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Investigating Polymer Degradation Using High-resolution Mass Spectroscopy

MS&T Review

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Organic Materials

Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the United States Department of Energy's National Nuclear Security Administration under contract DE-AC04-94AL85000.

Motivation and Goal

Problem:

- **Polymer aging is a degradation process that can adversely impact stockpile reliability.**
- **Polymer degradation mechanisms are complex and elusive**

Objective:

- **Develop a novel and more effective experimental methodology to characterize and understand polymer-aging mechanisms**

Age-related changes in polymer properties can only be predicted with science-based tools.

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Approach

Infer chemical mechanisms for polymer degradation through the study of volatiles evolved during the breakdown of the polymer molecular structure.

Steps:

1. **Choose a polymer: polypropylene**
2. **Age polymers in O_2 and $^{18}O_2$**
3. **Preconcentrate trace volatile organics**
   - **Cryofocusing preconcentration**
   - **Solid phase microextraction (SPME)**
4. **Analyze volatiles**
   - **Gas chromatography (trace organic separation)**
   - **Mass spectroscopy (electron impact and chemical ionization)**
   - **High-resolution mass spectroscopy (non-trace gases)**

Mass spectroscopy is ideally suited for generating this detailed information.

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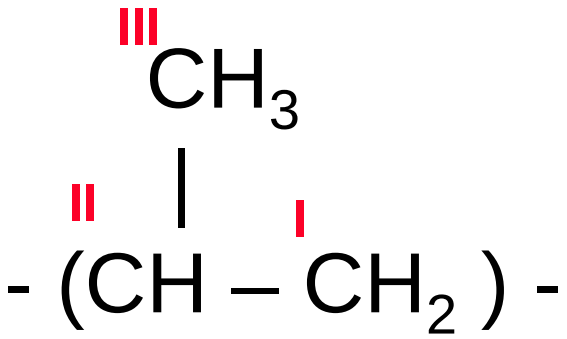
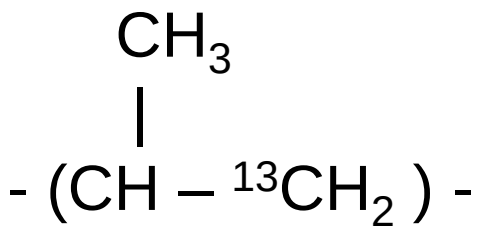
Advantages of using polypropylene for method development

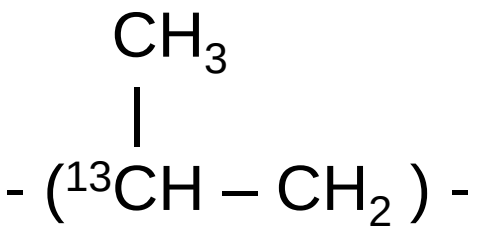
- **The polypropylene molecular structure is comprised of three unique, identifiable carbons**
- **An extensive knowledge base exists in the literature that is useful for validating the study findings.**
- **Carbon-13 isotopically labeled samples are available**



unlabeled



C(1)-labeled



C(2)-labeled

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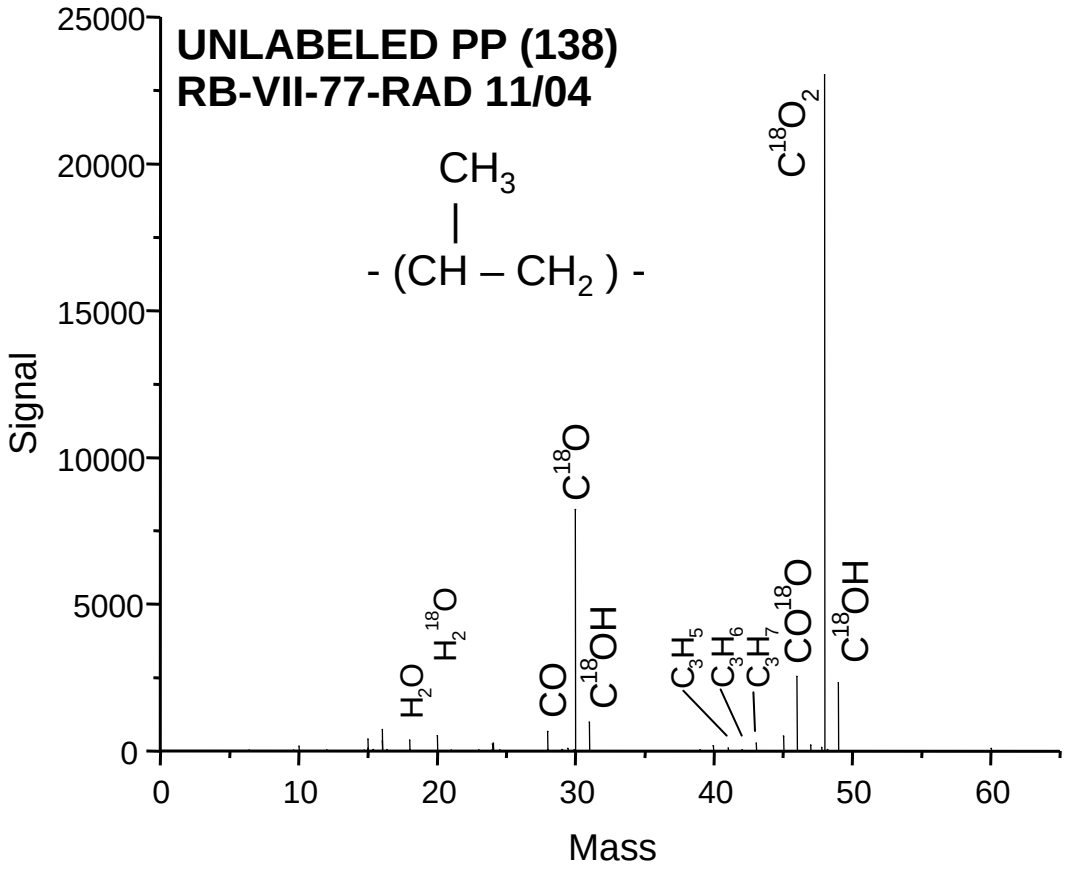
Unlabeled PP oxidized in $^{18}O_2$ shows isotopic shifts

