THERMAL DEGRADATION OF POLYPROPYLENE

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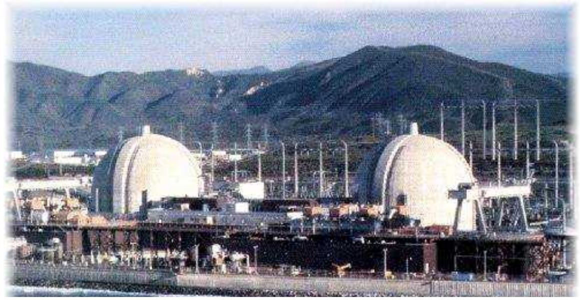
National Nuclear Security Administration

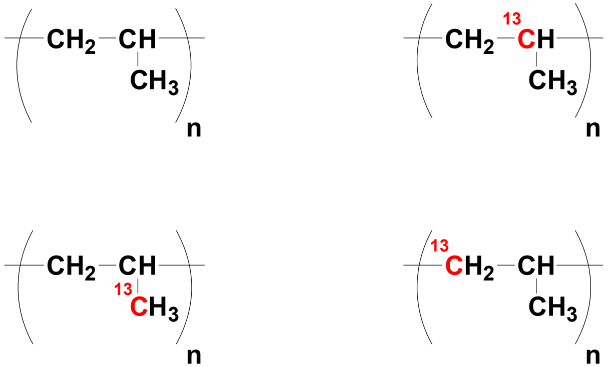
Organic Materials Aging and Degradation

O-rings

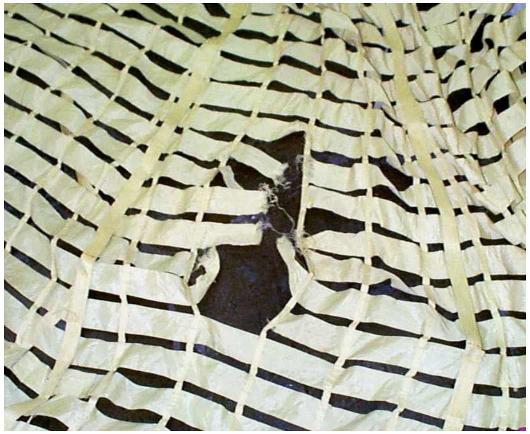


Nuclear Power Plant Cable Insulation

Aircraft Wire Insulation



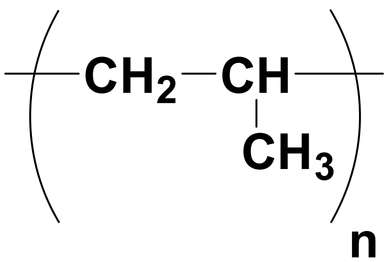
Labeled Polypropylene



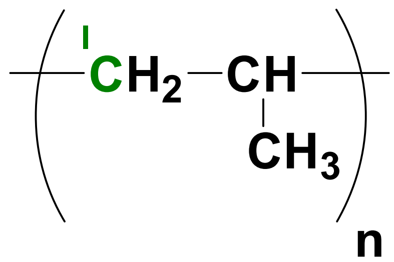
Textiles

Labeled Polypropylene

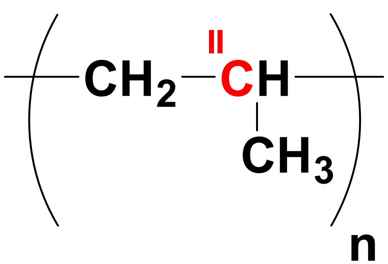
- Prepared 3 polypropylene samples with specific ^{13}C labels
- Goal: Map oxidation products back to macromolecular structure
- Analytical Techniques:
  - Solid-state NMR (solid products)
  - GC/ mass spec (volatile products)



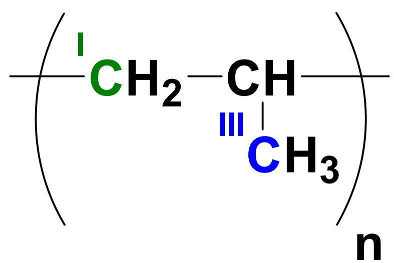
unlabeled



C(1)



