

# Analysis of butylene glycol oligomer samples by temperature-rising direct analysis in real time mass spectrometry (TR-DART-MS)

**ASMS 2015** TP 026

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### Introduction

DART (Direct Analysis in Real Time), a direct atmospheric pressure ionization source, is capable of analyzing chemical materials with little or no sample preparation. In DART analysis, as samples are only introduced into the heated helium gas flow which is set at the preset temperature, they can be analyzed in a quite short time such as about 10 seconds.

We had developed the temperature rising device,

ionRocket, combined with DART-MS system (TR-DART-MS), which could make the heating temperature of sample rise with the passage of time. It became able to acquire a MS spectrum while changing the heating temperature successively by this. Here, we report the analyses of 1,3-butylene glycol oligomer samples using this temperature rising device.

### Methods and Materials

Two kinds of butylene glycol oligomer different in each average molecular weight and polyethylene bag, which was often used at a convenience store, were used as analysis target samples. Butylene glycol oligomer samples, as they were liquid, applied directly. Polyethylene bag, as it was a solid sample, was cut with a cutter in the suitable size, then, it applied onto DART-MS analysis.

The DART-OS ion source with the temperature rising device, ionRocket, was interfaced onto the triple quadrupole mass spectrometer LCMS-8030. LCMS-8030 can achieve the polarity switching time of 15 msec and the scanning speed of up to 15000 u/sec, therefore the loop time can be set at less than 1 second despite the relatively large scanning range of 50-1500 u.

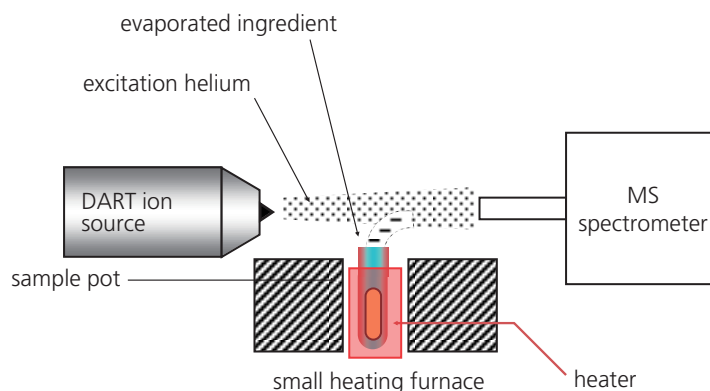
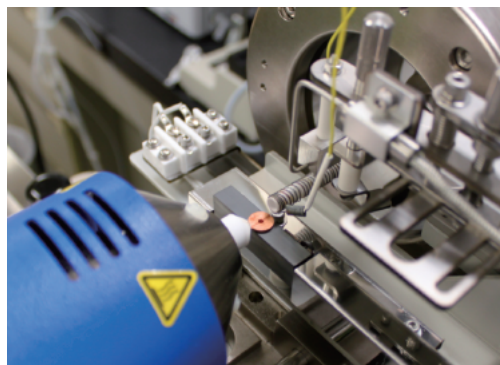


Figure 1 TR-DART-MS System; DART-MS integrated with the temperature rising device, ionRocket

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- Ultra Fast Polarity Switching
  - 15 msec
- Ultra Fast Scanning
  - 15,000 u/sec
- Ultra Fast MRM
  - Max. 555 transition /sec

Figure 2 LCMS-8030 triple quadrupole mass spectrometer

## Result

### Analysis by DART-OS

Two kinds of butylene glycol oligomer, sample A and sample B were analyzed by DART-OS. The heating temperature of DART was set at 450 Celsius degrees. Both sample A and B had detected several strong signals in positive and negative spectra. Rudder shape

signals of butylene glycol origin (72 u interval) were detected intensively in a positive mass spectrum of sample A around  $m/z$  500-700, but not detected so intensively in sample B.

Analytical condition	
Ionization	: DART-OS Ion Source
Measuring mode (MS)	: Q1 scanning, positive/negative simultaneously
Mass range	: $m/z$ 50 - 1500