Data from Siemens Quantra ion cyclotron resonance mass spectrometer

Major products are:

- **$C^{18}O$**
- **$C^{18}O_2$**



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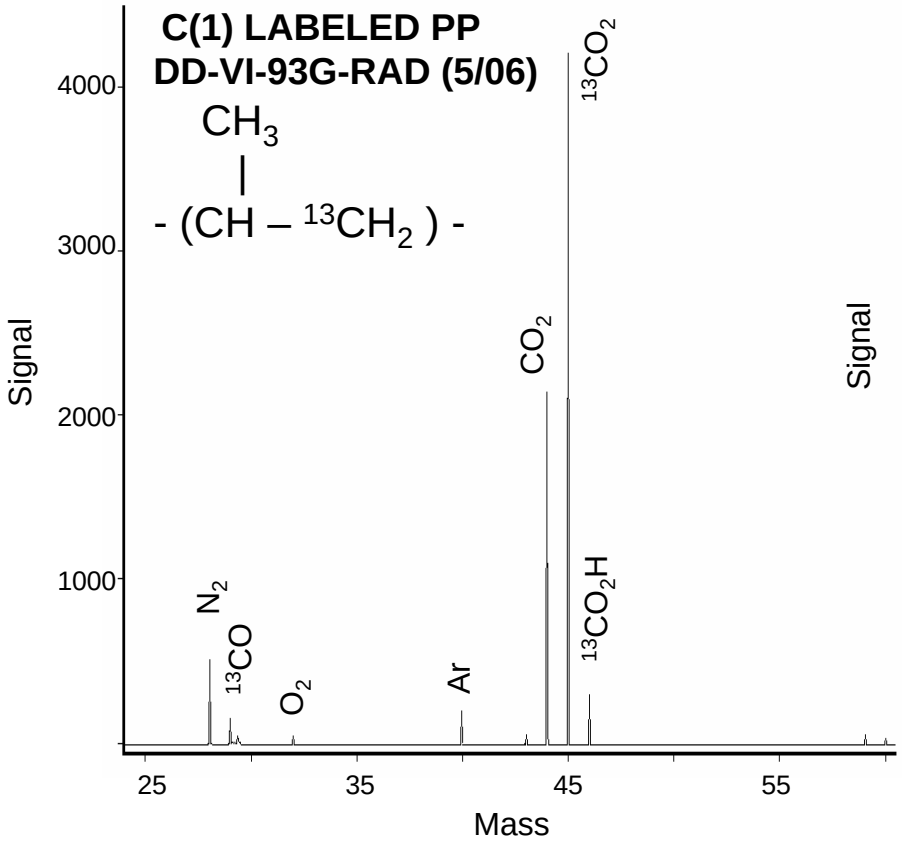
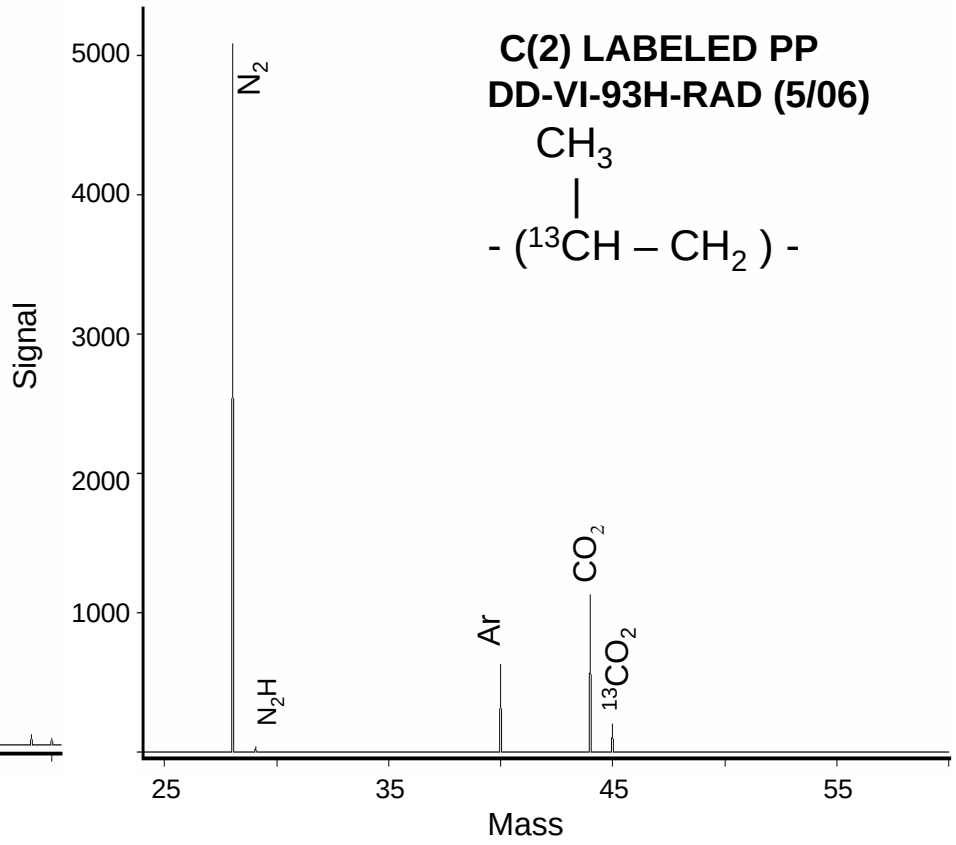
CO and CO2 products contain minimal C(2)



