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Radiation Aging and Post-Irradiation Aging Products in Polypropylene Samples Selectively Labeled with ^{13}C

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Thermal and Radiation Exposure of Polypropylene

- Degradation / Aging
  - o-rings, seals
  - cable jackets
- Processing (radiation)
  - sterilization of medical equipment
  - processing aid: scission/crosslink modifier
  - activation of surface for subsequent grafting

Polypropylene staining trays used for biological and medical applications. These trays can be repeatedly radiation-sterilized.

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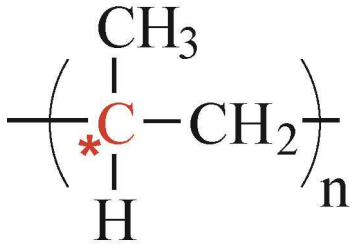
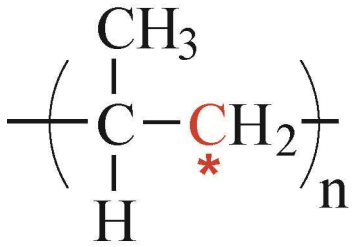
Selective Labeling of Polypropylene

Selective isotopic labeling with carbon-13

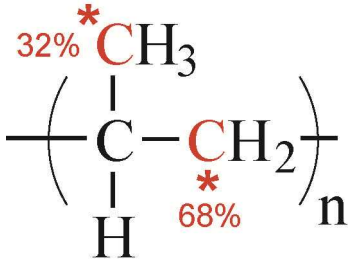
C(2) labeling



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.

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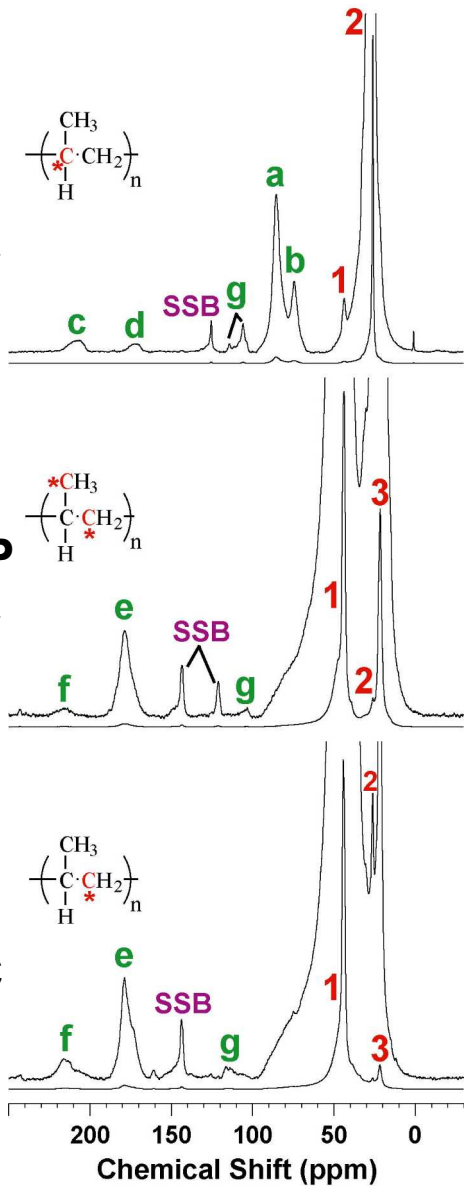
^{13}C DP/MAS Spectra of Aged Polypropylene Samples

C(2) labeled PP
aged 211 d at 50°C

C(1,3) labeled PP
aged 211 d at 50°C

C(1) labeled PP
aged 42 h at 109°C



Major ^{13}C Resonances

Main-chain PP resonances:

(1) Secondary/methylene (CH_2) carbon
(2) Tertiary/methine (CH) carbon
(3) Primary/methyl (CH_3) carbon

Functional group resonances:

(a) Tertiary hydroperoxides and/or dialkyl peroxides
(b) Tertiary alcohols
(c) Methyl ketones
(d) Esters and/or peresters
(e) Esters (chain-end)
(f) In-chain ketones
(g) Ketals

SSB ≡ Spinning sidebands of the main-chain resonances due to MAS at 10 kHz

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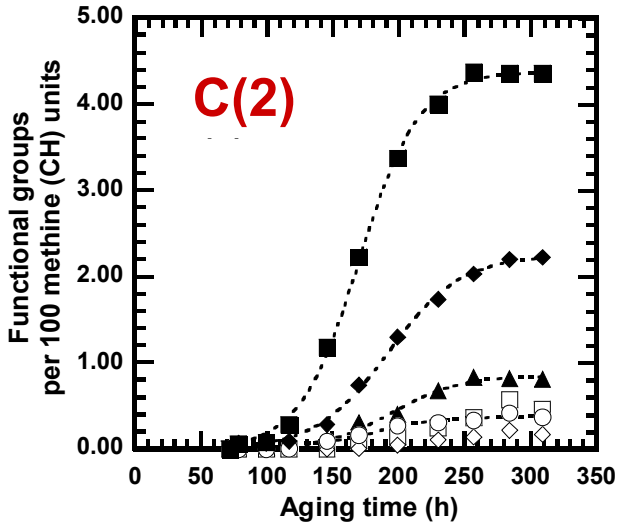
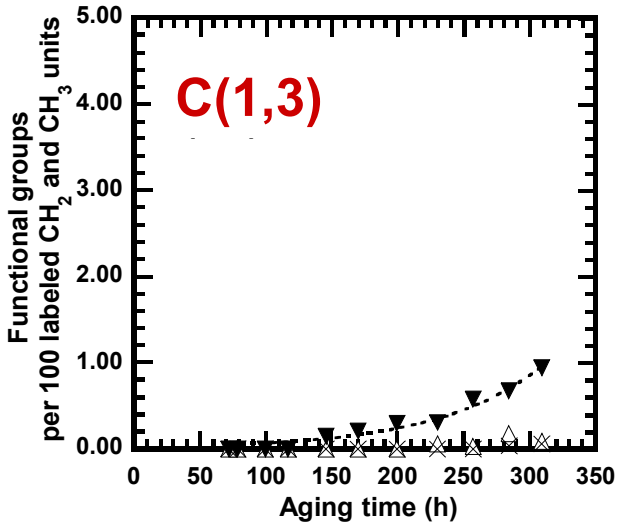
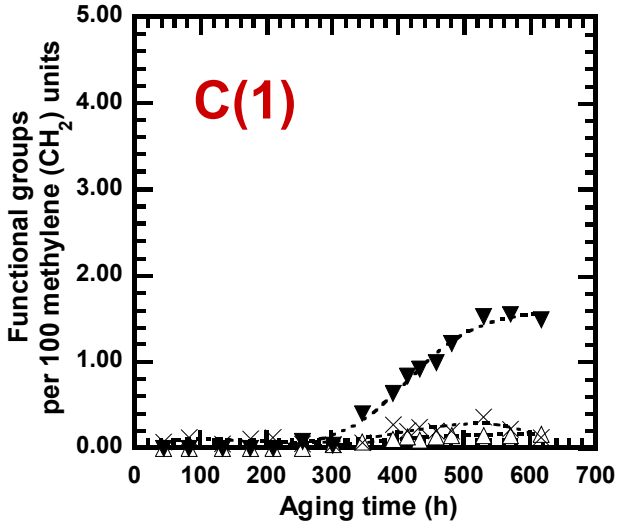
Thermo-Oxidative Aging at 80°C
Kinetic Accumulation of Oxidation Products







