Mass Spectrometry of Synthetic Polymers

Árpád Somogyi

CCIC MSP

OSU Summer Workshop

Problems with polymer analysis

• Sample preparation
  – Several polymers are not well soluble in conventional solvents
  – Solventless technique
  – Cationizing with Na\(^+\), K\(^+\), and Ag\(^+\) by spiking
  – Synthesis of tailor (home) made matrices

• Degradation during ionization (especially with MALDI)
  – Photodissociation in MALDI (MALDI/ESI comparison desirable)

• End group analysis reliable but better to have high resolution/accurate mass (FT-ICR)
Molecular weight distribution defines polydispersity of polymers


\[
M_w = \sum (N_i M_i) / \sum N_i
\]

\[
M_D = \sum (N_i M_i^2) / \sum N_i M_i
\]

Polymersity (PD) = M_w/M_n

---

MS is an absolute method for MW determination (but remember possible degradation!)

<table>
<thead>
<tr>
<th>Polymer standard</th>
<th>Molecular weight and polydispersity</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>By classical methods*</td>
</tr>
<tr>
<td>Polystyrene 5050</td>
<td></td>
</tr>
<tr>
<td>(M_w) 4755 (GPC)</td>
<td>(M_w) 5189 (0.5% RSD)</td>
</tr>
<tr>
<td>(M_n) 4982 (GPC)</td>
<td>(M_n) 5320 (0.5% RSD)</td>
</tr>
<tr>
<td>(M_D) 4720 (VPO)</td>
<td>PD = 1.027 ± 0.001</td>
</tr>
<tr>
<td>(M_D) 4950 (IV)</td>
<td>PD = 1.05 (GPC)</td>
</tr>
<tr>
<td>PD = 1.05 (GPC)</td>
<td>PD = 1.05 (GPC)</td>
</tr>
<tr>
<td>Polystyrene 7000</td>
<td></td>
</tr>
<tr>
<td>(M_w) 6170 (GPC)</td>
<td>(M_w) 6988 (0.4% RSD)</td>
</tr>
<tr>
<td>(M_n) 6962 (GPC)</td>
<td>(M_n) 7132 (0.4% RSD)</td>
</tr>
<tr>
<td>(M_D) 7170 (LLS)</td>
<td>PD = 1.019 ± 0.001</td>
</tr>
<tr>
<td>(M_D) 6943 (IV)</td>
<td>PD = 1.02 (GPC)</td>
</tr>
<tr>
<td>PD = 1.02 (GPC)</td>
<td>PD = 1.02 (GPC)</td>
</tr>
<tr>
<td>Polystyrene 11,600</td>
<td></td>
</tr>
<tr>
<td>(M_w) 11,356 (GPC)</td>
<td>(M_w) 11,074 (0.3% RSD)</td>
</tr>
<tr>
<td>(M_n) 11,697 (GPC)</td>
<td>(M_n) 11,187 (0.3% RSD)</td>
</tr>
<tr>
<td>(M_D) 11,000 (LLS)</td>
<td>(M_D) 11,000 (LLS)</td>
</tr>
<tr>
<td>(M_D) 10,720 (IV)</td>
<td>PD = 1.03 (GPC)</td>
</tr>
<tr>
<td>PD = 1.03 (GPC)</td>
<td>PD = 1.03 (GPC)</td>
</tr>
</tbody>
</table>

*Those results are provided by the suppliers; GPC, gel permeation chromatography; VPO, vapor pressure osmometry; N, intrinsic viscosity; LLS, laser light scattering.
†From five trials.
Repeating unit masses of polymers

http://www.polymerprocessing.com/polymers/alpha.html

- [CH₂-C] -
- [CH₂-O-CH₂-O-]

Poly(styrene) (PS)  
C₈H₈O (192.042259)

Poly(ethylene terephthalate) (PET)  
C₁₀H₈O₄ (192.042259)

Poly(methyl methacrylate) (PMMA)  
C₅H₈O₂ (100.052430)

Poly(vinyl alcohol) (PVA)  
C₂H₄O (44.026215)

Poly(ethylene glycol) (PEG)

