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SAND2012-7089C

Sandia National Laboratories

Detection and Characterization of Volatile Thermal-Oxidative Nylon 6.6 Degradation Products *via* Selective Isotopic Labeling and Cryo-GC/MS

James M. Hochrein,[1] Jonell N. Smith,[1] Gregory V. White II,[2] Michael I. White,[1] Megan R. Pearl,[1] and Robert Bernstein[2]

[1]*Materials Reliability Department (1825)* & [2]*Organic Materials Department (1821)*

7th MoDeSt 2012 Conference | Sept 2-6, 2012 | Prague, Czech Republic

U.S. DEPARTMENT OF ENERGY NNSA National Nuclear Security Administration

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PlainsCapitalBank

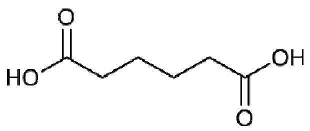
Processing and Environmental Technology Laboratory (PETL)

Nylon is Used in Numerous Applications

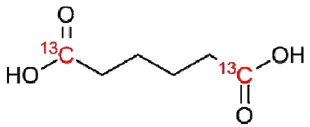
Sample Preparation

Monomers

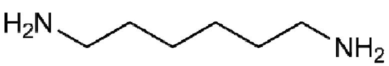
unlabeled adipic acid



C-13 labeled adipic acid (99% enriched)

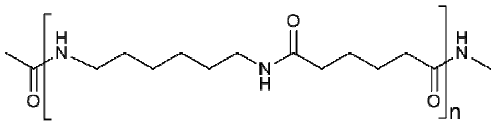


unlabeled 1,6-hexanediamine



Polymer

unlabeled nylon 6.6 (99% pure)



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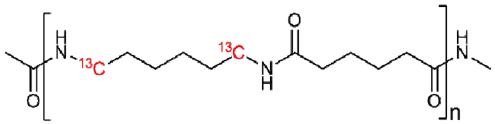
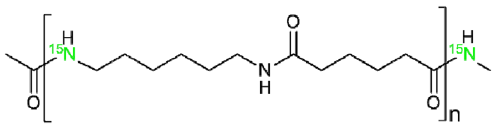


N-15 labeled nylon 6.6 (51.4% enriched)



Polymer synthesis:
- unlabeled and isotopically labeled polymer and monomers
- vacuum bake purification

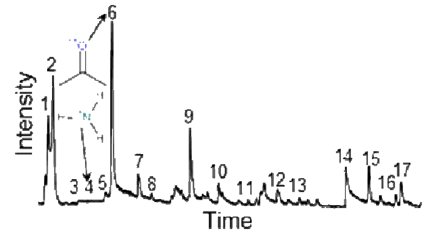
Accelerated aging:
- 1 to 243 days
- 138 °C
- 5 cc SS vessels
- O_2 or $^{18}O_2$ atmosphere

Detection and Analysis

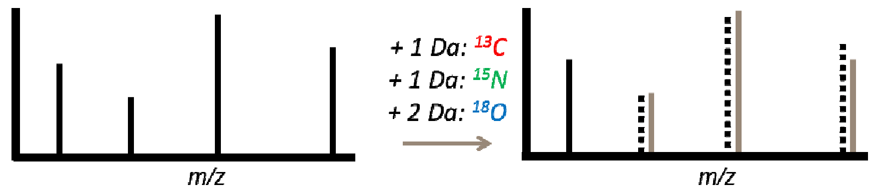
Headspace gas analysis:
- 10 cc gas injection
- cryofocusing gas chromatography MS (cryo-GC/MS)

JEOL GCMate II

Identify degradation products:
- 18 volatiles identified with cryo-GC/MS[1]



Locate isotopically labeled atoms:
- Monitor mass spectra for shifts and compare to ion fragmentation pathway

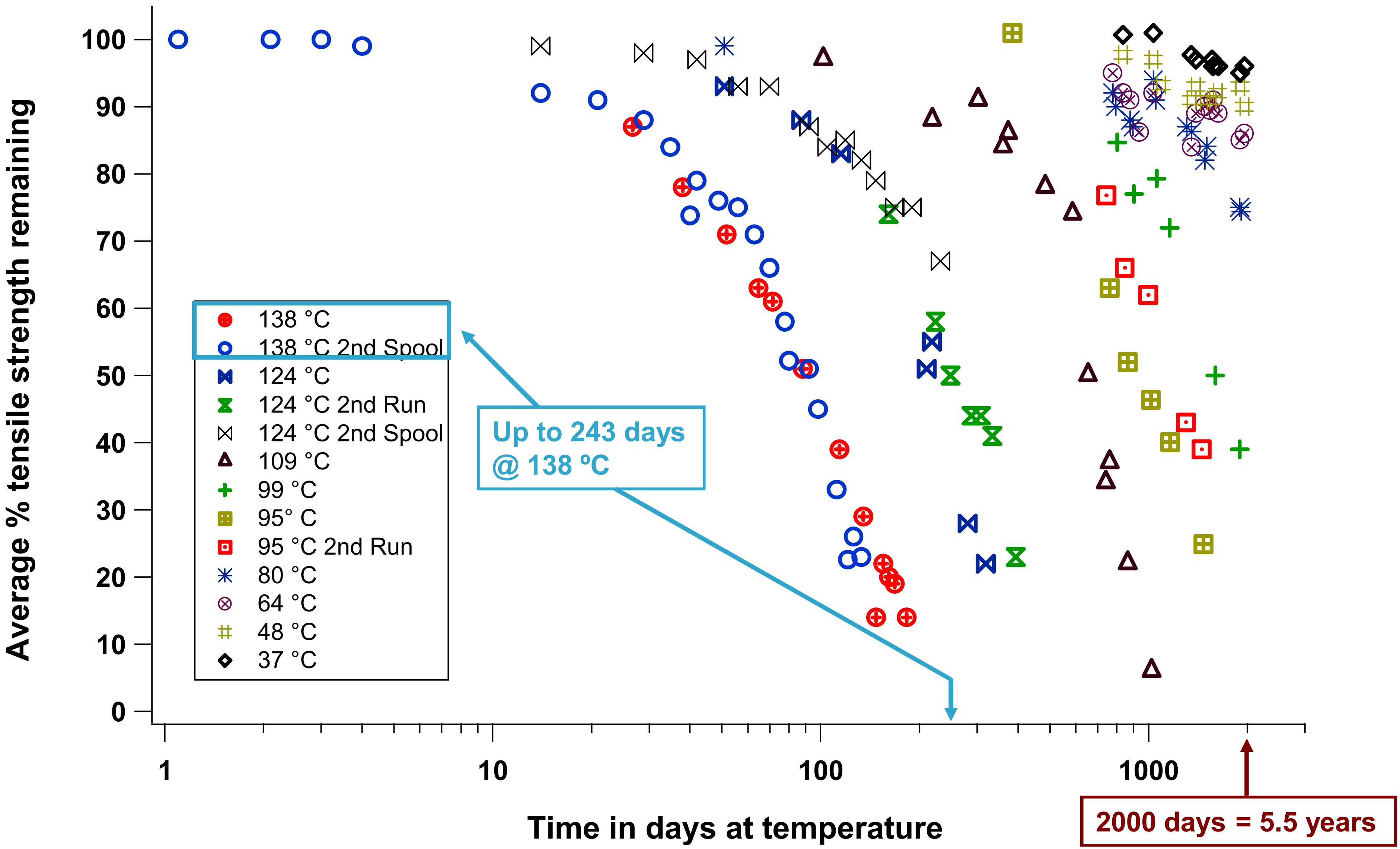


elucidate degradation mechanisms[2,3]

develop chemical sensors to monitor material degradation

[1] Smith, J.N., *et al. JASMS, in press* (2012) [2] White II, G.V., *et al. Polym. Degrad. Stab., in press* (2012) [3] White II, G.V., *et al. Polym. Degrad. Stab., in preparation* (2012)

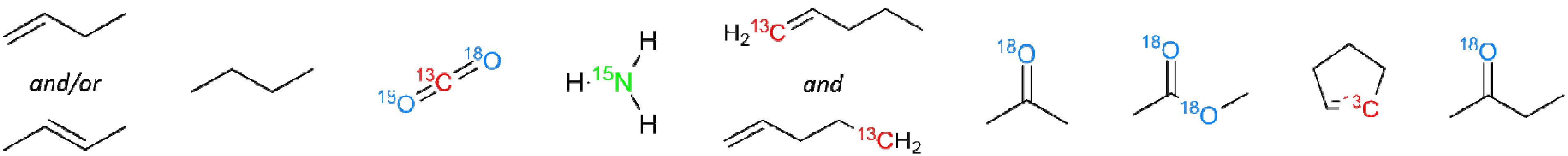
Tensile Strength Relates to Selected Aging Conditions



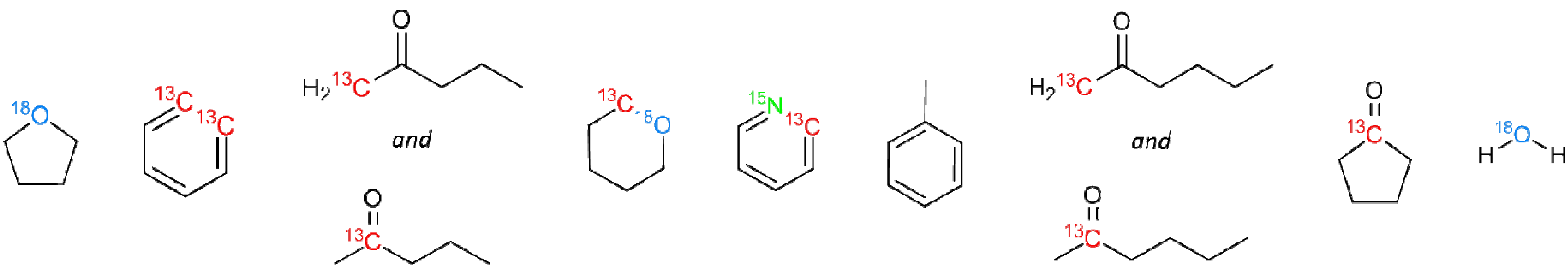
Bernstein, R., *et al. Polym. Degrad. Stab.*, **95**, 1471 (2010)

