MALDI mass spectrometry of polyethylene glycol fatty acid ester

MALDI mass spectrometry is capable of clearly assigning end group fatty acids of polyethylene glycol.

Keywords: autoflex maX, polymerix, polymer, polyethyleneglycol

Overview

In this application note, we will describe an example of a detailed analysis of end groups for two types of commercially available polyethylene glycol fatty acid esters.

Introduction

Polyethylene glycol fatty acid esters are important materials to our day-to-day lives due to their varied application and use as surfactants, and they can be used for different purposes by changing the type of fatty acid used to modify their material properties. However, generally commercially-available polyethylene glycol fatty acid esters may contain unreacted polyethylene glycol or differing fatty acids, and, strictly speaking, are thought to have variations in molecular structure.

MALDI-TOF MS is well-known as one of the available methods for the characterization of polymer samples and is used to calculate average molecular weight and analyze end groups. It is particularly beneficial due to the relative ease of obtaining information that is difficult to obtain through analysis methods other than mass spectrometry, particularly in terms of end group analysis, where, for example, it is capable of clearly identifying mixtures of end groups, which are observed as discontinuous peaks, provided that the masses (molecular weights) of these differ. In this application note, we will describe an example of detailed analysis using MALDI-TOF MS for two types of commercially-available poly-

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ethylene glycol fatty acid esters. The detected and identified components also include isobaric molecules that differ by only 0.09 Da.

Sample Preparation

We purchased commercially-available polyethylene glycol monooleate (Mn approx. 860) and polyethylene glycol dioleate (Mn approx. 914), and used tetrahydrofuran to make 20 mg/ml solutions. They were mixed with a matrix solution (DCTB 20 mg/ml in THF) and a cationizing agent solution (sodium trifluoroacetate 2 mg/ml in THF) and were then applied onto a target plate (MTP 384 Ground Steel), which were subsequently dried.

MALDI-TOF Measurement Conditions

We used autoflex maX mass spectrometer. This model has a rapid measurement capability due to its 2000 Hz laser and also offers an improved dynamic range due to its integrated 10-bit digitizer. Spectra were taken in Positive Reflector mode and analyzed using Sierra Analytics' polymer spectral analysis software, Polymerix 3.0.

Analysis Results

Figure 1 shows the mass spectra of the two samples. In each spectrum, regular intervals of 44 Da corresponding to the polyethylene glycol (PEG) unit confirm that the monomer unit is ethylene glycol. The fact that there are several series observed in shifted positions in the same 44 Da intervals indicates that they are mixtures of multiple components with different end groups. Figure 2 shows magnified spectra. While end group assignment results are also included, it can be seen that some of the molecules are isobaric, and differ by only 0.09 Da. Figure 3 shows the result of polyethylene glycol monooleate sample spectral analysis performed using Polymerix. In the figure, Ole indicates oleic acid, ol for hydroxyl, and Lin for linolenic acid end group. Monooleate is observed with the highest intensity, as the reagent name suggests, though its intensity is around 47%; diol and monolinoleate are also detected with relatively high intensity, at 24% and 15%, respectively.

