Mechanistic Study of the Thermal Degradation of Polypropylene

SAND2008-0992C

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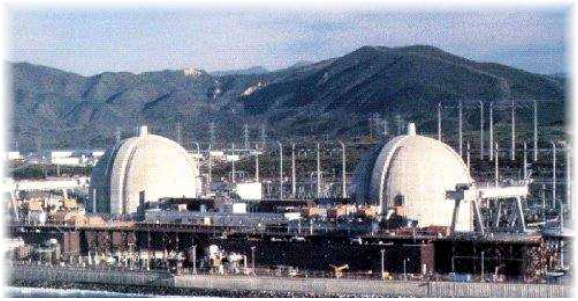
National Nuclear Security Administration

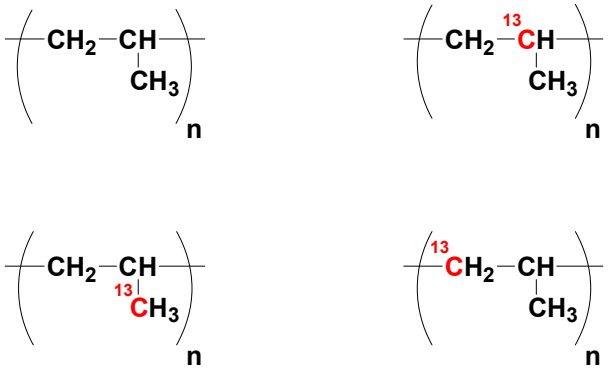
Organic Materials Aging and Degradation

O-rings

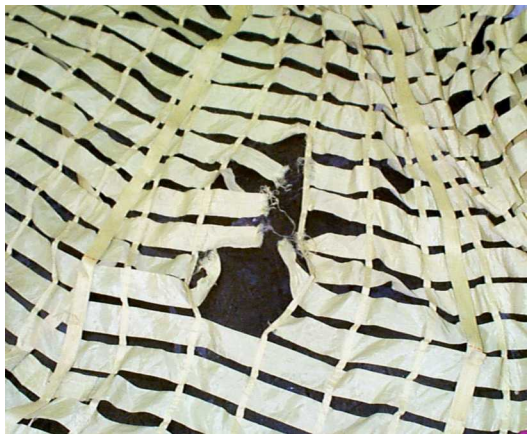


Nuclear Power Plant Cable Insulation

Aircraft Wire Insulation



Labeled Polypropylene



Textiles

Background…

Usual Projects:

Physical property changes as a function of time

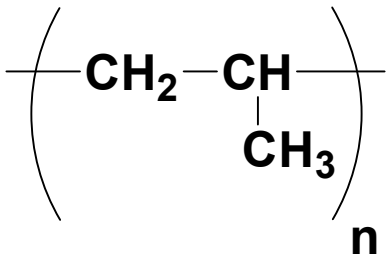
Labeled Polymers Studies:

Understand chemical mechanism for degradation

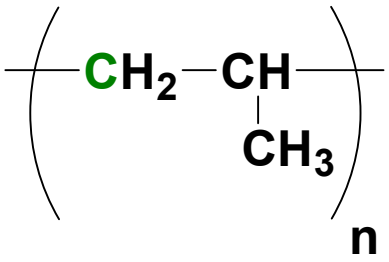
Labeled Polypropylene

- Prepared 3 polypropylene samples with specific ^{13}C labels
- Goal: Map oxidation products back to macromolecular structure
- Analytical Techniques:
  - Solid-state NMR (solid products)
  - GC/ mass spec (volatile products)

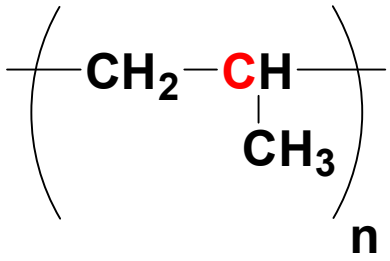
Sample	CH	CH_2	CH_3
C(1)	1.0	96.7	2.3
C(2)	98.5	0.8	0.8
C(1,3)	0.9	68.3	30.8



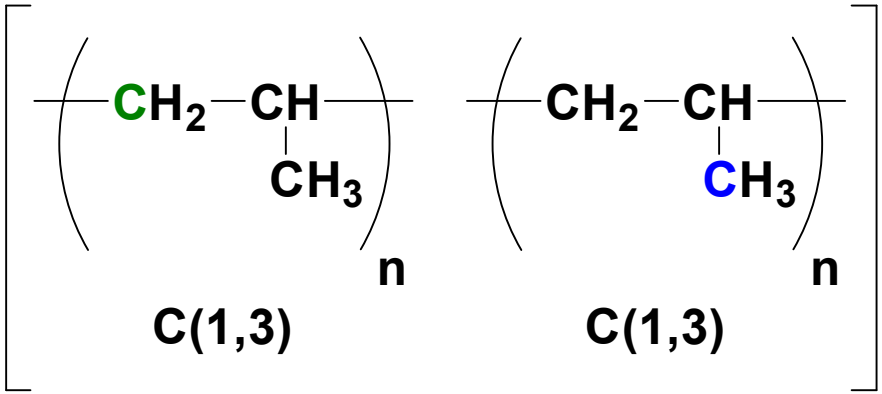
unlabeled



C(1)

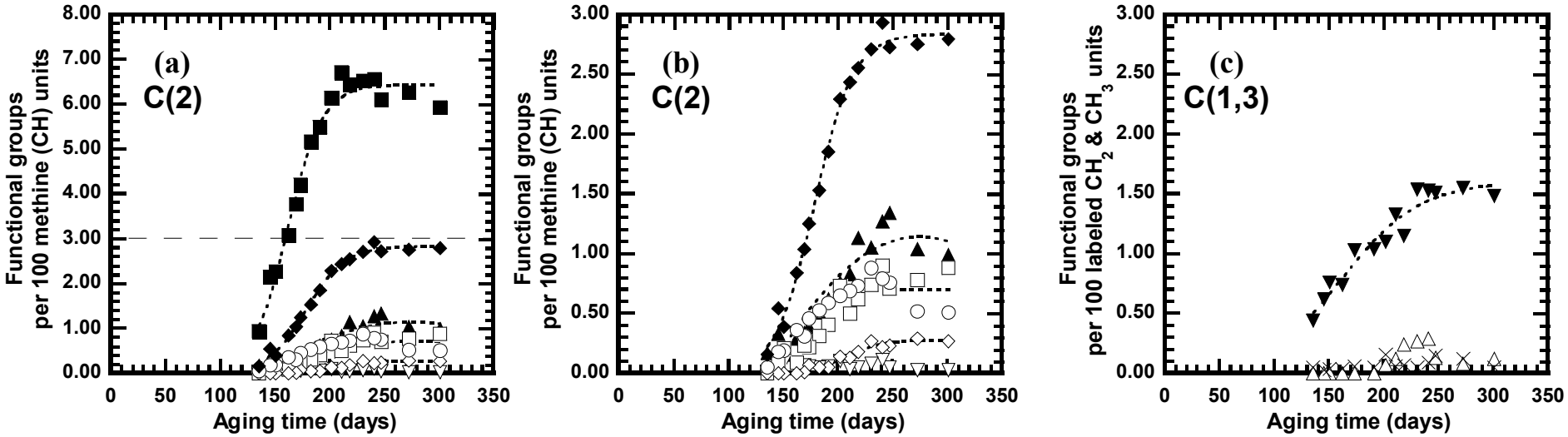


C(2)



C(1,3) C(1,3)

Solid State; It is all about the 3° carbon!

