DART Mass Spectrometry of Non Polar Polymers and Development of a Novel Data Analysis Program (MIRA-MER)

This paper describes objective technical results and analysis. Any subjective views or opinions that might be expressed in the paper do not necessarily represent the views of the U.S. Department of Energy or the United States Government.

Materials Characterization and Performance (01819)

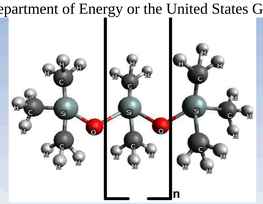
Alex Mirabal[1,2], Michael Brumbach[1], Curtis Mowry[1], Adam Pimentel[1]
[1]Sandia National Laboratory, [2]University of New Mexico

Sand2014-16123D

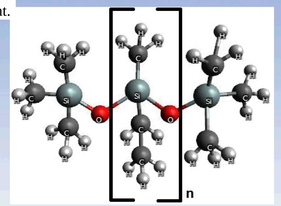
Sandia National Laboratories

U.S. DEPARTMENT OF ENERGY

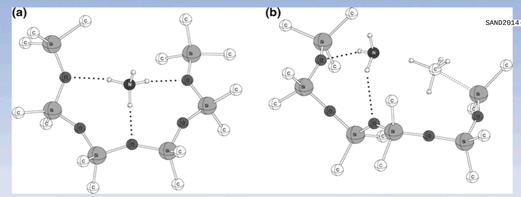
THE UNIVERSITY of NEW MEXICO



PDMS



PMES

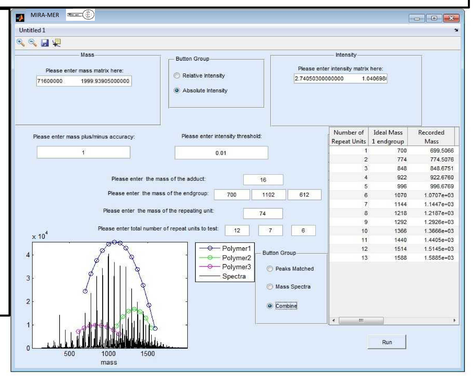


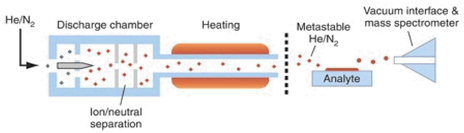
Ammonium Adduct

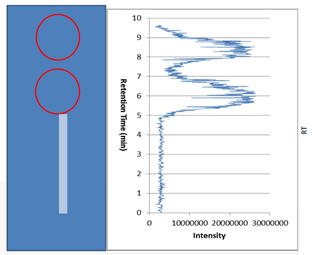
Abstract:
Silicone solutions are typically a heterogeneous mixture of silicone species. Identifying the molecular length distribution and chemistry can be important to the compatibility of the polymer for its intended use and its properties, such as viscosity. The aim of this project was to ascertain the chemical composition of silicones using a self-written code to analyze data from a newer technique, DART Mass Spectrometry. DART Mass Spectrometry was a helpful characterization tool but a data analysis tool was required to process the data in a useful manner.

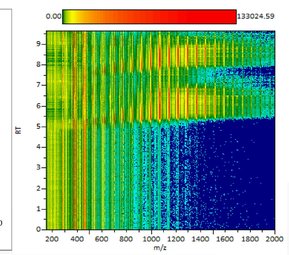
(**D**)irect (**A**)nalysis in (**R**)eal (**T**)ime (**M**)ass (**S**)pectrometry

- Atmospheric pressure (soft) Ionization in real time
- Invented in 2005
- The gas source is excited
- Charged particles are filtered out.
- The excited molecules can then be heated
- Neutral excited gas is then aimed at the sample.
- After cationization, the sample flows with the gas stream towards the analyzer.
- This technique lowers the detection limit, analysis time and sample preparation/amount.
- It also removes sample preparation steps
  - It can be done directly on the sample whether liquid, gas, or solid.
- Has become common in pharmaceuticals, health, and explosive industries.
- Not used for non polar molecules yet









Repreinted with permission from R. G. Cooks, Z. Ouyang, Z. Takats and J. M. Wiseman, Science, 2006, **311,** 1566-1570. Copyright © 2006, American Association for the Advancement of Science