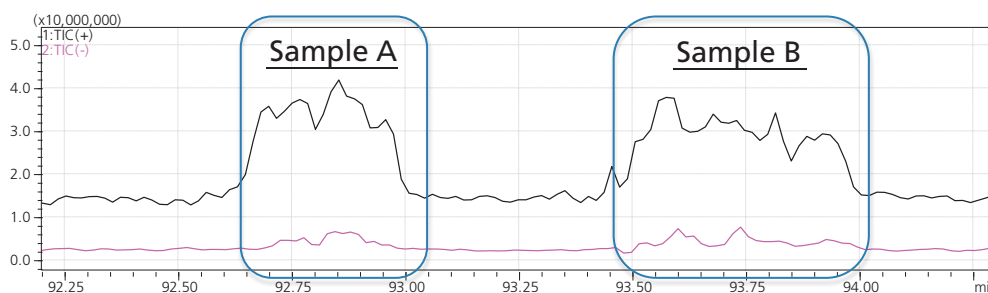
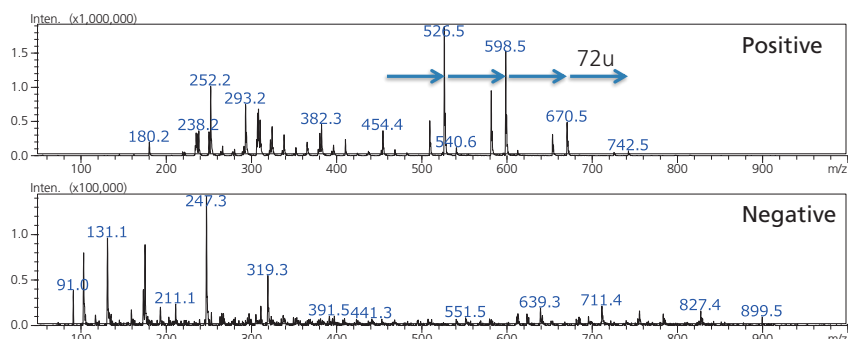


Figure 3 TIC chromatogram of two kinds of butylene glycol oligomer, sample A and sample B; black: positive TIC  $m/z$  50-1500, pink: negative TIC  $m/z$  50-1500

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## Sample A



## Sample B

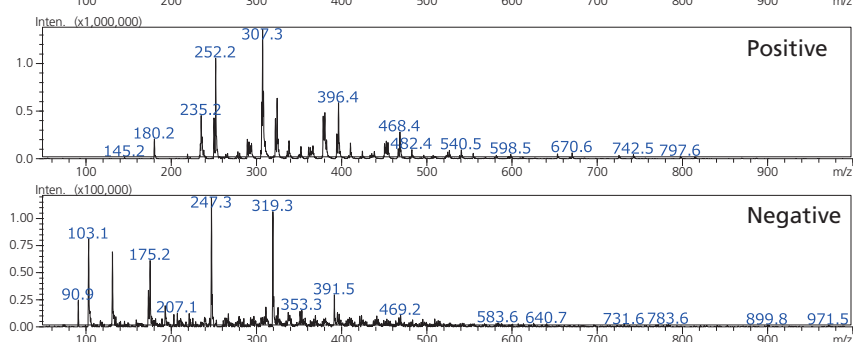


Figure 4 Mass spectra of butylene glycol oligomer, sample A and sample B

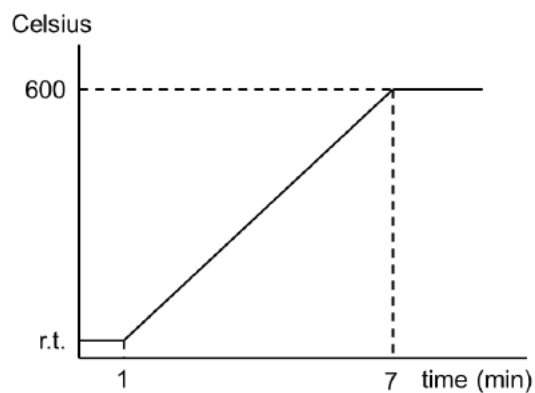
## Analysis by TR-DART-MS

Next, the DART-OS with the temperature rising device was interfaced onto LC-MS/MS and these samples were analyzed. Samples were subject to treatment of thermal

gradient from room temperature to 600 Celsius degrees for 6 minutes by the temperature rising device.

### Analytical Condition

Ionization	: TR-DART-MS
Heater Temperature (DART)	: 450 Celsius
Temperature control (ionRocket)	: 0-1min room temp., 7min 600 Celsius
Measuring mode (MS)	: Q1 scanning, positive/negative simultaneously



# Analysis of butylene glycol oligomer samples by temperature-rising direct analysis in real time mass spectrometry (TR-DART-MS)

