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Leveraging Isotopic Labels to Elucidate the Underlying Degradation Chemistries of Nylon 6.6

Gregory Von White II,[a] Roger L. Clough,[a] Jonell N. Smith,[b]
Michael I. White,[b] James M. Hochrein,[b] Robert Bernstein[a]
Sandia National Laboratories, Albuquerque, NM 87185
Org. 1821—Organic Materials[a] and Org. 1825—Materials Reliability[b]

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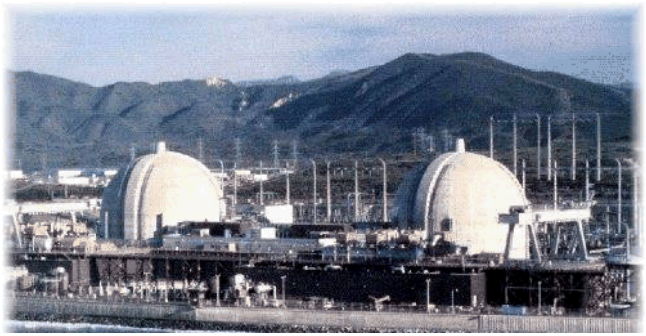
National Nuclear Security Administration

Outline

- Motivation
- Background
- Methodologies
- Quantitative Analysis of Product Formation
- Degradation Mechanisms

Organic Materials Employed in Service for Decades in Critical High Reliability and Performance Applications

O-rings



Nuclear Power Plant Cable Insulation

Aircraft Wire Insulation

Textiles/Fibers

Protective Clothing

Polymer Aging - Approaches/Goals

Macroscopic level

Physical Properties

Tensile Property

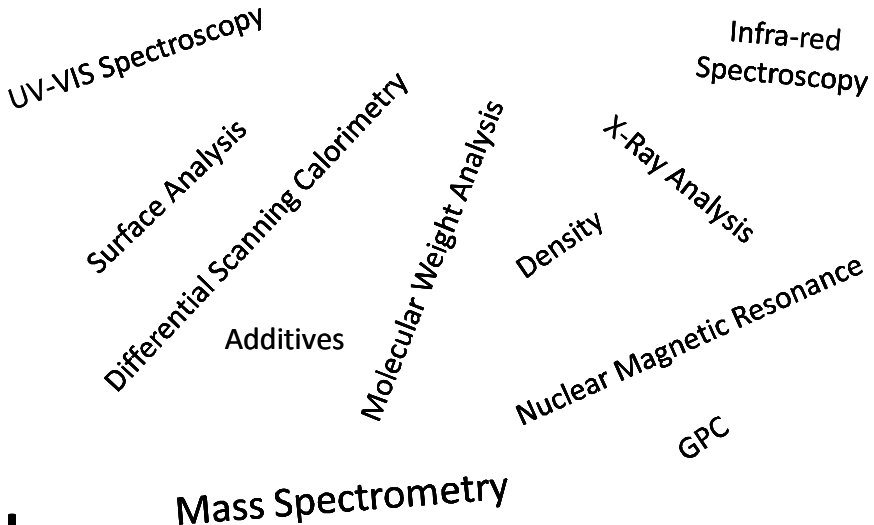
Permeation

Elongation

Dimensional changes

Molecular Level

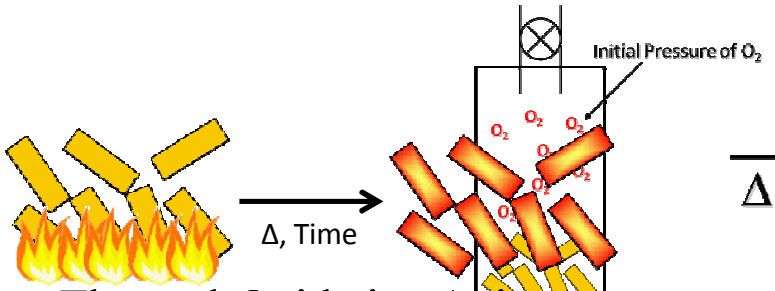
Chemical Properties



Goals

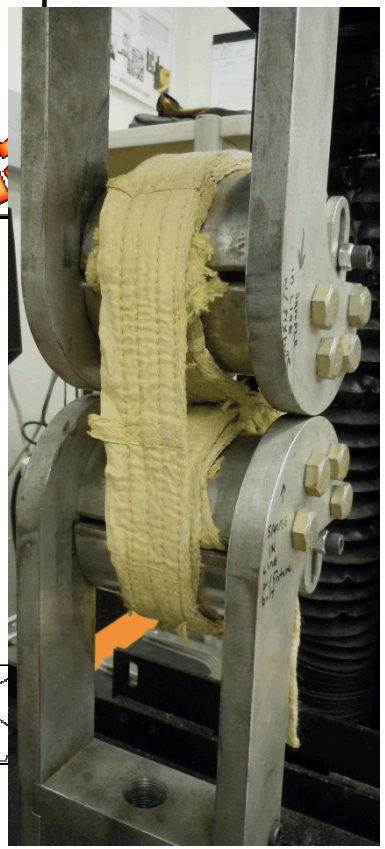
- **Prediction of physical properties vs. time**
  - **Predict remaining physical properties of field materials**
- Develop condition monitoring method

Methodologies

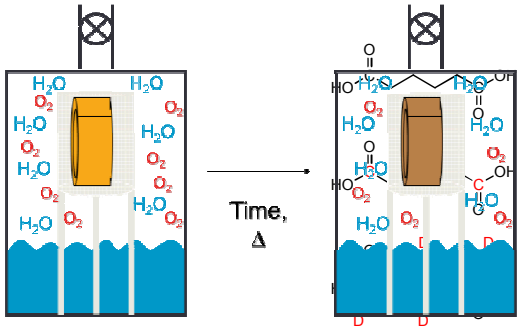


Thermal-Oxidative Aging

Oxygen Consumption



Tensile Testing

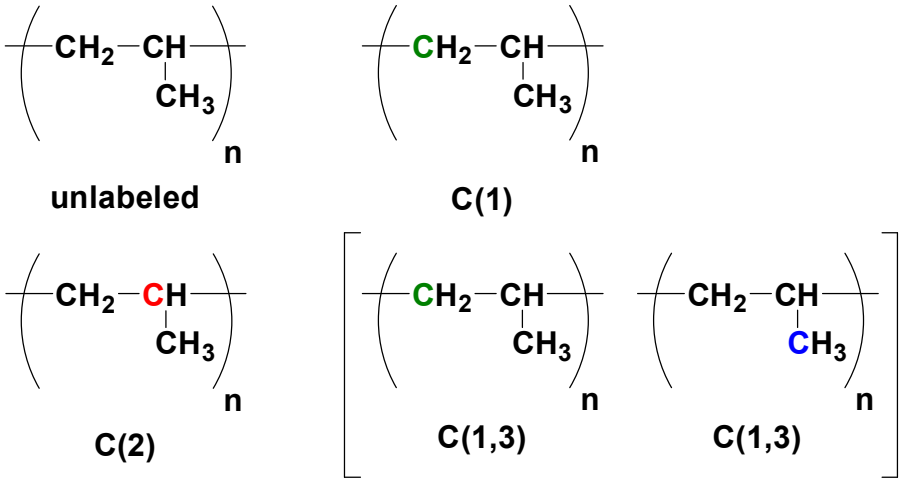


Humidity Aging

Isotopically Labeled Polymers

Polypropylene studies served as the model for nylon studies

- Polypropylene was isotopically labeled
- Aged under thermal-oxidative conditions
- Characterized using mass spectrometry to identify mass shifts and degradation products
- Piece puzzle together to establish mechanism for oxidative attack and decomposition



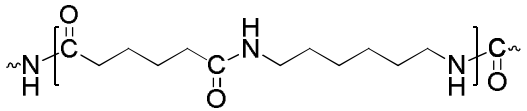
Relative ^{13}C abundance (%) of selectively-labeled polypropylene samples

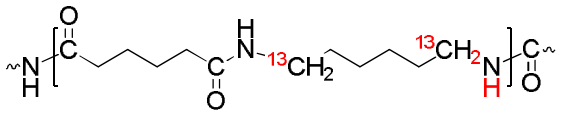
Sample	CH	CH_2	CH_3
C(1)	1.0	96.7	2.3
C(2)	98.5	0.8	0.8
C(1,3)	0.9	68.3	30.8

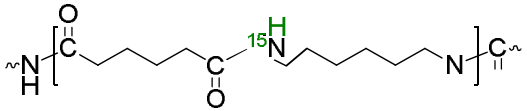
Mowery et al. *Macromol.* **2005**, 38, 5035-5046.
Thornberg et al. *Macromol.* **2006**, 39, 5592-5594.
Mowery et al. *Rad. Phys. Chem.* **2007**, 76, 864-878.
Mowery et al. *Macromol.* **2007**, 40, 3615-3623.
Thornberg et al. *Polym. Degrad. Stab.* **2007**, 92, 94-102.
Bernstein et al. *Polym. Degrad. Stab.* **2007**, 92, 2076-2094.
Bernstein et al. *Nucl. Instr. Meth. B* **2007**, 265, 8-17.
Bernstein et al. *Polym. Degrad. Stab.* **2008**, 93, 854-870.

Why Nylon?

- Nylon is used in a wide variety of products
- Oxidation reduces the overall lifetime of nylon which directly alters performance
- Underlying mechanisms must be understood to predict degradation product formation and serves as the foundation for future sensor development for condition monitoring

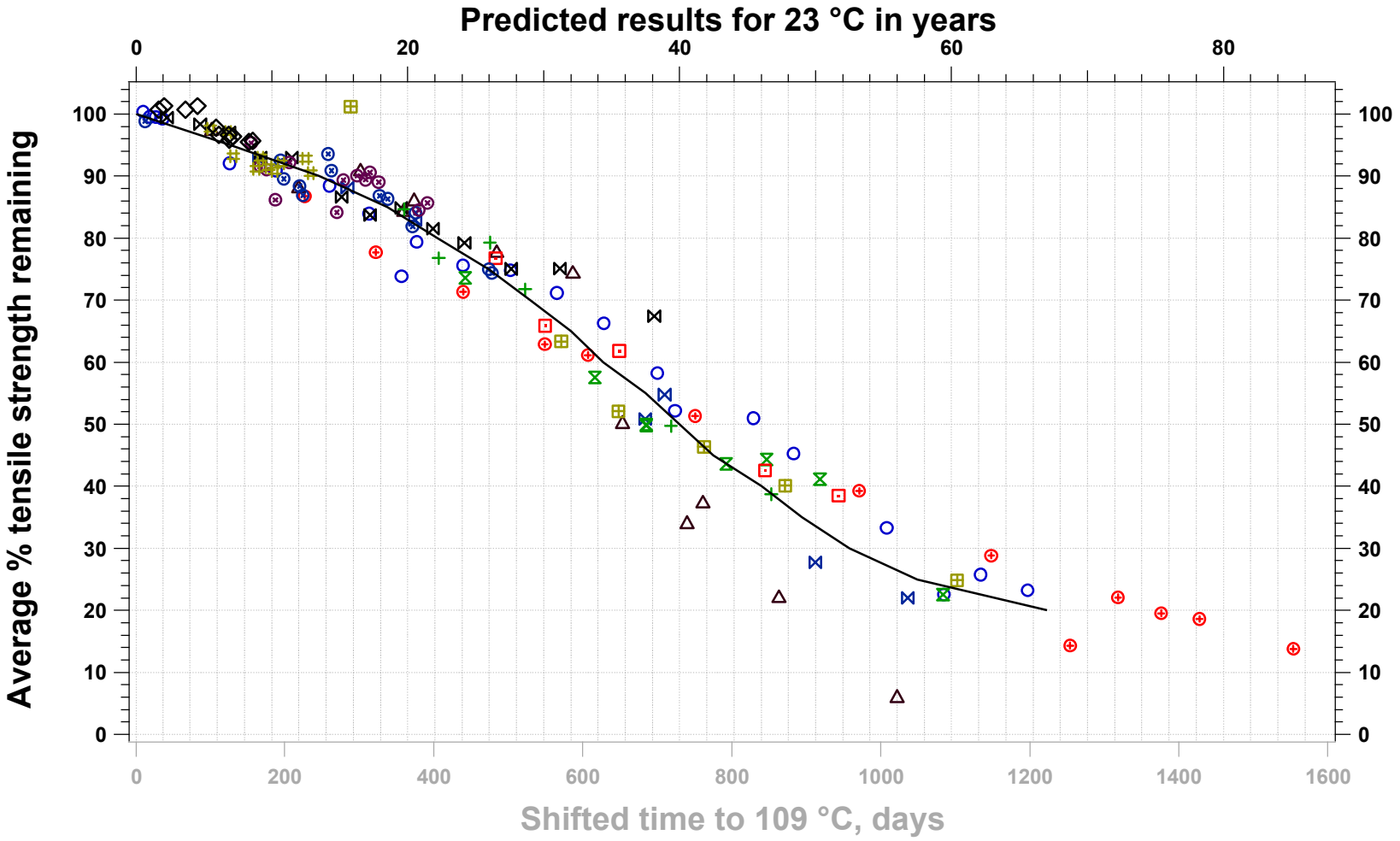






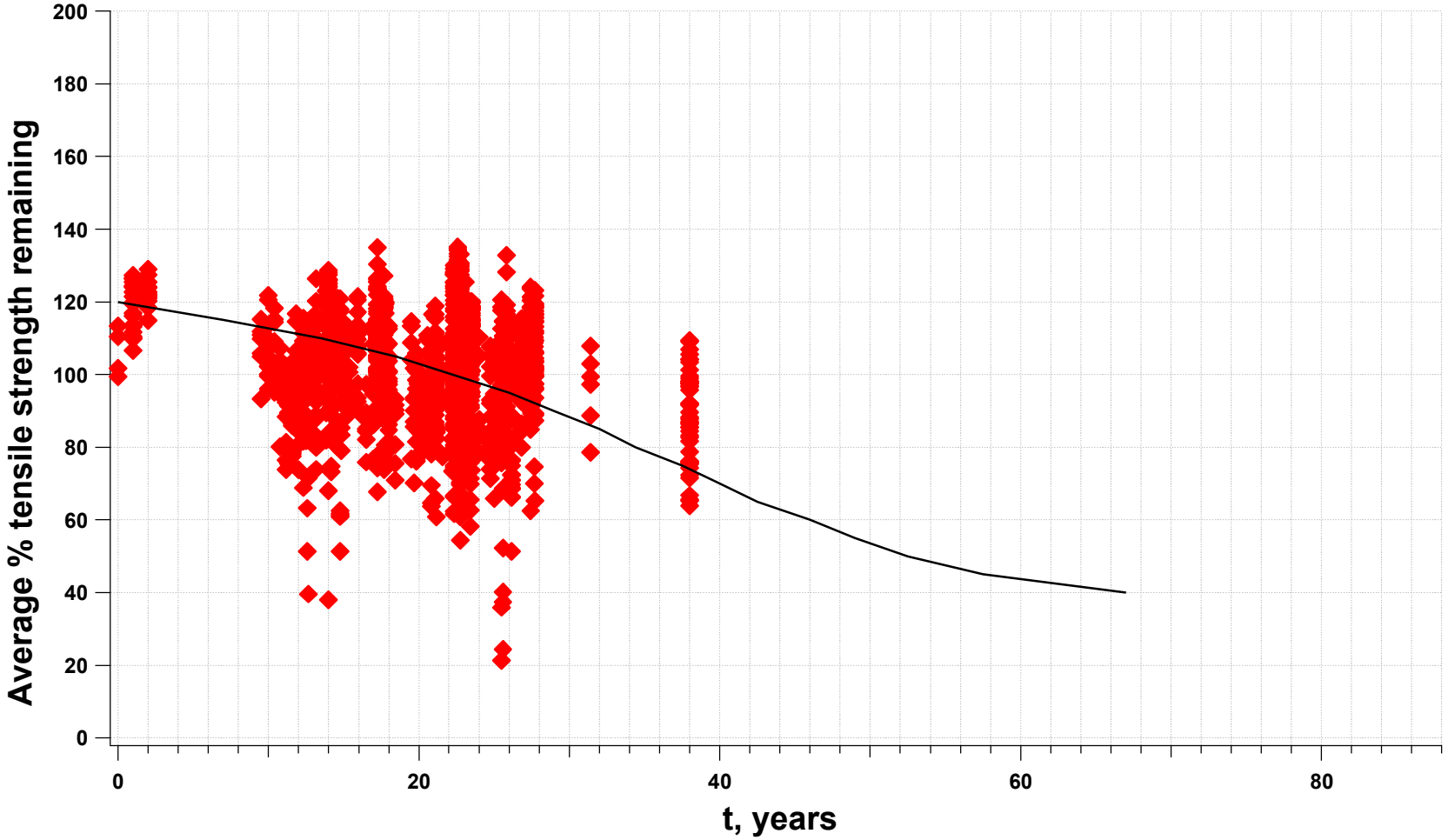
Karstens *Makromol Chem.* **1989**, 190, 3033-3053.
Groning et al. *J. Appl. Polym. Sci.* **2002**, 86, 3396-3407.
Shamey et al. *Rev. Prog. Color* **2003**, 33, 93-107.
Bernstein et al. *Polym. Degrad. Stab.* **2005**, 88, 480-488.
Bernstein et al. *Polym. Degrad. Stab.* **2010**, 95, 1471-1479.
White II et al. *Polym. Degrad. Stab.* **2012** In Review.