^{13}C products observed.



Few ^{13}C products observed.

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Each carbon contributes to the formation of CO and CO_2 differently

- **CO and CO_2 are the major products of polypropylene oxidation**
- **Contributions from labeled and unlabeled products (CO, CO_2) were summed to get the totals**

Carbon	%CO	%CO_2
C(1)	90%	65%
C(2)	<5%	9%
C(3)	<5%	26%

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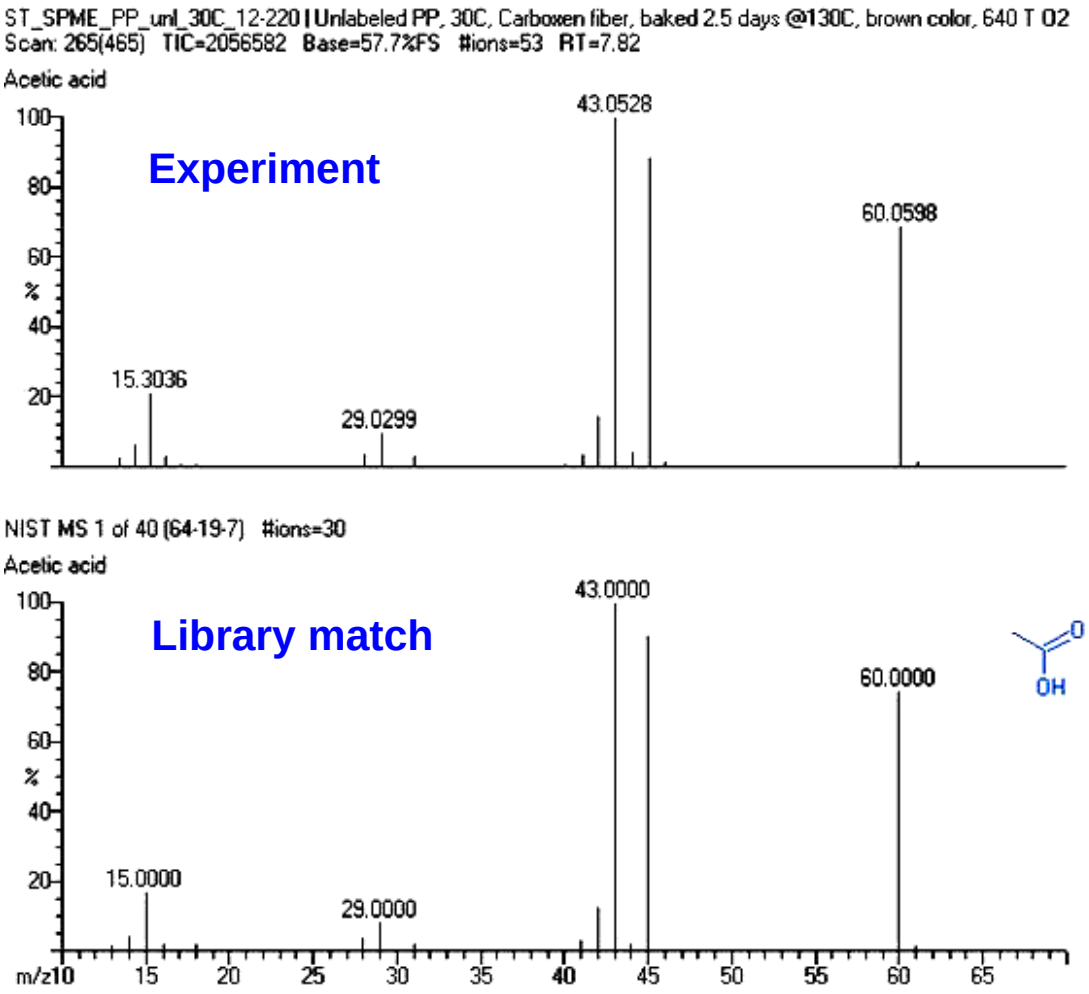
Step 1: Library match

