spectrometry Business Unit
JEOL Ltd.

No.110

Analysis of block copolymer by field desorption (FD) using JMS-T100GC "AccuTOF GC"

Introduction

A commercially available PO (polyoxypropylene) - EO (polyoxyethylene) block copolymer was analyzed by field desorption (FD) on JMS-T100GC "AccuTOF GC" and group-type analysis was performed on the obtained mass spectrum.

Methods

Sample — Poly(ethylene glycol)-*block*-poly(propylene glycol)-*block*-poly(ethylene glycol) (Aldrich 435406; BASF Pluronic® L-31), M_n = 1,100, 50 mg/mL in THF

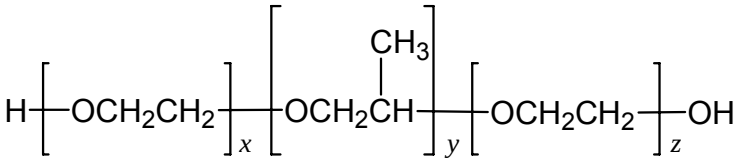

Fig.1 Structural formula of the sample

MS conditions

Mass spectrometer:	JMS-T100GC "AccuTOF GC"
Ionization mode:	FD (+)
Cathode potential:	-10 kV
Emitter current:	0 mA → 51.2 mA/min → 40 mA
Acquired mass range:	*m/z* 35 – 1,600
Spectral recording interval:	1.0 sec

Results and discussion

The obtained FD mass spectrum is shown in Fig.2.

The base peak was observed at *m/z* 1,005.7. Other significant peaks were observed with 58 interval (corresponds to C_3H_6O) at m/z 947.7, m/z 889.7, etc. These ions correspond to the structure shown in Fig. 1 with x = 0, y = 15, 16, 17, and z = 0.

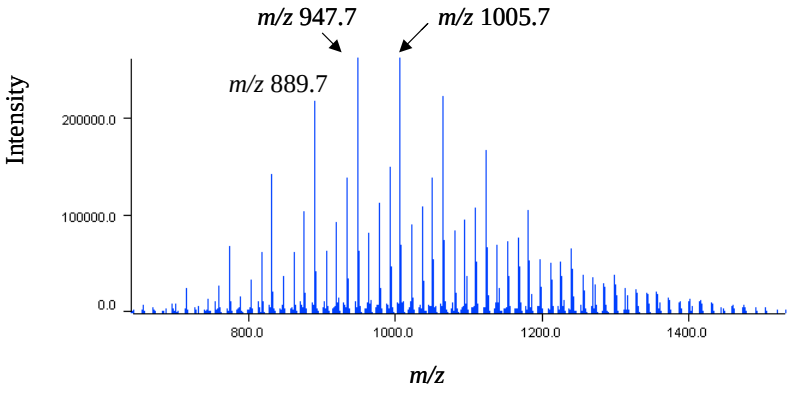

Fig.2 FD mass spectrum

For group-type analysis, the following parameters were used. Even though the sample was an EO-PO-EO triblock copolymer, only two repeat units, PO and EO, were specified since two of the three blocks were EO.

Group-type analysis parameters

Software	Polymerix™ (Sierra Analytics)
Repeat unit A:	C_3H_6O
Repeat unit B:	C_2H_4O
α end group:	H
ω end group:	OH
Adduct:	H
Match tolerance:	± 0.05 u

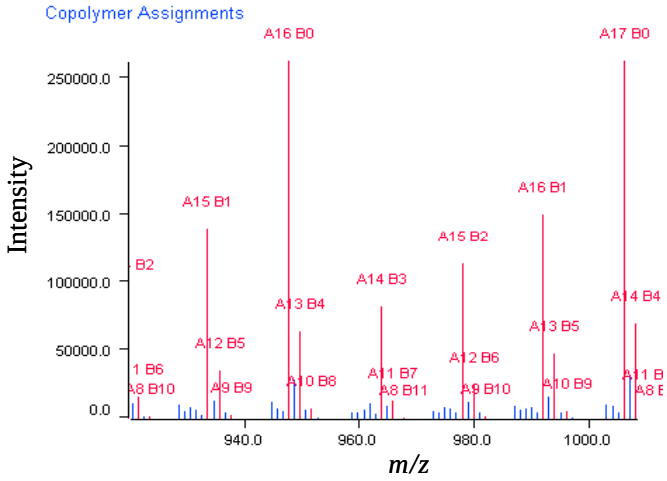

Fig.3 Type analysis assignments (*m/z* 920−1020)

Some of the assignments made by the software with the parameters settings from above are shown in Fig. 3; “A” means C3H6O, “B” means C2H4O, and the number following “A” or “B” means the number of the repeat. In Fig. 3, the peaks that correspond to A = 12 to 17 and B = 0 to 10 are assigned.

The distribution of the numbers of the repeat units, A (PO) and B (EO,) are shown in Fig. 4 and the average molecular weights and other metrics derived from the group-type analysis are shown in Table 1.

		Copolymer Distribution											
		Repeat B											
		0	1	2	3	4	5	6	7	8	9	10	11
Repeat A	6												
	7												
	8												
	9					1.08	1.66	1.27	1.33	1.61			
	10			1.63	2.17	4.19	4.24	3.04	2.26	2.58	1.72		
	11	2.65	3.42	5.09	6.17	8.20	7.60	5.81	4.63	4.34	2.42		
	12	9.58	10.37	12.54	14.00	15.99	13.09	9.23	5.62	4.32	3.27	2.19	1.40
	13	25.98	23.80	23.46	24.20	23.93	17.79	12.39	7.36	6.81	3.56	2.24	1.22
	14	54.36	39.41	35.20	31.16	26.41	20.61	13.98	9.37	7.03	4.81	2.82	1.11
	15	83.18	52.75	43.08	34.49	28.19	19.84	14.31	9.97	6.35	2.97	2.14	1.09
	16	99.99	56.93	41.44	32.28	25.35	18.00	12.60	8.69	6.50	3.50		
	17	100.00	52.72	36.53	26.54	20.38	14.20	10.73	6.67	3.61			
	18	84.89	41.17	27.92	20.53	16.96	9.92	7.72	4.55	3.09	1.37		
	19	63.64	29.20	19.25	14.66	10.89	7.26	4.05	3.16	1.73			
	20	40.33	19.86	13.74	9.46	6.85	4.96	1.56	1.69				
	21	25.17	11.41	8.93	5.77	4.50	3.04	2.11					
	22	14.63	7.35	3.67	3.55	2.94							
	23	7.94	4.08	1.86									
	24	4.44	2.56										
	25	1.69											
	26												

Fig.4 Copolymer distribution

Table 1 Type analysis result

	M_n	M_w	M_z	PD
$(H[C_3H_6O]_n[C_2H_4O]_mOH)+H^+$	1053.2	1077.1	1100.9	1.03

By analyzing the FD mass spectrum of triblock copolymer with a suitable group-type analysis software, metrics such as ratios and distribution among constituents, number average molecular weight (M_w,) weight average molecular weight (M_w,) Z average molecular weight (M_z,) polydispersity (PD,) were easily obtained.