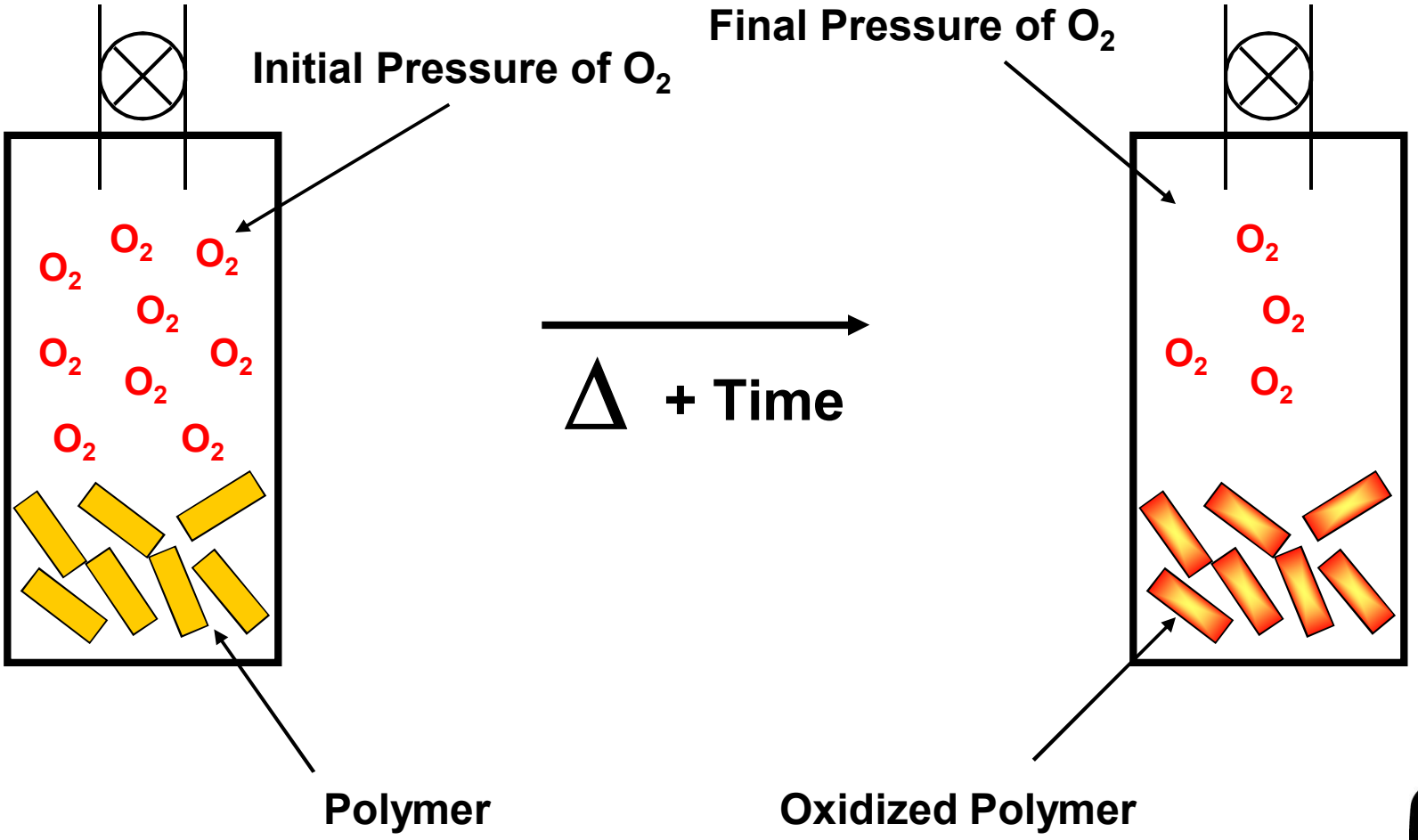


Kinetic accumulation of oxidation products in solid polypropylene samples thermally aged at 50 °C. (a) C(2) labeled sample, all products; (b) C(2) labeled sample, low concentration products; (c) C(1,3) labeled sample. Functional groups: (■) tertiary hydroperoxides and/or dialkyl peroxides; (♦) tertiary alcohols; (▲) methyl ketones; (Δ) in-chain ketones; (∇) carboxylic acids on C(2) carbon; (□) esters and/or peresters on C(2) carbon; (▼) carboxylic acids and/or esters on C(1) carbon; (◊) ketals and/or acetals on C(2) carbon (114.1 ppm); (○) ketals and/or acetals on C(2) carbon (105.7 ppm); (×) ketals and/or acetals on C(1) carbon (100–117 ppm). Dotted lines are guides to the eye.

Most of the oxidation products that formed on the polymer chain originated through chemical reactions at the PP tertiary carbons

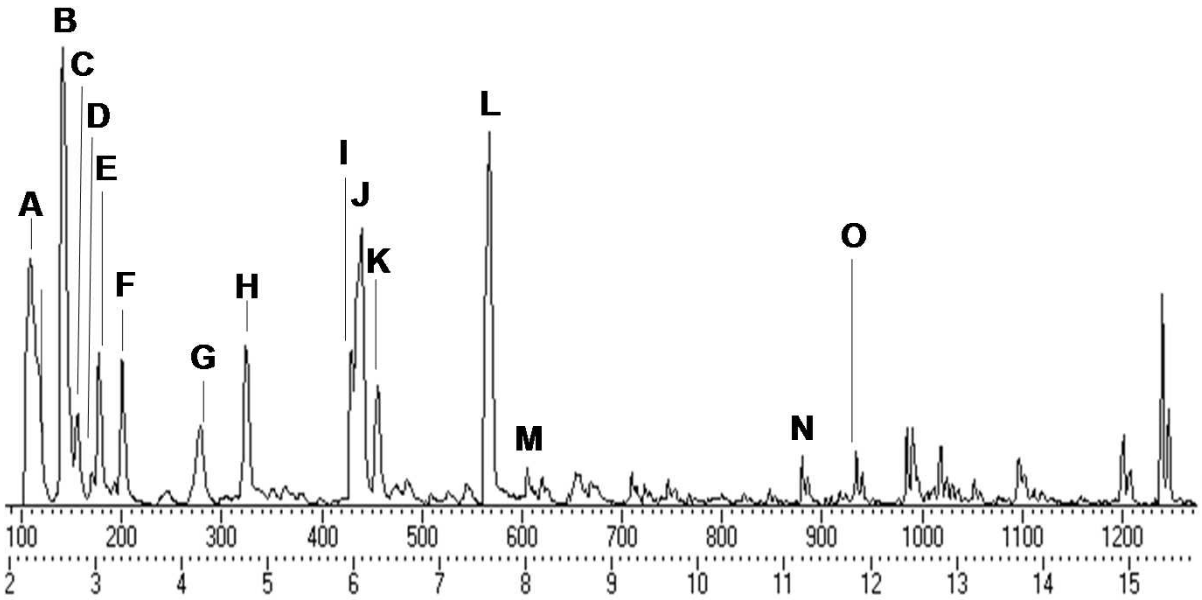
Mowery, D. M.; Assink, R. A.; Derzon, D. K.; Klamo, S. B.; Clough, R. L.; Bernstein, R. *Macromolecules,* Solid-State ^{13}C NMR Investigation of the Oxidative Degradation of Selectively Labeled Polypropylene by Thermal Aging and Gamma-Irradiation 2005, *38*, 5035-5046.