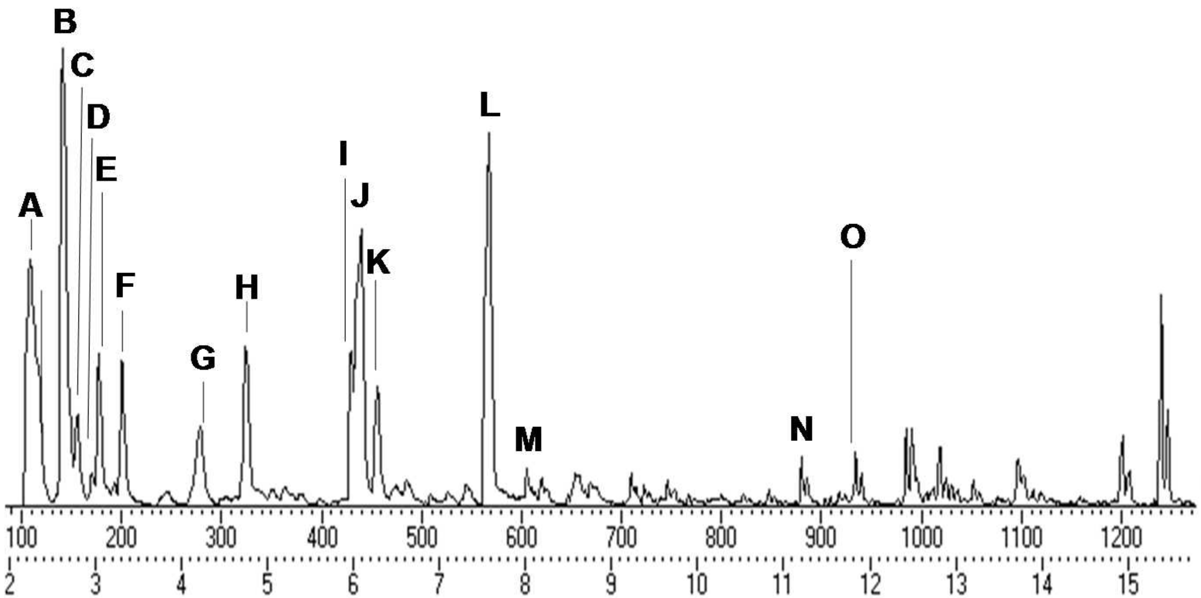
C(2)



C(1,3)

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

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

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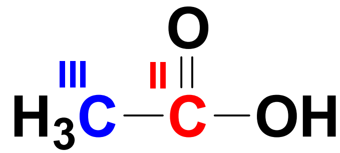
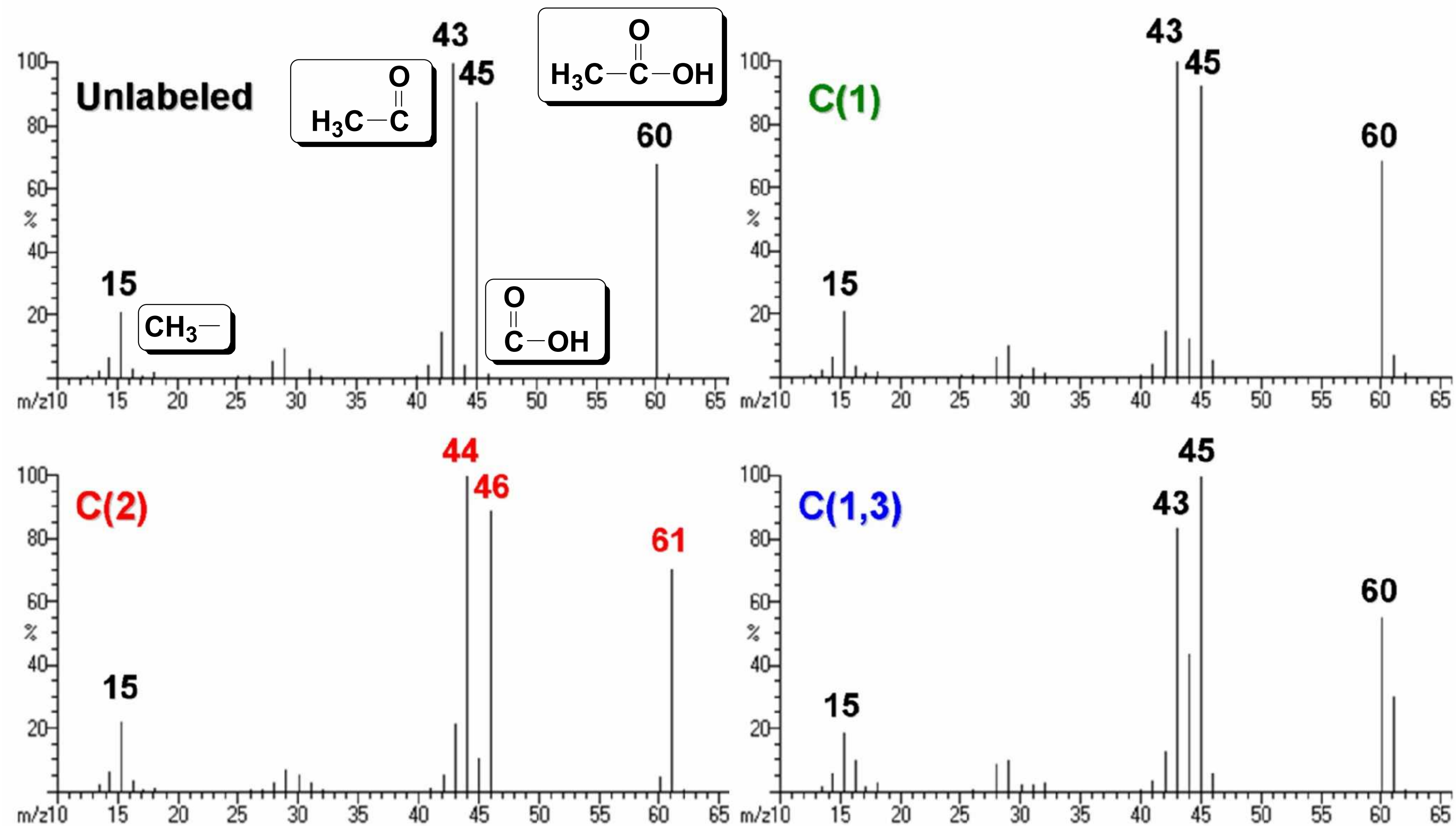
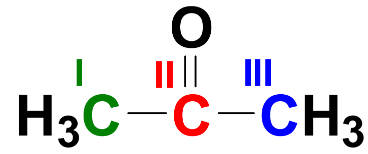
Acetic Acid

