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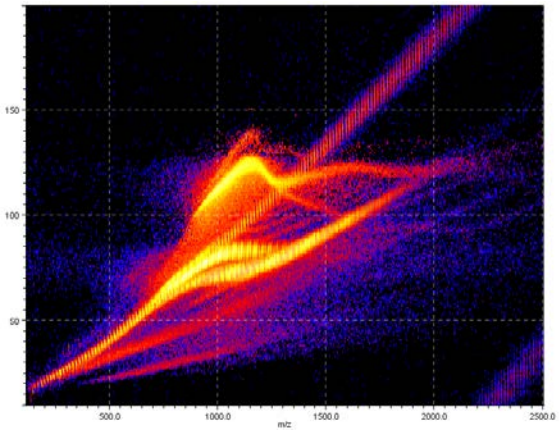
The Potential and Possibilities of Mass Spectrometry and Ion Mobility for the Analysis of Polymeric Materials

Kirsten Craven

GPC Polymer Symposium - Oct 2014



Contents

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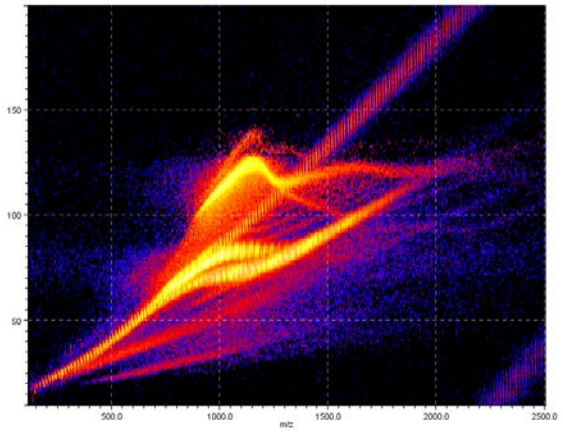
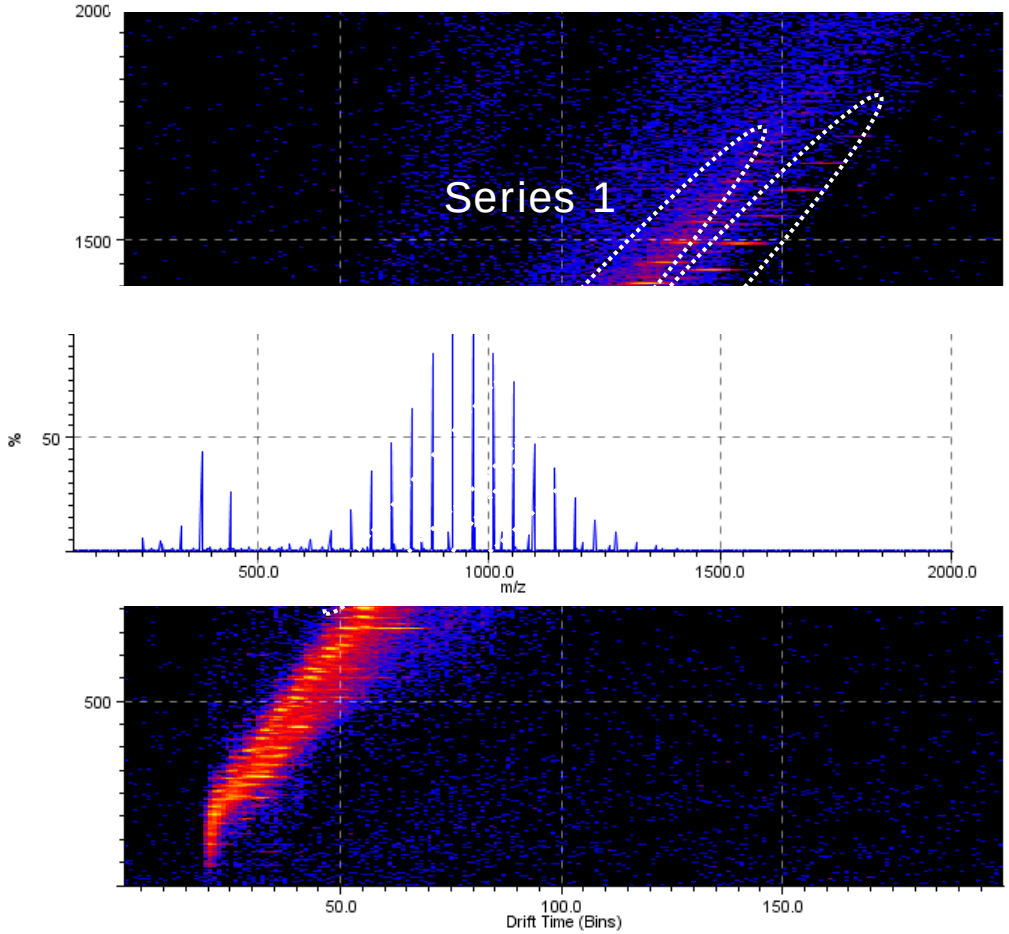
- **How is it Possible?**
  - SYNAPT Technology
  - Introduction to Ion Mobility
- **So What...?**
  - Simplification
  - Identification
  - Backbone Characterisation using MS/MS
  - Folding Patterns

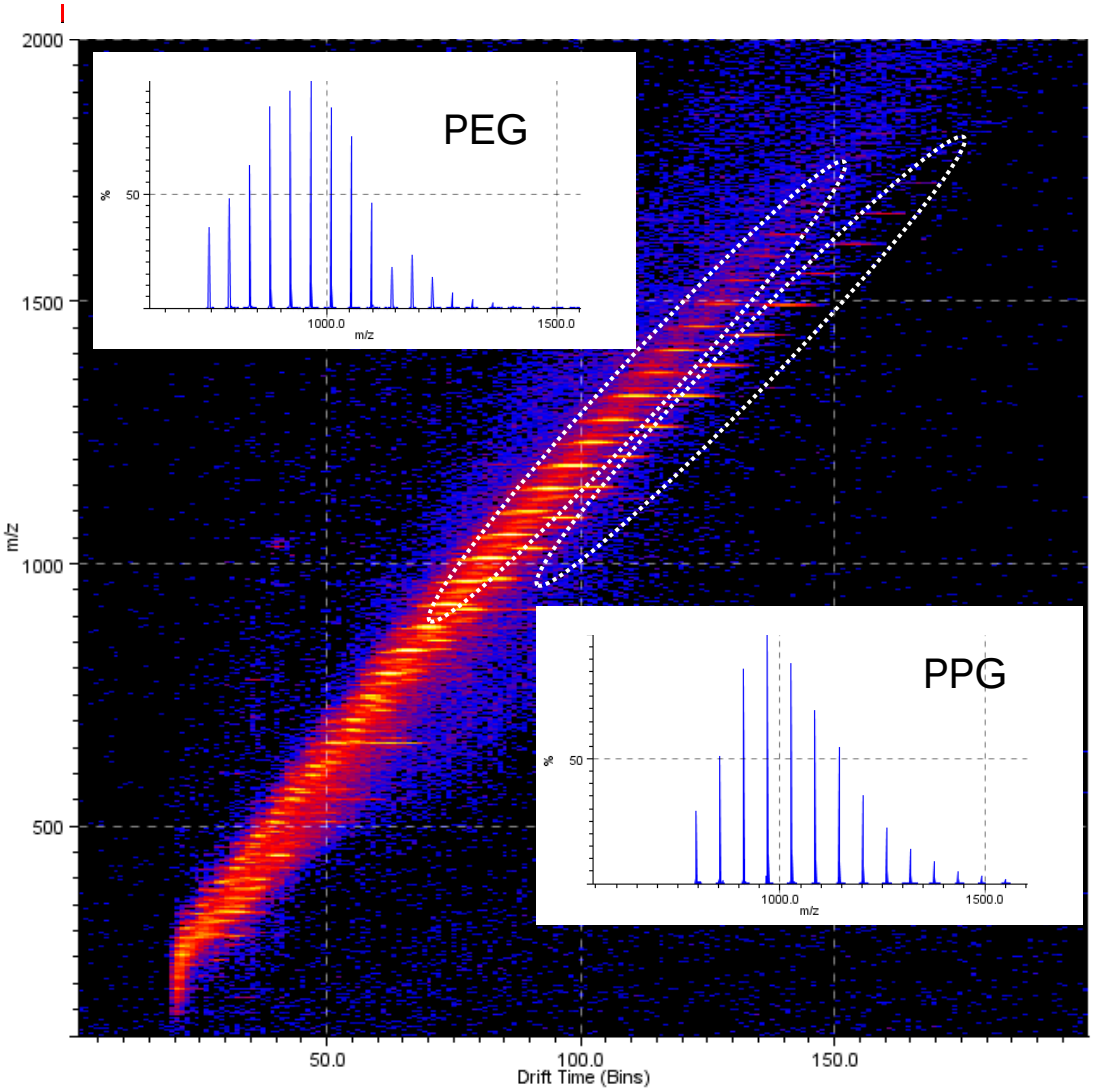
What is Possible?



MALDI Data



Spectral Selection



DriftScope™

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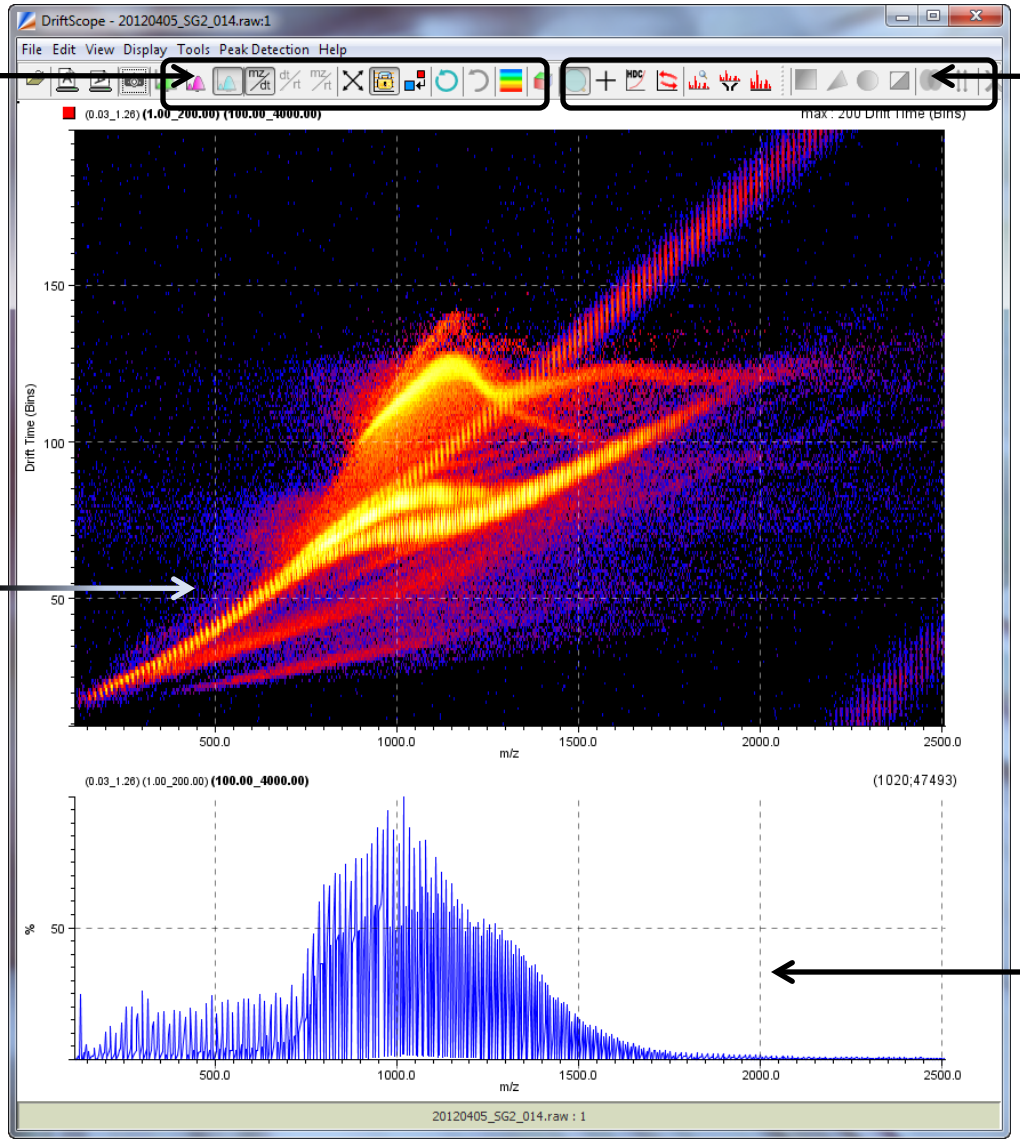
Data viewing tools

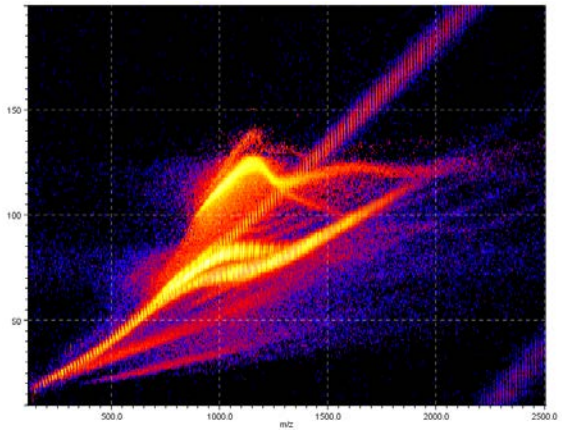
Data selection and peak detection tools



"Mobilogram" with *m/z* and drift time on the x and y-axes. Ion intensity is represented by colour.