- Data from Jeol GCMate II
- Sampling by solid phase microextraction (SPME)
- The match of the experimentally-obtained mass spectrum is excellent.



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Step 2: Exact mass determination

Exp'l (amu)	Exact (amu)	Error (ppm)	Empirical Formula
43.0185	43.0184	2	C_2H_3O
44.9968	44.9977	-20	CO_2H
60.0201	60.0211	-17	$C_2H_4O_2$

Exact mass determination gives provides the empirical formulae for oxidation products.

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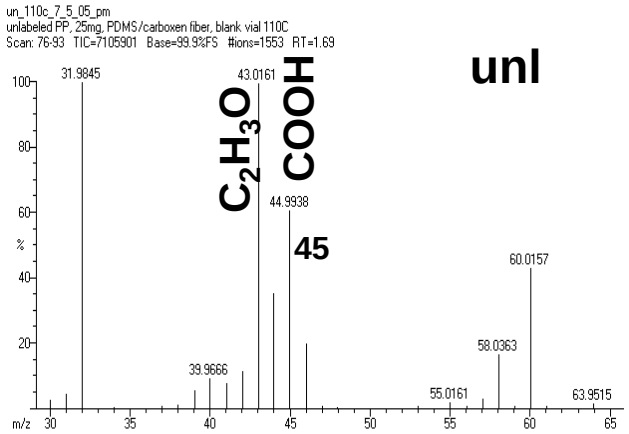
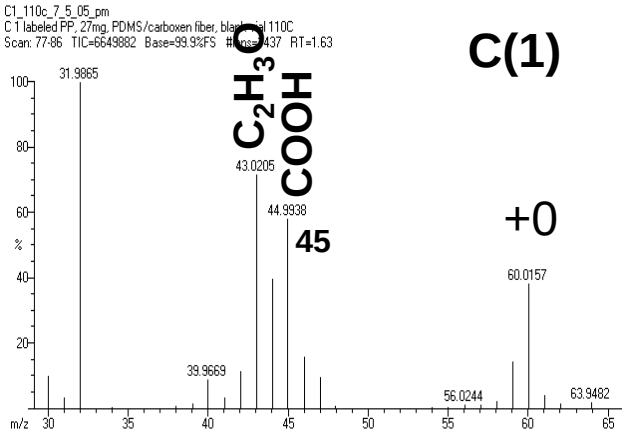
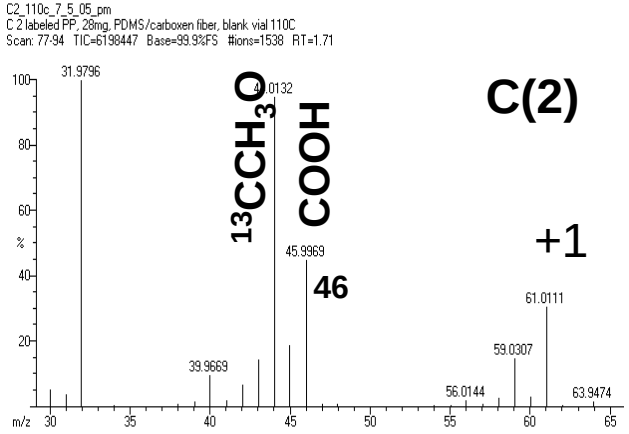
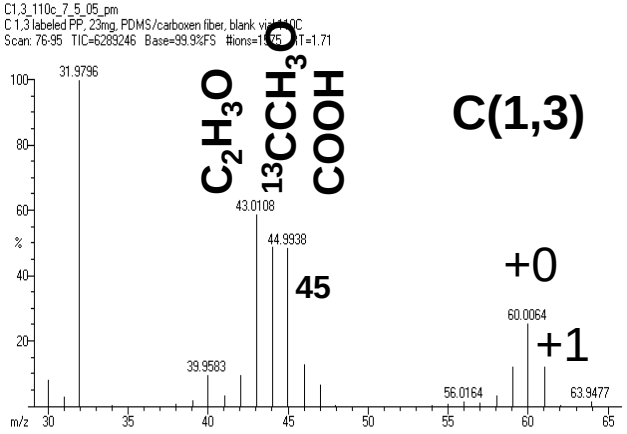
Step 3. Analyze isotopically labeled samples.

