The Abdus Salam
International Centre for Theoretical Physics

United Nations
Educational, Scientific and
Cultural Organization

IAEA
International Atomic Energy Agency

2227-4

Joint ICTP-IAEA Workshop on Radiation Resistant Polymers

14 - 18 March 2011

Radiation oxidation mechanisms in polyolefins, studied by isotopic labeling: O-17 and C-13

Roger L. Clough

Albuquerque
New Mexico
USA

Radiation oxidation mechanisms in polyolefins, studied by isotopic labeling: O-17 and C-13

---

*Analytical techniques: NMR and Mass Spectroscopy

Robert Bernstein, Steven M. Thornberg, Roger A. Assink, Daniel M. Mowery, M. Kathleen Alam, James M. Hochrein, Jason R. Brown, Adriane Irwin, Dora K. Derzon, Sara B. Klamo and Roger L. Clough

Sandia National Laboratories, Albuquerque, NM, 87185, and Arnold and Mabel Beckman Laboratories of Chemical Synthesis, California Institute of Technology, Pasadena, CA 91125

Polymer Processing with Controlled Degradation as Desired Result

- PTFE (Teflon) irradiation (MW and particle size decrease, oxidation)
  - Compatabilization; additive for inks, lubricant

- Polypropylene irradiation (alteration of MW distribution)
  - Improved processing properties, higher melt flow index

- Viscose process (partial degradation of cellulose) for making Rayon

- Irradiation of other natural polymers (chitin, etc)

- Surface modification of polymers (adhesion, wetting)

- Polymer recycling

- "Peroxidation" method of grafting (oxidation is an intermediate step in the processing)

Polymer Processing in which Degradation is an Unwanted Byproduct

- **Radiation sterilization of disposable medical items**
  - **(Polypropylene syringes, rubber gloves, cell culture dishes, etc.)**

- **Radiation treatment of UHMWPE: hip and knee joint replacement**
  - **Improved wear properties, plus sterilization**

- **Numerous crosslinking and curing applications**

- ***In these cases, the desired result is to minimize degradation to the extent possible***
  - **(process conditions, stabilizer additives, post-irradiation annealing)**

- **Stability of polymers in long-term radiation environments, in the presence of air**
  - **containment buildings of nuclear power plants (cable insulation, etc.)**
  - **radioisotope processing facilities**
  - **large particle physics facilities (CERN, Fermilab, etc.)**

Most Applications of Polymers plus Radiation Involve Exposure to O_2, Either During or After Irradiation (or Both)

- **Oxidation Chemistry typically dominates the Irradiation Chemistry**

We set out to provide a better method for detailed understanding of the mechanisms of radiation-oxidative degradation of polymers

Goals of detailed studies of polymer oxidation mechanisms

- Identify molecular structures on the polymer backbone, after irradiation, including “unstable” species, such as peroxides
- Conduct chemical analysis directly on intact (solid) polymers, without dissolving
- Follow the evolution of various oxidation products as a function of time
- Identify low molecular weight oxidation products (organic compounds) resulting from chain cleavage in oxidizing polymers, and determine the mechanisms (chemistry) of their formation
- Understand the mechanism by which CO and CO_2 are formed from polymers, during radiation oxidation
- Begin correlating oxidation chemistry with changes in macroscopic properties observed in earlier studies

There are Few Methods to <u>Directly</u> Observe Hydroperoxides

Indirect

(chemical modification & often dissolution)

- **colorimetric**
  - iodometric analysis
  - ferrometric complexation
- **infrared detection**
  - hydrosulfates
  - nitrate groups

Direct

- **infrared detection**
  - isolated hydroperoxides
- **NMR**
  - solution

    Cheng, Schilling, Bovey
    Macromol. **1976**, *9*, 363.
    Jelinski *et. al.*
    Macromol. **1984**, *17*, 1650.

Goal: direct observation without dissolution - real time observation in the solid state.

A very short course in NMR Spectroscopy.

The three most common elements in aged organic materials are hydrogen carbon and oxygen:

Active Isotope	Natural Abundance	Enriched
☐ ^{1}H	99.98 %	
^{13}C	1.1 %	99 %
^{17}O	0.037 %	80 %

Although hydrogen has an abundant active isotope, it is not the most useful for chemical analysis.

Carbon is most useful for characterizing the polymer chain.

Oxygen is useful for characterizing oxidation.

Isotope labeling will provide increased sensitivity and enable us to selectively examine the aging process.

Isotopic Labeling + NMR for Understanding Polymer Irradiation Effects (Degradation, Oxidation, Hydrolysis)

- **Label the Polymer**

^{13}C

- **Enhanced Sensitivity**
- **Morphology Changes**
- **Labeling of Specific Sites within the Macromolecule for More In-depth Mechanistic Information**

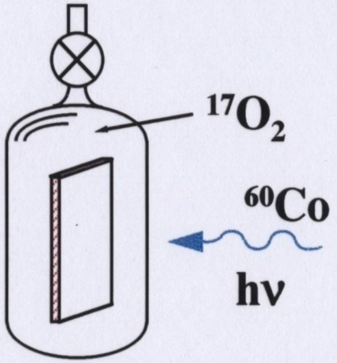
- **Label the Environment**

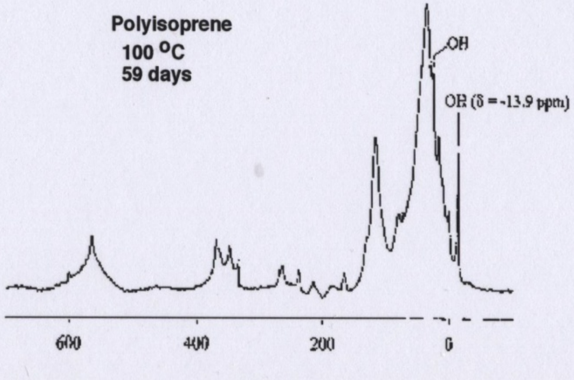
$^{17}O_2$ $H_2{}^{17}O$

^{15}NO $^{15}NO_2$

Every Peak in the NMR Spectrum is a Reaction Product

Oxidation of Organic Materials is being Investigated by ^{17}O Isotope Labeling

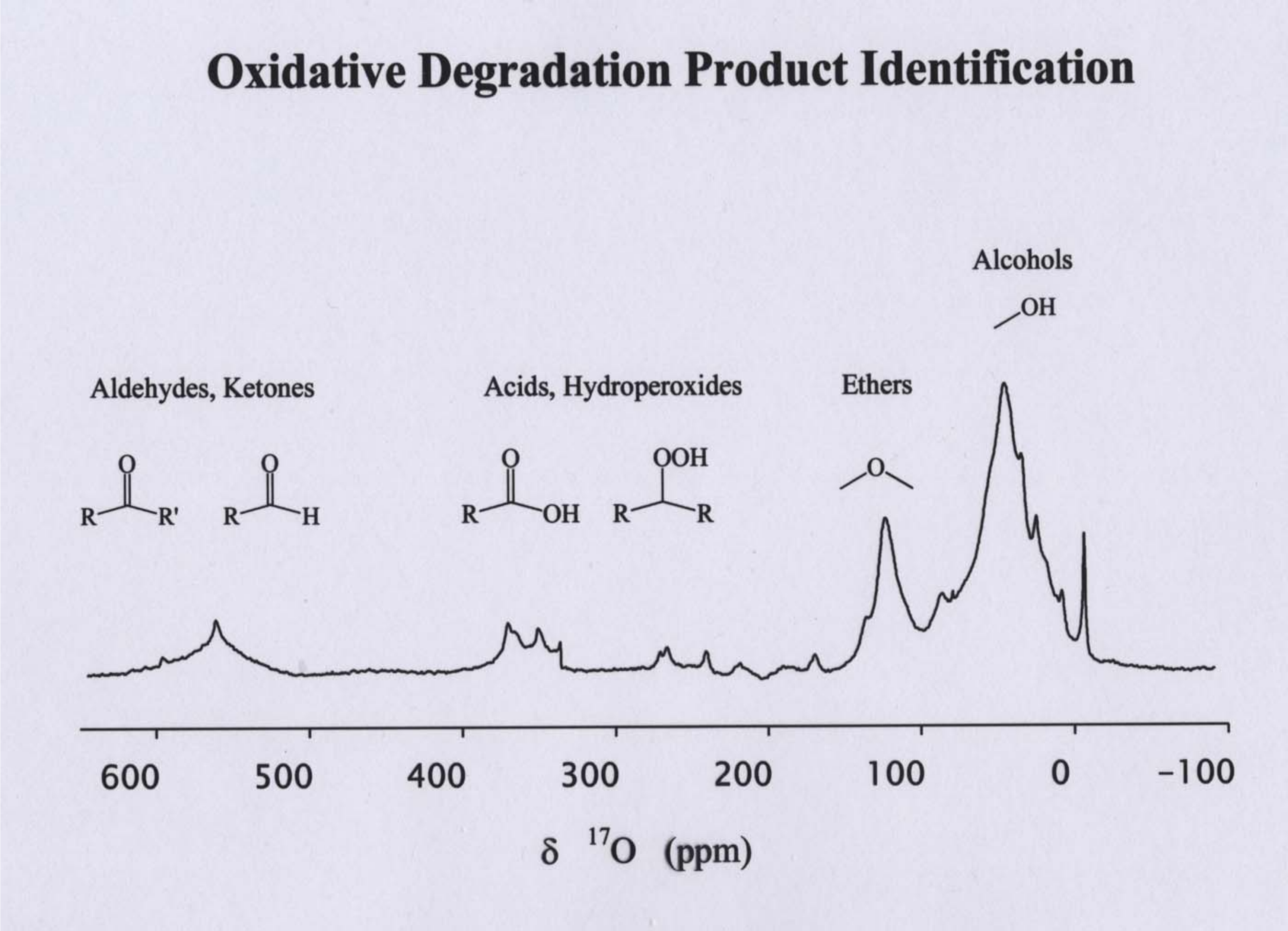




- This slide demonstrates the use of isotopically enriched oxygen gas to study the oxidative degradation of organic materials under environmental stress
- The NMR spectrum shows the complex mix of products formed by polyisoprene; each resonance corresponds to a specific chemical structure

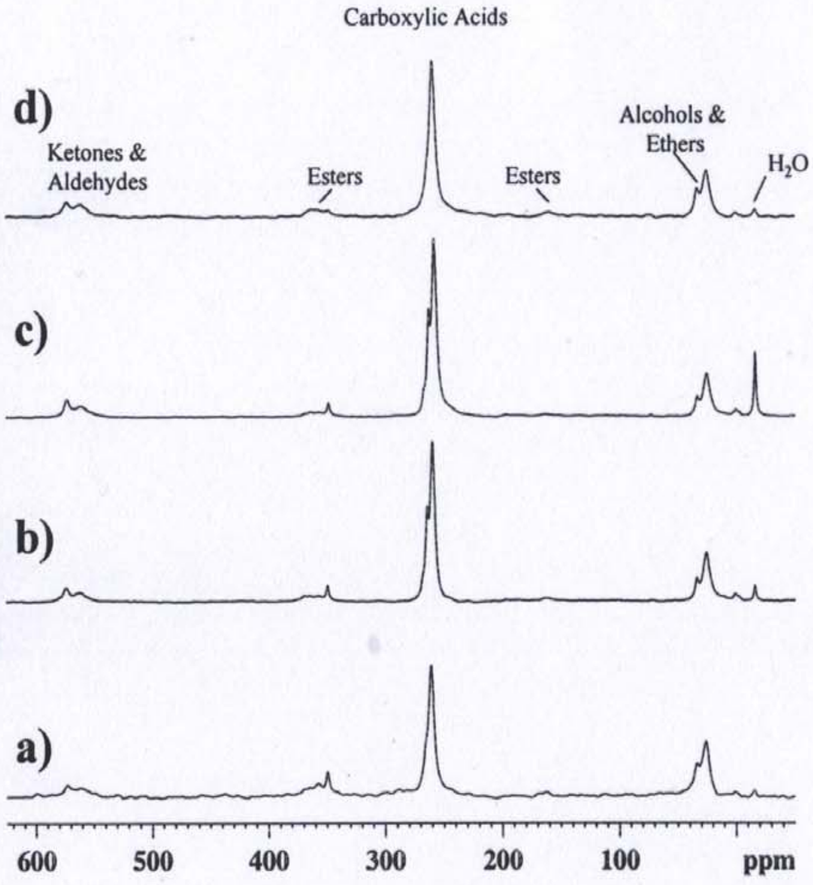
Isotope labeling combined with NMR spectroscopy provides a sensitive probe of the degradation products