"Traditional" mass spectrum view

How is it Possible?



SYNAPT® HDMS™ Technology

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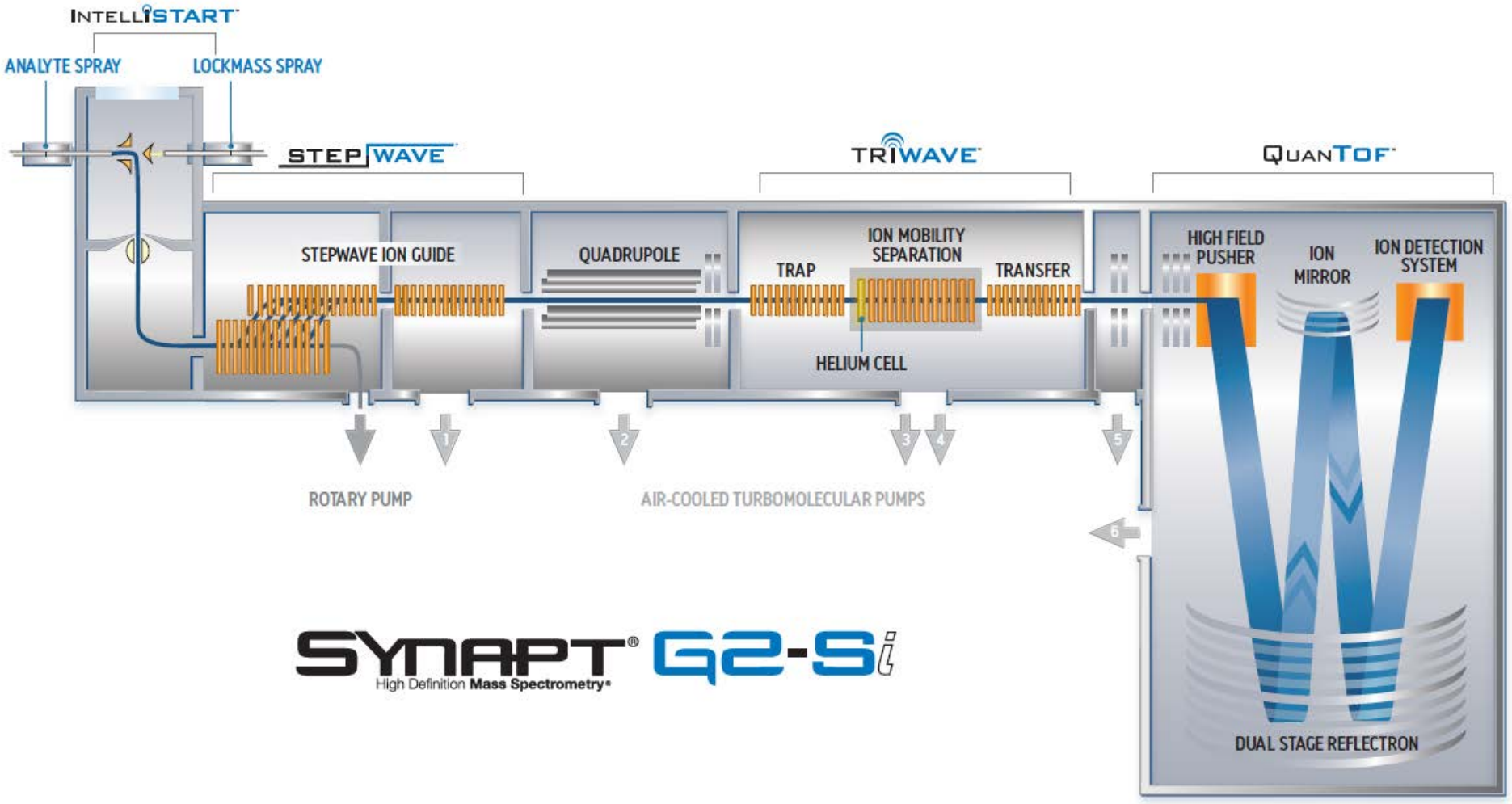
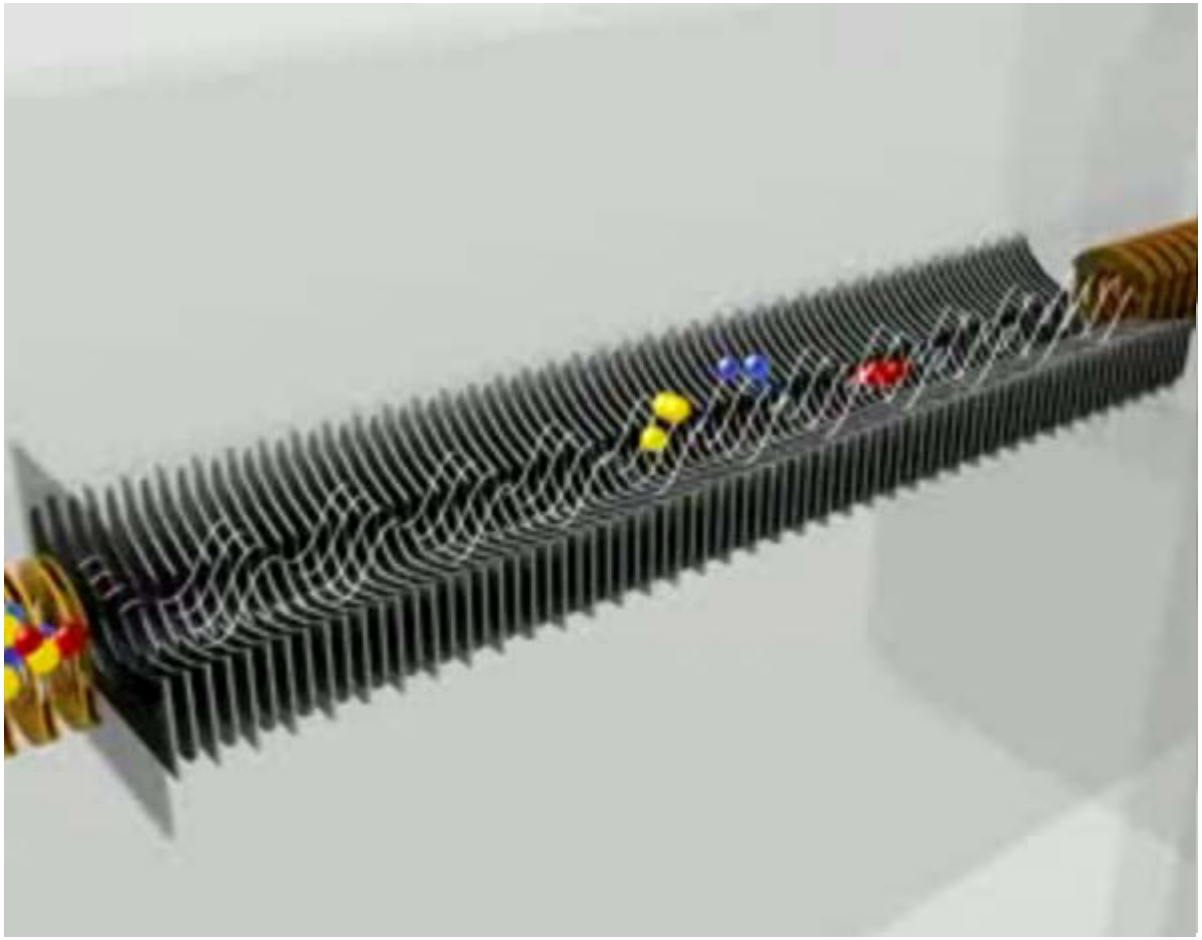


SYNAPT® G2-Si
High Definition Mass Spectrometry®

Tri-Wave



Tri Wave Region

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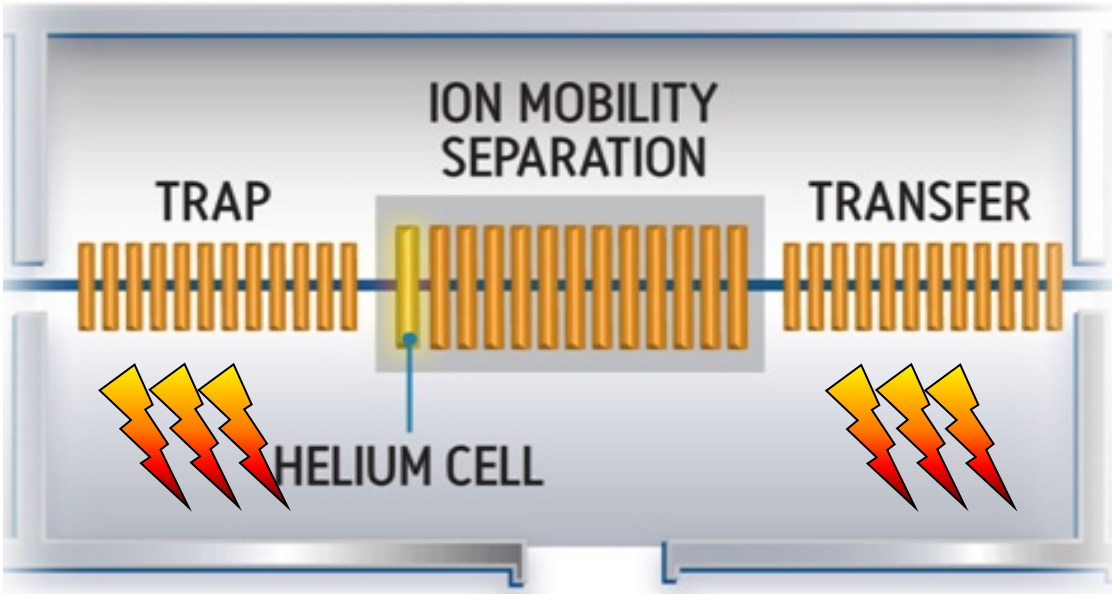
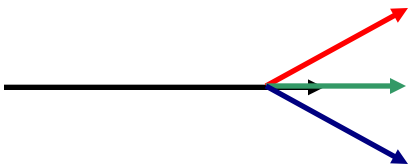
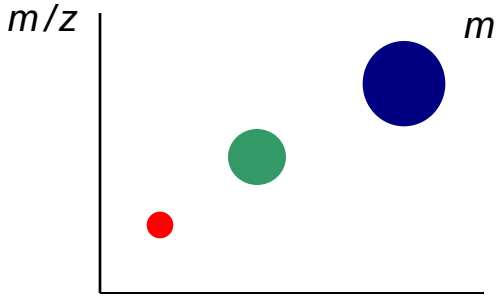
Ion isolated by quadrupole

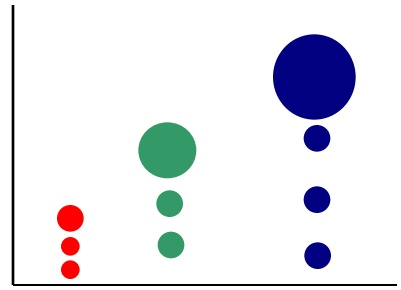




Precursor ion FRAGMENTED

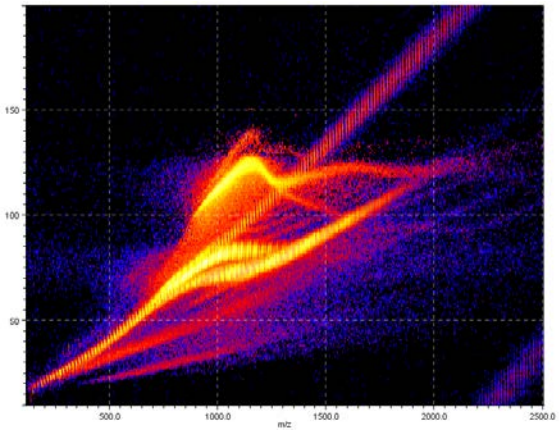


Product ions separated by IMS



1st & 2nd generation product ions are TIME ALIGNED

So What…?