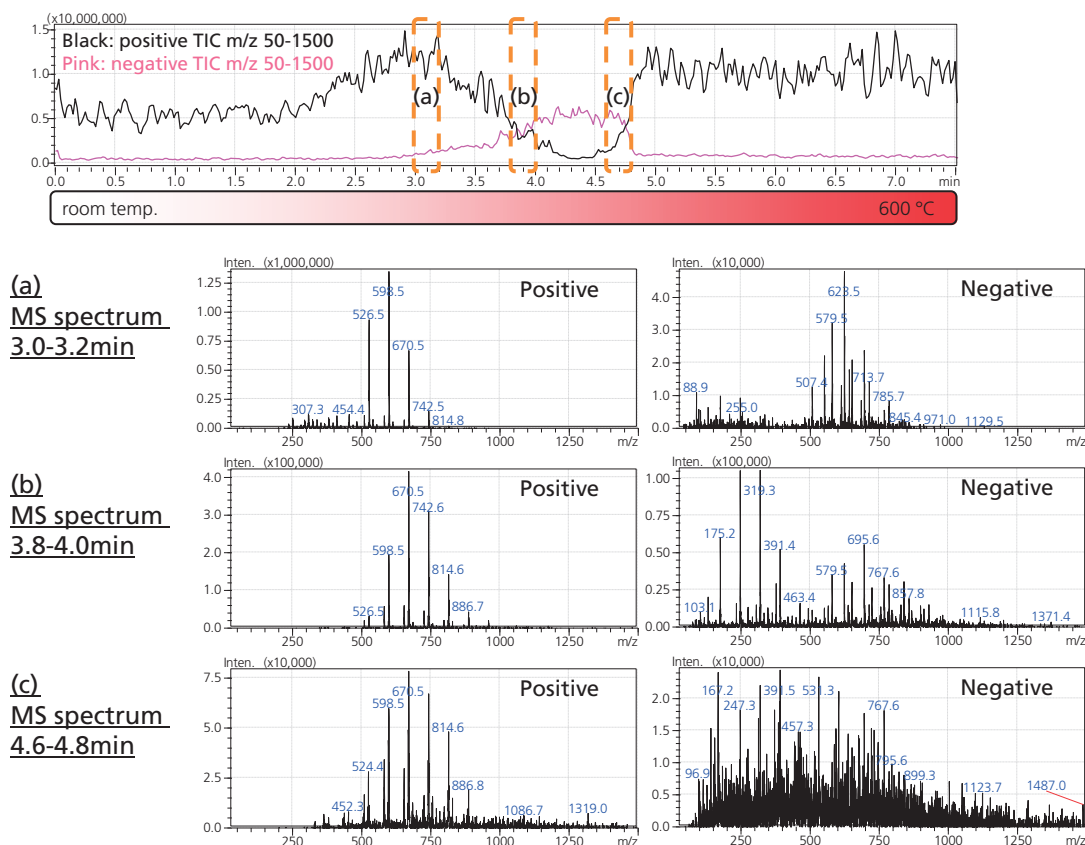


Figure 3 TIC chromatogram of sample A data and its typical MS spectra

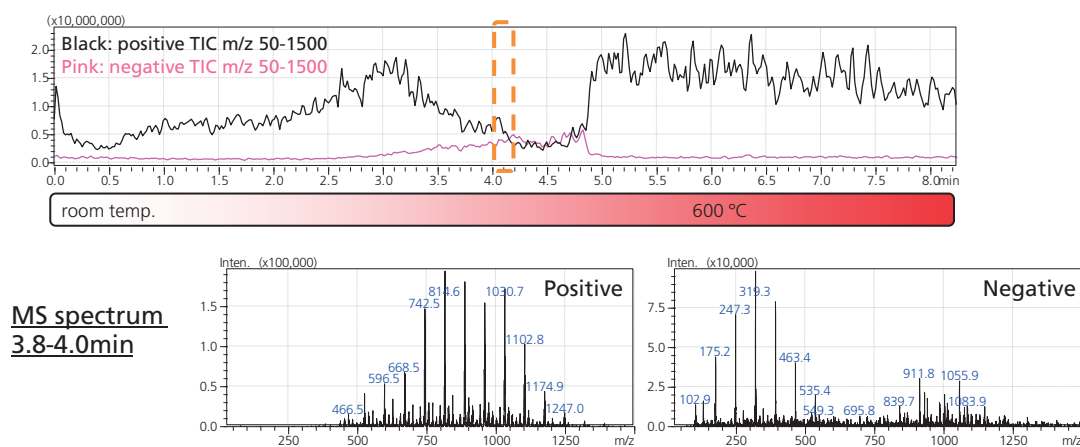


Figure 4 TIC chromatogram of sample B data and its typical MS spectra

## Analysis of butylene glycol oligomer samples by temperature-rising direct analysis in real time mass spectrometry (TR-DART-MS)

As a result of sample A analysis, the signals which seemed rudder shape of butylene glycol were detected at around 2.5 minutes and the rudder range was shifted to higher in m/z over time. The rudder range of sample A was detected in highest m/z (around m/z 600-900) at 4 - 5 minutes. The result of sample B analysis was mostly similar with that of sample A. However, the rudder range of sample B detected in highest was distributed around m/z 500-1300. These meant that the average molecular weight of sample B was bigger than that of sample A.

