ASMS 2024, WP 805

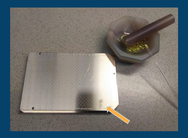
MALDI-TOF MS Analysis of Mechanopolymers and Vitrimers

Kushal Modi[1], Mark A. Arnould[1], Chrys Wesdemiotis[2], Calum Bochenek[2] and Tyler Arntz[2]

[1]Bruker Daltonics Inc., 40 Manning Road, Billerica, MA 01821, USA. [2]Chemistry Department, The University of Akron, Akron, OH 44325, USA.

Rapiflex

Solid Sample Preparation – Evaporative Grinding



Solution Sample Preparation:

- DCTB at 60 mg/ml, NaTFA at 5 mg/ml and Polymer at 10 mg/ml
- Mix in a 20:1:1 ratio (Matrix:Cation:Polymer)
- Spot 0.5 µl onto the target with gentle blowing

Solid Sample Preparation – Evaporative Grinding:

- Place a small amount of sample on target, add a very small amount NaTFA, add a slight excess of matrix
- Add 10 µl of acetone and grind on the target surface, scrape of the excess to a thin layer and remove the powder with clean air

Data Processing:

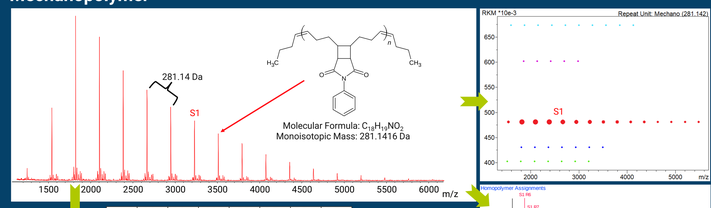
- Data analysis was accomplished using **Polytools (Bruker)** and **Polymerix** from **Sierra Analytics**

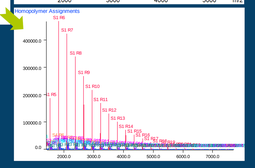
Mechanopolymers and Vitrimers:

- Mechanopolymers are unique materials that possess mechanically labile bonds allowing them to change their properties upon the application of external stimuli (degradable on demand)
  - light, heat, pH, or redox potential
- This ability has led to various useful properties such as color/fluorescence change, isomerization and efficient degradation pathways

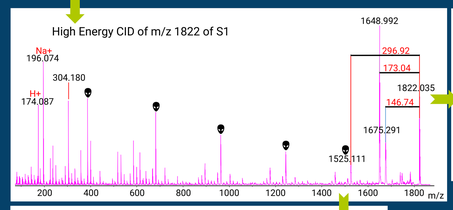
- Vitrimers are compounds derived from thermosets and are very similar to them
- Vitrimers consist of molecular, covalent networks that change their topology by thermally activated bond-exchange reactions
- At high temperatures they can flow like viscoelastic liquids but at low temperatures the bond-exchange reactions are slow, they behave like classical thermosets
- Their behavior opens new possibilities in the application of thermosets like self-healing material or simple processibility in a wide temperature range.

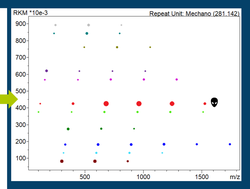
Mechanopolymer

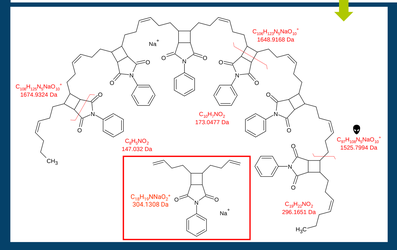




	Mn	Mw	Mz	PD	DPn	DPw	DPz
Total	3219	3976	4665	1.23	11	14	16
S1	2927	3441	4048	1.18	10	12	14
S2	3606	4547	5312	1.26	12	16	18
S3	3984	5408	6104	1.36	14	19	22
S4	3510	4599	5514	1.31	12	16	19
S5	3512	4611	5453	1.31	12	16	19
S7	3684	4783	5576	1.30	13	16	19





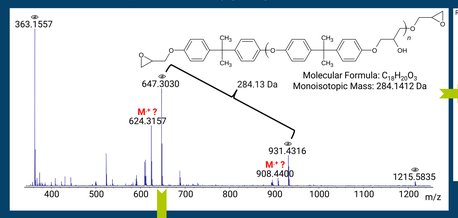


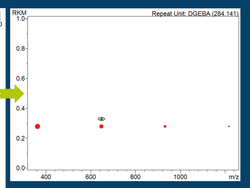
Fragments:

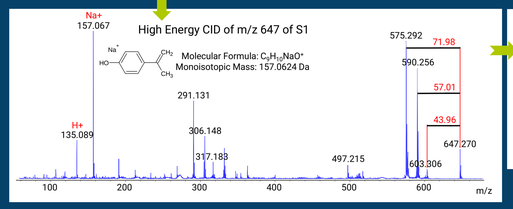
- Proton Transfers and Simple Rearrangements (Sodium not participating in the rearrangement) = Charge Remote
- Sodium Lost with the Fragment = Charge Induced
- Transannular bond cleavage across the rings (cyclobutene and phenyl pyrrolidinedione) readily observed

