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Understanding the Thermal-Oxidative Degradation of Nylon 6.6 using Isotopically Labeled Polymers

Gregory Von White II,[a] Roger L. Clough,[a] Jonell N. Smith,[b]
Mike I. White,[b] James M. Hochrein,[b] Robert Bernstein[a]
Sandia National Laboratories, Albuquerque, NM 87185
Org. 1821—Organic Materials[a] and Org. 1825—Materials Reliability[b]

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National Nuclear Security Administration

Polymer aging in general

- Polymers used for essentially every application in today's society (automotive, medical, food, defense, clothing, etc…)

- Thermal degradation for many materials has been actively pursued using techniques such as pyrolysis and TGA
  - Fast/inexpensive
  - Provides information about thermal degradation products
  - Mechanisms altered; not good representation of real world (low temp long times)

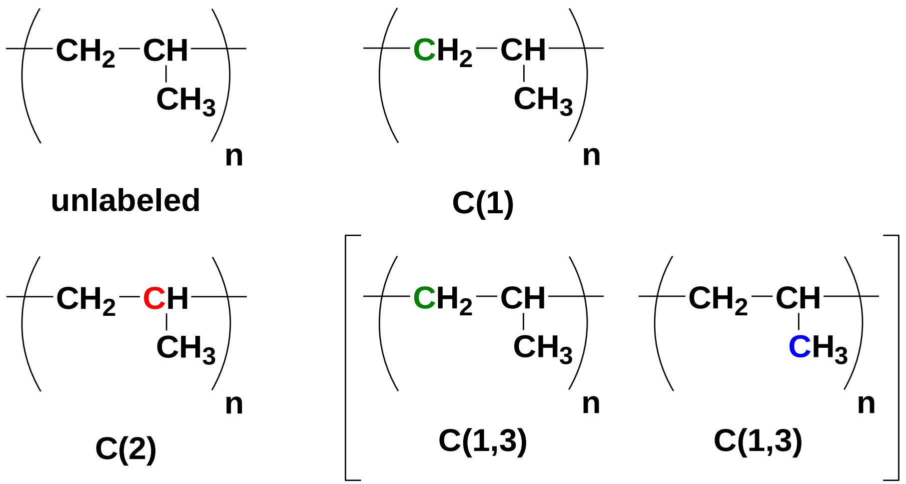
- Detailed oxidative degradation mechanisms and products that are formed are not as well understood for many polymers
  - Aging dependent and time dependent
  - Formulation dependent (fillers, additives, antioxidants, lubricants, etc.)

- Isotopic labeling of polymers can reveal detailed mechanistic information about oxidative degradation to gain insights into realistic lifetimes of materials

- Understanding degradation mechanisms is the gateway for sensor development to identify unique volatile degradation products for condition monitoring
  - Early warning system
  - Establish real-time status update

Polypropylene studies served as the model for nylon studies

- Polypropylene was isotopically labeled
- Aged under thermal-oxidative conditions
- Characterized using mass spectrometry to identify mass shifts and degradation products
- Piece puzzle together to establish mechanism for oxidative attack and decomposition



Relative ^{13}C abundance (%) of selectively-labeled polypropylene samples

Sample	CH	CH_2	CH_3
C(1)	1.0	96.7	2.3
C(2)	98.5	0.8	0.8
C(1,3)	0.9	68.3	30.8

Polypropylene published and 'done'

(1) Mowery, D. M.; Assink, R. A.; Derzon, D. K.; Klamo, S. B.; Bernstein, R.; Clough, R. L. *Radiation Physics and Chemistry,* Radiation Oxidation of Polypropylene: A Solid-State 13C NMR Study using Selective Isotopic Labeling **2007**, *76*, 864-878.

(2) Mowery, D. M.; Assink, R. A.; Derzon, D. K.; Klamo, S. B.; Clough, R. L.; Bernstein, R. *Macromolecules,* Solid-State 13C NMR Investigation of the Oxidative Degradation of Selectively Labeled Polypropylene by Thermal Aging and gamma-Irradiation **2005**, *38*, 5035-5046.

(3) Mowery, D. M.; Clough, R. L.; Assink, R. A. *Macromolecules,* Identification of Oxidation Products in Selectively Labeled Polypropylene with Solid-State 13C NMR Techniques **2007**, *40*, 3615-3623.

(4) Thornberg, S. M.; Bernstein, R.; Derzon, D. K.; Irwin, A. N.; Klamo, S. B.; Clough, R. L. *Polymer Degradation and Stability,* The Genesis of CO2 and CO in the Thermooxidative Degradation of Polypropylene **2007**, *92*, 94-102.

(5) Thornberg, S. M.; Bernstein, R.; Mowery, D. M.; Klamo, S. B.; Hochrein, J. M.; Brown, J. R.; Derzon, D. K.; Clough, R. L. *Macromolecules,* Insights into Oxidation Pathways, from Volatile Products of Polypropylene with Selective Isotopic Labeling **2006**, *39*, 5592-5594.

(6) Bernstein, R.; Thornberg, S. M.; Assink, R. A.; Irwin, A. N.; Hochrein, J. M.; Brown, J. R.; Derzon, D. K.; Klamo, S. B.; Clough, R. L. *Polymer Degradation and Stability,* The origins of volatile oxidation products in the thermal degradation of polypropylene, identified by selective isotopic labeling **2007**, *92*, 2076-2094.

(7) Bernstein, R.; Thornberg, S. M.; Assink, R. A.; Mowery, D. M.; Alam, M. K.; Irwin, A. N.; Hochrein, J. M.; Derzon, D. K.; Klamo, S. B.; Clough, R. L. *Nuclear Instruments and Methods in Physics Research B,* Insights into Oxidation Mechanisms in Gamma-Irradiated Polypropylene, Utilizing Selective Isotopic Labeling with Analysis by GC/MS, NMR and FTIR **2007**, Accepted for Publication.