18 Low-Molecular Weight Volatiles Detected

- 18 thermal-oxidative degradation species were identified
  - C-13, N-15, and O-18 labels were located within each structure



{1} {2} {3} {4} {5} {6} {7} {8} {9}

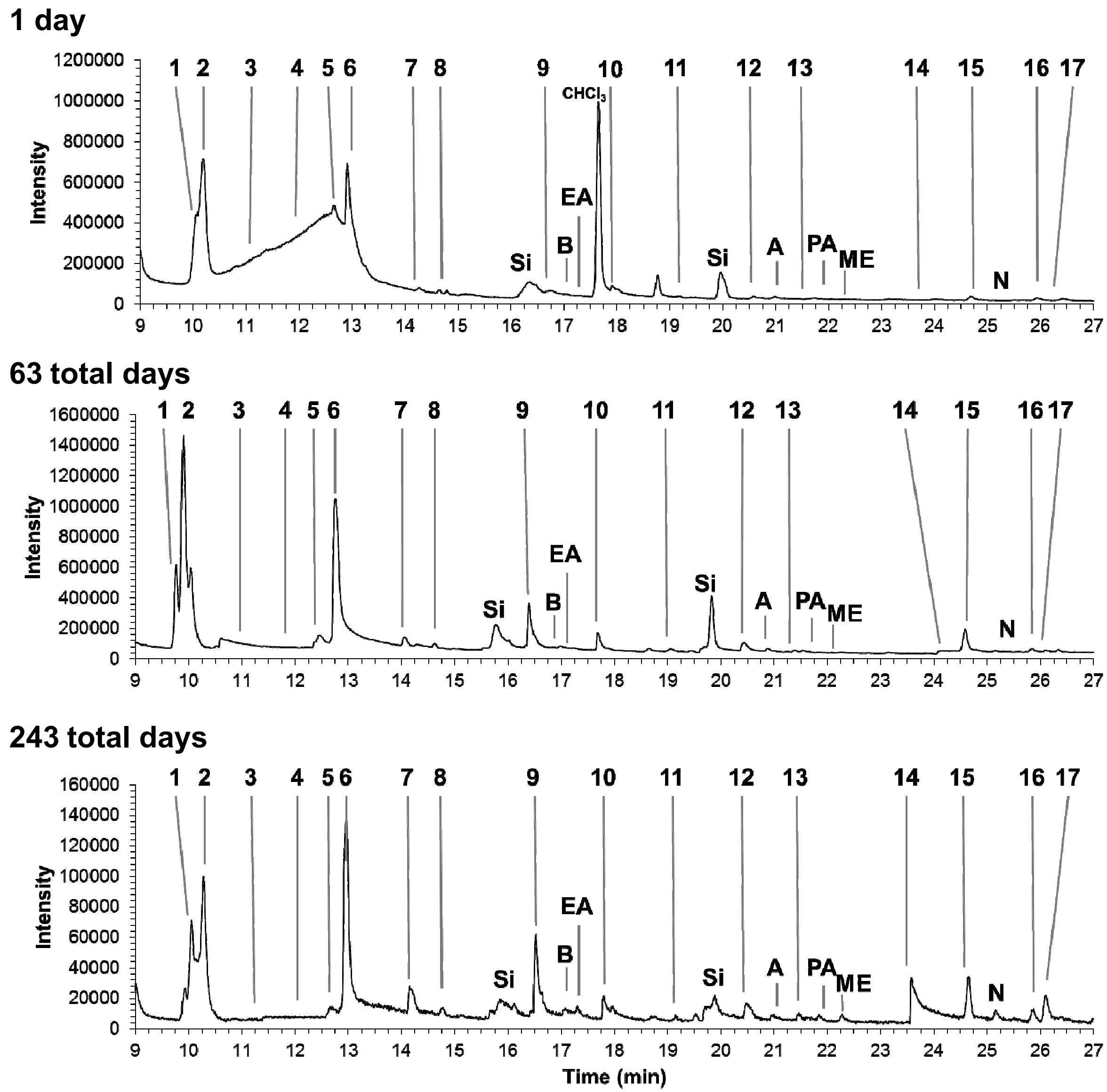


{10} {11} {12} {13} {14} {15} {16} {17} {18}

Adipic Acid Origins *1,6-Hexanediamine Origins* *Origins from Both Monomers*

Products have Reproducible Retention Times

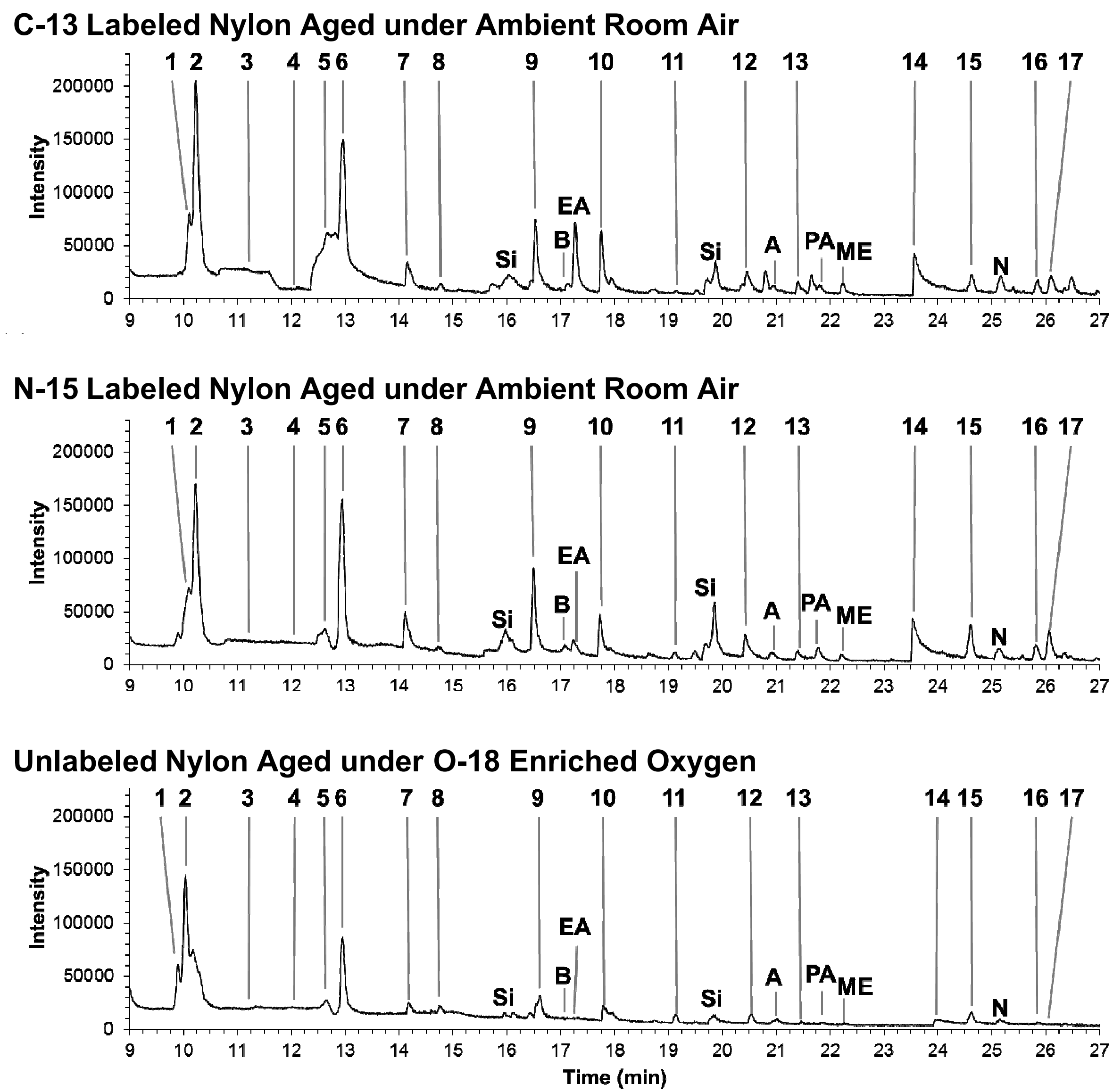
- Degradation product retention times align for all aging experiments
  - 1, 34, 63, 153, and 243 total days
- CO_2 **{3}** and NH_3 **{4}** source exhausted at early aging times
  - Leaving from end groups
- Water **{18}** was detected in the injection artifact, background, and final chromatogram minutes
- Unidentifiable species: **Si**, **B**, **EA**, **A**, **PA**, **ME**, and **N**



Smith, J.N., *et al. JASMS, in press* (2012)

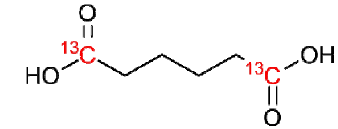
Isotopic Labeling does not Affect Mechanisms