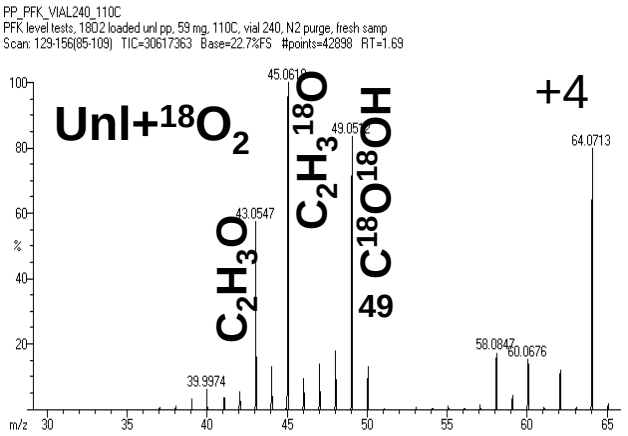








$C(3)H_3C(2)OOH$



$C_2H_4O_2$

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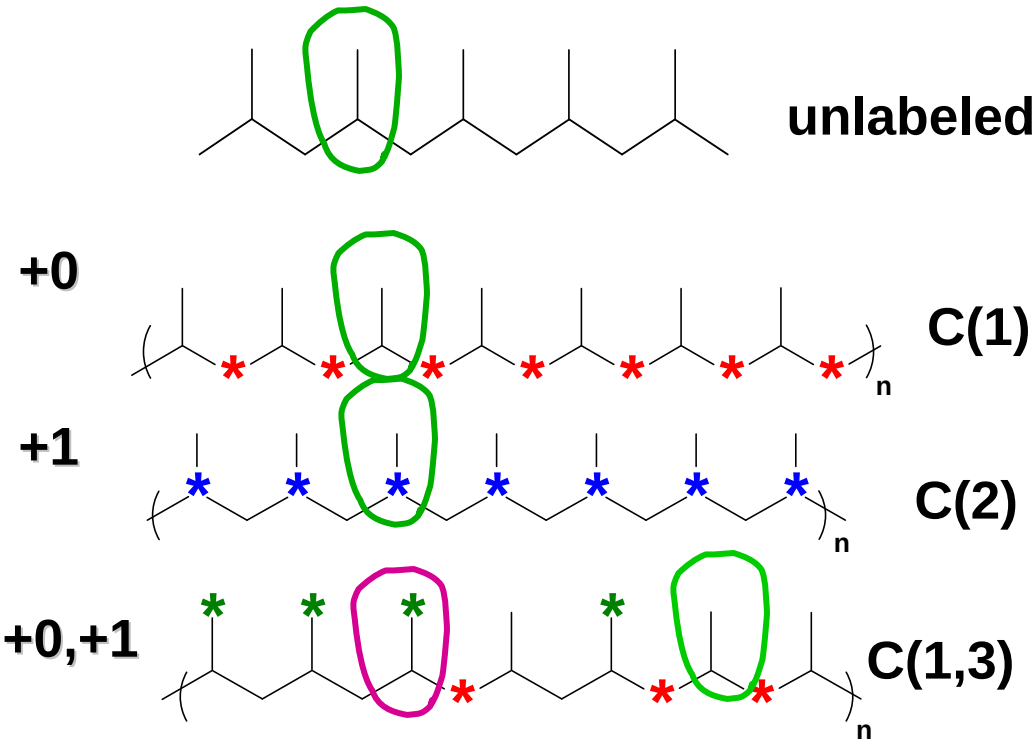
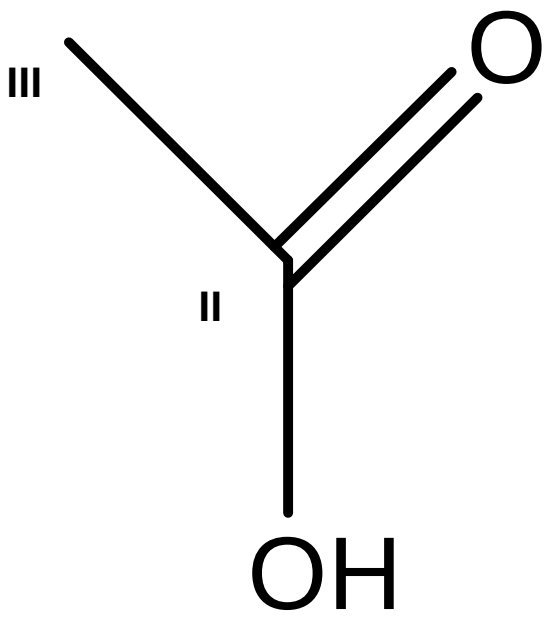
Origin of acetic acid on the polymer backbone is now known

$C_2H_4O_2$



Consistent w/ mass spectrum.



