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Sandia National Laboratories

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

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

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

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

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# Outline

## OBJECTIVE

- Enhance the current knowledgebase of polymer aging, in particular nylon, as a means to correlate degradation product formation to physical properties

## APPROACH

- Use selective isotopic labeling in conjunction with cryo-GC/MS to identify low-molecular weight volatile thermal-oxidative degradation products of nylon 6.6 and its monomers

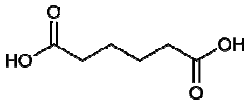
## IMPACT

- Understanding polymer degradation mechanisms that can be monitored and correlate to their useful lifetimes and reliability

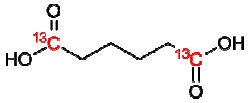
# Nylon is Used in Numerous Applications

# Methods

unlabeled adipic acid

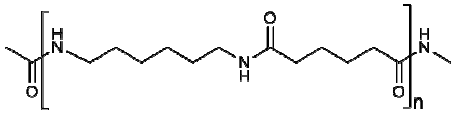


C-13 labeled adipic acid (99% enriched)

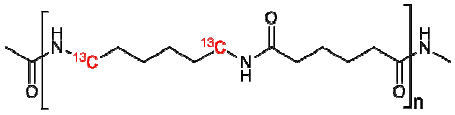


unlabeled 1,6-hexanediamine

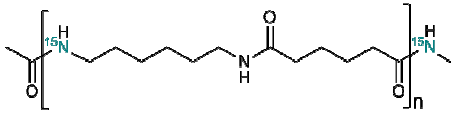
unlabeled nylon 6.6 (99% pure)



C-13 labeled nylon 6.6 (99% enriched)



N-15 labeled nylon 6.6 (51.4% enriched)

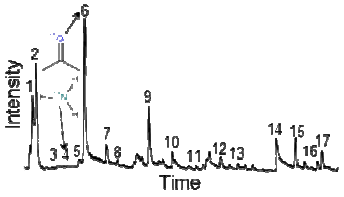


***Polymer synthesis:***
- unlabeled and isotopically labeled polymer and monomers
- vacuum bake purification

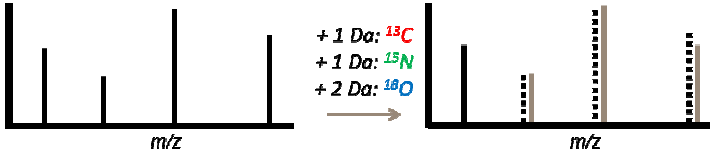
***Accelerated aging:***
- 1 to 243 days
- 138 °C
- 5 cc SS vessels
- $O_2$ or $^{18}O_2$ atmosphere

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

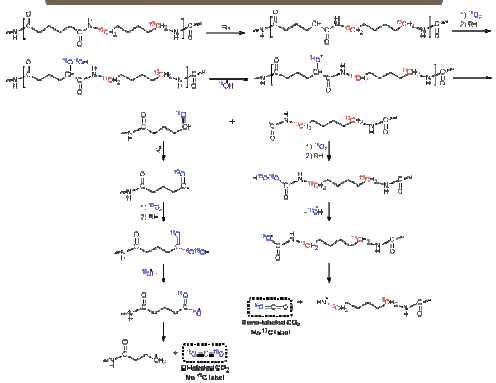
***Identify degradation products:***
- 18 volatile compounds identified