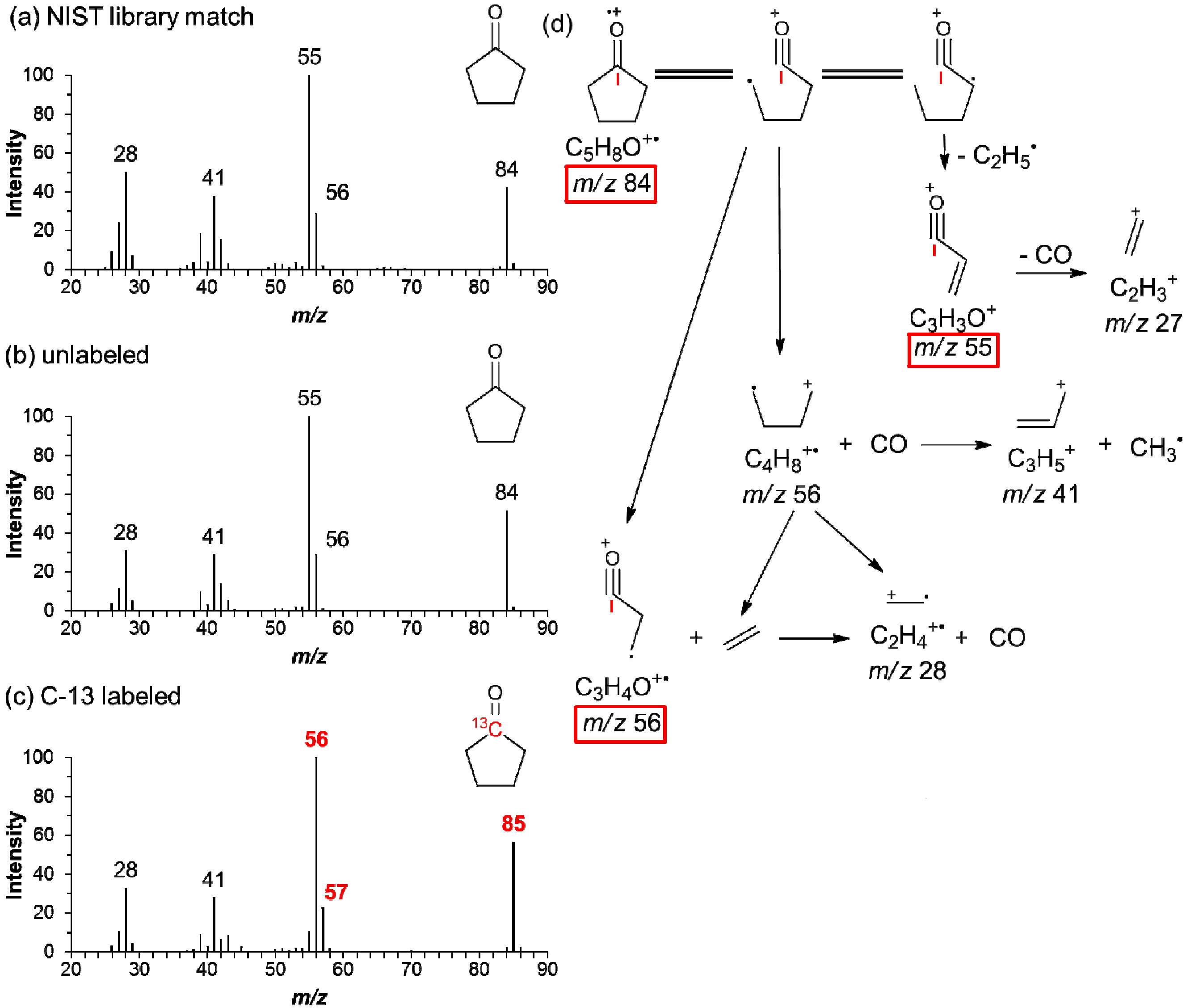
- Retention times for aged unlabeled *(not shown)* and all isotopically labeled nylon 6.6 samples align
- Isotopic labels did not change the underlying nylon 6.6 degradation mechanisms



Cyclopentanone

C-13 labeled adipic acid (99% enriched)

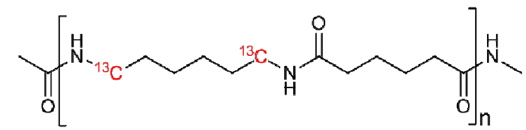


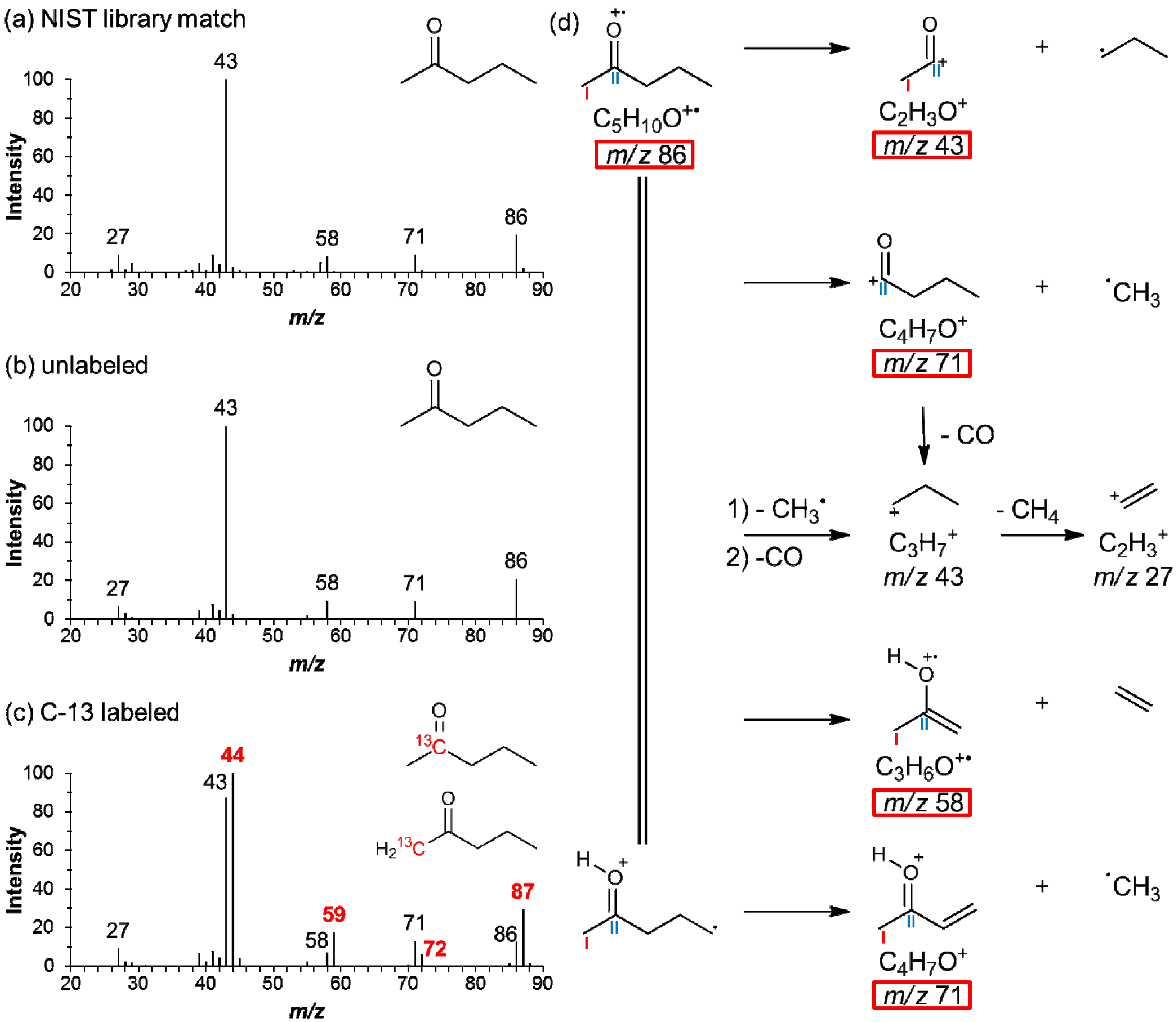


- One C-13 atom
  - *m/z* 84 → *m/z* 85
- C-1, C-2, or C-3
  - +1 Da: *m/z* 56 ($C_3H_4O^{+•}$)
  - +1 Da: *m/z* 55 ($C_3H_3O^{+}$)
- Not C-2 or C-3
  - +0 Da: *m/z* 27 ($C_2H_3^{+}$)
  - +0 Da: *m/z* 56 ($C_4H_8^{+•}$)
  - +0 Da: *m/z* 28 ($C_2H_4^{+•}$)
  - +0 Da: *m/z* 41 ($C_3H_5^{+}$)
- C-13 at the C-1 carbonyl position
  - Agrees with C-13 atom location in the C-13 adipic acid monomer

2-Pentanone

C-13 labeled nylon 6.6 (99% enriched)