Nylon 6.6 Accelerated Aging Studies



Bernstein, R.; Gillen, K. T. *Polym. Degrad. Stab.* **2010**, *95*, 1471-1479.

Lifetime Prediction Validation with Field Aged Data



Nylon Field Aged Materials and our Thermal-Oxidative Prediction Line at 23 °C

Approaches/Goals

Macroscopic level

Physical Properties

Tensile Property

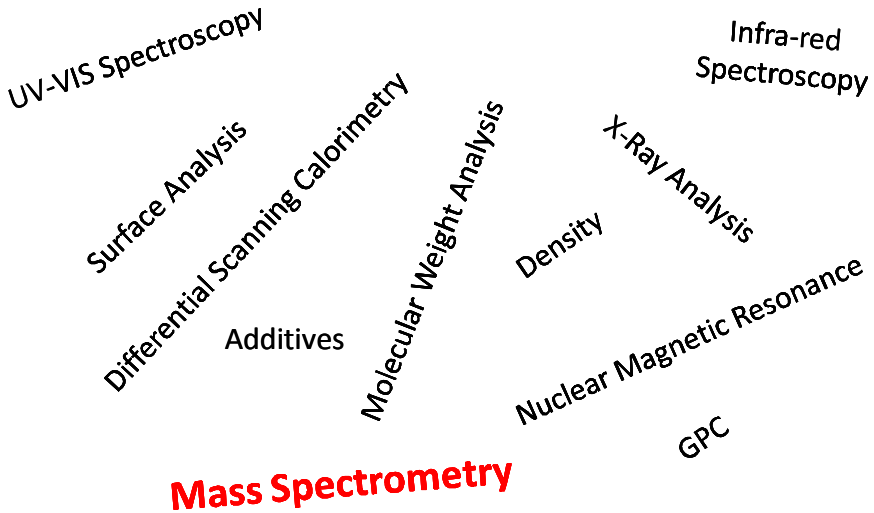
Permeation

Elongation

Dimensional changes

Molecular Level

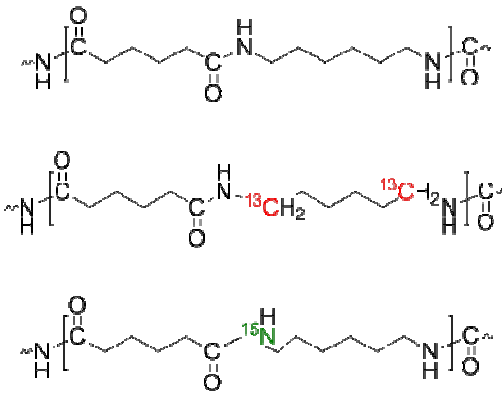
Chemical Properties



Goals

- Prediction of physical properties vs. time
  - Predict remaining physical properties of field materials
- **Develop condition monitoring method**

Methodologies

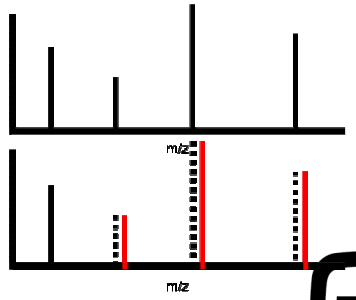


Isotopically labeled and unlabeled nylon 6.6 were aged in 5 cm^3 stainless steel vessels between 1 and 243 days at 109 °C and 138 °C

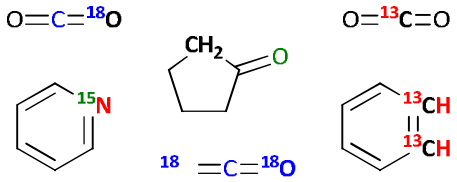
Cryo-GC/MS

Identify degradation products

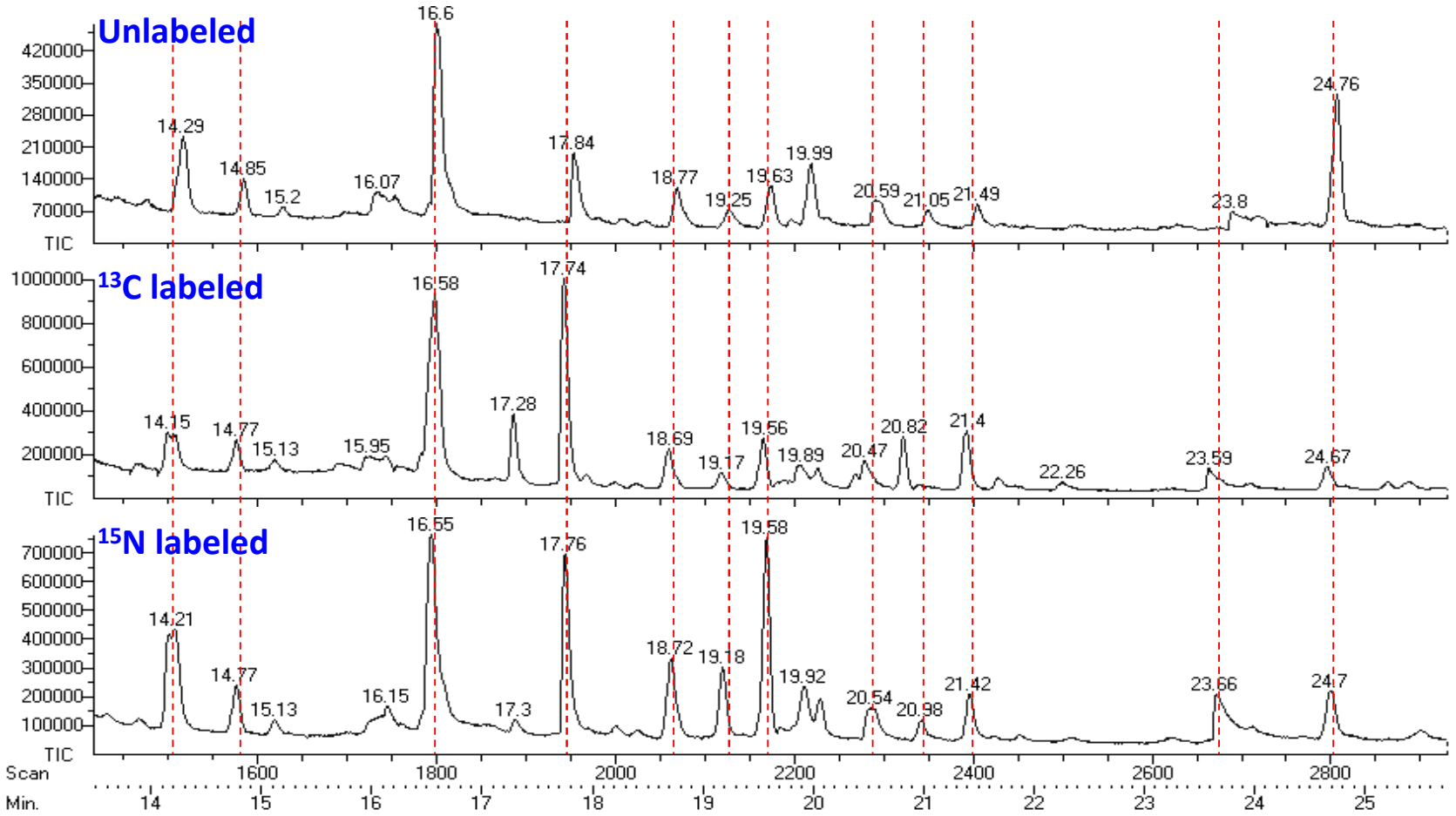
Monitor mass spectra for shifts



Use mass shifts to determine degradation mechanisms

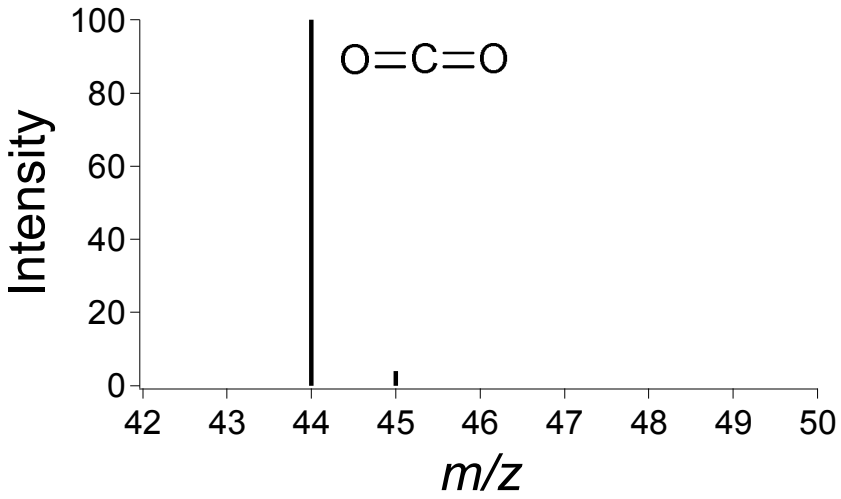


Selected region of TIC for the three nylons tested

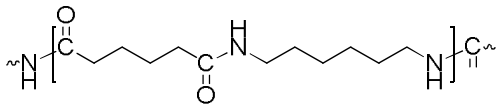


Nylon degradation follows similar mechanism for all variants.
Chromatograms show high reproducibility.

Example: Carbon Dioxide



A representative carbon dioxide mass spectrum from oxidation of unlabeled nylon 6.6



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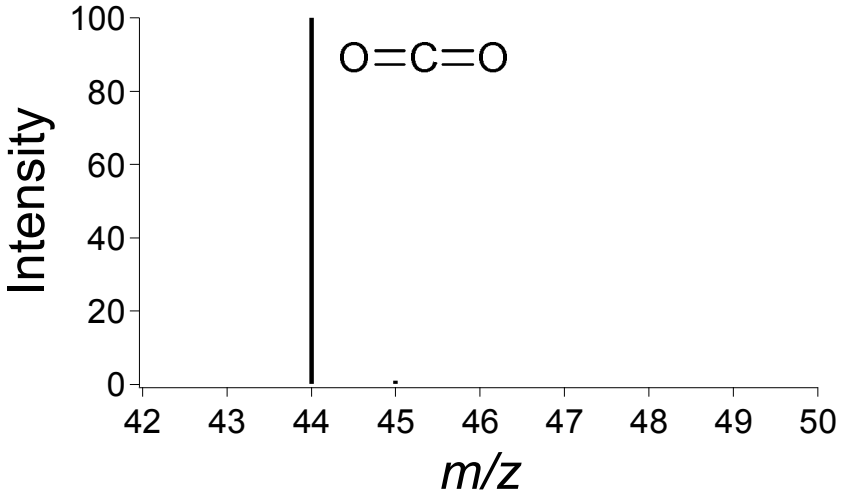
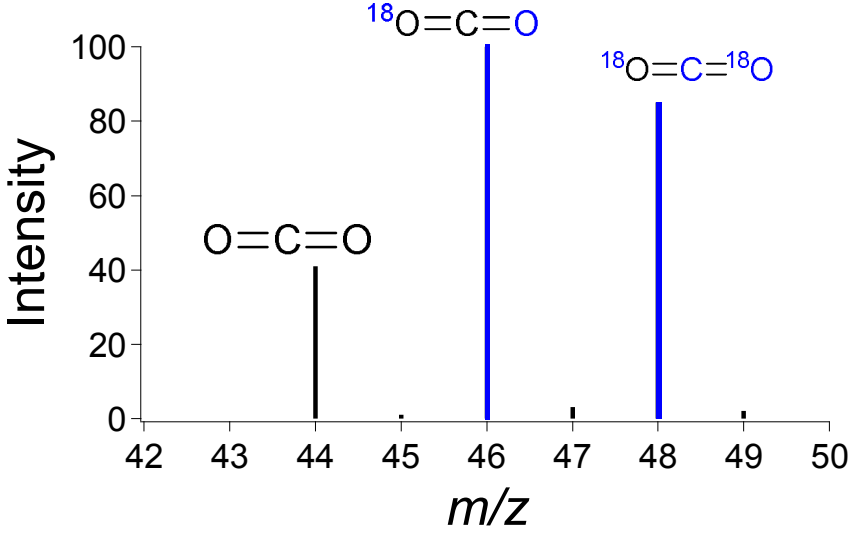
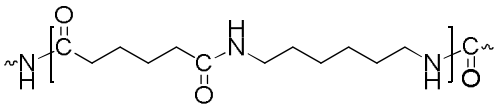


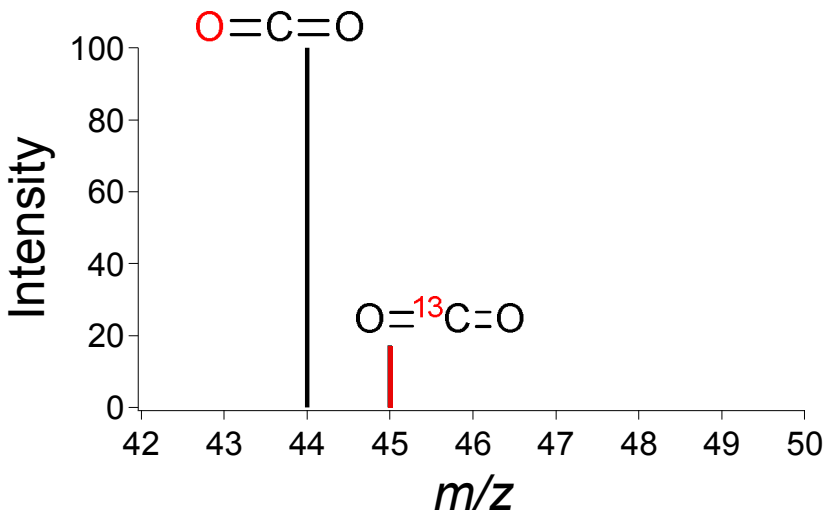
Mass spectrum of carbon dioxide from the NIST Spectral database