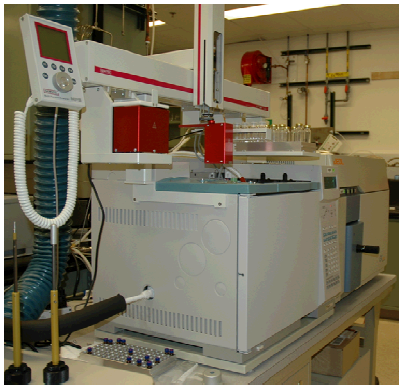



***Locate isotopically labeled atoms:***
- Monitor mass spectra for shifts and compare to ion fragmentation pathway




***elucidate degradation mechanisms[2,3]***



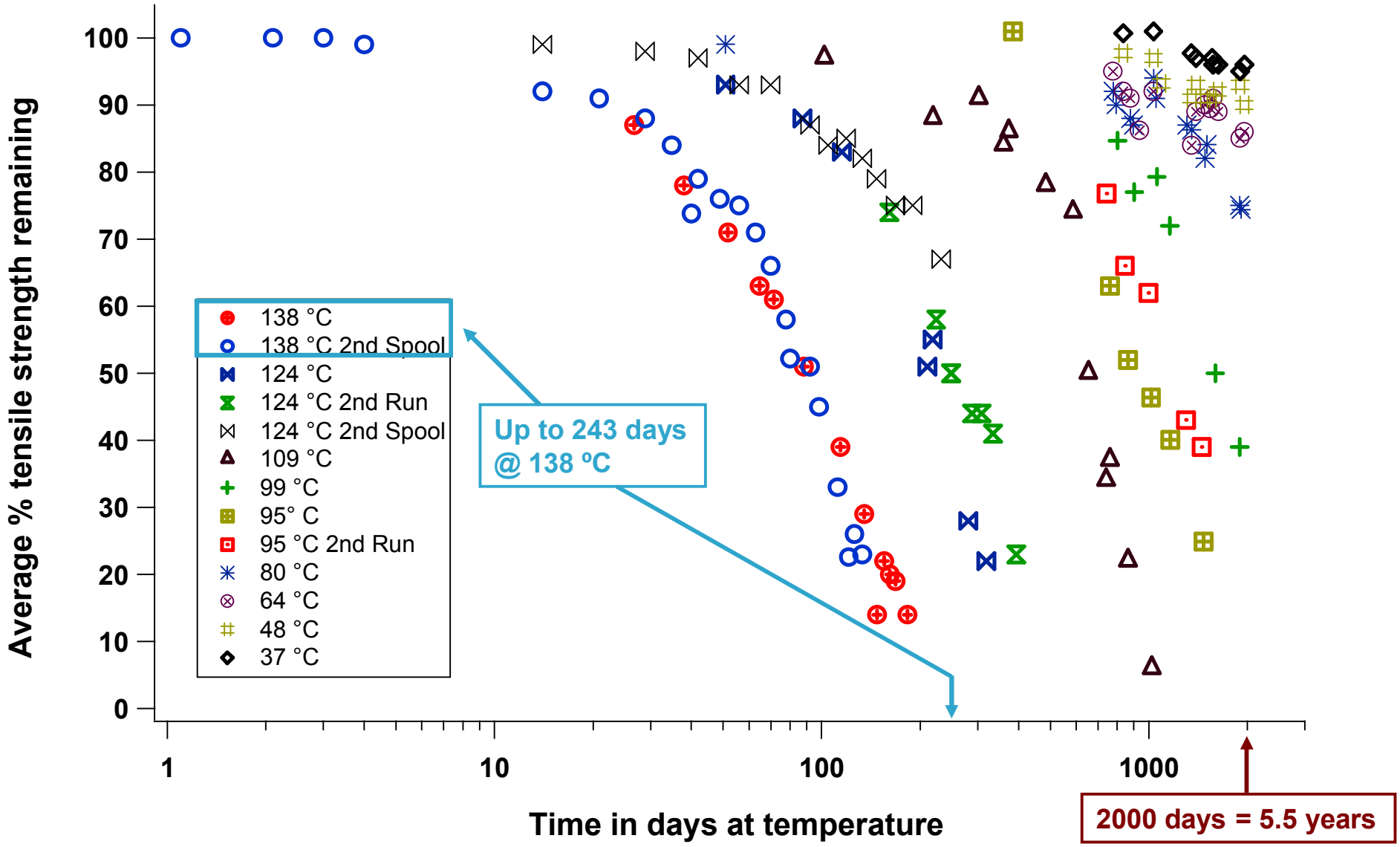


JEOL Gcmate II



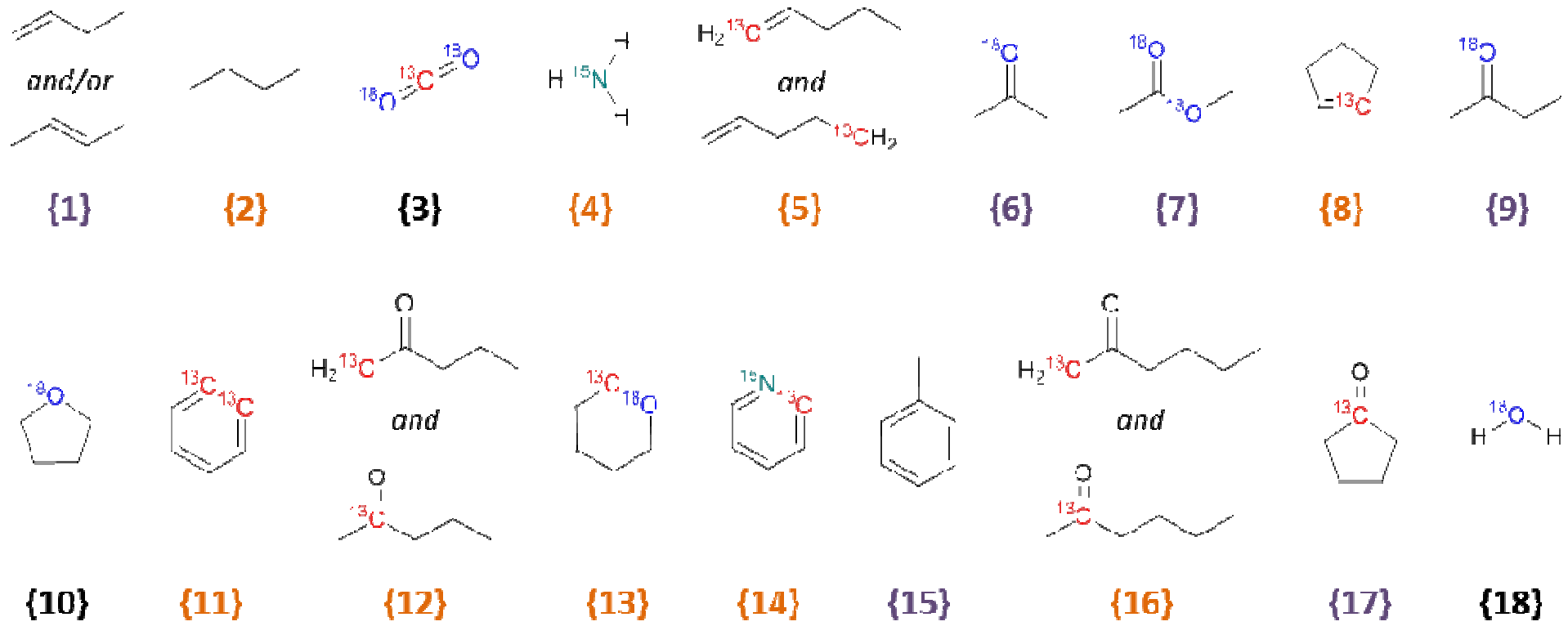
[2] White II, G.V., *et al.*: The Origins of $CO_2$ and $NH_3$ in the Thermal-Oxidative Degradation of Nylon 6.6. *Polym. Degrad. Stab., in press* (2012) [3] White II, G.V., *et al.*: Understanding the Long Term Thermal-Oxidative Aging Effects of Nylon 6.6 Using Isotopically Labeled Polymers. *Polym. Degrad. Stab., in preparation* (2012)