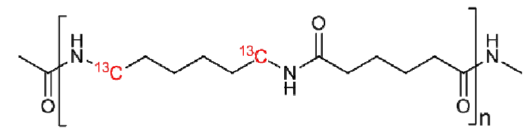


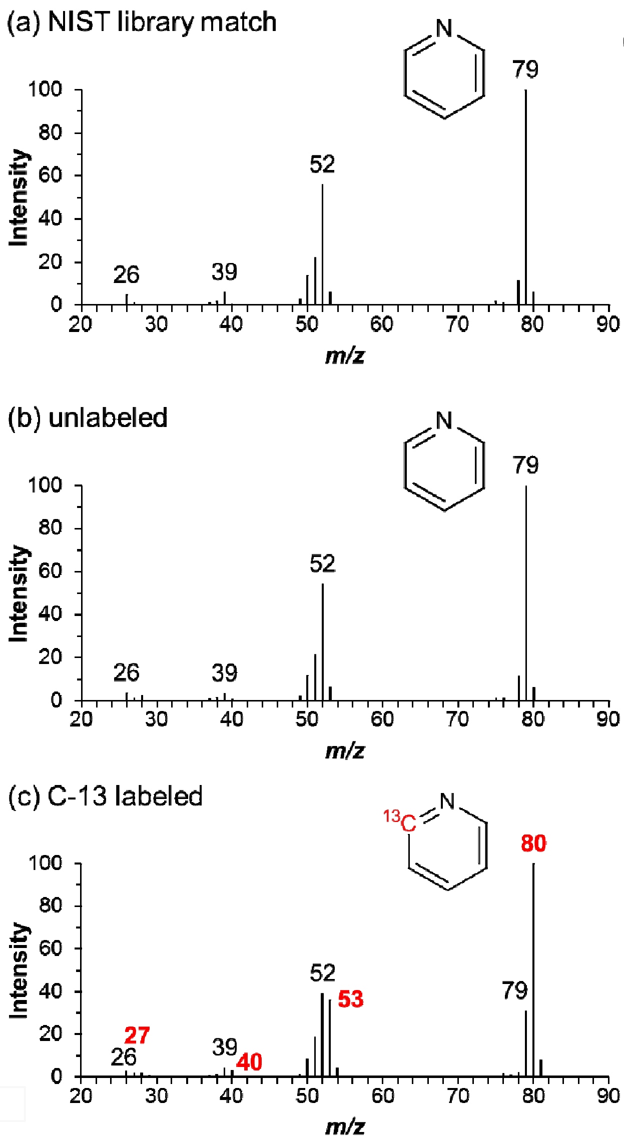


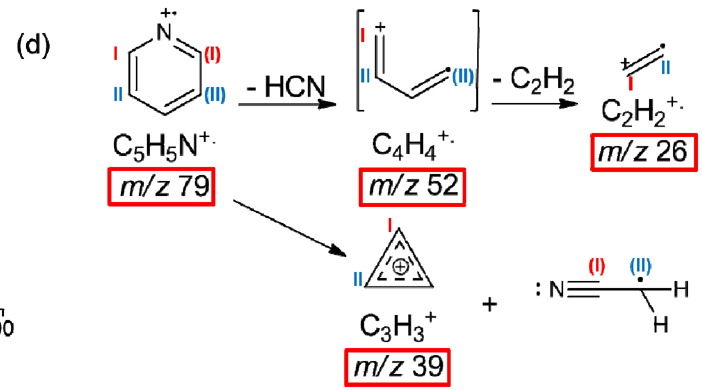
- One C-13 atom
  - *m/z* 86 → *m/z* 87
- C-1, C-2, or C-3
  - +1 Da: *m/z* 58 ($C_3H_6O^{+\bullet}$)
  - +1 Da: *m/z* 71 ($C_4H_7O^+$)
    - Two structures
- Not C-3
  - +1 Da: *m/z* 43 ($C_2H_3O^+$)
  - +0 Da: *m/z* 43 ($C_3H_7^+$)
  - +0 Da: *m/z* 27 ($C_2H_3^+$)
- Mixture of C-1 and C-2
  - *m/z* 43:44 is about 1:1
- 1,6-hexanediamine origins, which does not contain oxygen atoms
  - Unlabeled present
  - 2-hexanone is analogous

Pyridine

C-13 labeled nylon 6.6 (99% enriched)







- One C-13 atom
  - *m/z* 79 → *m/z* 80
- C-1, C-2, or C-3
  - +1 Da: *m/z* 52 ($C_4H_4^{+\bullet}$)
  - +1 Da: *m/z* 39 ($C_3H_3^{+}$)
- Not C-3
  - +1 Da: *m/z* 26 ($C_2H_2^{+\bullet}$)

Example:

- Loss of $H^{13}CN$ → *m/z* 52
- Loss of HCN → *m/z* 53

If C-2, you would have a larger *m/z* 53 contribution.

- Not C-2 → C-1 only
  - Branching ratio of nearly one for:
    - *m/z* 52:53
    - *m/z* 39:40
    - *m/z* 26:27
- C-13 location has good agreement with 1,6-hexanediamine origins

Factor Analysis

- Data exploration & reduction using principal component analysis.

What is this?...

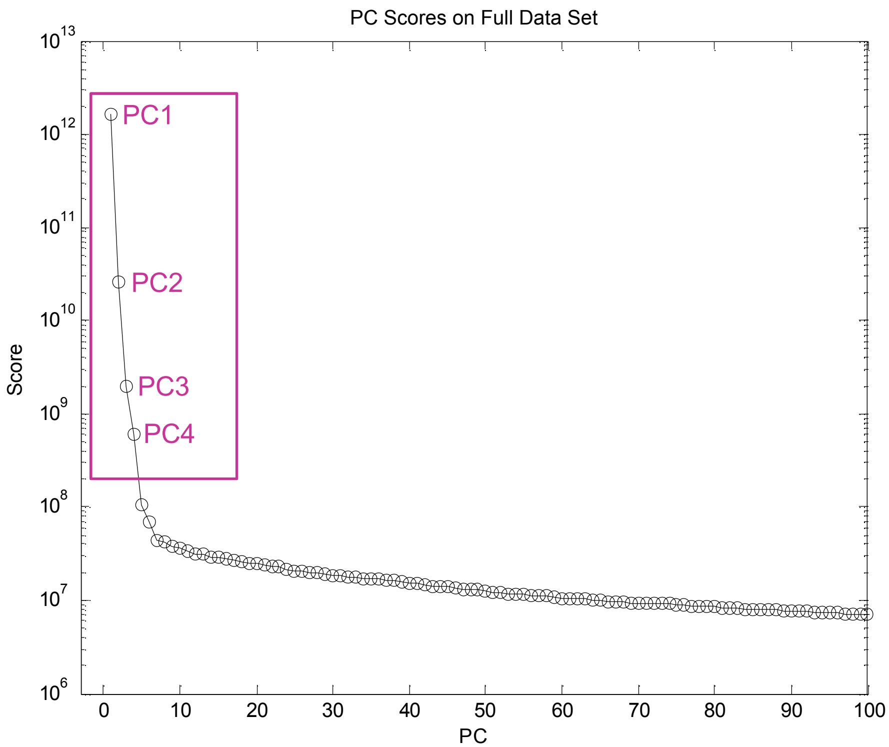
...a circle?…

...a mirror?...

…the bean!

Factor Analysis

- Data exploration & reduction using principal component analysis.
- Factor analysis to decompose the data into n factors.



Factor Analysis

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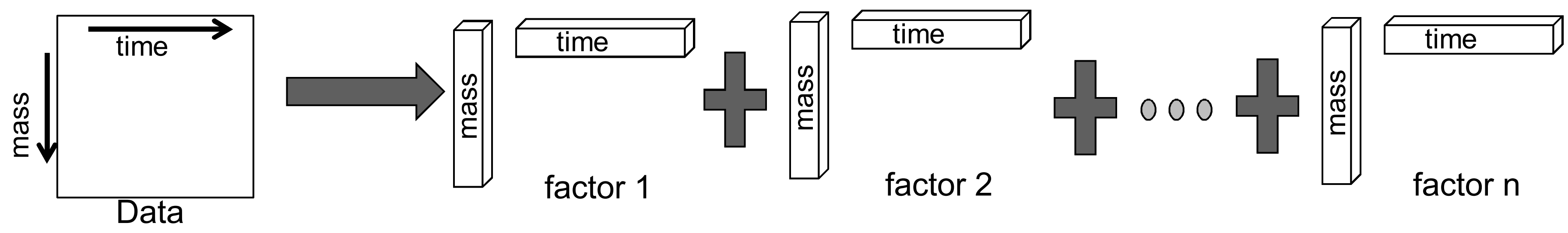
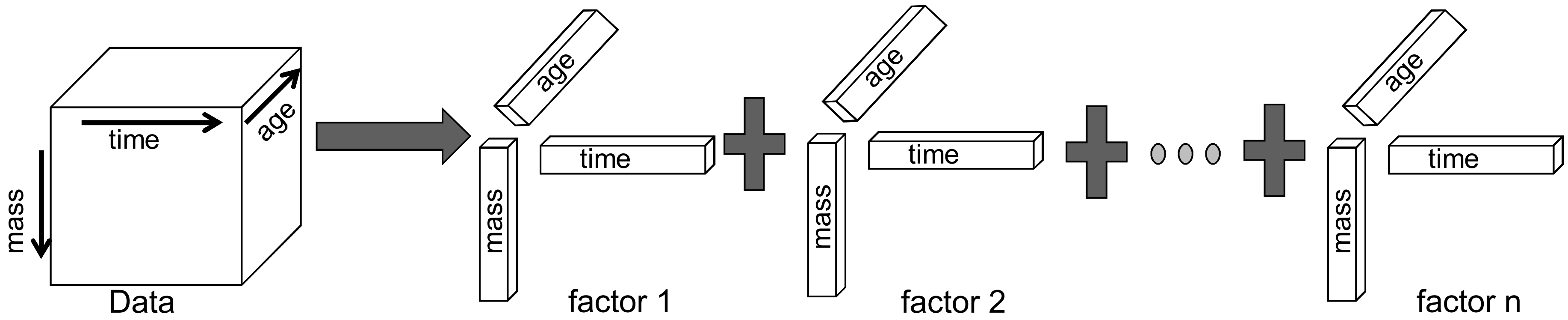
- Factor analysis options:
  - Multivariate Curve Resolution (MCR) → Resolve compounds at single age



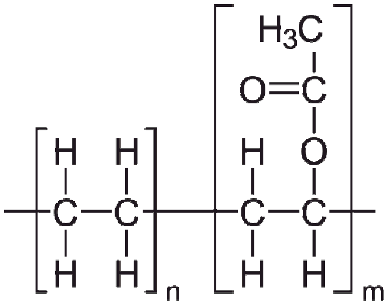
Factor Analysis

- Data exploration & reduction using principal component analysis.
- Factor analysis to decompose the data into n factors.
- Factor analysis options:
  - Multivariate Curve Resolution (MCR) → Resolve compounds at single age
  - Parallel Factor Analysis (PARAFAC2) → Changes in compounds with time