Synthetic Polymer Analysis by MS (MALDI-TOF)

m/z

1664.205 1728.231 1772.260 1816.292 1860.310

44 44 44 44
Polymer analysis

Clues to polymer identity (Repeated patterns)
- 1655.7-1639.7 = 16  Possibly Na (23) and K (39) adducts
- 1639.7-1595.7 = 44  Polyethylene glycol (CH₂CH₂O)

Possible formula for 1639.7 peak:
- C 73 O 37 H 148 Na 1
- Hydrogen increases mass by 1
- (Nitrogen rule not broken)
- 1640 = measured
- -23 = subtract Na
- 1617 = polymer mass
- -1885 = 36 PEG units
- 32 = END GROUP

Must be methoxy-PEG

\[
\text{CH}_3\text{-(OCH}_2\text{CH}_2\text{)-OH}
\]

\[
\text{CH}_3\text{OH exact mass: 32.0262 u}
\]

<table>
<thead>
<tr>
<th># of Atoms</th>
<th>Exact</th>
<th>Mass</th>
<th>Total</th>
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<tr>
<td>C 73</td>
<td></td>
<td>12.000000</td>
<td>676.0000</td>
</tr>
<tr>
<td>O 37</td>
<td></td>
<td>15.994914</td>
<td>591.8118</td>
</tr>
<tr>
<td>H 148</td>
<td></td>
<td>1.007825</td>
<td>149.1581</td>
</tr>
<tr>
<td>Na 1</td>
<td></td>
<td>22.989769</td>
<td>22.9898</td>
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1630.9597

<table>
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<tr>
<th># of Atoms</th>
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<th>Total</th>
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</thead>
<tbody>
<tr>
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<td>12.000000</td>
<td>864.0000</td>
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<tr>
<td>O 36</td>
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<td>15.994914</td>
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<tr>
<td>H 144</td>
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<td>1.007825</td>
<td>145.1268</td>
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<tr>
<td>Na 0</td>
<td></td>
<td>22.989769</td>
<td>0.0000</td>
</tr>
</tbody>
</table>

1564.9437
FT-ICR - Accurate Mass Measurements
(ESI Ionization, MeOH:ACN 1:1)

**C_{45}H_{42}O_{16}Na^{+}**

**C_{45}H_{42}O_{16}NH_{4}^{+}**

FT-ICR - Accurate Mass Measurements

**C_{45}H_{42}O_{16}Na^{+}**

**C_{45}H_{42}O_{16}NH_{4}^{+}**

--

**Note: For n = 2000, elements C, H, N, and O are considered indistinguishable.**

**Formulas:**

<table>
<thead>
<tr>
<th>Mn</th>
<th>C_{45}H_{42}O_{16}Na^{+}</th>
<th>C_{45}H_{42}O_{16}NH_{4}^{+}</th>
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<tbody>
<tr>
<td>856.2811</td>
<td>065.202</td>
<td>065.202</td>
</tr>
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<td>857.2845</td>
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<td>065.202</td>
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<td>858.2873</td>
<td>065.202</td>
<td>065.202</td>
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<tr>
<td>859.2900</td>
<td>065.202</td>
<td>065.202</td>
</tr>
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</table>

**Intensities:**

<table>
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<tr>
<th>Int.</th>
<th>0.00</th>
<th>0.25</th>
<th>0.50</th>
<th>0.75</th>
<th>1.00</th>
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</thead>
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<tr>
<td>7x10^3</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**FT-ICR - Accurate Mass Measurements**
MS/MS spectra of polymers depend on

- The cationizing agent (sample preparation)
- Instrument type, ion activation method
  - Low energy (eV) collisions (Q-TOF, FT-ICR (SORI, IRMPD)
  - High energy (keV) collisions (TOF-TOF)

Renaissance, due to sophisticated instrumentation

Main goal is to determine polymer structure but basic studies such as comparison of different activation methods are emerging

Survival yield curve

- M/(M+ΣF)
- SY50: characteristic; easy spectra evaluation
- Low energy spectrum, little fragmentation correct MW distribution
- High energy spectrum, lot of fragments good “fingerprint”
The effect of the variation of cation in the matrix-assisted laser desorption/ionisation-collision induced dissociation (MALDI-CID) spectra of oligomeric systems