# Tensile Strength Relates to Selected Aging Conditions



# 18 Low-Molecular Weight Volatiles Detected

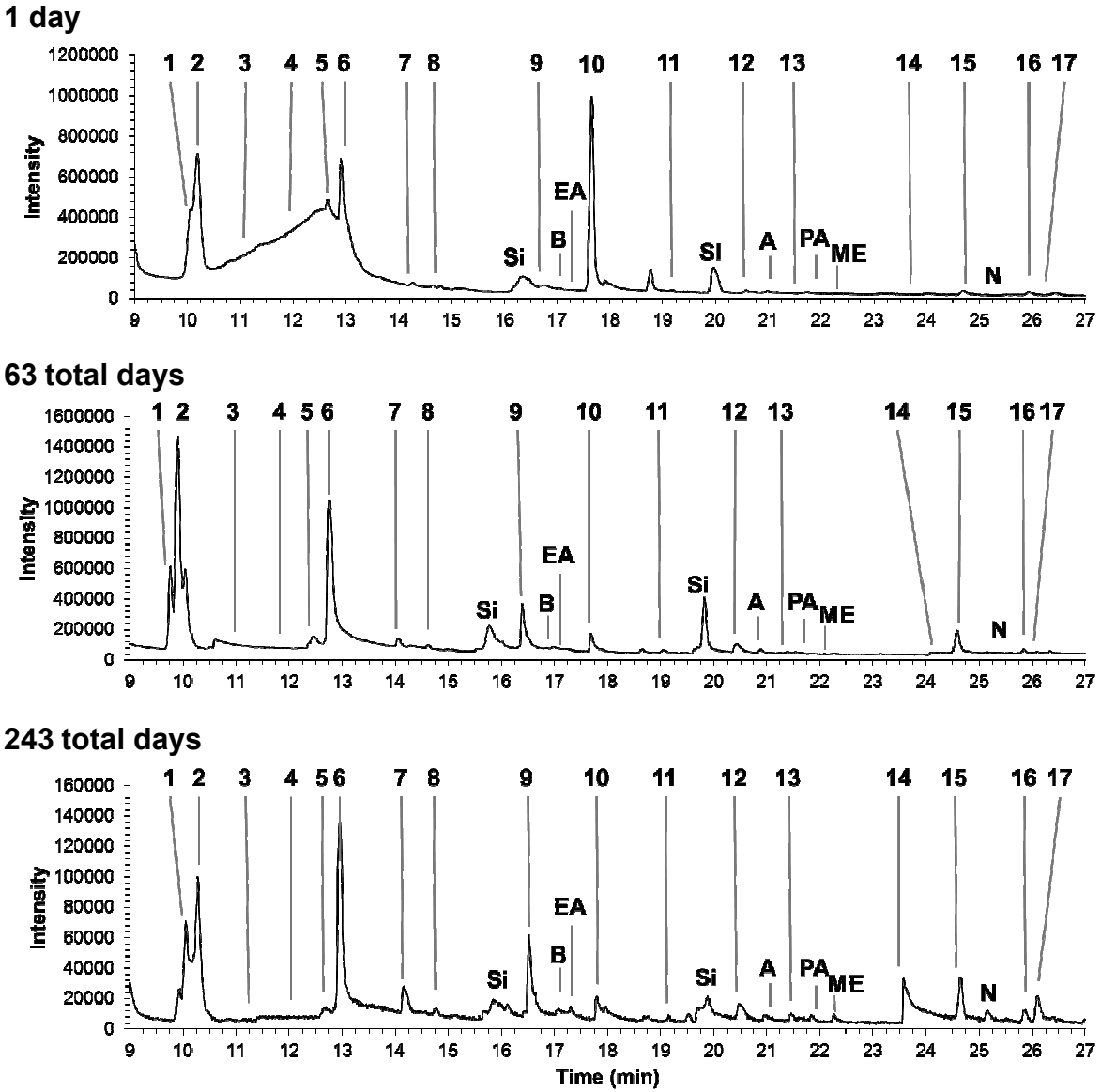
- 18 thermal-oxidative degradation species were identified
  - C-13, N-15, and O-18 labels were located within each structure




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

# Products have Reproducible Retention Times

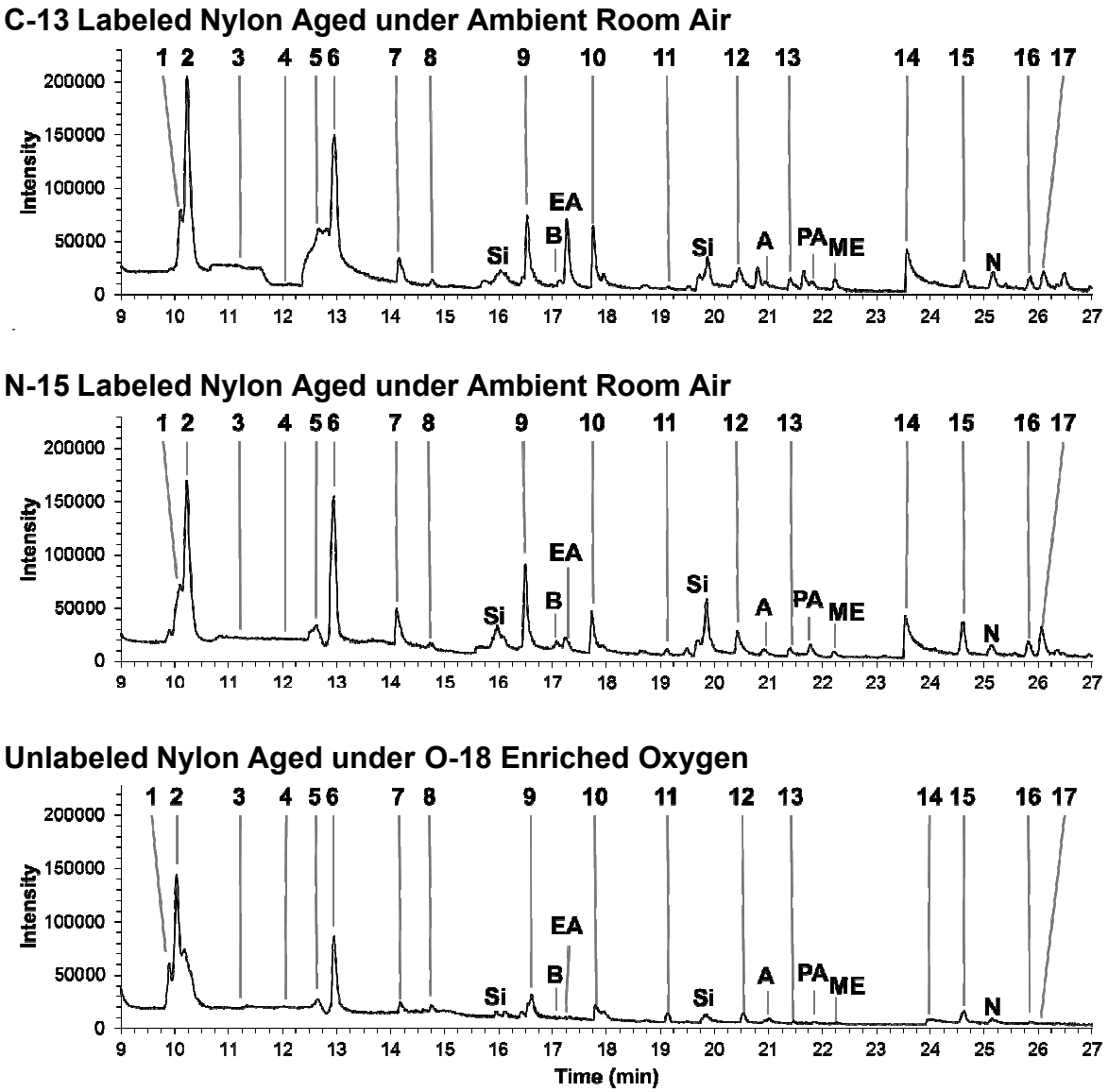
- Degradation product retention times align for all aging experiments
  - 1, 34, 63, 153, and 243 total days
- $CO_2$ **{3}** and $NH_3$ **{4}** source exhausted at early aging times
  - Leaving from end groups
- Water **{18}** was detected in the injection artifact, background, and final chromatogram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