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)

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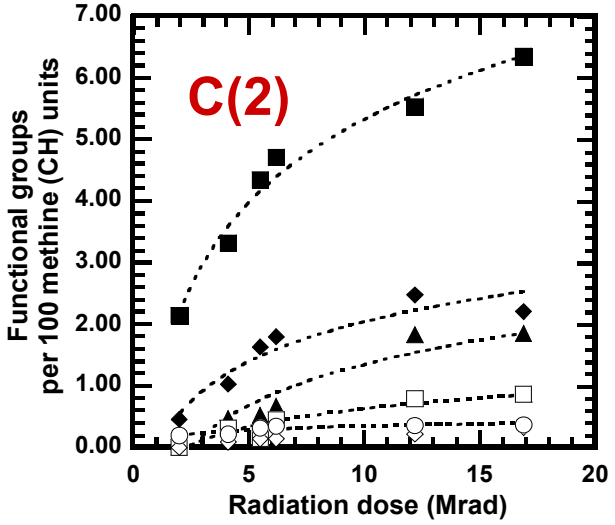
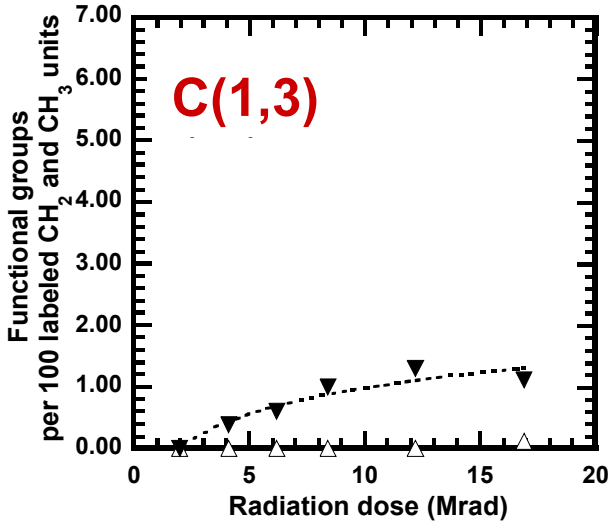
γ-Radiation Oxidation at 80°C
Kinetic Accumulation of Oxidation Products





- **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.**

γ-Radiation aging: 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.

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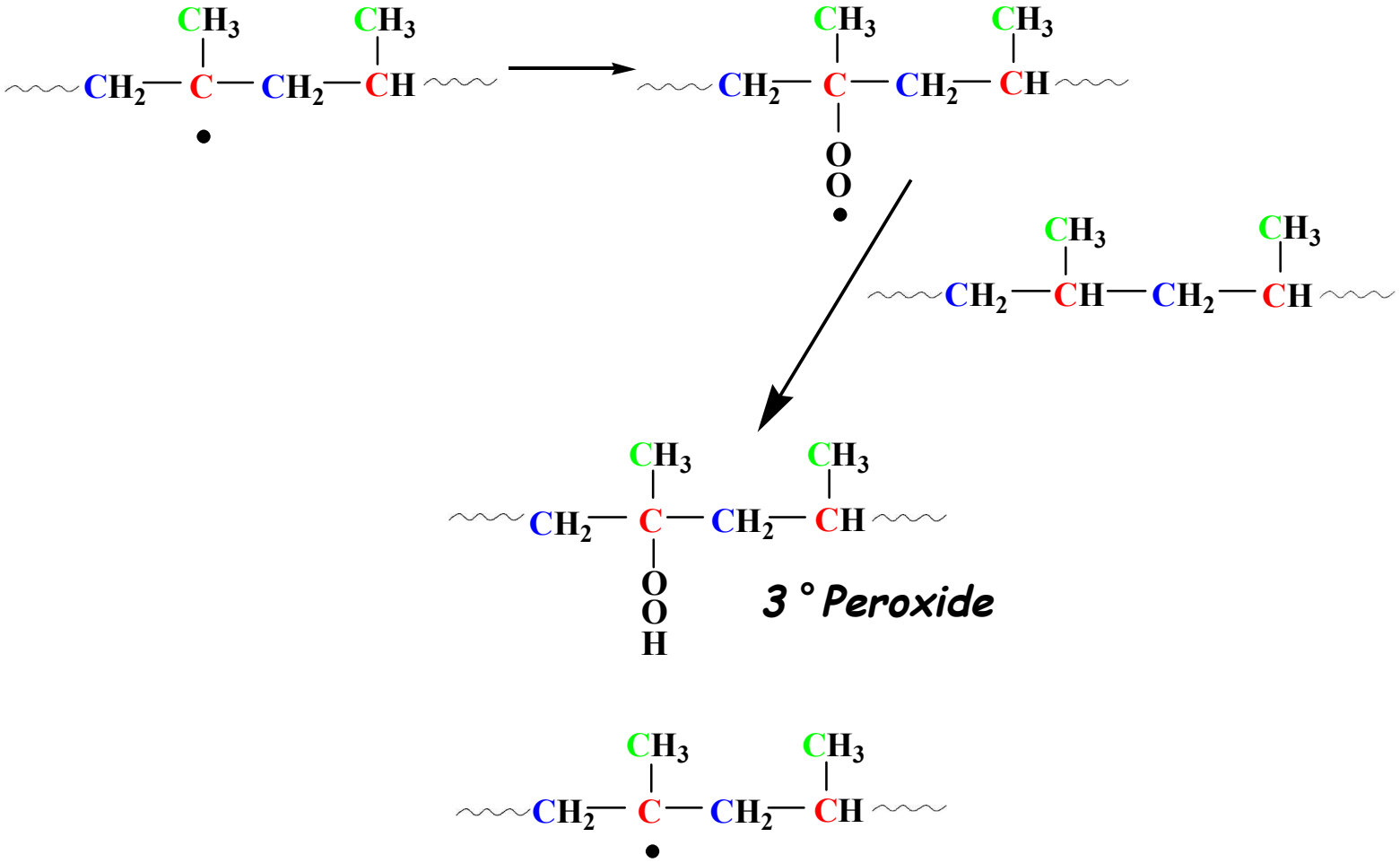
Chemical Mechanism for the Formation of Tertiary Peroxides