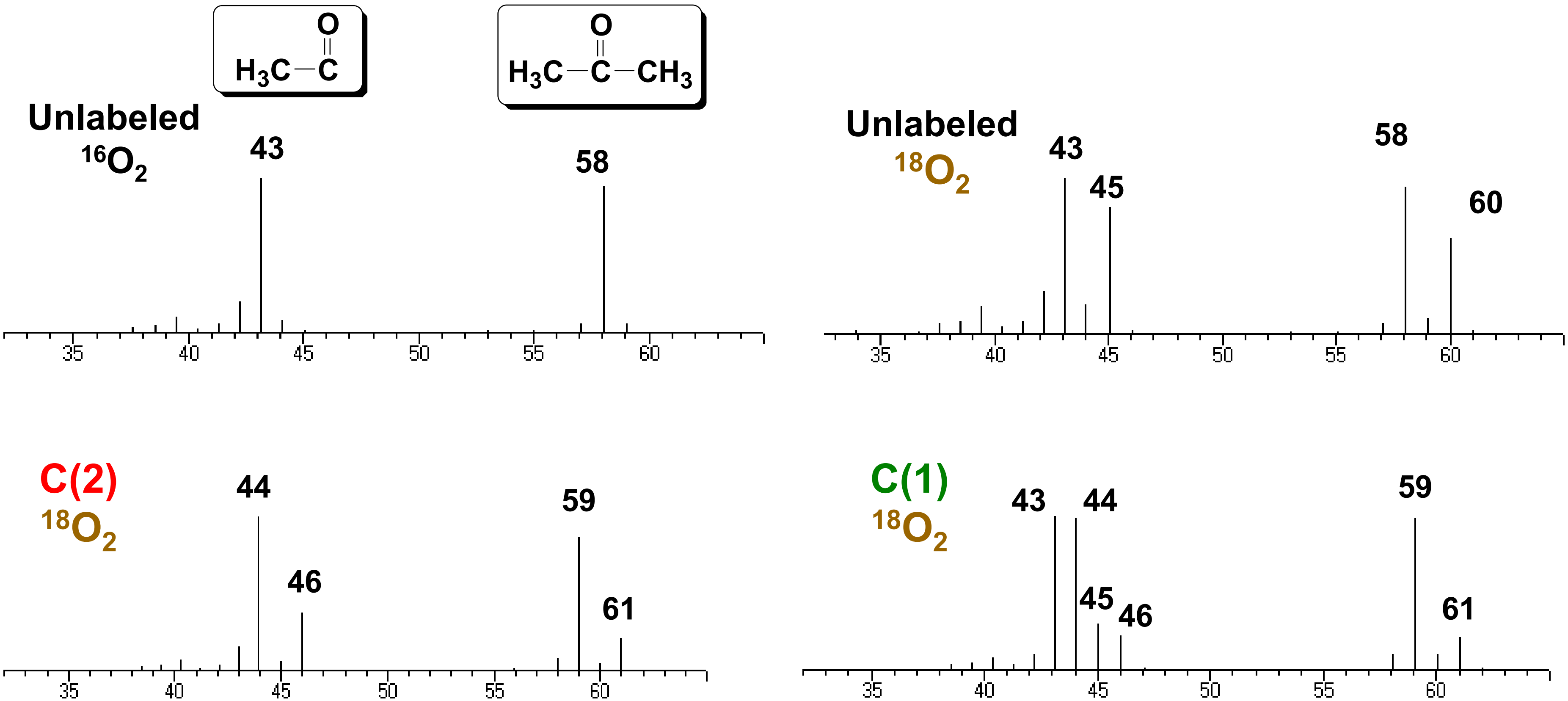




Thornberg, S. M.; Bernstein, R.; Mowery, D. M.; Klamo, S. B.; Hochrein, J. M.; Brown, J. R.; Derzon, D. K.; Clough, R. L. *Macromolecules,* Insights into Oxidation Pathways, from Volatile Products of Polypropylene with Selective Isotopic Labeling **2006**, *39*, 5592-5594.