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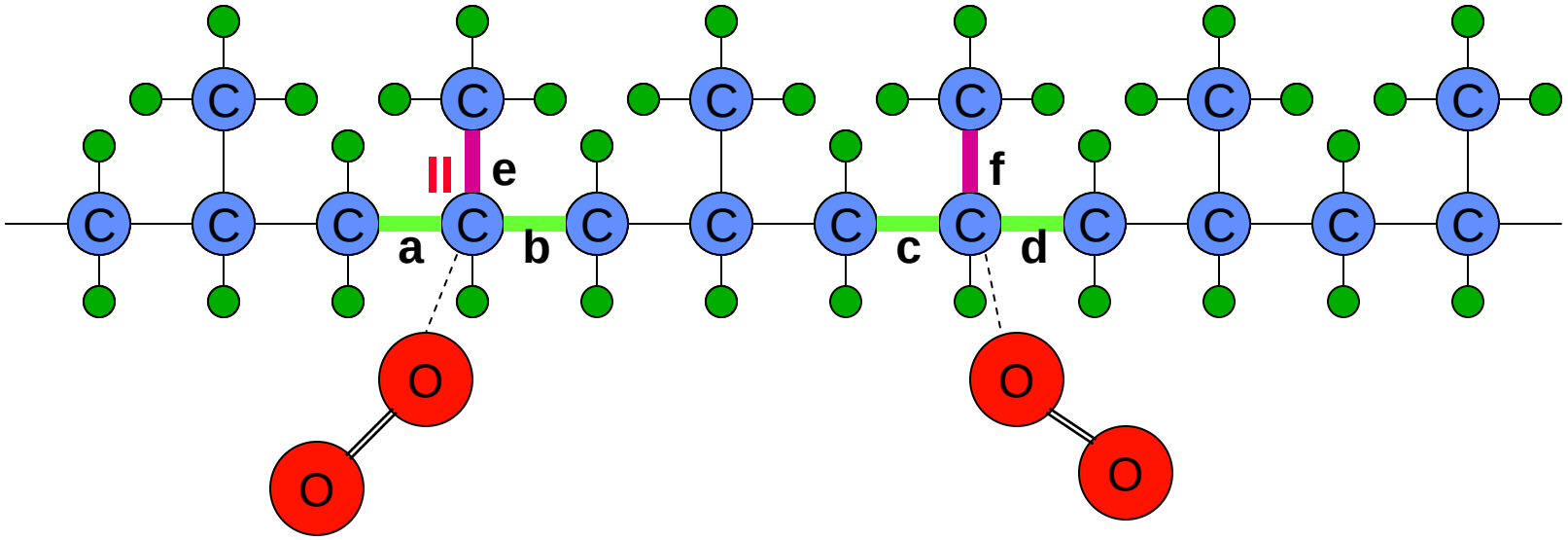
An oxygen molecule attacks, then liberates fragments of the polymeric chain

- The mass spectra is consistent with a mechanism where two bonds on the backbone chain are cleaved to release the molecule detected.
- The bond to the CH_3 group can be cleaved to produce other variations.



- The dominant series observed arises from a-c or b-d bonds being cleaved (symmetric).

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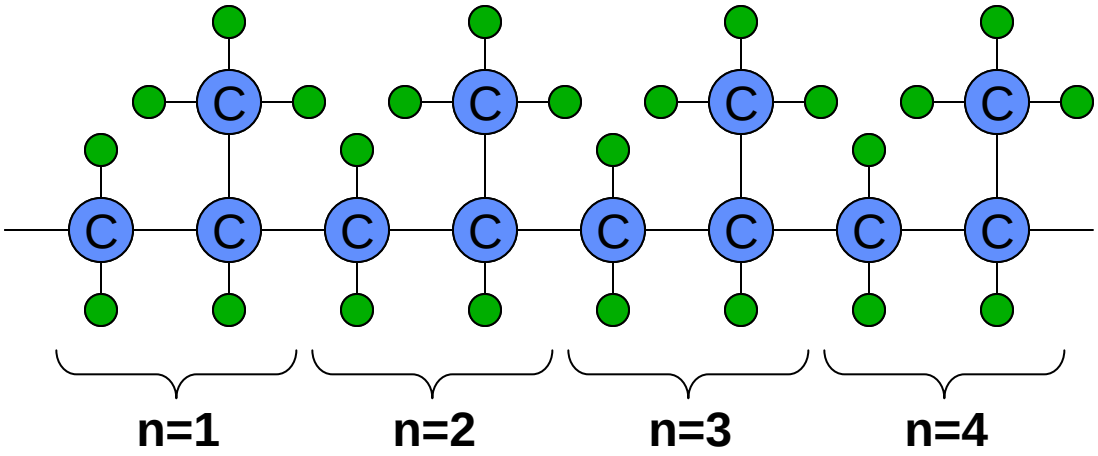
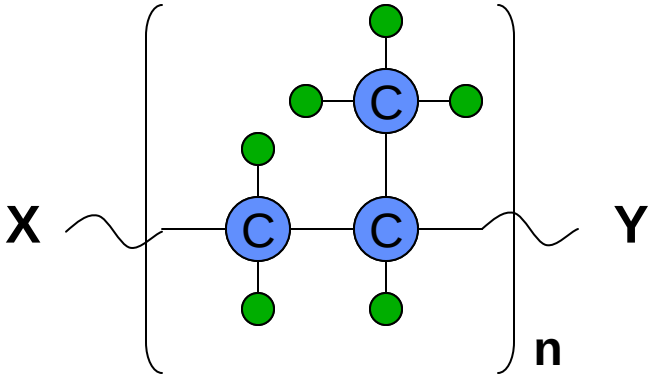
Relationship Between Polypropylene and Mass Spectral Fragments

