Investigation of hydrodynamic radius of ethylene-oxide propylene-oxide copolymers as a function of their chemical composition

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Introduction

The hydrodynamic radius of a copolymer highly depends on its chemical composition and molecular weight, therefore the molecular weight measurement using GPC (gel permeation chromatography) is challenging. The hydrodynamic radius dependence on the chemical composition can be determined by known copolymers, however, standards are not available for most copolymers.

In this paper, we investigated the correlation between the hydrodynamic radius (GPC elution time) and the chemical composition of the ethylene-oxide propylene oxide copolymers.

With the fractionation of the copolymers (EO-PO), the separation of compounds based on size was performed and the chemical compositions of the fractions were analyzed by MALDI TOF MS. Mass remainder analysis was applied to evaluate all the spectra. [1] Our result can be used to achieve higher accuracy for copolymer molecular weight determination by GPC

Experiment

The mass spectrometric measurements were carried out with Autoflex Speed MALDI-TOF mass spectrometer (Bruker, Bremen, Germany). The GPC separation was performed by the Waters separation module equipped with Waters Styragel columns and a refractive index detector. The samples (M-1170 and L-121 Polymers) were dissolved in THF and injected into the GPC. Anthracentriol, sodium trifluoroacetate, methanol were used as the matrix, ionization agent, and solvent, respectively in MALDI-TOF measurements.

Results and discussion

We performed the separation of two polymers with different molecular weights using GPC. The first question concerns the presence of homopolymers in the copolymer system. **Fig. 1** illustrates the mass spectra of two different fractions of L-121 copolymer as well as the presence of PO series.
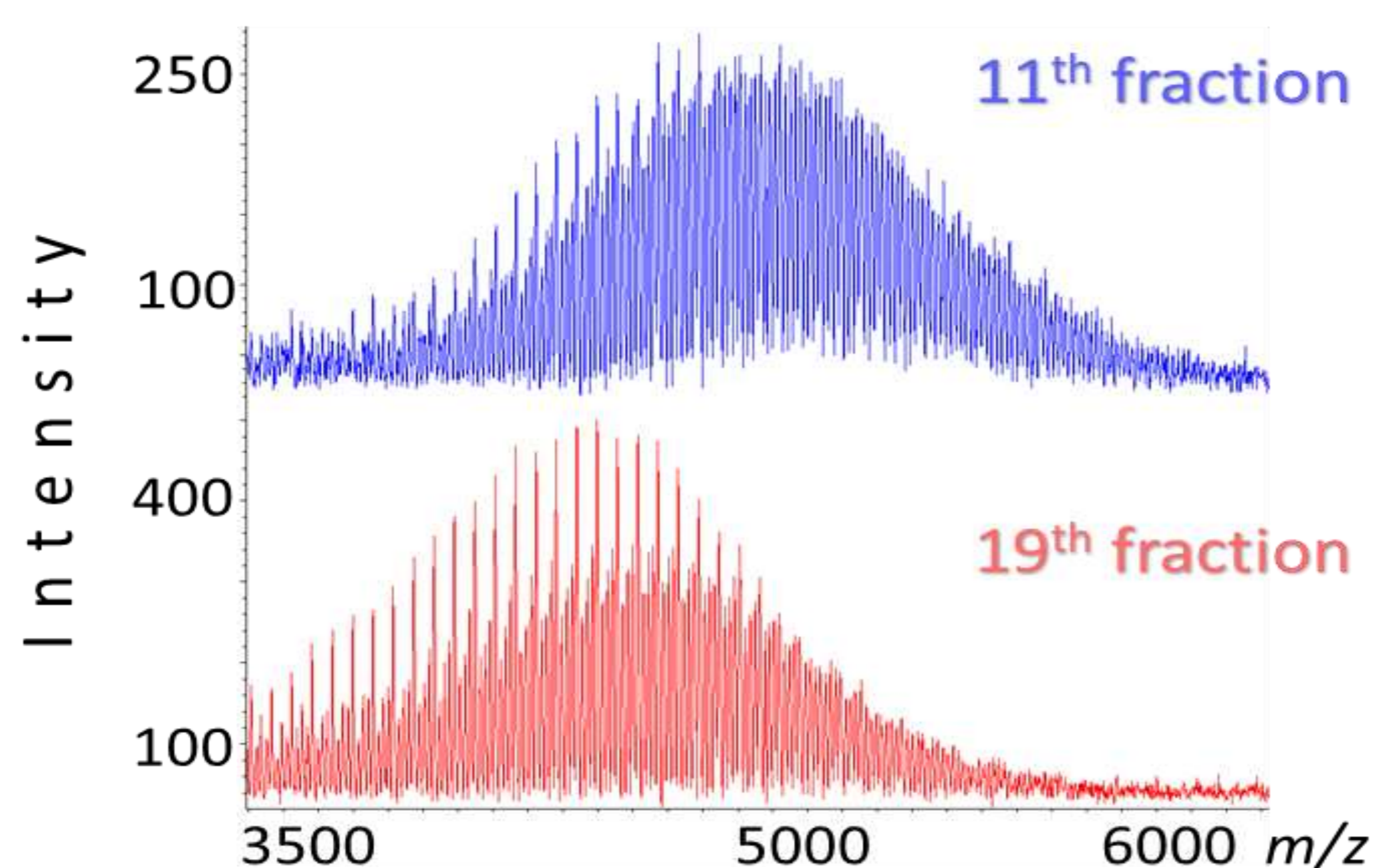