Acetone with $^{18}O_2$





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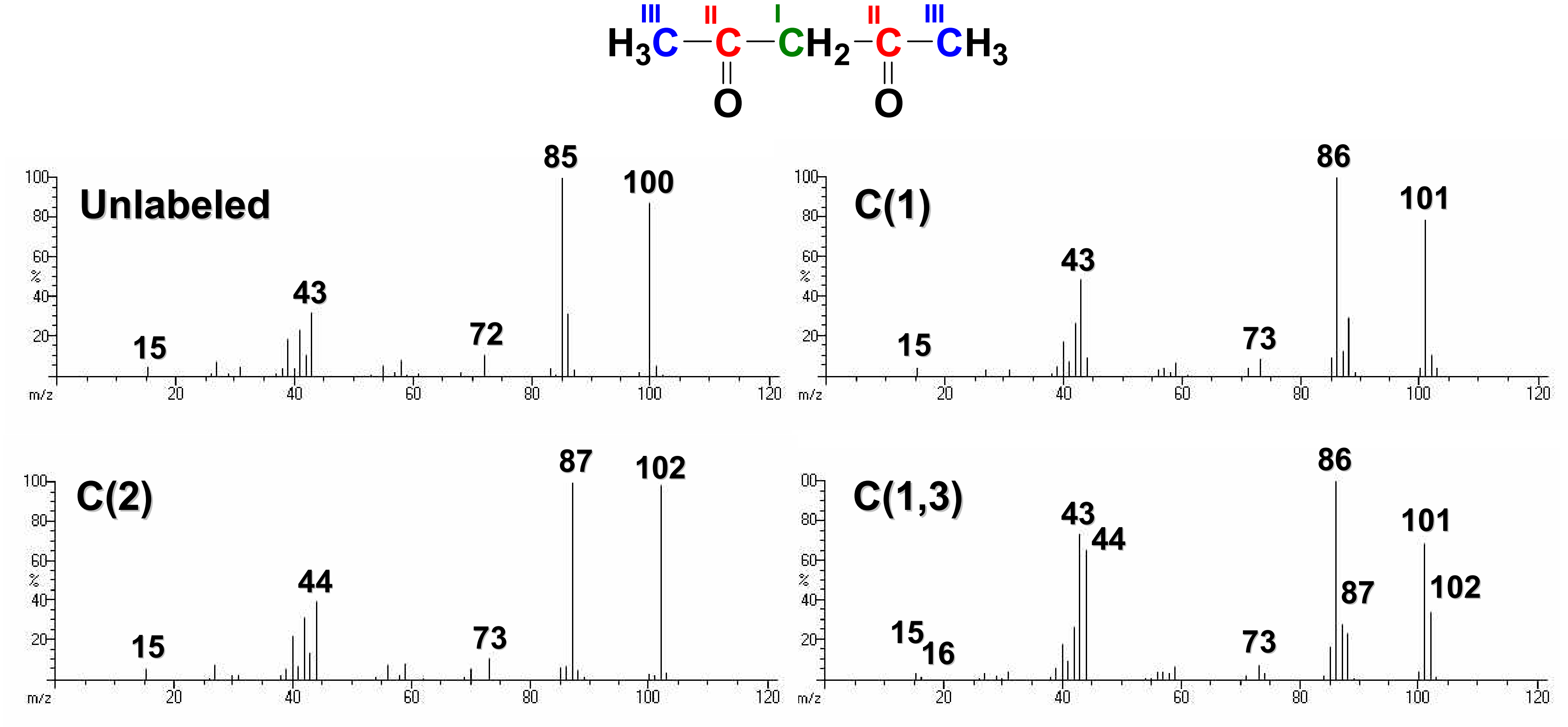
Pentane-2,4-dione