Polypropylene



Molecular species Observed in the mass spectra.



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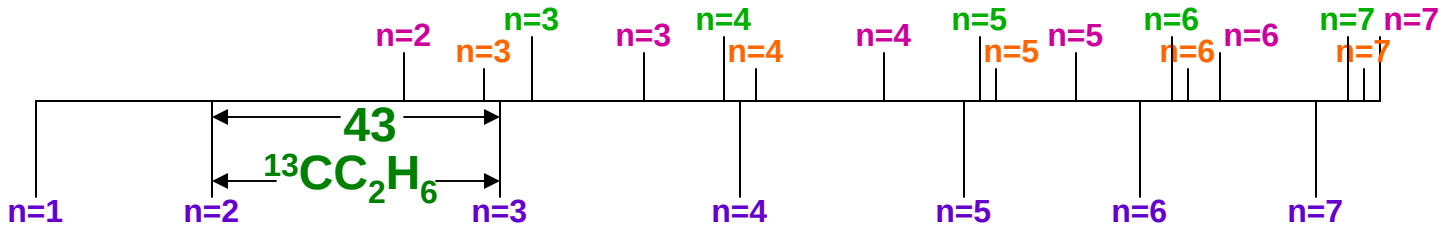
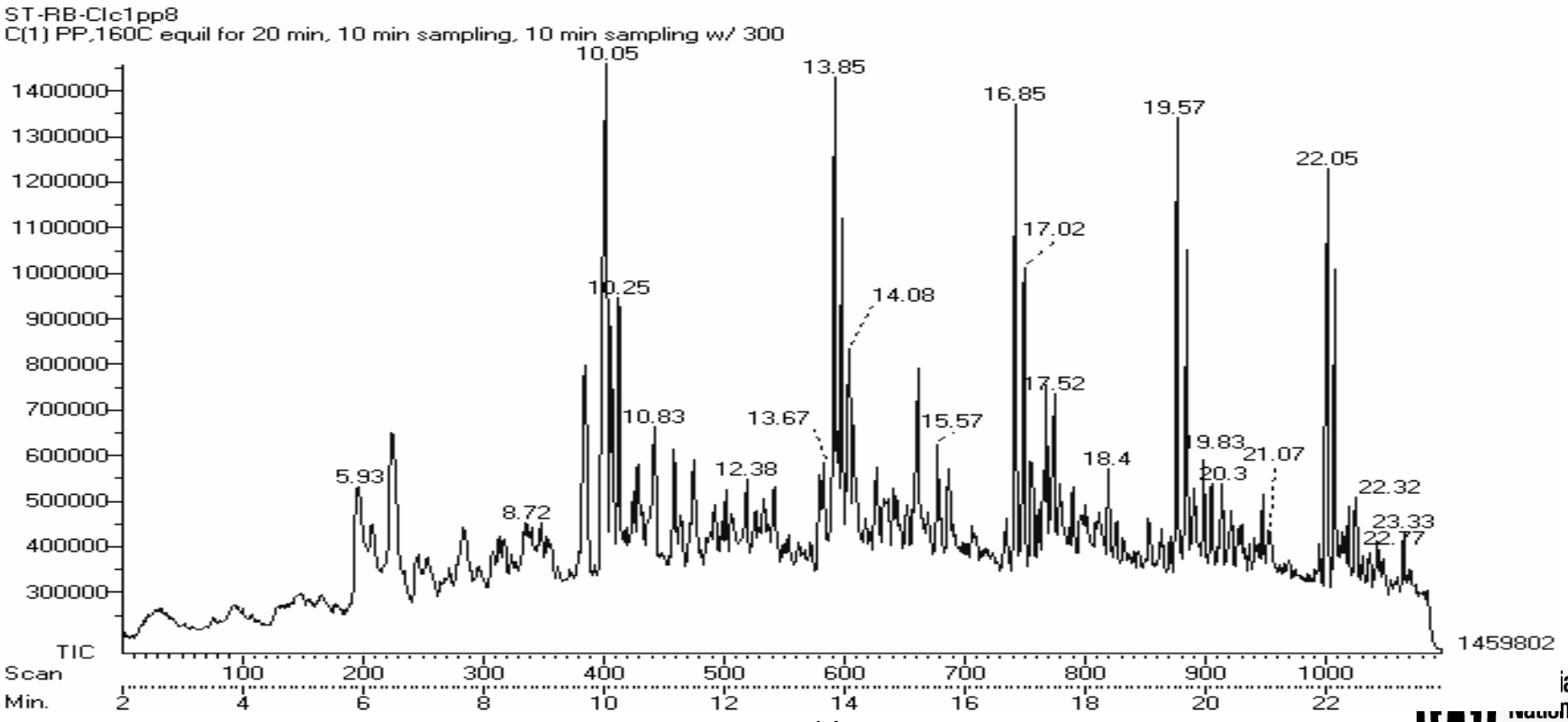
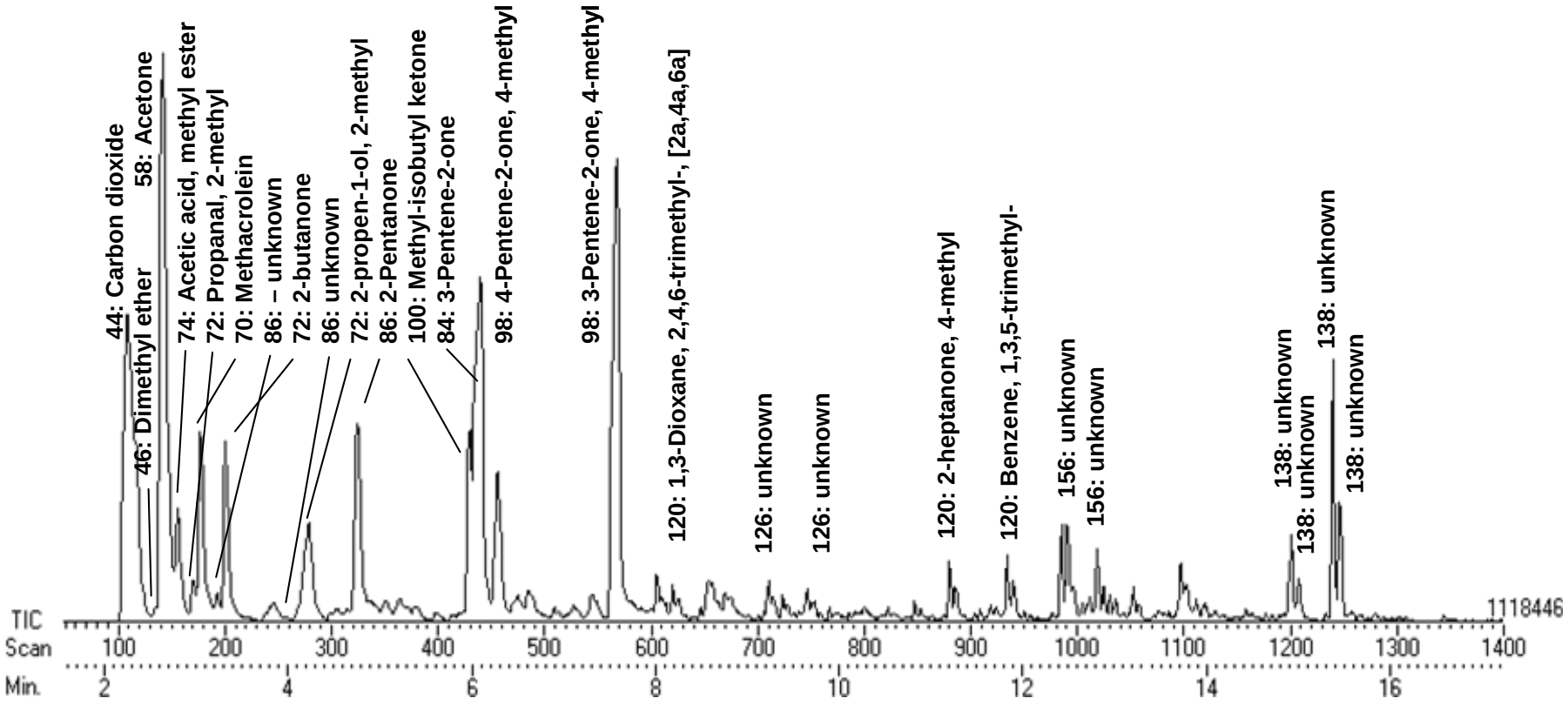
Series of compounds seen in chemical ionization data





Compound identification in Cryo/GC/MS data



Many polypropylene oxidation products have been positively identified, carbon atom assignments, and form the basis for a polypropylene oxidation product compound library.

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Conclusion

- **Methods developed provide an unprecedented level of understanding of the source of volatile products in polymer degradation**
- **Isotopic labeling is extremely valuable in product identification**
- **Kinetic information can provide information about the rate of polymer degradation**
- ***Methods developed can now be applied to more complex polymer systems of interest in weapons***

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