Characterization of Ethylene-oxide propylene-oxide copolymers by MALDI-TOF MS

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INTRODUCTION

The mass spectrometric characterization of copolymers is stimulating because of the numerous detected peaks, especially in the case of higher molecular weight copolymers where overlaps of monoisotopic and isotopic peaks are common. Therefore, manual analysis is impossible. An effective data processing method is necessary for the data evaluation, to handle the overlapping peaks. My aim is to characterize high molecular weight ethylene-oxide propylene-oxide (EO-PO) copolymers and determine the number average, weight average molecular weight, the average number of EO and PO units, and composition drift. Matrix-Assisted Laser Desorption/Ionization Time of Flight (MALDI-TOF) mass spectrometry was applied to measure the copolymer samples. After the automatized evaluation, the polymer compositions were determined, and further structural information was also obtained by the composition drift plots.

EXPERIMENTAL

Autoflex Speed MALDI-TOF Mass Spectrometer (Bruker, Bremen, Germany) was applied for the measurements. The polymers (M-1170 and L-121) were dissolved in the concentration of 10 mg/mL with THF. 2,5-dihydroxy benzoic acid (DHB) matrix was used in the concentration of 20 mg/mL, while NaTFA (sodium trifluoroacetic acid) was the ionizing agent (5 mg/mL). The samples, the matrix, and the ionizing agent were mixed in the ratio of 2:10:1, respectively. 0.25 µL of the mixtures were deposited on the MALDI target plate.

RESULTS AND DISCUSSION

In order to effectively characterize relatively higher molecular weight copolymers, the need for an effective copolymer analysis method is deployed such as Mass-remainder Analysis. The measured spectra are shown in **Fig 1**, which shows that mass spectra are complex and contain over 1000 complex peaks and many overlaps are obtained. The main difference between the peaks is 14. The overlaps come as a result of the replacement of the EO-PO change, replacing 3 PO units with 4 EO units. The difference in this case will be 2, therefore non-isotopic and isotopic peaks merge to form the overlaps. This is shown in **Fig 2**, where we can observe peak series which contain many different copolymer chains (with different chemical compositions).

Therefore in order to handle such complex spectra, the Mass-remainder analysis is applied to identify special polymer properties such as M_n (number-average), M_w (weight-average) molecular weights, the polydispersity index M_w/M_n, the number-average number of monomer units and weight-average number of monomer units for X, nn X, and nw X, respectively, where X represents a monomer unit. The L-121 is a linear block copolymer with 10 wt. % of EO content and molecular weight of 4400 Da (based on the provider), while based on the experiment we carried out 11.18 wt. % and 4950 Da of EO content and molecular weight, respectively **(Table 1)**. M1170 is a glycerol type of random copolymer with unknown wt. % of EO content by provider however, we investigated EO content is 71.12 wt. % **(Table 2).**

L-121	mPO	nwPO	nnEO	nwEO	Mn	Mw	Mw/Mn	m%PO	m%EO
	75.09	75.45	12.46	16.00	4950	4990	1.00	88.82	11.18

Table. 1 Chemical Compositions of L-121

M1170	mPO	nwPO	nnEO	nwEO	Mn	Mw	Mw/Mn	m%PO	m%EO
	22.90	26.93	74.34	77.90	4720	4770	1.01	28.88	71.12