O-17 NMR

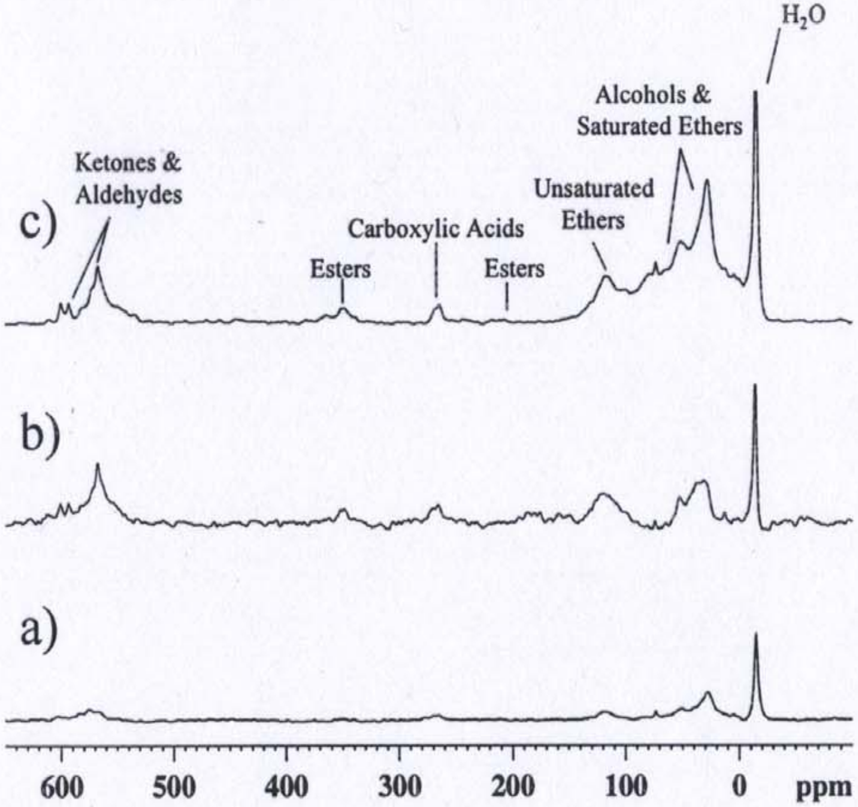


Oxidative Degradation Product Identification

O-17 NMR Spectra of Material Following γ-Irradiation Under O-17 Labeled O_2



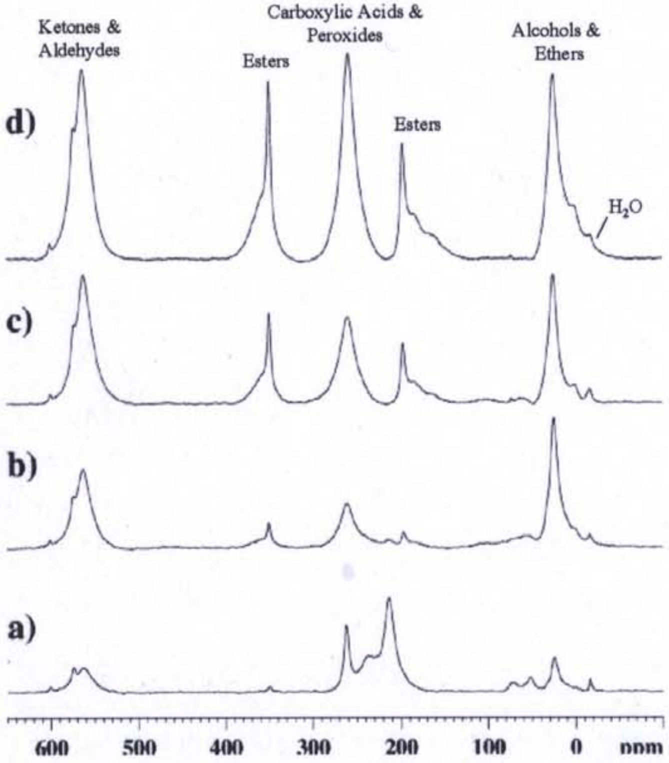
pentacontane



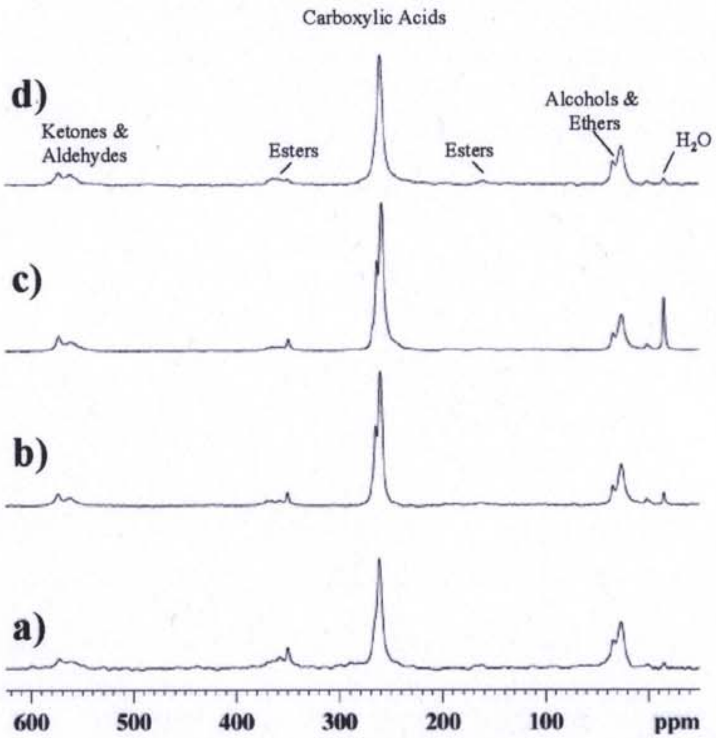
polyisoprene

Mechanistic Differences Between Radiolytic and Thermal Oxidation

Pentacontane - 125 °C



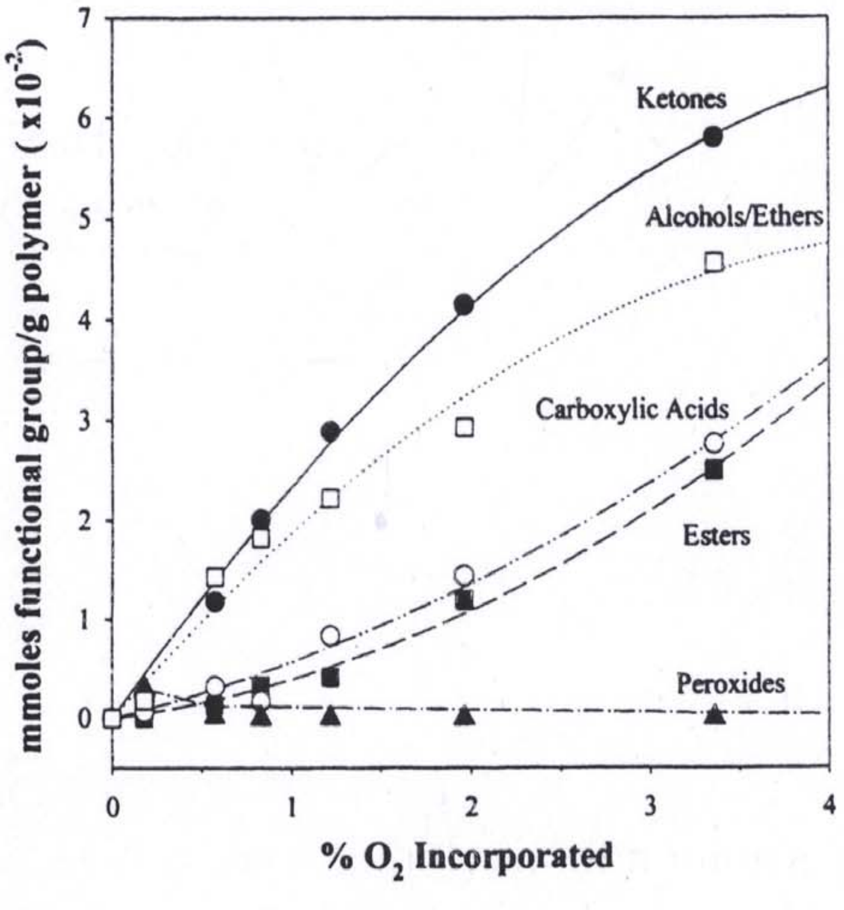
Pentacontane - γ irradiation



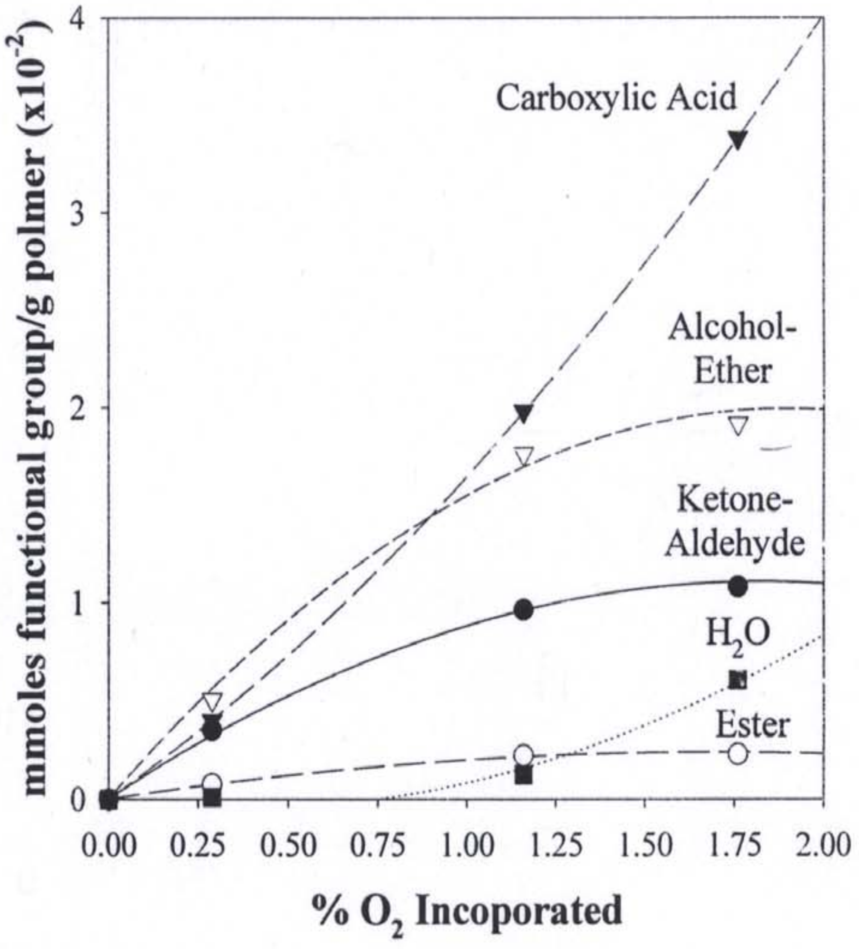
- **Under radiolytic oxidation the formation of carboxylic acids becomes dominant in long chain hydrocarbons.**

Oxidation Products in Pentacontane ($C_{50}H_{102}$) by O-17 NMR

Thermal Oxidation



Gamma Irradiation in Air



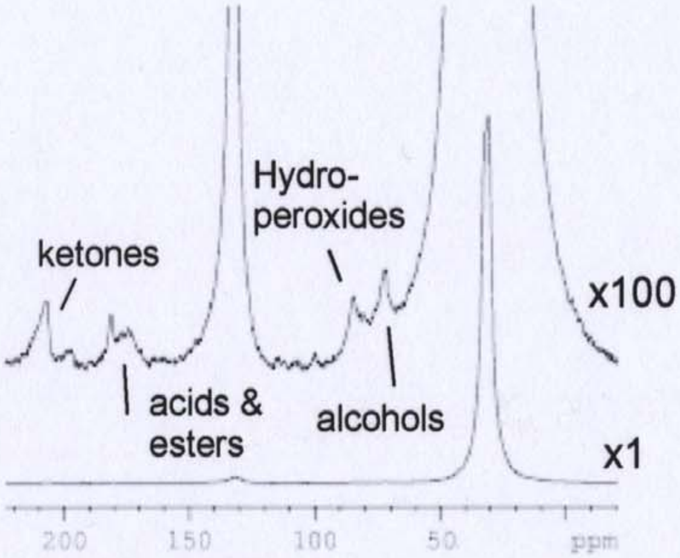
- **Isotopic labeling of the polymer (prior to irradiation experiments)**

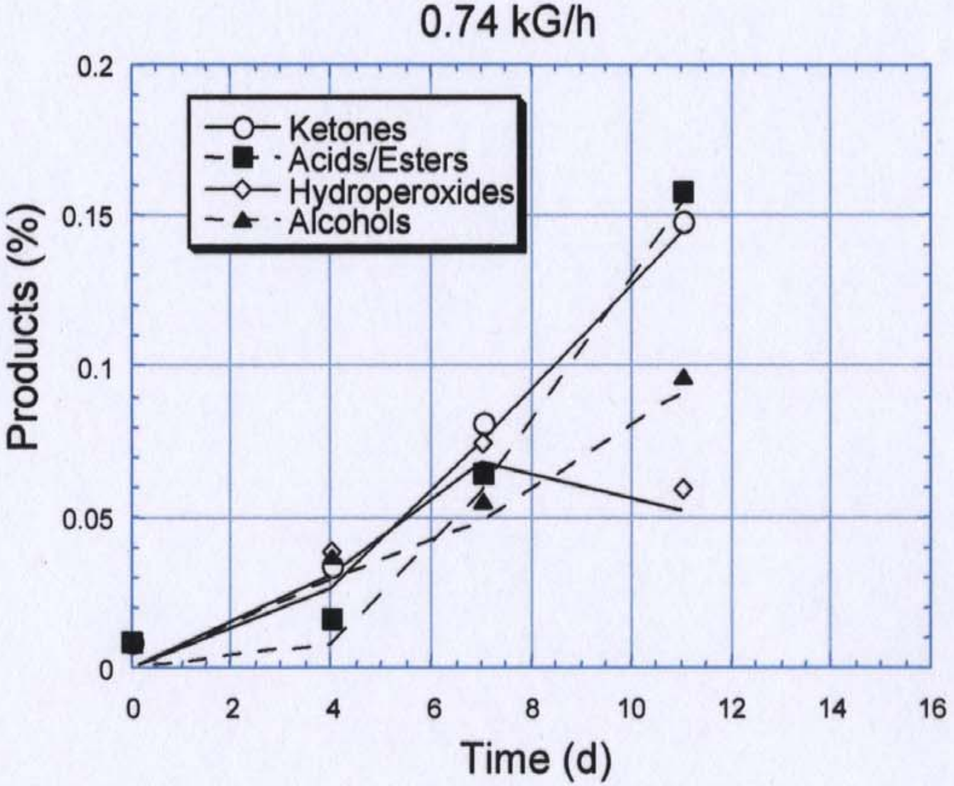
- **C-13 Labeling of:**
  - **Polyethylene**
  - **Polypropylene**

- **Irradiation Experiments are conducted under “ordinary” air atmosphere [O-16]**

- **Measurements by C-13 NMR**

Polyethylene-$^{13}C_2$ was Enriched at the 99 % Level.





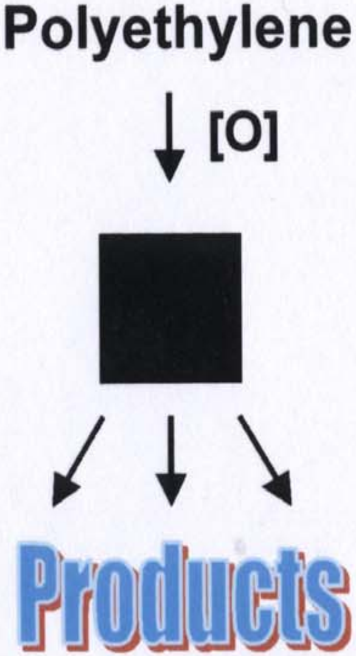
Compared to Natural Abundance:

1. **20 min vs 20 hr**
2. **0.02 % vs 0.1%**
3. **solid vs liquid**

Direct observation of the hydroperoxide species at RT.

Annealing Experiments Were Used to Distinguish Between Reaction Pathways.

- **Several reaction pathways have been proposed in the literature.**

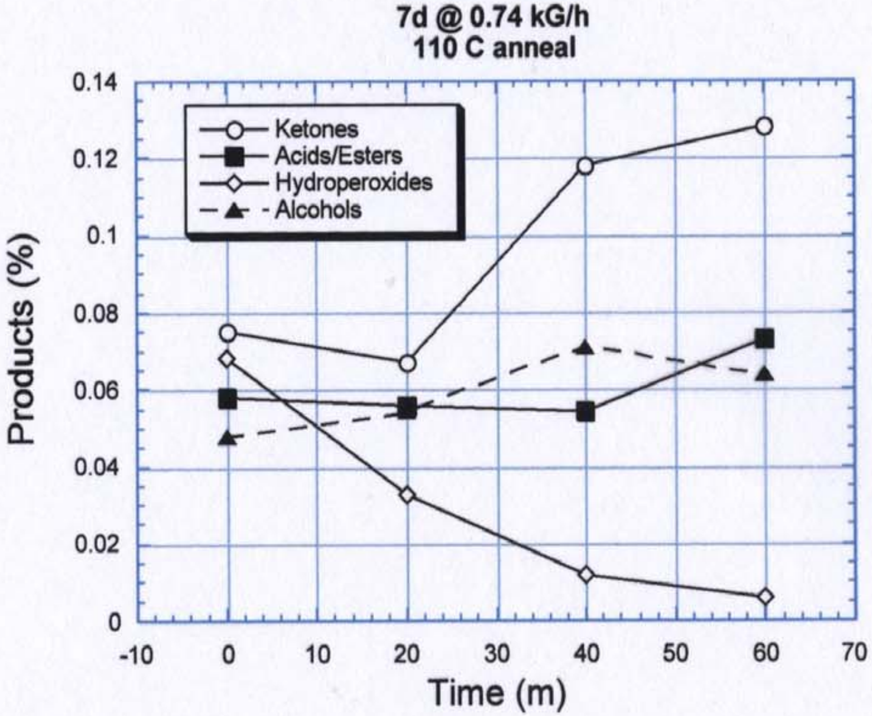


Polyethylene

[O]

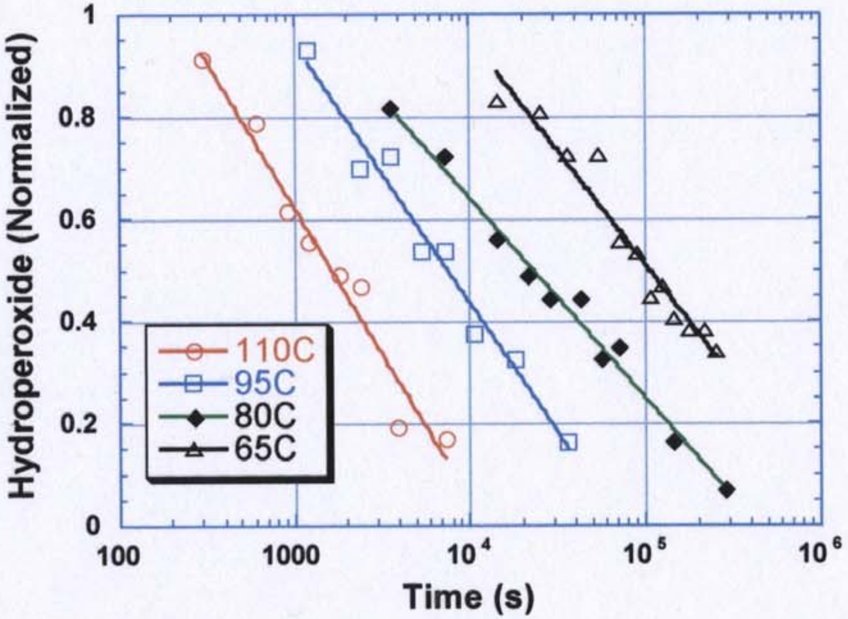
Products

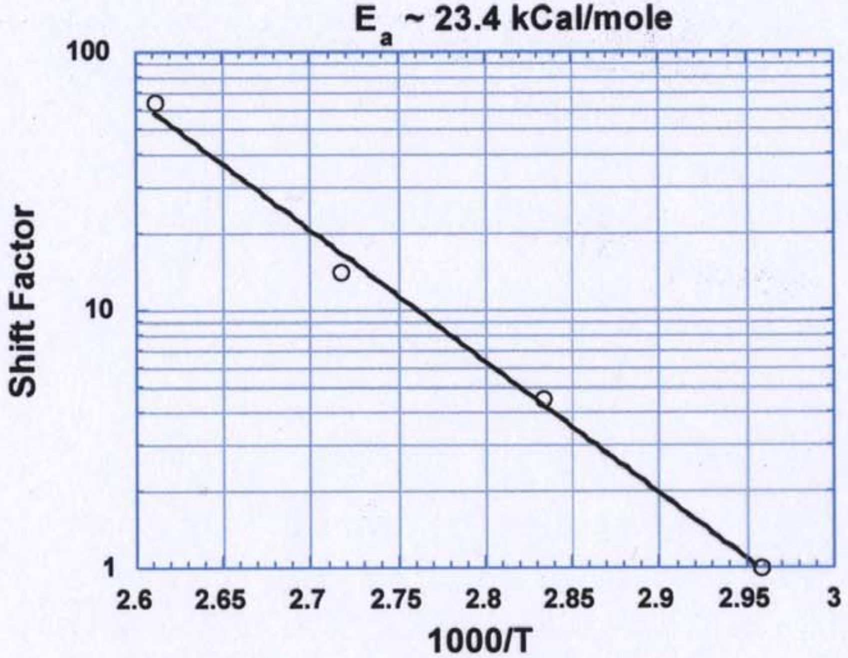
- **After radiation aging for 7 days, the sample is annealed at 110 C for 20, 40 and 60 minutes.**



- **We find that the hydroperoxide is converted primarily to ketones.**

Annealing at Various Temperatures Enables One to Measure the Activation Energy.





- Annealing was done *in situ* for intermediate temperatures.
- Shift factors for the hydroperoxide half-life were cal'c. Half-life of species ~ 4 months at ambient temps.

Using C-13 (labeled polymer)

- Readily see oxidation products at low extent of conversion

- Direct quantitative measurements on oxidized SOLID polymer
  - (no dissolving, heating, or other sample treatment)

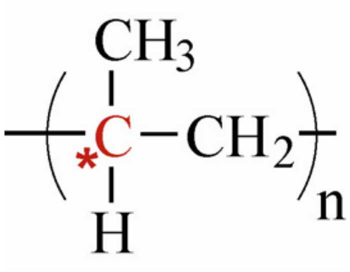
- Have followed thermal decomposition of peroxides formed in PE after γ irradiation in air:
  - Measured E_a in solid phase (23.4 kcal/mol)
  - Followed appearance of oxidation products as the peroxides decomposed (ketones predominate)

- Also measure radiation-induced changes in crystallinity in PE

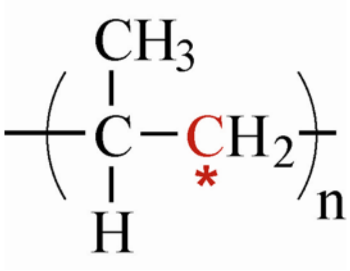
Selective Labeling of Polymers for Irradiation Experiments: [*Polypropylene*]

Selective isotopic labeling with carbon-13

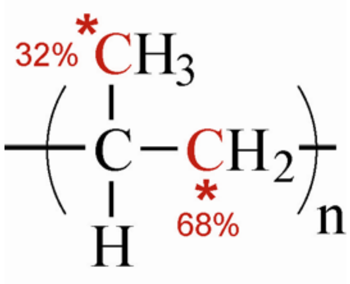
C(2) labeling



C(1) labeling



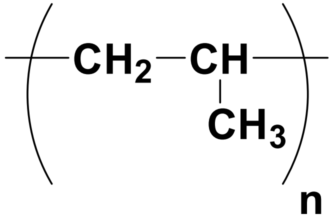
C(1,3) labeling



For the C(1,3) labeled PP, the 68/32 distribution was the result of scrambling during polymerization.

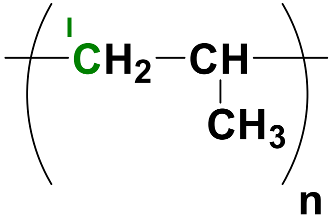
Selective ^{13}C labels allow for the identification of oxidation products, their origin on the PP chain, and their relative concentrations with increased sensitivity.

- **Prepared 3 polypropylene samples with specific Carbon-13 labels**



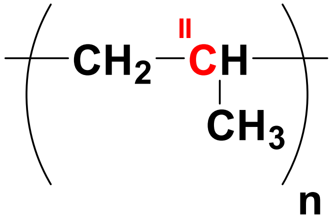
$$\left(CH_2 - \underset{CH_3}{\underset{|}{CH}} \right)_n$$

unlabeled



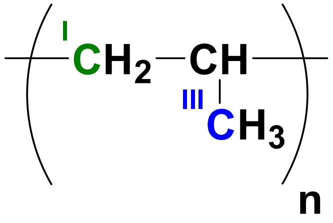
$$\left(\overset{I}{C}H_2 - \underset{CH_3}{\underset{|}{CH}} \right)_n$$

C(1)



$$\left(CH_2 - \underset{CH_3}{\underset{|}{\overset{II}{C}H}} \right)_n$$

C(2)



$$\left(\overset{I}{C}H_2 - \underset{{}^{III}CH_3}{\underset{|}{CH}} \right)_n$$

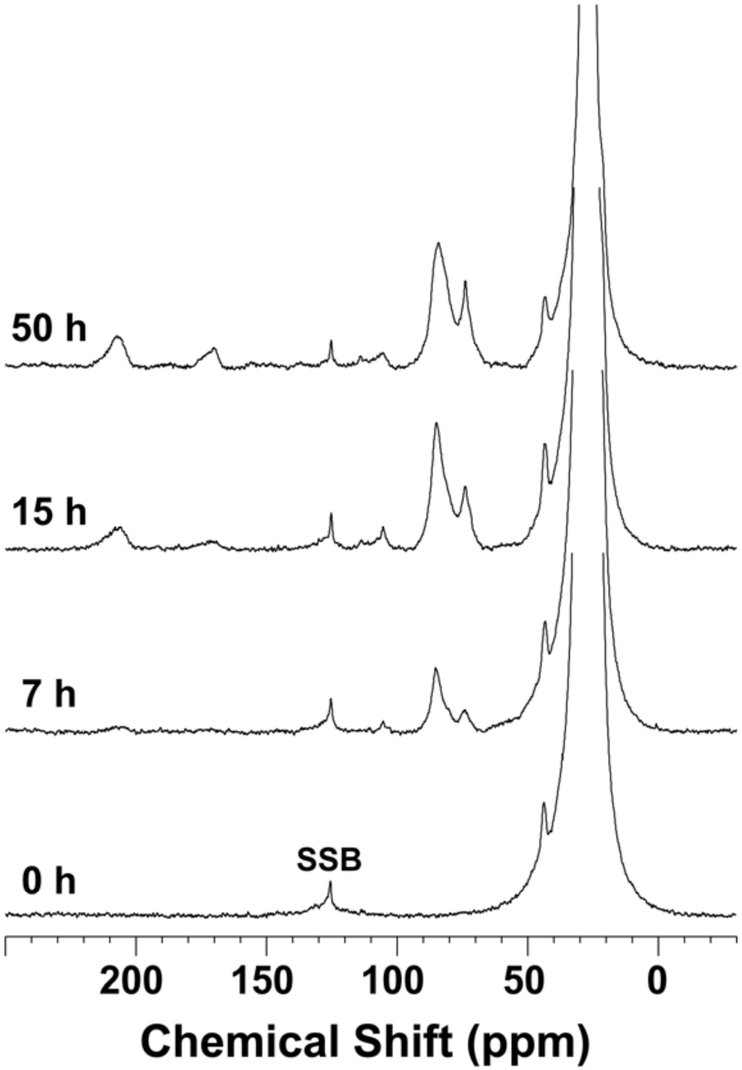
C(1,3)