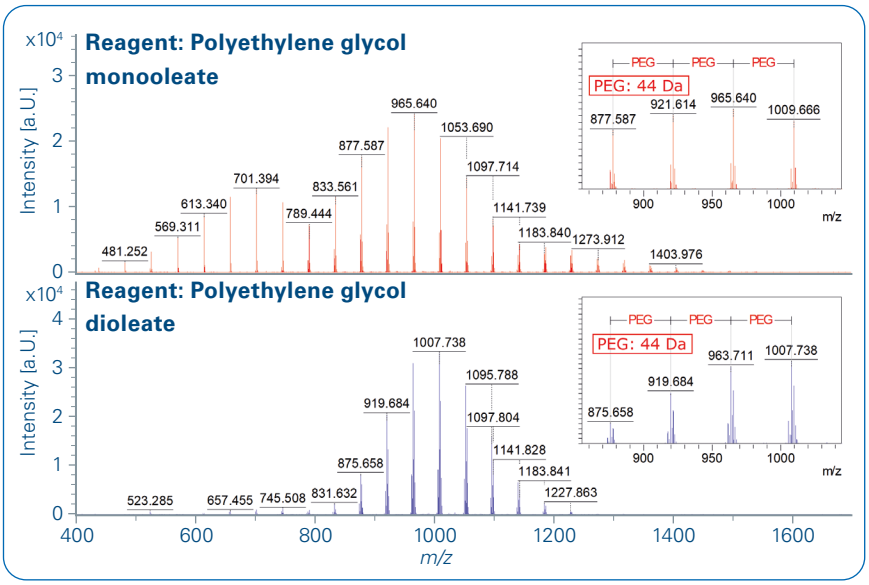

Figure 1: Mass spectra of polyethylene glycol monooleate (top) and dioleate (bottom). This indicates that the monomer unit is ethylene glycol and that they are both mixtures of structurally different end groups.

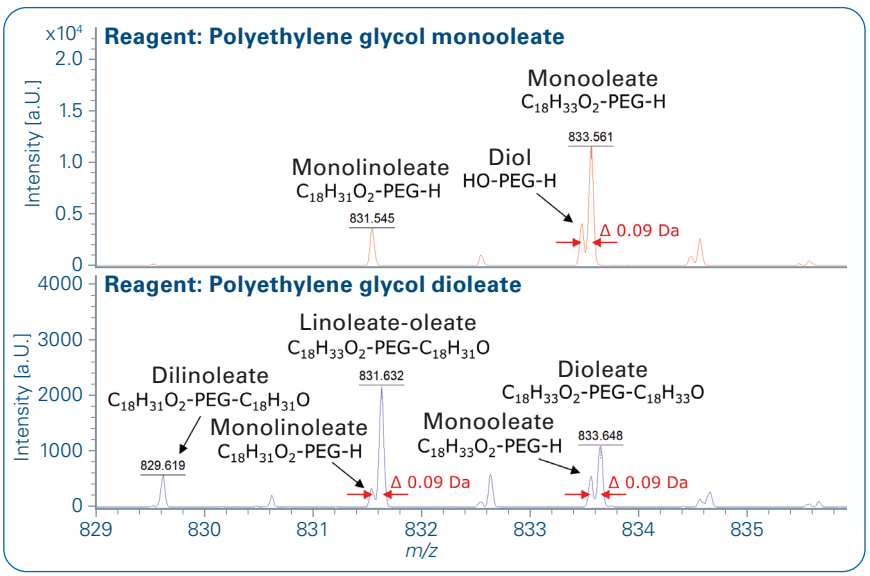

Figure 2: Magnified spectra. End group assignments based on results of analysis performed by Polymerix. Detected/identified components include isobars with a 0.09 Da difference.

Figure 4 shows the result of polyethylene glycol dioleate sample analysis performed using Polymerix. Here, it is not dioleate that is observed with the highest intensity (27%), but linoleate-oleate (59%). It also shows that while components with the hydroxyl group unchanged on one side are detected, components with the hydroxyl group on both ends are not detected.

Table 1 is a comparison of total detection intensity for the end groups calculated from the aforementioned results. For the ethylene glycol dioleate sample in particular, the ratio for the linolenic acid end group is estimated to be close to the oleic acid terminal group. Although the effect on the ionization efficiency of fatty acids and other factors must be addressed when discussing precise quantification, the information provided should be useful as a rough estimate. It is possible to obtain the end group data as an average of samples similar to those shown in Table 1 by other means than MS; however, one of the advantages of MS is its ability to provide individual data, as shown in Figures 3 and 4.