(8) Bernstein, R.; Thornberg, S. M.; Irwin, A. N.; Hochrein, J. M.; Derzon, D. K.; Klamo, S. B.; Clough, R. L. *Polymer Degradation and Stability,* Radiation-oxidation mechanisms: Volatile organic degradation products from polypropylene having selective C-13 labeling, studied by GC/MS **2008**, *93*, 854-870.

Many high reliability military and civilian products are made of nylon

- Nylon used for wide variety of products
- Oxidation reduces the overall lifetime of high reliability materials altering performance
- Mechanism must be understood to predict degradation product formation and develop sensors enabling early warning




Approaches/Goals

Macroscopic level

Physical Properties

Tensile Property

Permeation

Elongation

Dimensional changes

Molecular Level

Chemical Properties

UV-VIS Spectroscopy

Infra-red Spectroscopy

Surface Analysis

Differential Scanning Calorimetry

Molecular Weight Analysis

X-Ray Analysis

Density

Additives

Nuclear Magnetic Resonance

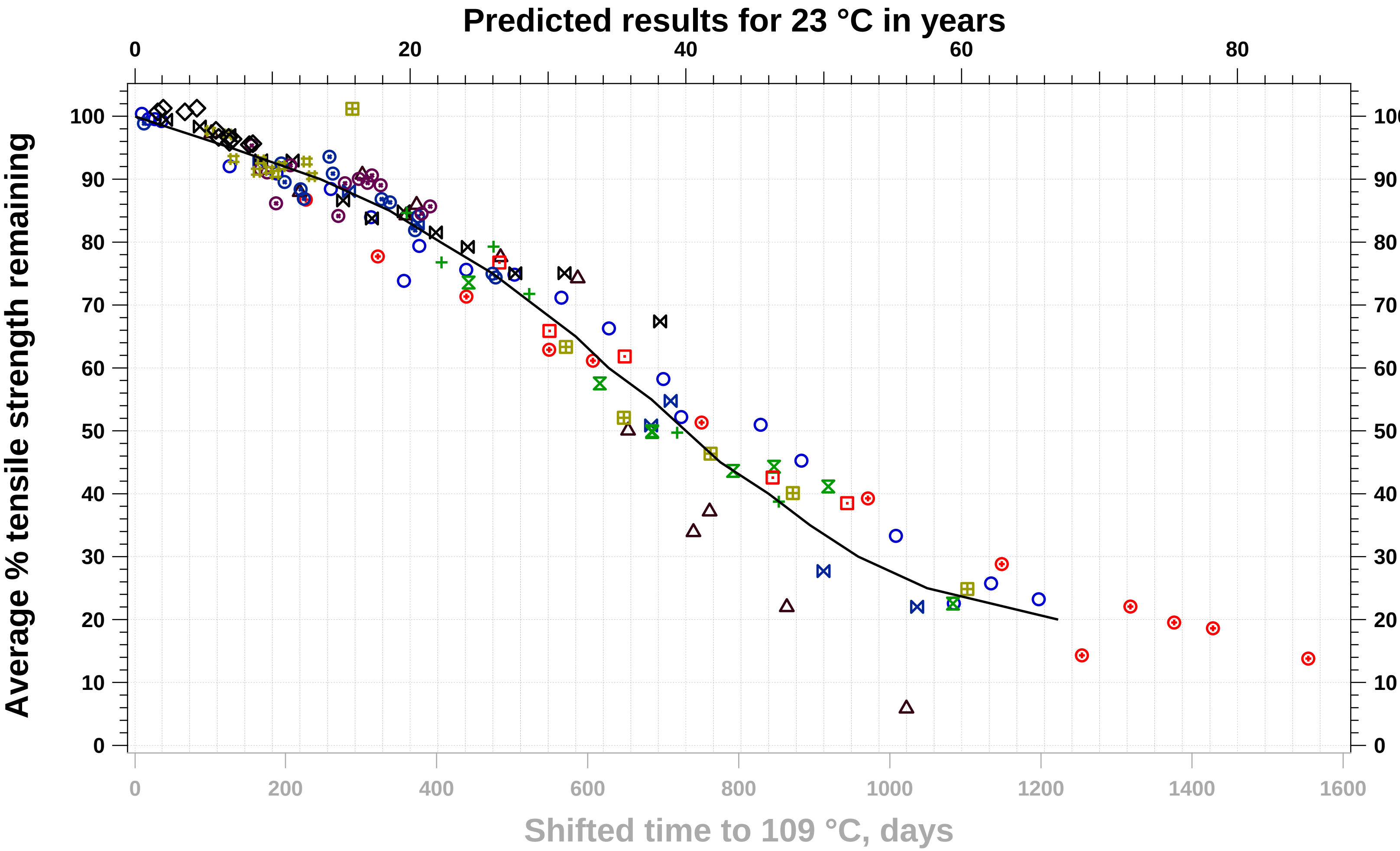
GPC

Mass Spectrometry

Goals