Schematic of Vials



Volatiles Studies

GC Separation of Volatiles

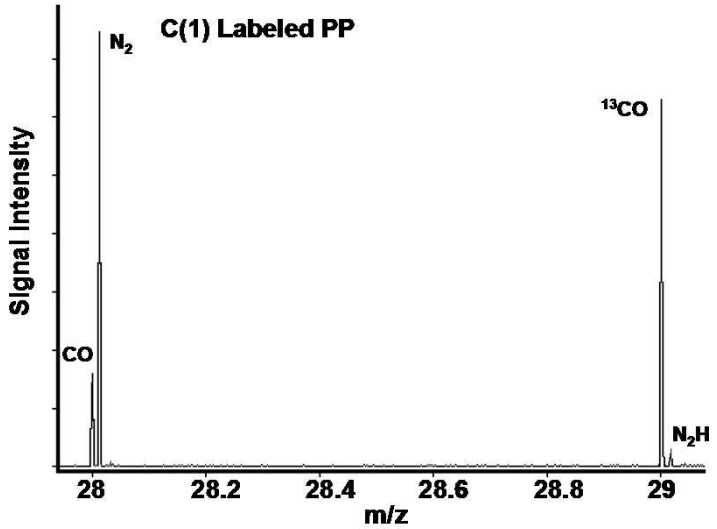


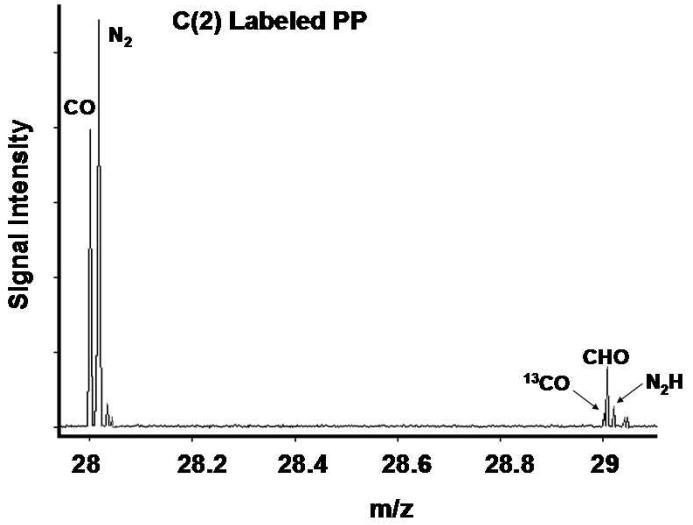
Peak	Chemical Structure
A	Carbon Dioxide
B	Acetone
C	Methyl acetate
D	2-methylpropanal
E	Methacrolein
F	2-Butanone
G	2-Methyl-2-propen-1-ol
H	2-Pentanone
I	Methyl-isobutyl ketone
J	3-Pentene-2-one
K	4-Methyl-4-pentene-2-one
L	4-Methyl-3-pentene-2-one
M	2,4,6-Trimetyl-1,3-dioxane
N	4-Methyl-2-heptanone
O	1,3,5-Trimethylbenzene

Numerous volatile compounds separated
Not all identified

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

CO Studies

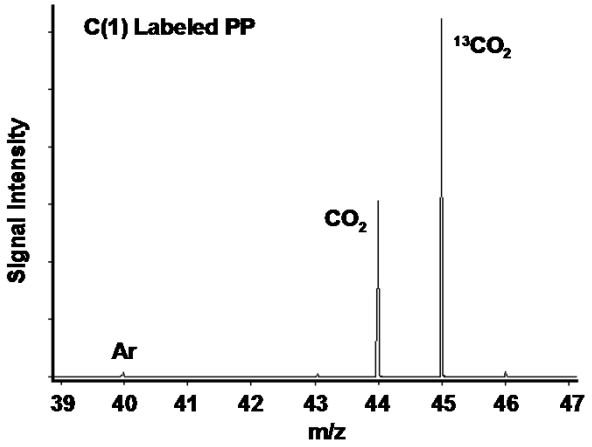


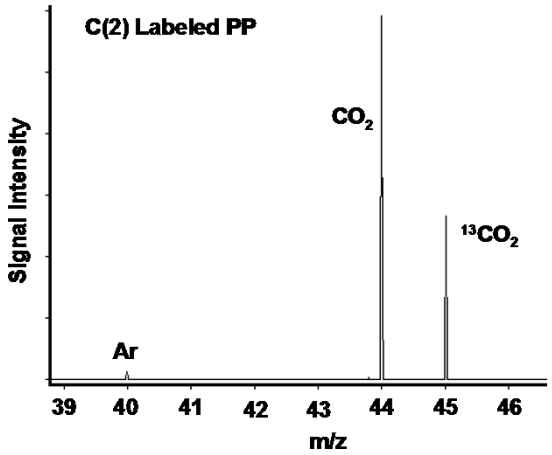


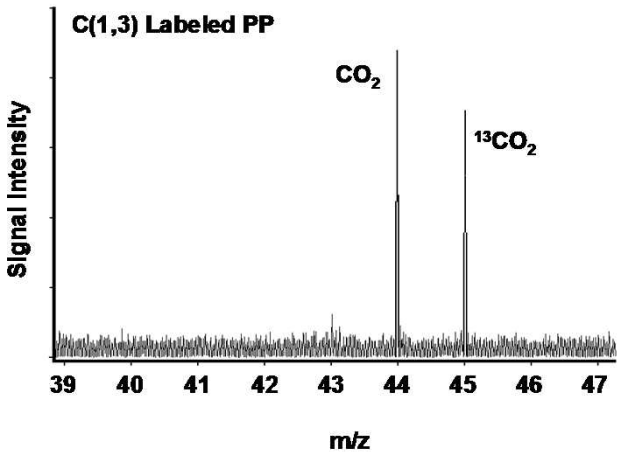
Carbon atom within the polymer	% CO from this position
C(1) [methylene]	≥80% [± 10%]
C(2) [tertiary]	≤5% [± 10%]
C(3) [methyl group]	Not determined

Thornberg, S. M.; Bernstein, R.; Derzon, D. K.; Irwin, A. N.; Klamo, S. B.; Clough, R. L. *Polymer Degradation and Stability,* The Genesis of CO_2 and CO in the Thermooxidative Degradation of Polypropylene **2007**, *92*, 94-102.

CO_2 Studies



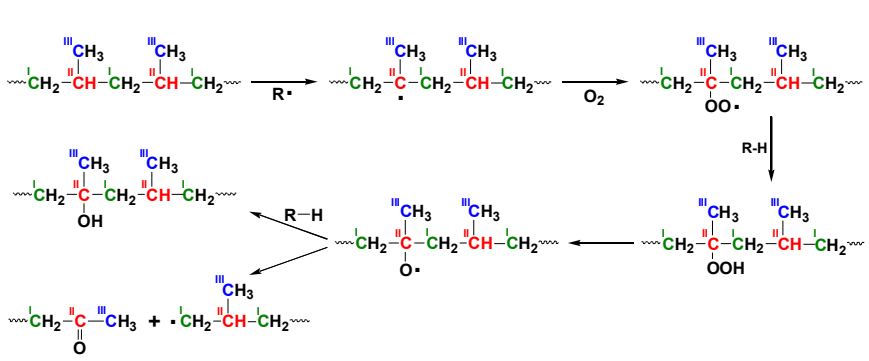


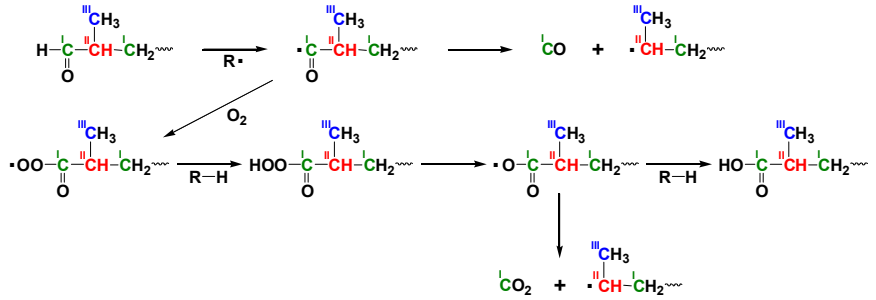


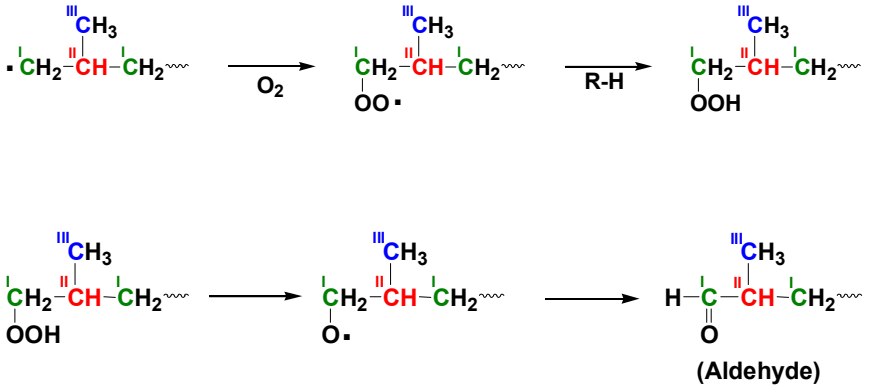
Carbon atom within the polymer	% CO_2 from this position
C(1) [methylene]	66% [± 5%]
C(2) [tertiary]	33% [± 5%]
C(3) [methyl group]	0% [< 5%]

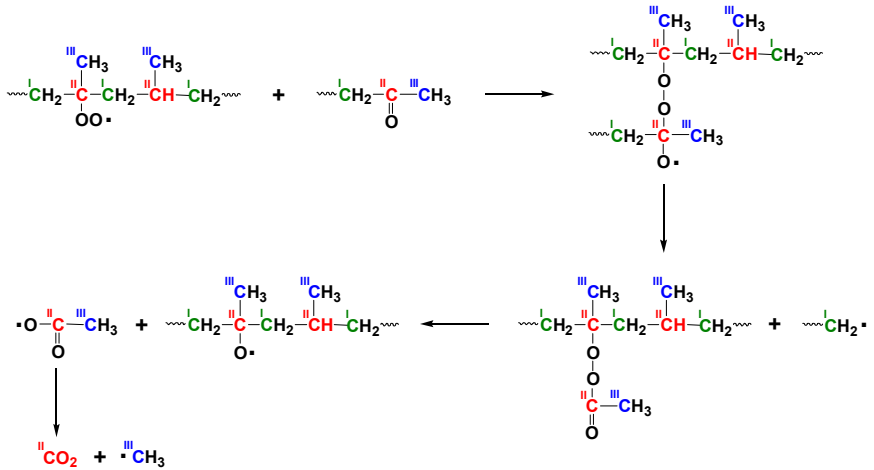
Thornberg, S. M.; Bernstein, R.; Derzon, D. K.; Irwin, A. N.; Klamo, S. B.; Clough, R. L. *Polymer Degradation and Stability,* The Genesis of CO_2 and CO in the Thermooxidative Degradation of Polypropylene **2007**, *92*, 94-102.