Example: Carbon Dioxide

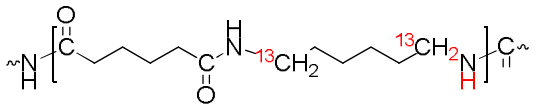


Carbon dioxide mass spectrum from oxidation of unlabeled nylon 6.6 in an ^{18}O enriched environment

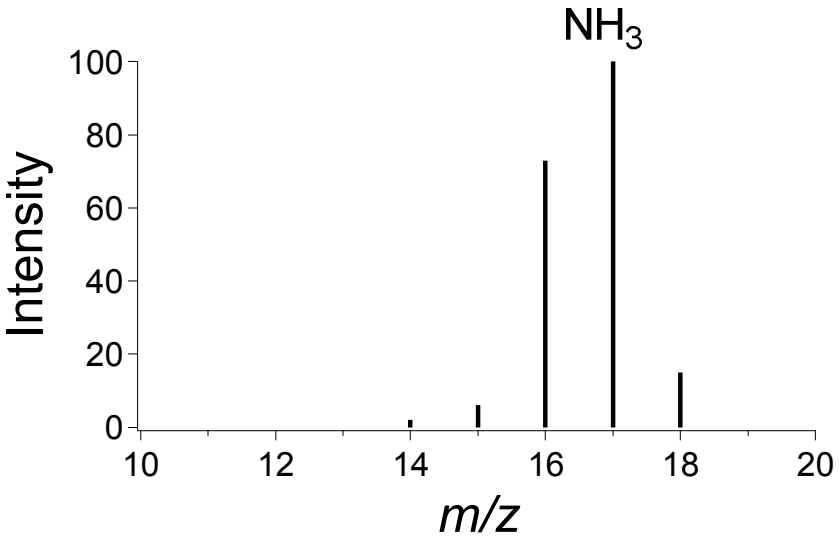




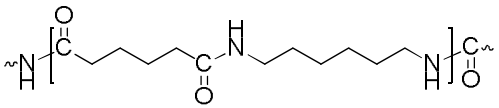
Carbon dioxide mass spectrum from oxidation of ^{13}C labeled nylon 6.6 in an oxygen environment

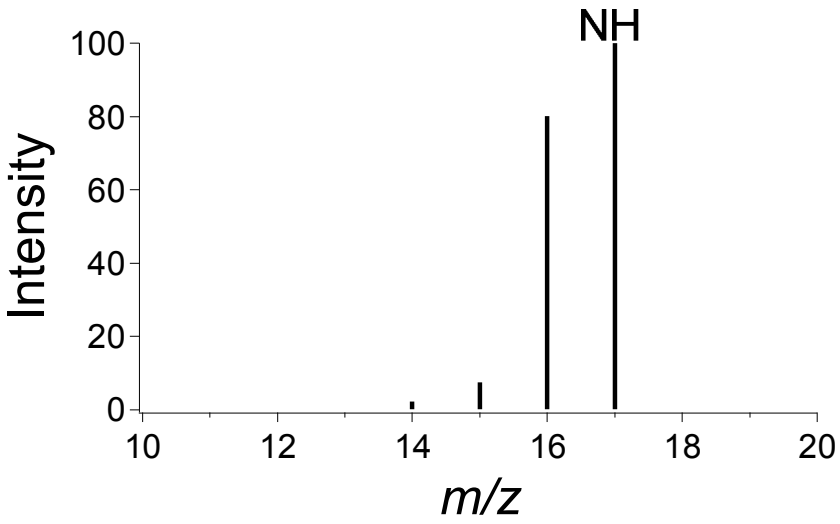


Example: Ammonia

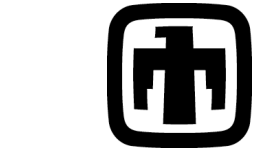


A representative ammonia mass spectrum from oxidation of unlabeled nylon 6.6

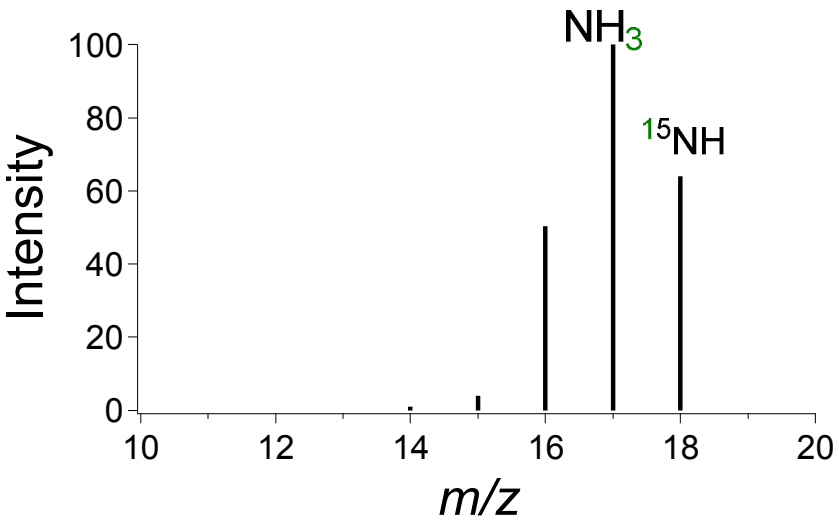




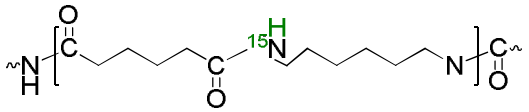
Mass spectrum of ammonia from the NIST Spectral database



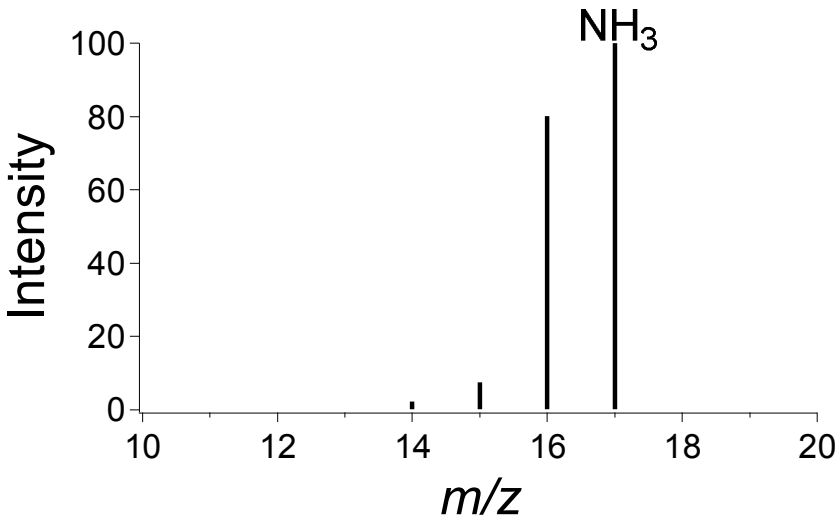
Example: Ammonia



A representative ammonia mass spectrum from oxidation of ^{15}N labeled nylon 6.6



Isotopically labeled nylon 6.6 was 51.4% min atom ^{15}N per the manufacturer's quality assurance



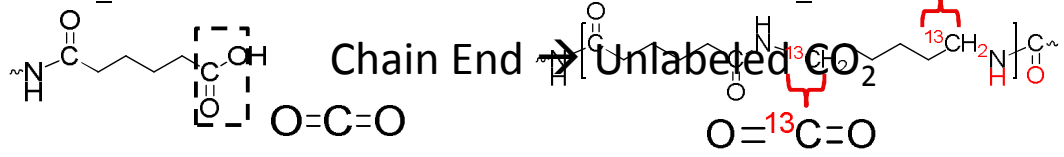
Mass spectrum of ammonia from the NIST Spectral database

Quantitative Analysis of CO_2 Formation

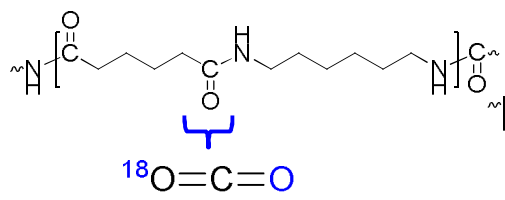
m/z	Assignment	Relative MS Intensity (%)	Functional Group
44	$CO_2^{+\bullet}$	17.6 ± 0.5	Chain End
46	$CO^{18}O^{+\bullet}$	42.3 ± 2.7	Amide Carbonyl
48	$C^{18}O^{18}O^{+\bullet}$	40.1 ± 3.3	Methylene

m/z	Assignment	Relative MS Intensity (%)	Functional Group
44	$CO_2^{+\bullet}$	85.4 ± 0.2	Methylene
45	$^{13}CO_2^{+\bullet}$	14.6 ± 0.2	*N*-Vicinal Methylene

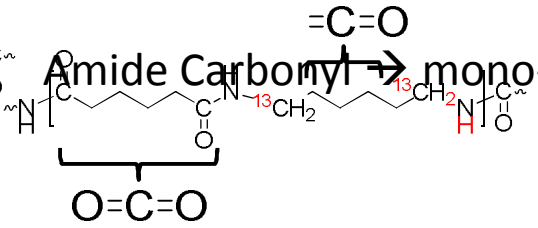
CO_2 Products formed when aged in $^{18}O_2$



Chain End → Unlabeled CO_2

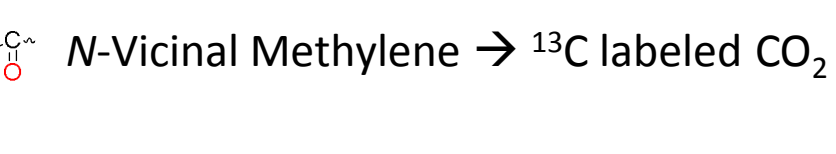


Amide Carbonyl → mono-labeled CO_2



Methylene → Unlabeled CO_2

CO_2 Products formed when aged in air

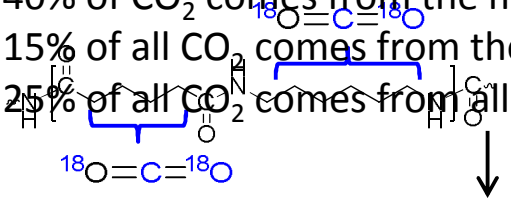


N-Vicinal Methylene → ^{13}C labeled CO_2

40% of CO_2 comes from the methylene groups

15% of all CO_2 comes from the *N*-Vicinal methylene groups

25% of all CO_2 comes from all other methylene groups

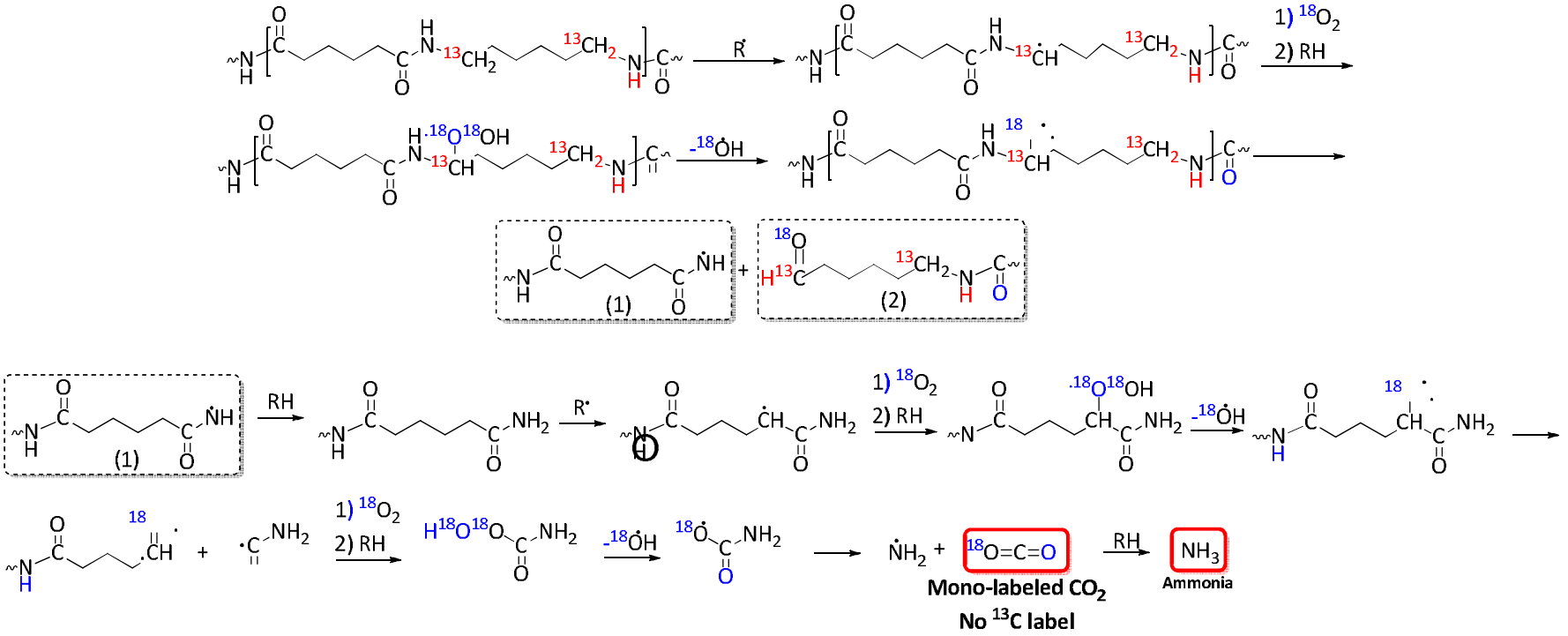


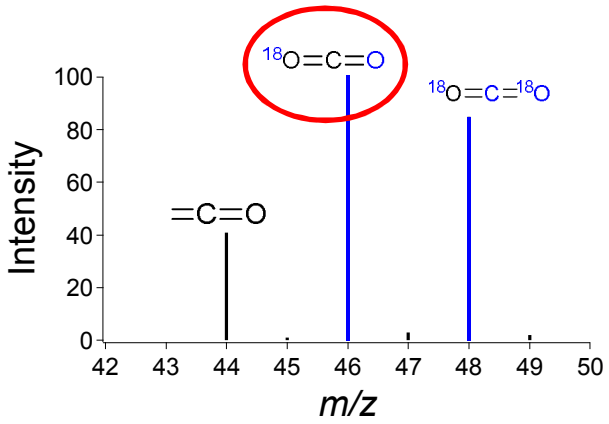
Methylene → di-labeled CO_2

N-Vicinal methylene groups contribute 38% of CO_2 formed from the methylene groups

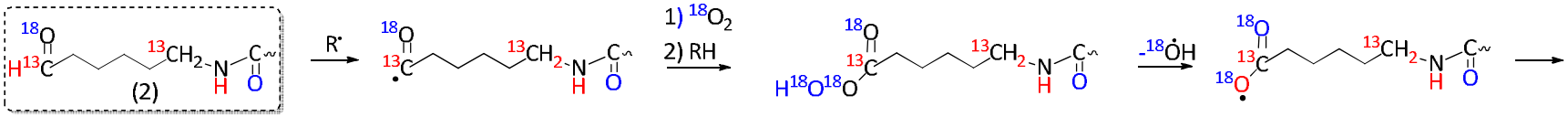
The other four types of methylene groups contribute 16% each to the CO_2 formed from the methylene groups. The most labile hydrogen in the nylon backbone is therefore in the *N*-Vicinal methylene group.