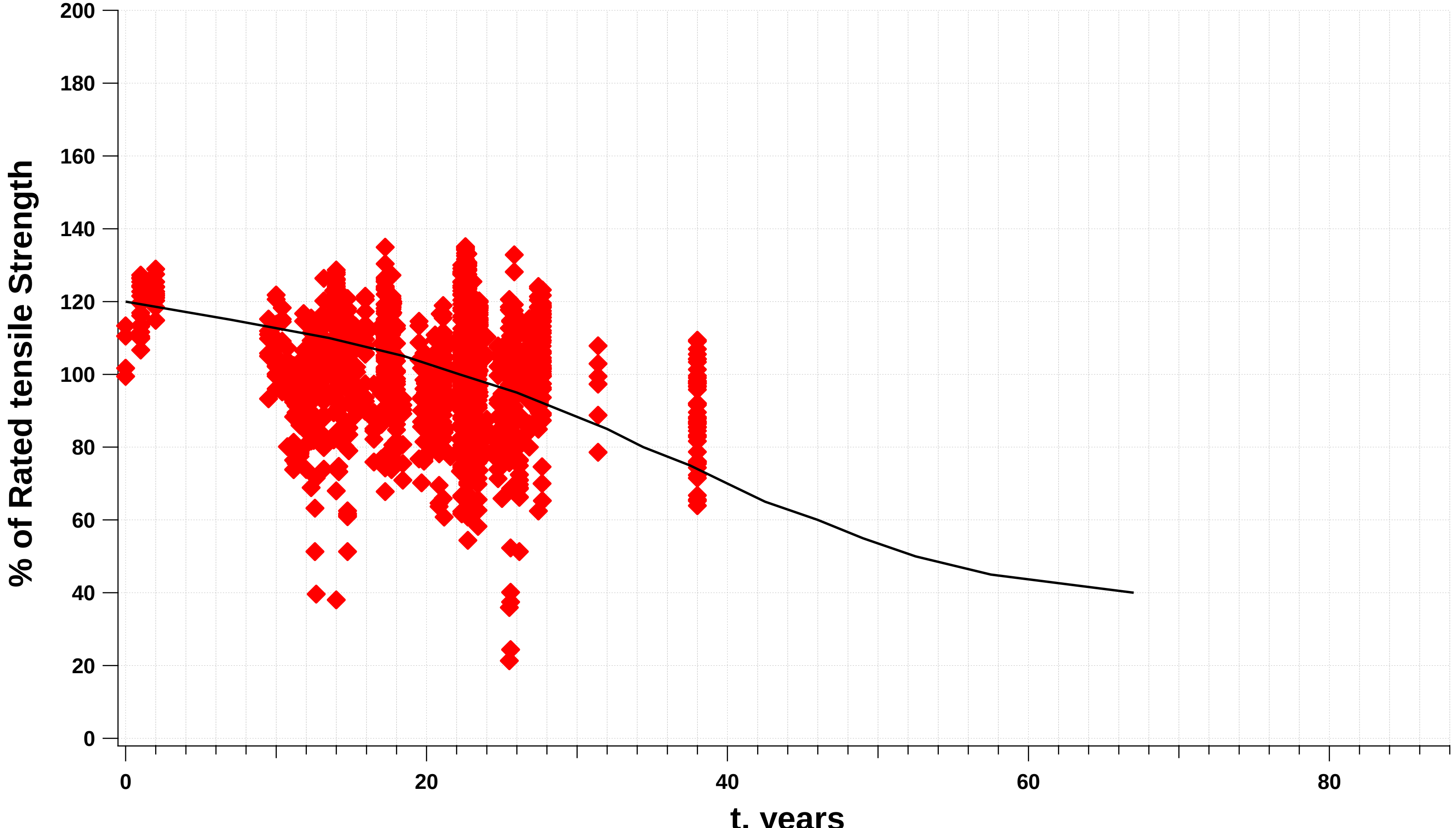
- **Prediction of physical properties vs. time**
  - **Predict remaining physical properties of field materials**
- Develop condition monitoring method

Nylon 6.6 Accelerated Aging Studies



Bernstein, R.; Gillen, K. T. *Polym. Degrad. Stab.* **2010**, *95*, 1471-1479.

Lifetime Prediction Validation with Field Aged Data



Nylon Field Aged Parachute Materials and our Thermal-Oxidative Prediction Line at 23 °C

Nylon Degradation Chemistry

"A considerable amount of work has already been carried out to investigate the mechanism of nylon degradation, but the exact mechanism of the degradation has still not been conclusively established."

Shamey, R.; Sinha, K. *Rev. Prog. Color.* **2003**, *33*, 93-107.

Approaches/Goals

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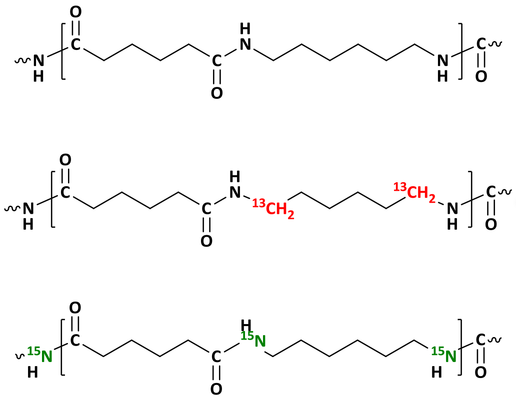
Methodologies

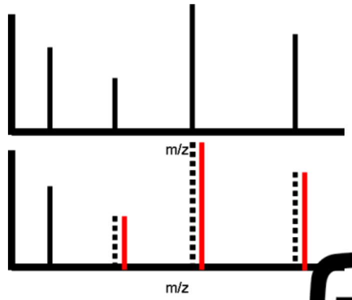


Isotopically labeled and unlabeled nylon 6.6 were aged in 5 mL stainless steel vessels between 1 and 243 days at 109 °C and 138 °C