Possible CO and CO_2 Mechanisms









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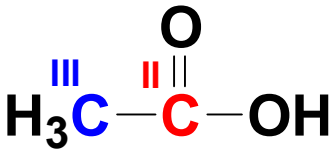
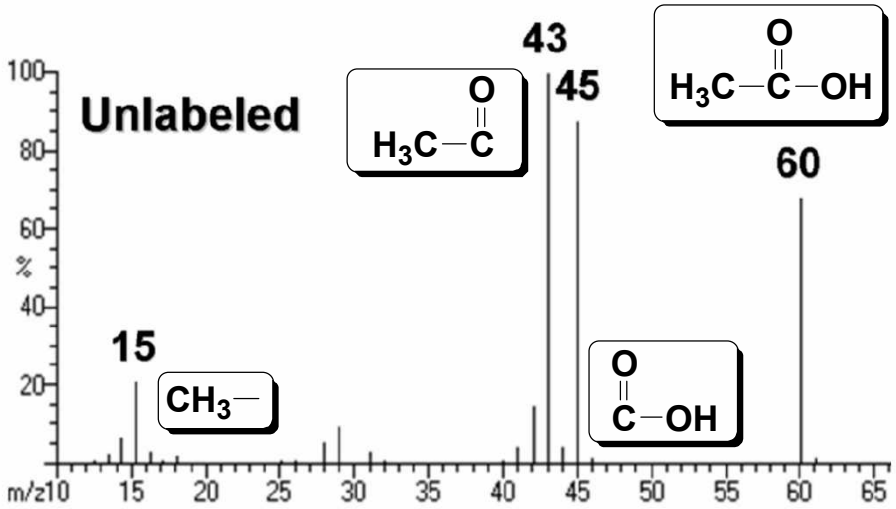
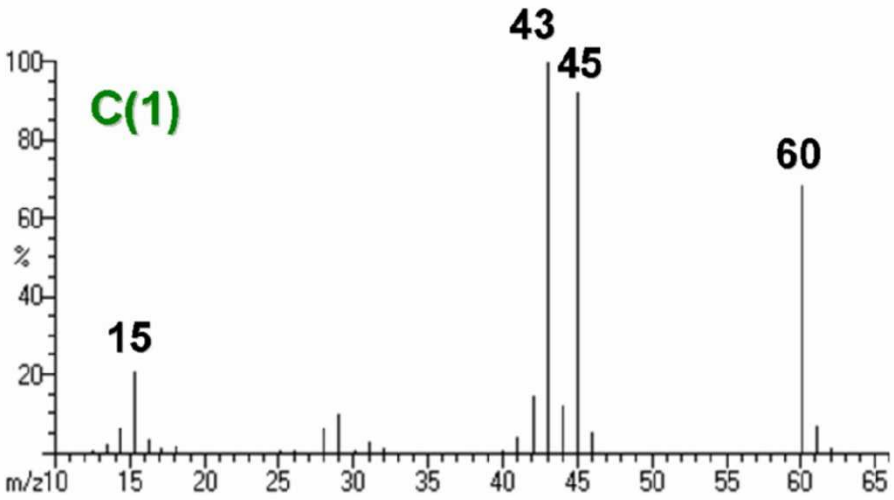
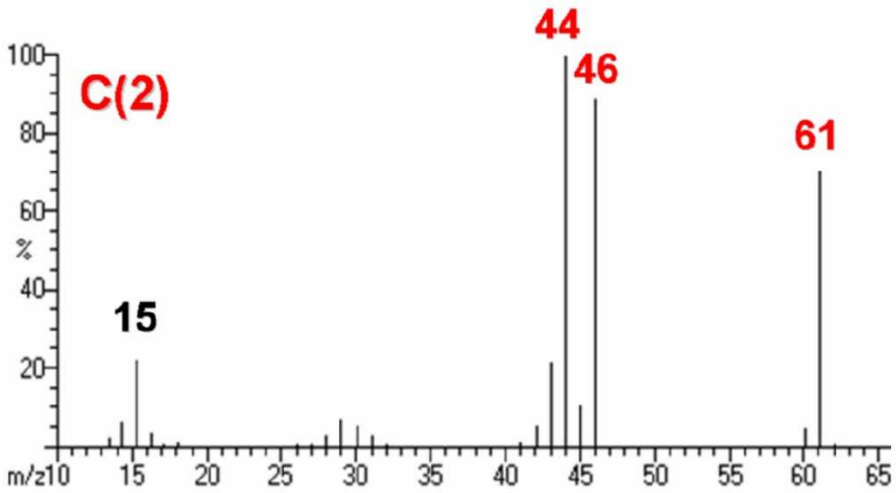
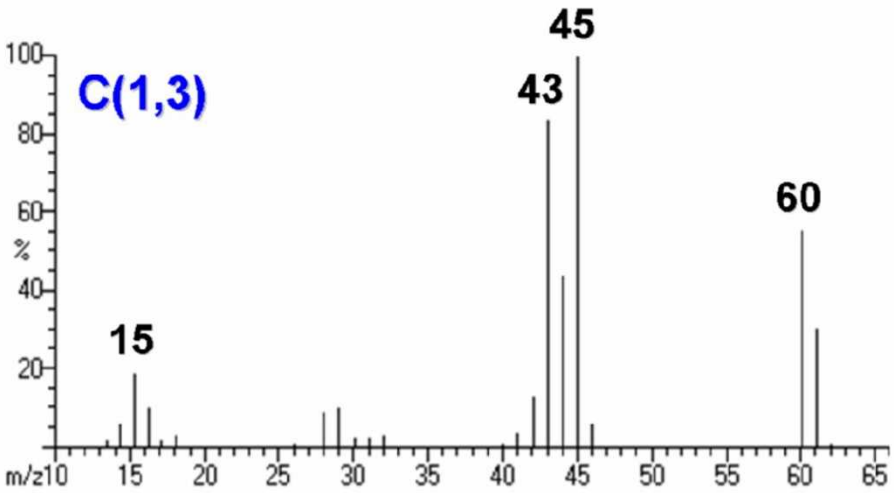
Acetic Acid