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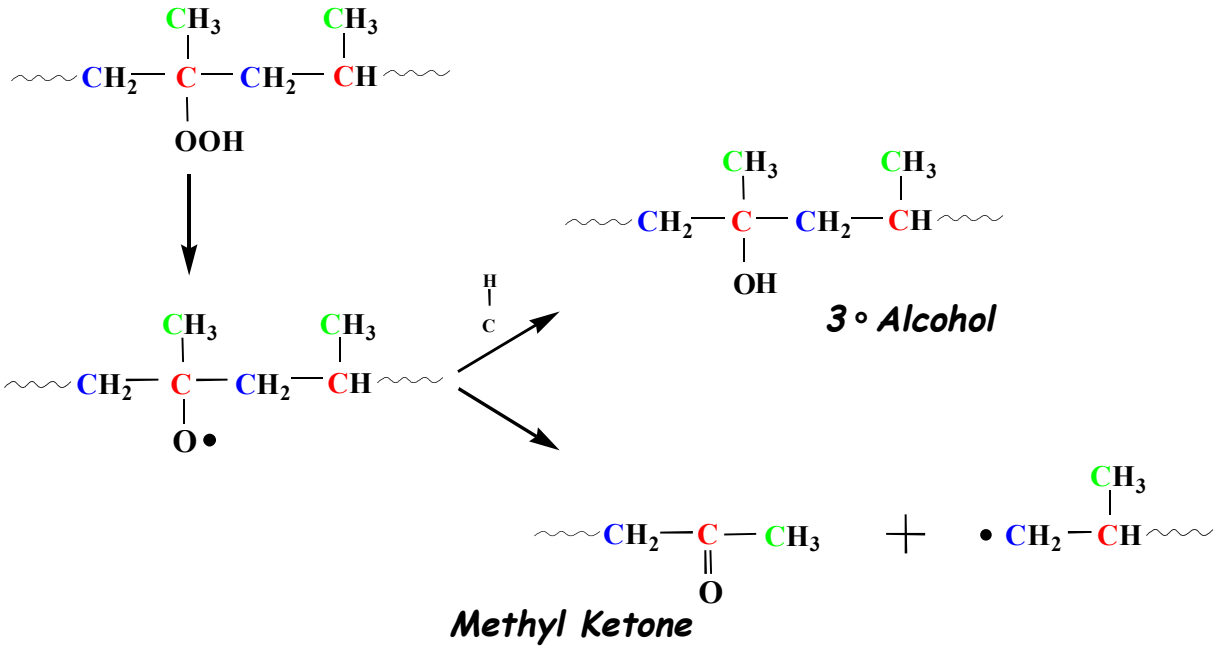
Chemical Mechanism for the Formation of Methyl Ketones

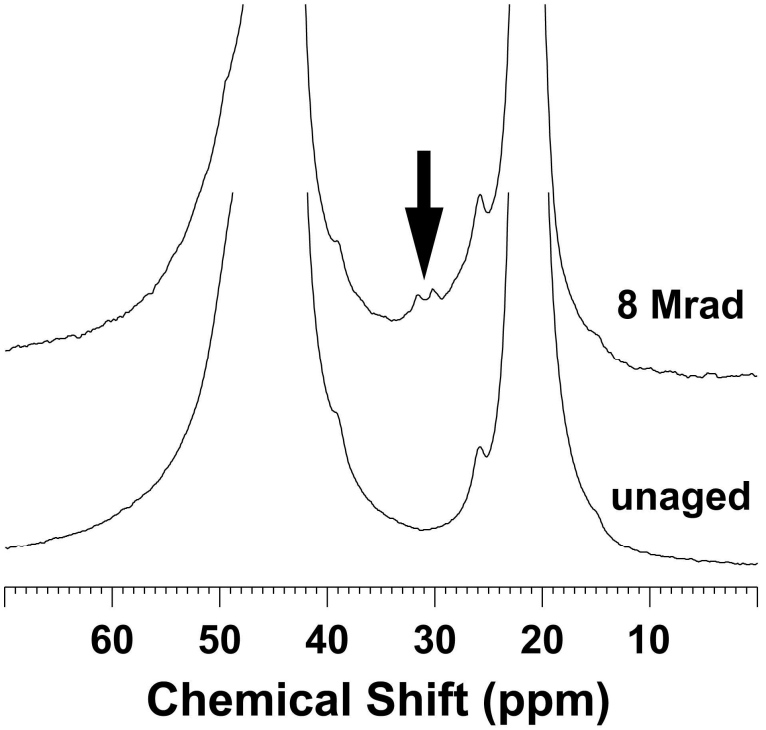


Formation of methyl ketones and 3° alcohols

Methyl Peaks Associated with Methyl Ketones

Previous scheme predicts a chain end methyl group and a methyl group attached to the 3^{o} alcohol.

Both should be associated with the C(3) carbon and are predicted to resonate in the 30 to 32 ppm range.



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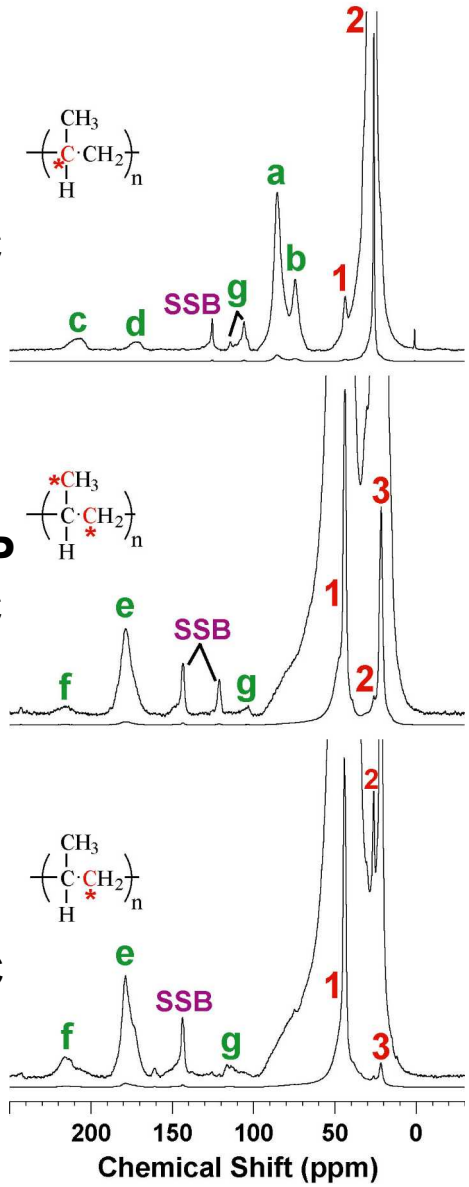
Identification of Resonances near 110 PPM