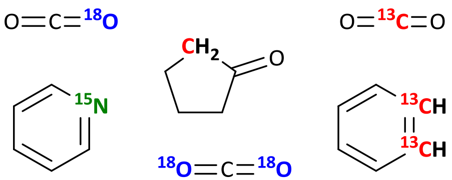
Cryo-GC/MS

Identify degradation products

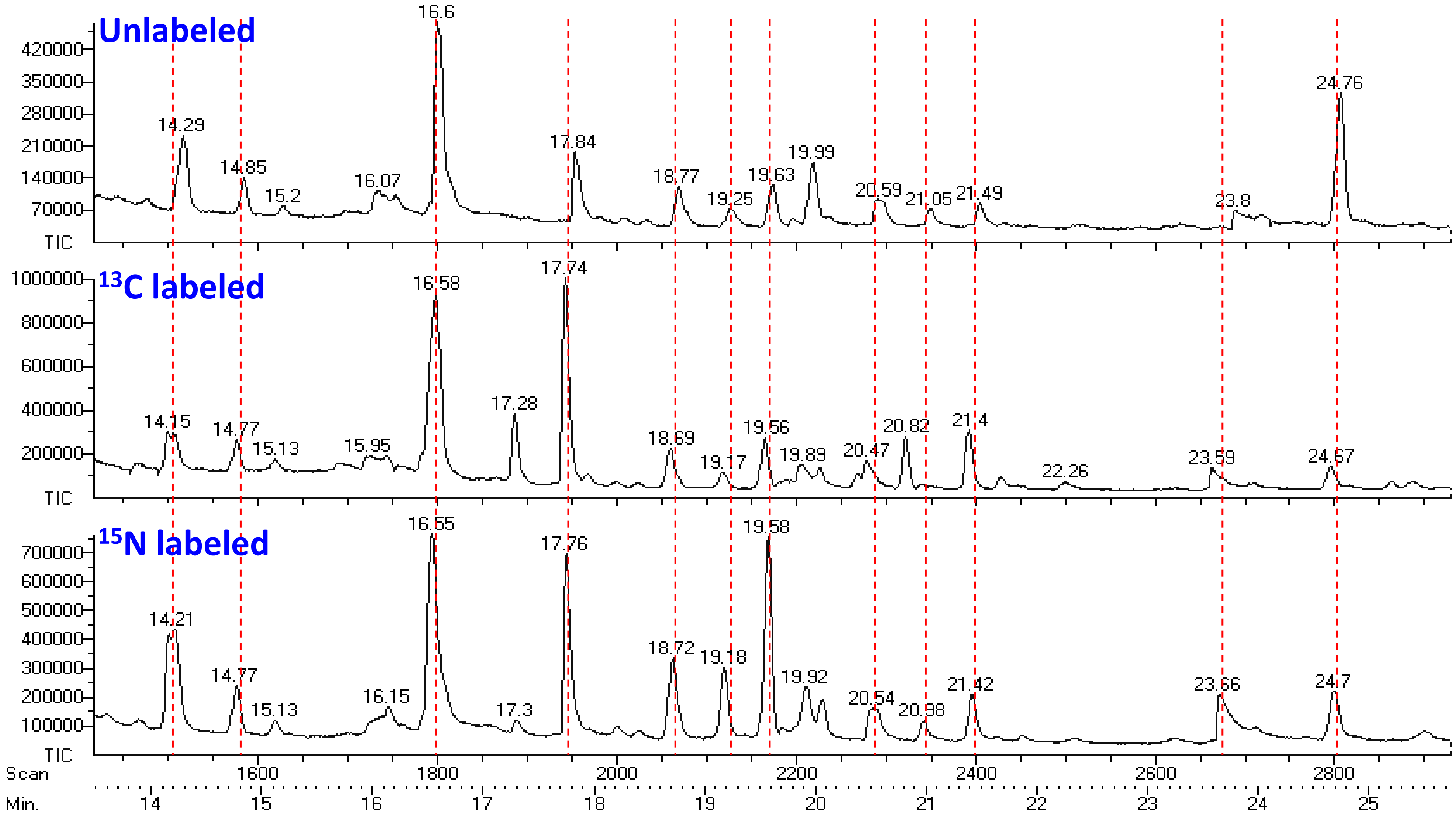
Monitor mass spectra for shifts



Use mass shifts to determine degradation mechanisms

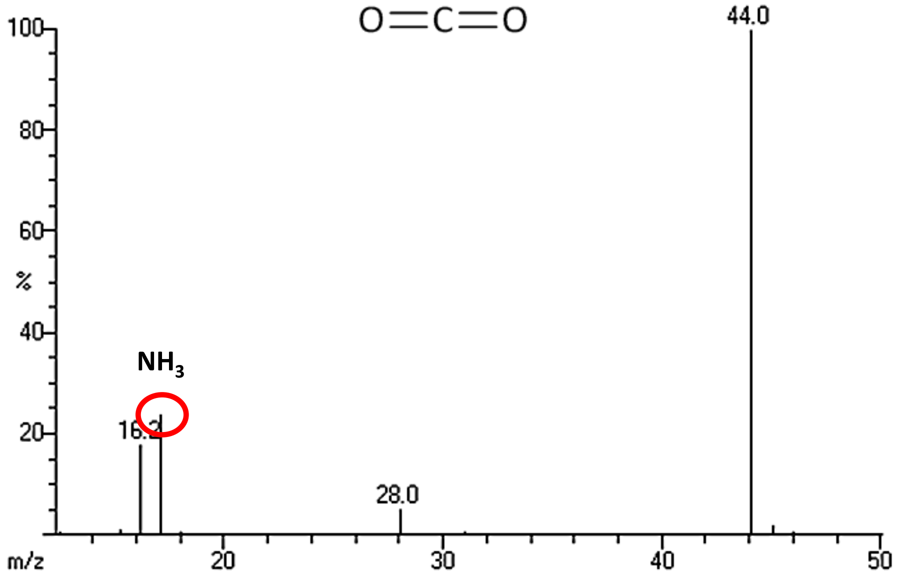


Selected region of TIC for the three nylons tested