Proposed Origins of CO_2 and NH_3



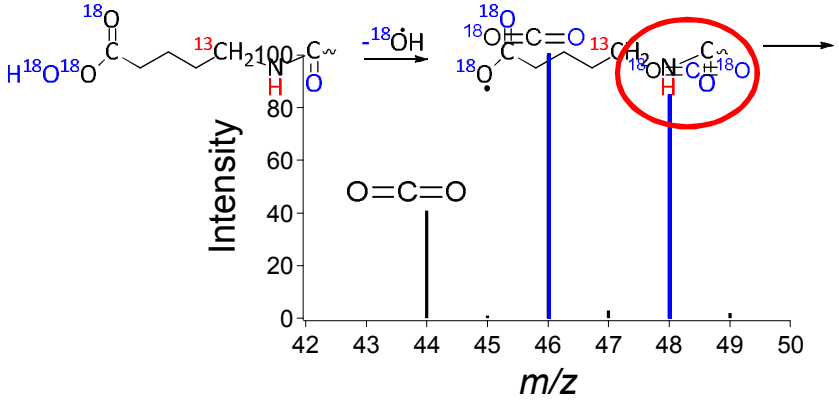


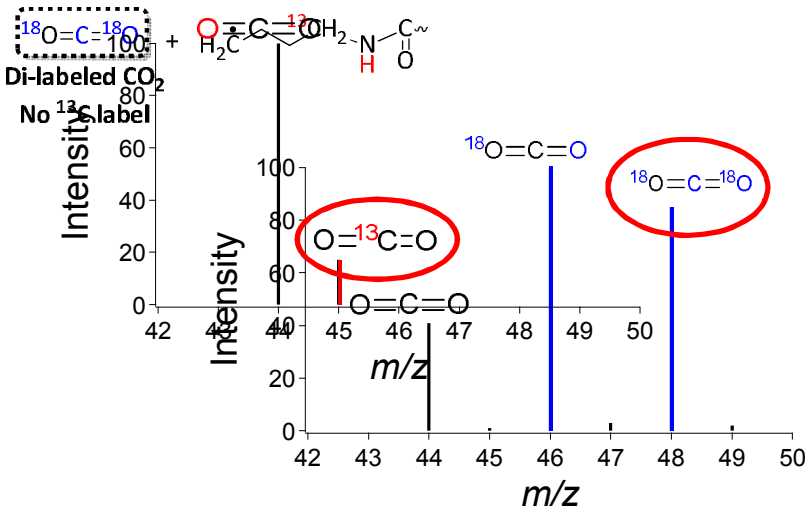
Proposed Origins of CO_2



$^{18}O{=}^{13}C{=}^{18}O$

^{18}O di-labeled or ^{13}C labeled CO_2





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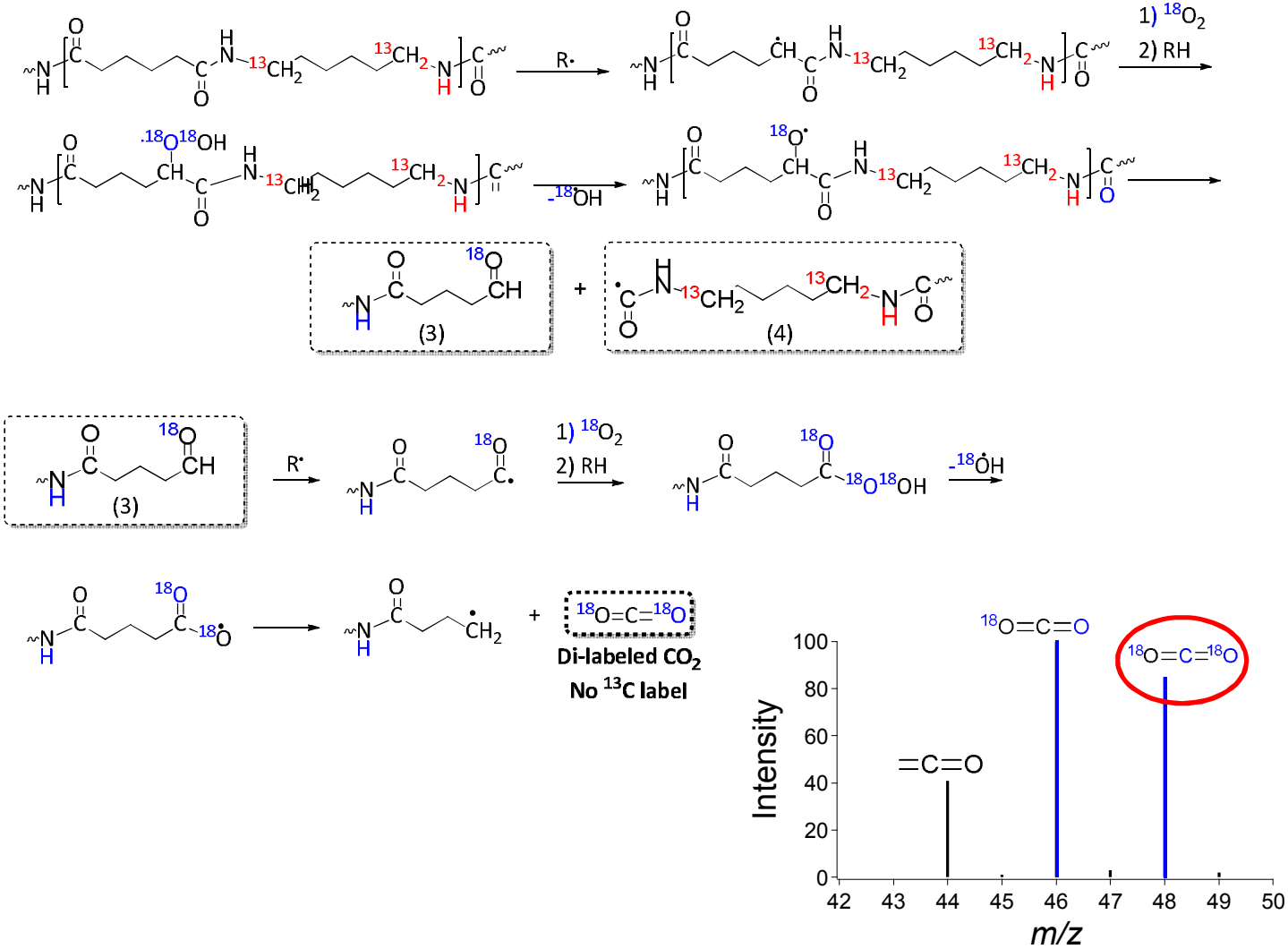
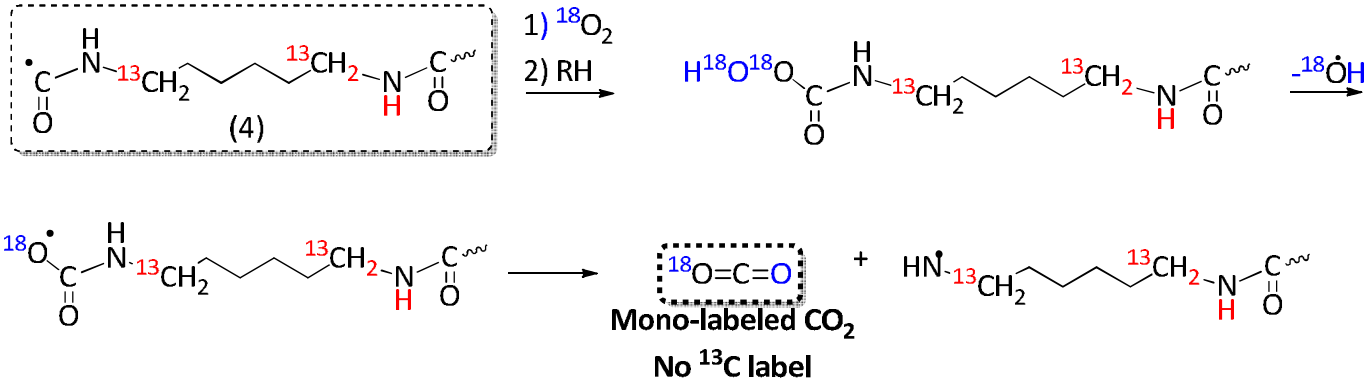
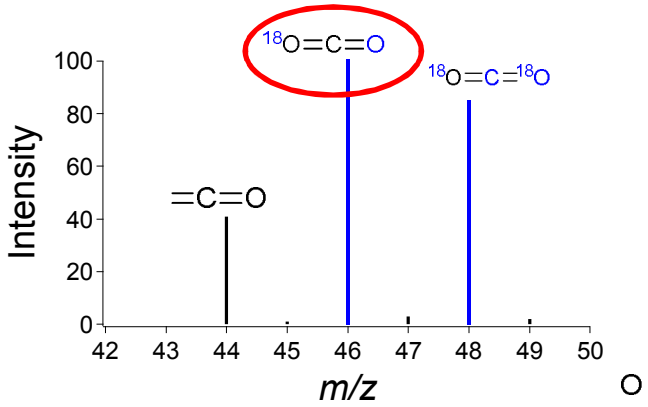
Proposed Origins of CO_2

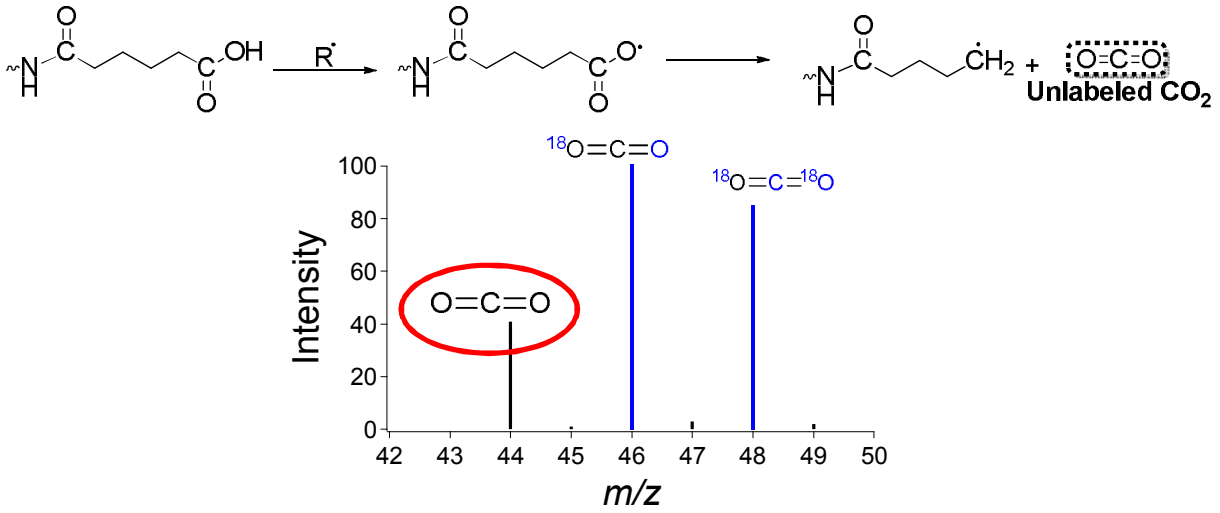


Proposed Origins of CO_2



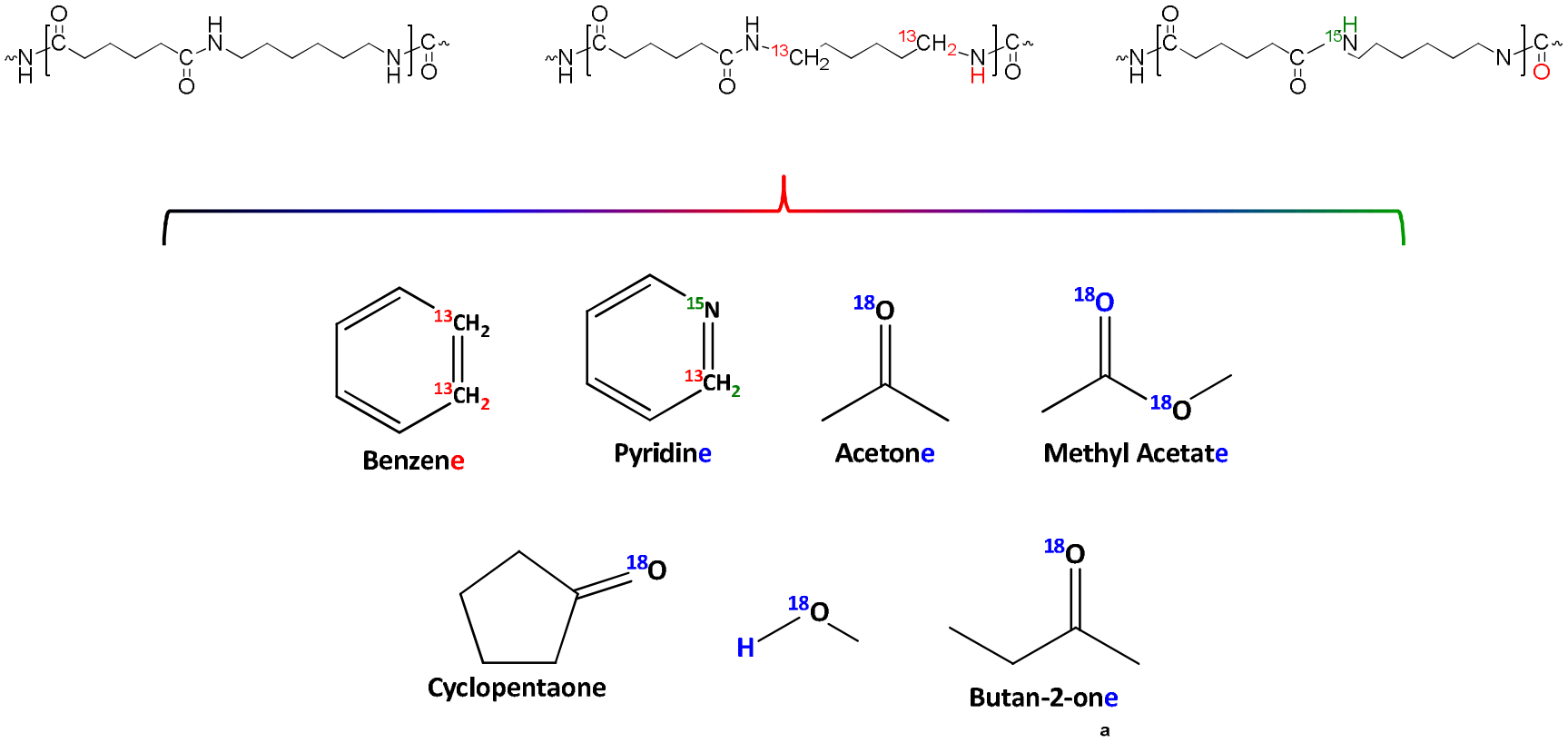


Proposed Origins of CO_2 and NH_3



We observed NH_3 and $^{15}NH_3$ in aging experiments that employed ^{15}N labeled nylon 6.6 with relative mass spectral contributions of 46 ± 13 and 54 ± 12%, respectively. This is consistent with TOF-SIMS analysis of the neat ^{15}N labeled polymer (51.6% min atom ^{15}N) and the manufacturer's quality analysis (51.4% min atom ^{15}N).