Different Polymers

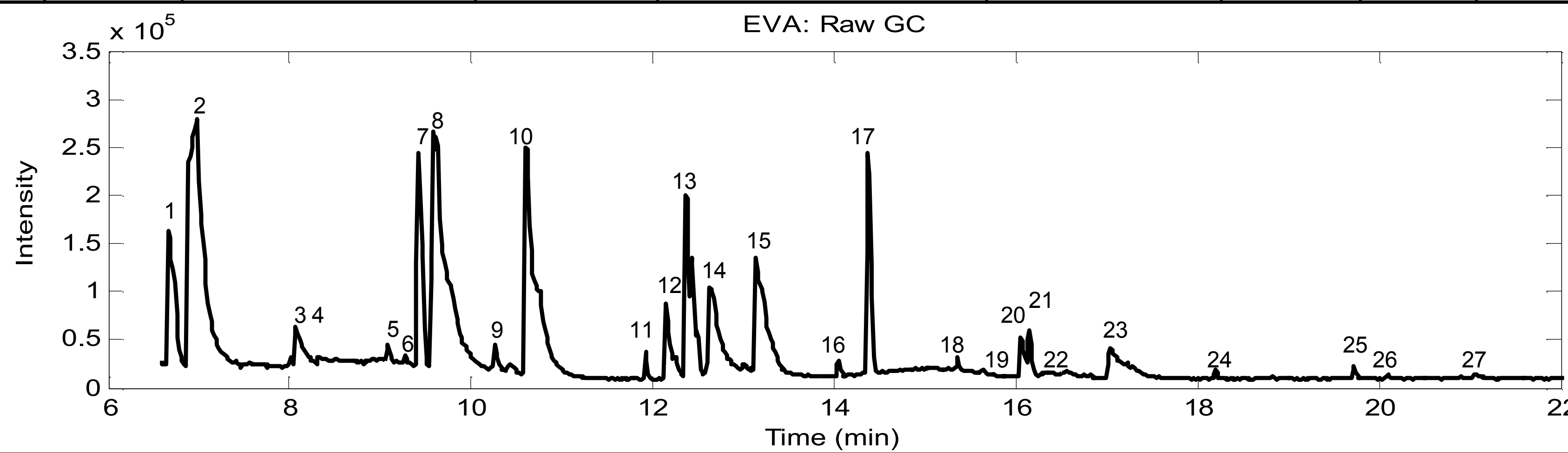
- Poly (ethylene-co-vinyl acetate) (EVA)
  - Hot glue sticks, ski boot padding, fishing rods, cigarette paper, plastic wrap clinginess enhancer



1	2	3	4	5	6	7	8	9
1-propene, 2-methyl	acetaldehyde	ethyl chloride	methyl formate	1-pentene	pentane	furan	propanal	acetone

10	11	12	13	14	15	16	17	18
acetic acid methyl ester	1-hexene	acetic acid ethenyl ester	butanal	2-butanone	ethyl acetate	butane, 1-chloro	benzene	1-heptene

19	20	21	22	23	24	25	26	27
heptane	pentanal	2-hexene, 5,5-dimethyl	2-pentanone	2-pentene, 3,4,4-trimethyl	Pentane, 1-chloro	1-octene	octane	hexanal



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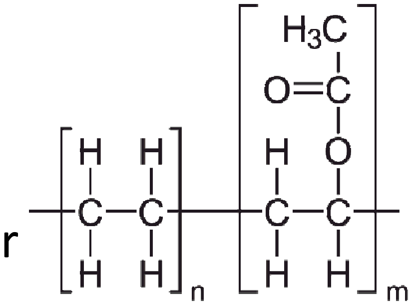

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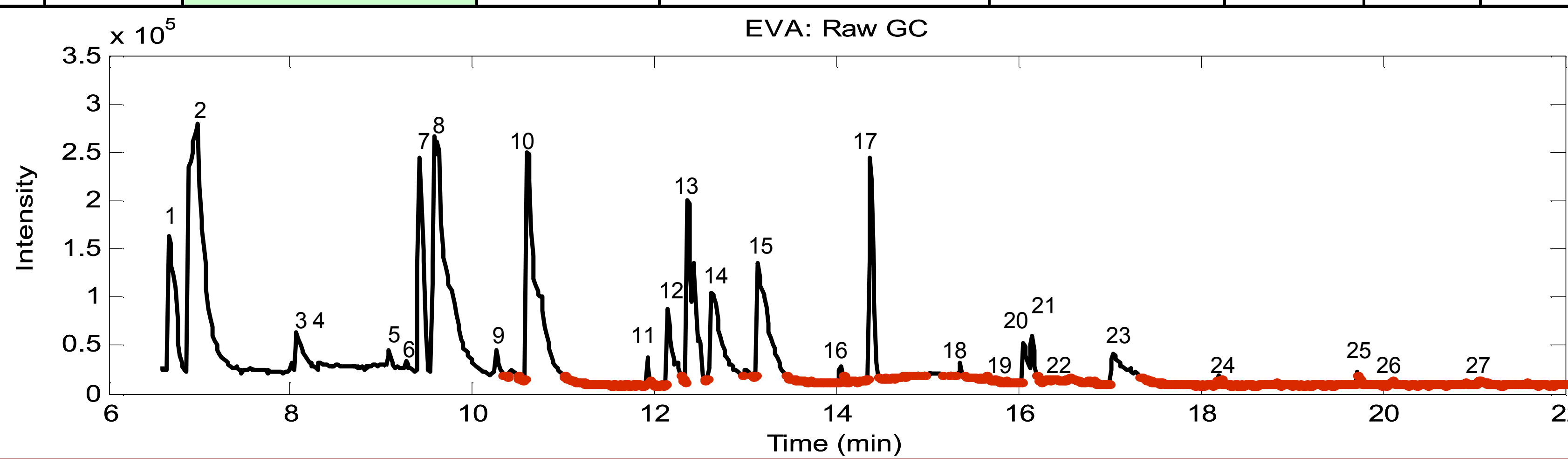
19	20	21	22	23	24	25	26	27
heptane	pentanal	2-hexene, 5,5-dimethyl	2-pentanone	2-pentene, 3,4,4-trimethyl	Pentane, 1-chloro	1-octene	octane	hexanal



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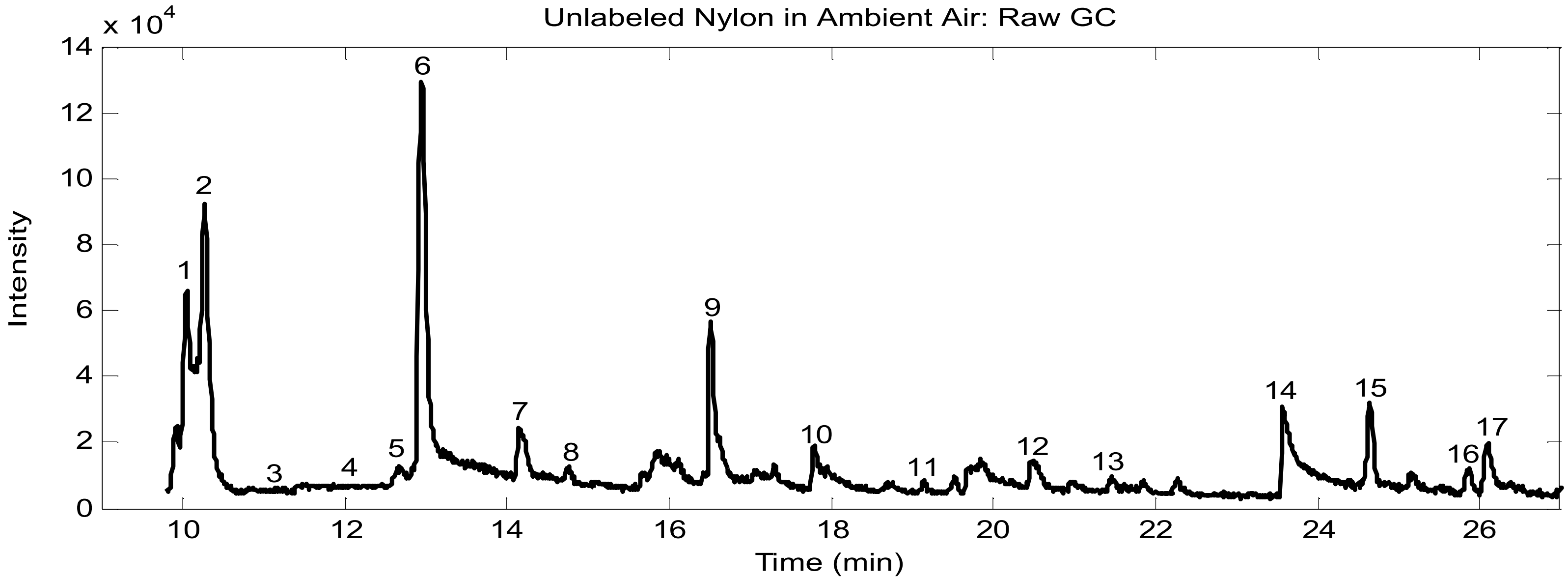
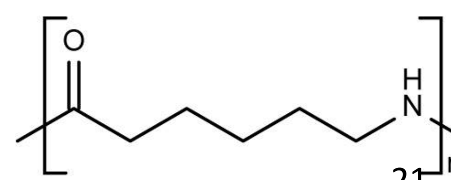


1	2	3	4	5	6	7	8	9
butene	butane	carbon dioxide	ammonia	1-pentene	acetone	methyl acetate	cyclopentene	2-butanone

10	11	12	13	14	15	16	17
Tetrahydro furan	benzene	2-pentanone	tetrahydropyran	pyridine	toluene	2-hexanone	cyclopentanone

- Nylon
  - Bridal veils, screws, vehicle tires, toothbrush, musical strings, fabrics…and many other commercial items