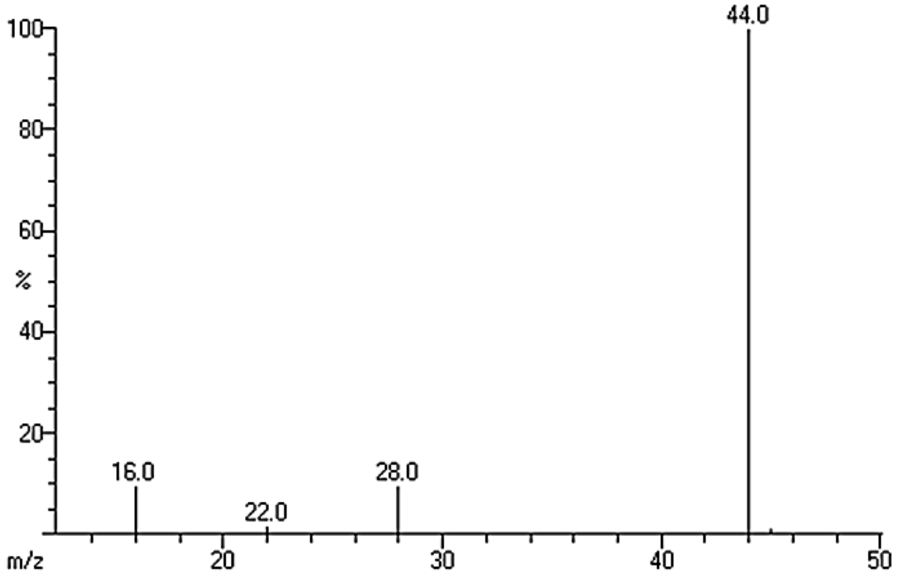


Nylon degradation follows similar mechanism for all variants.
Chromatograms show high reproducibility .

Example: Carbon Dioxide

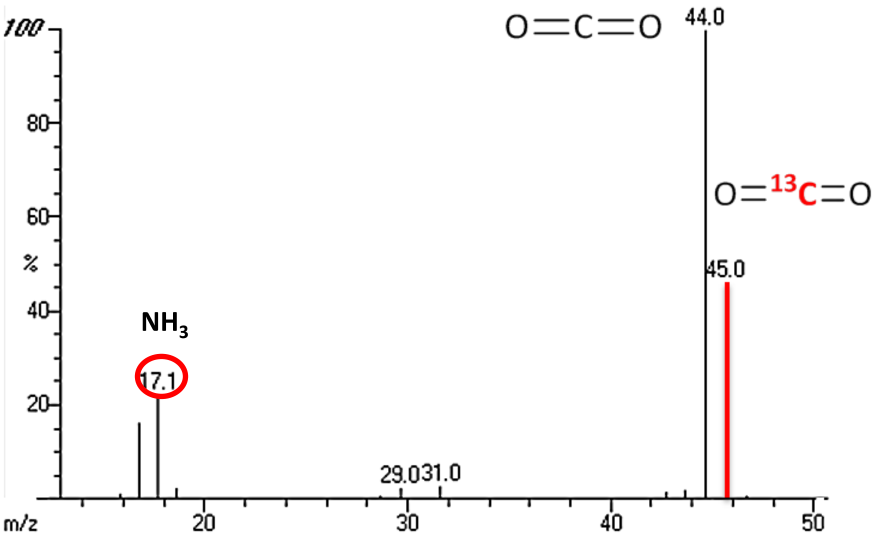


A representative carbon dioxide mass spectrum from oxidation of unlabeled nylon 6.6

