Detailed characterization of Ethylene-oxide propylene-oxide triblock copolymers by MALDI-TOF MS

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1 Introduction

The triblock copolymers of polyethyelene oxide and polypropylene oxide were analyzed by Matrix-Assisted Laser Desorption/Ionization Time of Flight (MALDI-TOF) mass spectrometry. The mass spectrum was analyzed by using the detected peaks however, incase of high molecular weight copolymers the overlapping isotopic peaks made it challenging to evaluate the data manually. RPE and PE type copolymers were studied and differences between their structures were further identified from their results. Two step calibration was necessary to the process to reduce any effects of overlapping peaks that would alter the accuracy of the results. The calibrant employed was PEG homopolymers. In this study, characterization of the copolymers assisted the determination of the structure which wasn't disclosed accurately by the provider of the products. The importance of such a study comes from devising a structure-property corelation between the composition of the copolymer and a specific property that the copolymer has been tested for, ex:antifoaming activity.

2 Experimental

The experiment involves injecting a sample mixture of the copolymer, matrix, and ionizing agent into the target metal plate and placing it inside the Bruker MALDI instrument. 20 µl of PE3100 at concentration of 10mg/ml was mixed with 50µl of DCTB(matrix) at concentration of 20mg/ml and 10µl of NaTFA at concentration 5mg/ml. Using a pipette a drop of the well mixed sample was injected into the metal plate and placed inside the Bruker MALDI instrument. The same procedure was repeated for 17R4. For the PEG calibrant sample: PEG 1100, 2000,3350 and 4000 were mixed with a ratio of 2:2:8:6 repectively and injected into the metal plate using a pipette.

Acknowledgements

3 Results and Discussion

The spectrums obtained for polymers PE3100 and 17R4 are shown to be very complex with numerous peaks some which are overlapping. Figure 1 shows the spectrum for both PE3100 and 17R4. It can be clearly seen from the spectra that PE3100 has a lower molecular weight range than 17R4. PE3100 has a molecular weight range from 1100-1400 with the highest intensity peak at approximetely 1000. 17R4 has high molecular weight range from 2100 to 3500 and the highest intensity peak at 2800. The highest intensity peak of the spectrums represent the average molecular weight of the copolymer.

The table below shows the automated evaluation of 17R4 and PE3100 including their estimated and actualy molecular weight and EO% content,PO% content, nnPO/EO , and nwPO/EO.

Copolymer name	nnPO	nwPO	nnEO	nwEO	theoratical		measured	m%PO	m%EO
					Mn	Mw	Mw		
Pluronic PE3100	16	16	2	4	990	1027	1000	93	7
Pluronic 17R4	28	28	26	27	2797	2824	2650	58	42

Table 1: chemical compositionof PE3100 and 17R4

Table 1 illustrates the difference between the theoratical or expected molecular weight and this represents the relevance and importance of the experiment. Analyzing the evaluating the mass spectrum helps us find the exact composition of the copolymers and shows all the substances present that werent disclosed by the producer. This can also be shown in figure 2. The difference between the highest intensity peaks in each peak pack is 58 which represents the molecular weight of PO. Thus the sample of PE3100 contains homopolymers of EO. Similarly, figure 3, shows the magnified spectrum of 17R4 where the difference of the highest intensity peaks in each peak pack is 14.This represents the replacement of 3 PO units with 4 EO units to get to the next set of peaks and result in the overlapping of peaks. In this copolymer sample, no homopolymers is found, only the triblock copolymers of 17R4.
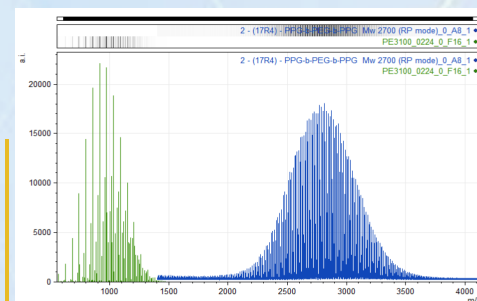

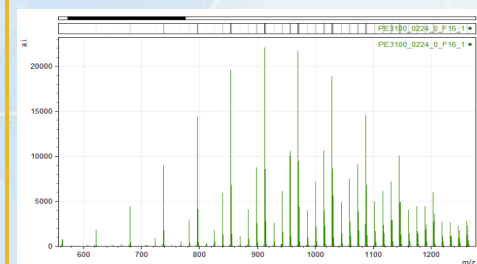**Figure 1: mass spectrum of PE3100 (green) and 17R4 (blue)**

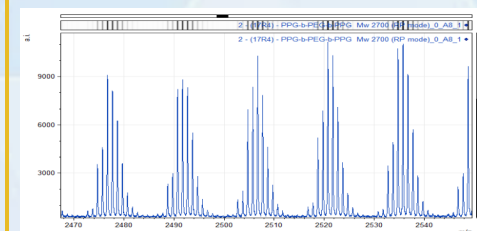**Figure 2: magnified mass spectrum of PE3100**

Figure 2: magnified mass spectrum of 17R4

4 Conclusion

Copolymers 17R4 and PE3100 were analyzed using MALDI. 17R4 is an RPE type polymer and the obtained information about the chemical composition shows that it has 60:40 ratio of PO:EO in the structure of the polymer. However, the PE3100 is a PE with 9:1 ratio of PO:EO. The molecular weight of PE3100 is in aggrement with the expected molecular weight with a difference of only 2.6%, while the difference in the expected and measured molecular weight of 17R4 is almost double at 6.1%. The obtained information about the structure could be used for further investigation to determine some kind of structure-property correlation of the polymers using the molecular weight or even the EO%/PO%.

References

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