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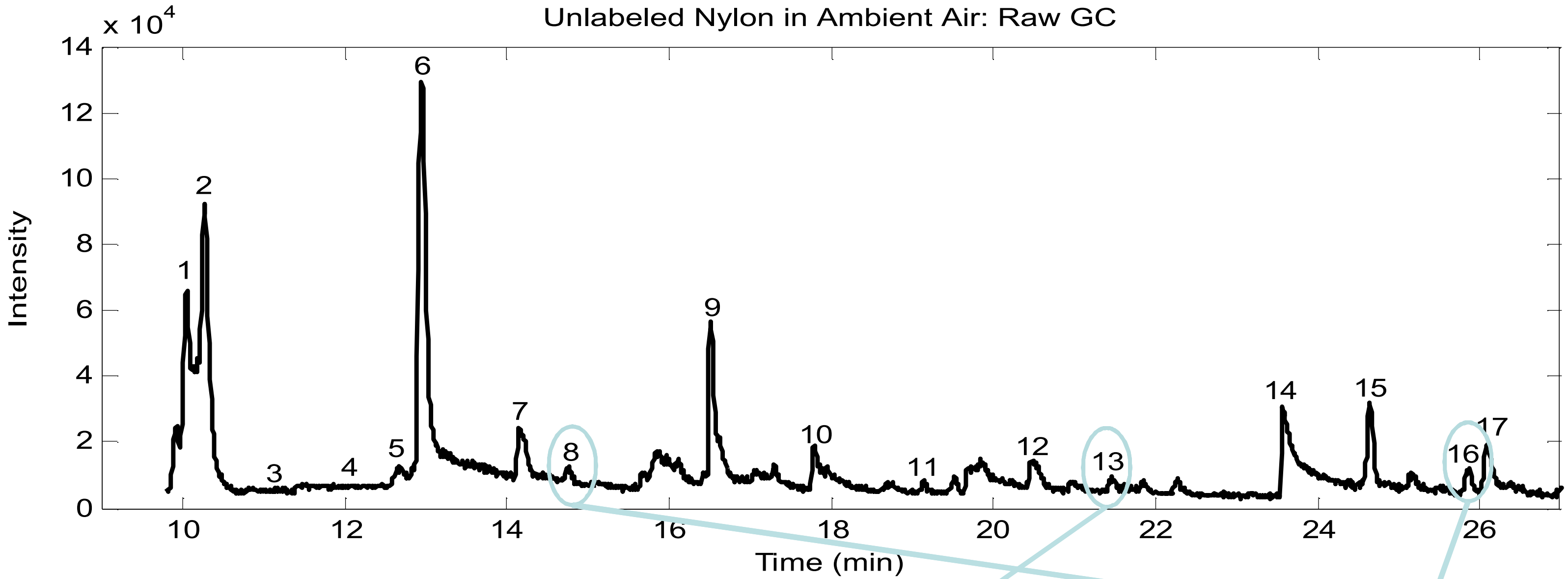

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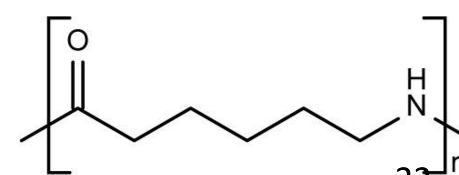
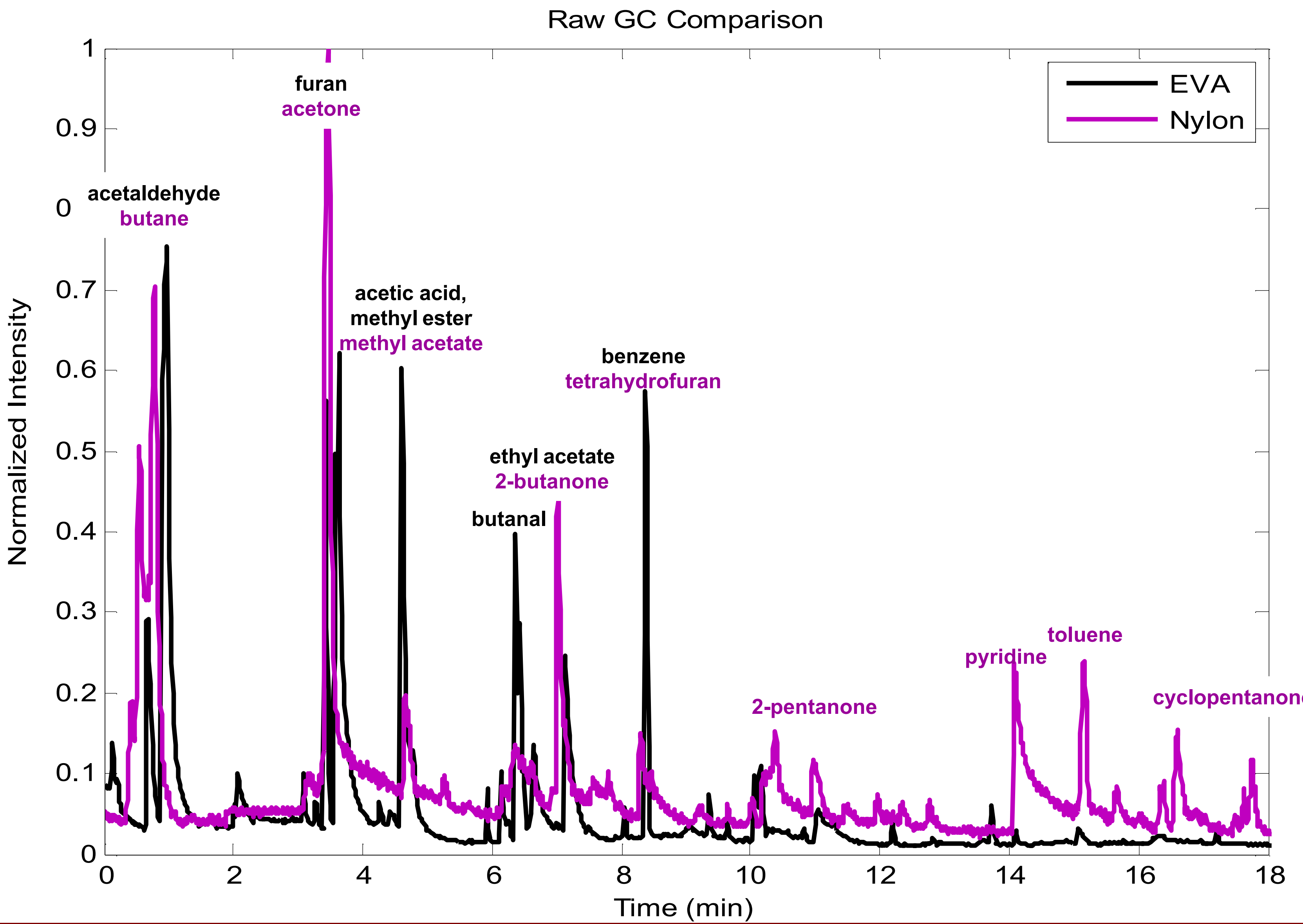
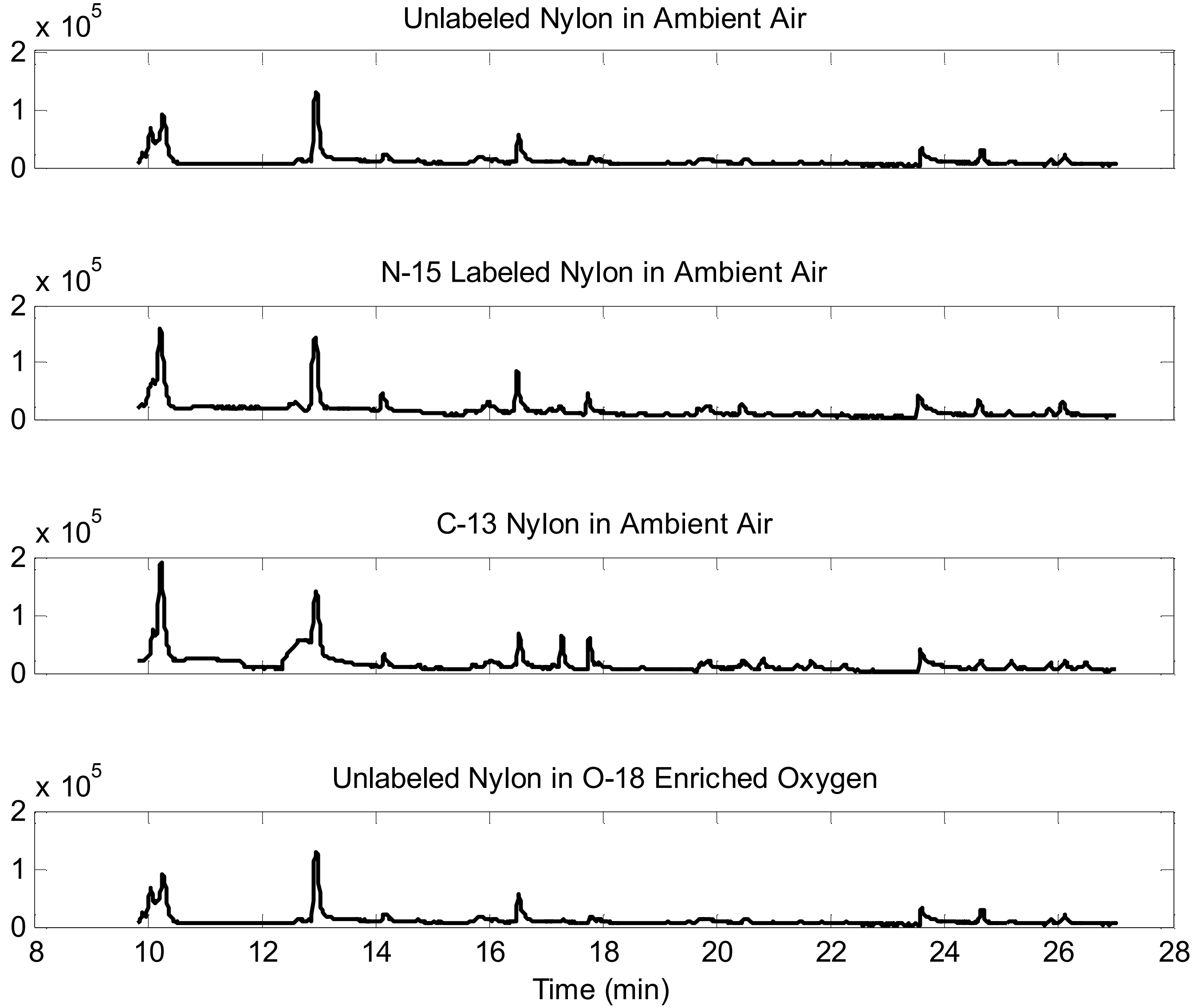