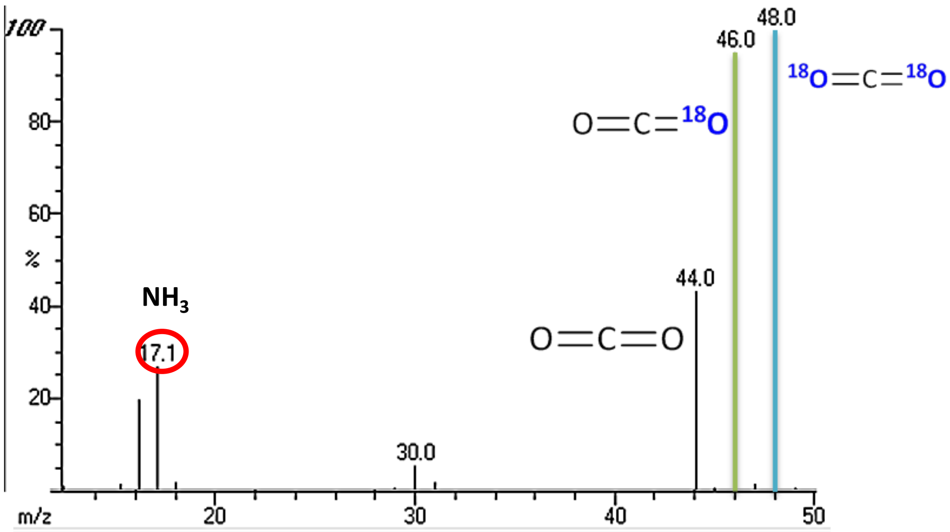


NIST Mass Spectral Library match of carbon dioxide spectrum

Example: Carbon Dioxide

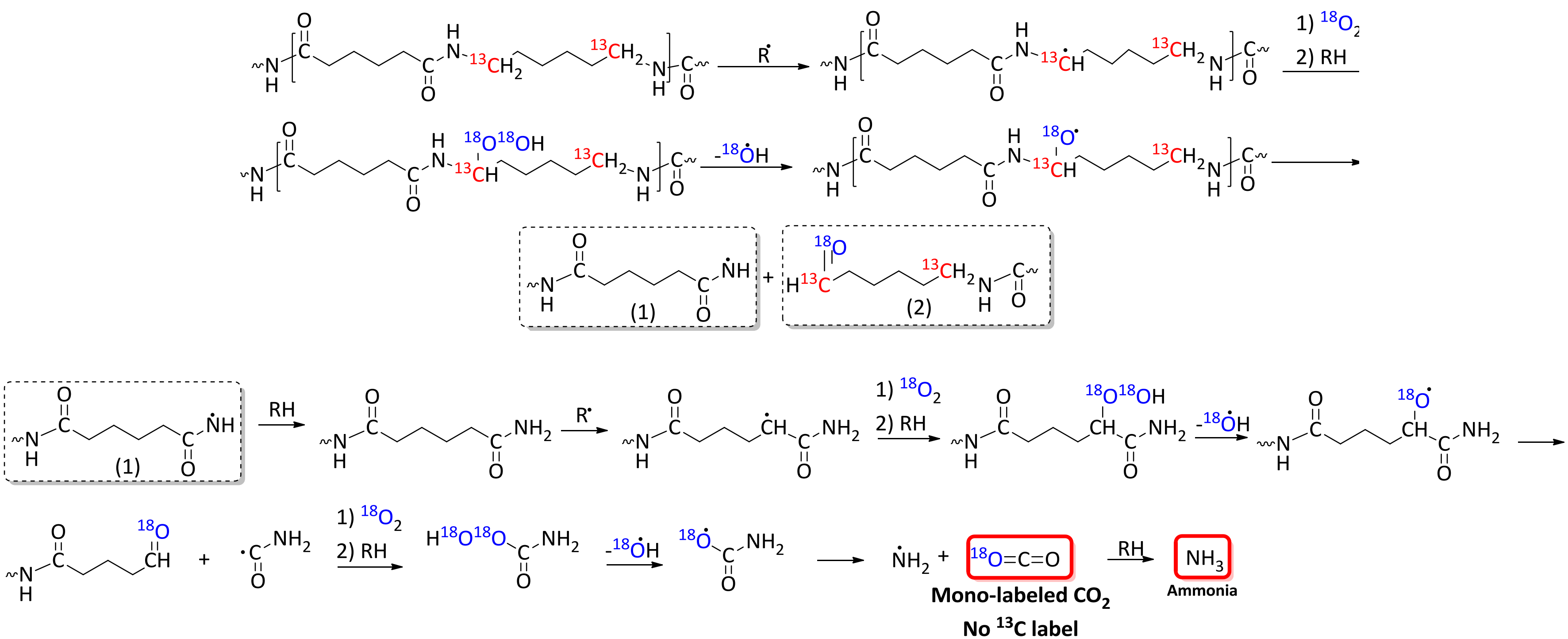


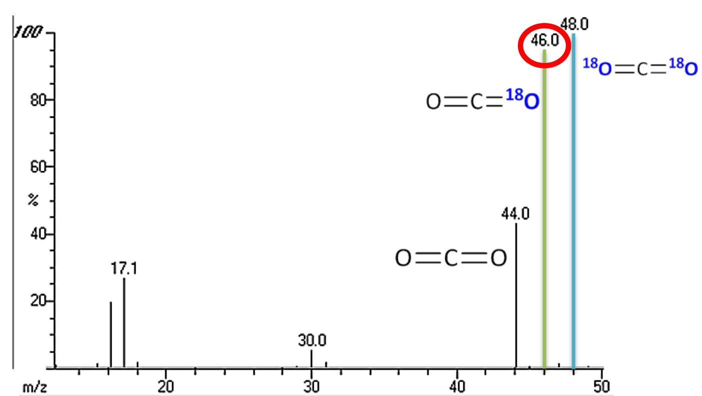
Carbon dioxide mass spectrum from oxidation of ^{13}C labeled nylon 6.6 in an oxygen environment