Copolymers

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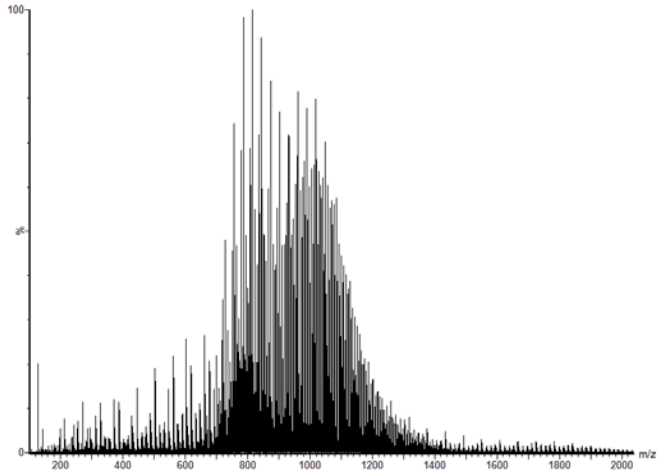
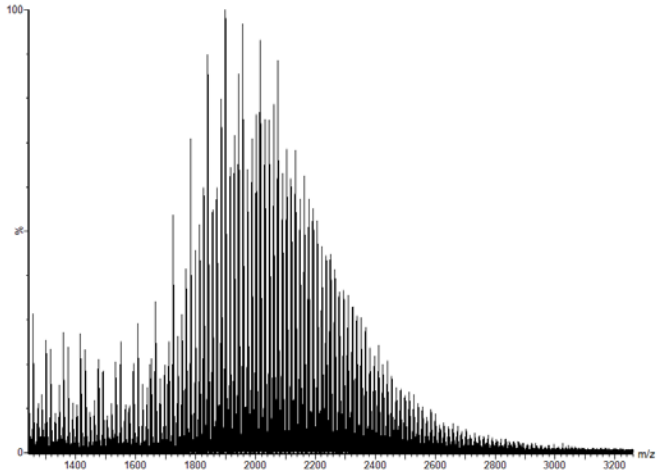
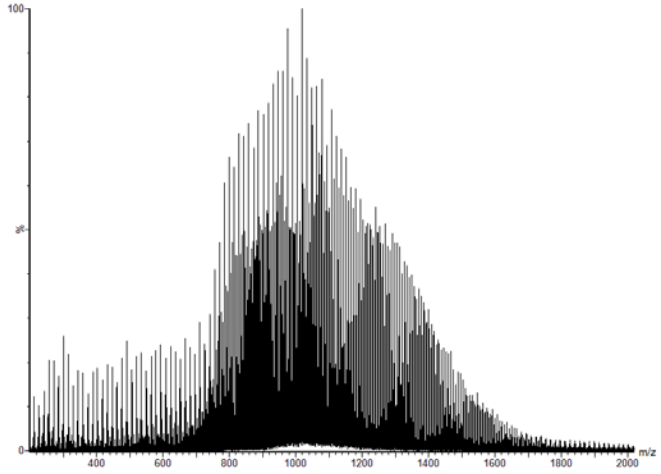
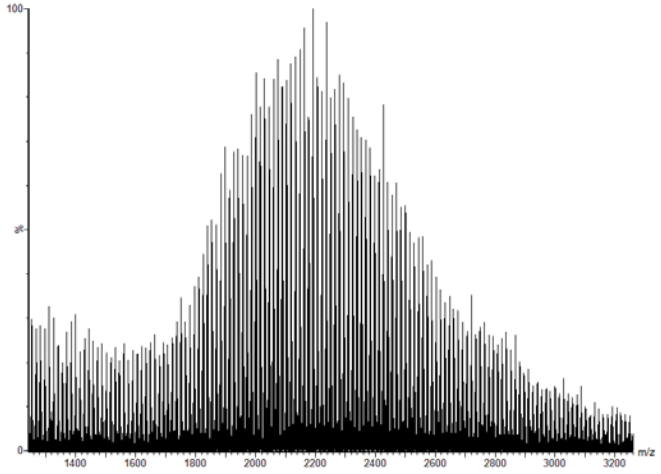
	ESI+	MALDI+
2K PEG-b-PPG-b-PEG		
2K PEG-r-PPG		

IMS Separation of Copolymers

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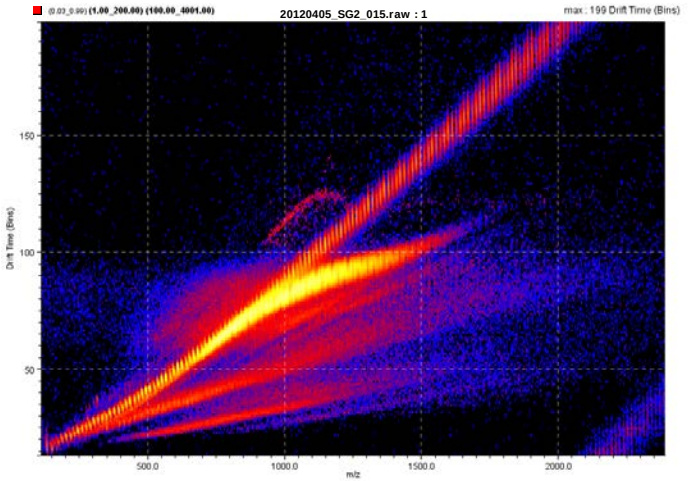
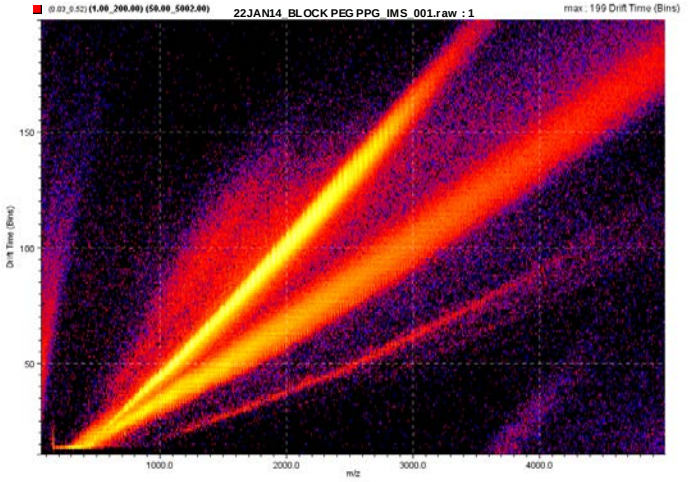
ESI+