J.H. Scrivens\textsuperscript{a}, A.T. Jackson\textsuperscript{a,*}, H.T. Yates\textsuperscript{a}, M.R. Green\textsuperscript{b}, G. Critchley\textsuperscript{b}, J. Brown\textsuperscript{b}, R.H. Bateman\textsuperscript{b}, M.T. Bowers\textsuperscript{b}, J. Gidden\textsuperscript{b}


Abstract

The effect of the variation of the cation, on the matrix-assisted laser desorption/ionisation collision induced dissociation (MALDI-CID) spectra obtained, has been studied in a hybrid sector-orthogonal acceleration-time of flight tandem mass spectrometer for some synthetic oligomeric systems. Oligomers of poly(acryl methyl methacrylate) and poly(styrene) in the molecular weight range of approximately 1000–3000 u were analysed. They were ionised by attachment of various alkali metal and copper and silver ions, respectively. The MALDI-CID spectra are shown to vary with different cations more from precursor ions of lower than those of higher mass-to-charge ratio. © 1997
Q-CID MS/MS spectra of ammoniated (NH$_4^+$) and sodiated (Na$^+$) ions of 3-OEB polymers in a FT-ICR instrument (ApexQh)

Somogyi et al., unpublished
Some Examples for Tailor-Made Matrices

Synthesis and MALDI-TOF analysis of non-conventional Polymers (Polyhedral Oligomeric Silsesquioxanes, POSS)

Figure 2. Ethyl isobutyrate POSS PMA oligomers synthesized using ATRP techniques.


Practical importances of phenanthroline-functionalized PEGs


- stabilization of magnetic nanoparticles (e.g. Fe₃O₄)
- hydrophilic networks by complex formation
Change of the absorbance at 515 nm versus molar ratio of the added Fe(II)-ions and phenanthroline functions of PEGs

- **Fe**^{2+}: phen/PEG = 2:3
- **Fe**^{2+}: PEG/phen = 1:3

CT transition

Absorbance (515 nm)

- \( \varepsilon = 11090 \text{ M}^{-1}\text{cm}^{-1} \)
- \( \varepsilon = 10300 \text{ M}^{-1}\text{cm}^{-1} \)

**Synthesis of phenanthroline-functionalized PEGs**

1. \( \text{N} \text{N} \text{HO} \text{N} \text{N} \text{OH} \) in \( c c \text{H}_2\text{SO}_4 \), reflux, 1 h
2. 50% NaOH, pH=7, reflux, 72 h
3. \( \text{SOCl}_2 \), abs. toluene
4. NaH, abs. DMF, reflux, 48 h
5. \( \text{Cl} \text{CH}_2 \text{CH}_2 \text{O} \text{CH}_2 \text{CH}_2 \text{Cl} \) (M\(_n\) = 1100 g/mol)
6. \( \text{Cl} \text{CH}_2 \text{CH}_2 \text{O} \text{CH}_2 \text{CH}_2 \text{Cl} \) (M\(_n\) = 1500 g/mol)
ESI-MS spectrum of Fe(PEG\_phen)$_3^{2+}$

![Graph showing the ESI-MS spectrum with peaks labeled as [FeL$_3$+3NH$_4$+Na]$^{6+}$, [FeL$_3$+2NH$_4$+Na]$^{5+}$, [FeL$_3$+2NH$_4$]$^{4+}$, [FeL$_3$+NH$_4$]$^{3+}$, Fe$_3^{2+}$, and L = PEG\_phen.]