C(2) labeled PP
aged 211 d at 50°C

C(1,3) labeled PP
aged 211 d at 50°C

C(1) labeled PP
aged 42 h at 109°C



- **Peaks (g):**
  - Carbons in a double bond (C=C) or di-oxygenated alkyl carbons (O−C−O), such as ketals or acetals?
  - In previous high-temperature, solution-state ^{13}C NMR studies of oxidatively degraded PP, a peak at 111.5 ppm was seen and identified with the vinylidene carbon ($=CH_2$).
  - Double bonds could indicate cross linking.
- **Peaks (d) and (e):**
  - Esters or carboxylic acids?

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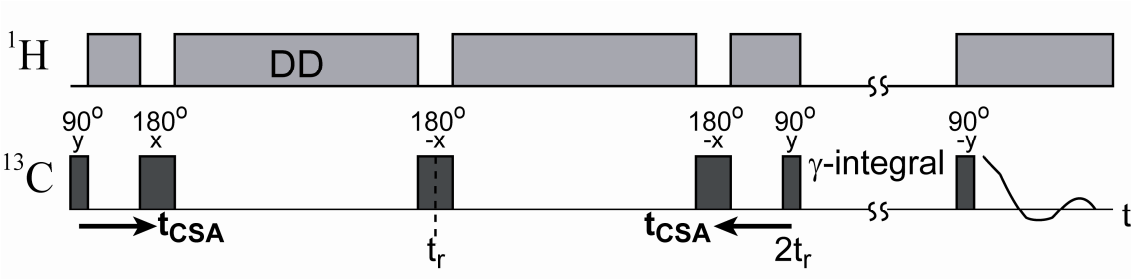
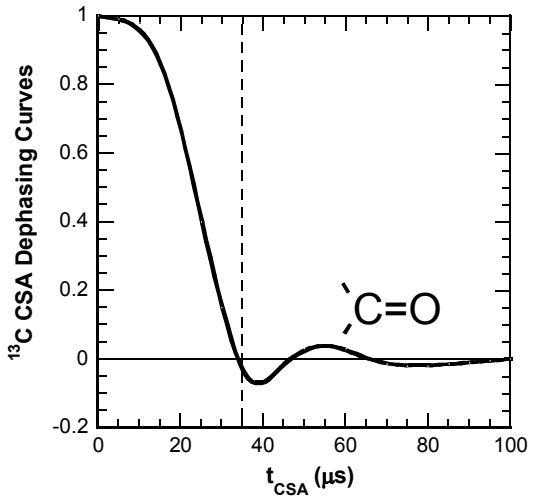
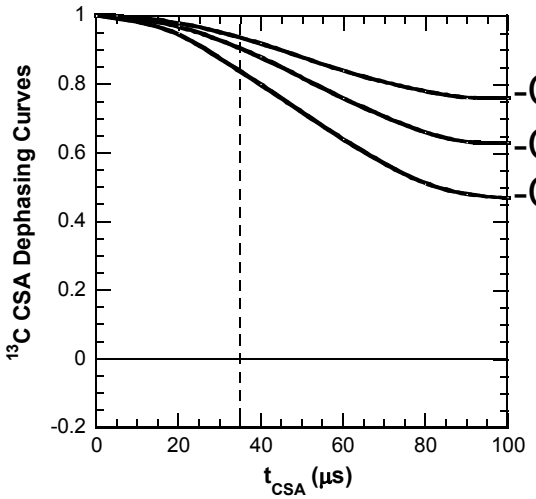
Separation of ^{13}C NMR Resonances by a CSA Filter

Recently, Mao and Schmidt-Rohr* presented CSA recoupling pulse sequences that suppress the ^{13}C NMR signals of sp- and sp^2-hybridized carbons (such as aromatic and vinylidene carbons) while selecting the signals of sp^3-hybridized carbons, particularly alkyl carbons. This selection is achieved by exploiting the symmetry-based, systematic difference in the ^{13}C chemical shift anisotropies (CSAs) between the carbon sites.







Typical ^{13}C CSA dephasing curves for different carbon sites, based on simulated curves (B_o=9.4 T, v_r=5 kHz) from Mao and Schmidt-Rohr*.

*J.-D. Mao; K. Schmidt-Rohr *Solid State Nucl. Magn. Reson.* **2004**, *26*, 36-45.

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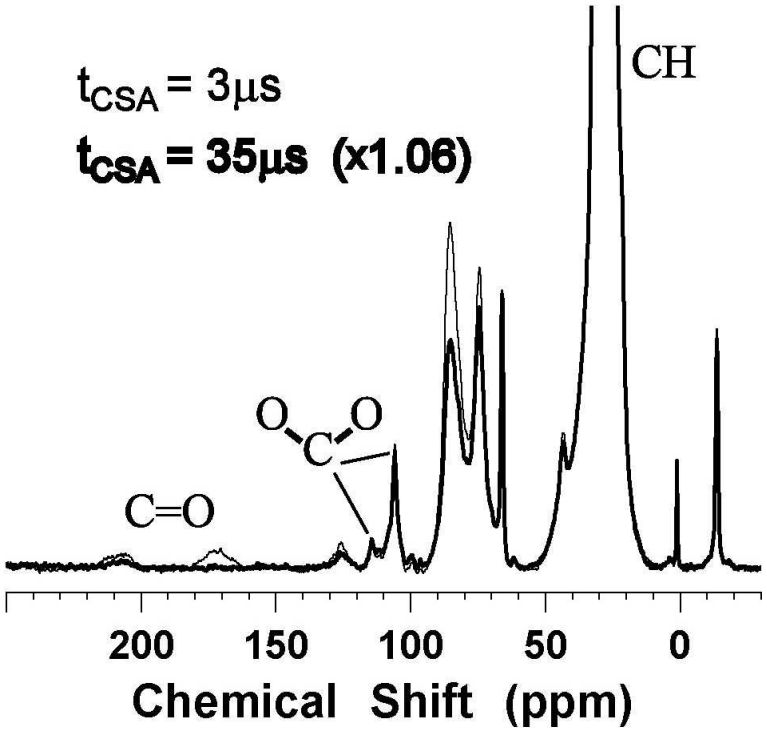
^{13}C CSA Filter Applied to Aged Polypropylene



DP/MAS spectra of a C(2) labeled PP thermally aged 293 h at 80°C. A reference spectrum and a CSA-filtered spectrum are presented.