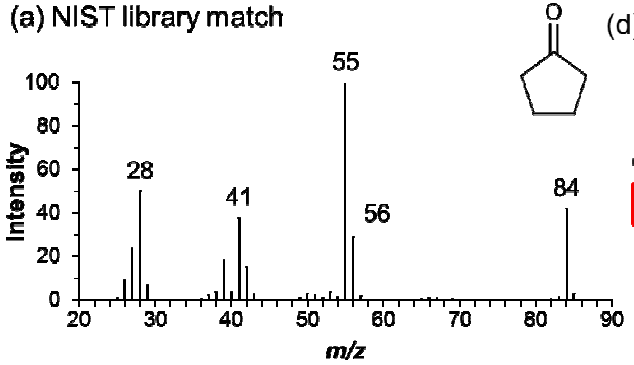
# Isotopic Labeling does not Effect Mechanisms

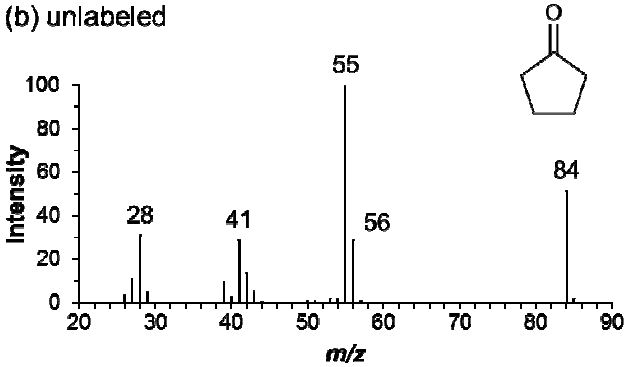
- Retention times for aged unlabeled *(not shown)* and all isotopically labeled nylon 6.6 samples align

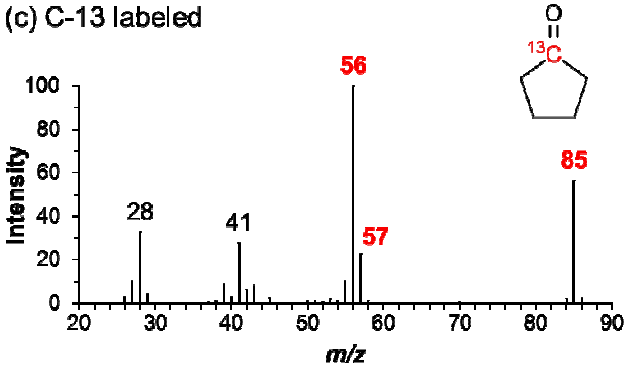
- Isotopic labels did not change the underlying nylon 6.6 degradation mechanisms