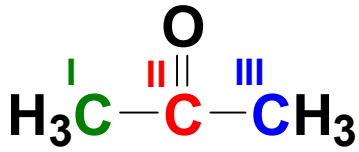


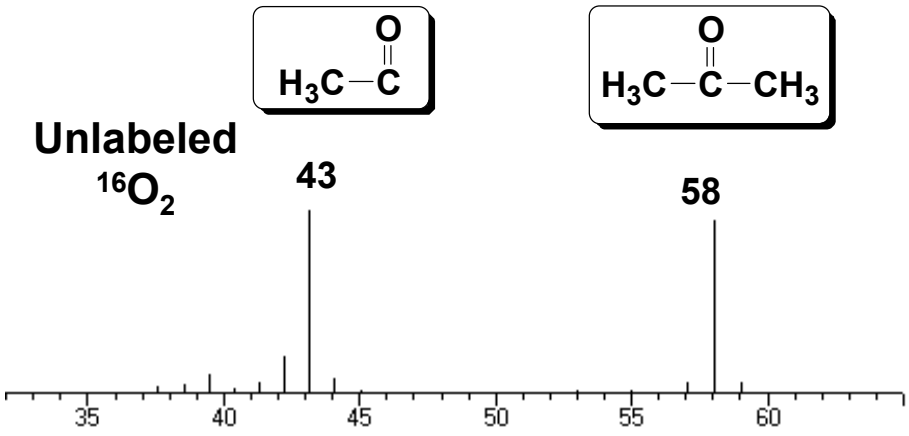


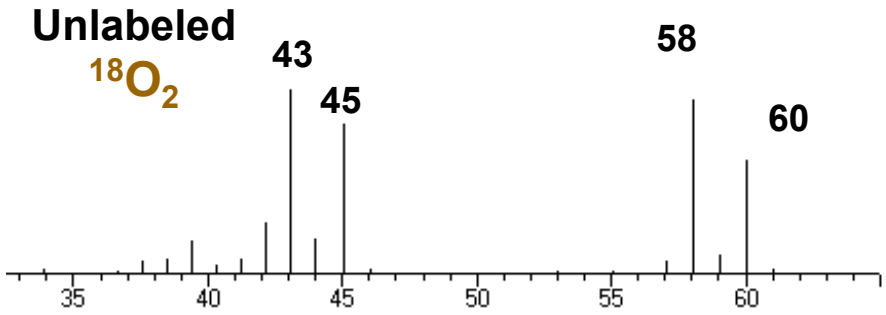


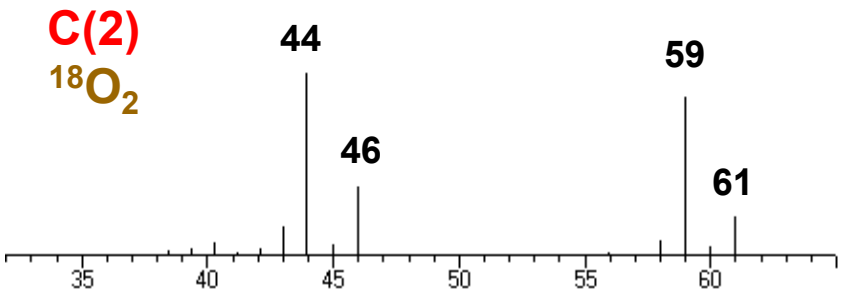
Thornberg, S. M.; Bernstein, R.; Mowery, D. M.; Klamo, S. B.; Hochrein, J. M.; Brown, J. R.; Derzon, D. K.; Clough, R. L. *Macromolecules,* Insights into Oxidation Pathways, from Volatile Products of Polypropylene with Selective Isotopic Labeling **2006**, *39*, 5592-5594.

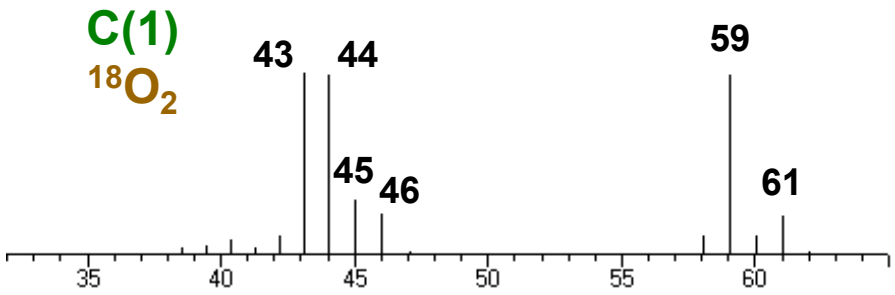
Acetone with $^{18}O_2$











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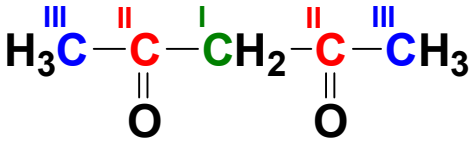
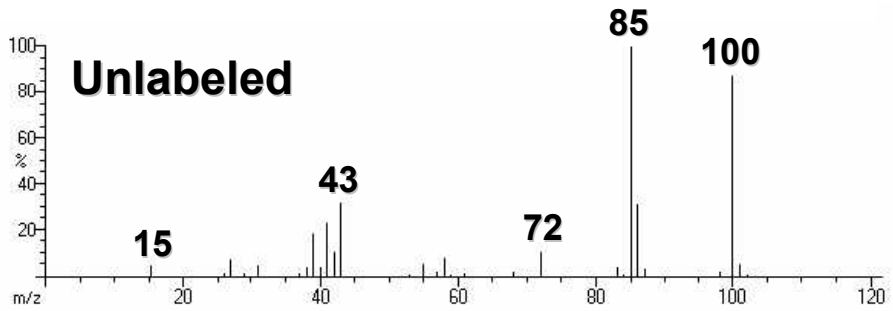
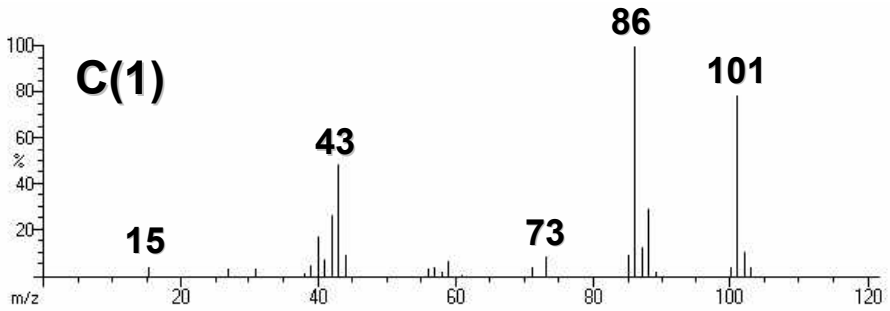
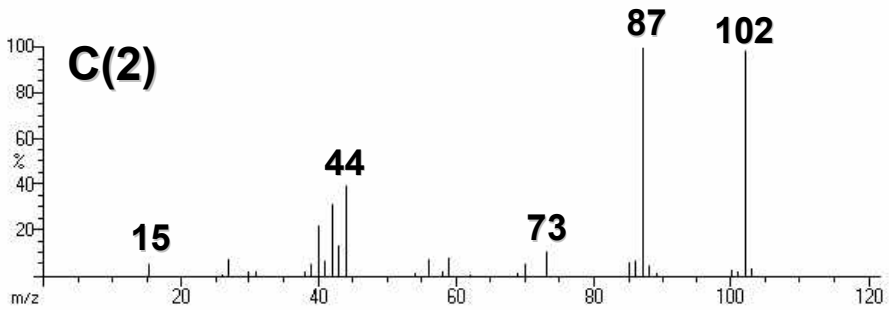
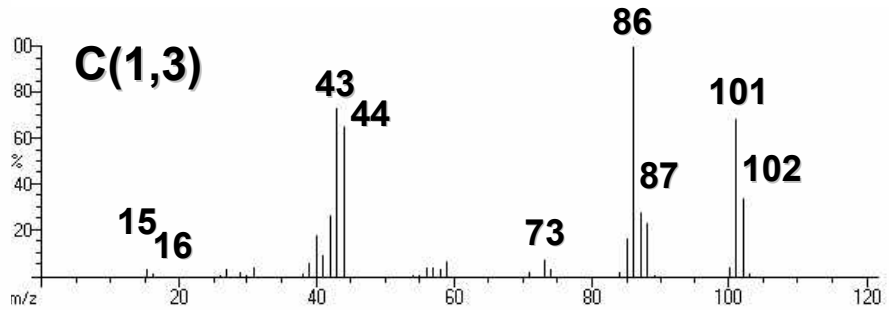
Pentane-2,4-dione











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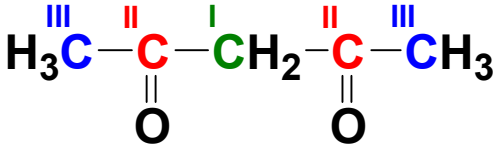
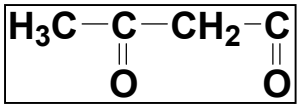
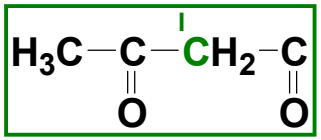
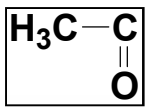
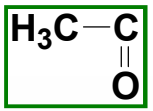
Pentane-2,4-dione