Fig. 1 Mass spectra of PEG-PPG-PEG block copolymer (Pluronics® L-121). Blue: 11th fraction Red: 19th fraction eluted by GPC
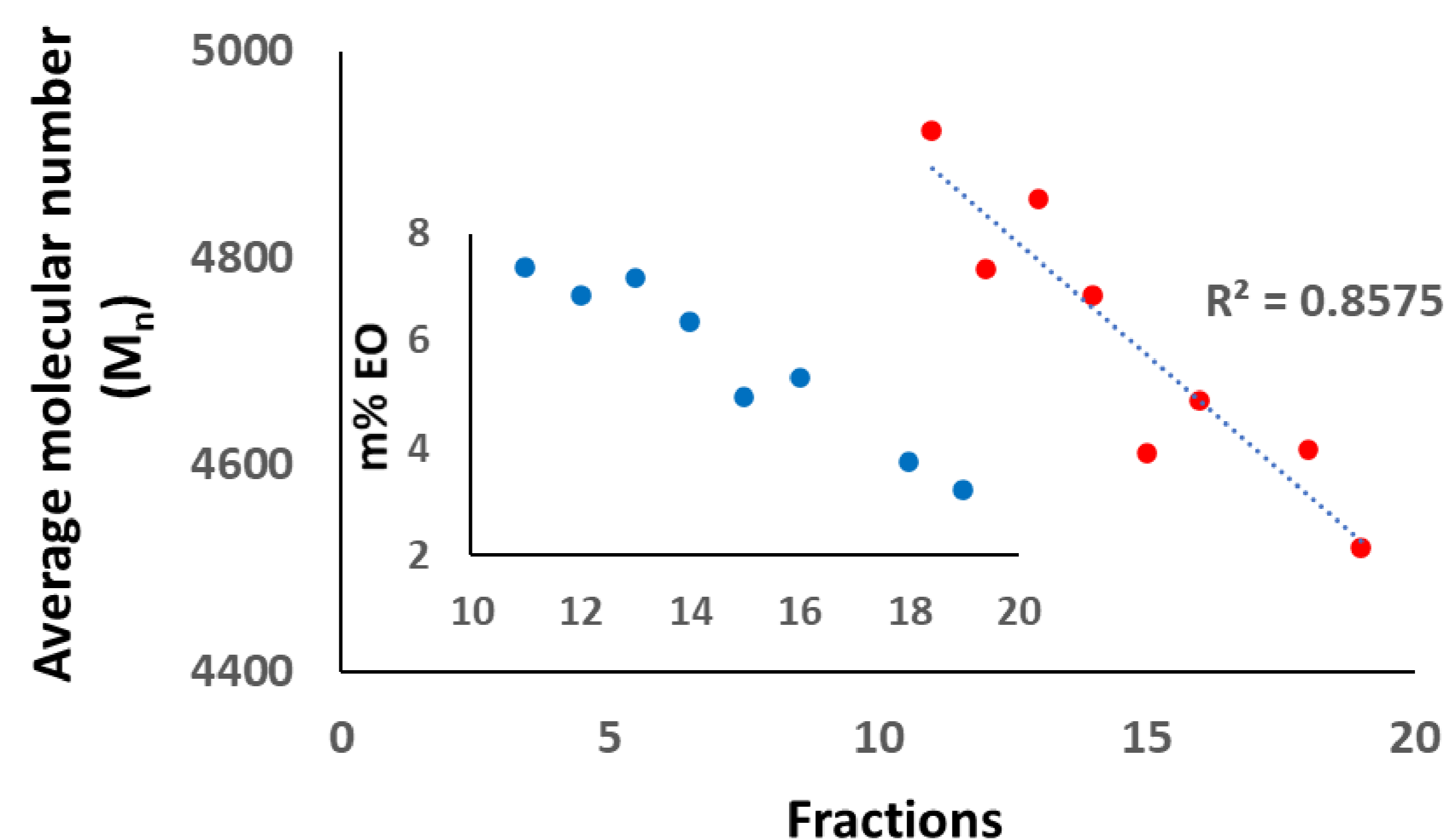