- The CSA filter of Mao and Schmidt-Rohr (five-pulse sequence) was applied to a highly aged C(2) PP sample.
- The filter clearly suppresses the signals of the carbonyl carbons (160-220 ppm), which are sp^2-hybridized.
- The signal of the main-chain methine carbon (25.9 ppm) shows little dephasing.
- Most importantly, the resonances from 100-117 ppm do not significantly dephase, convincingly identifying these resonances with ketal and acetal groups, not vinylidene structures.

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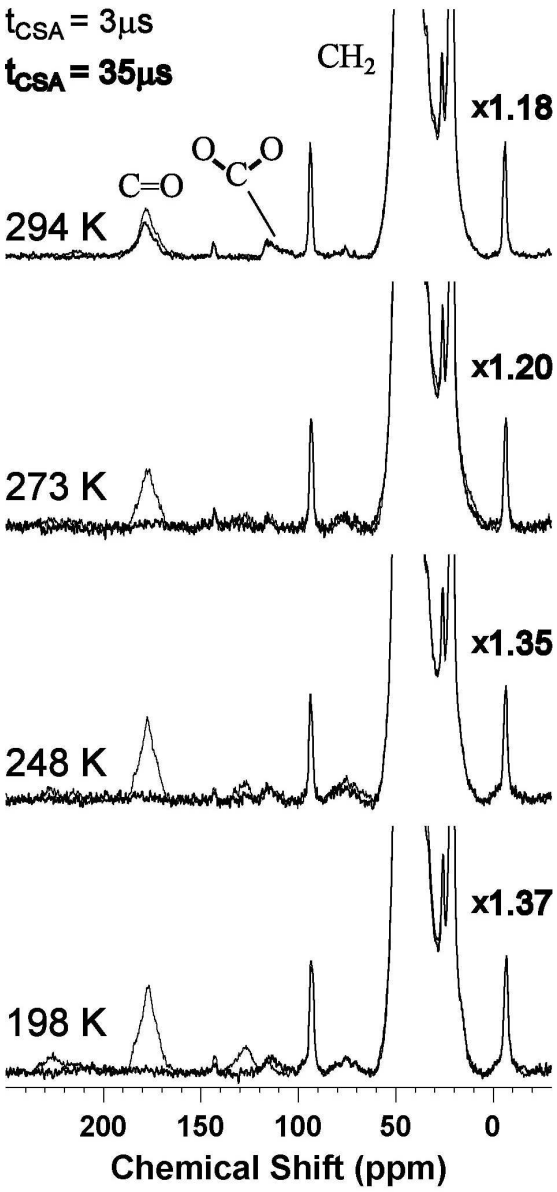
Variable Temperature CSA Filtering



DP/MAS spectra of a C(1) labeled PP thermally aged 41 h at 109°C.

- At room temperature (294 K), the carbonyl (C=O) signals at ~179 ppm are not effectively suppressed by the filter, although carbonyl carbons typically have large CSAs.
- At lower temperatures, however, the filter clearly suppresses the carbonyl resonance at ~179 ppm.
- The temperature-dependant difference in the effectiveness of filter suppression implies mobility in the specific carbonyl group.
  - **At room temperature, the mobility is enough to partially average the CSA.**
- Note that at all temperatures, the resonances in the range 100-117 ppm do not significantly dephase, again identifying these resonances with ketal and acetal groups.

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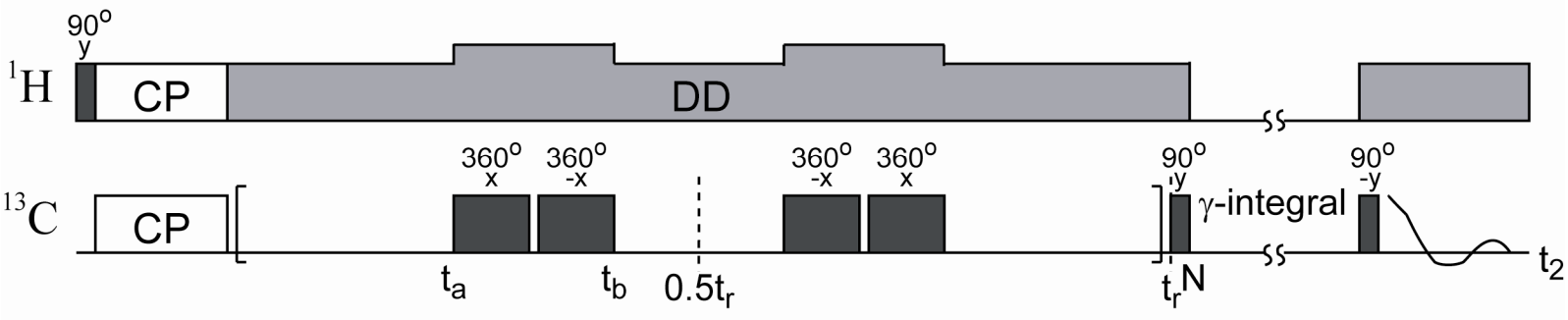
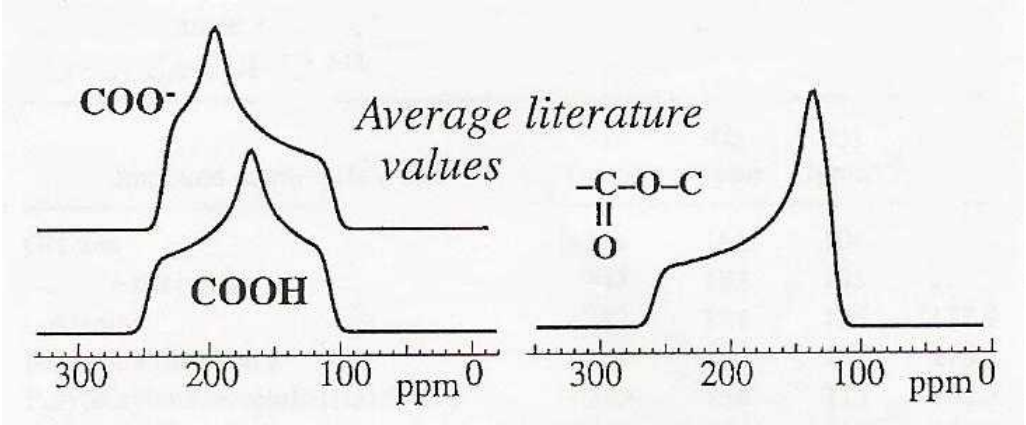
SUPER Experiment

Schmidt-Rohr and co-workers* recently developed an MAS experiment for separating quasi-static CSA patterns by the isotropic chemical shift. The method, termed Separation of Undistorted Powder patterns by Effortless Recoupling (SUPER), allows for effective assignment of ^{13}C resonances by their respective CSA patterns.