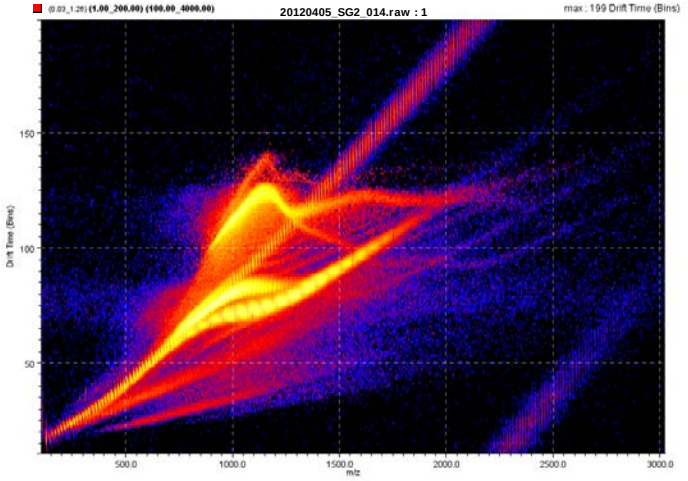
MALDI+

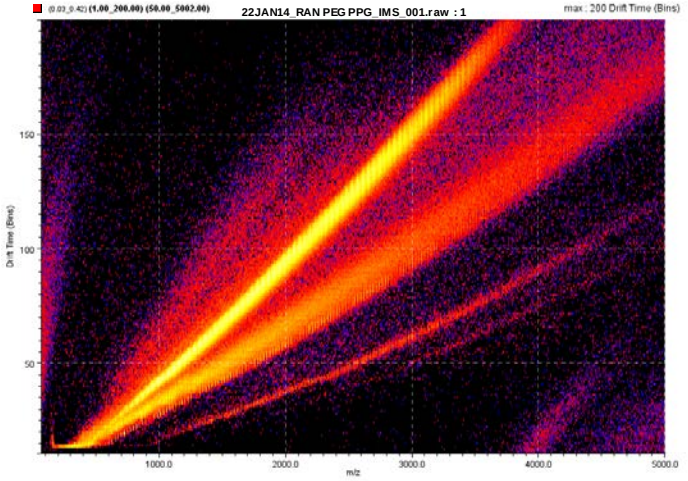
Block
PEG and PPG





Random
PEG and PPG





Mixture of Copolymers

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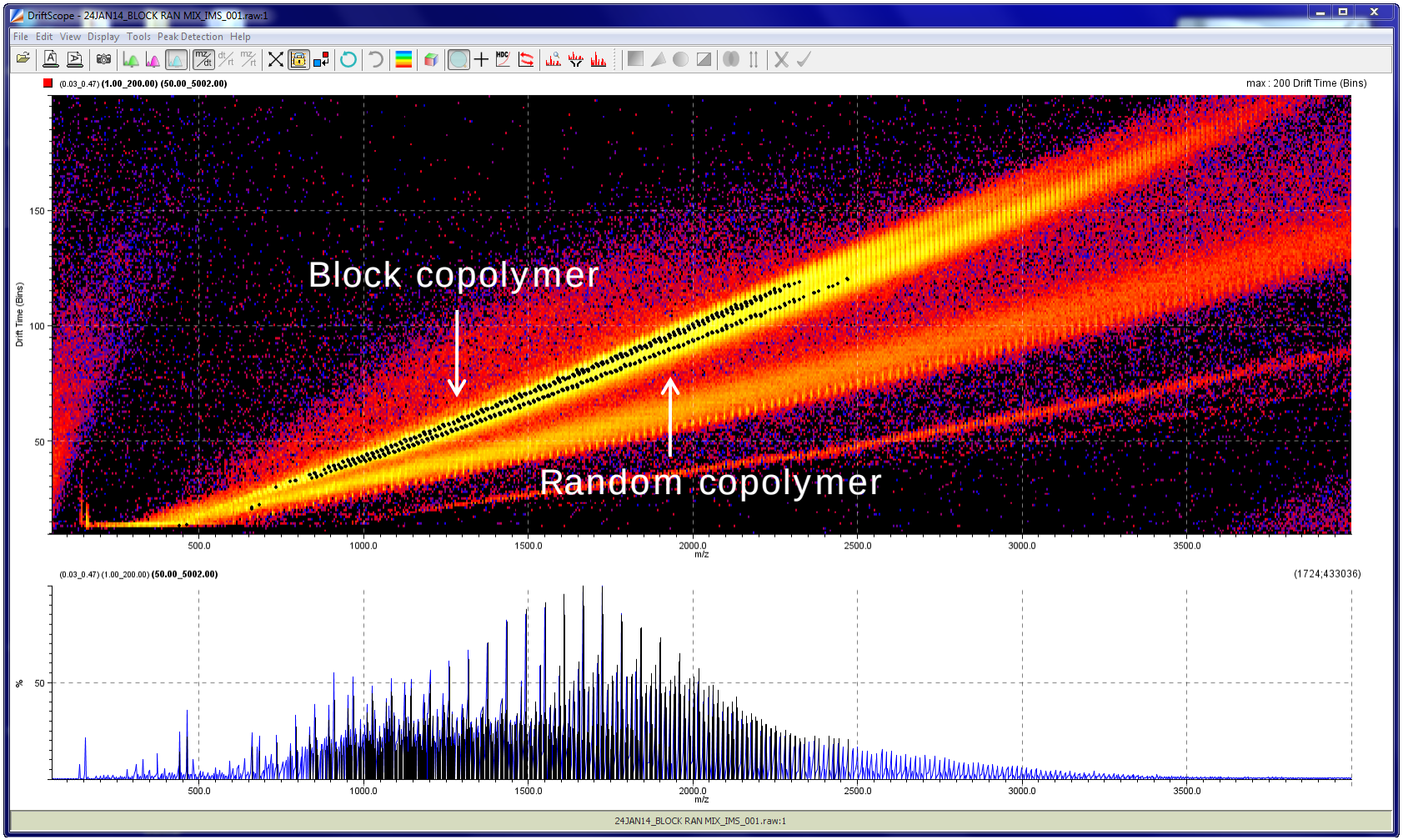
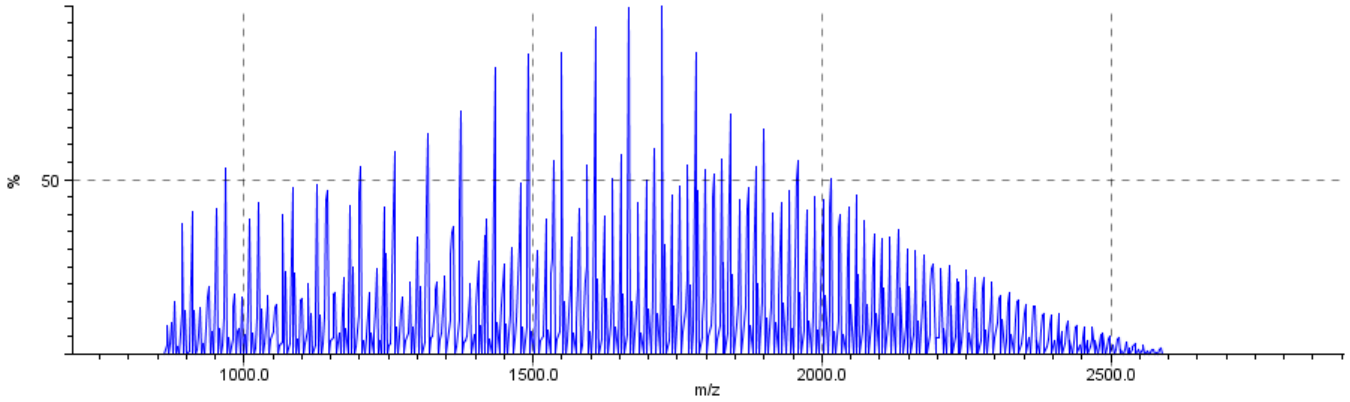
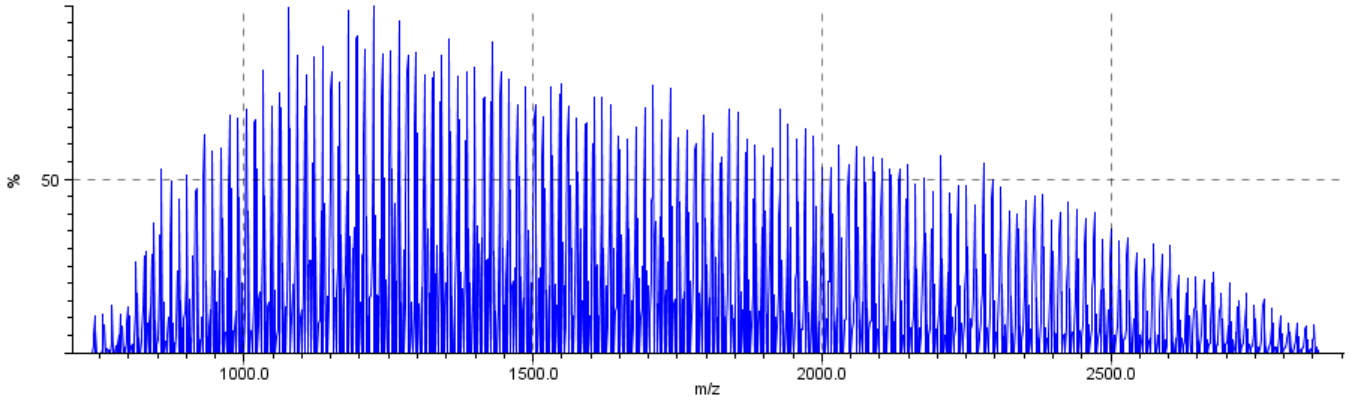


Isolated Ion Series

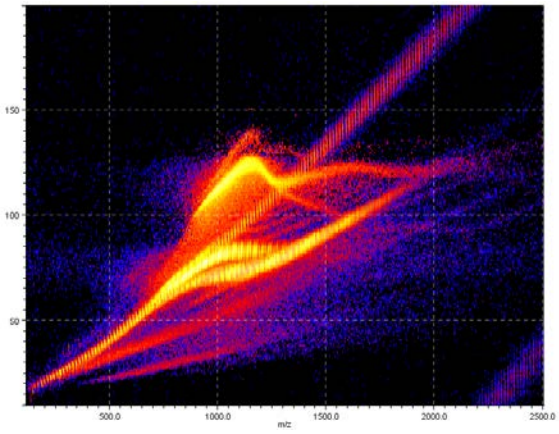


Top ion series
Block copolymer

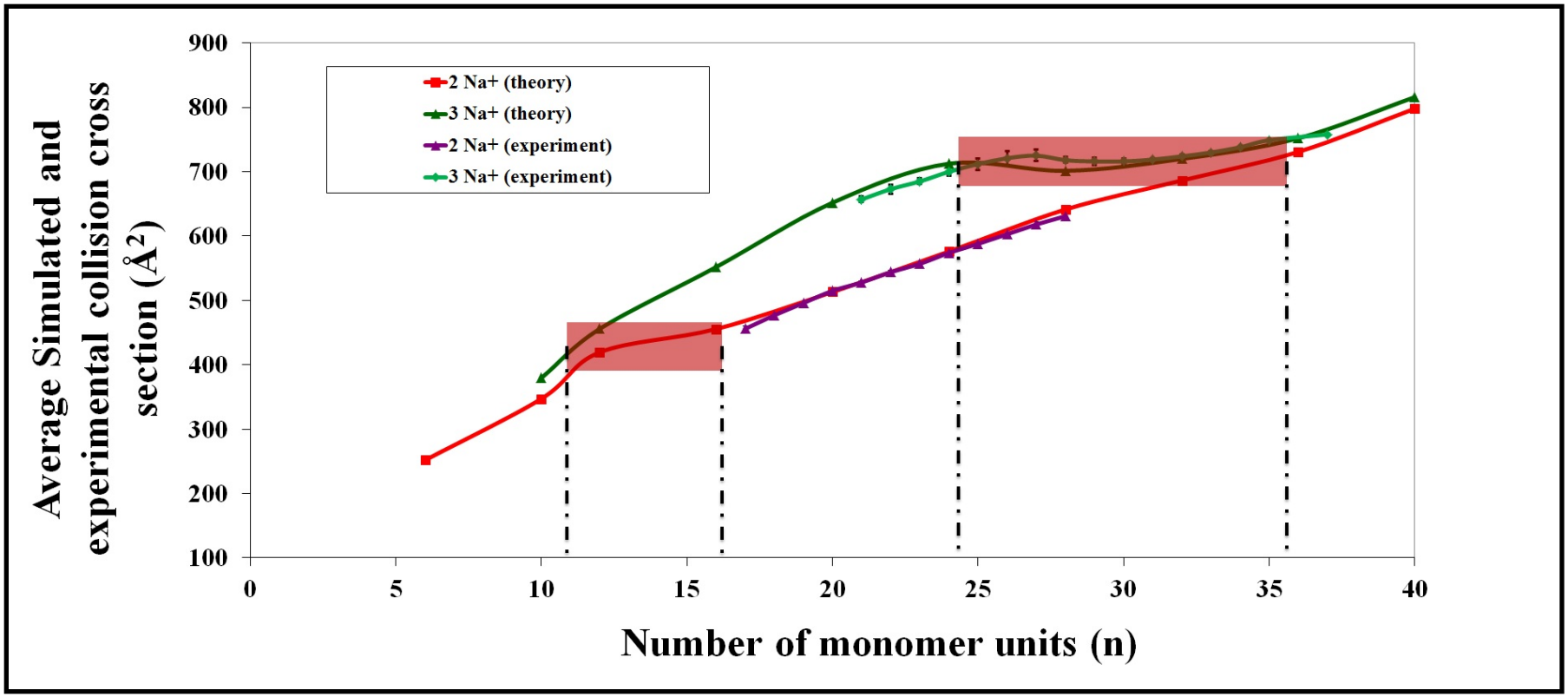


Bottom ion series
Random copolymer

Folding Patterns



Polylactide Analysis



J De Winter, *et al*. Chem. Eur. J. 2011, 17, 9738-9745

Sodiated Polylactide (+3)

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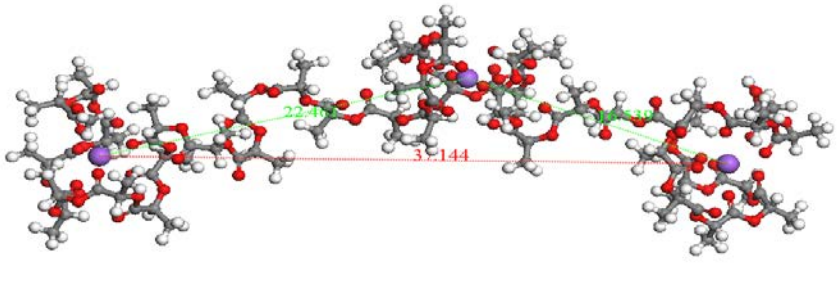
n = 20



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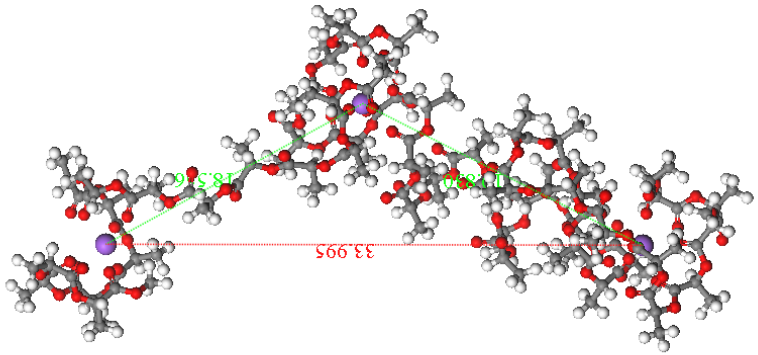

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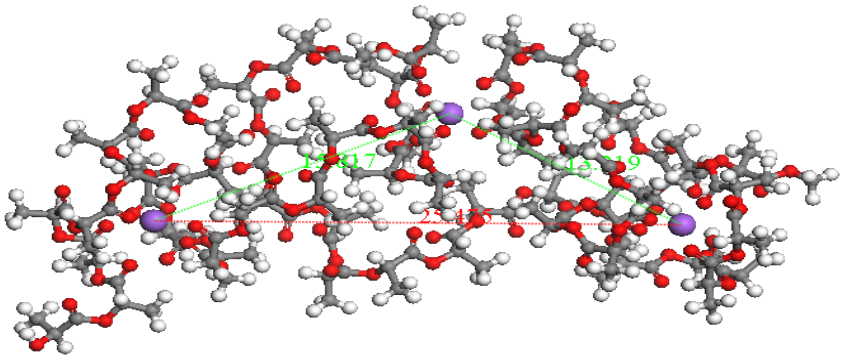
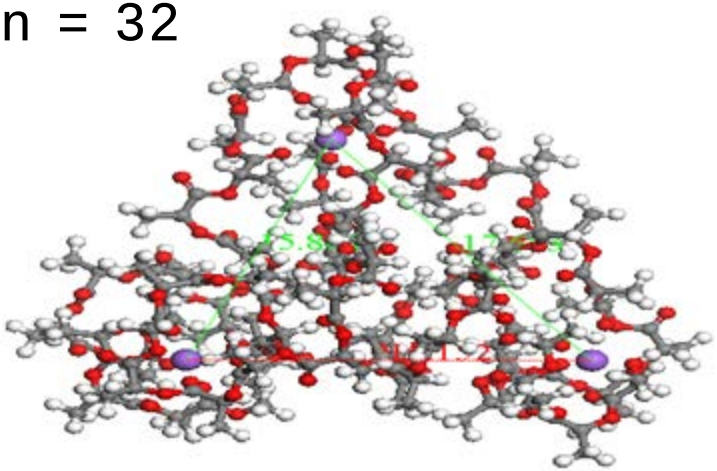