- **Goal: Map oxidation products back to macromolecular structure**

- **Analytical Techniques:**

Solid-state ^{13}C NMR	**(solid products)**
FTIR	**(solid products)**
GC/ mass spec	**(volatile products)**

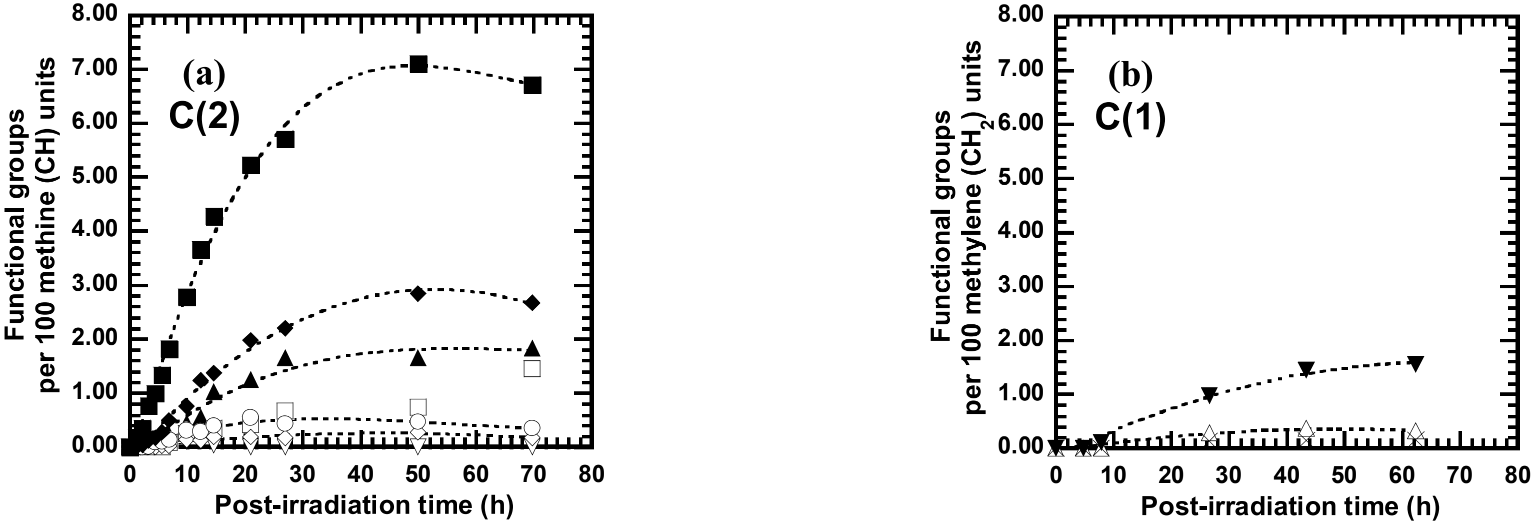
^{13}C NMR Spectra of Post-Irradiation Thermally Aged Polypropylene



C(2) labeled polypropylene exposed to 24 Mrad of γ-radiation in argon at 24°C and then subjected to post-irradiation thermal aging in air at 109°C.

The major degradation products are tertiary peroxides, tertiary alcohols and methyl ketones.

Product Distribution of Post-Irradiation Polypropylene (irradiated in argon, then held in air at 109^{o}C)

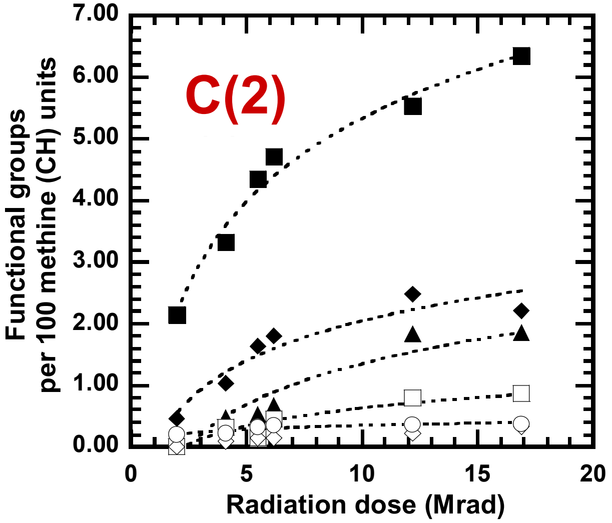


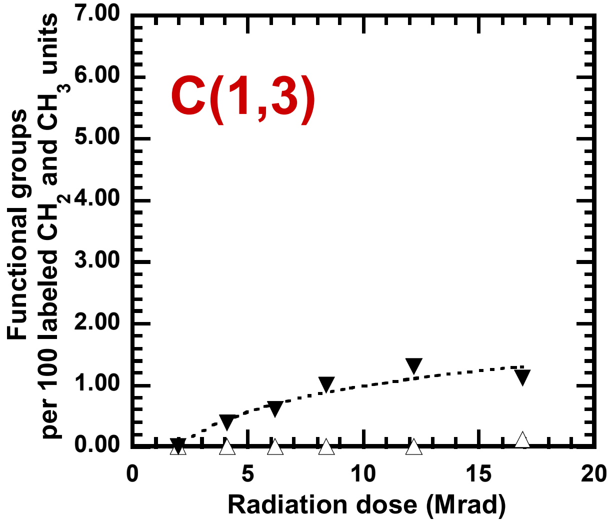
Functional group resonances:

(■) tertiary hydroperoxides / dialkyl peroxides
(♦) tertiary alcohols
(▲) methyl ketones
(Δ) in-chain ketones
(□) esters and/or peresters on C(2) carbon
(▼) esters on C(1) carbon
(◊) ketals on C(2) carbon (114.1 ppm)
(○) ketals on C(2) carbon (105.7 ppm)
(×) ketals on C(1) carbon (100–117 ppm)

The product distribution for both the C(2) and C(1) carbons are similar to thermally aged samples.

γ-Radiation Oxidation at 80°C
Kinetic Accumulation of Oxidation Products

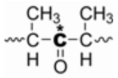
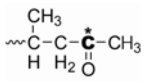
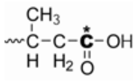
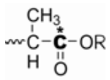
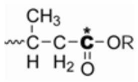
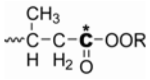
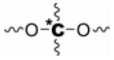
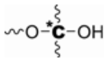
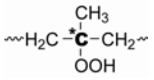
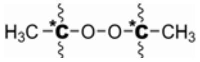
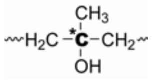




- Unlike thermo-oxidative aging, no apparent induction period is present with product accumulation in γ-radiation oxidation.
- The product accumulation is also much faster with γ-irradiation.

<u>γ-Radiation aging</u>: Film samples were subjected to γ-irradiation under flowing air at room temperature (24°C) and at 80°C. The γ-radiation was generated with a ^{60}Co source at a dose rate of 80-90 krad/h.

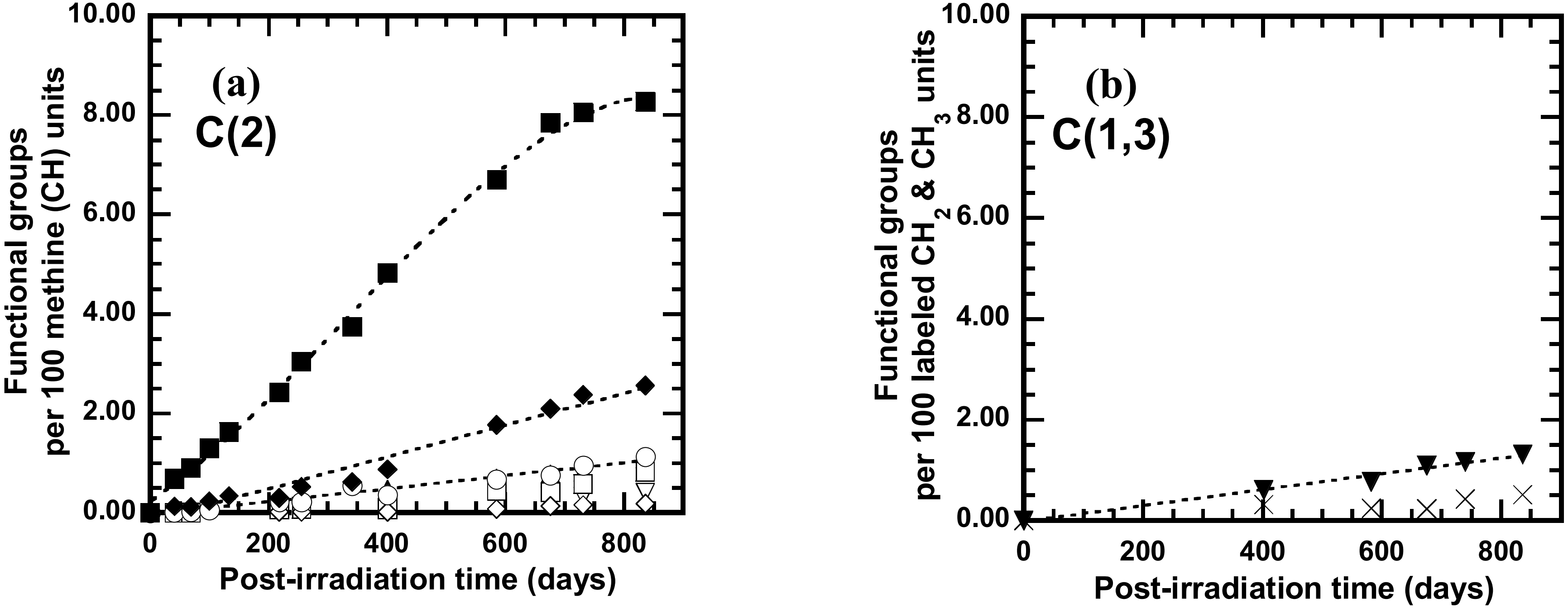
13C Resonances of Oxidation-Induced Functional Groups Observed in Solid-State NMR Spectra of Selectively Labeled Polypropylene Samples.

^{13}C chemical shift (ppm)	Oxidative functional group	PP position of origin	Aging conditions observed*
~215 (broad)	 in-chain ketone	C(1)	γ (80°C) γ' (109°C)
~207 (broad)	 methyl (chain-end) ketone	C(2)	γ (24°C, 80°C) γ' (22°C – 109°C)
~185 (broad)	 carboxylic acid	C(2)	γ (24°C) γ' (22°C)
~179 (broad)	 ester	C(1)	γ (24°C, 80°C) γ' (22°C, 109°C)
170–175 (broad)	 ester	C(2)	γ (24°C, 80°C) γ' (22°C – 109°C)
	 perester		
100–117 (several peaks)	 ketal	C(1) C(2)	γ (24°C, 80°C) γ' (22°C – 109°C)
	 hemiketal		
85.3	 tertiary hydroperoxide	C(2)	γ (24°C, 80°C) γ' (22°C – 109°C)
	 dialkyl peroxide		
74.2	 tertiary alcohol	C(2)	γ (24°C, 80°C) γ' (22°C – 109°C)

γ = exposure to γ-radiation in air

γ' = exposure to γ-radiation in 24°C argon,
followed by post-irradiation thermal aging in air

NMR: Irradiated Polymer held at room temperature in air, for over 2 years



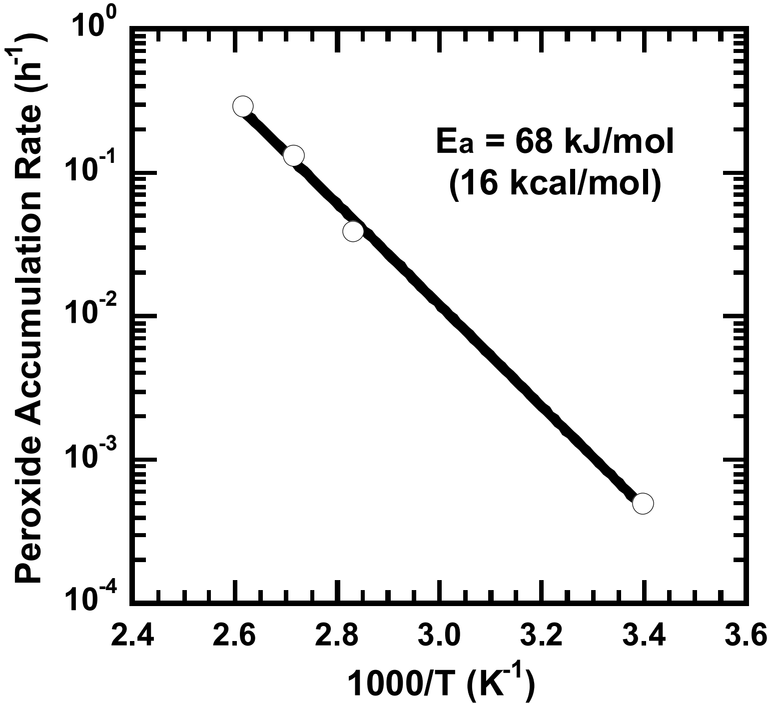
Oxidation products in PP exposed to γ-radiation (240 kGy) in 24 °C argon followed by post-irradiation thermal aging in 22 °C air. (a) C(2) labeled sample; (b) C(1,3) labeled sample. (■) tertiary hydroperoxides and/or dialkyl peroxides; (♦) tertiary alcohols; (▲) methyl ketones; (△) in-chain ketones; (▽) carboxylic acids on C(2) carbon; (□) esters and/or peresters on C(2) carbon; (▼) esters and/or peresters on C(1) carbon; (◊) ketals on C(2) carbon (114.1 ppm); (○) ketals on C(2) carbon (105.7 ppm); (×) ketals on C(1) carbon (100–117 ppm).

The Activation Energy for Accumulation of Tertiary Peroxides

An Arrhenius plot of the tertiary peroxide accumulation rate for C(2) labeled polypropylene.

γ-radiation in argon at 24°C followed by thermal aging in air.

E_a ~ 68 kJ/mol (16 kcal/mol)



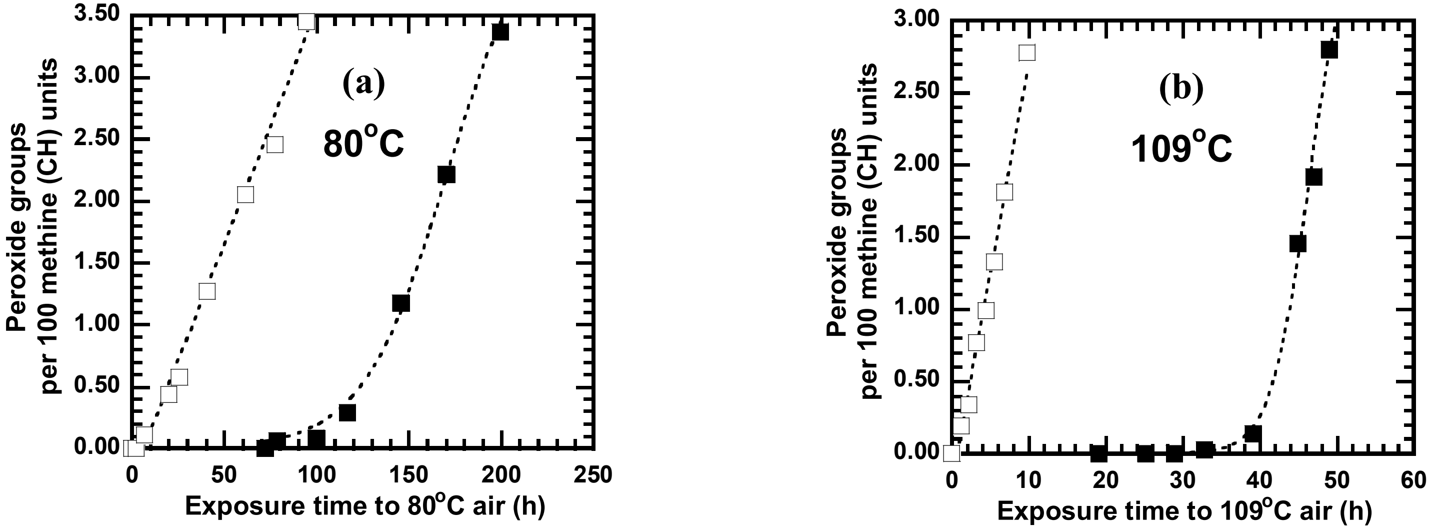
- **Polypropylene vs. Polyethylene (previous study)**
  - PP: Peroxides = largest product, remarkably stable at elevated temp
    alcohols are next largest product.
  - PE: Peroxides in low concentration, disappear rapidly on heating,
    not seen for irradiation at elevated temp.
    Largest product depends on dose and temp; acids and esters
    favored at high dose, ketones at lower dose

Further Comparison of Aging Mechanisms in Polypropylene and Polyethylene

- **Peroxide Concentration**
  - Radiation aging
    - Polyethylene: ~ 0.1%
    - Polypropylene: > 6%

- **Peroxide Stability**
  - Polyethylene: ½ life of < 30 hrs at 65°C
  - Polypropylene: very long lifetime during extended periods at elevated temperatures (even 110°C)

Pre-irradiation Eliminates the Induction Time Associated with Thermal Degradation



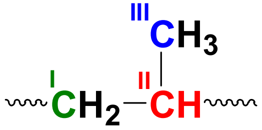
Accumulation of tertiary peroxide groups in solid C(2) labeled polypropylene:

(□) samples exposed to γ-radiation (24 Mrad) in argon at 24°C followed by post-irradiation thermal aging in air

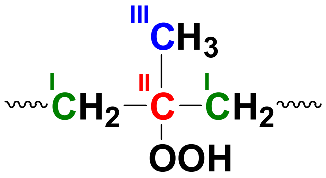
(■) thermally aged in the absence of γ-radiation

The kinetics for the two processes are similar in the linear portion of the buildup region.