SUPER NMR pulse sequence*



Carboxyl groups, which have overlapping isotropic chemical shift ranges, can be readily distinguished by the shape of their CSA patterns (different σ_{22}).

*S.-F. Liu; J.-D. Mao; K. Schmidt-Rohr *J. Magn. Reson.* **2002**, *155*, 15-28.

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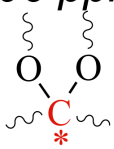
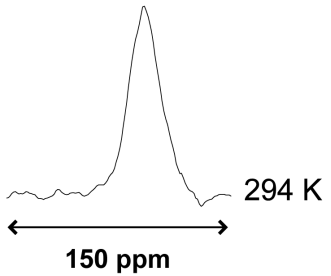
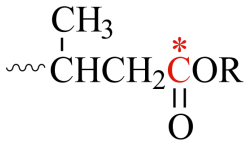
SUPER Experiment Applied to Aged Polypropylene

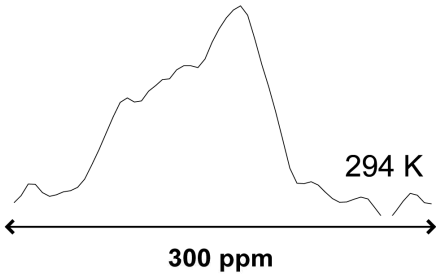
C(2)
106 ppm



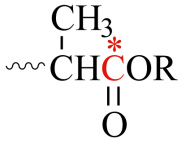


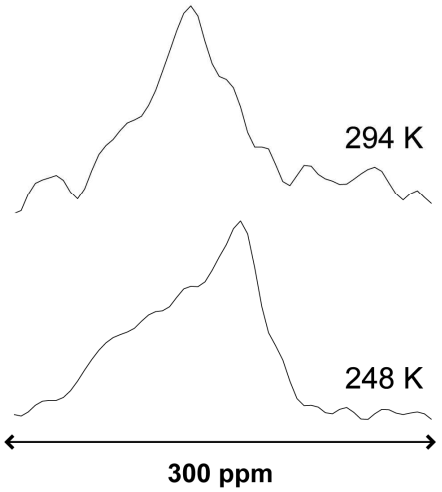
C(2)
170 ppm





C(1)
179 ppm





- The CSA patterns of resonances from 100-117 ppm are much narrower than carbonyl patterns, typical of sp^3-hybridized carbons.
  - consistent with results of the CSA-filtered experiments
- Both of the carboxyl resonances in question for aged PP show CSA patterns typical of ester groups, not carboxylic acids.
- As with the CSA-filtered experiments, SUPER is temperature dependent, due to functional group mobility.
  - The mobility of the C(1) resonance at ~179 ppm implies chain-end esters.

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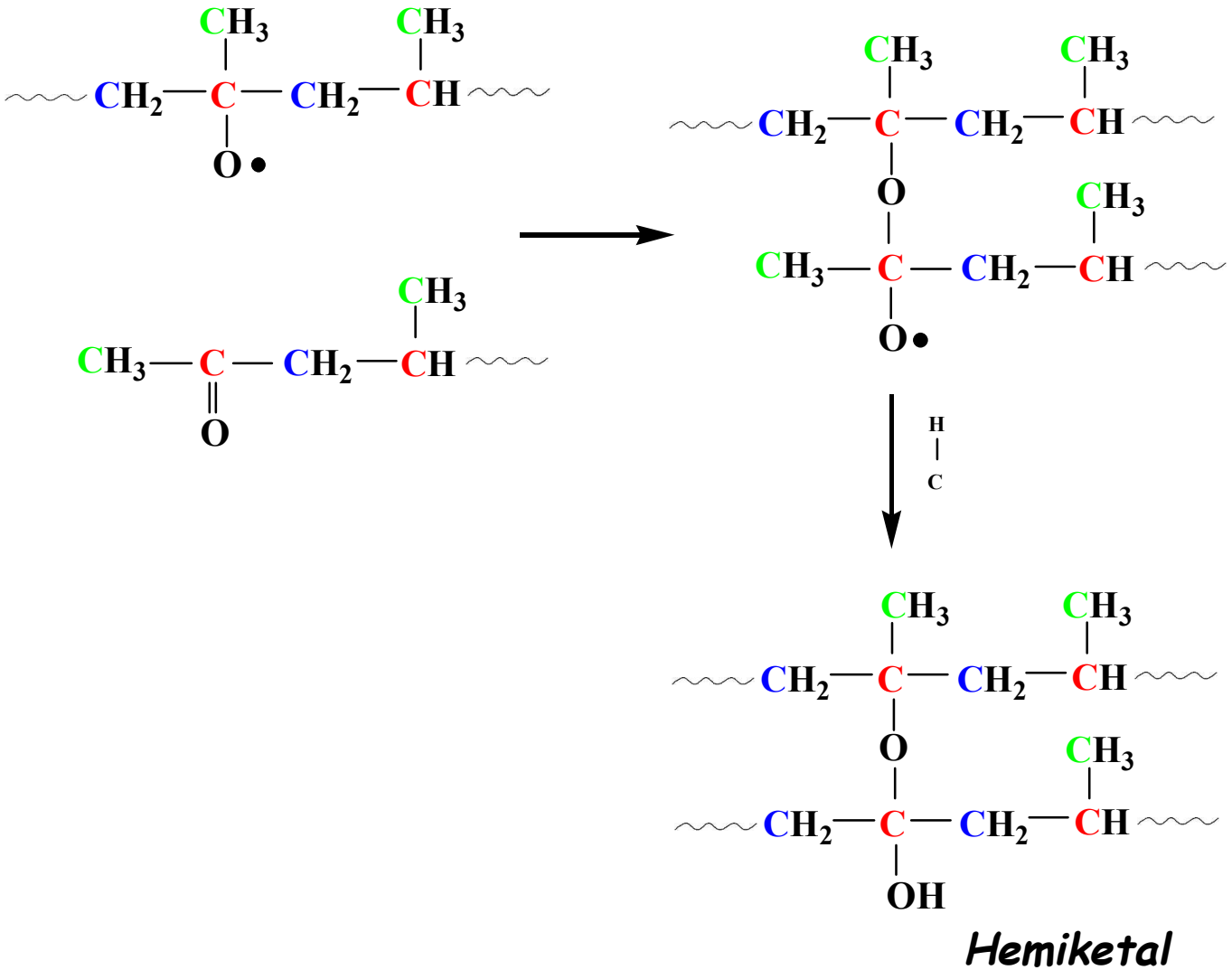
Chemical Mechanism for the Formation of Hemiketals