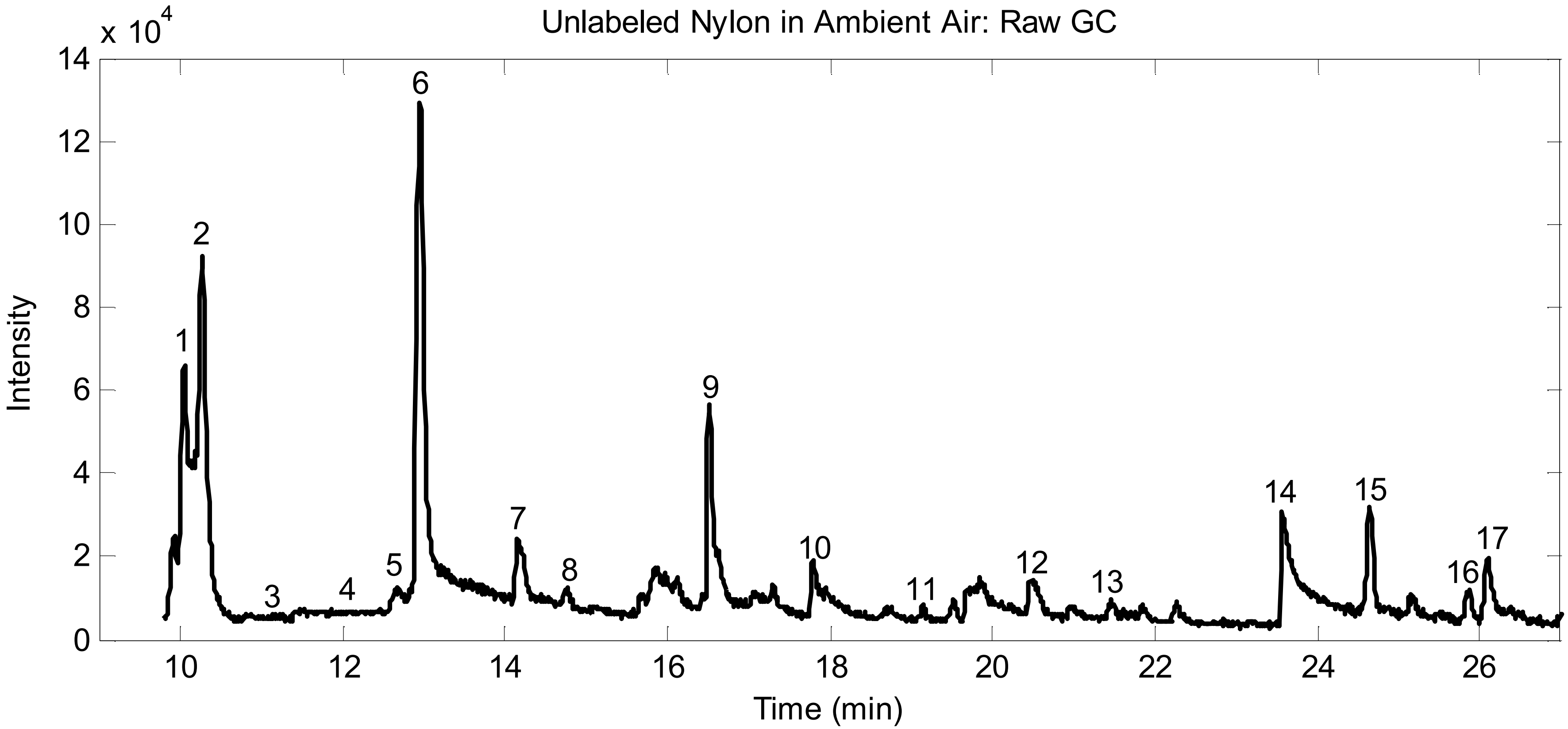
Different Polymers



Labeled vs. Unlabeled: GC



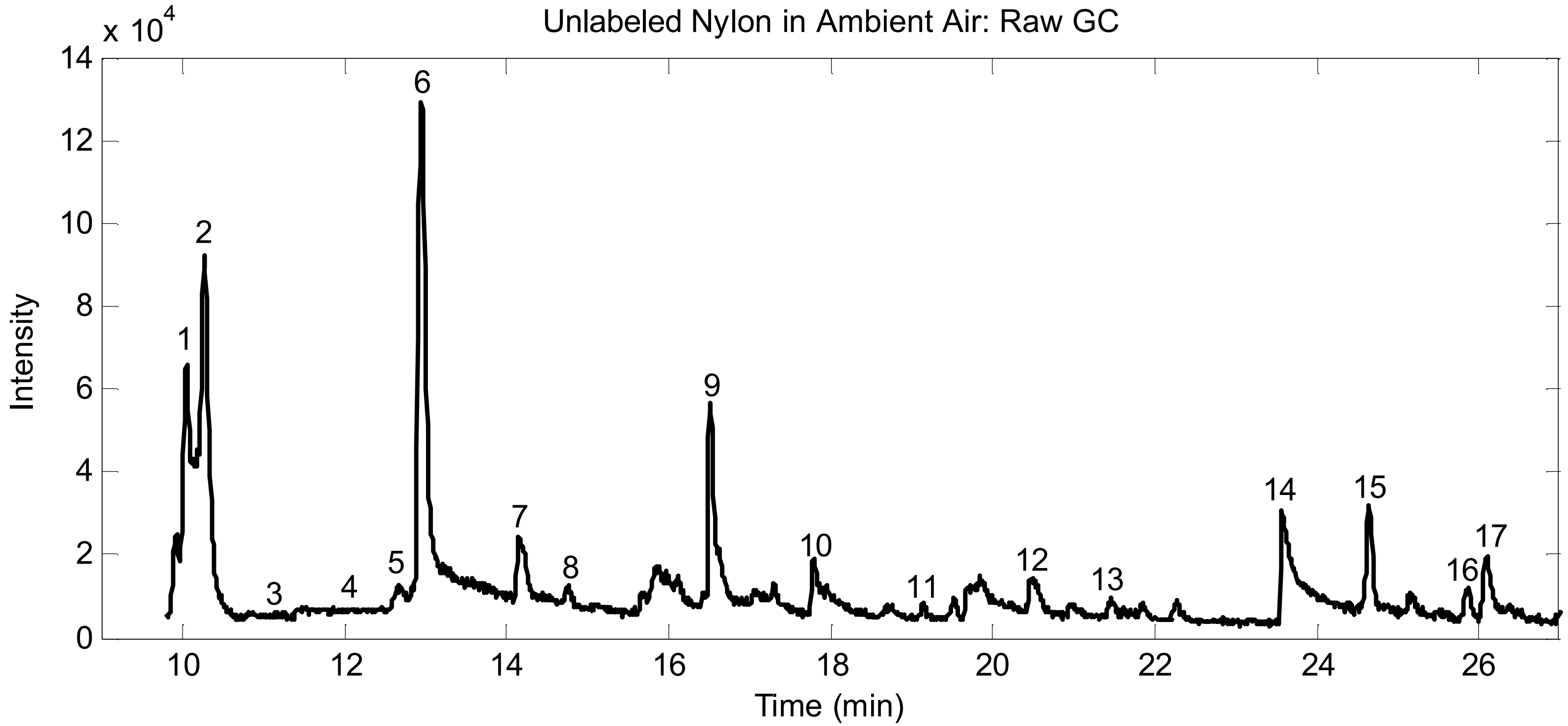
Labeled vs. Unlabeled: GC



Labeled vs. Unlabeled: MS

1	2	3	4	5	6	7	8	9
butene	butane	carbon dioxide	ammonia	1-pentene	acetone	methyl acetate	cyclopentene	2-butanone

10	11	12	13	14	15	16	17
tetrahydrofuran	benzene	2-pentanone	tetrahydropyran	pyridine	toluene	2-hexanone	cyclopentanone



Labeled vs. Unlabeled: MS

1	2	3	4	5	6	7	8	9
butene	butane	carbon dioxide	ammonia	1-pentene	acetone	methyl acetate	cyclopentene	2-butanone