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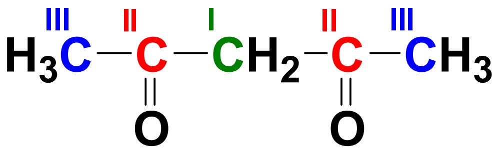
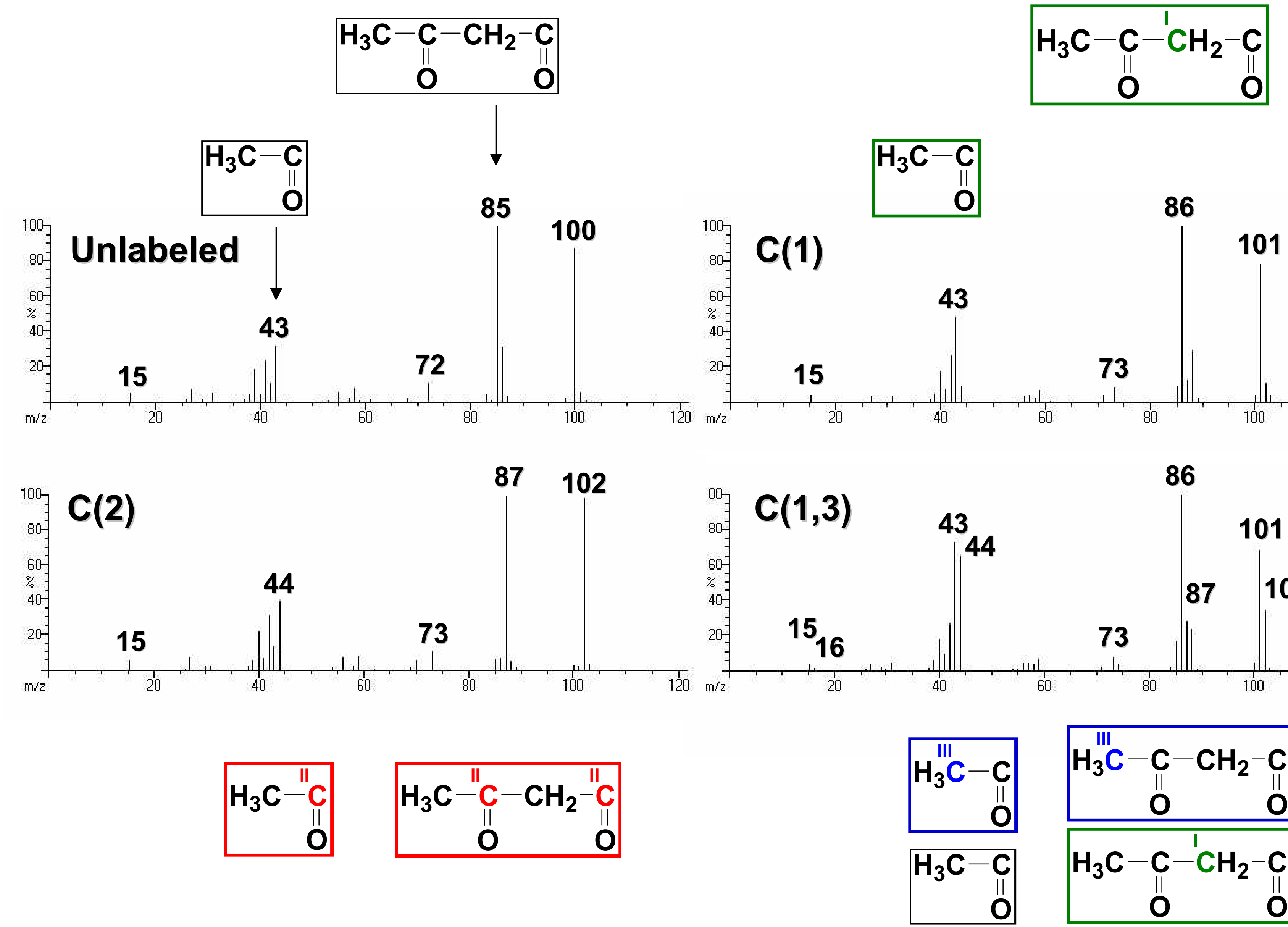
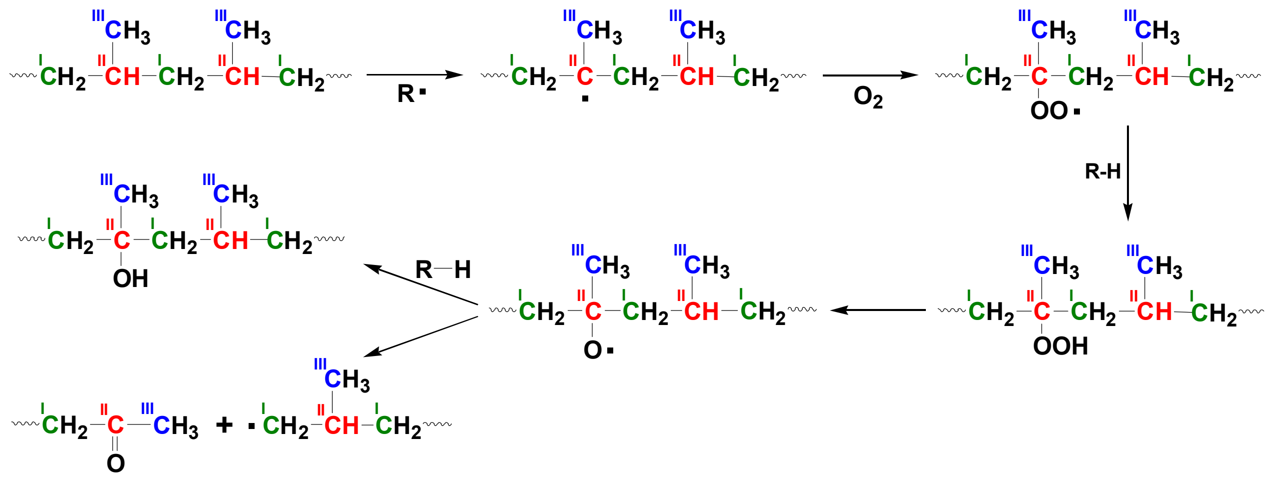
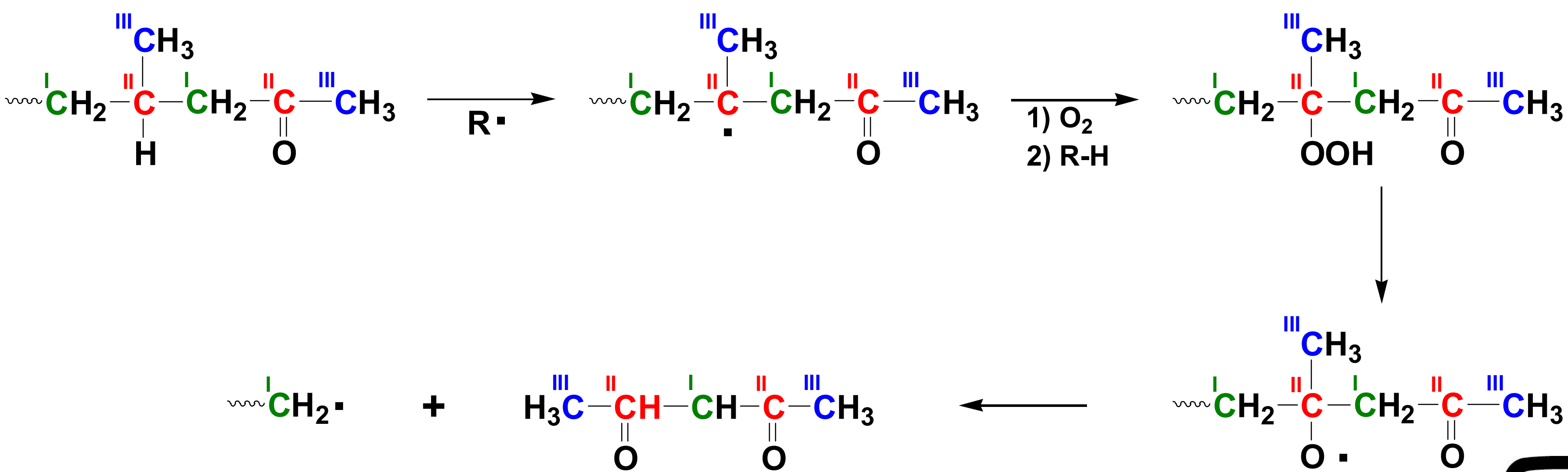