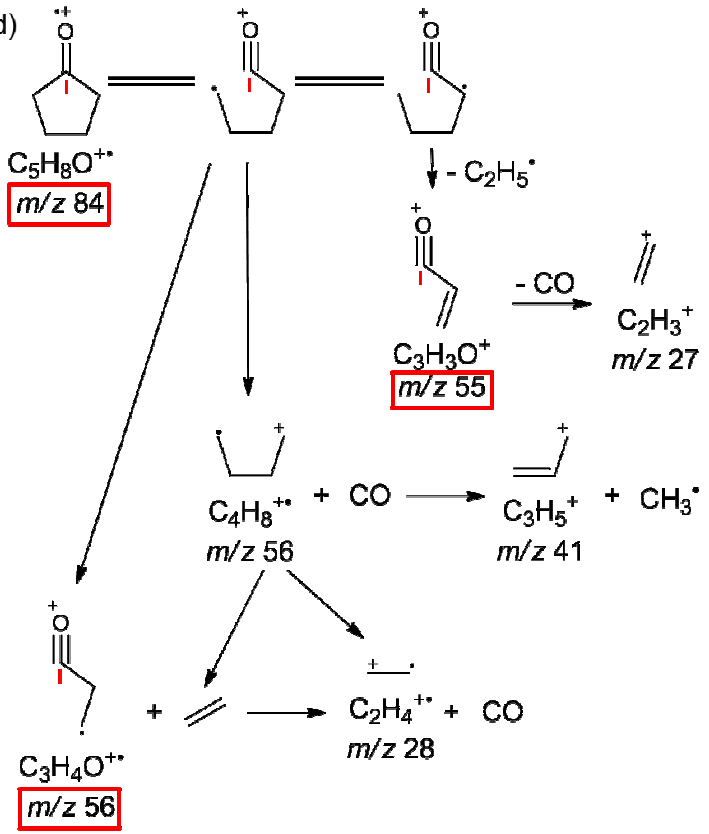


# Cyclopentanone

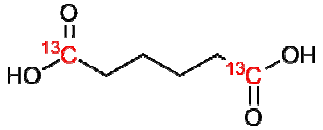


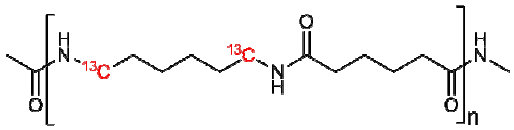

*C-13 labeled adipic acid (99% enriched)*

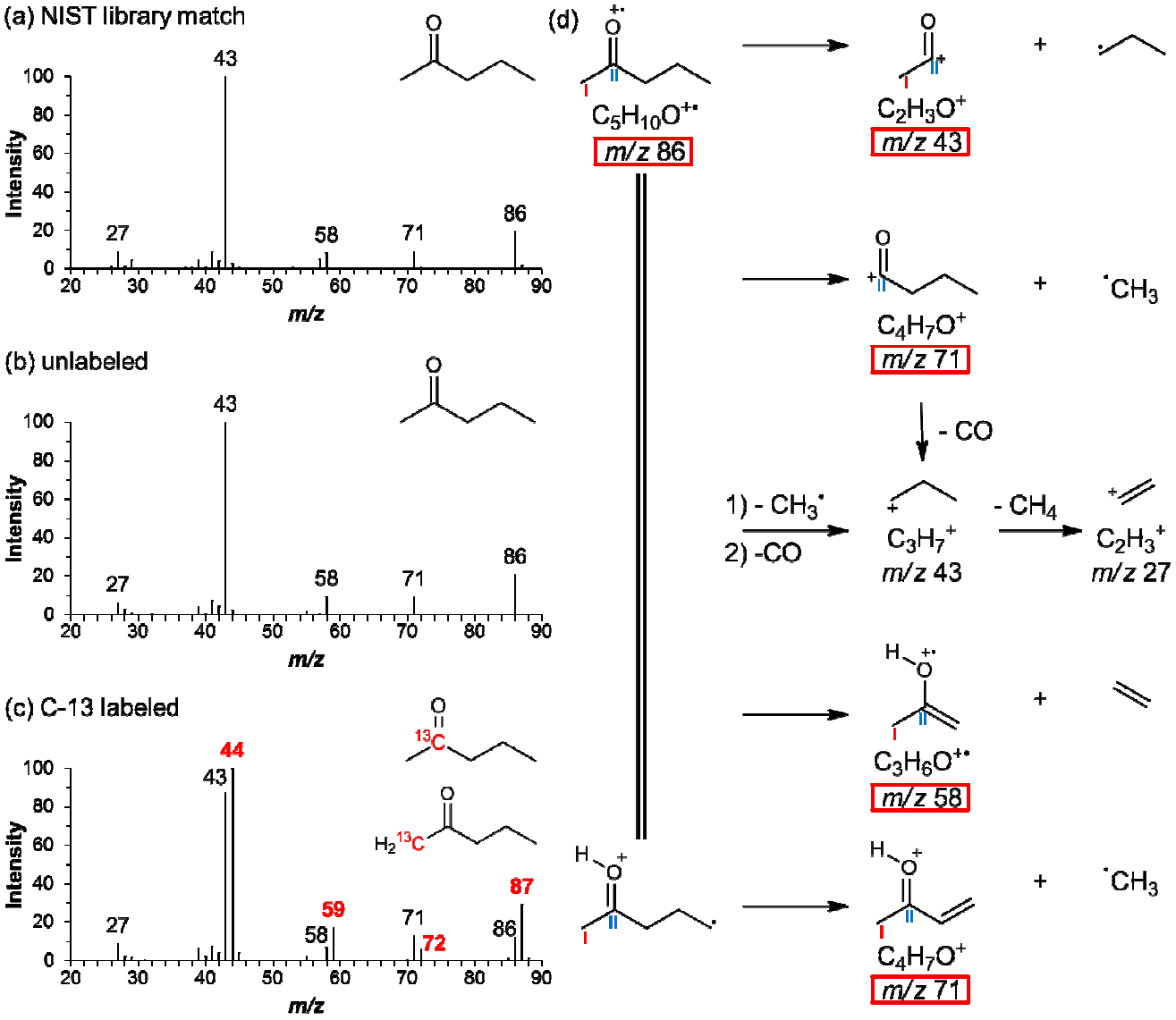



- One C-13 atom
  - *m/z* 84 → *m/z* 85
- C-1, C-2, or C-3
  - +1 Da: *m/z* 56 ($C_3H_4O^{+\bullet}$)
  - +1 Da: *m/z* 55 ($C_3H_3O^{+}$)
- Not C-2 or C-3
  - +0 Da: *m/z* 27 ($C_2H_3^{+}$)
  - +0 Da: *m/z* 56 ($C_4H_8^{+\bullet}$)
  - +0 Da: *m/z* 28 ($C_2H_4^{+\bullet}$)