ESI-MS intensity distribution of PEG\_phen and Fe(PEG\_phen)$_3^{2+}$

Fe$^{2+}$ + L$_i$ + L$_j$ + L$_k$ → FeL$_{i+j+k}^{2+}$ (n=i+j+k)

**Theoretical model:**

$$P_n = \sum_{i,j,k=1}^{\infty} P_i P_j P_k$$

+Fe(II)

![Graph showing the probability of EO units and normalized intensity with measured and simulated data.]
ESI-MS/MS of Fe(PEG phen)$_3^{2+}$

Fe(PEG phen)$_3^{2+}$ → Fe(PEG phen)$_2^{2+}$ + PEG phen

Fe(PEG phen)$_2^{2+}$ → Fe(PEG phen)$_{2+}$ + PEG phen

Tandem Mass Spectrometry Characteristics of Silver-Cationized Polystyrenes: Backbone Degradation via Free Radical Chemistry

Michael J. Peice, 1,2 Manuela Ocampo, 3 Roderic P. Quirk, 3 and Chrys Wesdemiotis 1,4

Departments of Chemistry and Polymer Science, The University of Akron, Akron, Ohio 44325

Figure 1. MALDI-CAD spectrum of silverated C_{6}H_{10}[CH_{2}CH_{2}Ph]_{n=18}-H (m/z 2038.1). The complete isotopic cluster was mass-selected for CAD with Ar at \(E_a = 130\ eV (E_{cm} = 2.5\ eV)\). The inset shows an expanded trace of the m/z 600–1000 range. Above m/z 1500, traces of the \(a_7/y_7\) series are detected up to \(n = 15\).

(a)

\[
\begin{align*}
\text{C}_6\text{H}_{10} & \rightarrow \text{C}_6\text{H}_{10} \text{CH}_2 \text{CH}_2 \text{CH} \text{CH}_2 \text{CH}_2 \text{CH}_2 \text{CH} \\
\text{Ph} & \text{Ph} \text{Ph} \text{Ph} \text{Ph} \text{Ph} \text{Ph} \\
\text{not observed} & \\
\text{C}_6\text{H}_{10} & \rightarrow \text{C}_6\text{H}_{10} \text{CH}_2 \text{CH}_2 \text{CH} \text{CH}_2 \text{CH}_2 \text{CH}_2 \text{CH} \\
\text{Ph} & \text{Ph} \text{Ph} \text{Ph} \text{Ph} \text{Ph} \text{Ph} \\
\text{not observed} & \\
\text{C}_6\text{H}_{10} & \rightarrow \text{C}_6\text{H}_{10} \text{CH}_2 \text{CH}_2 \text{CH} \text{CH}_2 \text{CH}_2 \text{CH}_2 \text{CH} \\
\text{Ph} & \text{Ph} \text{Ph} \text{Ph} \text{Ph} \text{Ph} \text{Ph} \\
\text{Y}_{n+1} & \text{Ph} \text{Ph} \text{Ph} \text{Ph} \text{Ph} \text{Ph} \\
\text{not observed} & \\
\end{align*}
\]

(b)

\[
\begin{align*}
\text{C}_6\text{H}_{10} & \rightarrow \text{C}_6\text{H}_{10} \text{CH}_2 \text{CH}_2 \text{C} \text{CH}_2 \text{CH}_2 \text{CH}_2 \text{CH} \\
\text{Ph} & \text{Ph} \text{Ph} \text{Ph} \text{Ph} \text{Ph} \\
\text{a}_{n+1} & \\
\text{C}_6\text{H}_{10} & \rightarrow \text{C}_6\text{H}_{10} \text{CH}_2 \text{CH}_2 \text{C} \text{CH}_2 \text{CH}_2 \text{CH}_2 \text{CH} \\
\text{Ph} & \text{Ph} \text{Ph} \text{Ph} \text{Ph} \text{Ph} \\
\text{Z}_{n+1} & \text{Ph} \text{Ph} \text{Ph} \text{Ph} \text{Ph} \\
\text{not observed} & \\
\text{C}_6\text{H}_{10} & \rightarrow \text{C}_6\text{H}_{10} \text{CH}_2 \text{CH}_2 \text{C} \text{CH}_2 \text{CH}_2 \text{CH}_2 \text{CH} \\
\text{Ph} & \text{Ph} \text{Ph} \text{Ph} \text{Ph} \text{Ph} \\
\text{a}_{n+5} & \\
\text{C}_6\text{H}_{10} & \rightarrow \text{C}_6\text{H}_{10} \text{CH}_2 \text{CH}_2 \text{C} \text{CH}_2 \text{CH}_2 \text{CH}_2 \text{CH} \\
\text{Ph} & \text{Ph} \text{Ph} \text{Ph} \text{Ph} \text{Ph} \\
\text{y}_{n} & \text{Ph} \text{Ph} \text{Ph} \text{Ph} \text{Ph} \\
\text{not observed} & \\
\end{align*}
\]