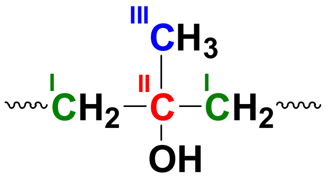
Polymeric Oxidation Products



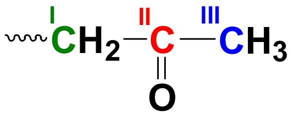
85-90% C(2)
10-15% C(1)
0% C(3)



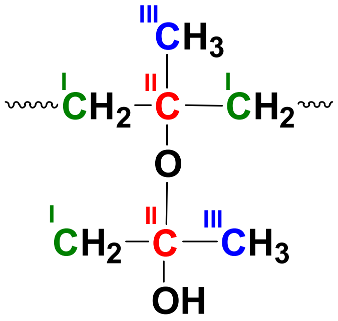
Peroxide



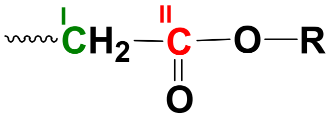
Alcohol



Methyl Ketone

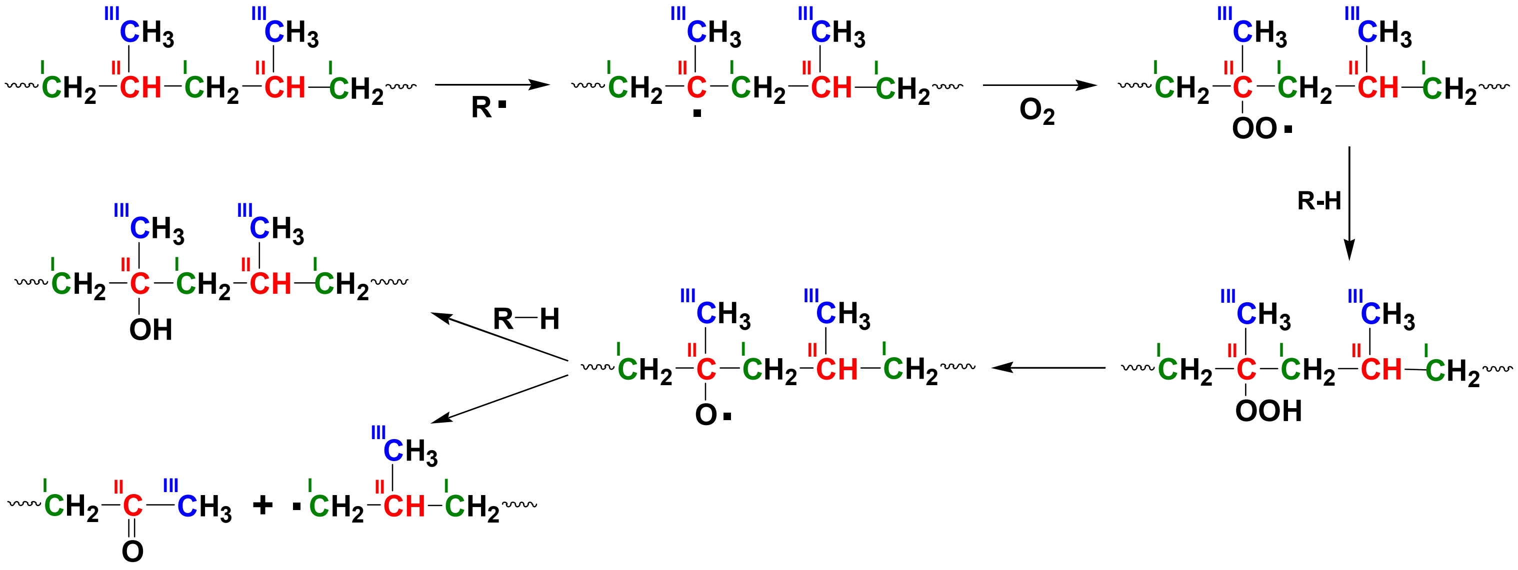


Hemiketal



Ester

Radiation Oxidation of Polypropylene



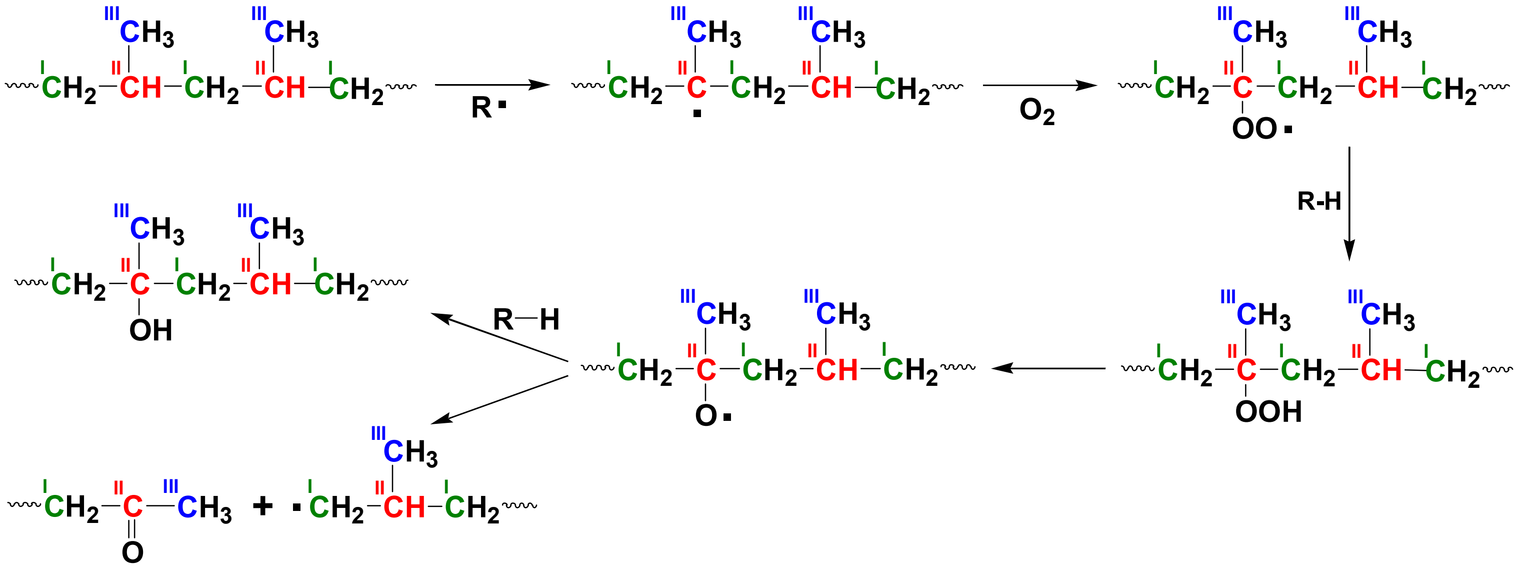
Oxidation-Induced Functional Groups Observed on the C(2) Carbon in Polypropylene Samples γ-Irradiated in Argon Followed by Post-Irradiation Thermal Aging in Air

Functional group	**Post-irradiation aging temperature and time**			
	22°C **675 – 731 d**	**80°C** **145 – 229 h**	**95°C** **55 – 80 h**	**109°C** **50 – 70 h**
Tertiary hydroperoxides/ dialkyl peroxides	62.2	55.9	54.4	50.3
tertiary alcohols	17.4	20.7	19.2	20.2
methyl ketones	**6.2**	**10.3**	**13.1**	**14.8**
carboxylic acids	2.6	0.7	0.2	—
esters/peresters	3.9	5.5	6.5	9.9
ketals (114.1 ppm)	1.1	2.1	2.4	1.5
ketals (105.7 ppm)	6.6	4.8	4.2	3.3

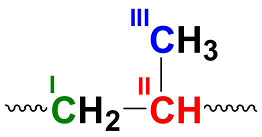
Functional Groups Observed by NMR in Polypropylene Samples Exposed to γ-Radiation or Thermal Aging in Air

Functional group	Aging temperature and radiation dose / thermal aging time after induction period					
	24°C, 230 kGy irradiation		80°C, 170 kGy irradiation		80°C, ~175 h no irradiation	
	C(2)[b]	C(1,3)[c]	C(2)[b]	C(1,3)[c]	C(2)[b]	C(1,3)[c]
tertiary hydroperoxides/ dialkyl peroxides	58.5	—	46.0	—	42.7	—
tertiary alcohols	**11.7**	—	**16.0**	—	**21.6**	—
methyl ketones	**5.9**	—	**13.5**	—	**8.0**	—
carboxylic acids on C(2) carbon	1.6	—	—	—	—	—
esters/peresters on C(2) carbon	11.1	—	6.3	—	5.6	—
esters/peresters on C(1) carbon	—	5.8	—	11.9	—	13.8
in-chain ketones	—	—	—	1.3	—	1.3
ketals on C(2) carbon (114.1 ppm)	—	—	2.3	—	2.2	—
ketals on C(2) carbon (105.7 ppm)	4.4	—	2.7	—	4.1	—
ketals on C(1) carbon	—	1.0	—	—	—	0.7

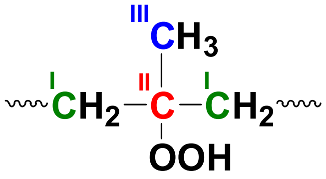
Radiation Oxidation of Polypropylene



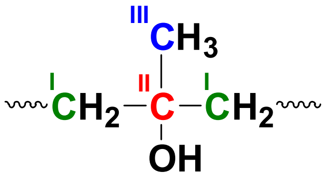
Polymeric Oxidation Products



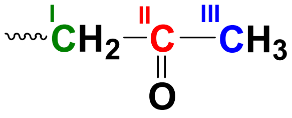
85-90% C(2)
10-15% C(1)
0% C(3)



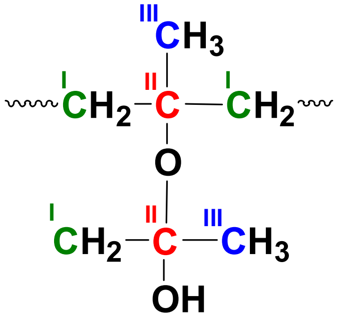
Peroxide



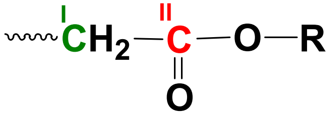
Alcohol



Methyl Ketone



Hemiketal

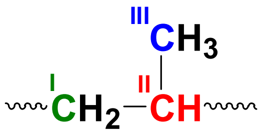


Ester

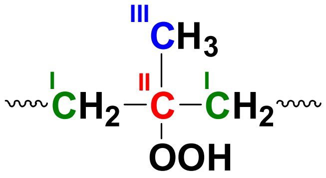
- Chain scission indicator: C(2) methyl ketone: Yield rises more than C(2) alcohol at elevated temperature

- This change in mechanism at higher temperatures explains radiation/thermal "synergism" in mechanical property changes, during "combined environment" degradation experiments

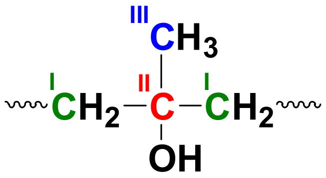
Polymeric Oxidation Products



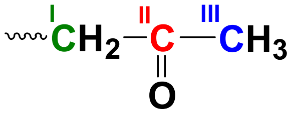
85-90% C(2)
10-15% C(1)
0% C(3)



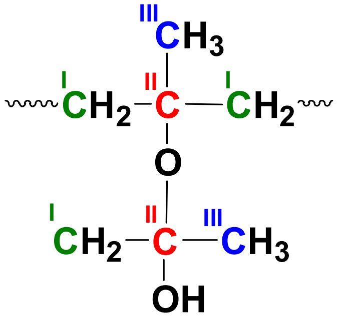
Peroxide



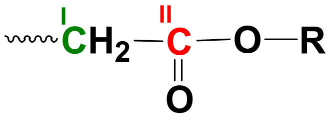
Alcohol



Methyl Ketone



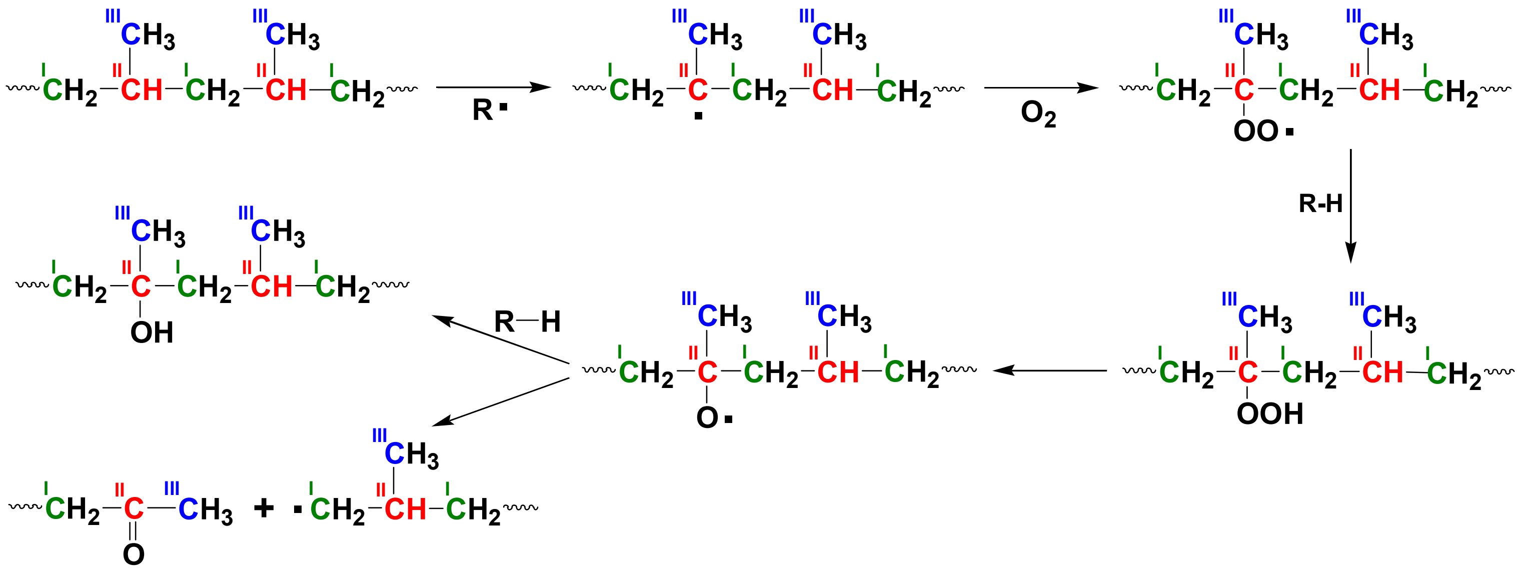
Hemiketal



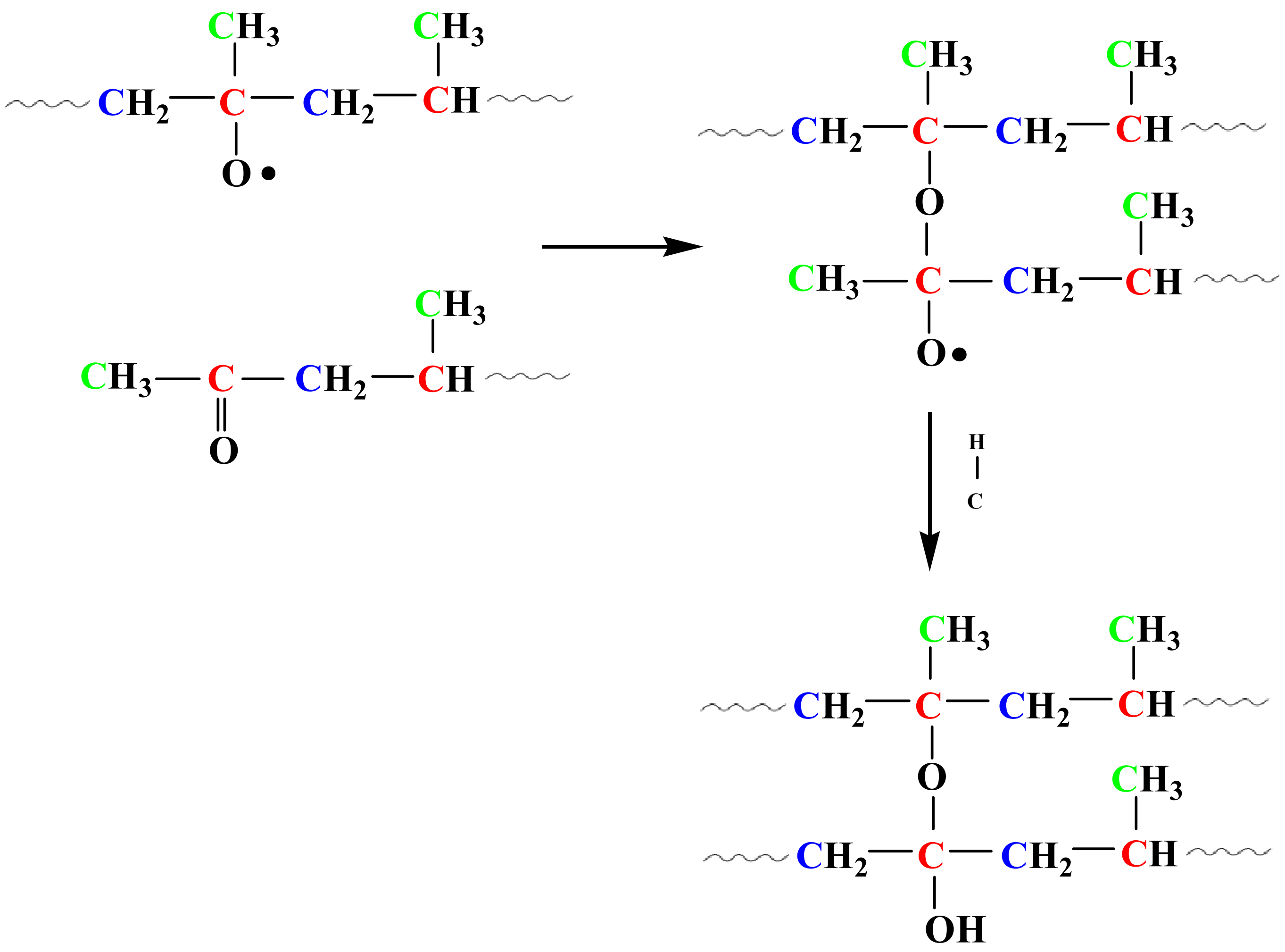
Ester

- **New degradation product identified (Hemiketal)**

Radiation Oxidation of Polypropylene

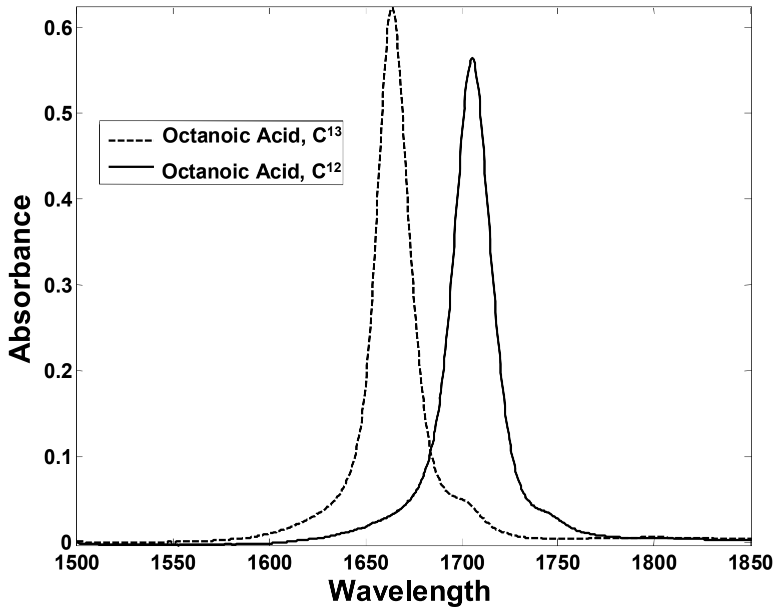


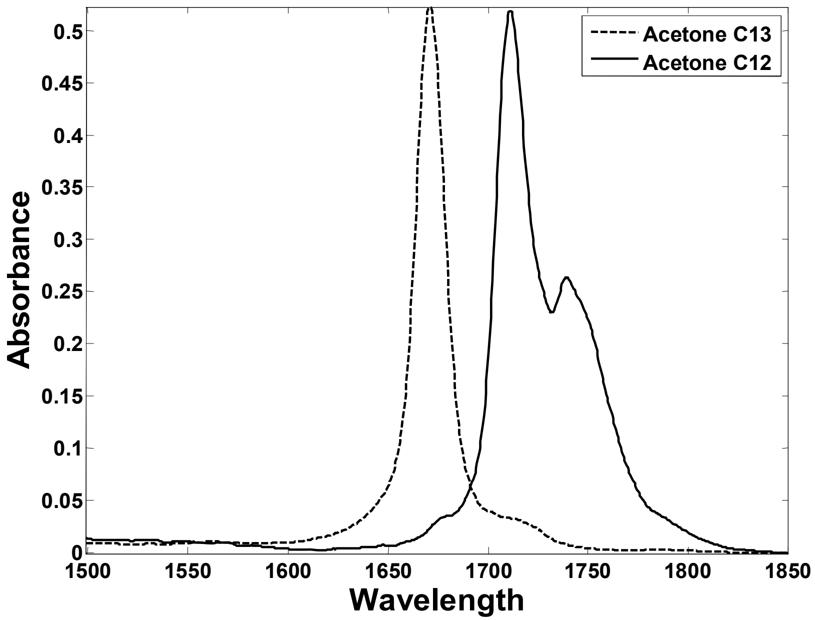
Chemical Mechanism for the Formation of Hemiketals

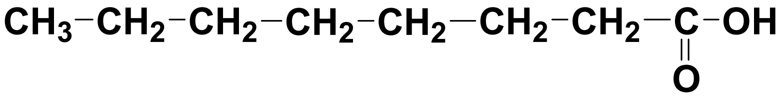


Hemiketal

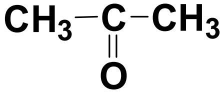
FTIR: Spectra of C-13 labeled small molecules [model compounds]