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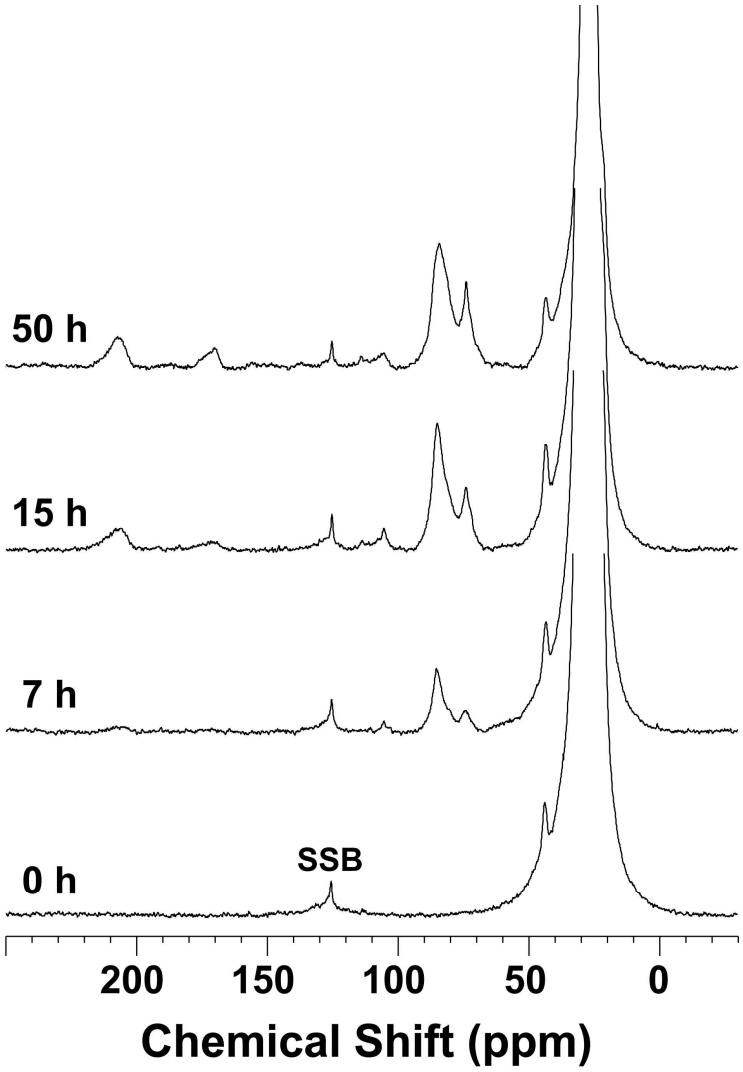
^{13}C NMR Spectra of Post-Irradiation Thermally Aged Polypropylene



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.

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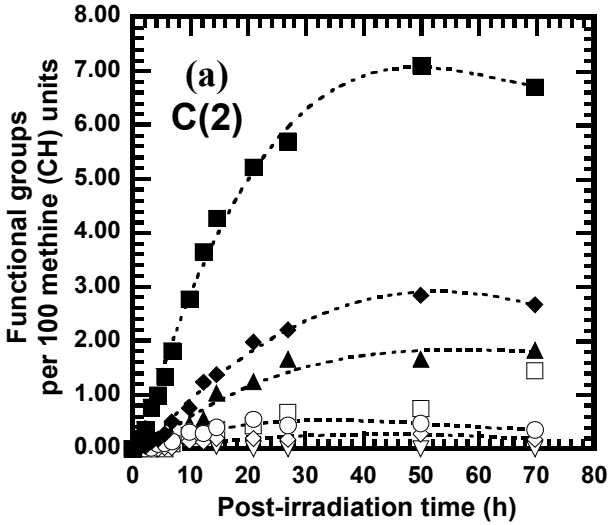
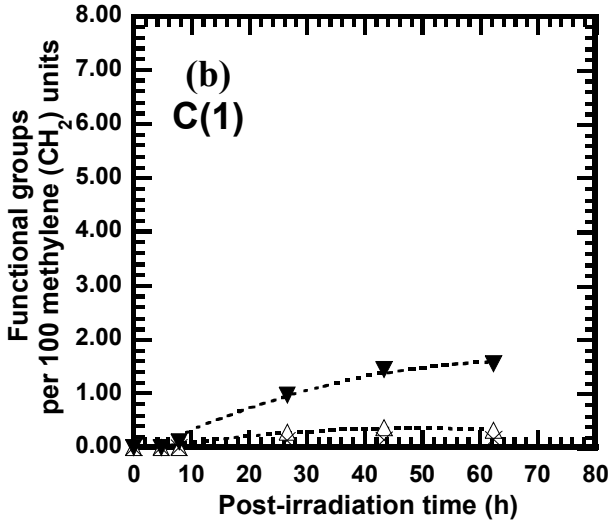
Product Distribution of Post-Irradiation Thermally Aged Polypropylene





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

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)