n = 32



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Polylactide Analysis

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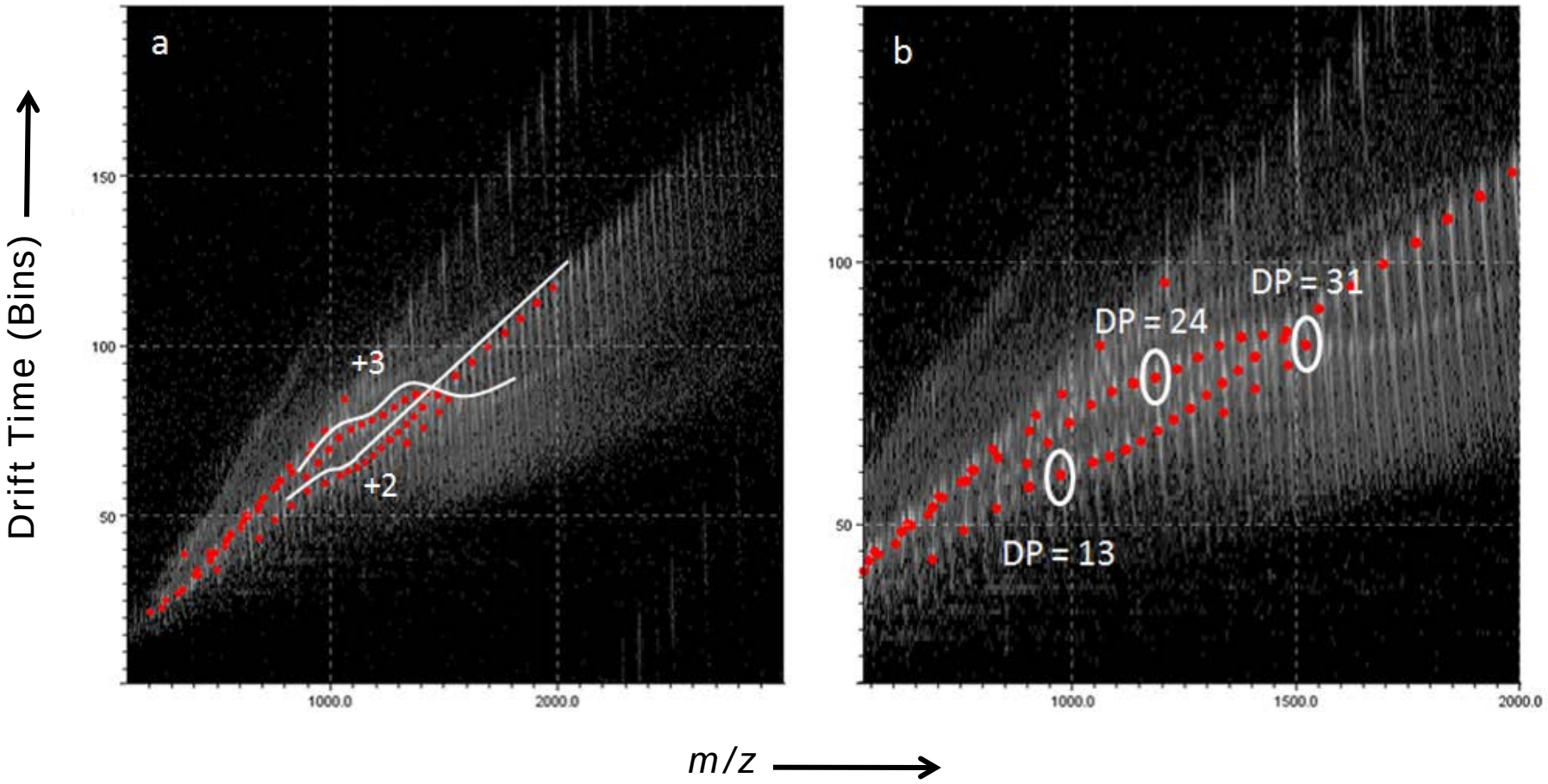
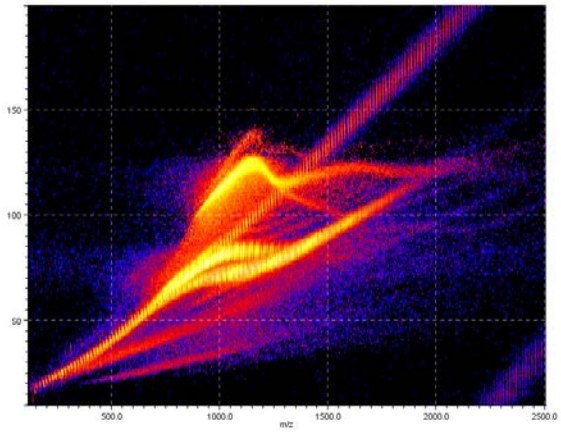


Identification



Problem Solving

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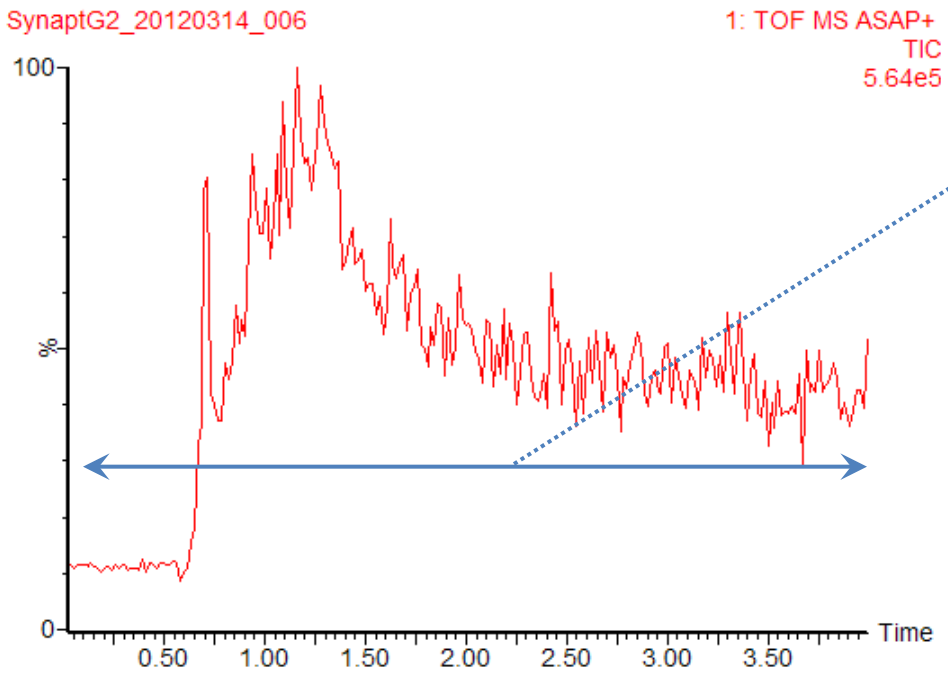
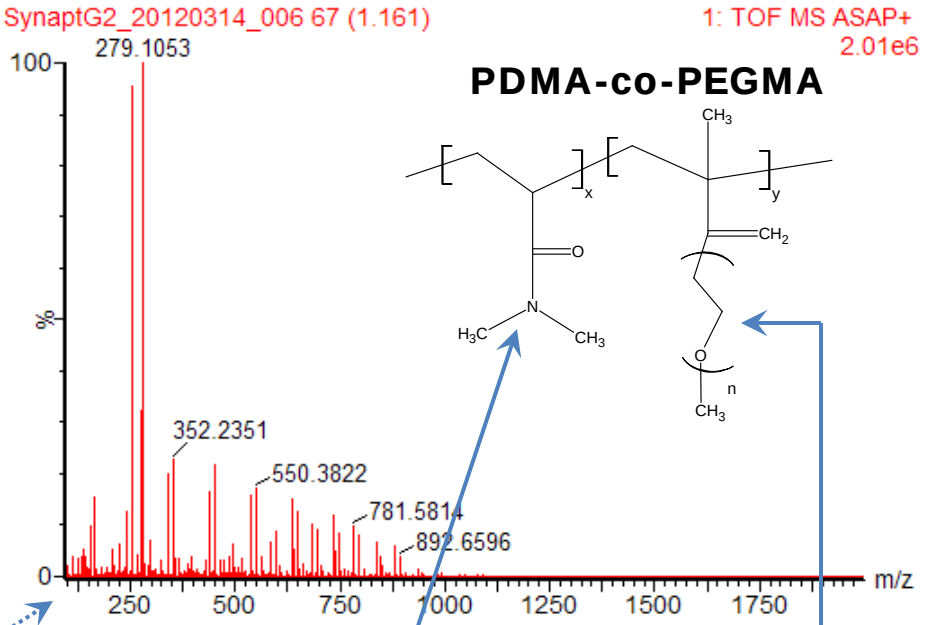
ASAP





PDMA-co-PEGMA

99 Da Repeat Unit
(PDMA)

44 Da Repeat Unit
(PEG)

Problem Solving

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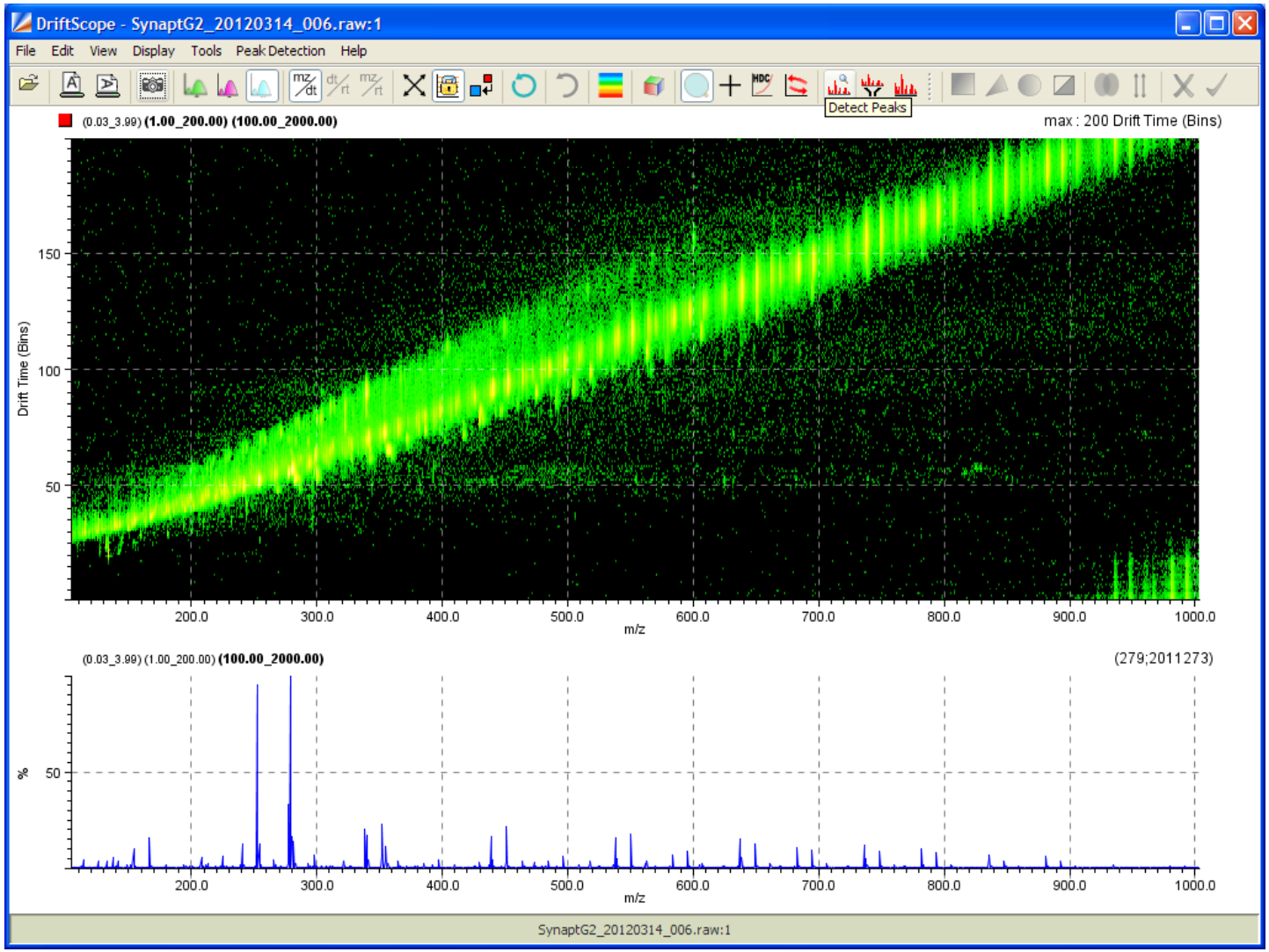
Emerald Forest, Log Scale