Table. 2 Chemical Compositions of M1170

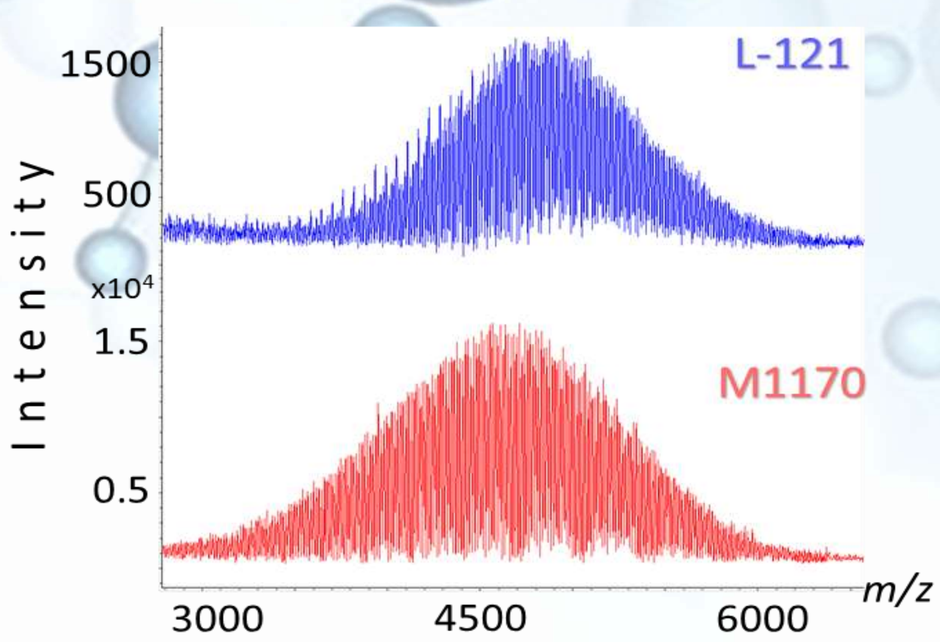

Figure 1. Spectra of Polymers. Blue: L-121 Red: M1170

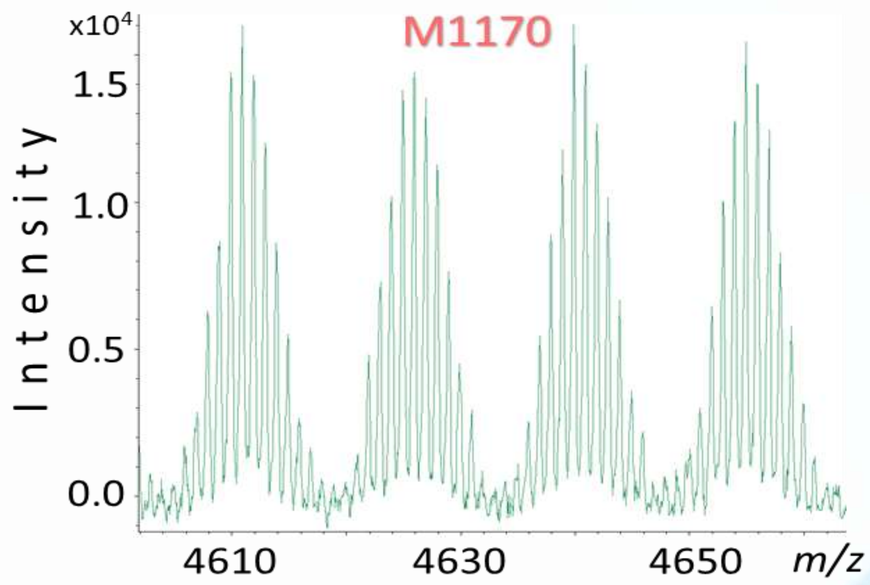

Figure 2. Zoomed spectrum of M1170

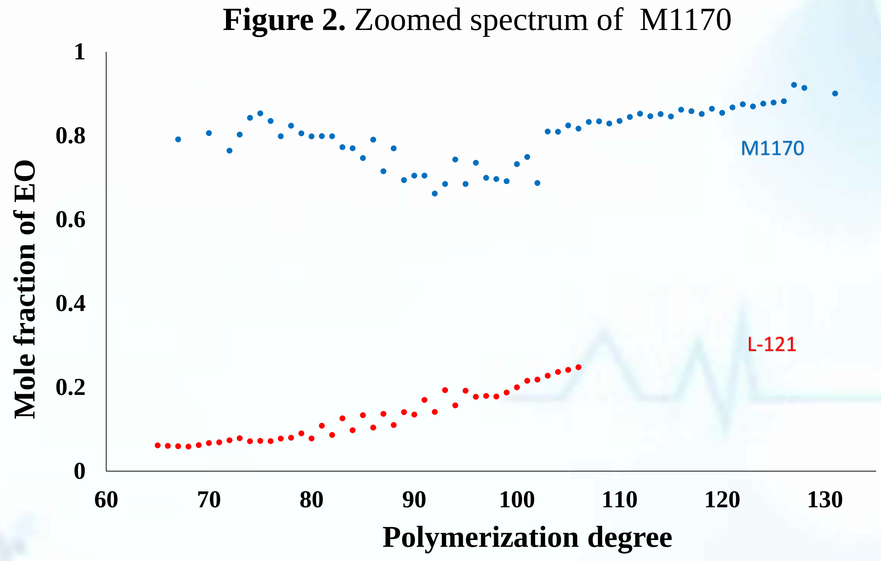

Figure 3. Composition Drift of Polymers. Blue: M1170 Red: L-121

Additionally, by applying the Mass-remainder analysis the composition drift diagrams are also constructed. This is shown in **Fig 3**. where the EO content was shown versus the polymerization degree. If the EO molar fraction is changing by the polymerization degree this shows the presence of block copolymer, as shown for the L121 polymer. This confirms the data given by the provider to be a triblock copolymer. However, for the M1171 such information is not available. Based on the figure **(Fig 3)** it shows that it is not a block copolymer, the figure does not reflect the clear change of the EO by the polymerization degree.

CONCLUSION

Two different polymers were measured by MALDI TOF mass spectrometry, Mass-remainder analysis was used to identify special polymer quantities. The results show for L-121 had a higher molecular weight than expected while the EO content was in good agreement with the value, given by the provider. For the M1170, 4770 Da number average molecular weight and 71.12 wt. % EO was obtained. Furthermore, the composition drift diagrams were used to confirm the structure of L-121 as a triblock copolymer while the M1170 was identified as either random or alternating.

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