Fig. 2 M_n and m/m% EO as a function of number of the fractions (Pluronics® L-121)

Fig. 1 represents that the average molecular weight of the 11th fraction is higher than that of the 19th fraction because the higher molecular weight fraction elutes faster through the GPC column. A Previous study proposed L-121 contains 10% EO by mass however, **Fig. 2** shows the number average molecular weight and mass percentage of EO content of the fractions decrease (from 7% to 3%) as fraction number increases. The decrease in EO content (7% instead of 10%) is due to the low peak intensities. M-1170 copolymer does not have a direct correlation (**Table. 1**) as compared to the L-121 block copolymer, which is a polyether polyol, a statistical copolymer of EO and PO based on glycerine. In the same retention time at 18.8 min, the number of molecular weight of L-121 is much higher than the number of molecular weight of M-1170.

L-121				M-1170				
Fraction	M_n Da	M_w Da	Retention time (min)	m% EO	Fraction	M_n Da	M_w Da	m% EO	Retention time (min)
11	4922	4970	18.8	7.4	17	4734	4782	76.5	17.9
12	4788	4835	19.0	6.9	18	4612	4667	74.6	18.1
13	4856	4900	19.2	7.2	19	4539	4598	78.0	18.3
14	4764	4813	19.4	6.4	20	4534	4574	77.8	18.5
15	4611	4653	19.6	5.0	21	4412	4470	76.8	18.7
16	4662	4706	19.8	5.3	22	4429	4482	72.6	18.9
18	4614	4655	20.4	3.7	23	4267	4321	75.7	19.1
19	4520	4561	20.6	3.2	24	4290	4333	73.1	19.3

Table. 1 Chemical composition of L-121 and M-1170

Conclusion

We successfully characterized the copolymer fractions, and all polymer quantities were determined. Based on the chemical composition change by a fraction, we showed that L-121 copolymer is a block copolymer while M-1170 is not. The results suggest that besides the size separation, the chemical composition has an effect on the separation however further experiments and analysis are required to confirm that observation.

References

1. Nagy T, Kuki Á, Nagy M, Zsuga M, Kéki S., Mass-Remainder Analysis (MARA): An Improved Method for Elemental Composition Assignment in Petroleomics. **Anal. Chem.** 2019, 91(10), 6479-6486.

Acknowlegdement