Figure 3. (a) Benzylic and primary radical ions arising by random homolytic C–C bond cleavages in a polystyrene chain with C_{6}H_{10} and –H substituents at the α and ω chain ends, respectively. Only some benzylic radical ions (encircled) are observed in the CAD spectra. (b) Closed-shell fragment ion series produced by \(n\)-scission from the radical ions. Encircled are the major products.
Scheme 1. Backbiting (1,5-H Rearrangement) and Subsequent \( C - C \) Bond Scissions in the Benzylc Radical Ions \( b_n^+ \) and \( z_n^+ \) Generated by Random \( C - C \) Homolyces of Silverated Polystyrene Chains. \( R = \text{C}_6\text{H}_5 \) for \( b_n^+ \) and \( a_n^+ \); \( R = \text{CH}_3\text{Ph} \) for \( z_n^+ \) and \( y_n^+ \).

**Novel Software for the Assignment of Peaks from Tandem Mass Spectrometry Spectra of Synthetic Polymers**

Konstantinos Thalassinos,Anthony T. Jackson,Jonathan P. Williams,Gillian R. Hilton,Susan E. Slade, and James H. Scrivens

\(^a\) Department of Biological Sciences, University of Warwick, Gibbet Hill Road, Coventry, UK
\(^b\) Measurement Science Group, KCI plc., Wilton Centre, Redcar, Cleveland, UK

(J Am Soc Mass Spectrom 2007, 18, 1324–1331)
A few recent polymer MS and MS/MS articles in JASMS (April, 2011)


Astrobiology

Anybody else is out there in the Galaxy??

Motivation and Aims

“Titan is an Organic Paradise”
Why?

Origin of Color – Origin of Life???
Pre-biotic Earth: pre-biotic chemistry?
The Role of Tholins?
Why to use Mass Spectrometry in Space Science?

Lots of charged particles out there in space (not only H+ and e-)

Small neutrals also there (in the gas phase), easy to ionize

Need to shoot mass specs into space

“Visitors” (meteorites) from space come to us

Experimentally modeling (atmospheric) ion-molecule reactions and checking chemical potential of atmospheric products on the planet surface

No need to shoot and we can use “fancy” mass specs, e.g., with ultrahigh resolution
General Conclusions on the Role of MS in Atmospheric (Space) Science and Astrobiology

• MS in space
  – Provides data from “real” environment
  – Kg/$$ expensive
  – Long travel time (advance design desirable)
  – Resolution limited, ambiguous assignments
  – m/z limit

• MS on Earth
  – Does not provide data on “real” environment
  – Nevertheless, model reactions can be easily varied and/or modified and these studies are useful for mission design (Intelligent? Design!)
  – Ultrahigh resolution, accurate mass, repetitive measurements
  – Expensive but much cheaper than in space

One of the great successful missions: INMS Data from Titan atmosphere

Ambiguous assignments due to low resolution; “isobaric” ions are not resolved
Questions and Answers

- Why Titan?
- What (and where) is Organic Paradise?
- Why Ultrahigh Resolution MS and MS/MS?
- Why laboratory (model) experiments?
- Why do we care about “simple” organic (?) reactions in the gas-phase (or the origin of life)?
- Atmosphere (N$_2$/CH$_4$) and NH$_3$/ice on surface
- Wide variety of chemical reactions (mass specs!)
- Individual (and not bulk) properties/information
- Titan is too far (far away)
- Just because we are curious human beings

Aerosol growth
Lavvas et al.
PNAS, 2013
PAHs ?
Dinelli et al.
Geophys Res Lett. 2013
Chemical Ionization

- Ion-molecule reaction(s) between a reagent gas and the sample at a relatively high pressure