  - +0 Da: *m/z* 41 ($C_3H_5^{+}$)
- 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)*

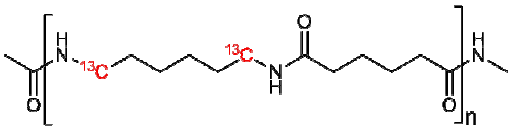




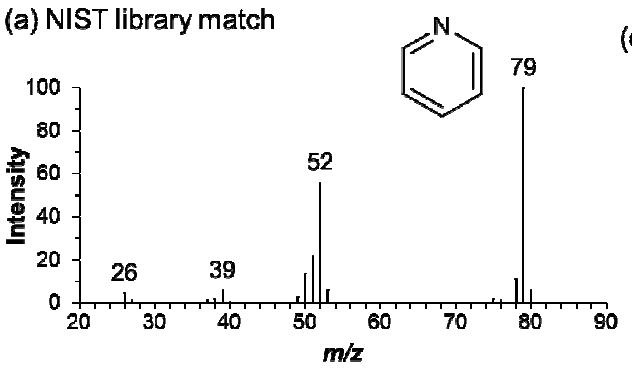

- One C-13 atom
  - *m/z* 86 → *m/z* 87
- C-1, C-2, or C-3
  - +1 Da: *m/z* 58 ($C_3H_6O^{+\bullet}$)
  - +1 Da: *m/z* 71 ($C_4H_7O^+$)
    - Two structures
- Not C-3
  - +1 Da: *m/z* 43 ($C_2H_3O^+$)
  - +0 Da: *m/z* 43 ($C_3H_7^+$)
  - +0 Da: *m/z* 27 ($C_2H_3^+$)
- Mixture of C-1 and C-2
  - *m/z*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