	Repeat Unit:	PDMS		PMES
Sample	End Group:	Trimethyl	ethyl-di-methyl	Trimethyl
cSt 5		61.73	26.73	
cSt 10		61.63	27.1	
cSt 50		68.62	19.38	
Frekote		20.25	12.77	
Frekote 75C		30.2	15.54	
Frekote 100C		24.22	15.68	
Frekote 150C		23.89	37.08	
Ultra II		26.4	24.07	15.13
Ultra II 75C		32.72	26.55	5.98
Ultra II 100C		28.18	22.11	5.01
Ultra II 150C		31.16	46.66	3.63
RAM 225		38.58	23.67	

This table shows the percent of the spectrum attributed to these polymers

Procedure

- Place drops of sample on glass slide
- Let dry/oven dry
- Run through DART Mass Spectrometer
- Remove background
- Average over high intensity peak
- Analyze peaks using MIRA-MER, Mass++, and Polymerix

Method of Data Analysis

MIRA-MER, Polymerix, and Mass++ were three programs used analyze the data acquired from DART Mass Spectrometry.

Building MIRA-MER Mass Spectrometry Software:

- Data had to be binned into peaks
- Peaks below a threshold value were removed
- The peaks were compared against a simulated data from input
  - Including the mass of the end-groups and repeating groups as well as the number of repeat units to test for.
- Possible Ammonium adducts attach to the polymers when they are removed from the surface
- Envelopes of repeating peaks can be used to identify a polymer by using the mass of the repeat unit.
- Backtrack to find the mass of the end groups.
- Multiple envelopes and the mass by which the envelopes are offset provide key clues about the molecule of interest

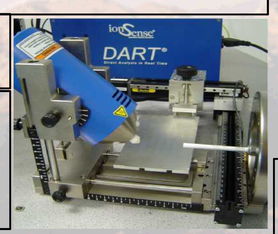
Mira-mer

Mass++

- Mass Spectrometry software that views Raw Data files
- 3D display of time(distance on glass slide), mass, and intensity

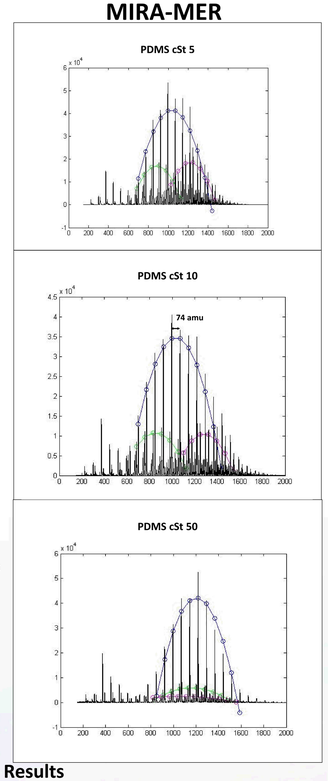
Polymerix

- Mass spectrometry software for polymers.
- Accounts for isotopic envelopes
- Displays match through color
- Accounts for adducts
- Overlapping isotopic envelopes can be discerned with difficulty



Comparison of Polydimethylsiloxane Standards:
Comparison of PDMS standards identified by their viscosity in centistokes(cSt) was done to verify the validity of the MATLAB code and to provide a basis for which to further analyze other samples.

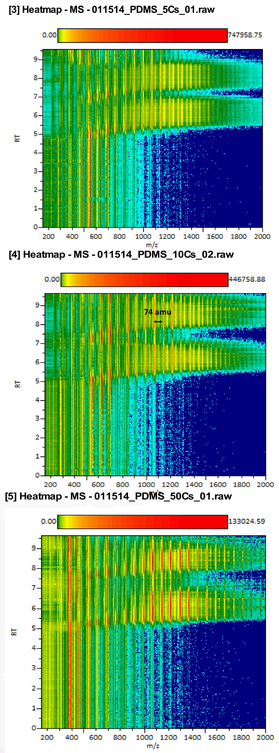
MIRA-MER



Results

- PDMS 5, 10, and 50 cSt peak envelope ~ 1000, 1000, and 1200 amu respectively.
- 1200 amu is appx. Location of 2nd small envelope for 5 and 10 cSt