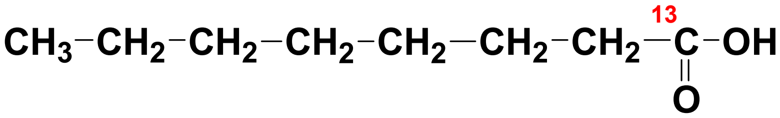




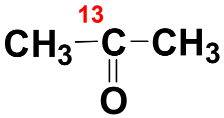
$CH_3{-}CH_2{-}CH_2{-}CH_2{-}CH_2{-}CH_2{-}CH_2{-}\underset{\underset{O}{\|}}{C}{-}OH$



$CH_3{-}\underset{\underset{O}{\|}}{C}{-}CH_3$

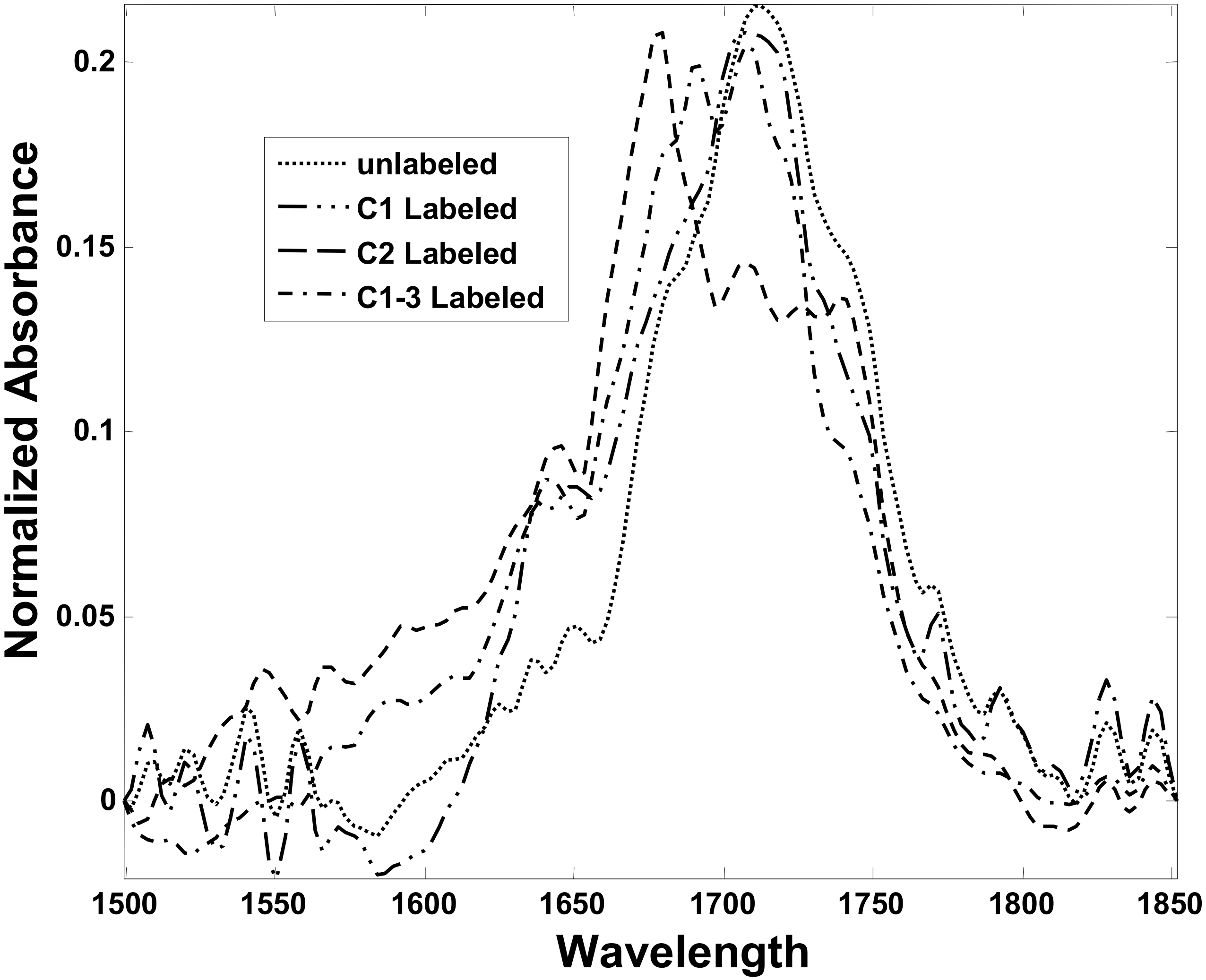


$CH_3{-}CH_2{-}CH_2{-}CH_2{-}CH_2{-}CH_2{-}CH_2{-}\overset{13}{\underset{\underset{O}{\|}}{C}}{-}OH$



$CH_3{-}\overset{13}{\underset{\underset{O}{\|}}{C}}{-}CH_3$

IR spectra obtained from polypropylene following irradiation in oxygen



GC/ mass spec

Analysis of Volatile Radiolysis Products:
CO_2; CO; and Small Organic Molecules

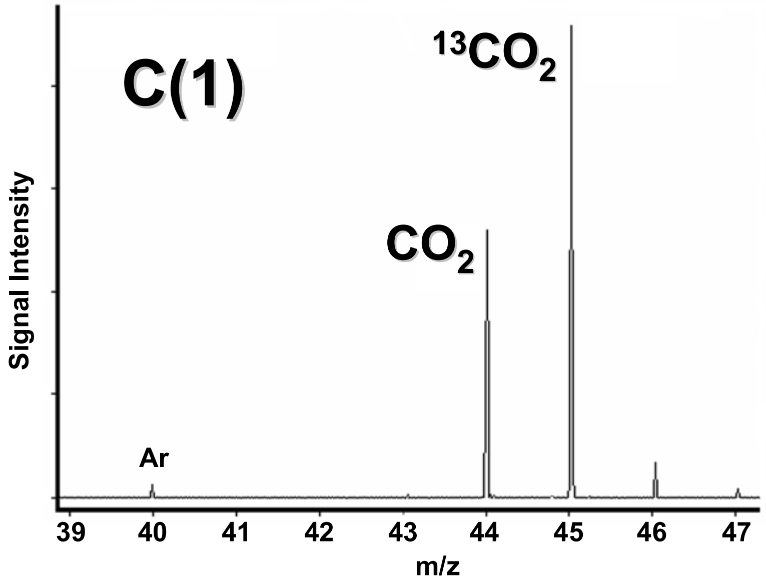
- **Volatile (gaseous) products well known to form under irradiation**

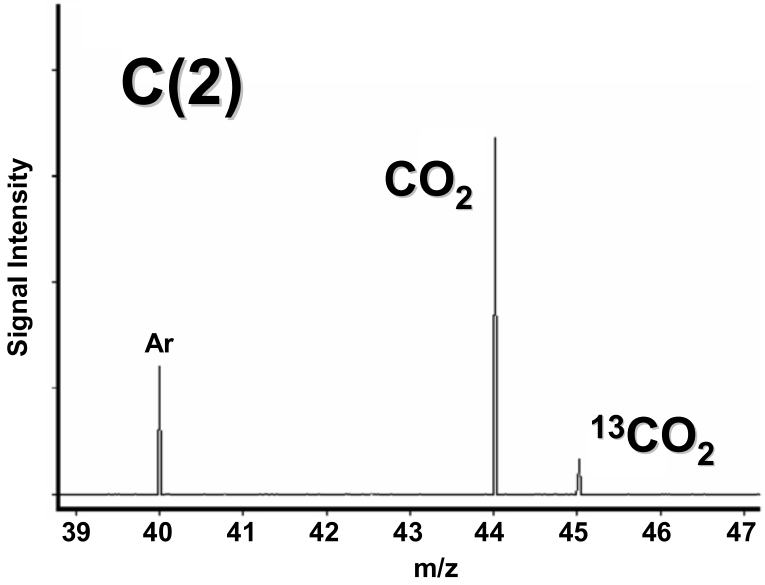
- **These molecular fragments** *can offer insights into radiation-degradation chemistry*

- **Because they are small molecules, exact molecular structural identification is possible**

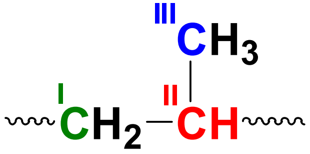
- **Analysis by Gas Chromatography, Mass Spectroscopy**

Ratio of $^{13}CO_2$ versus $^{12}CO_2$ by Mass Spec





% CO_2



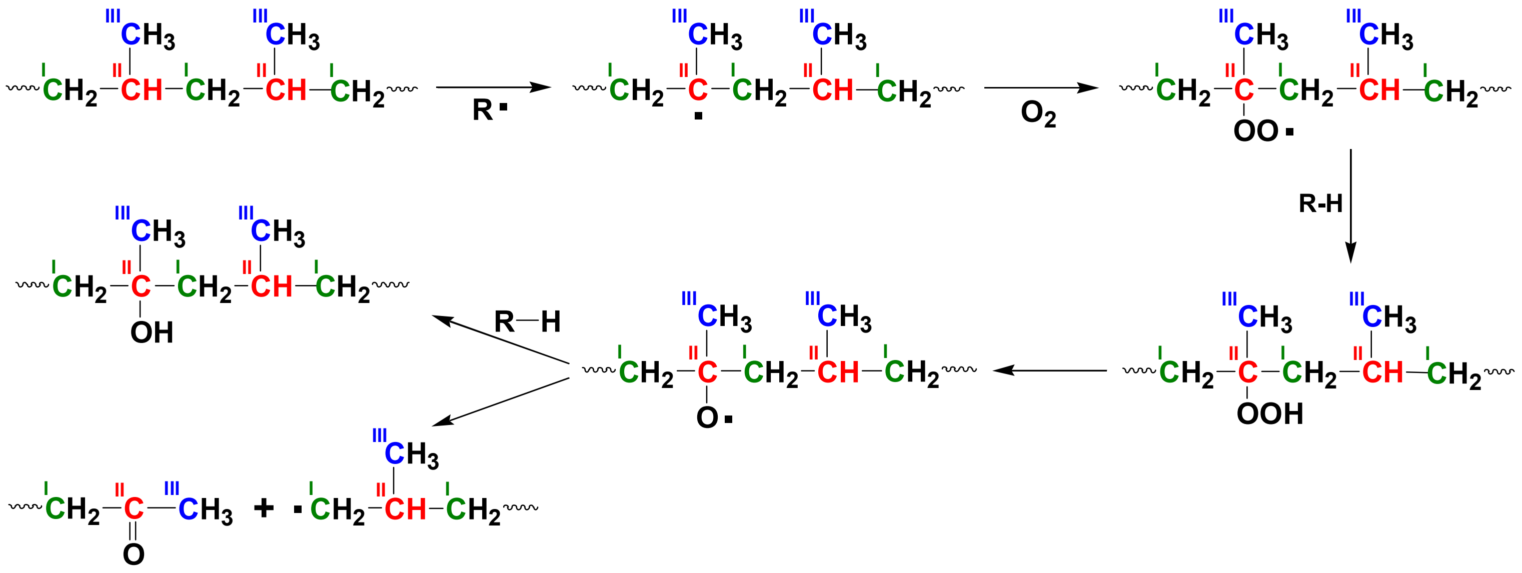
C(1)	60%	[± 10%]
C(2)	10%	[± 10%]
C(3)	30%	[± 15%]

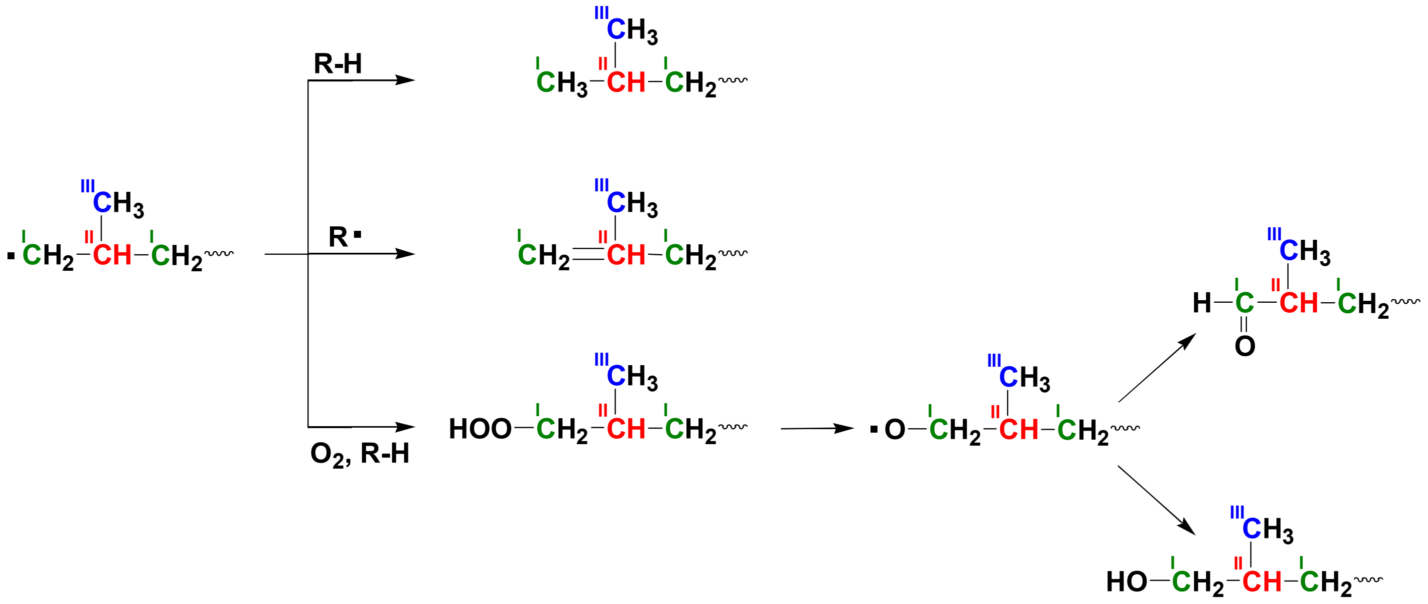
% CO

Similar Mass Spec Measurements were made for ^{13}CO versus ^{12}CO

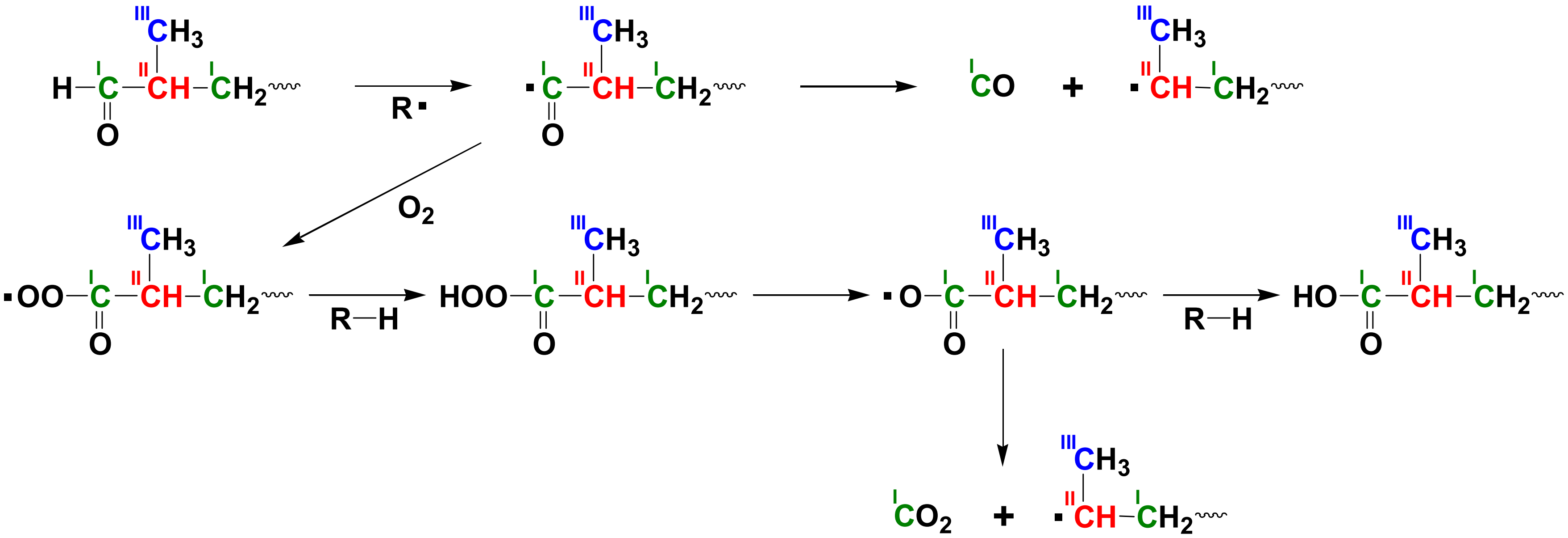
C(1)	90%	[± 10%]
C(2)	5%	[± 10%]
C(3)	5%	[± 10%]

Radiation Oxidation of Polypropylene

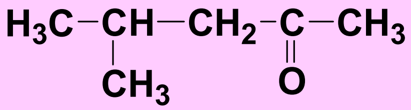




Formation of CO and CO_2 at C(1)



Many volatile products are formed when polymers are irradiated.
With GC/MS, we can gain insight into the radiation chemistry that led to their formation An example:

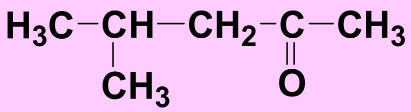


$H_3C-CH(CH_3)-CH_2-C(=O)-CH_3$

Methylisobutylketone

Many volatile products are formed when polymers are irradiated. With GC/MS, we can gain insight into the radiation chemistry that led to their formation

100

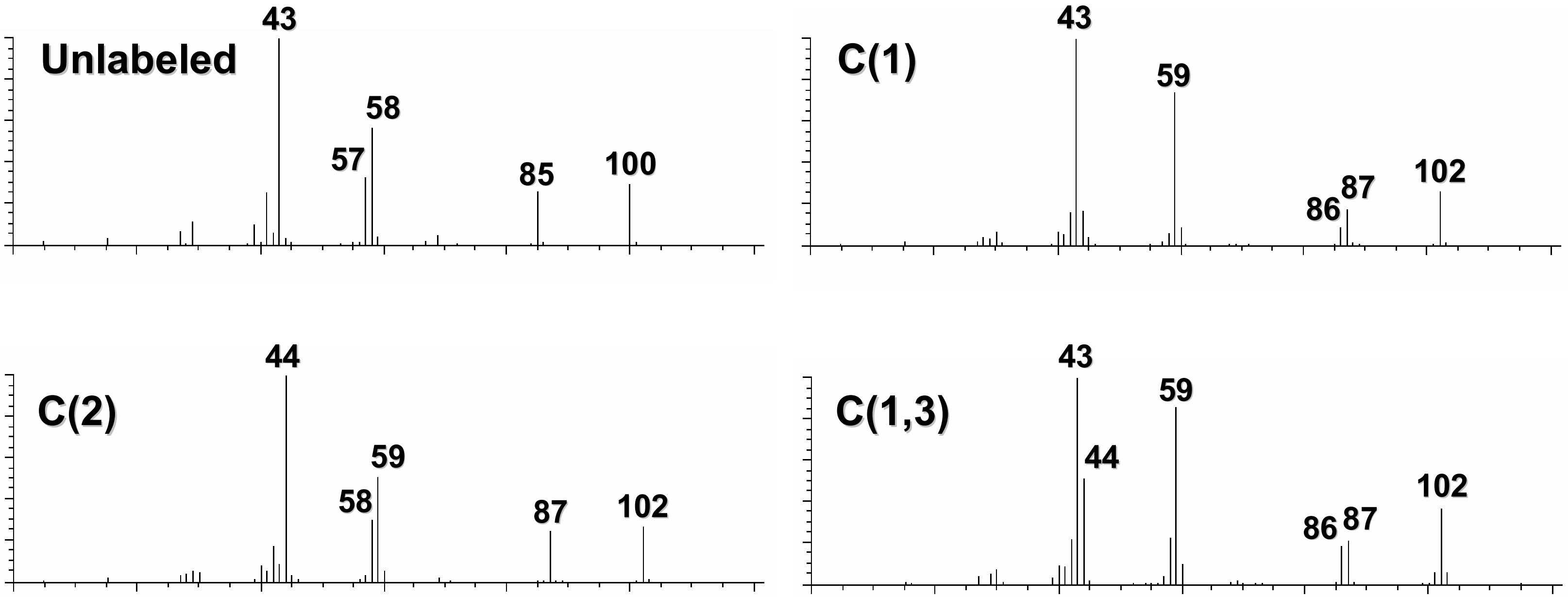


$$H_3C-\underset{\displaystyle CH_3}{CH}-CH_2-\underset{\displaystyle O}{\overset{}{C}}-CH_3$$