Problem Solving

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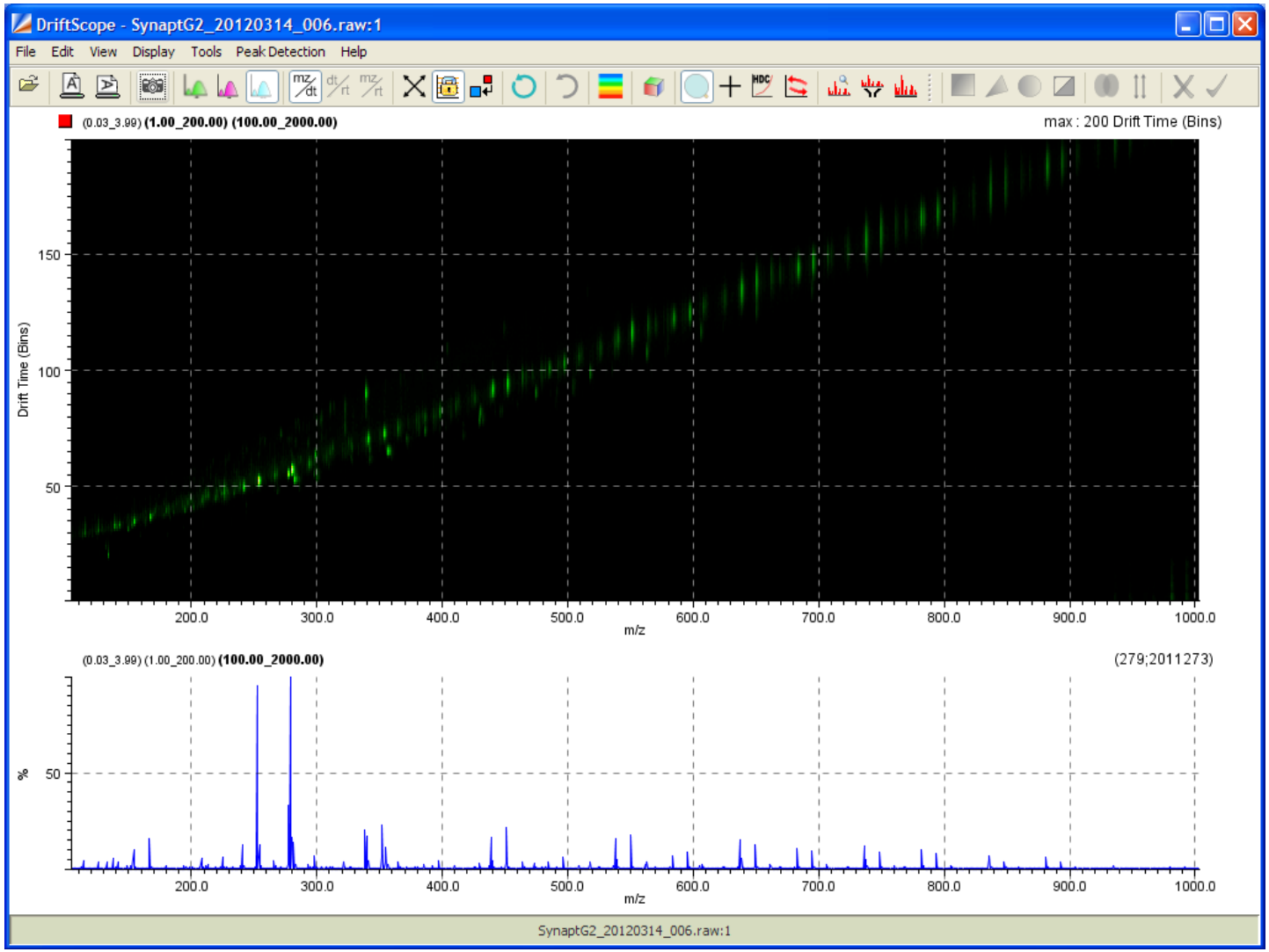
Emerald Forest, Square Root Scale



Problem Solving

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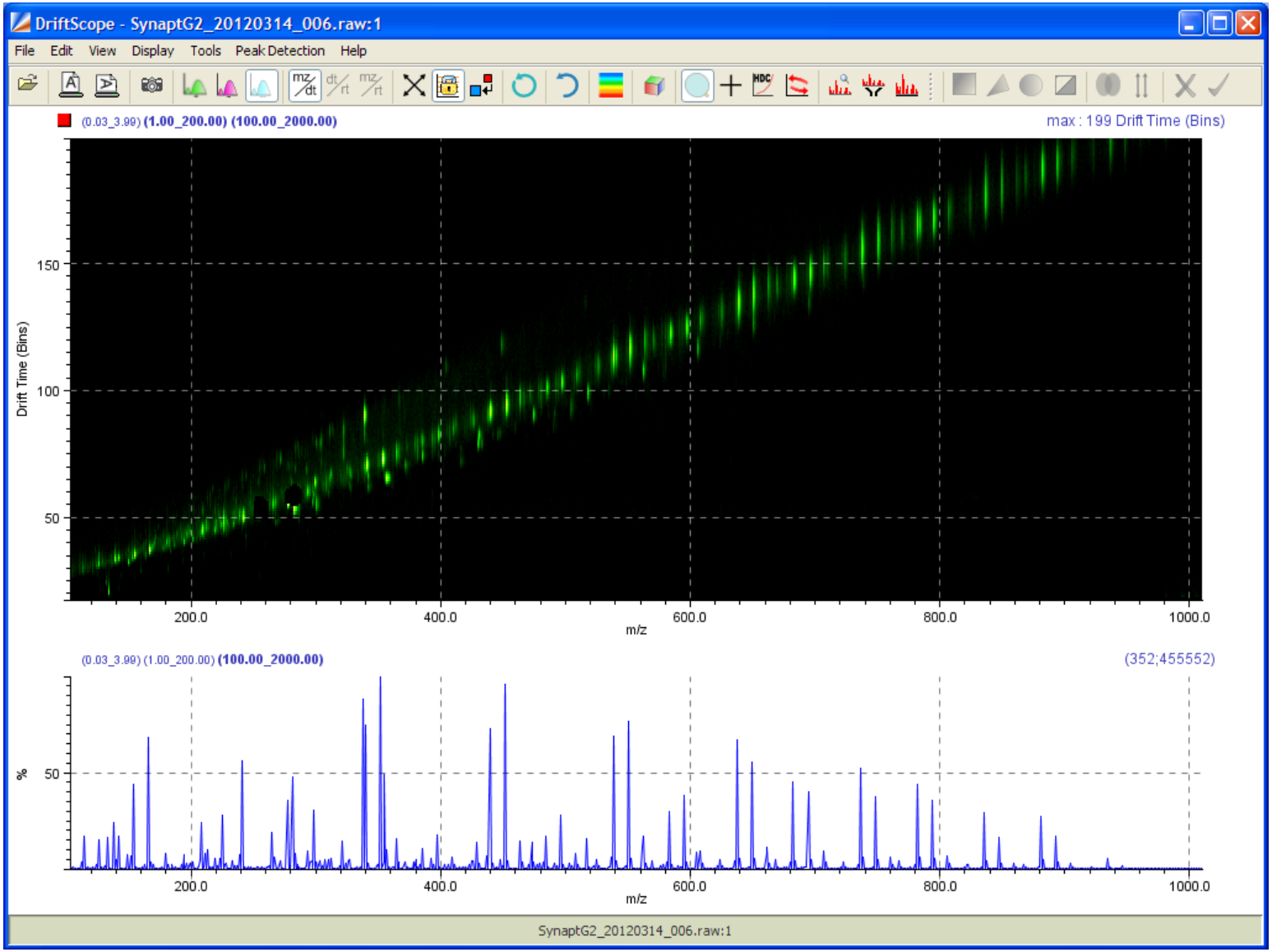

Problem Solving

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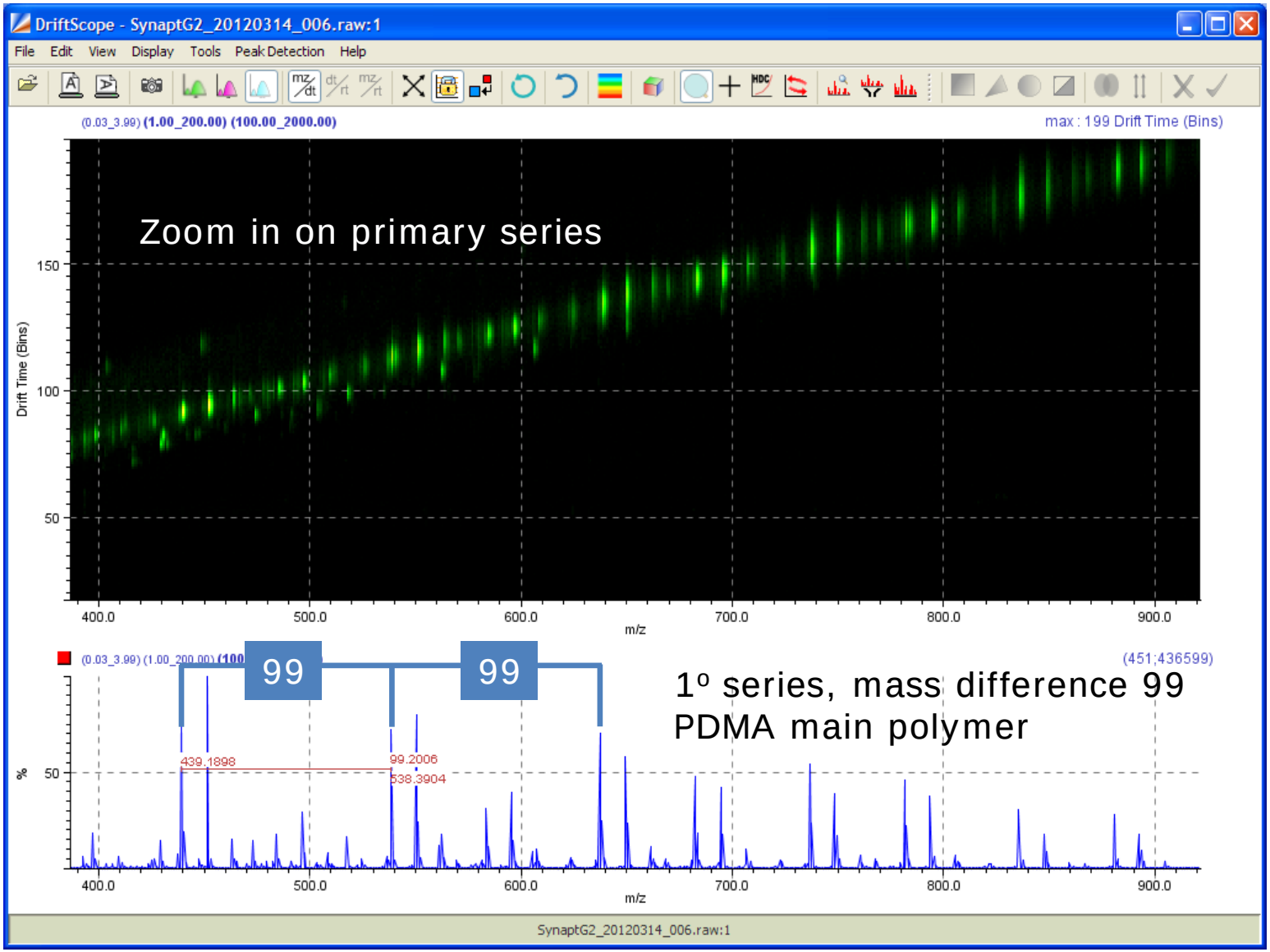