Other Key Labeled Species Identified

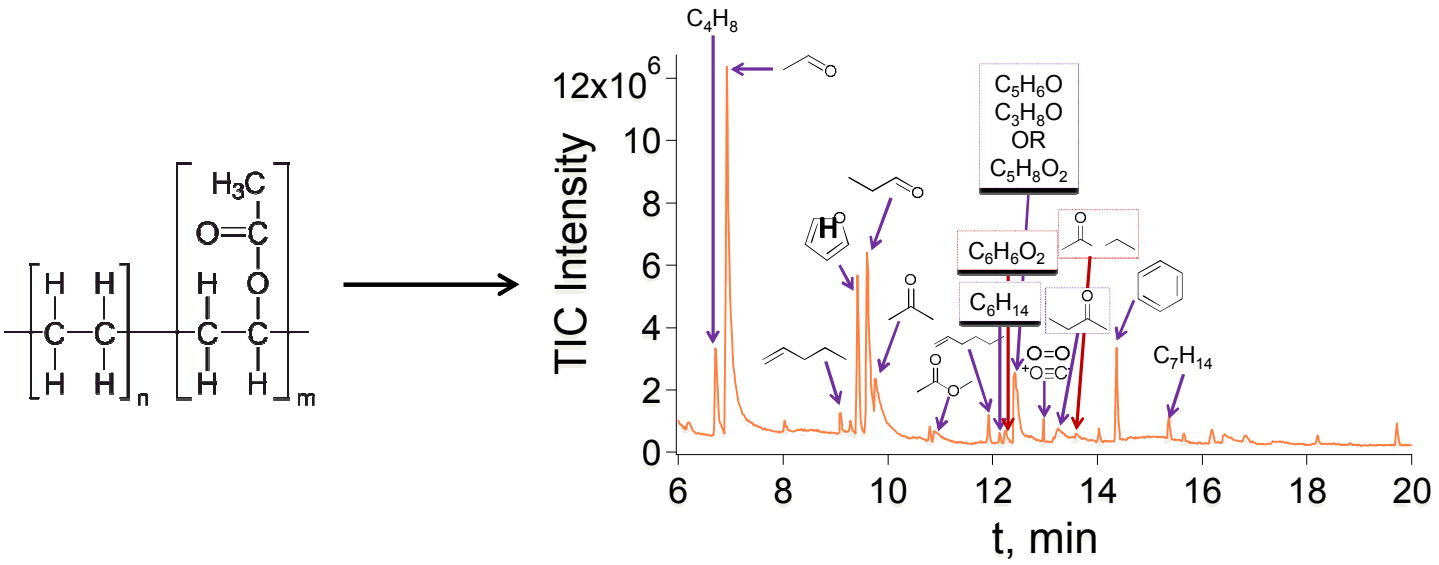


Conclusions

- By leveraging cryo-GC/MS in conjunction with isotopically labeled air, we have demonstrated the novel ability to discriminate between oxygen originating from the polymer backbone and oxygen from the environment.
- Experiments employing isotopically labeled and unlabeled nylon afforded the opportunity to propose the underlying formation mechanisms of carbon dioxide and ammonia
- We have identified and are proposing degradation mechanisms for other low molecular weight thermal-oxidative and hydrolytic degradation products

Future Work

- Complete the investigation of the hydrolytic degradation mechanisms of nylon 6.6
- Initiate the thermal-oxidative degradation of poly(ethylene co-vinyl acetate), EVA



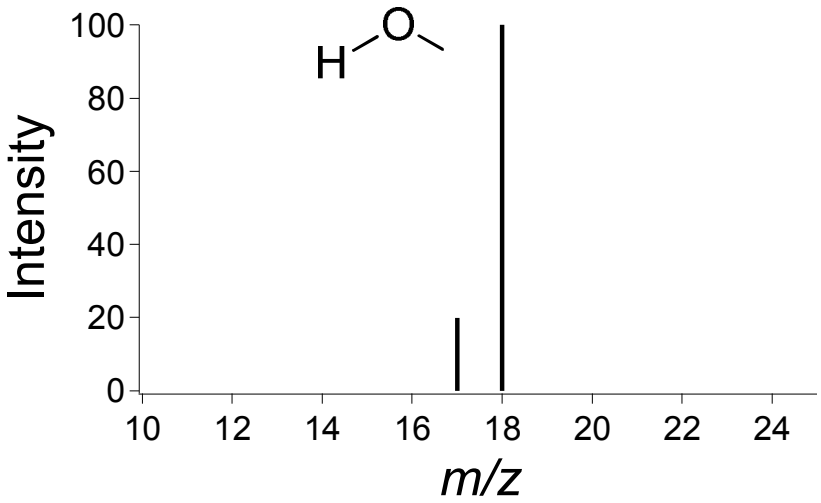
Acknowledgements

- Sandia National Laboratories
- Department of Energy
- Donald Bradley

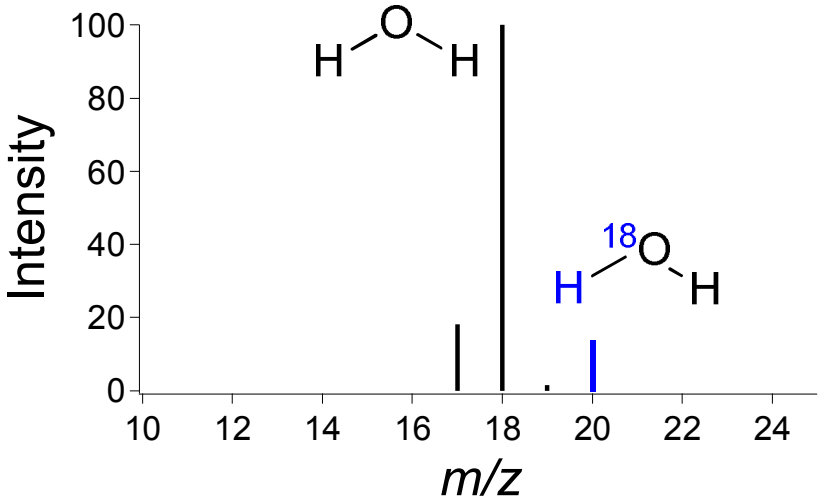
QUESTIONS?

Backup Slides

Example: Water

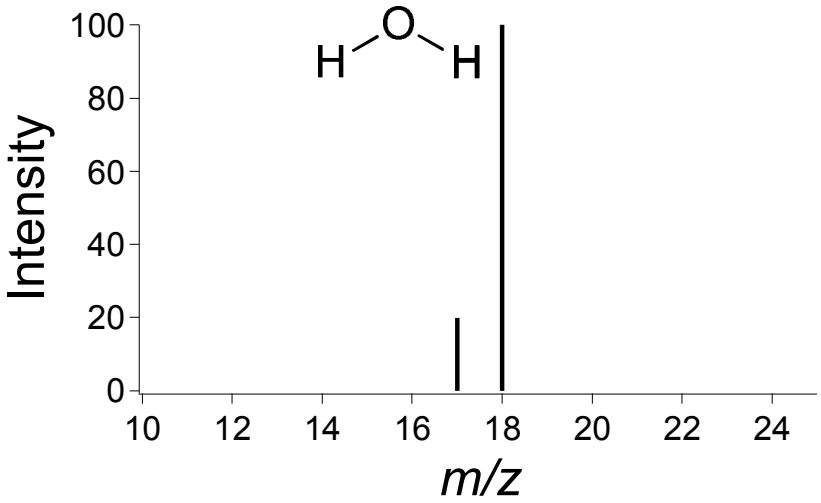


Mass spectrum of ammonia from the NIST Spectral database

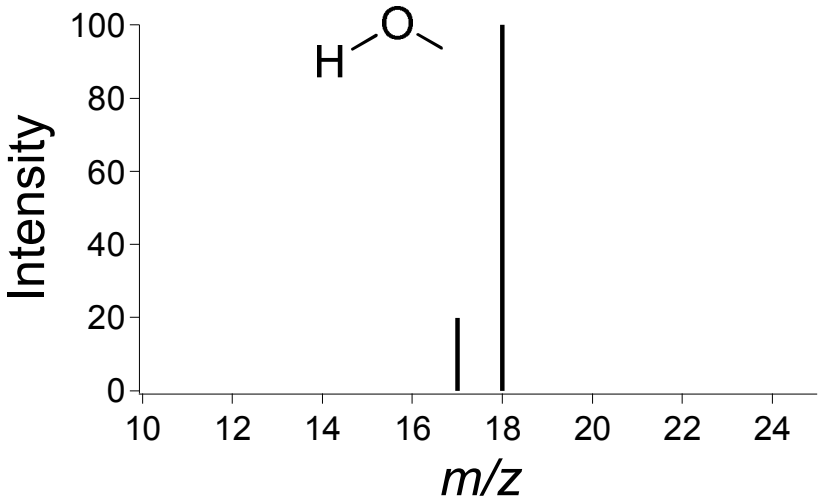


Water mass spectrum from oxidation of unlabeled nylon 6.6 in an ^{18}O enriched environment

Example: Water



A representative water mass spectrum from oxidation of unlabeled nylon 6.6



Mass spectrum of water from the NIST Spectral database

Polymer Aging

- Polymers used for essentially every application in today's society (automotive, medical, food, defense, clothing, etc…)
- Thermal degradation for many materials has been actively pursued using techniques such as pyrolysis and TGA
  - Fast/inexpensive
  - Provides information about thermal degradation products
  - Mechanisms altered; not good representation of real world (low temp long times)
- Detailed oxidative degradation mechanisms and products that are formed are not as well understood for many polymers
  - Aging dependent and time dependent
  - Formulation dependent (fillers, additives, antioxidants, lubricants, etc.)
- Isotopic labeling of polymers can reveal detailed mechanistic information about oxidative degradation to gain insights into realistic lifetimes of materials
- Understanding degradation mechanisms is the gateway for sensor development to identify unique volatile degradation products for condition monitoring
  - Early warning system
  - Establish real-time status update

Polypropylene published and 'done'

(1) Mowery, D. M.; Assink, R. A.; Derzon, D. K.; Klamo, S. B.; Bernstein, R.; Clough, R. L. *Radiation Physics and Chemistry,* Radiation Oxidation of Polypropylene: A Solid-State 13C NMR Study using Selective Isotopic Labeling **2007**, *76*, 864-878.

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

(3) Mowery, D. M.; Clough, R. L.; Assink, R. A. *Macromolecules,* Identification of Oxidation Products in Selectively Labeled Polypropylene with Solid-State 13C NMR Techniques **2007**, *40*, 3615-3623.

(4) Thornberg, S. M.; Bernstein, R.; Derzon, D. K.; Irwin, A. N.; Klamo, S. B.; Clough, R. L. *Polymer Degradation and Stability,* The Genesis of CO2 and CO in the Thermooxidative Degradation of Polypropylene **2007**, *92*, 94-102.

(5) 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.

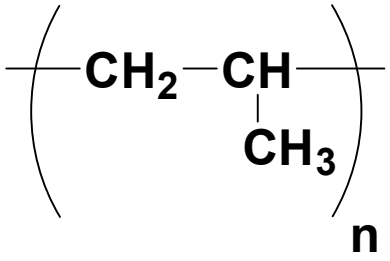
(6) Bernstein, R.; Thornberg, S. M.; Assink, R. A.; Irwin, A. N.; Hochrein, J. M.; Brown, J. R.; Derzon, D. K.; Klamo, S. B.; Clough, R. L. *Polymer Degradation and Stability,* The origins of volatile oxidation products in the thermal degradation of polypropylene, identified by selective isotopic labeling **2007**, *92*, 2076-2094.

(7) Bernstein, R.; Thornberg, S. M.; Assink, R. A.; Mowery, D. M.; Alam, M. K.; Irwin, A. N.; Hochrein, J. M.; Derzon, D. K.; Klamo, S. B.; Clough, R. L. *Nuclear Instruments and Methods in Physics Research B,* Insights into Oxidation Mechanisms in Gamma-Irradiated Polypropylene, Utilizing Selective Isotopic Labeling with Analysis by GC/MS, NMR and FTIR **2007**, 265 (1), 8-17.

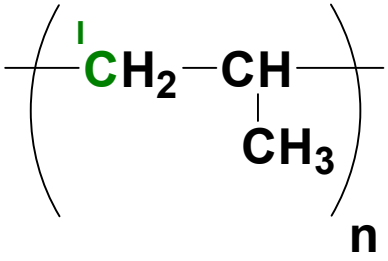
(8) Bernstein, R.; Thornberg, S. M.; Irwin, A. N.; Hochrein, J. M.; Derzon, D. K.; Klamo, S. B.; Clough, R. L. *Polymer Degradation and Stability,* Radiation-oxidation mechanisms: Volatile organic degradation products from polypropylene having selective C-13 labeling, studied by GC/MS **2008**, *93*, 854-870.

Labeled Polypropylene

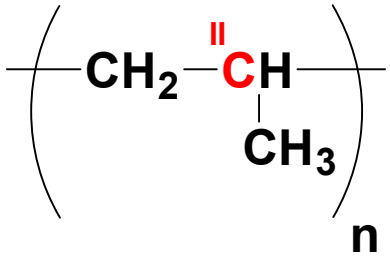
Purchased from Isotec



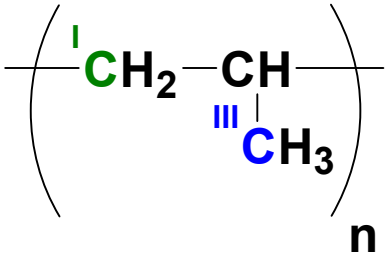
unlabeled



C(1)



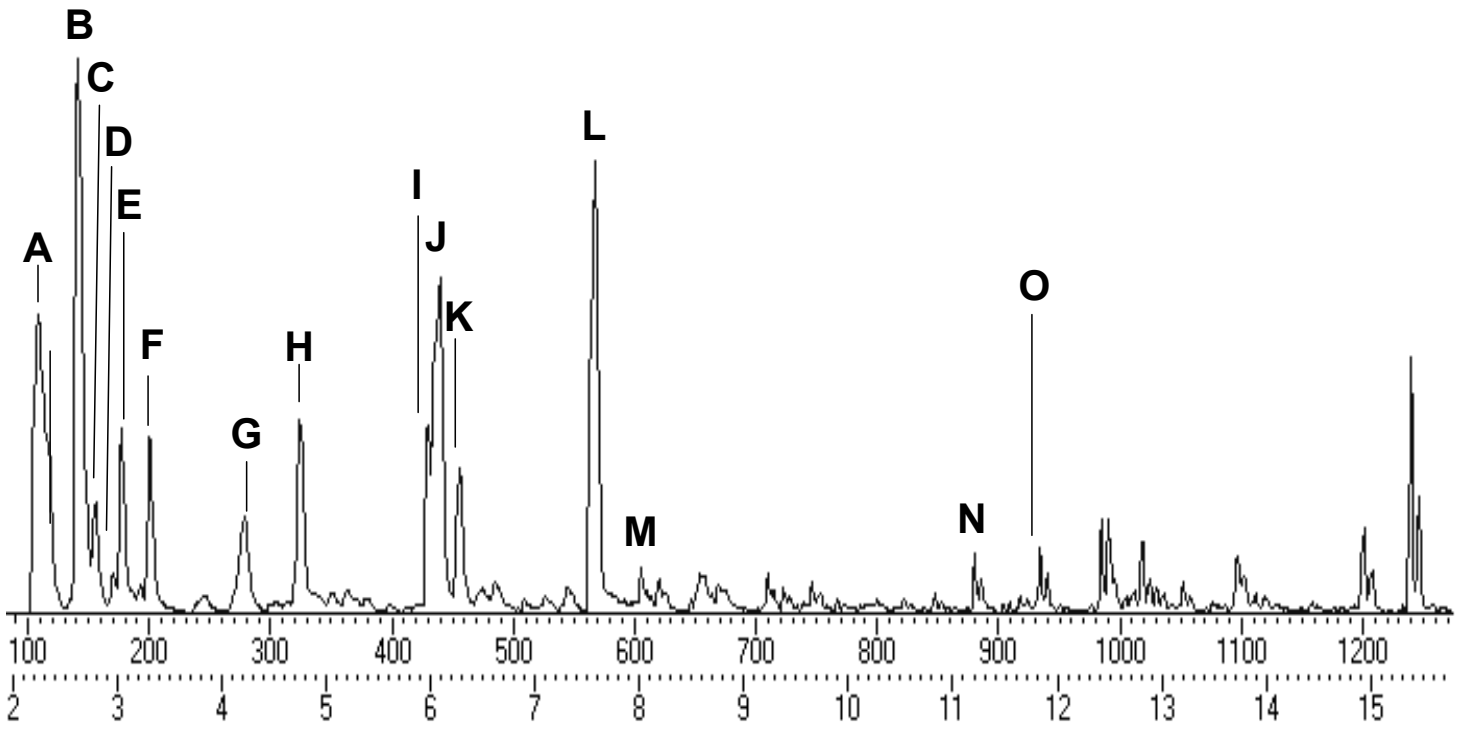
C(2)