- Most common reagent gases
  – methane, isobutane, ammonia

- Mechanisms
  – \( \text{CH}_4 + e^- \rightarrow \text{CH}_4^+ \), \( \text{CH}_3^+ \), \( \text{CH}_2^+ \), ...
  – \( \text{CH}_4^+ + \text{CH}_4 \rightarrow \text{CH}_5^+ + \text{CH}_3 \)
  – \( \text{CH}_3^+ + \text{CH}_4 \rightarrow \text{C}_2\text{H}_5^+ + \text{H}_2 \)
  – \( \text{CH}_3^+ + M \rightarrow [\text{M}+\text{H}]^+ + \text{CH}_4 \)
  – \( \text{C}_2\text{H}_6^+ + M \rightarrow [\text{M}-\text{H}]^+ + \text{C}_2\text{H}_6 \)
  – \( \text{C}_2\text{H}_5^+ + M \rightarrow [\text{M}+\text{C}_2\text{H}_5]^+ \)
The 11th Commandment…

The Second Law of Thermodynamics

For spontaneous processes:

$$\Delta G = \Delta H - T \Delta S < 0$$

For isolated systems:

$$\Delta S > 0$$

Of course, we also need a “good” Big Bang, “heavy” atoms (C, N, O…) from first generations stars, at least second generation stars and compressed dust (planets, rocks), and a lot of time and luck….

Tholins: Analog material produced in plasma reactors

UHV Discharge reactor
Mark Smith’s lab
(Tucson/Houston)
Low temperature tholins

65% N₂, 35% CH₄ with adjustable flow rate

Glass tube to collect tholins at 195 K

Pampre cold plasma reactor
Nathalie Carrasco’s lab (LATMOS - Versailles)
Tholins in levitation
Ultrahigh vacuum (UHV) plasma generator to synthesize “tholins” (CxHyNz) in oxygen free environment (Mark Smith’s lab)

The Necessity of Ultrahigh Resolution and MS/MS: Organic Environment on Saturn’s Moon, Titan

- Sarker, N.; Somogyi, Á.; Lunine, J. I.; Smith, M. A. Astrobiology, 2003, 3, 719-726.
**Bruker 9.4 T Apex Qh FT-ICR with a dual source (Tucson, Thermo LTQ-Orbitrap (Grenoble, France))**

**ESI/ APCI**

**HRMS is mandatory for Tholins analysis**

Early works:
Somogyi et al., JASMS 2005
Tholinomics data reduction tools: Pernot et al., Anal. Chem. 2010
FT-ICR of Complex Organic Aggregates (UHVT_001)

Positive Ions: ESI

Positive Ions: LDI

Negative Ions: ESI

Negative Ions: LDI

Not the same protonated/deprotonated neutral species in +/- modes
Modified van Krevelen diagram for LDI ions

Red: positive LDI (FT-ICR)
Blue: negative LDI (FT-ICR)

 QCID MS/MS spectra of C$_7$H$_{N_4}$
### MS/MS Fragmentation Matrix

<table>
<thead>
<tr>
<th>Compound</th>
<th>MS/MS Fragment m/z</th>
<th>Intensity</th>
<th>Charge State</th>
<th>Precursor m/z</th>
</tr>
</thead>
<tbody>
<tr>
<td>C7HN4</td>
<td>(141.02067)</td>
<td>89.01</td>
<td>2</td>
<td>141.02067</td>
</tr>
<tr>
<td>C6N3</td>
<td>(114.00977)</td>
<td>69.02</td>
<td>2</td>
<td>114.00977</td>
</tr>
<tr>
<td>C2H3N4</td>
<td>(83.03632)</td>
<td>67.02</td>
<td>2</td>
<td>83.03632</td>
</tr>
<tr>
<td>C3HN4</td>
<td>(93.02067)</td>
<td>52.01</td>
<td>2</td>
<td>93.02067</td>
</tr>
<tr>
<td>C3H2N5</td>
<td>(108.03157)</td>
<td>47.02</td>
<td>2</td>
<td>108.03157</td>
</tr>
<tr>
<td>C4H2N3</td>
<td>(92.02542)</td>
<td>43.01</td>
<td>2</td>
<td>92.02542</td>
</tr>
<tr>
<td>C2N3</td>
<td>(66.00978)</td>
<td>30.01</td>
<td>2</td>
<td>66.00978</td>
</tr>
<tr>
<td>-HCN</td>
<td></td>
<td>25.01</td>
<td>2</td>
<td>-15.001</td>
</tr>
</tbody>
</table>