Then, a polyethylene bag was analyzed. Sample was cut with a cutter into small peace and it was subjected. Heating program was performed by the above-mentioned condition. The signal which seemed additives (oxide of irgafos 168) was detected in m/z 663 and the rudder signals of 14u interval which seemed polyethylene origin were detected around m/z 300-600 at about 4 minutes. Since the sample was heated at high temperature, it was considered that the pyrolyzed polyethylene was detected.

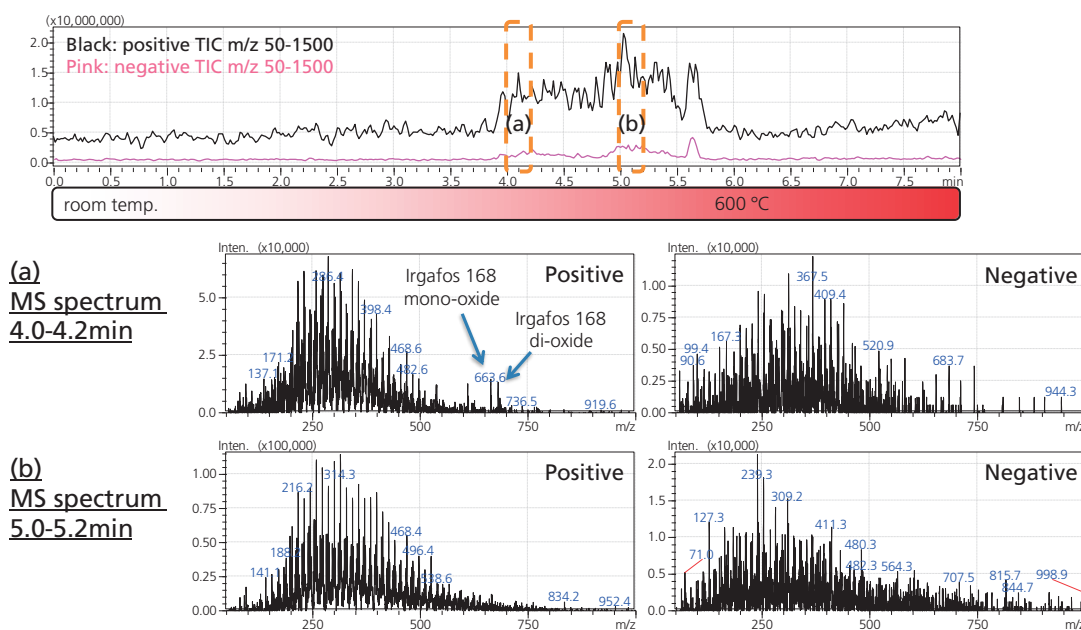


Figure 5 TIC chromatogram of polyethylene bag data and its typical MS spectra

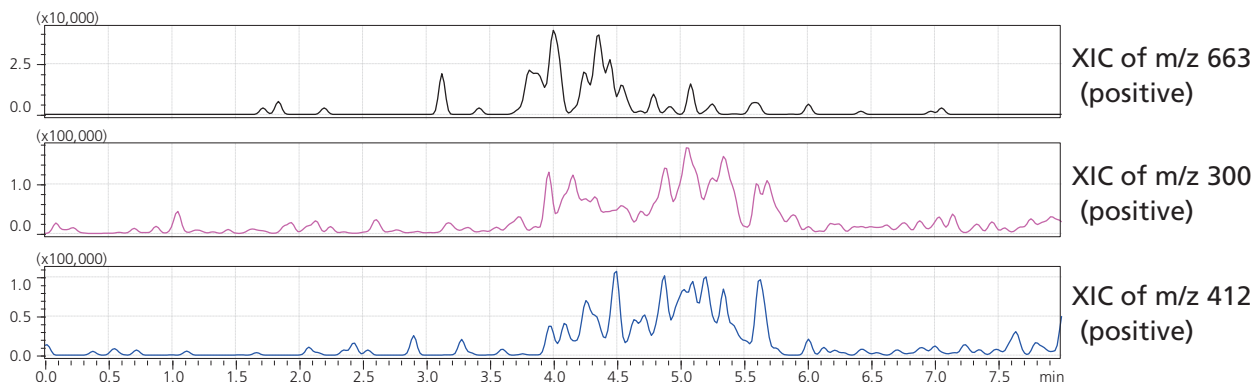


Figure 6 XIC chromatograms of polyethylene bag data

XIC of m/z 663, which was considered to be an oxide of irgafos 168, detected 3.7-4.5min, while XIC of m/z 300 and 412, the pyrolyzed polyethylene, detected 4-5.5min.

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### Conclusions

- TR-DART-MS, DART-MS with the temperature, rising device enabled to acquire a mass spectrum while raising the sample heating temperature successively.
- Signals of larger  $m/z$  value could be detected in TR-DART-MS analysis of butylene glycol oligomer.
- Detection of additives and pyrolyzed polyethylene was available in TR-DART-MS analysis of polyethylene.