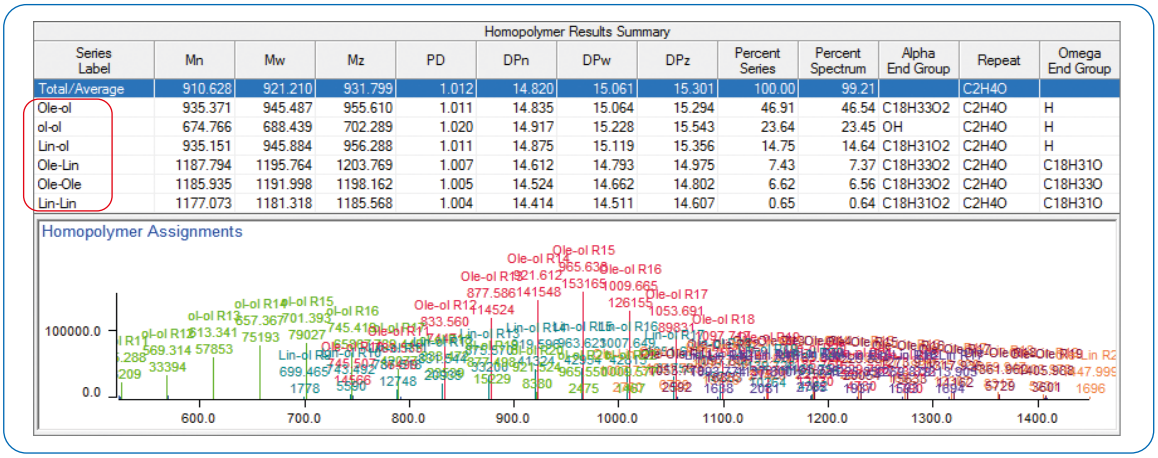

Figure 3: Result of polyethylene glycol monooleate sample spectral analysis performed using Polymerix. The end group series labels are shown inside the red box on the figure, with Ole indicating oleic acid, Lin for linoleic acid and ol for hydroxyl end group. Mean molecular weight, polydispersity, degree of polymerization, and detection intensity are listed for each series. The mean molecular weight changes depending on the end group, but the degree of polymerization (DPn, DPw, DPz) is almost constant.

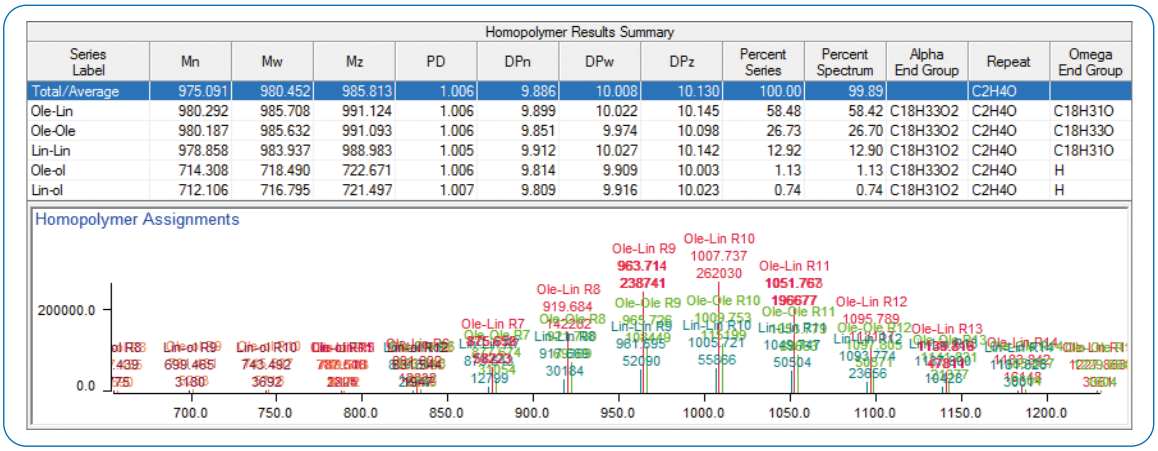

Figure 4: Result of polyethylene glycol dioleate sample spectral analysis performed using Polymerix. Oleate linoleate, rather than dioleate, is detected with the highest intensity.

Conclusion

We performed an analysis of the end groups of two commercially available polyethylene glycol esters using MALDI-TOF MS. The ability to provide individual data, rather than mean data, is an advantage of mass spectrometry. The significance of detailed polymer material analysis for quality management purposes will continue to grow as surfactants and other various materials with high performance and advanced functionalities continue to be developed.

Reagent	Monooleate	Dioleate
Terminal oleic acid %	33.8	56.5
Terminal linoleic acid %	11.7	42.5
Terminal hydroxy group %	54.5	0.9
Fatty acid: hydroxy group ratio	1:1.20	1:0.01
Oleic acid: linoleic acid ratio	1:0.35	1:0.75

Table 1: Total intensity (%) and ratio for each terminal group structure, as calculated by detection intensity values obtained using Polymerix

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