**Diagram:**

- **I:** \( C_{14}H_{26}N_{2} \) (141.02067)
- **B:** \( C_{6}H_{12}N_{3} \) (114.00977)
- **E:** \( C_{12}H_{24}N_{5} \) (108.03157)
- **C:** \( C_{10}H_{12}N_{4} \) (93.02067)
- **F:** \( C_{8}H_{12}N_{5} \) (83.03632)
- **D:** \( C_{6}H_{12}N_{2} \) (66.00978)
- **G:** \( C_{5}H_{8}N_{2} \) (52.01)
- **H:** \( C_{4}H_{8}N_{2} \) (47.02)
- **I:** \( C_{3}H_{6}N_{2} \) (43.01)
- **J:** \( C_{2}H_{4}N_{2} \) (30.01)
- **K:** \( C_{2}H_{4}N_{2} \) (25.01)

**Chemical Reactions:**

- **I → B:** Amination with HCN
- **C → E:** Amination with HCN
- **D → F:** Amination with HCN
- **G → H:** Amination with HCN

**Notes:**

- The matrix represents the fragmentation patterns of the compounds listed.
- The intensities indicate the relative abundance of each fragment.
- The charge state is given in parentheses for each fragment.
CLIO, variable wavelength IRMPD in a FTICR cell (7T Bruker)

- Action spectroscopy of ions in the cell,
  « only ions which absorb photons will fragment »
Maitre et al., Nucl. Inst. & Meth., 2003

Vw IRMPD (FT-ICR) measurements at CLIO (Orsay, France)

C:\Tholin_Stuff\from_CLIO\2011-06-22-thissen\PolyCN_Grenoble_ESI_neg_smallmass_newturene_IRMPD_107_000001.d

Good agreement with our CLIO gas-phase spectrum of the deprotonated HCN tetramer
Blue-shift due to isotope effect!

\[ \text{C}_2\text{H}_2\text{N}_5^+ \quad (108.03157) \]

\[ \text{C}_2\text{N}_3^- \quad (66.00978) \]

\[ \text{C}_2\text{N}_3^- \quad (15\text{N}) \quad (67.00699) \]

\[ \text{C}_2\text{N}_3^- \quad (13\text{C}) \quad (67.01324) \]
Two positively charged ions
Two different spectroscopy

Congested spectra, very rich info
\[ \lambda \approx 1550 \text{ cm}^{-1} \]

\[ \lambda \approx 1610 \text{ cm}^{-1} \]

Large scale Quantum chemical calculations are needed

Red arrows indicate possible protonation sites

\[ \text{C}_4\text{H}_8\text{N}_4 \]
\[ \text{C}_3\text{H}_7\text{N}_5 \]

Source of oxygen is water

Oxygen incorporation is faster and higher in ammonia solution than in pure water

Tholin reacts with NH$_3$

Quantitative kinetic studies to determine hydrolysis rate constants and Arrhenius activation energies in 14% NH$_3$/water

Kinetic "growing" curves at four different temperatures

Arrhenius plot from hydrolysis rate constants
The distribution of Arrhenius activation energies

Incorporation of oxygen atoms can occur in 3,000-10,000 years on the surface of Titan

Conclusion

Titan is planet-scale chemical laboratory, with astrobiological relevance

Interpretation of Cassini-Huygens data requests for permanent feedback of information from Physical Chemistry and MS community

Tholins appear as a good analog to study the potential composition of Titan aerosols. High resolution mass spectrometry is mandatory to evaluate their composition

Positive and negative ion spectra are characteristically different indicating more saturated amino/imino compounds (positive mode) and highly unsaturated (CN containing) species with H/C < 1 (negative mode)

Chemical formulae can be unambiguously determined but structural isomerism exists

MS/MS with vV IRMPD and theoretical calculations are required to determine fine structural details

Studies of new concepts of ion handling and analysis are required for future space exploration
(The Funny) Conclusions

All we are just dust in the wind…

Come from gas and return to gas