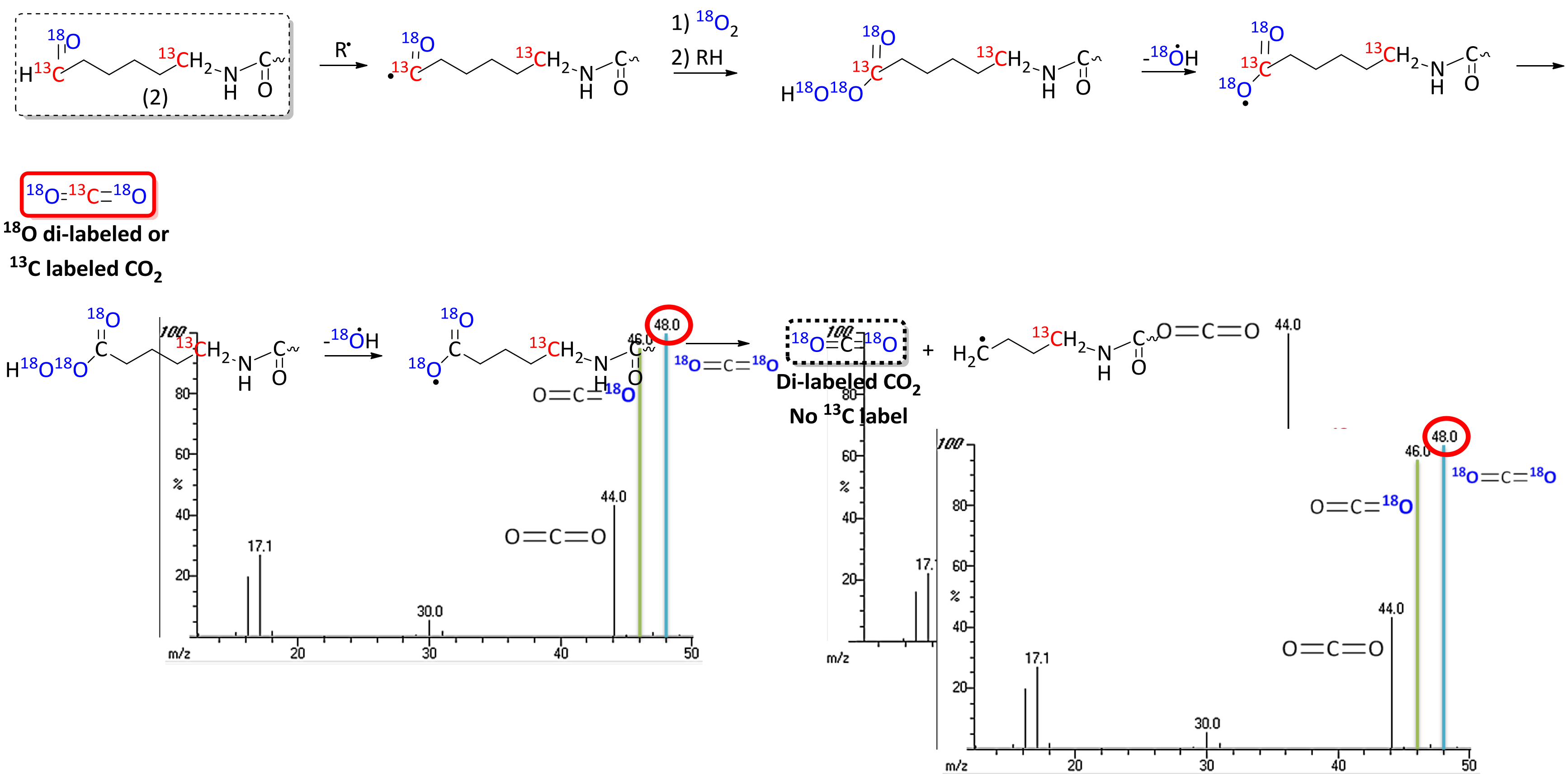
Carbon dioxide mass spectrum from oxidation of unlabeled nylon 6.6 in an ^{18}O enriched environment