# Pyridine

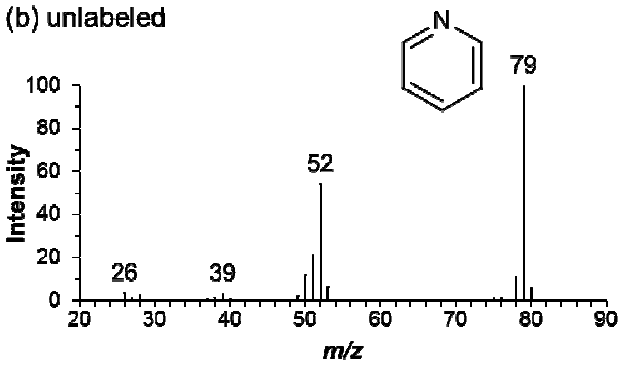
*C-13 labeled nylon 6.6 (99% enriched)*



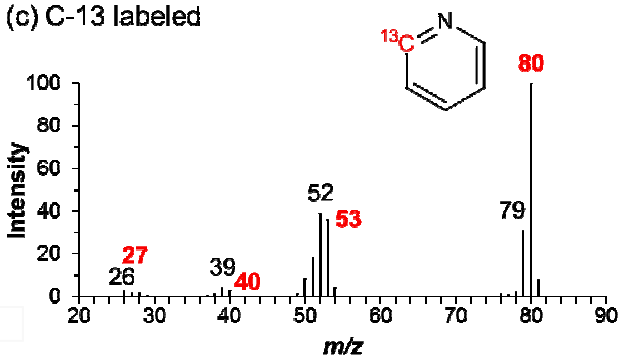
(a) NIST library match



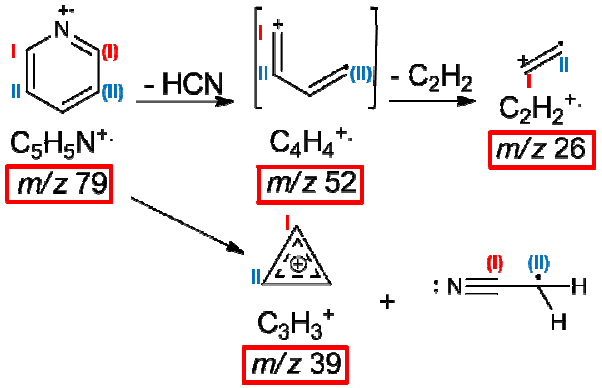

(b) unlabeled




(c) C-13 labeled




(d)




*Example:*

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

- 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 ($C_2H_2^{+\bullet}$)
- 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

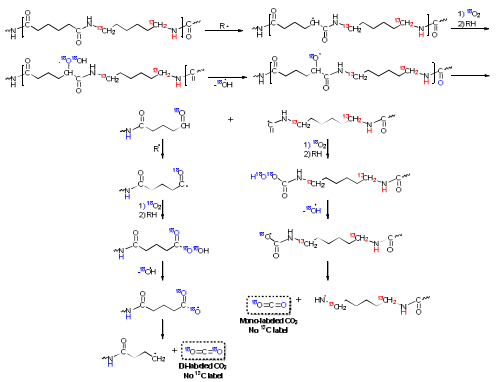
# Conclusions

- 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[1]

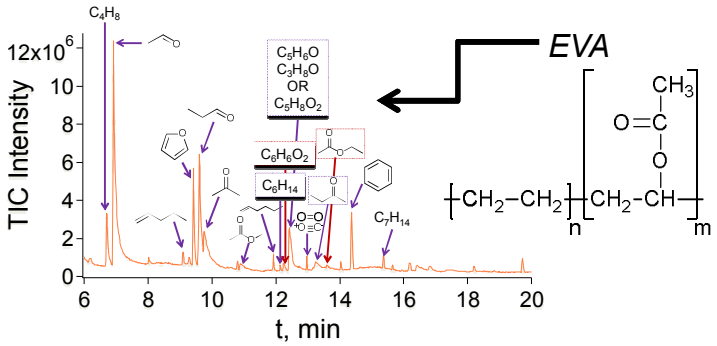

[1] Smith, J.N., *et al.*: Characterization of Volatile Nylon 6.6 Thermal-Oxidative Degradation Products by Selective Isotopic Labeling and Cryo-GC/MS. *JASMS, in press* (2012)

# Future Directions

- Elucidating nylon 6.6 degradation mechanisms
  - Talk directly following this presentation
    - Presenter: *Gregory V. White II*



- Poly(ethylene-co-vinyl acetate) (EVA)
  - Preliminary results → Wednesday poster
    - Presenter: *Jonell N. Smith*




# Acknowledgments


- Project Funding:
  - National Nuclear Security Administration (NNSA)
    - Enhanced Surveillance Campaign (ESC)