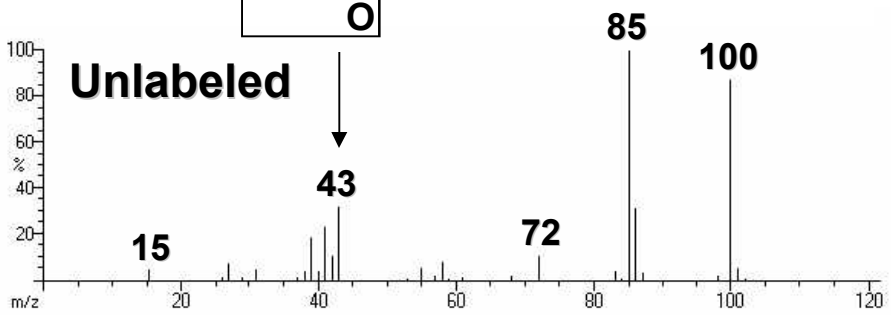


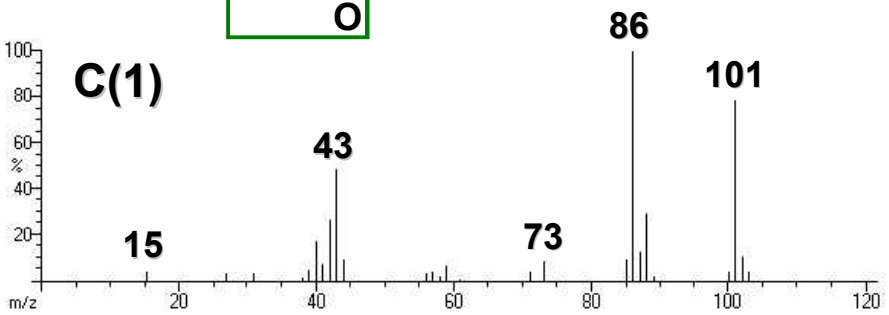


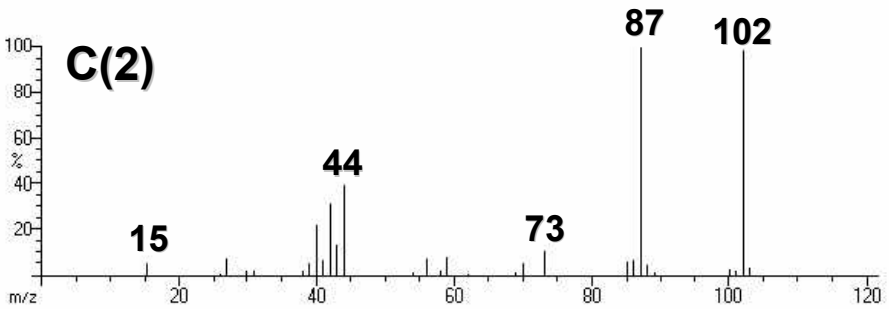


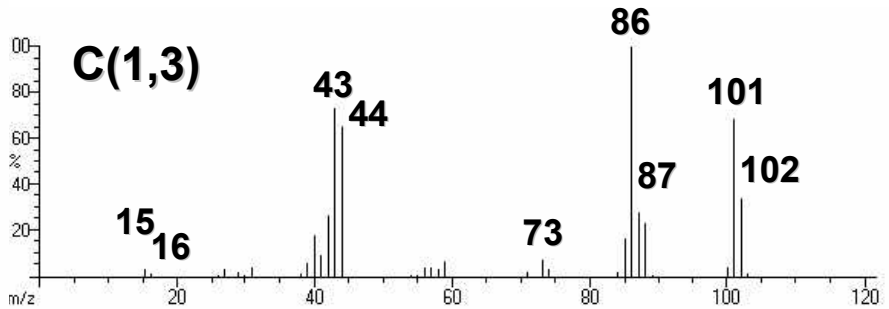


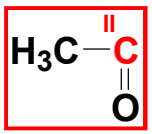


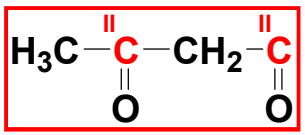


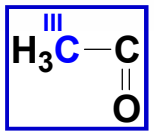


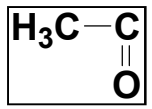


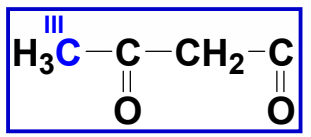


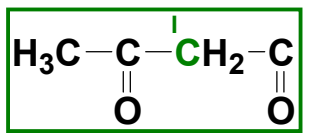




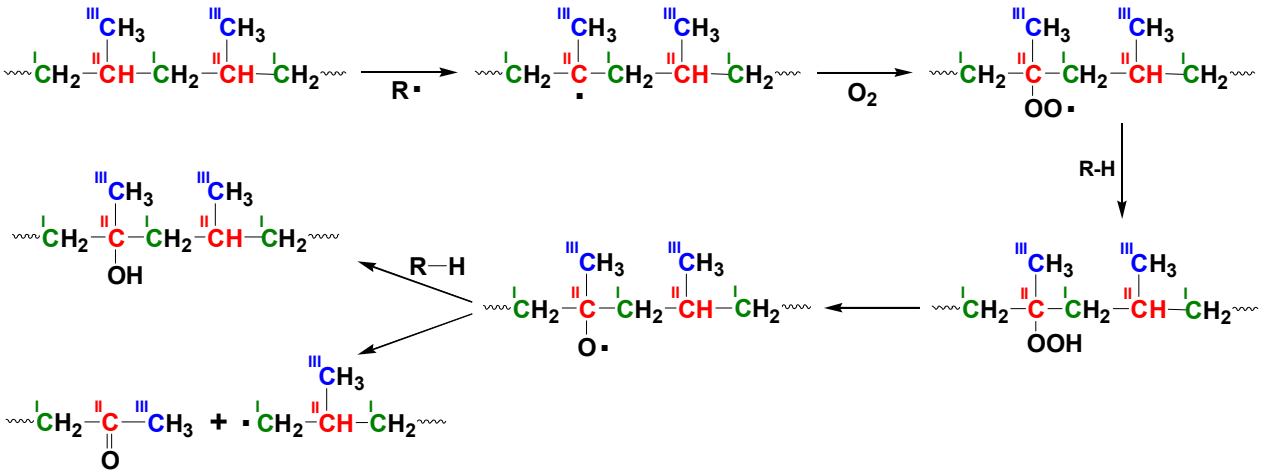


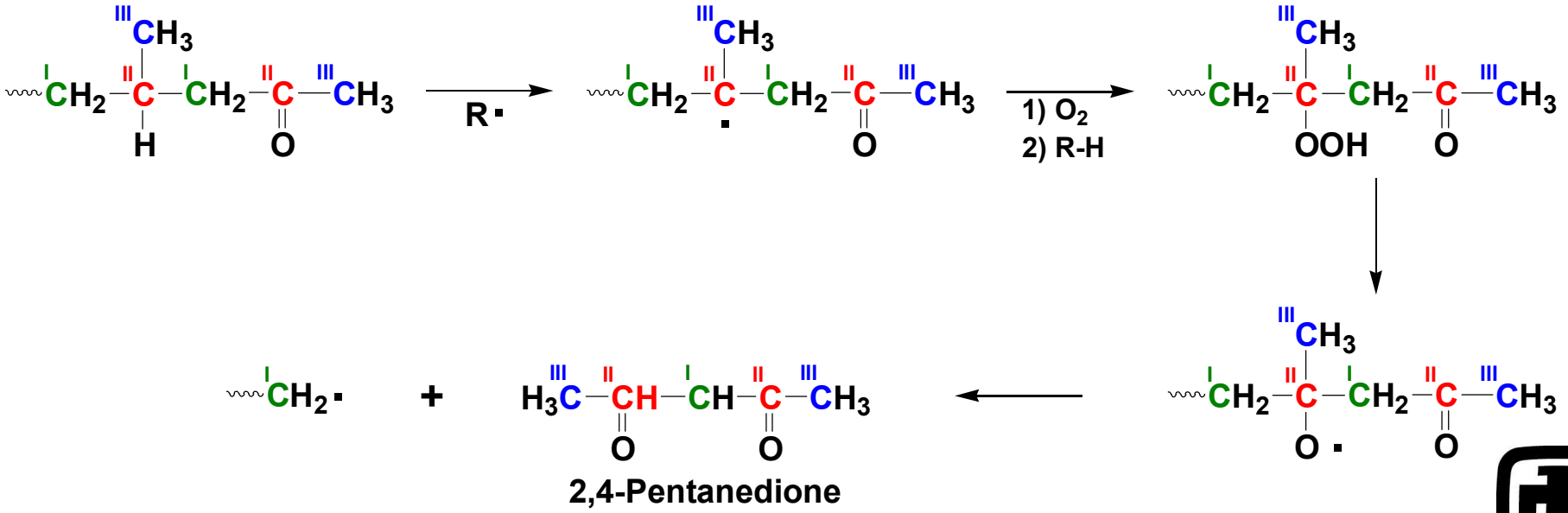




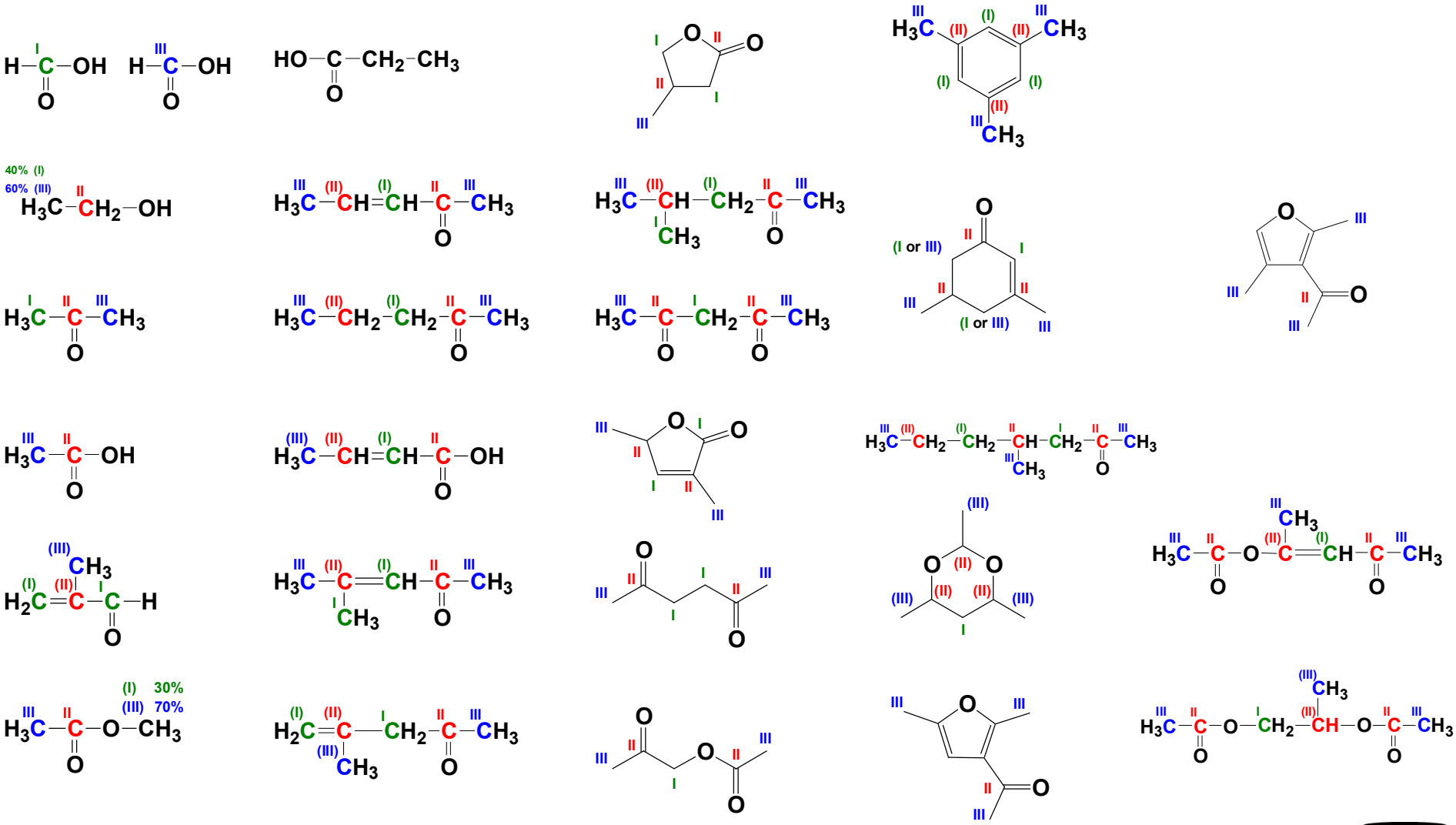