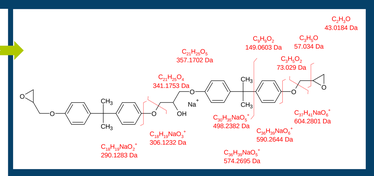
Vitrimer Component

EPON 828 - Bisphenol A diglycidyl ether:



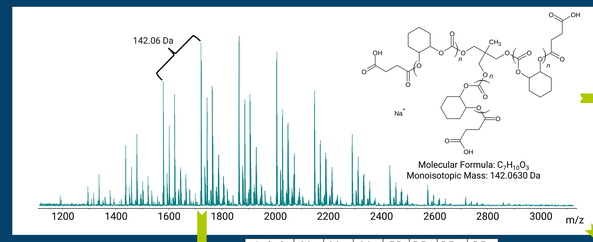


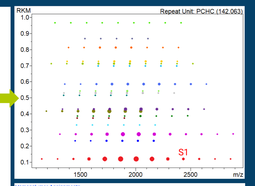


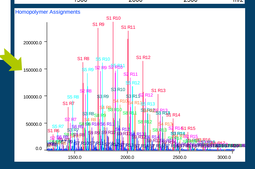


Vitrimer Component

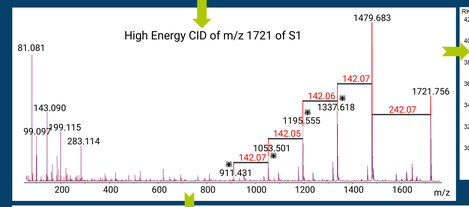
Tri-PCHC - poly(cyclohexene carbonate):

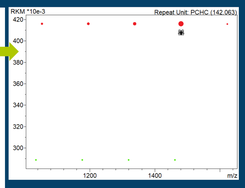






Label	Mn	Mw	Mz	PD	DPn	DPw	DPz
Average	2356	3044	4132	1.29	14	19	26
S1	2151	2617	3576	1.22	12	15	22
S2	2243	2822	3898	1.26	13	17	24
S3	2366	3034	4162	1.28	13	18	26
S4	2522	3305	4474	1.31	14	20	28
S5	2127	2681	3767	1.26	13	17	24
S6	2670	3925	5220	1.47	17	26	35
S7	3805	5173	5958	1.36	26	36	41
S8	2368	3121	4322	1.32	14	19	27
S9	2921	4165	5387	1.43	18	27	35

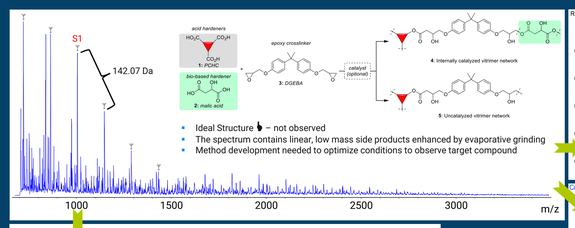


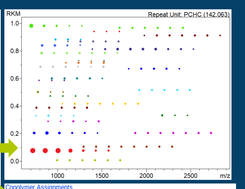


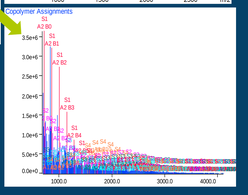
Fragments:

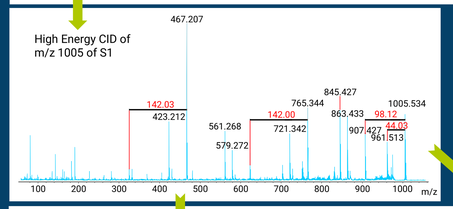
- The structure shown is not what exists in the gas-phase but was drawn this way for easy visualization of the fragmentation
- Each arm should have the same amount of repeat units

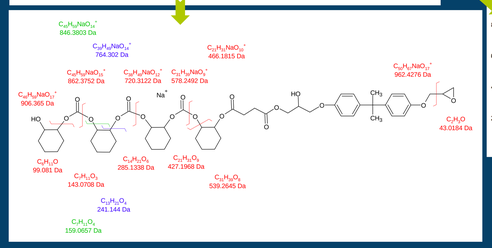
Vitrimer:











Fragments:

- The structure shown is the best fit to the observed MS/MS data
- Possibly cyclic?

- MALDI MS easily characterizes polymeric/oligomeric samples allowing for complete characterization of synthesized or purchased materials
- Complete characterization is necessary to understand synthetic routes of novel materials such as the Mechanopolymer, which helps decrease undesired products
- Understanding materials used in the synthesis of additional products (vitrimer) is paramount in avoiding impure materials not suitable for reaction and avoiding contamination of the final material with products resulting from side reactions
- The complete characterization of a network like the vitrimer is extremely difficult due to insolubility and desorption/ionization of a large branched molecule
- Evaporative grinding (solid sample prep) enabled the acquisition of preliminary data showing side and/or degradation products – more work needed to optimize