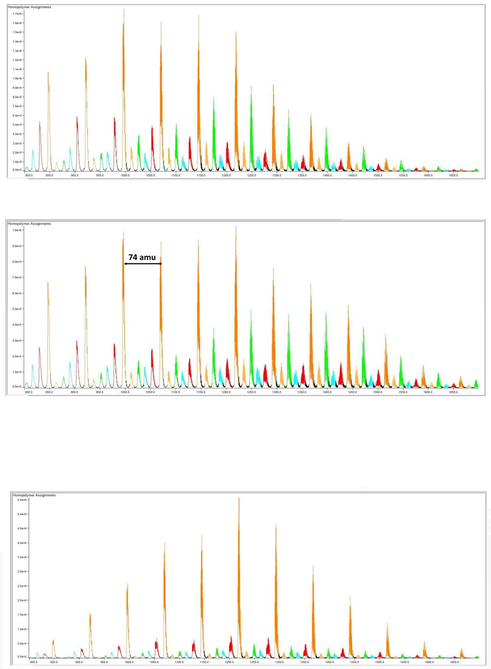
Mass++



Results

- Shift in chain length distribution envelope for spots across glass slide

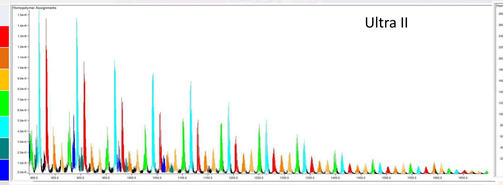
Polymerix

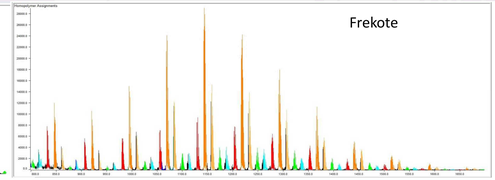


Results

- Mass range 800-1700 amu
- 10 cSt PDMS combination of 5 and 50 cSt PDMS
- Primarily trimethyl PDMS with ammonium adduct

End Group	Repeat	End Group	Adduct
$(CH_3)_2SiO$	$(CH_3)_2SiO$	$(CH_3)_3Si$	H
$(CH_3)_2SiO$	$(CH_3)_2SiO$	$(CH_3)_3Si$	NH_3
$(CH_3)_2SiO$	$(CH_3)_2SiO$	$(CH_3)_3Si$	NH_3+O
$(CH_3)_2CH_2SiO$	$(CH_3)_2SiO$	$(CH_3)_2CH_2Si$	NH_3+H_2
$(CH_3)_2CH_2SiO$	$(CH_3)_2SiO$	$(CH_3)_2CH_2Si$	(NH_3)+O
$(CH_3)_2SiO$	$(CH_3)_2CH_2SiO$	$(CH_3)_3Si$	NH_3+O
(CH3)$_2$SiO	$(CH_3)_2CH_2SiO$	$(CH_3)_3Si$	NH_3





Results

- Ultra II
  - Primarily PDMS with trimethyl and ethyldimethyl end groups
  - Shows some PMES
  - The majority of the Ethyldimethyl PDMS has multiple adducts
- Frekote
  - Primarily PDMS with trimethyl end group and an Ammonium Adduct or Ammonium and Oxygen adducts

Conclusion

We were able to successfully analyze non-polar polymers , collected by DART Mass Spectrometry, using a self-written matlab code and verified/further analyzed using the software Mass++ and Polymerix. I was able to deepen my understanding of the nuances associated with mass spectrometry and ,in particular, DART, while also further solidifying my understanding of the chemistry that occurs to make this process possible. The mathematical considerations in the analysis of data provided multiple opportunities to think about the processes occurring.

U.S. DEPARTMENT OF ENERGY

Sandia National Laboratories is a multi-program laboratory operated by Sandia Corporation, a wholly owned subsidiary of Lockheed Martin Corporation, for the U.S. Department of Energy's National Nuclear Security Administration under contract DE-AC04-94AL85000.

Acknowledgements:
[illegible] ject. I also thank Curtis Mowry and Adam Pimentel who provided the instrument, tools for analysis, and [illegible]
Sandia National Laboratories is a multimission laboratory managed and operated by National Technology & Engineering Solutions of Sandia, LLC, a wholly owned [illegible] subsidiary of Honeywell International Inc., for the U.S. Department of Energy's National Nuclear Security Administration under contract DE-NA0003525.

Sandia National Laboratories