Problem Solving

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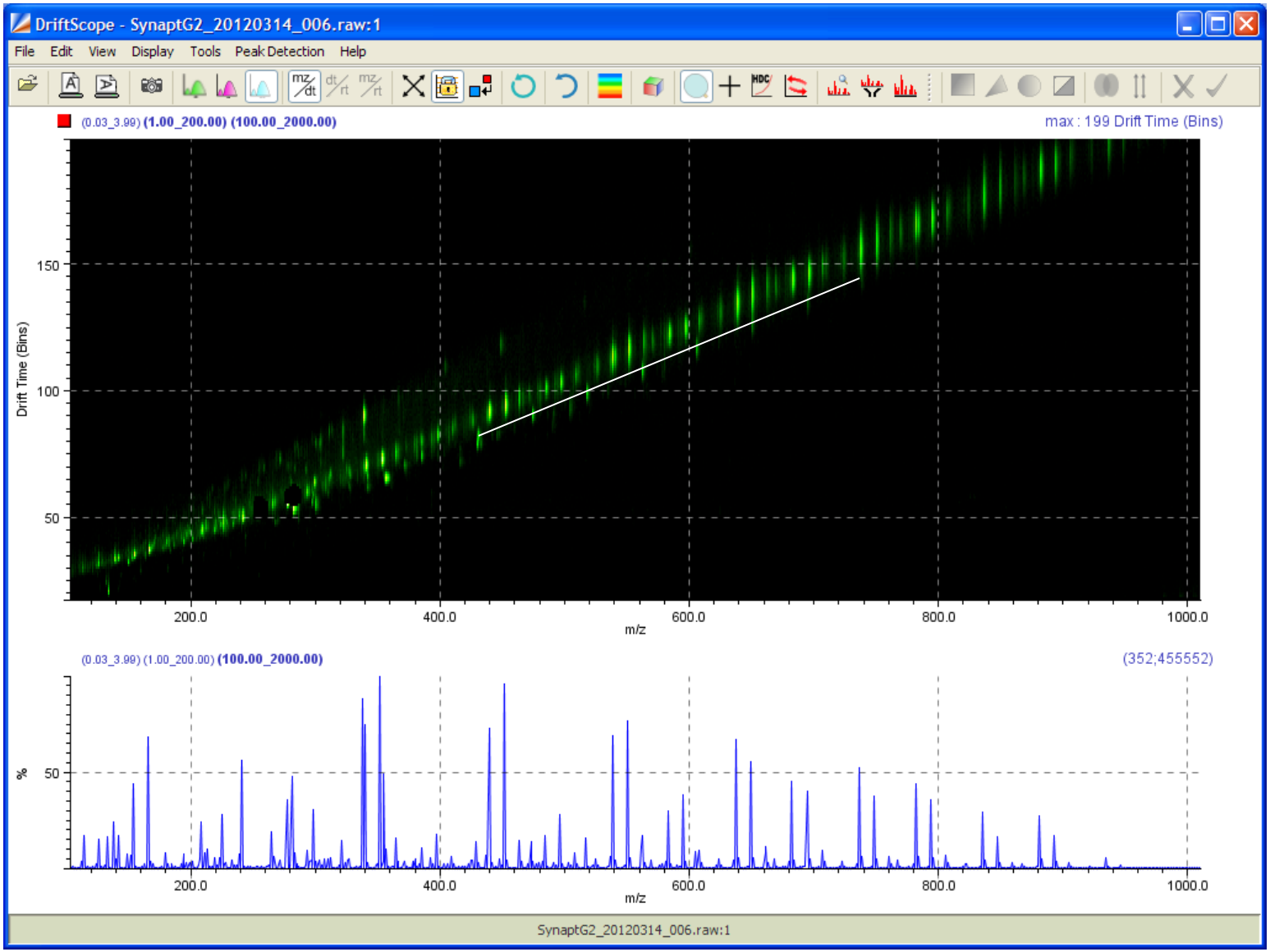
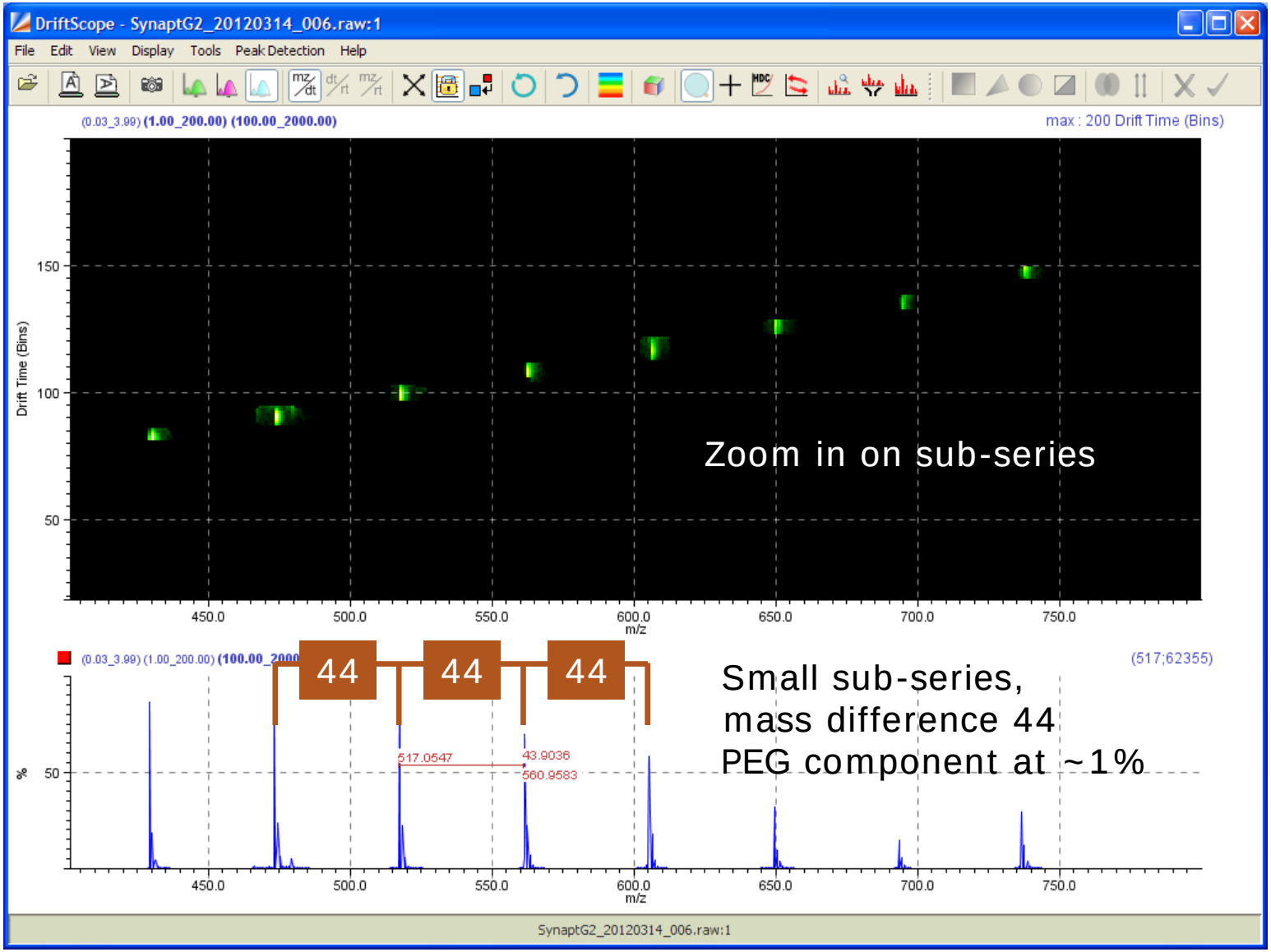
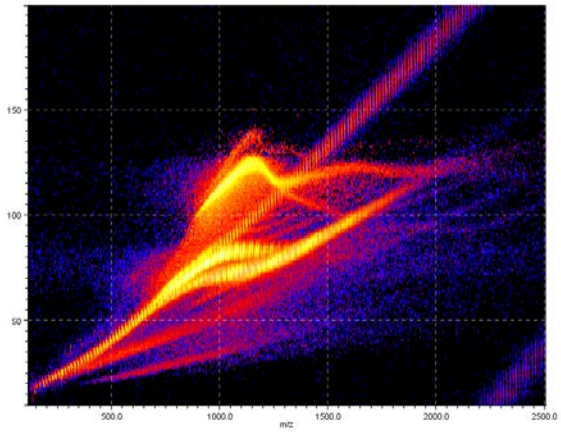


Problem Solving



Characterization using ETD for MS/MS Experiments



MS/MS - Fragmentation Methods

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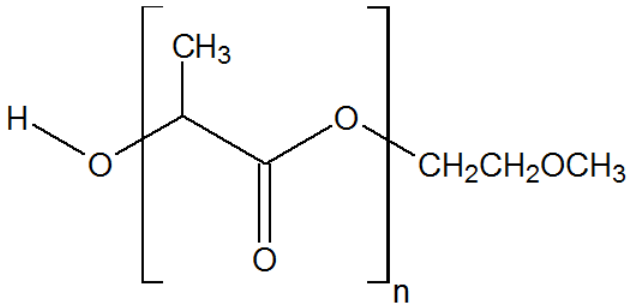
- Two fragmentation methods have been compared

- **C**ollision **I**nduced **D**issociation (CID)
  - Transitional energy is converted to internal energy
  - Energy is distributed until the weakest bond breaks
  - Newly formed fragment ions may undergo further CID fragmentation (creating fragments of fragments)

- **E**lectron **T**ransfer **D**issociation (ETD)
  - A complementary fragmentation mechanism.
  - Multiply charged precursor ions cleave due to ion-ion reactions with a reagent radical ion of the opposite charge
  - The reagent ion energetically excites the precursor ion causing decomposition
  - ETD fragmentation mechanism is currently not well published in the literature for polymers

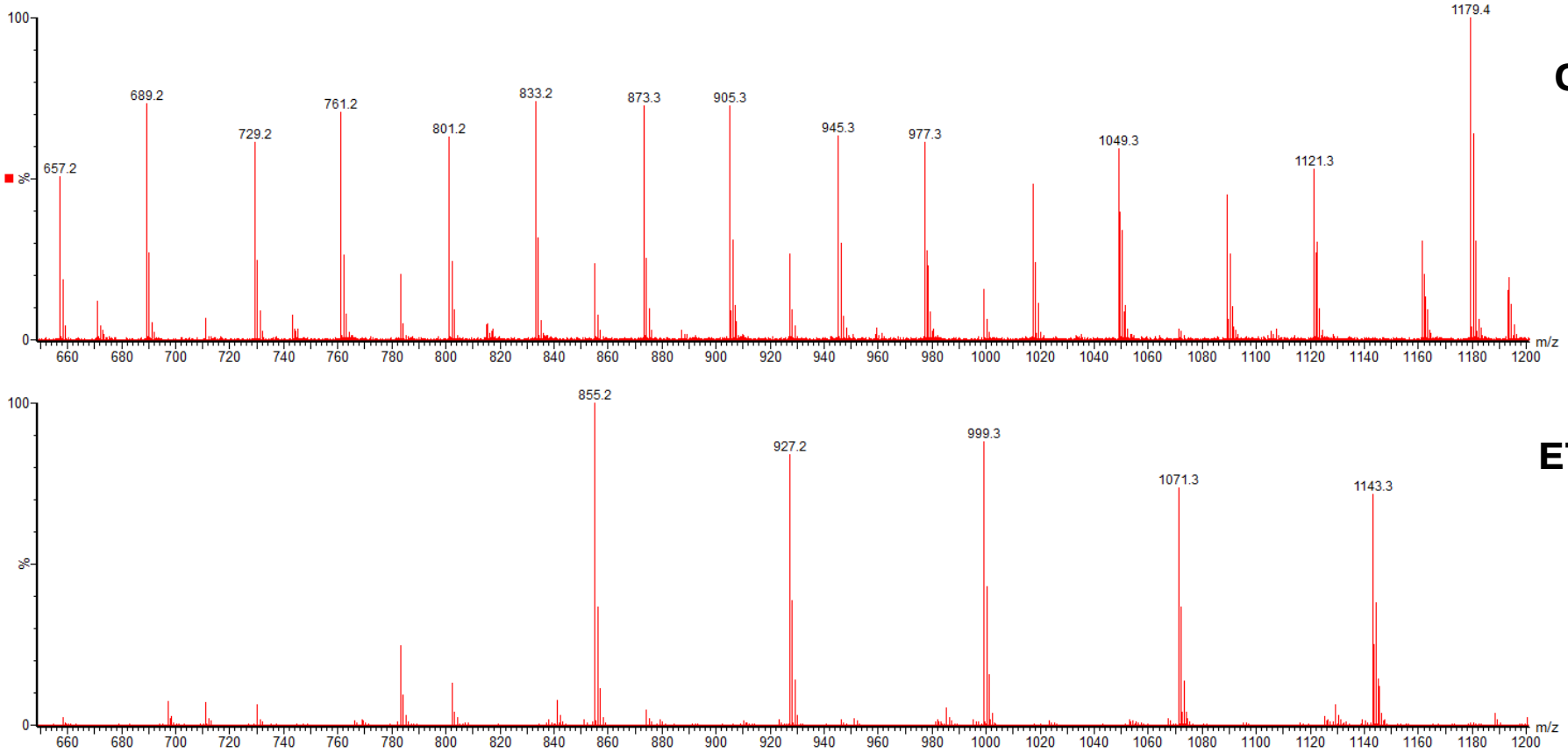
Polylactide

- To demonstrate the difference between two fragmentation techniques for polymers, polylactide was used.
- The sodiated 16-mer was selected for MS/MS analysis by both CID and ETD