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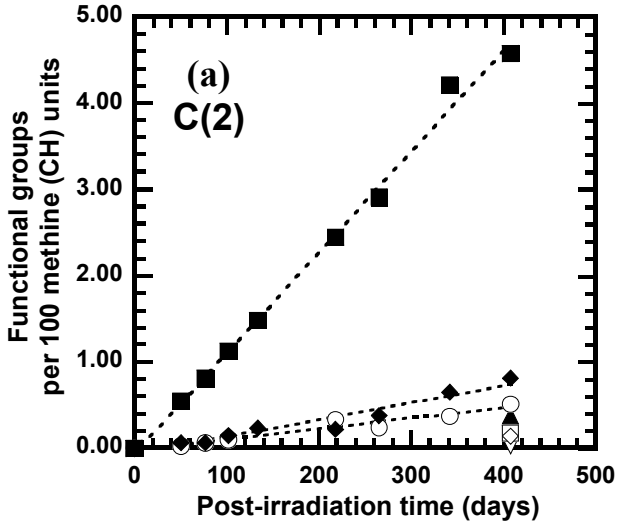
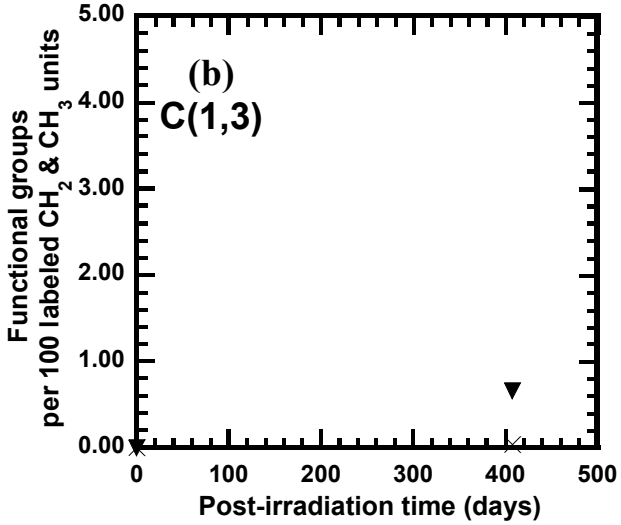
Post-Irradiation Thermally Aging of Polypropylene at 22°C





The product distributions at 22°C are similar to those at 109°C.

Note the rapid buildup of product at 22°C for these samples.

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)

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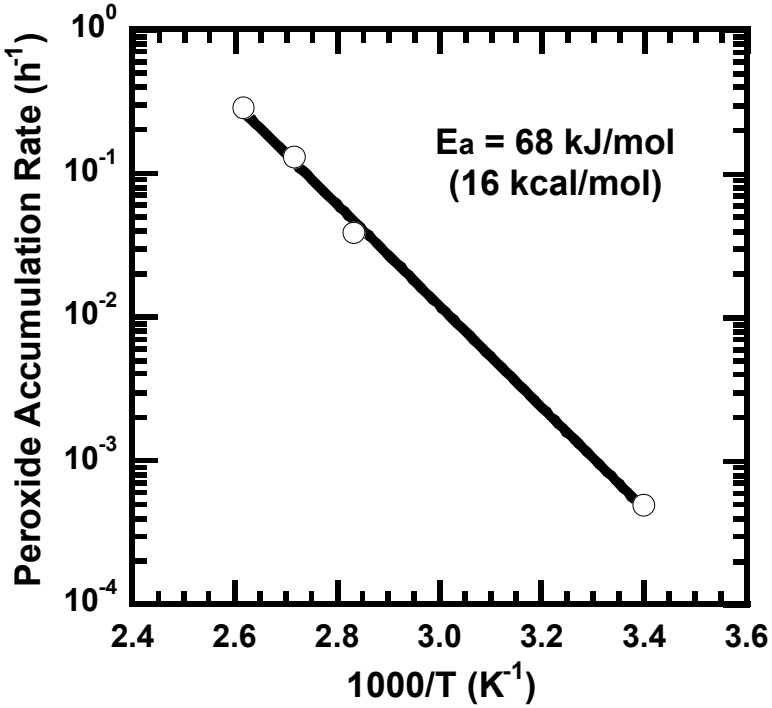
The Activation Energy for Accumulation of Tertiary Peroxides

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)



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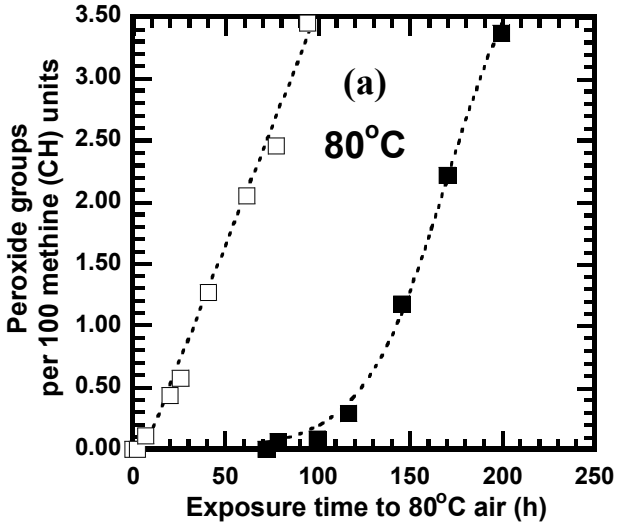
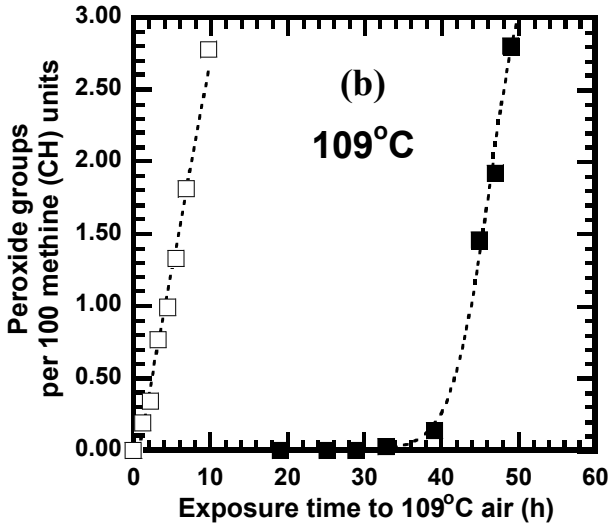
Pre-irradiation Eliminates the Induction Time Associated with Thermal Aging





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

Pre-irradiation eliminates the induction time associated with the degradation process.

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

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Comparison of Aging in Polypropylene and Polyethylene

- **Peroxide Concentration**
  - Thermal aging
    - Polyethylene: none
    - Polypropylene: ~ 4%
  - Radiation aging
    - Polyethylene: ~ 0.1%
    - Polypropylene: > 6%
- **Peroxide Stability**
  - Polyethylene: ½ life of < 30 hrs at 65°C
  - Polypropylene: little effect for extended periods at 110°C

Additional Work:

FTIR: isotope shifts of functional groups

Mass Spectroscopy: origin of gaseous and low MW products

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