C(1,3)

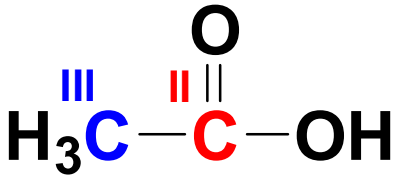
~68/31 mix

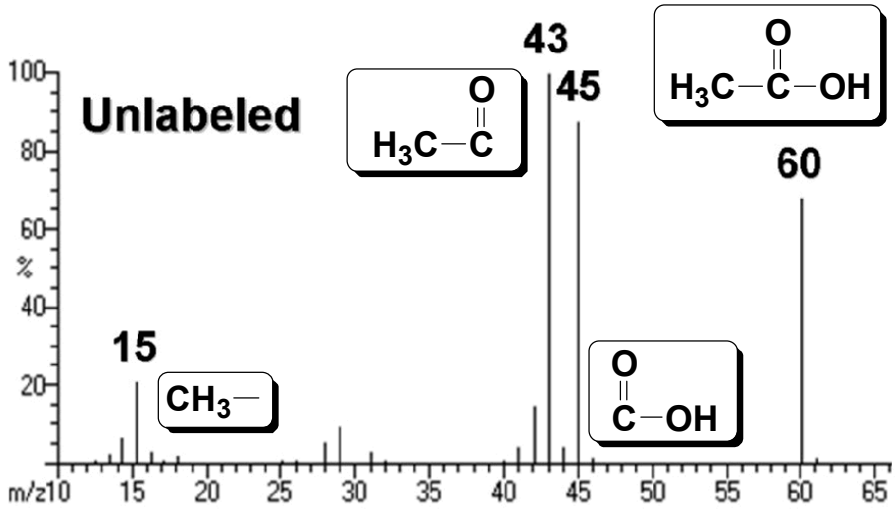
Example of Thermal-oxidation Products

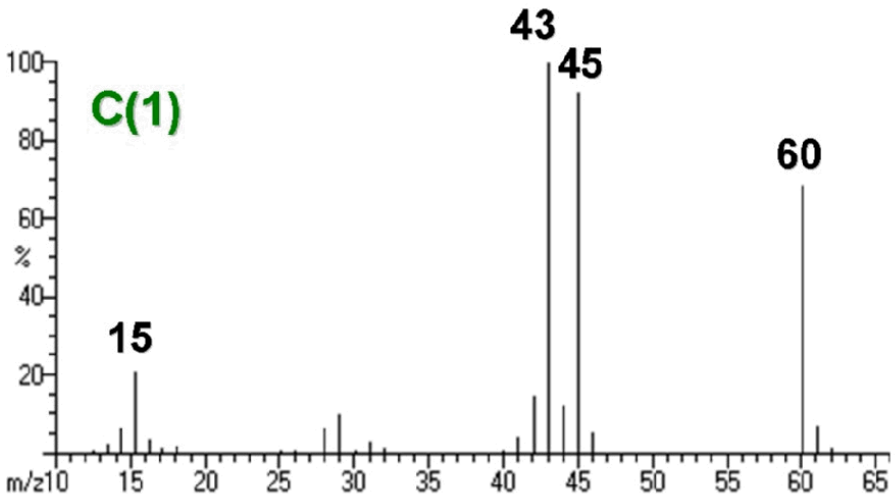


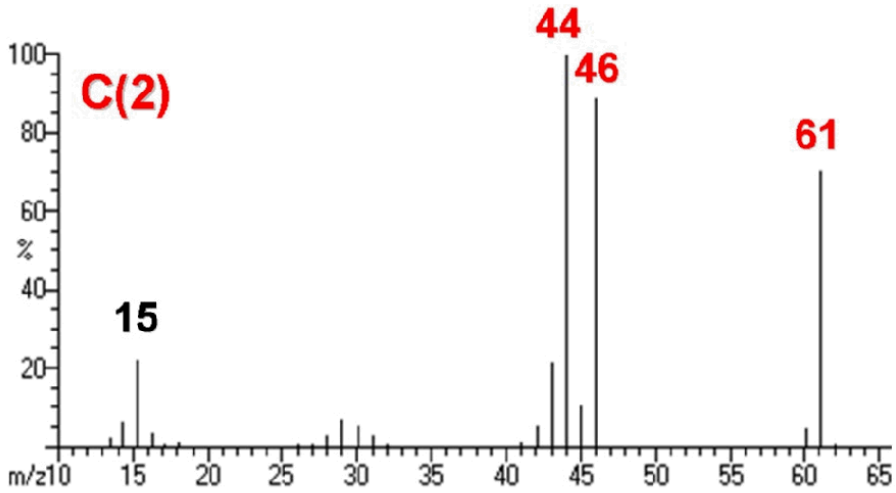
Peak	Chemical Structure
A	Carbon Dioxide
B	Acetone
C	Methyl acetate
D	2-methylpropanal
E	Methacrolein
F	2-Butanone
G	2-Methyl-2-propen-1-ol
H	2-Pentanone
I	Methyl-isobutyl ketone
J	3-Pentene-2-one
K	4-Methyl-4-pentene-2-one
L	4-Methyl-3-pentene-2-one
M	2,4,6-Trimetyl-1,3-dioxane
N	4-Methyl-2-heptanone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

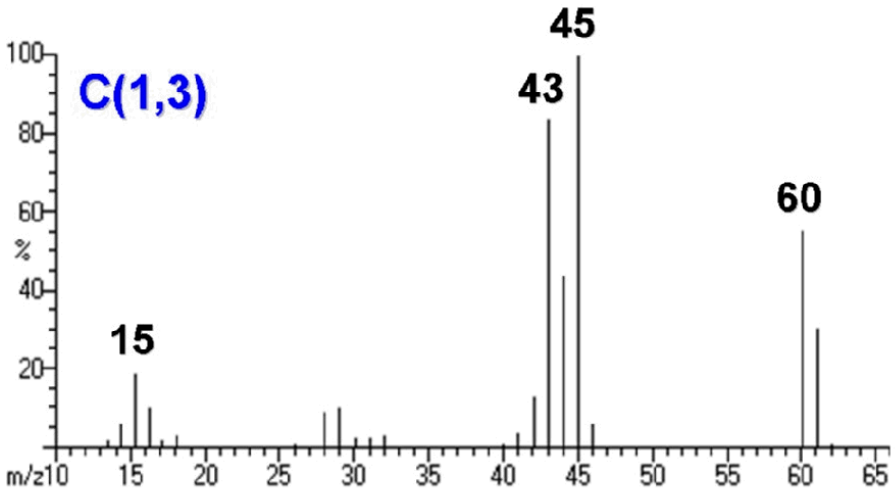
Acetic Acid





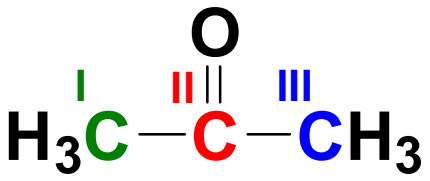


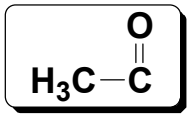


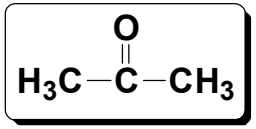


Bernstein et al. *Polym. Degrad. Stab.* **2007**, 92, 2076-2094.
Bernstein et al. *Nucl. Instr. Meth. B* **2007**, 265, 8-17.
Bernstein et al. *Polym. Degrad. Stab.* **2008**, 93, 854-870.

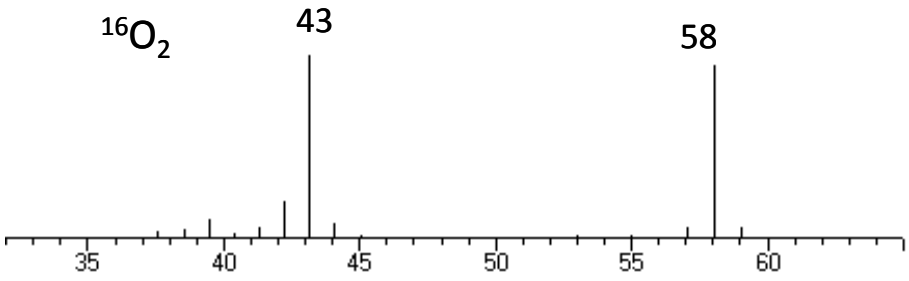
Acetone with $^{18}O_2$







Unlabeled
$^{16}O_2$



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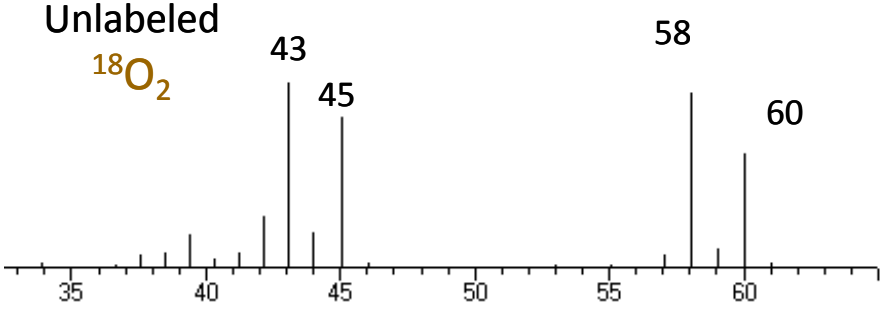
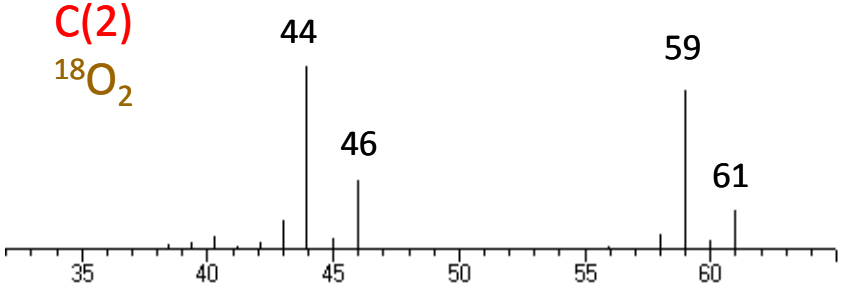
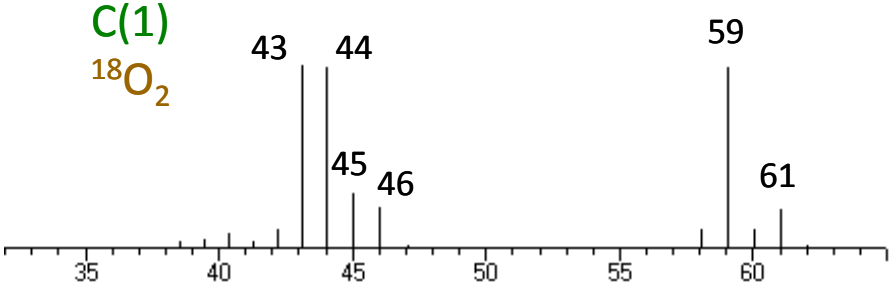


C(2)
$^{18}O_2$

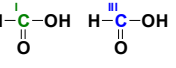
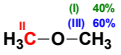
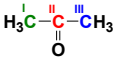
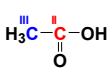
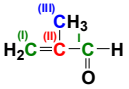
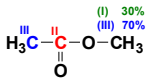
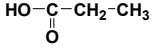
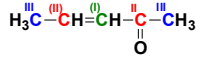
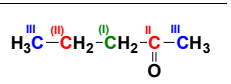
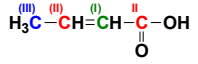
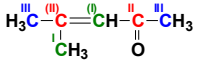
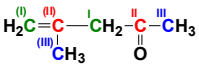
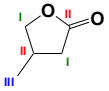
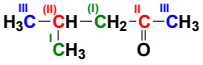
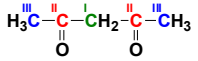
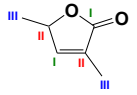
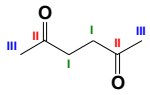
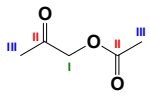
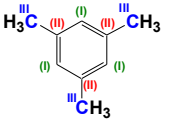
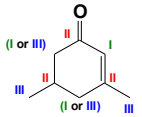


C(1)
$^{18}O_2$



Bernstein et al. *Polym. Degrad. Stab.* **2007**, 92, 2076-2094.
Bernstein et al. *Nucl. Instr. Meth. B* **2007**, 265, 8-17.
Bernstein et al. *Polym. Degrad. Stab.* **2008**, 93, 854-870.