Proposed Origins of CO_2

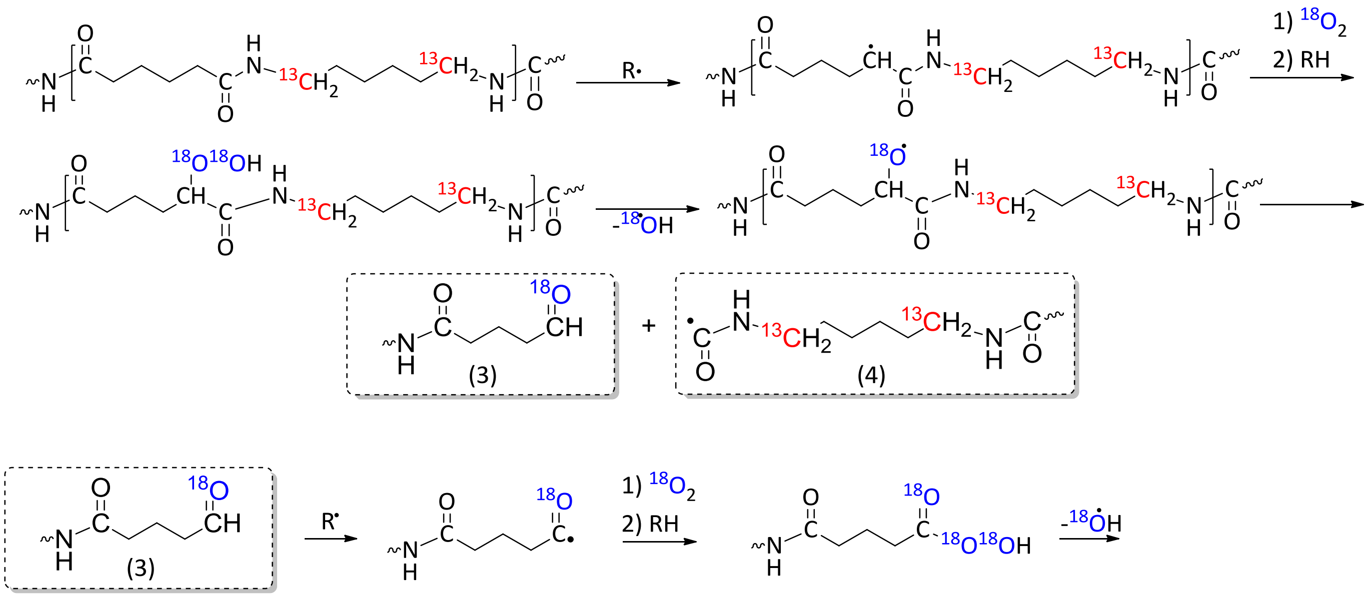


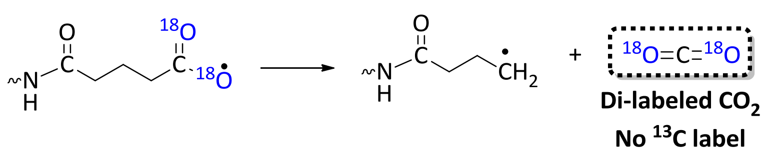


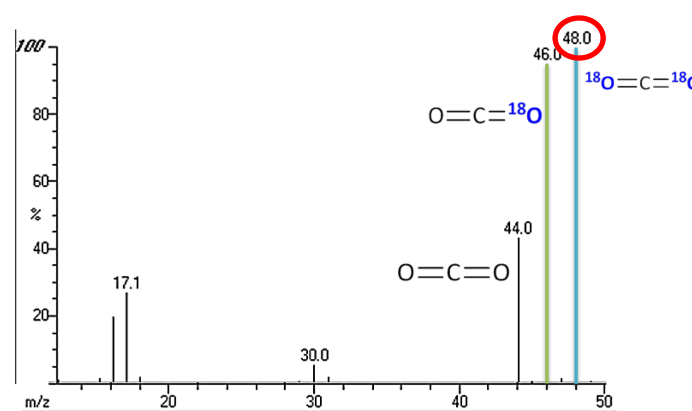
Proposed Origins of CO_2



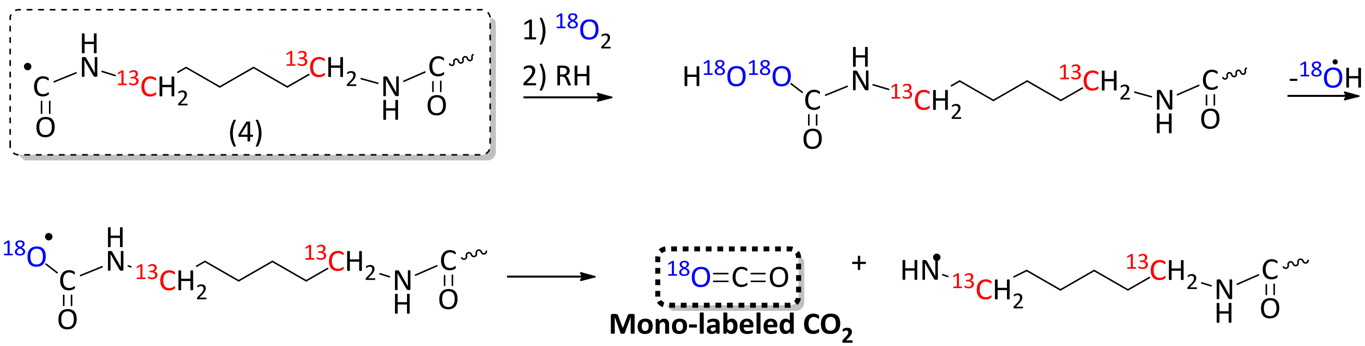
Proposed Origins of CO_2





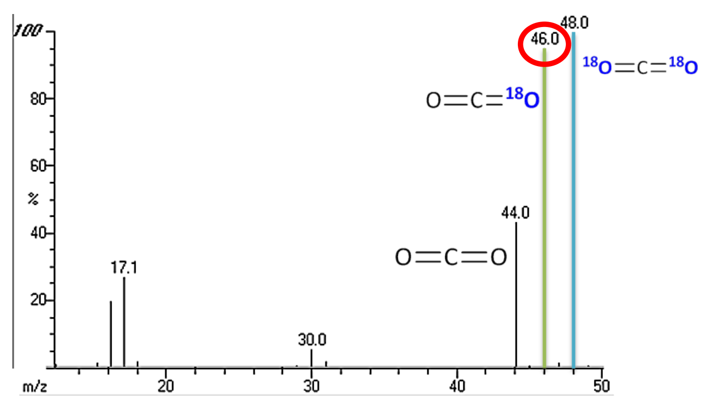


Proposed Origins of CO_2

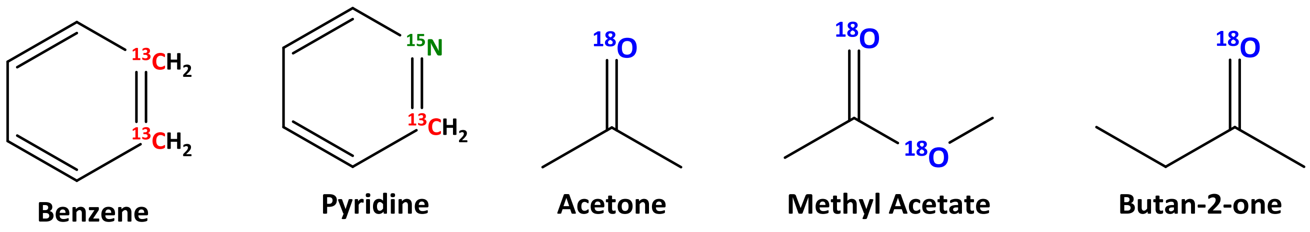


Mono-labeled CO_2

No ^{13}C label



Other Molecules Identified



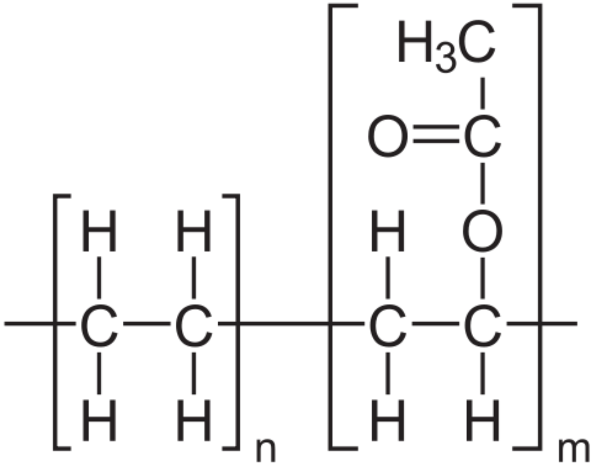
Future work will include the identification of the underlying chemistries which lead to the formation of the above molecules

Conclusions

- By leveraging isotopic labels, we have proposed the origins of carbon dioxide and several possible degradation mechanisms
- We have identified and are proposing degradation mechanisms for other low molecular weight thermal-oxidative degradation products

Future Work

- Investigate the hydrolytic degradation mechanisms of nylon 6.6
- Initiate accelerated aging studies on poly(ethylene co-vinyl acetate), EVA



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QUESTIONS?