Possible Mechanistic Schemes



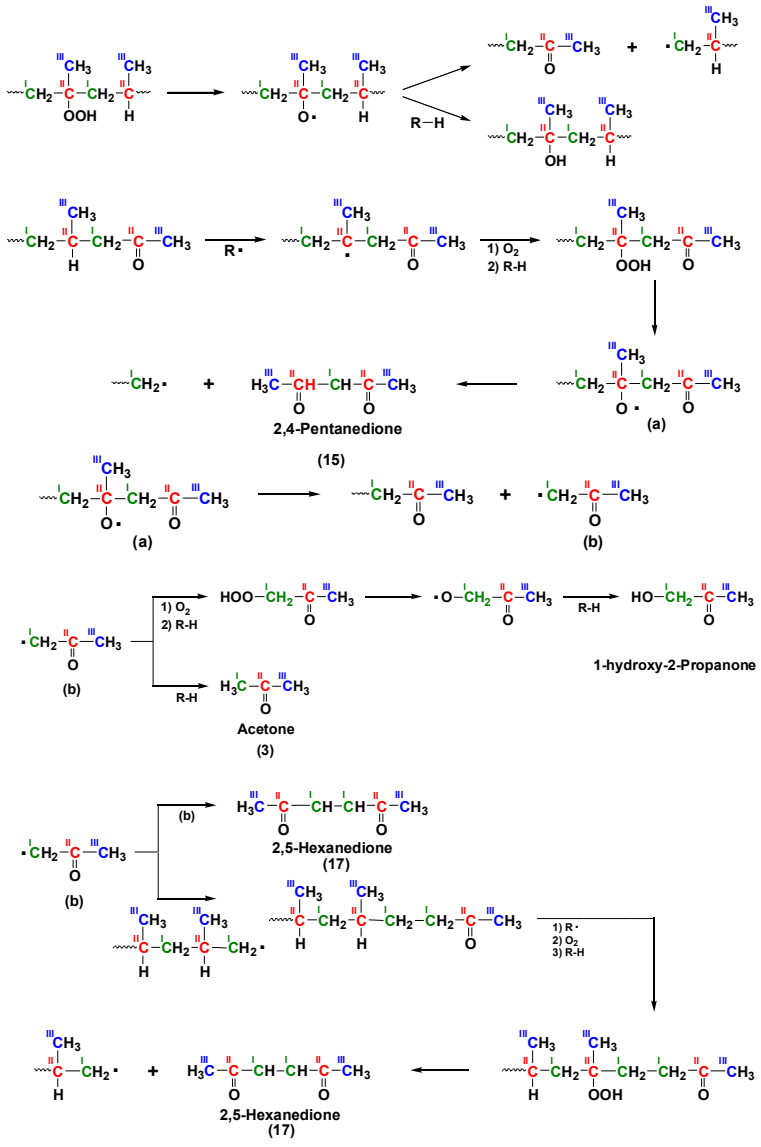


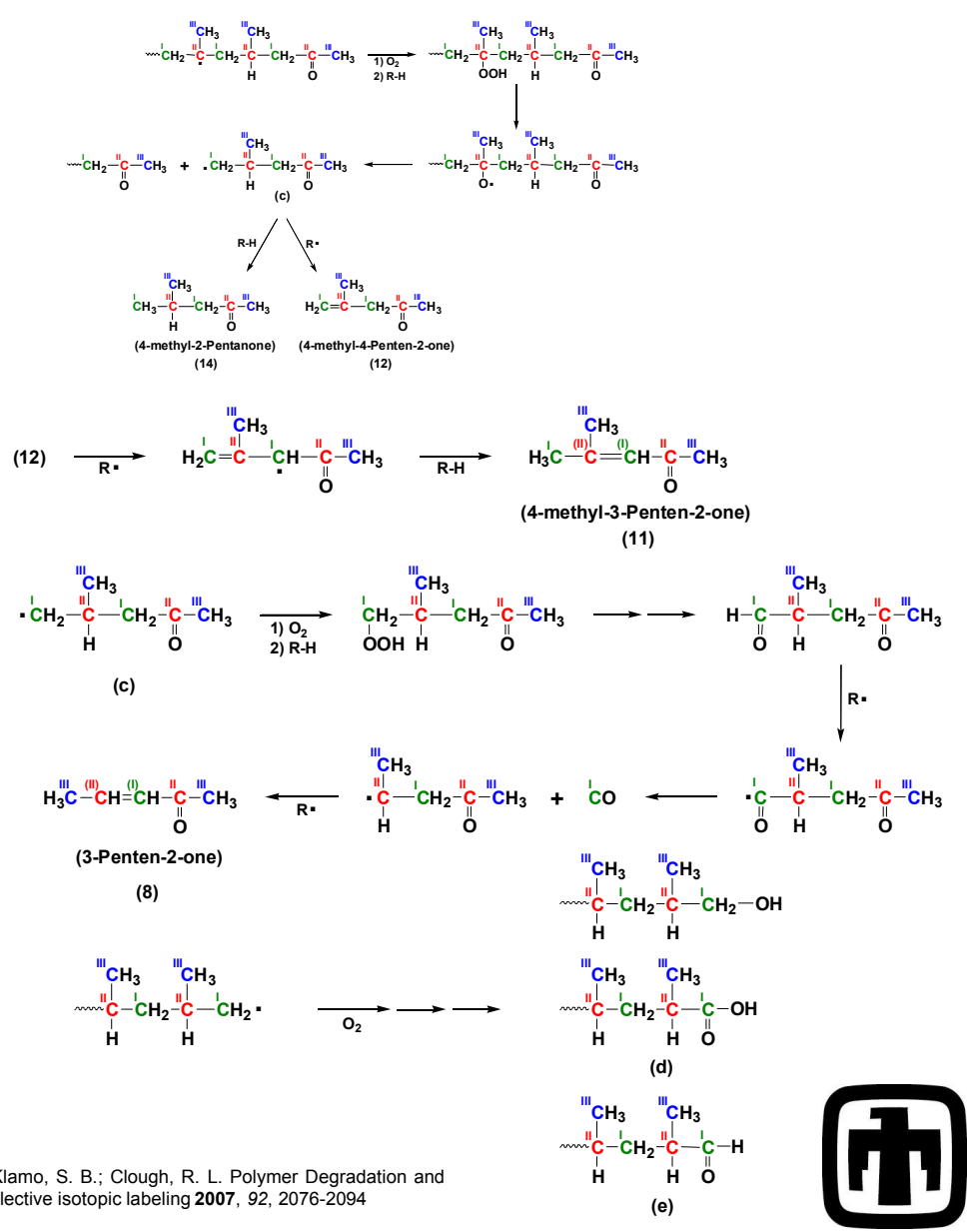
Various Thermal-oxidative Degradation Products



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

Reaction Mechanisms





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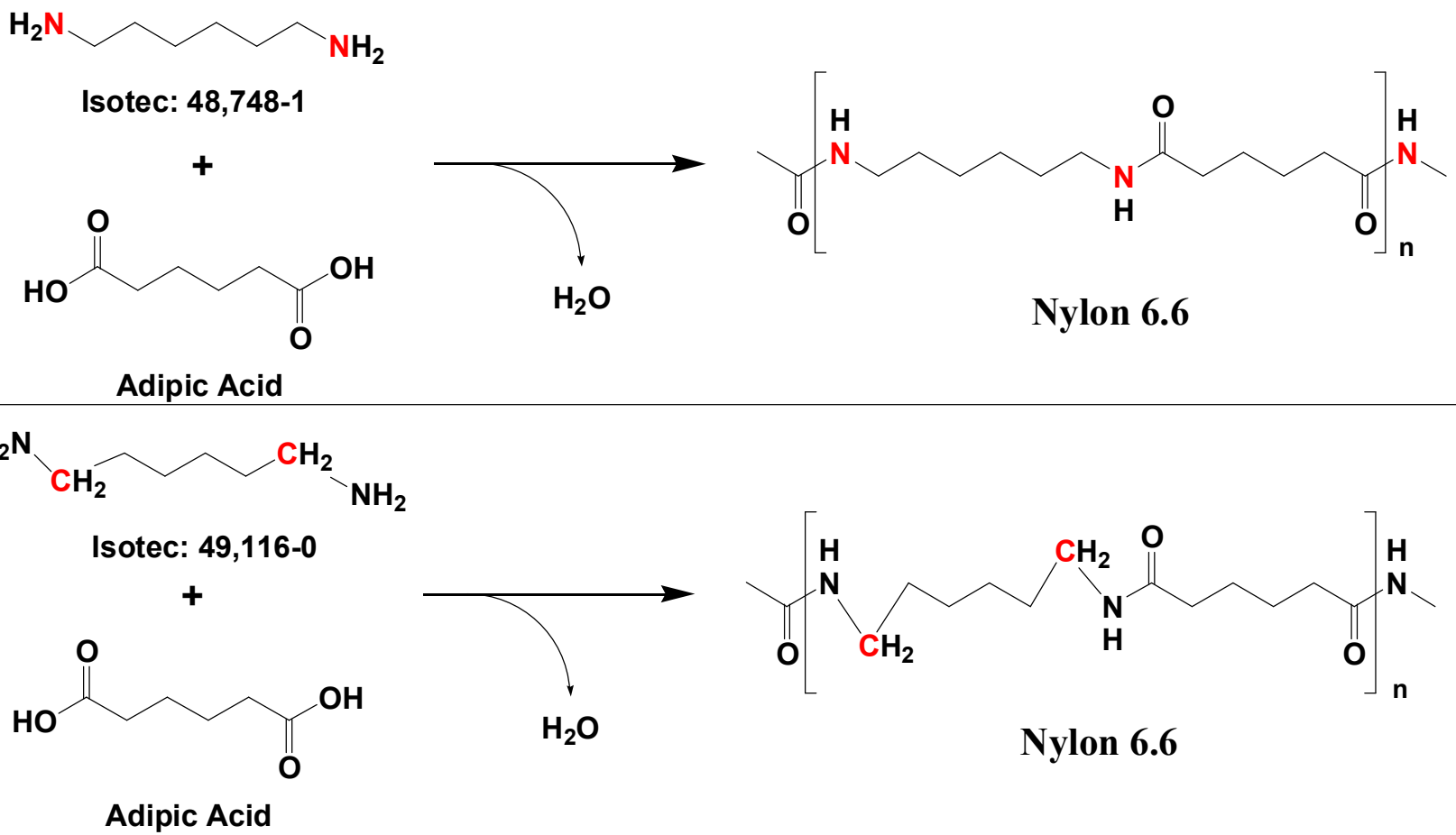
Labeled Nylon

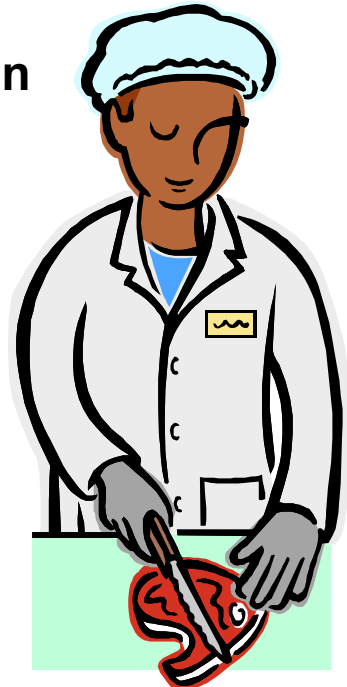


Thermal-oxidative vs. Hydrolysis

Summary

- Methodology for detailed tracking of (complex) polymer degradation
- Polymer samples are prepared with selective isotopic labeling (This study used polypropylene, with ^{13}C)
- Analysis by NMR (macromolecular products), and by GC/MS (volatile products)
- Allows "mapping" of products onto positions of origin from original polymer
- Provides insights into mechanisms of polymer degradation

A comment on "Mother Nature's" butcher shop



Future Work / Acknowledgments

Studies on the degradation of polypropylene via radiation

Comparison of radiation to thermal mechanistic pathways

Isotopically labeled Nylon 6.6

Search for the next labeled polymer to study

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Questions?