Various Thermal-oxidative Degradation Products

#	MW	# Oxygen by O-18	Carbon Atom Composition from PP Structure	Structure
1	46	1	1 C(1) or 1 C(3)	
2	46	1	0 or 1 C(1) 1 C(2) 0 or 1 C(3)	
3	58	1	1 C(1) 1 C(2) 1 C(3)	
4	60	2	0 C(1) 1 C(2) 1 C(3)	
5	70	1	2 C(1) 1 C(2) 1 C(3)	
6	74	2	0 or 1 C(1) 1 C(2) 1 or 2 C(3)	
7	74	1	1 C(1) 1 C(2) 1 C(3)	
8	84	1	1 C(1) 2 C(2) 2 C(3)	
9	86	1	1 C(1) 2 C(2) 2 C(3)	
10	86	2	1 C(1) 2 C(2) 1 C(3)	 ±
11	98	1	2 C(1) 2 C(2) 2 C(3)	
12	98	1	2 C(1) 2 C(2) 2 C(3)	
13	100	2	2 C(1) 2 C(2) 1 C(3)	
14	100	1	2 C(1) 2 C(2) 2 C(3)	
15	100	2	1 C(1) 2 C(2) 2 C(3)	
16	112	2	2 C(1) 2 C(2) 2 C(3)	
17	114	2	2 C(1) 2 C(2) 2 C(3)	
18	116	3	1 C(1) 2 C(2) 2 C(3)	
19	120	0	3 C(1) 3 C(2) 3 C(3)	
20	124	1	2 C(1) 3 C(2) 3 C(3)	
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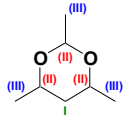
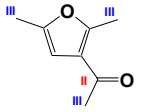
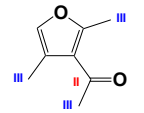
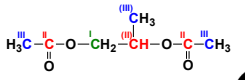
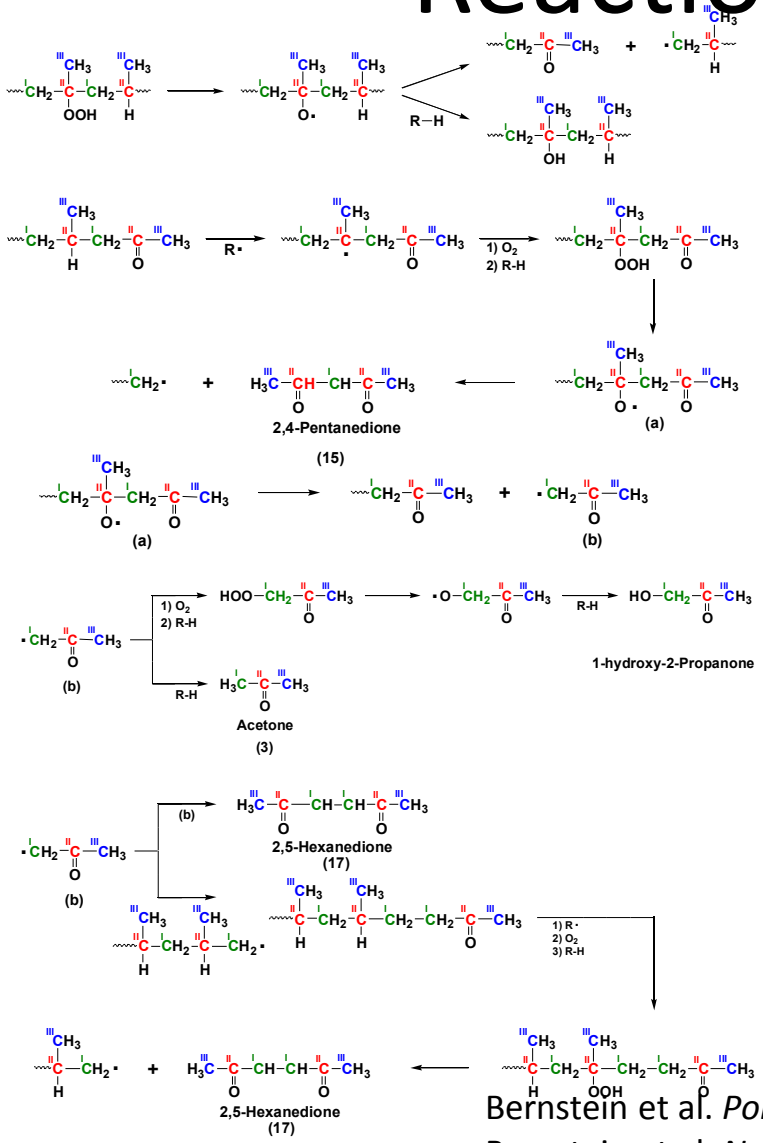
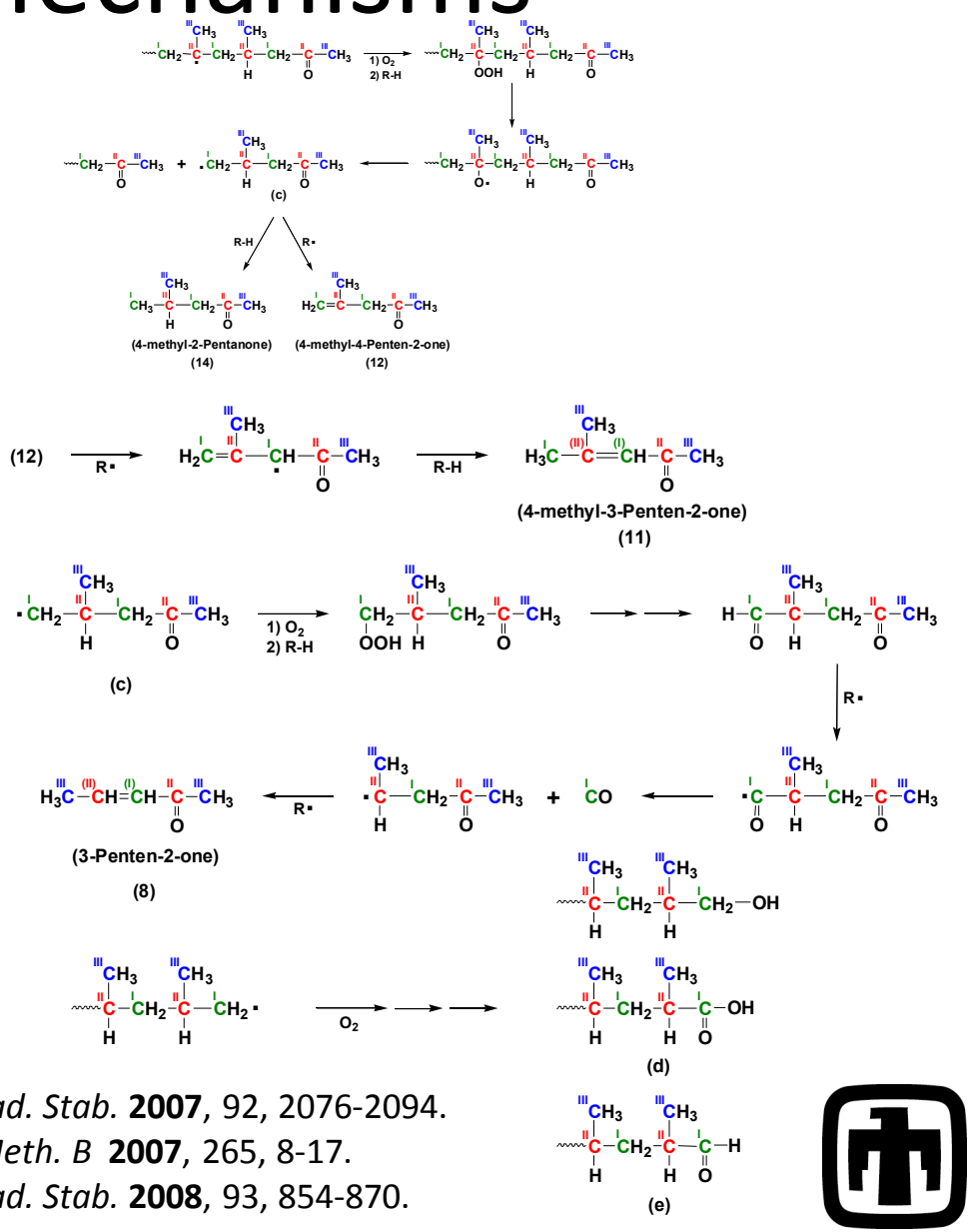
22	130	2	1 C(1) 3 C(2) 3 C(3)	
23	138	2	2 C(1) 3 C(2) 3 C(3)	
24	138	2	2 C(1) 3 C(2) 3 C(3)	
25	142	2	1 C(1) 3 C(2) 3 C(3)	
26	160	4	1 C(1) 3 C(2) 3 C(3)	

Bernstein et al. *Polym. Degrad. Stab.* **2007**, 92, 2076-2094.
Bernstein et al. *Nucl. Instr. Meth. B* **2007**, 265, 8-17.
Bernstein et al. *Polym. Degrad. Stab.* **2008**, 93, 854-870.

Reaction Mechanisms



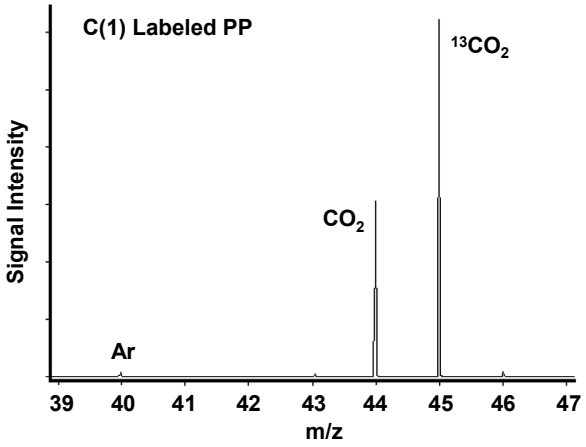


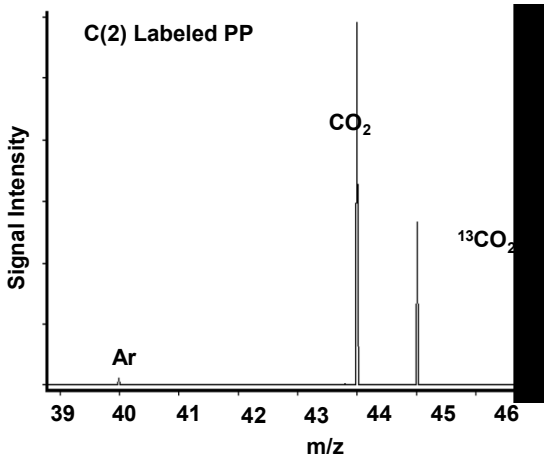
Bernstein et al. *Polym. Degrad. Stab.* **2007**, 92, 2076-2094.

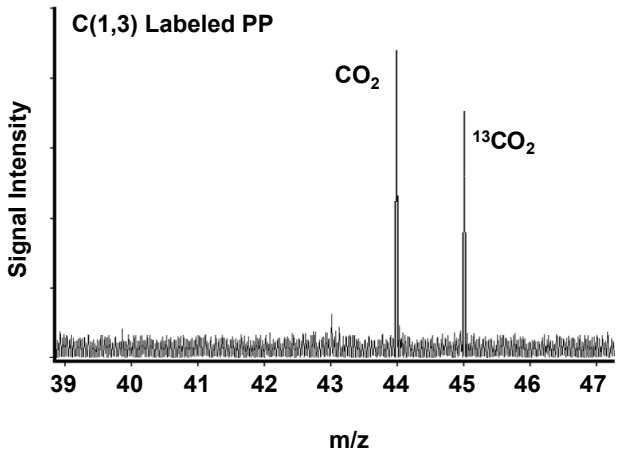
Bernstein et al. *Nucl. Instr. Meth. B* **2007**, 265, 8-17.

Bernstein et al. *Polym. Degrad. Stab.* **2008**, 93, 854-870.

CO_2 Studies



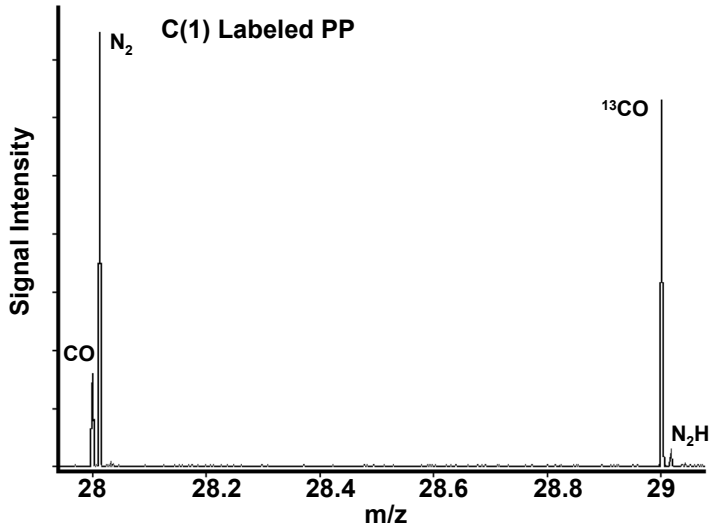


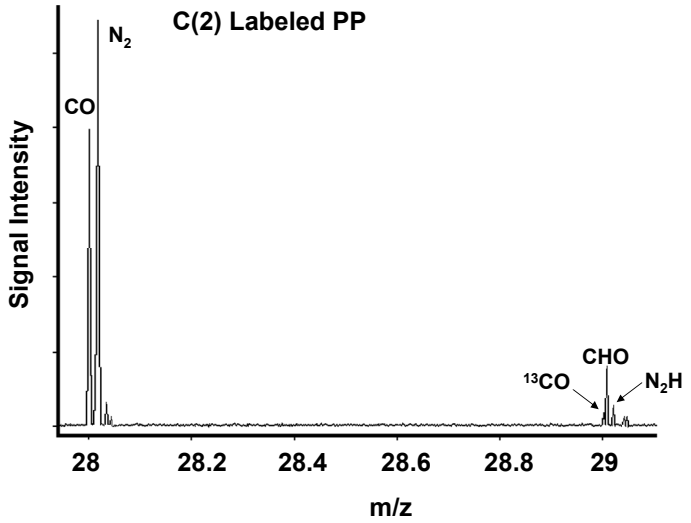


Carbon atom within the polymer	% CO_2 from this position
C(1) [methylene]	66% [± 5%]
C(2) [tertiary]	33% [± 5%]
C(3) [methyl group]	0% [< 5%]

Thornberg, S. M.; Bernstein, R.; Derzon, D. K.; Irwin, A. N.; Klamo, S. B.; Clough, R. L. *Polymer Degradation and Stability,* The Genesis of CO2 and CO in the Thermooxidative Degradation of Polypropylene Polymer Degradation and Stability, in press.

CO Studies

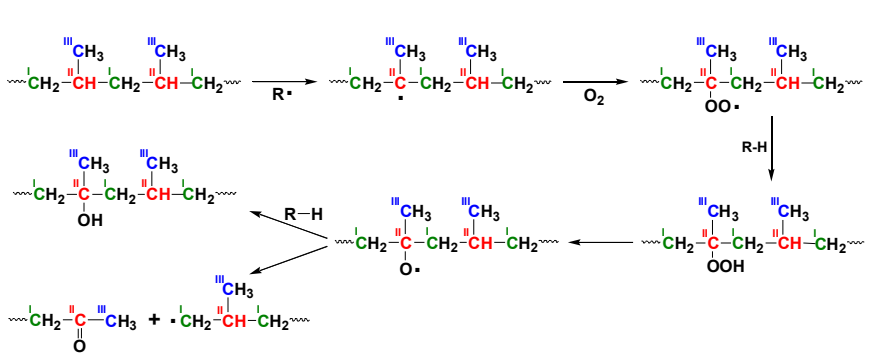


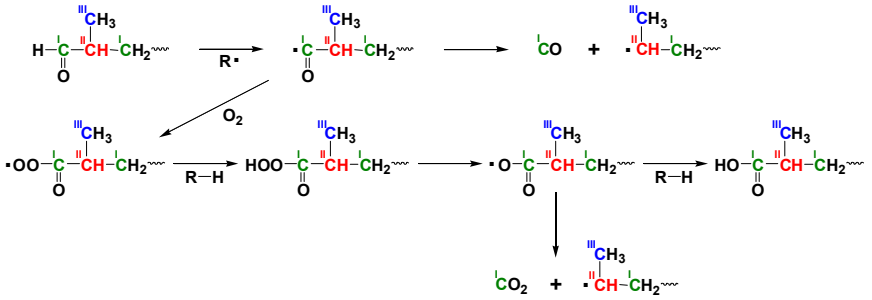


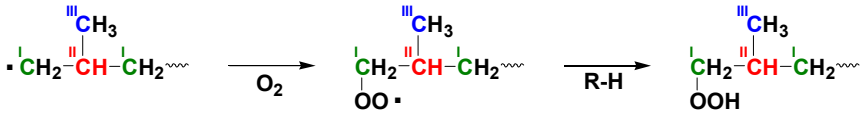
Carbon atom within the polymer	% CO from this position
C(1) [methylene]	≥80% [± 10%]
C(2) [tertiary]	≤5% [± 10%]
C(3) [methyl group]	Not determined

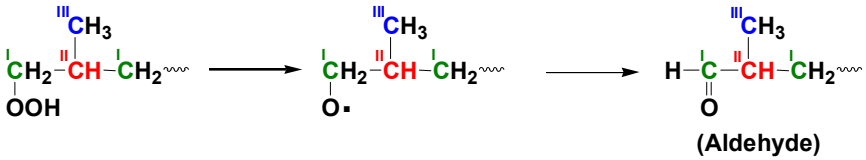
Thornberg, S. M.; Bernstein, R.; Derzon, D. K.; Irwin, A. N.; Klamo, S. B.; Clough, R. L. *Polymer Degradation and Stability,* The Genesis of CO2 and CO in the Thermooxidative Degradation of Polypropylene Polymer Degradation and Stability, in press.