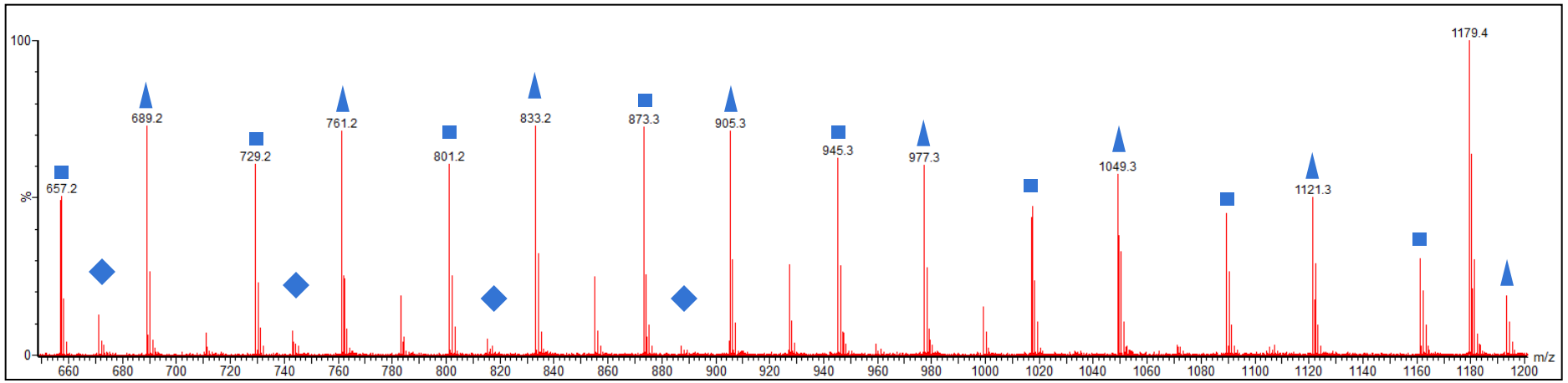


Results

- The two MS/MS spectra below are from the same polylactide sample using either CID or ETD fragmentation.
- The same precursor ion has been fragmented

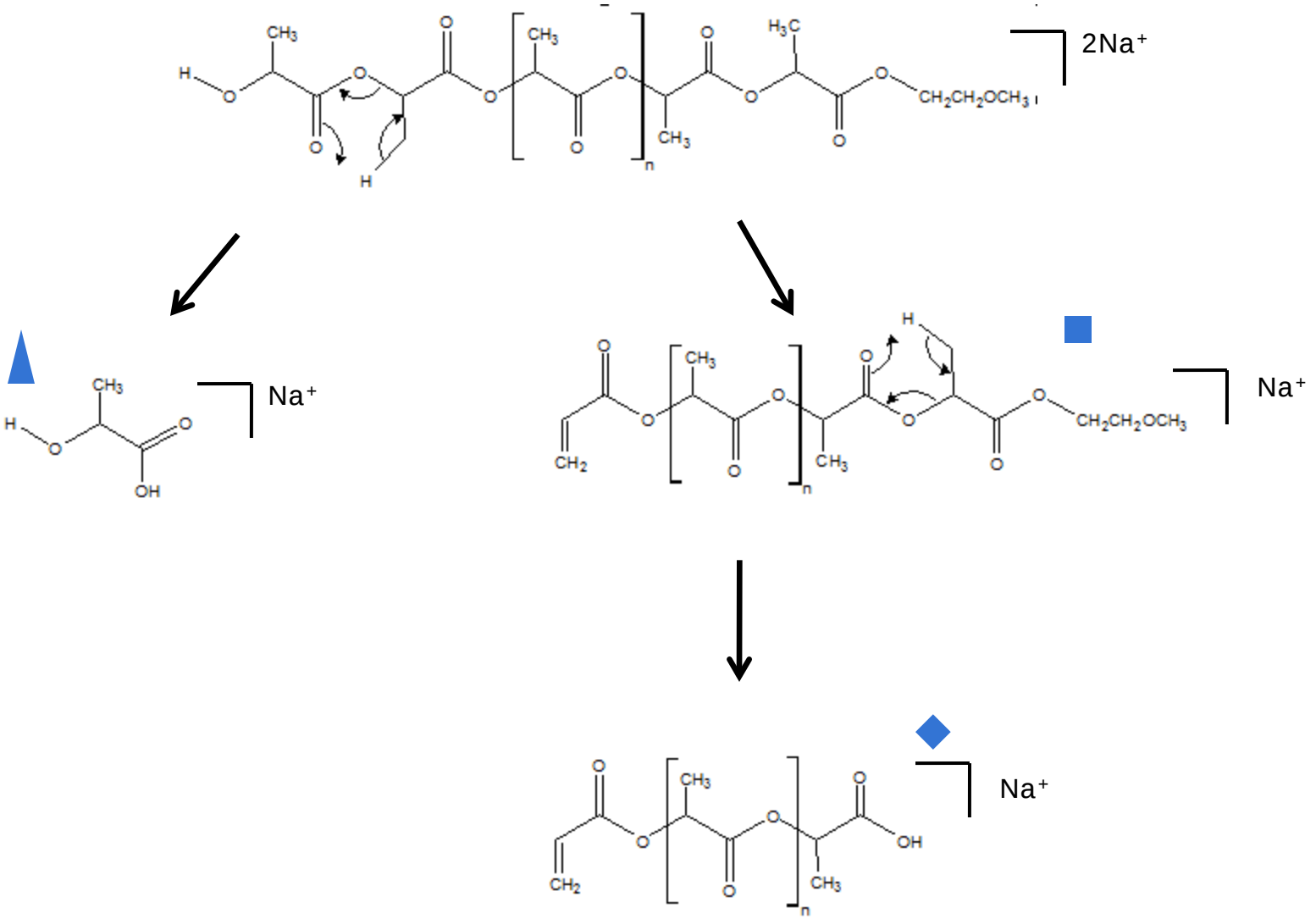


CID Mechanism for Polylactide



- CID can create many series of fragment ions due to the non-specific nature of the collision energy that is applied
  - Potentially first and second generation fragment ions are generated

CID Mechanism for Polylactide



ETD Pathways for Polylactide

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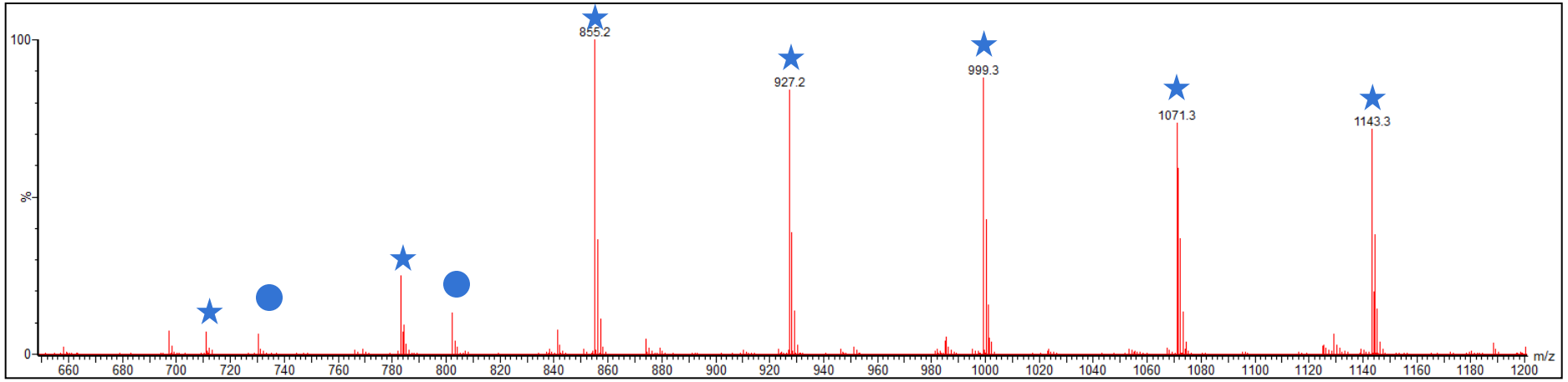
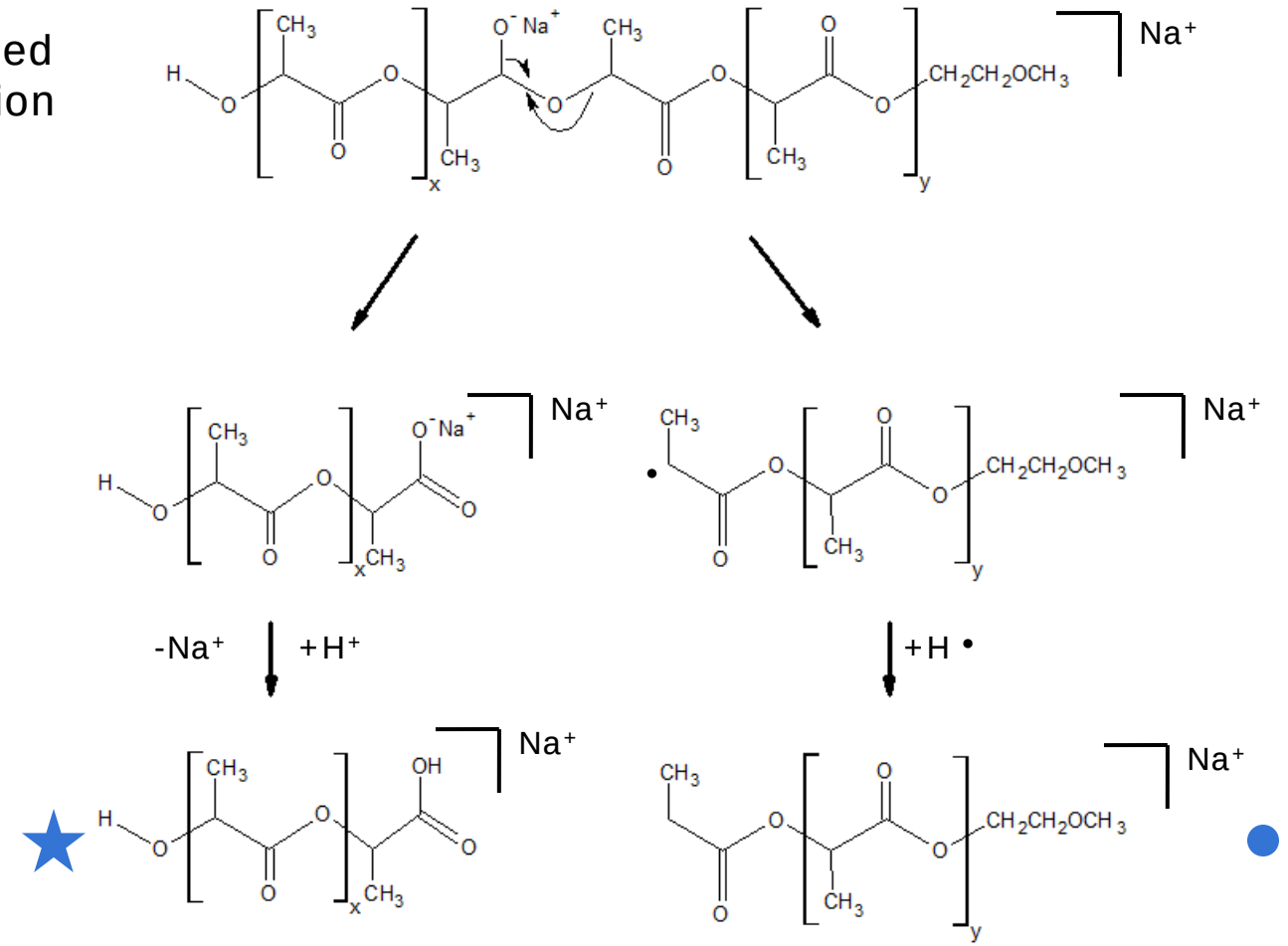
- ETD generate two series of ions due to the nature of the ion-ion reactions.
  - Each series of ions relates to an end group.



ETD Pathway

ETD generated free radical ion



Summary

- ETD generally creates less complex MS/MS spectra
- Using both CID and ETD fragmentation yields more detailed information than just one approach
  - It has been proved that two different fragmentation reactions take place
- If ion mobility is also being used CCS measurements can be used as additional confirmation that the end groups have been determined correctly.

Summary

- Ion mobility separation of complex material
- Dedicated software for data identification and interpretation
- Polymer characterization

Thank You