Methylisobutylketone

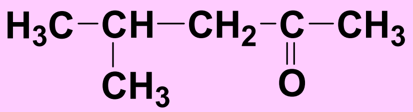
Parent Peak:

- 2 C(1)
- 2 C(2)
- 2 C(3)



Many volatile products are formed when polymers are irradiated. With GC/MS, we can gain insight into the radiation chemistry that led to their formation

100

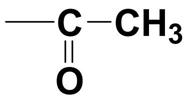

$H_3C-\underset{|\atop CH_3}{CH}-CH_2-\underset{\|\atop O}{C}-CH_3$

Methylisobutylketone

Parent Peak:

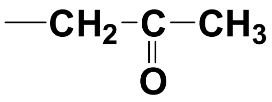
2 C(1)
2 C(2)
2 C(3)

43


$-\underset{\|\atop O}{C}-CH_3$

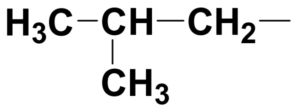
0 C(1)
1 C(2)
1 C(3)

58


$-CH_2-\underset{\|\atop O}{C}-CH_3$

1 C(1)
1 C(2)
1 C(3)

57

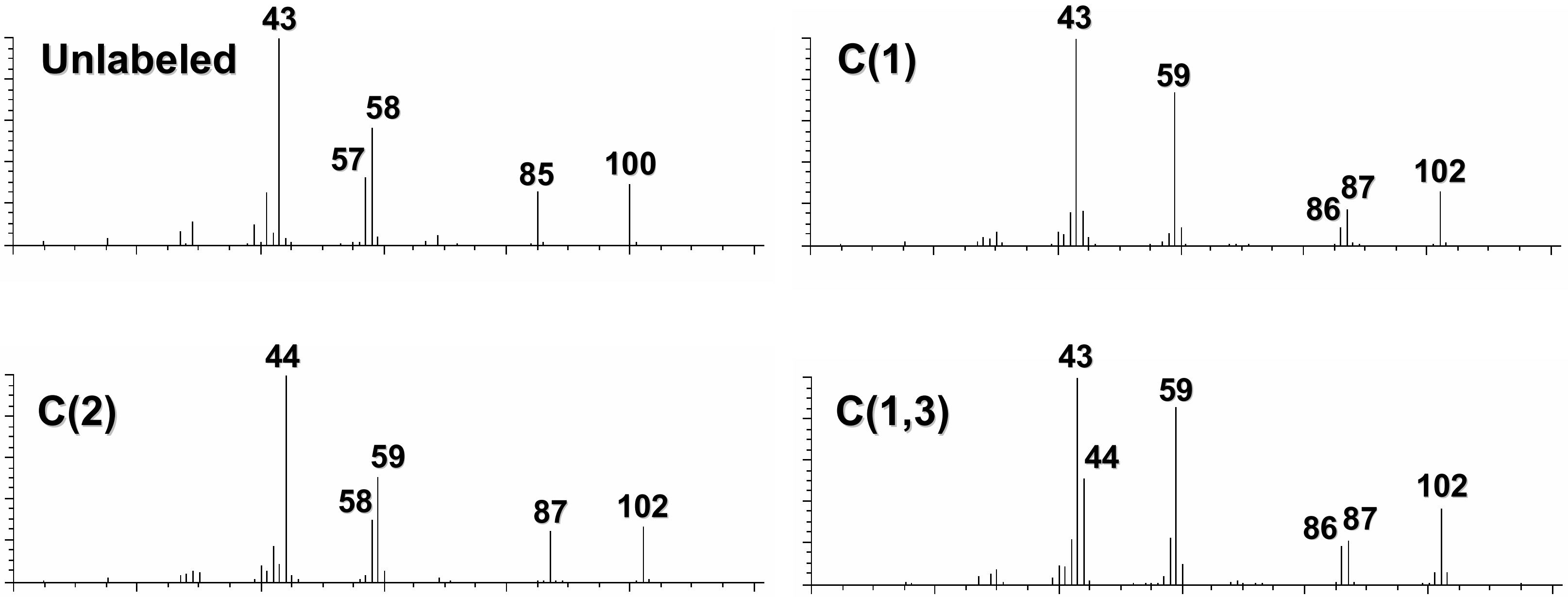

$H_3C-\underset{|\atop CH_3}{CH}-CH_2-$

2 C(1)
1 C(2)
1 C(3)

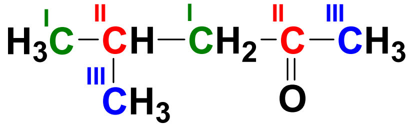
85

Loss of methyl

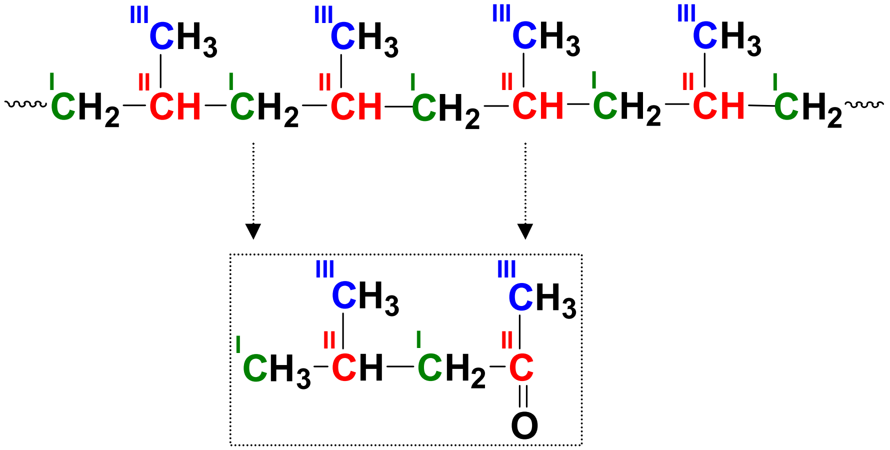
1 C(1)
0 C(2)
2 C(3)



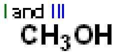
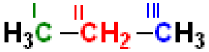
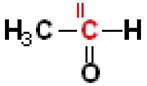
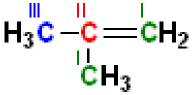
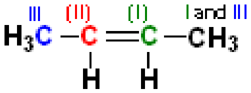
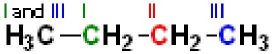
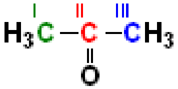
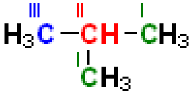
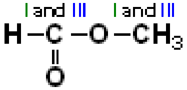
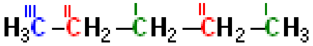
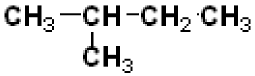
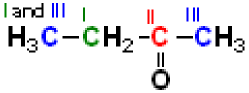
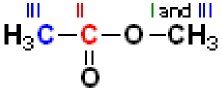
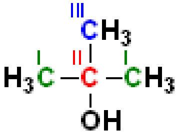
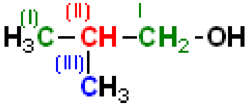
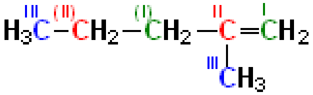
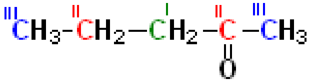
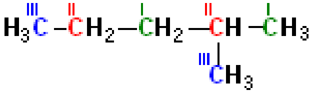
Assigned Structure of Methylisobutylketone

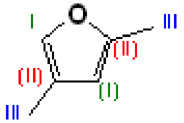
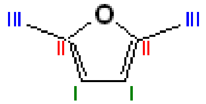
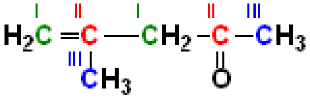
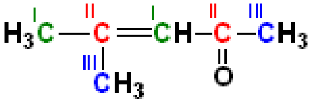
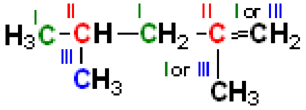
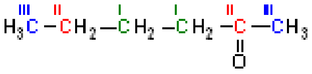
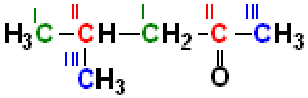
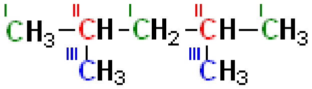


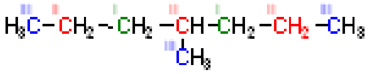
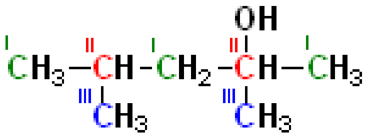
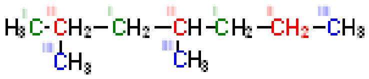
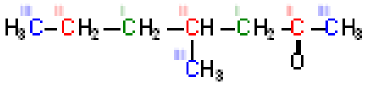
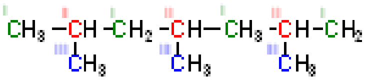
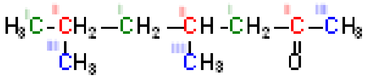
Labeling Specificity ≈ 100%
One predominate route



Mapping onto PP

#	MW	Carbon Atom Composition from PP Structure	Structure	Note
1	32	0 or 1 C(1) 0 C(2) 0 or 1 C(3)		†
2	44	1 C(1) 1 C(2) 1 C(3)		
3	44	? C(1) 1 C(2) ? C(3)		•
4	56	2 C(1) 1 C(2) 1 C(3)		
5	56	1 or2 C(1) 1 C(2) 1 or2 C(3)		△
6	58	1, or 2 C(1) 1 C(2) 1 or2 C(3)		≠
7	58	1 C(1) 1 C(2) 1 C(3)		
8	58	2 C(1) 1 C(2) 1 C(3)		
9	60	1 or2 C(1) 0 C(2) 1 or2 C(3)		‡
10	72	1 C(1) 2 C(2) 2 C(3)		
11	72	complex labeling		*
12	72	1 or2 C(1) 1 C(2) 1 or2 C(3)		#
13	74	0 or1 C(1) 1 C(2) 1 or2 C(3)		√
14	74	2 C(1) 1 C(2) 1 C(3)		
15	74	2 C(1) 1 C(2) 1 C(3)		o
16	84	2 C(1) 2 C(2) 2 C(3)		
17	86	1 C(1) 2 C(2) 2 C(3)		
18	86	2 C(1) 2 C(2) 2 C(3)		

19	86	2 C(1) 2 C(2) 2 C(3)	 $H_3C-CH_2-CH_2-CH_2-CH_2-CH_3$	§
20	96	2 C(1) 2 C(2) 2 C(3)		
21	96	2 C(1) 2 C(2) 2 C(3)		
22	98	2 C(1) 2 C(2) 2 C(3)	 $H_2C{=}C(CH_3)-CH_2-C(=O)-CH_3$	
23	98	2 C(1) 2 C(2) 2 C(3)	 $H_3C-C(CH_3){=}CH-C(=O)-CH_3$	
24	98	3 C(1) 2 C(2) 2 C(3)	 $H_3C-CH(CH_3)-CH_2-C(CH_3){=}CH_2$	
25	100	2 C(1) 2 C(2) 2 C(3)	 $H_3C-CH_2-CH_2-CH_2-C(=O)-CH_3$	
26	100	2 C(1) 2 C(2) 2 C(3)	 $H_3C-CH(CH_3)-CH_2-C(=O)-CH_3$	
27	100	3 C(1) 2 C(2) 2 C(3)	 $CH_3-CH(CH_3)-CH_2-CH(CH_3)-CH_3$	

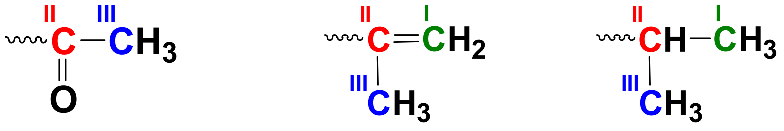
28	114	2 C(1) 3 C(2) 3 C(3)	 $H_3C-CH_2-CH_2-CH(CH_3)-CH_2-CH_2-CH_3$	
29	116	2 C(1) 2 C(2) 2 C(3)	 $CH_3-CH(CH_3)-CH_2-C(OH)(CH_3)-CH_3$	
30	128	3 C(1) 3 C(2) 3 C(3)	 $H_3C-CH_2(CH_3)-CH_2-CH(CH_3)-CH_2-CH_2-CH_3$	
31	128	2 C(1) 3 C(2) 3 C(3)	 $H_3C-CH_2-CH_2-CH(CH_3)-CH_2-C(=O)-CH_3$	
32	142	4 C(1) 3 C(2) 3 C(3)	 $CH_3-CH(CH_3)-CH_2-CH(CH_3)-CH_3-CH(CH_3)-CH_2$	
33	142	3 C(1) 3 C(2) 3 C(3)	 $H_3C-CH_2(CH_3)-CH_2-CH(CH_3)-CH_2-C(=O)-CH_3$	

33 volatile compounds from PP radiation-oxidation identified

Among the 31 “catenated’ products:

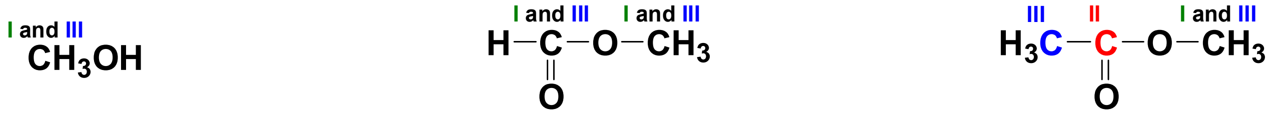
- 15 have oxidation at C(2)
- 9 are methyl ketones, with C(2) carbonyl and C(3) methyl
- 2 have oxidation at C(1) [an alcohol and an aldehyde]
- No oxidation at C(3). C(3) always methyl, connected to C(2)
- 26 retain the PP connectivity [no C(1)-C(1), no C(1)-C(3), no C(3)-C(3)]

- Can understand formation route as 2 chain scissions, by methyl ketone mechanism, and possibly direct C-C scission from irradiation



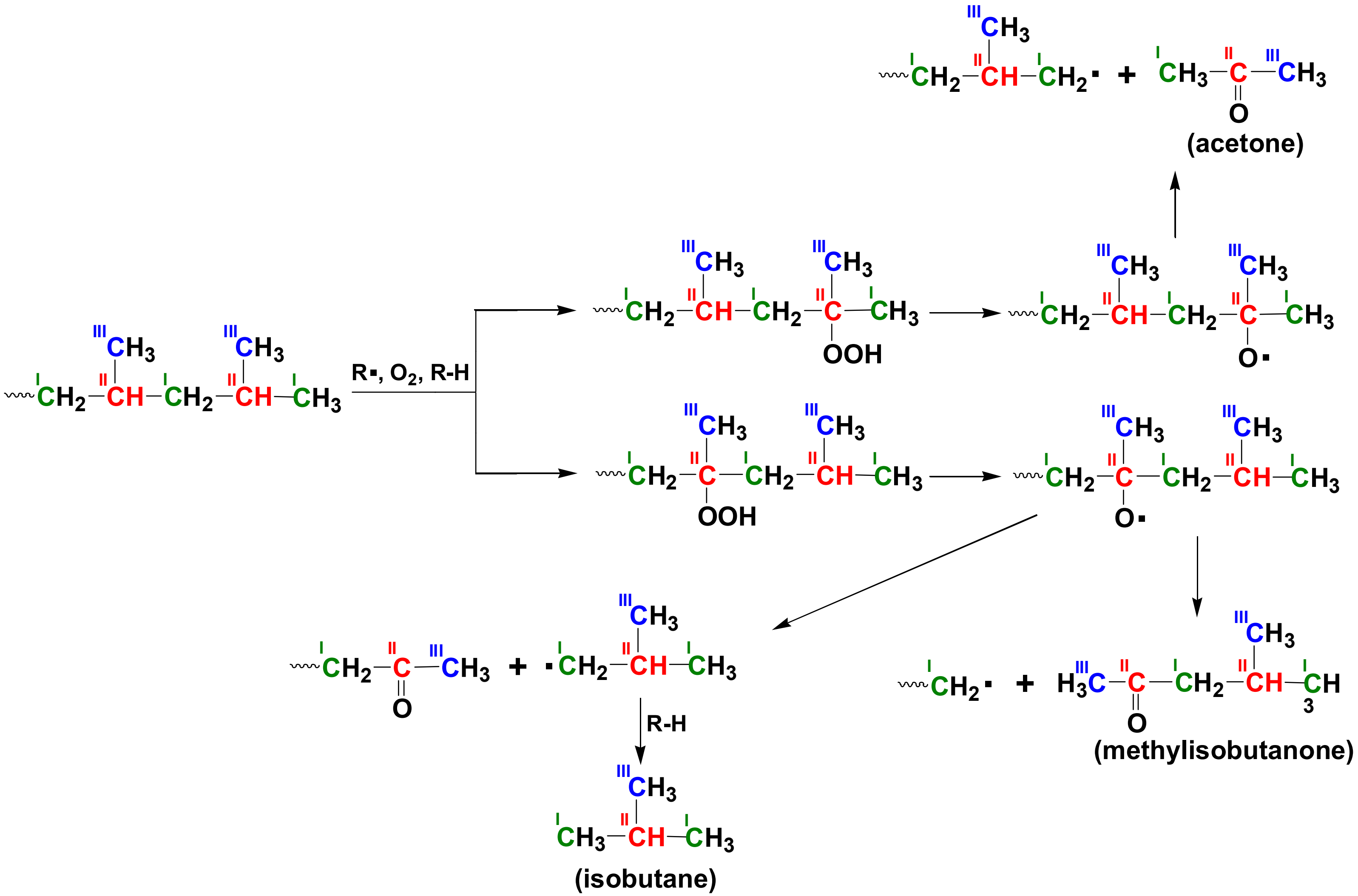
$\sim\!C(=O)-CH_3$ $\quad$ $\sim\!C(CH_3)=CH_2$ $\quad$ $\sim\!CH(CH_3)-CH_3$

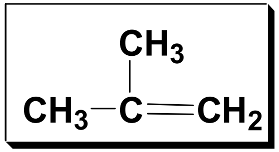
3 products have single carbon atoms. All are C(1) and C(3) mix



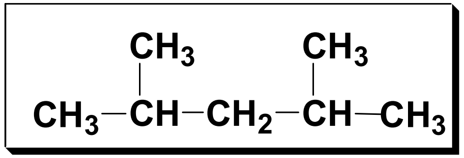
CH_3OH $\quad$ $H-C(=O)-O-CH_3$ $\quad$ $H_3C-C(=O)-O-CH_3$

Chemistry leading to 3 of the products found: *methylisobutylketone, acetone, isobutane*

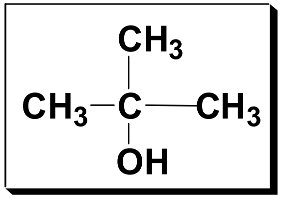




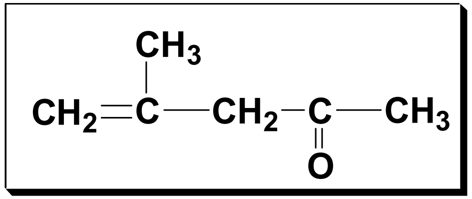
$$\mathrm{CH_3-\overset{\overset{\displaystyle CH_3}{|}}{C}=CH_2}$$