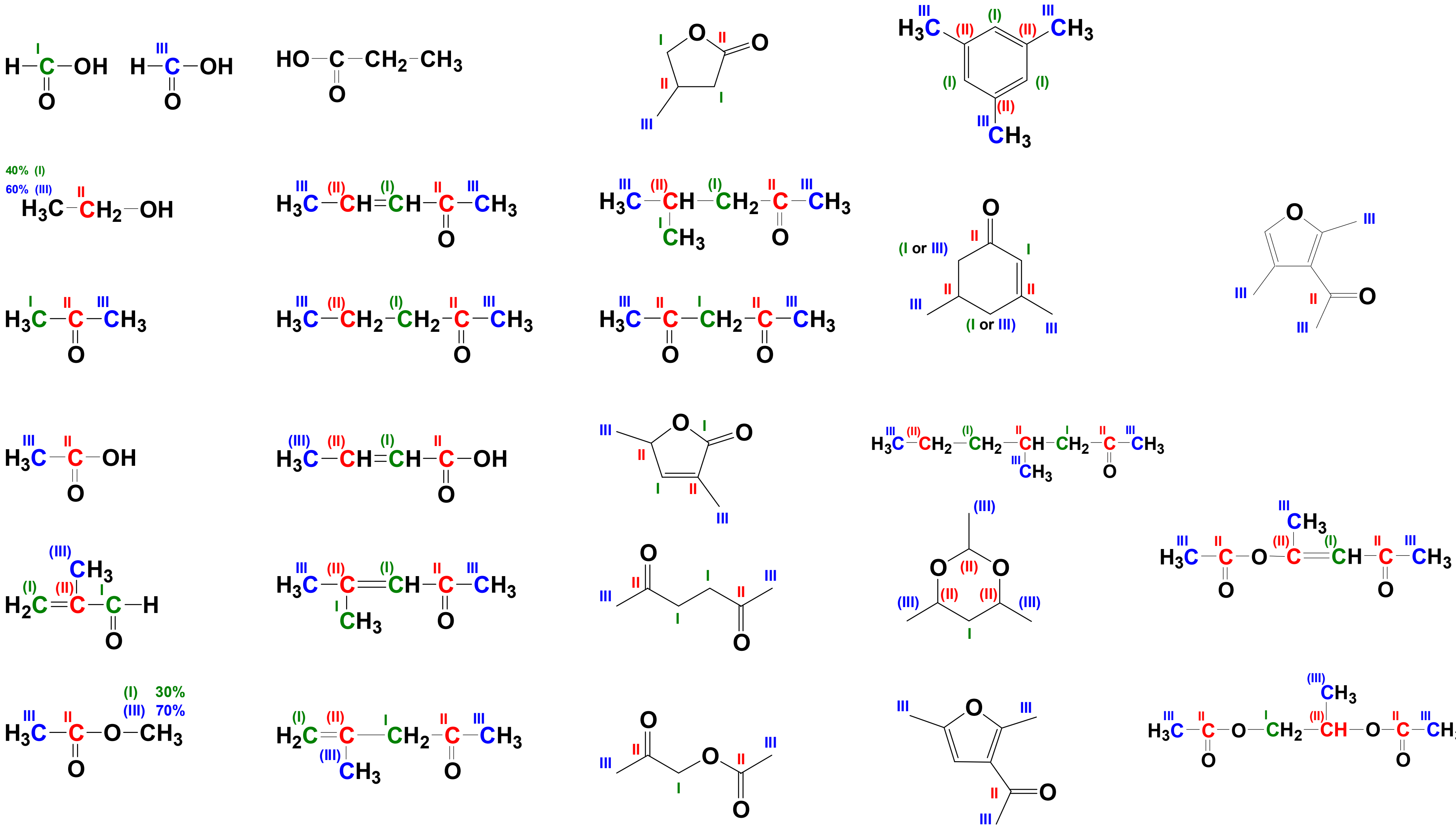


Possible Mechanistic Schemes





Various Thermal-oxidative Degradation Products



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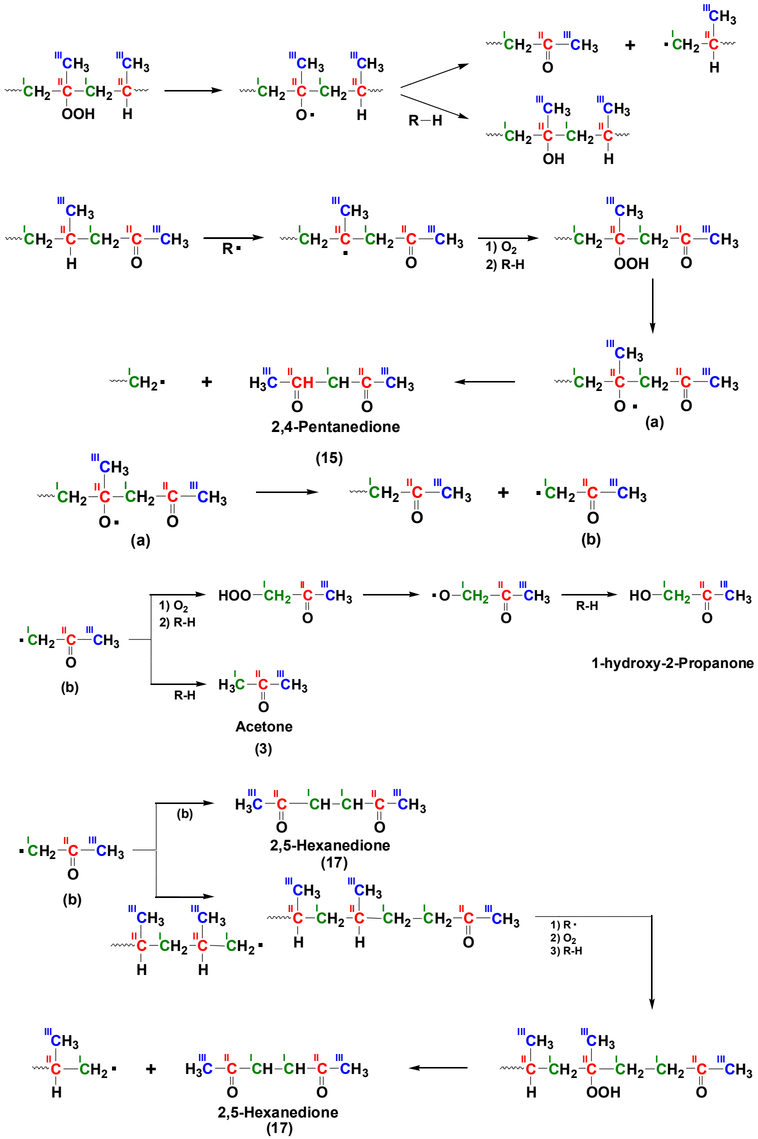
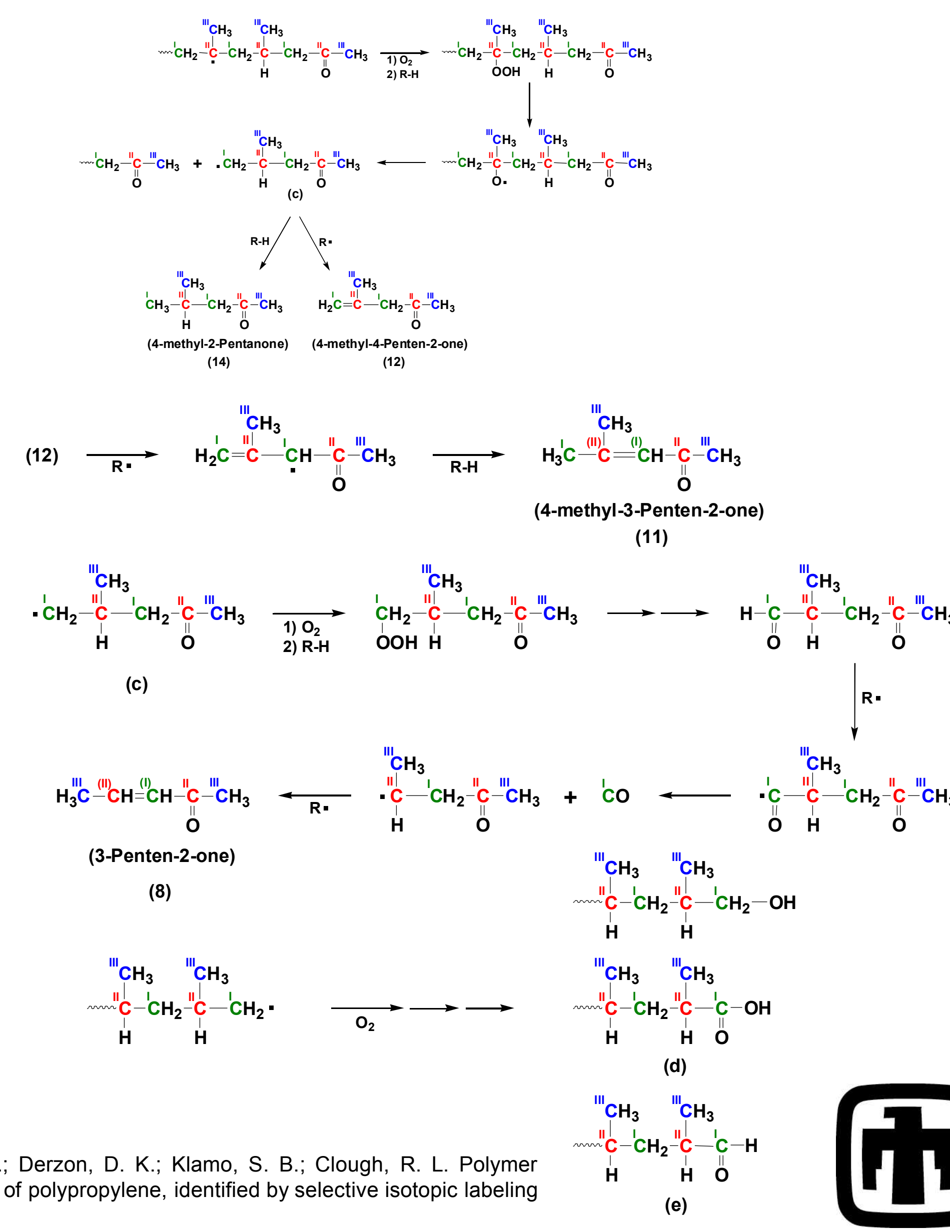
Reaction Mechanisms





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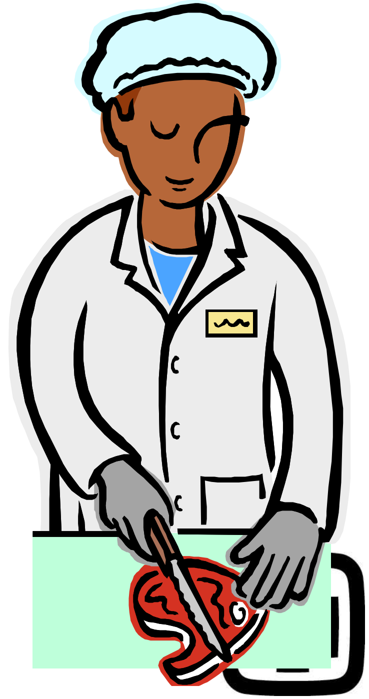
Summary

- 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 next labeled polymer for study

Acknowledgements: The authors thank Judith F. Banet, Rachael D. Boyd, and Jessica D. Leong for assistance in collating and reducing the GC/MS data.