10	11	12	13	14	15	16	17
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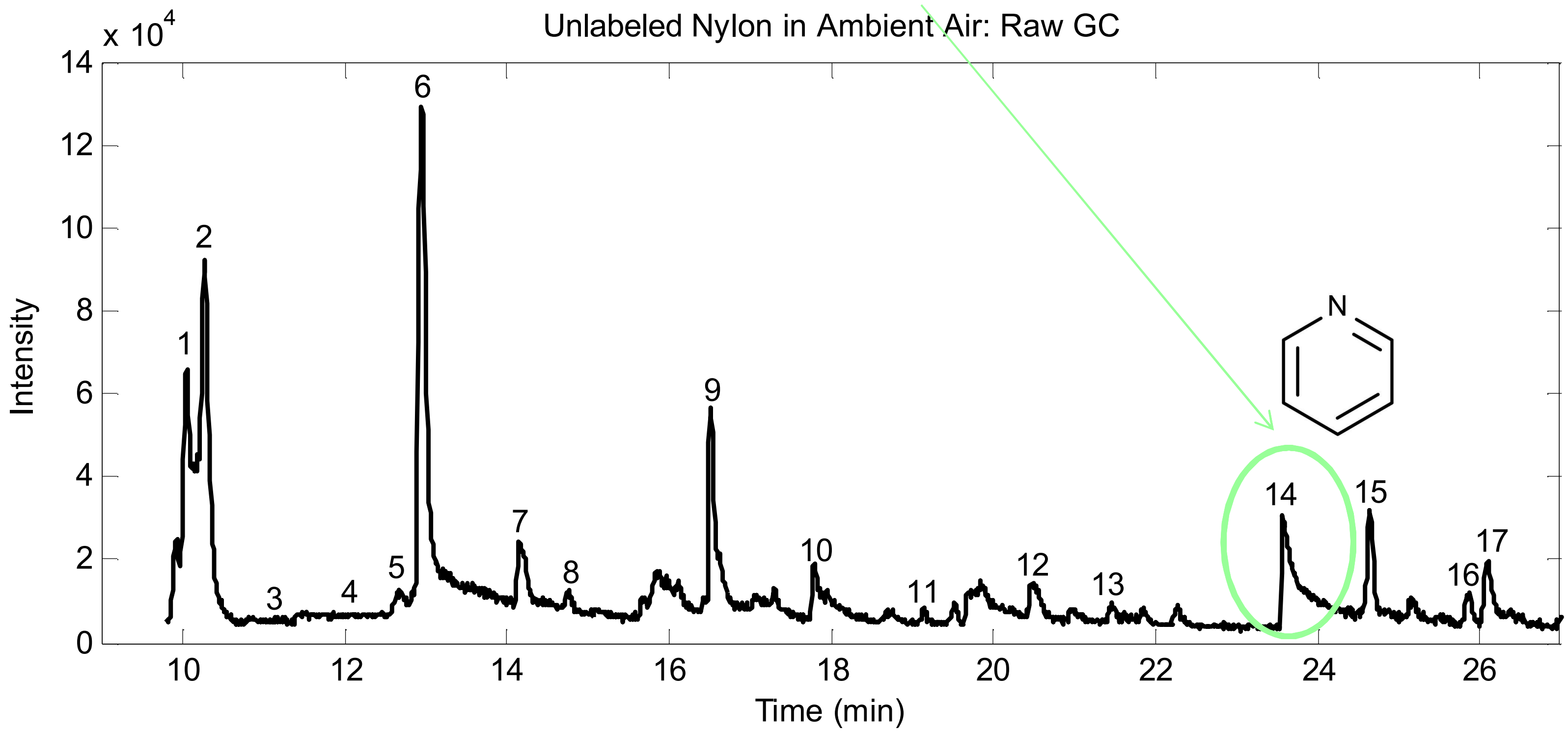
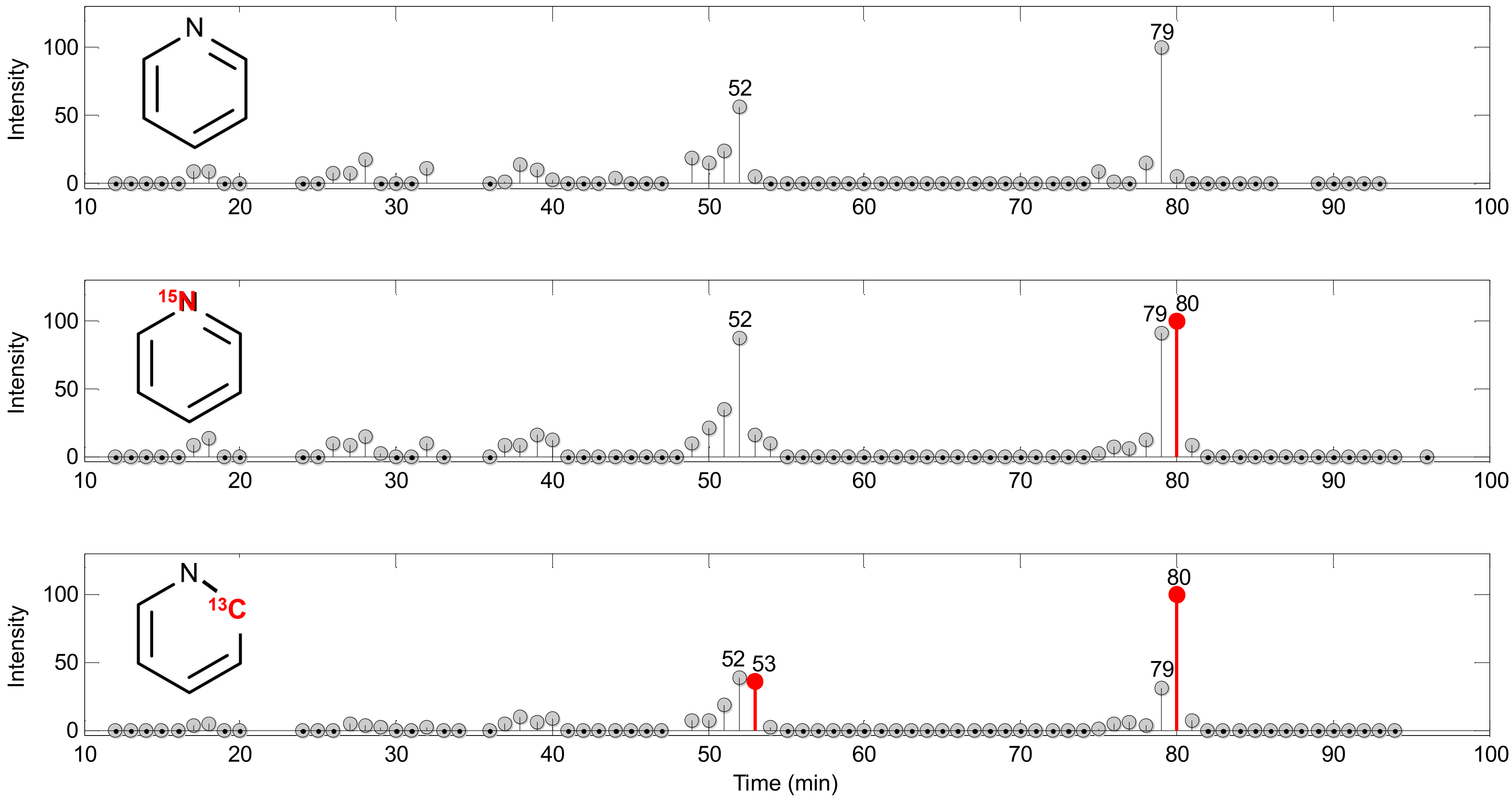


Labeled vs. Unlabeled: MCR Factors



Conclusion

- MCR is excellent data exploration tool.
  - Can find mass spectrum for every significant retention time.
  - Can resolve minor differences in mass spectra due to isotopic labels.
- Reduce analysis time from days or weeks to possibly a single day.
  - Eliminates sifting through data to find mass spectra.
  - Save significant amounts of time & money.
- Multi-experiment analysis of aging data can be quickly understood using PARAFAC2.

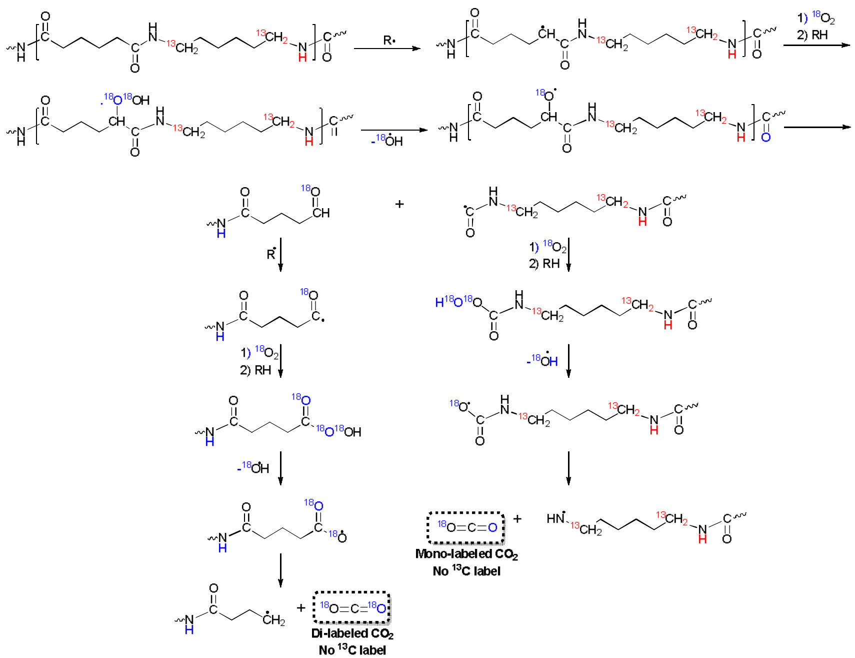
Conclusions

- Cryo-GC/MS and isotopic labeling were used to identify eighteen compounds that collected in the headspace over aged samples (up to 243 total days at 138 ^{o}C) of nylon 6.6 and its monomers
- Exact locations of isotopically labeled atom(s) were determined by comparing mass spectra to predicted ion fragmentation pathways
- Aging under an O-18 enriched environment aids in understanding the origin of oxygen in degradation products
- Relative ratios for unlabeled to isotopically labeled degradation products provided additional compound formation information

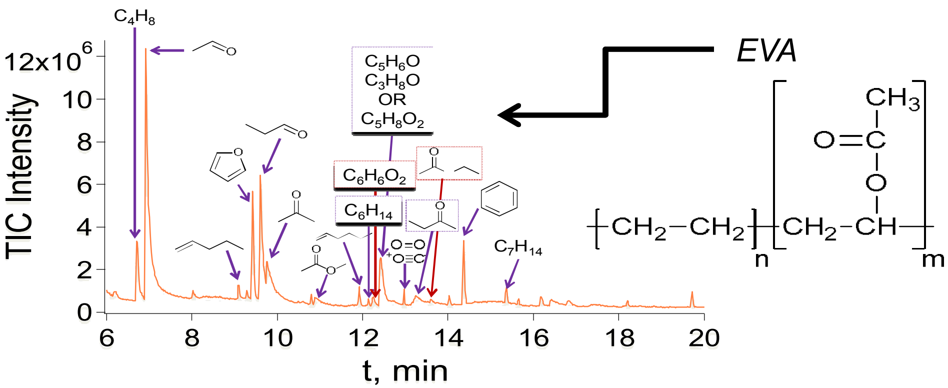
Smith, J.N., *et al. JASMS, in press* (2012)

Future Directions

- Nylon 6.6 degradation mechanisms
  - Talk following this presentation 1630 Rm.A
    - Presenter: Dr. *Robert Bernstein*



- Further development of embedded chemical sensors
- New materials of interest including Poly(ethylene-co-vinyl acetate) (EVA)



Acknowledgments

- Project Funding:
  - C8
- Collaborators:

  Cody Washburn, Shawn Dirk, Don Bradley