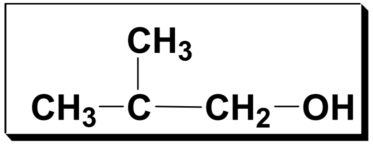
$$\mathrm{CH_3-\overset{\overset{\displaystyle CH_3}{|}}{CH}-CH_2-\overset{\overset{\displaystyle CH_3}{|}}{CH}-CH_3}$$



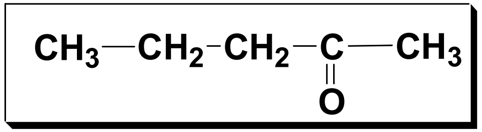
$$\mathrm{CH_3-\underset{\underset{\displaystyle OH}{|}}{\overset{\overset{\displaystyle CH_3}{|}}{C}}-CH_3}$$



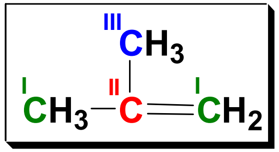
$$\mathrm{CH_2=\overset{\overset{\displaystyle CH_3}{|}}{C}-CH_2-\underset{\underset{\displaystyle O}{\|}}{C}-CH_3}$$



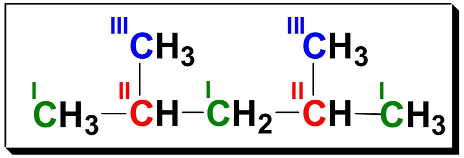
$$\mathrm{CH_3-\overset{\overset{\displaystyle CH_3}{|}}{C}-CH_2-OH}$$



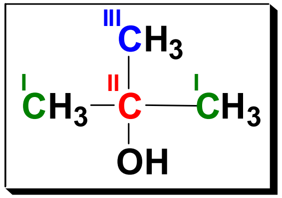
$$\mathrm{CH_3-CH_2-CH_2-\underset{\underset{\displaystyle O}{\|}}{C}-CH_3}$$



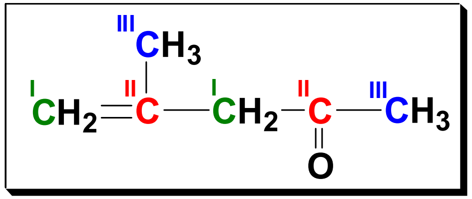
$$\overset{\mathrm{I}}{C}H_3-\overset{\mathrm{II}}{C}(\overset{\mathrm{III}}{C}H_3)=\overset{\mathrm{I}}{C}H_2$$



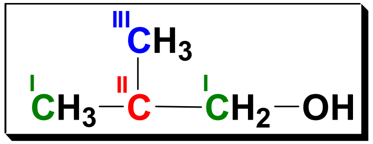
$$\overset{\mathrm{I}}{C}H_3-\overset{\mathrm{II}}{C}H(\overset{\mathrm{III}}{C}H_3)-\overset{\mathrm{I}}{C}H_2-\overset{\mathrm{II}}{C}H(\overset{\mathrm{III}}{C}H_3)-\overset{\mathrm{I}}{C}H_3$$



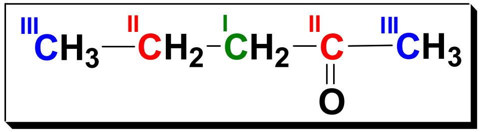
$$\overset{\mathrm{I}}{C}H_3-\overset{\mathrm{II}}{C}(\overset{\mathrm{III}}{C}H_3)(OH)-\overset{\mathrm{I}}{C}H_3$$



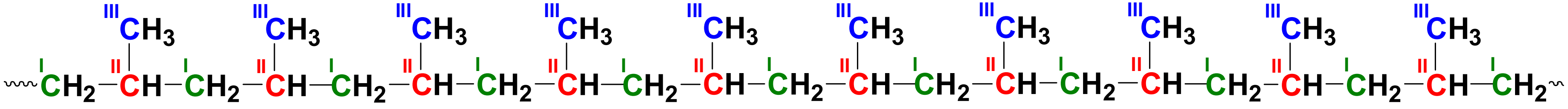
$$\overset{\mathrm{I}}{C}H_2=\overset{\mathrm{II}}{C}(\overset{\mathrm{III}}{C}H_3)-\overset{\mathrm{I}}{C}H_2-\overset{\mathrm{II}}{C}(=O)-\overset{\mathrm{III}}{C}H_3$$



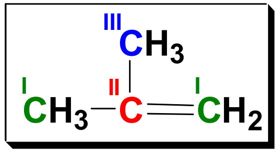
$$\overset{\mathrm{I}}{C}H_3-\overset{\mathrm{II}}{C}(\overset{\mathrm{III}}{C}H_3)-\overset{\mathrm{I}}{C}H_2-OH$$



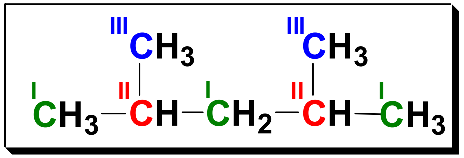
$$\overset{\mathrm{III}}{C}H_3-\overset{\mathrm{II}}{C}H_2-\overset{\mathrm{I}}{C}H_2-\overset{\mathrm{II}}{C}(=O)-\overset{\mathrm{III}}{C}H_3$$



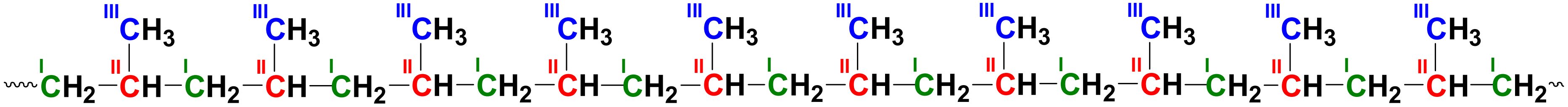
$\sim {}^{I}CH_2-{}^{II}CH({}^{III}CH_3)-{}^{I}CH_2-{}^{II}CH({}^{III}CH_3)-{}^{I}CH_2-{}^{II}CH({}^{III}CH_3)-{}^{I}CH_2-{}^{II}CH({}^{III}CH_3)-{}^{I}CH_2-{}^{II}CH({}^{III}CH_3)-{}^{I}CH_2-{}^{II}CH({}^{III}CH_3)-{}^{I}CH_2-{}^{II}CH({}^{III}CH_3)-{}^{I}CH_2-{}^{II}CH({}^{III}CH_3)-{}^{I}CH_2-{}^{II}CH({}^{III}CH_3)-{}^{I}CH_2-{}^{II}CH({}^{III}CH_3)-{}^{I}CH_2\sim$



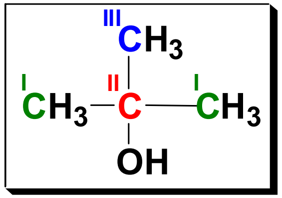
${}^{I}CH_3-{}^{II}C({}^{III}CH_3)={}^{I}CH_2$



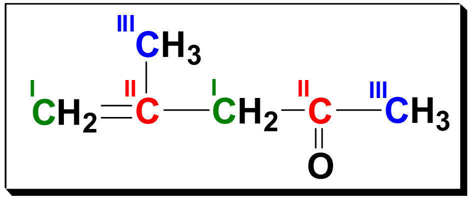
${}^{I}CH_3-{}^{II}CH({}^{III}CH_3)-{}^{I}CH_2-{}^{II}CH({}^{III}CH_3)-{}^{I}CH_3$



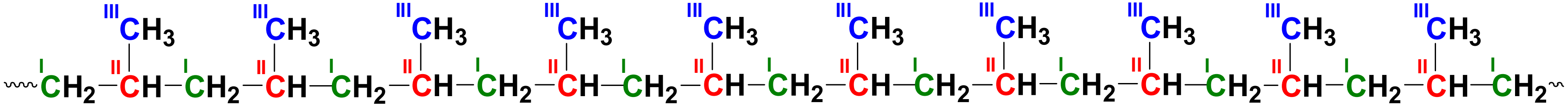
$\sim {}^{I}CH_2-{}^{II}CH({}^{III}CH_3)-{}^{I}CH_2-{}^{II}CH({}^{III}CH_3)-{}^{I}CH_2-{}^{II}CH({}^{III}CH_3)-{}^{I}CH_2-{}^{II}CH({}^{III}CH_3)-{}^{I}CH_2-{}^{II}CH({}^{III}CH_3)-{}^{I}CH_2-{}^{II}CH({}^{III}CH_3)-{}^{I}CH_2-{}^{II}CH({}^{III}CH_3)-{}^{I}CH_2-{}^{II}CH({}^{III}CH_3)-{}^{I}CH_2-{}^{II}CH({}^{III}CH_3)-{}^{I}CH_2-{}^{II}CH({}^{III}CH_3)-{}^{I}CH_2\sim$



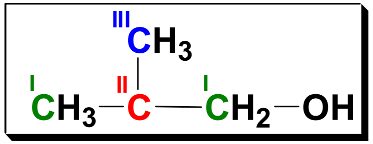
${}^{I}CH_3-{}^{II}C({}^{III}CH_3)(OH)-{}^{I}CH_3$



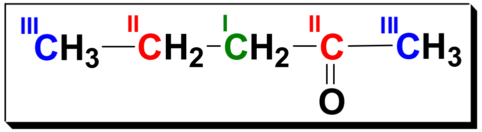
${}^{I}CH_2={}^{II}C({}^{III}CH_3)-{}^{I}CH_2-{}^{II}C(=O)-{}^{III}CH_3$



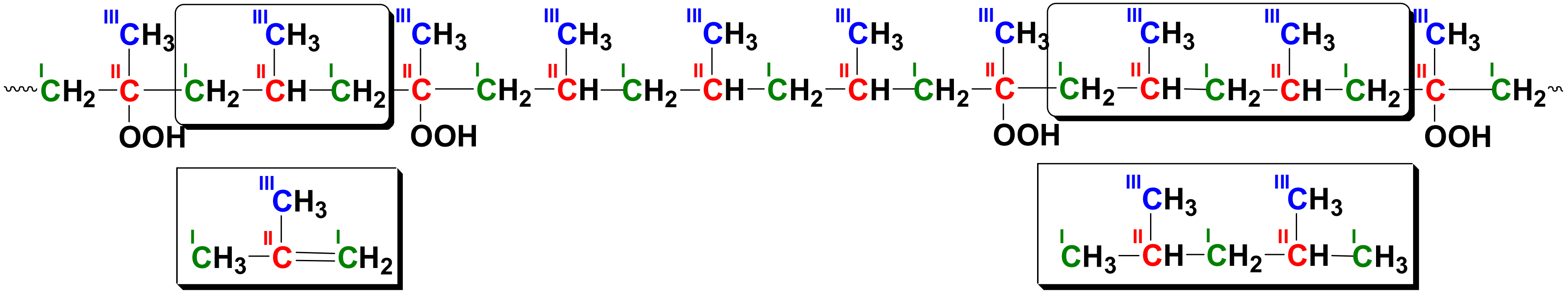
$\sim {}^{I}CH_2-{}^{II}CH({}^{III}CH_3)-{}^{I}CH_2-{}^{II}CH({}^{III}CH_3)-{}^{I}CH_2-{}^{II}CH({}^{III}CH_3)-{}^{I}CH_2-{}^{II}CH({}^{III}CH_3)-{}^{I}CH_2-{}^{II}CH({}^{III}CH_3)-{}^{I}CH_2-{}^{II}CH({}^{III}CH_3)-{}^{I}CH_2-{}^{II}CH({}^{III}CH_3)-{}^{I}CH_2-{}^{II}CH({}^{III}CH_3)-{}^{I}CH_2-{}^{II}CH({}^{III}CH_3)-{}^{I}CH_2-{}^{II}CH({}^{III}CH_3)-{}^{I}CH_2\sim$

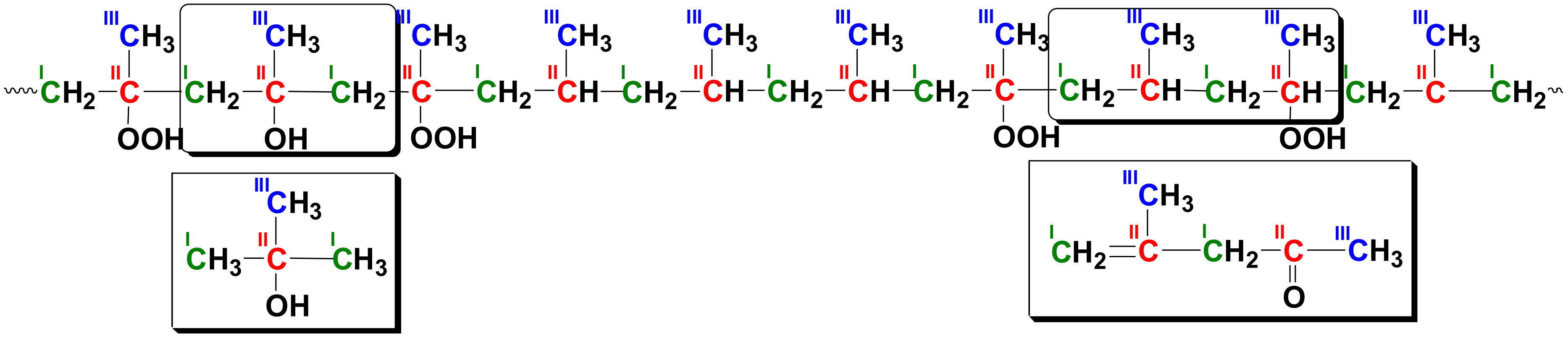


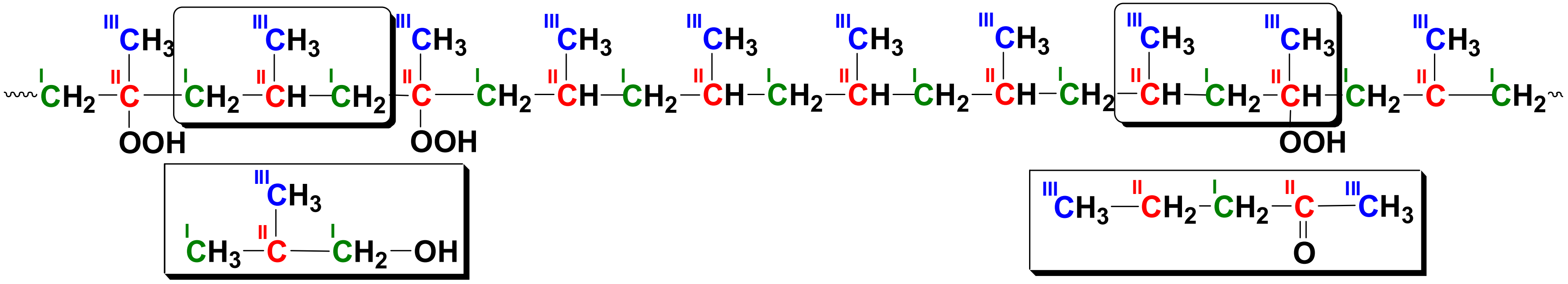
${}^{I}CH_3-{}^{II}C({}^{III}CH_3)-{}^{I}CH_2-OH$



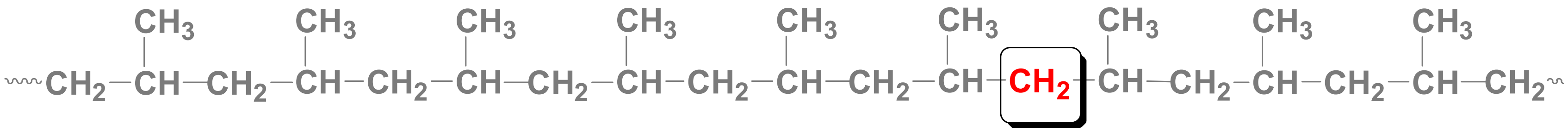
${}^{III}CH_3-{}^{II}CH_2-{}^{I}CH_2-{}^{II}C(=O)-{}^{III}CH_3$





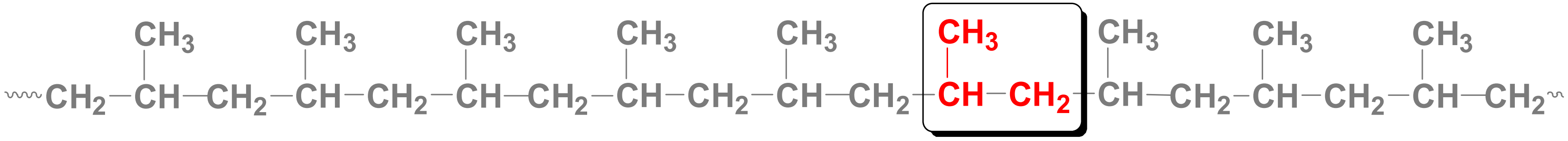


1



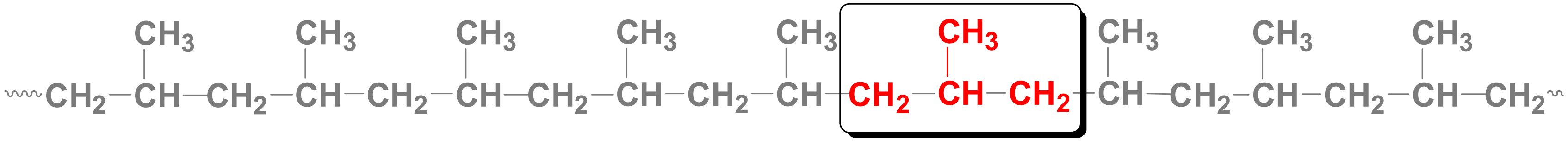
$$\sim \mathrm{CH_2}-\overset{\mathrm{CH_3}}{\mathrm{CH}}-\mathrm{CH_2}-\overset{\mathrm{CH_3}}{\mathrm{CH}}-\mathrm{CH_2}-\overset{\mathrm{CH_3}}{\mathrm{CH}}-\mathrm{CH_2}-\overset{\mathrm{CH_3}}{\mathrm{CH}}-\mathrm{CH_2}-\overset{\mathrm{CH_3}}{\mathrm{CH}}-\mathrm{CH_2}-\overset{\mathrm{CH_3}}{\mathrm{CH}}-\boxed{\mathrm{CH_2}}-\overset{\mathrm{CH_3}}{\mathrm{CH}}-\mathrm{CH_2}-\overset{\mathrm{CH_3}}{\mathrm{CH}}-\mathrm{CH_2}-\overset{\mathrm{CH_3}}{\mathrm{CH}}-\mathrm{CH_2}\sim$$

3



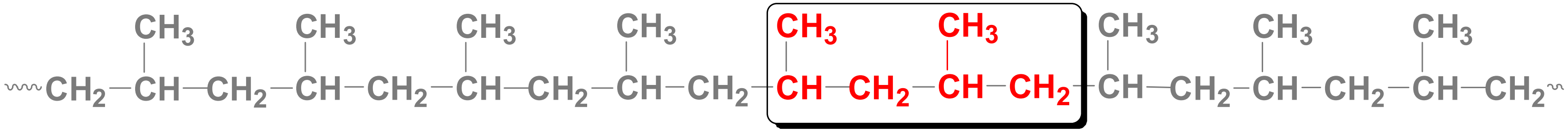
$$\sim \mathrm{CH_2}-\overset{\mathrm{CH_3}}{\mathrm{CH}}-\mathrm{CH_2}-\overset{\mathrm{CH_3}}{\mathrm{CH}}-\mathrm{CH_2}-\overset{\mathrm{CH_3}}{\mathrm{CH}}-\mathrm{CH_2}-\overset{\mathrm{CH_3}}{\mathrm{CH}}-\mathrm{CH_2}-\overset{\mathrm{CH_3}}{\mathrm{CH}}-\mathrm{CH_2}-\boxed{\overset{\mathrm{CH_3}}{\mathrm{CH}}-\mathrm{CH_2}}-\overset{\mathrm{CH_3}}{\mathrm{CH}}-\mathrm{CH_2}-\overset{\mathrm{CH_3}}{\mathrm{CH}}-\mathrm{CH_2}-\overset{\mathrm{CH_3}}{\mathrm{CH}}-\mathrm{CH_2}\sim$$

3



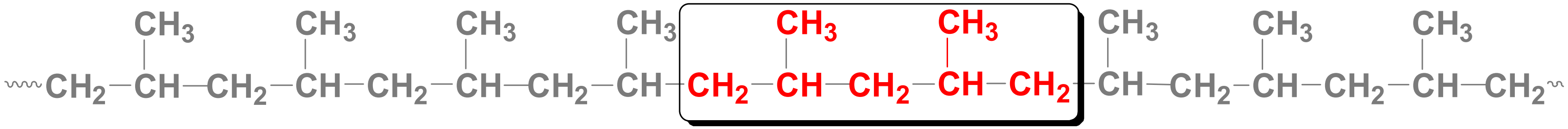
$$\sim \mathrm{CH_2}-\overset{\mathrm{CH_3}}{\mathrm{CH}}-\mathrm{CH_2}-\overset{\mathrm{CH_3}}{\mathrm{CH}}-\mathrm{CH_2}-\overset{\mathrm{CH_3}}{\mathrm{CH}}-\mathrm{CH_2}-\overset{\mathrm{CH_3}}{\mathrm{CH}}-\mathrm{CH_2}-\overset{\mathrm{CH_3}}{\mathrm{CH}}-\boxed{\mathrm{CH_2}-\overset{\mathrm{CH_3}}{\mathrm{CH}}-\mathrm{CH_2}}-\overset{\mathrm{CH_3}}{\mathrm{CH}}-\mathrm{CH_2}-\overset{\mathrm{CH_3}}{\mathrm{CH}}-\mathrm{CH_2}-\overset{\mathrm{CH_3}}{\mathrm{CH}}-\mathrm{CH_2}\sim$$

5



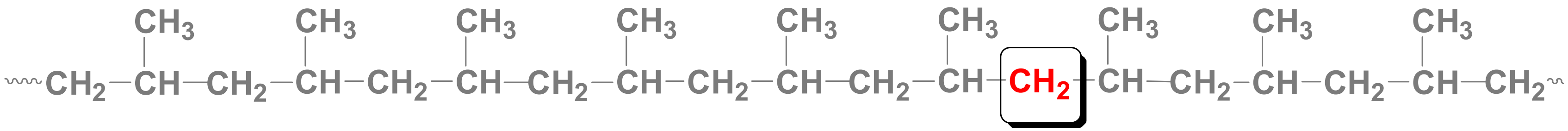
$$\sim \mathrm{CH_2}-\overset{\mathrm{CH_3}}{\mathrm{CH}}-\mathrm{CH_2}-\overset{\mathrm{CH_3}}{\mathrm{CH}}-\mathrm{CH_2}-\overset{\mathrm{CH_3}}{\mathrm{CH}}-\mathrm{CH_2}-\overset{\mathrm{CH_3}}{\mathrm{CH}}-\mathrm{CH_2}-\boxed{\overset{\mathrm{CH_3}}{\mathrm{CH}}-\mathrm{CH_2}-\overset{\mathrm{CH_3}}{\mathrm{CH}}-\mathrm{CH_2}}-\overset{\mathrm{CH_3}}{\mathrm{CH}}-\mathrm{CH_2}-\overset{\mathrm{CH_3}}{\mathrm{CH}}-\mathrm{CH_2}-\overset{\mathrm{CH_3}}{\mathrm{CH}}-\mathrm{CH_2}\sim$$

5



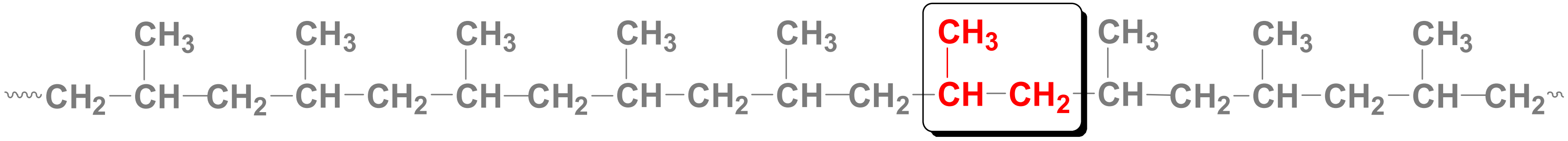
$$\sim \mathrm{CH_2}-\overset{\mathrm{CH_3}}{\mathrm{CH}}-\mathrm{CH_2}-\overset{\mathrm{CH_3}}{\mathrm{CH}}-\mathrm{CH_2}-\overset{\mathrm{CH_3}}{\mathrm{CH}}-\mathrm{CH_2}-\overset{\mathrm{CH_3}}{\mathrm{CH}}-\boxed{\mathrm{CH_2}-\overset{\mathrm{CH_3}}{\mathrm{CH}}-\mathrm{CH_2}-\overset{\mathrm{CH_3}}{\mathrm{CH}}-\mathrm{CH_2}}-\overset{\mathrm{CH_3}}{\mathrm{CH}}-\mathrm{CH_2}-\overset{\mathrm{CH_3}}{\mathrm{CH}}-\mathrm{CH_2}-\overset{\mathrm{CH_3}}{\mathrm{CH}}-\mathrm{CH_2}\sim$$

1



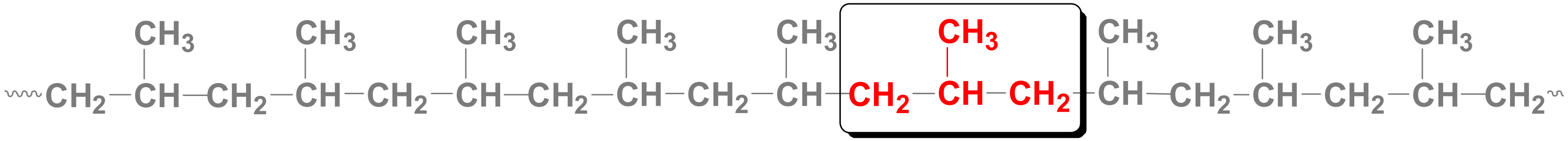
$$\sim CH_2-\overset{CH_3}{\overset{|}{CH}}-CH_2-\overset{CH_3}{\overset{|}{CH}}-CH_2-\overset{CH_3}{\overset{|}{CH}}-CH_2-\overset{CH_3}{\overset{|}{CH}}-CH_2-\overset{CH_3}{\overset{|}{CH}}-CH_2-\overset{CH_3}{\overset{|}{CH}}-\boxed{CH_2}-\overset{CH_3}{\overset{|}{CH}}-CH_2-\overset{CH_3}{\overset{|}{CH}}-CH_2-\overset{CH_3}{\overset{|}{CH}}-CH_2\sim$$

3



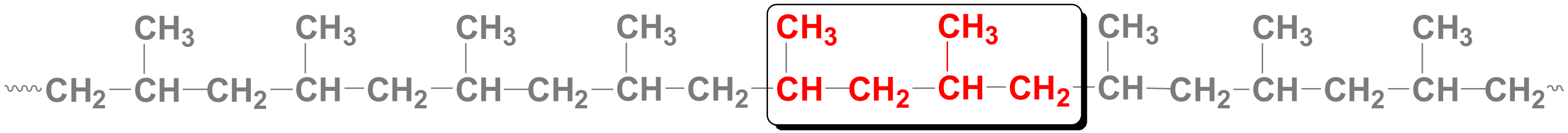
$$\sim CH_2-\overset{CH_3}{\overset{|}{CH}}-CH_2-\overset{CH_3}{\overset{|}{CH}}-CH_2-\overset{CH_3}{\overset{|}{CH}}-CH_2-\overset{CH_3}{\overset{|}{CH}}-CH_2-\overset{CH_3}{\overset{|}{CH}}-CH_2-\boxed{\overset{CH_3}{\overset{|}{CH}}-CH_2}-\overset{CH_3}{\overset{|}{CH}}-CH_2-\overset{CH_3}{\overset{|}{CH}}-CH_2-\overset{CH_3}{\overset{|}{CH}}-CH_2\sim$$

3



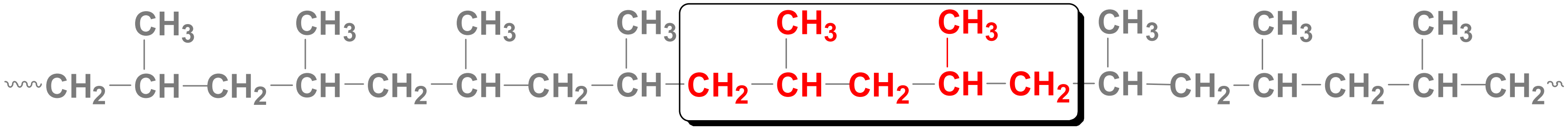
$$\sim CH_2-\overset{CH_3}{\overset{|}{CH}}-CH_2-\overset{CH_3}{\overset{|}{CH}}-CH_2-\overset{CH_3}{\overset{|}{CH}}-CH_2-\overset{CH_3}{\overset{|}{CH}}-CH_2-\overset{CH_3}{\overset{|}{CH}}-\boxed{CH_2-\overset{CH_3}{\overset{|}{CH}}-CH_2}-\overset{CH_3}{\overset{|}{CH}}-CH_2-\overset{CH_3}{\overset{|}{CH}}-CH_2-\overset{CH_3}{\overset{|}{CH}}-CH_2\sim$$

5



$$\sim CH_2-\overset{CH_3}{\overset{|}{CH}}-CH_2-\overset{CH_3}{\overset{|}{CH}}-CH_2-\overset{CH_3}{\overset{|}{CH}}-CH_2-\overset{CH_3}{\overset{|}{CH}}-CH_2-\boxed{\overset{CH_3}{\overset{|}{CH}}-CH_2-\overset{CH_3}{\overset{|}{CH}}-CH_2}-\overset{CH_3}{\overset{|}{CH}}-CH_2-\overset{CH_3}{\overset{|}{CH}}-CH_2-\overset{CH_3}{\overset{|}{CH}}-CH_2\sim$$

5

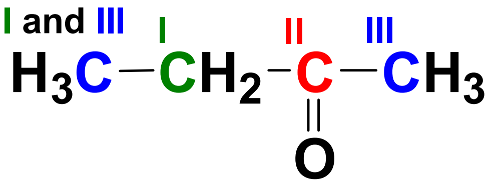


$$\sim CH_2-\overset{CH_3}{\overset{|}{CH}}-CH_2-\overset{CH_3}{\overset{|}{CH}}-CH_2-\overset{CH_3}{\overset{|}{CH}}-CH_2-\overset{CH_3}{\overset{|}{CH}}-\boxed{CH_2-\overset{CH_3}{\overset{|}{CH}}-CH_2-\overset{CH_3}{\overset{|}{CH}}-CH_2}-\overset{CH_3}{\overset{|}{CH}}-CH_2-\overset{CH_3}{\overset{|}{CH}}-CH_2-\overset{CH_3}{\overset{|}{CH}}-CH_2\sim$$

PP degradation products having > 2 interconnected C-atoms, which form from two chain cleavages without rearrangement, will always have an odd number of C atoms along their chain length.

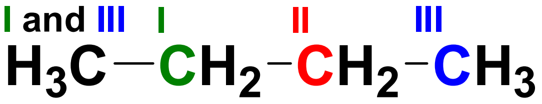
Some Compounds Have Mixed Isotopic Labeling

1 or 2 C(1)
1 C(2)
1 or 2 C(3)



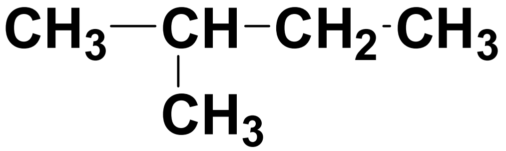
$$\overset{\text{I and III}}{H_3C}-\overset{\text{I}}{CH_2}-\overset{\text{II}}{\underset{\|}{C}}-\overset{\text{III}}{CH_3}\\ \quad O$$

1, or 2 C(1)
1 C(2)
1 or 2 C(3)



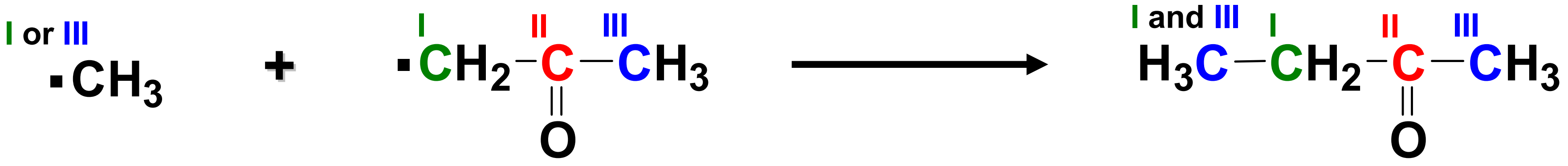
$$\overset{\text{I and III}}{H_3C}-\overset{\text{I}}{CH_2}-\overset{\text{II}}{CH_2}-\overset{\text{III}}{CH_3}$$

complex labeling

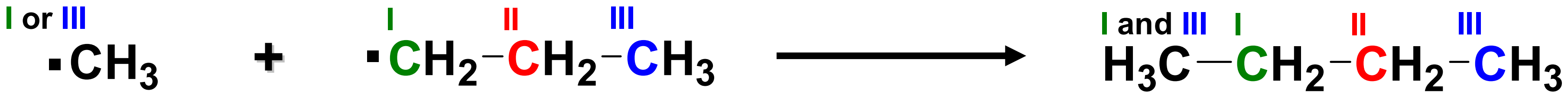


$$CH_3-\underset{\substack{|\\CH_3}}{CH}-CH_2-CH_3$$

Some Compounds Have Mixed Isotopic Labeling



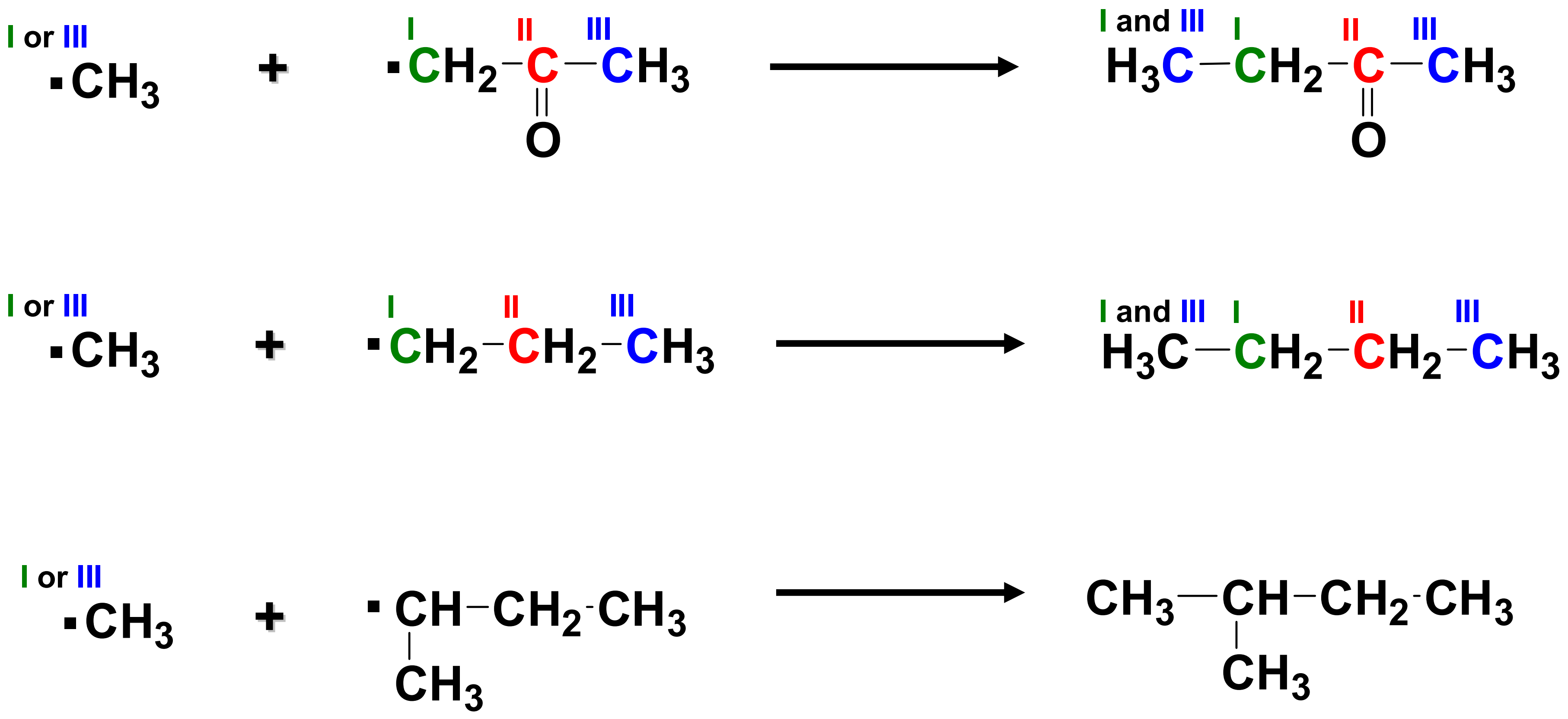
$$\overset{\text{I or III}}{\blacksquare CH_3} + \blacksquare\overset{\text{I}}{C}H_2-\overset{\text{II}}{\underset{\overset{\|}{O}}{C}}-\overset{\text{III}}{C}H_3 \longrightarrow \overset{\text{I and III}}{H_3C}-\overset{\text{I}}{C}H_2-\overset{\text{II}}{\underset{\overset{\|}{O}}{C}}-\overset{\text{III}}{C}H_3$$



$$\overset{\text{I or III}}{\blacksquare CH_3} + \blacksquare\overset{\text{I}}{C}H_2-\overset{\text{II}}{C}H_2-\overset{\text{III}}{C}H_3 \longrightarrow \overset{\text{I and III}}{H_3C}-\overset{\text{I}}{C}H_2-\overset{\text{II}}{C}H_2-\overset{\text{III}}{C}H_3$$

$$\overset{\text{I or III}}{\blacksquare CH_3} + \blacksquare\,\underset{\overset{|}{CH_3}}{CH}-CH_2-CH_3 \longrightarrow CH_3-\underset{\overset{|}{CH_3}}{CH}-CH_2-CH_3$$

Some Compounds Have Mixed Isotopic Labeling



$$\cdot CH_3 + \cdot CH_2-\underset{\overset{\|}{O}}{C}-CH_3 \longrightarrow H_3C-CH_2-\underset{\overset{\|}{O}}{C}-CH_3$$

$$\cdot CH_3 + \cdot CH_2-CH_2-CH_3 \longrightarrow H_3C-CH_2-CH_2-CH_3$$

$$\cdot CH_3 + \cdot \underset{\overset{|}{CH_3}}{CH}-CH_2-CH_3 \longrightarrow CH_3-\underset{\overset{|}{CH_3}}{CH}-CH_2-CH_3$$

For PP degradation products with > 2 interconnected C-atoms, an *even* number of C atoms along the chain length indicates formation via radical-radical coupling.

Final Summary

- Isotopic labeling (O-17 and C-13): New method for detailed tracking polymer radiation-chemistry, for oxidative degradation
- Polymer samples can be prepared with selective isotopic labeling (This study used 3 labeled polypropylene samples, each with C-13 in one of the three carbon positions along the chain)
- Analysis by NMR (macromolecular products), and by GC/MS (volatile products) allowed quantitative measurements of the time-dependent evolution of oxidation products
- Extensive characterization of Peroxides in PE (low concentration, low stability) vs. in PP (high concentration, higher stability), obtained, including concentrations, activation energies, and decomposition routes
- Previously unknown oxidation product (hemiketal) discovered

Final Summary

- Allows "mapping" of volatile (small molecule) oxidation products onto positions of origin from original polymer
- Small-molecule oxidation products coming "directly" from 2 chain scission events in PP, retain their original connectivity of carbon atoms, and always contain an "odd" number of carbon atoms (1,3,5,7,9….).
- In PP, most macromolecular oxidation products, and small-molecule oxidation products, result from oxidation at the C-2 carbon atom. However, CO and CO_2 result mainly from oxidation at the C-1 carbon atom.
- Provides insights into polymer radiation effects (such as synergism between radiation and elevated temperature).