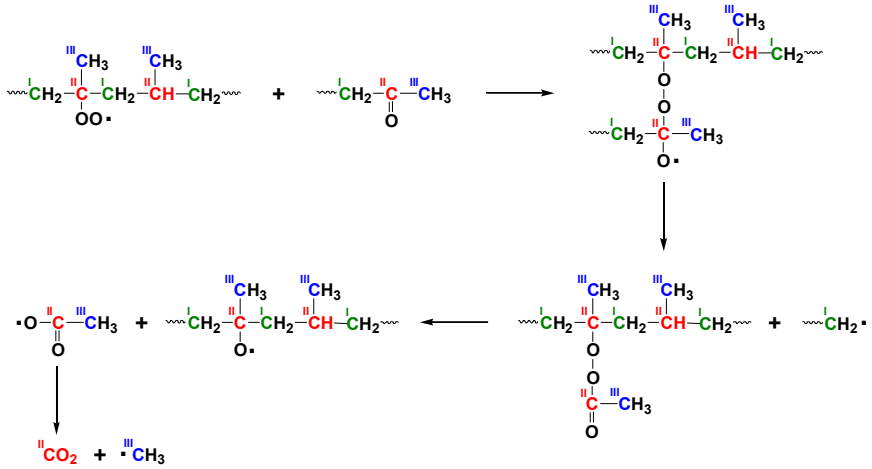
CO and CO_2 Mechanisms











Thornberg, S. M.; Bernstein, R.; Derzon, D. K.; Irwin, A. N.; Klamo, S. B.; Clough, R. L. *Polymer Degradation and Stability,* The Genesis of CO2 and CO in the Thermooxidative Degradation of Polypropylene Polymer Degradation and Stability, in press.

Previous and Future Work

- Methodology for detailed tracking of (complex) polymer chemistry
- Polymer samples were prepared with selective isotopic labeling. Previous work employed ^{13}C labeled polypropylene, current work uses ^{13}C and ^{15}N labeled Nylon.
- Analysis by NMR (solid state products), and by GC/MS (volatile products)
- Allows “mapping” of products onto positions of origin from original polymer

Nylon Degradation

”Despite the high level of activity and the large number of publications in this field, there is no generally mechanism for the thermal decomposition of aliphatic nylons.”

“However, there is no agreement in the literature as to which bond in the polymer chain predominantly undergoes scission at low or moderate temperatures.”

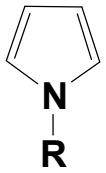
Levchik, S. V.; Weil, E. D.; Lewin, M. Polym Int, Thermal Decomposition of Aliphatic Nylons 1999, 48, 532-557.

“A considerable amount of work has already been carried out to investigate the mechanism of nylon degradation but the exact mechanism of the degradation has still not been conclusively established.”

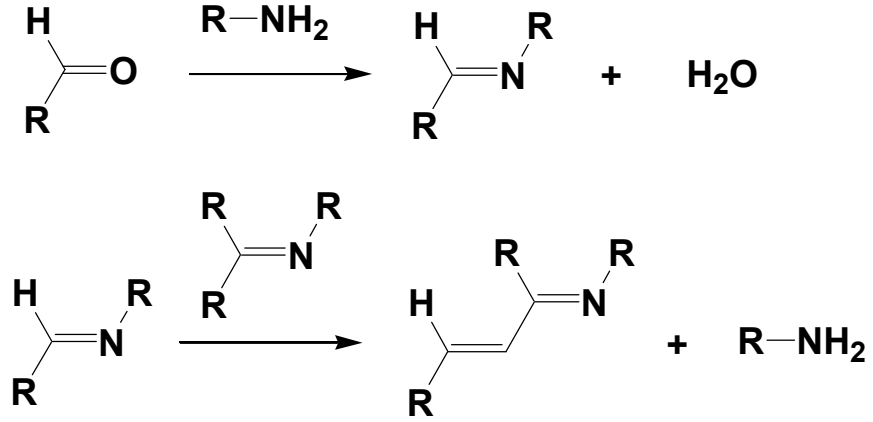
Shamey, R.; Sinha, K. In *Review of Progress in Coloration and Related Topics* A review of degradation of nylon 6.6 as a result of exposure to environmental conditions, 2003; Vol. 33, pp 93-107.

Nylon Yellow color

Source of chromophore in Nylon uncertain

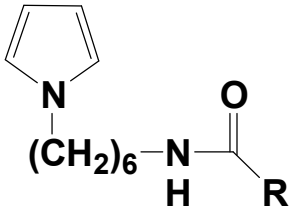


Pyrroles



Azomethines

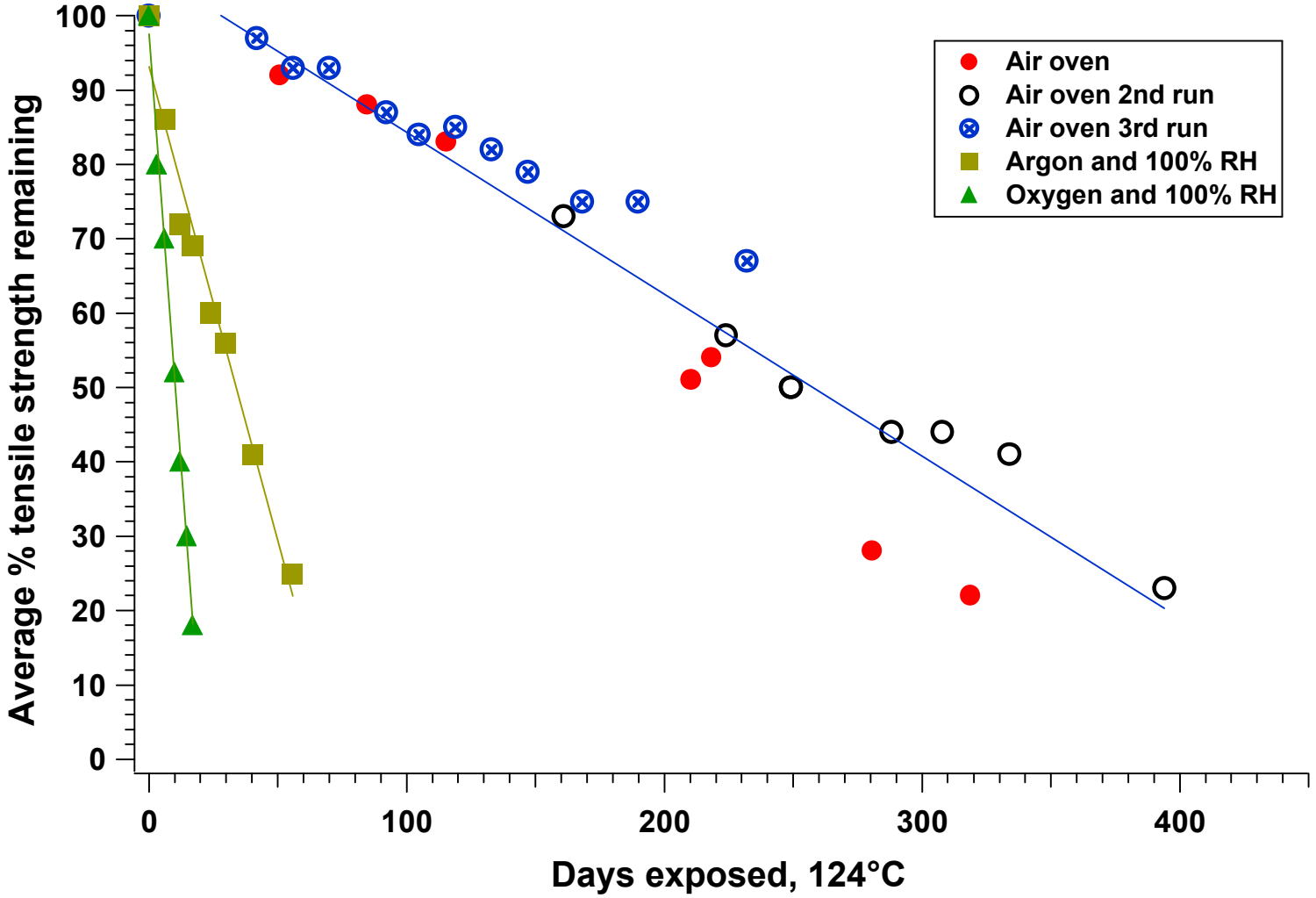
oligoeneamines



Allegedly ruled out by one group (George)

Holland, B. J.; Hay, J. N. *Polym. Int.,* Thermal degradation of nylon polymers 2000, *49*, 943-948.
Levchik, S. V.; Weil, E. D.; Lewin, M. *Polym Int,* Thermal Decomposition of Aliphatic Nylons 1999, *48*, 532-557.
Thanki, P. N.; Singh, R. P. *J Macromol Sci-Rev Macromol,* Progress in the area of degradation and stabilization of nylon 66 1998, *C38*, 595-614.
Karstens, T.; Rossbach, V. *Makromol. Chem.,* Thermo-oxidative Degradation of Polyamide 6 and 6.6 Kintetics of the Formation and Inhibition of UV/VIS-Active Chromophores 1989, *190*, 3033-3053.

Nylon Tensile Comparison



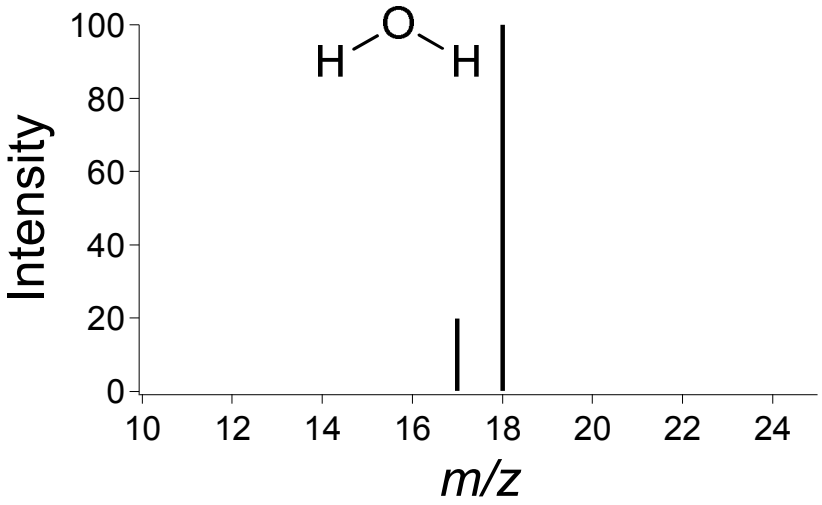
(1) Bernstein, R.; Derzon, D. K.; Gillen, K. T. Polymer Degradation and Stability, Nylon 6.6 accelerated aging studies: thermal-oxidative degradation and its interaction with hydrolysis 2005, 88, 480-488.
(2) Bernstein, R.; Derzon, D. K.; Gillen, K. T. Polymer Preprints (American Chemical Society, Division of Polymer Chemistry), Nylon degradation studies: Humidity and aging 2002, 43, 1349.

Nylon Tensile Comparison

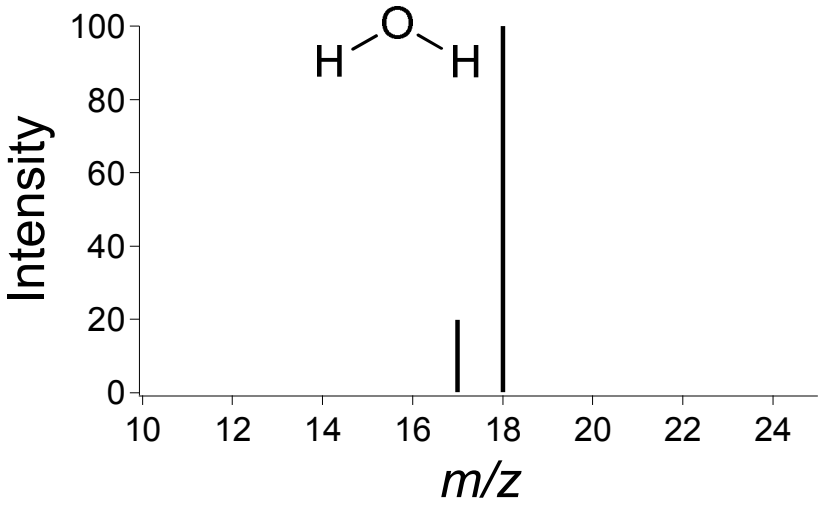
Conditions	Normalized Slope	
	124 ºC	109 ºC
Rate for Thermal and Oxygen	1.0	1.0
	8.4	15.6
Rate for Thermal, Argon, and 100% R_H	7.4	14.6
Rate for Thermal, Oxygen, and 100% R_H	22.9	45.0

Combined rate ca. 3 times sum of individual rates

Example: Water

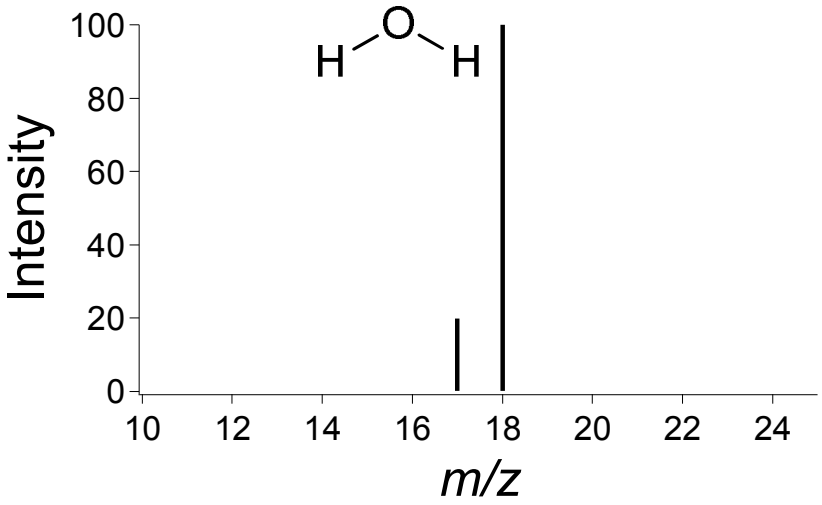


A representative water mass spectrum from oxidation of unlabeled nylon 6.6

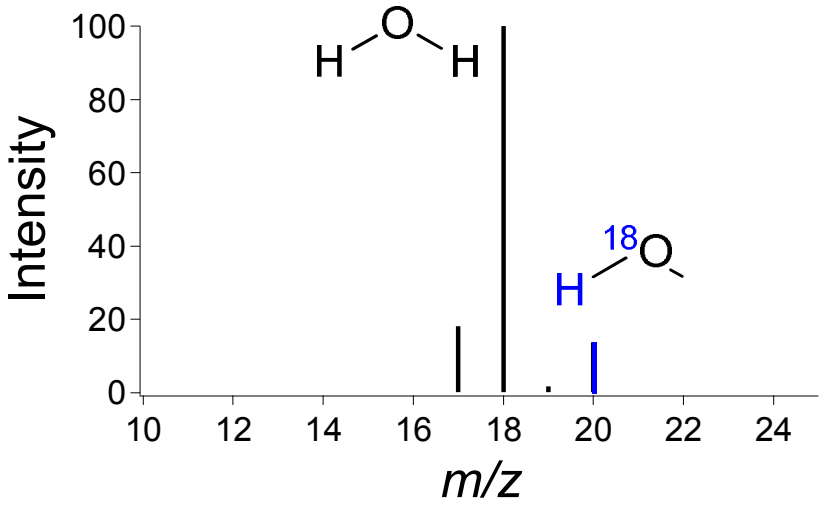


NIST Mass Spectral Library match of water spectrum

Example: Water



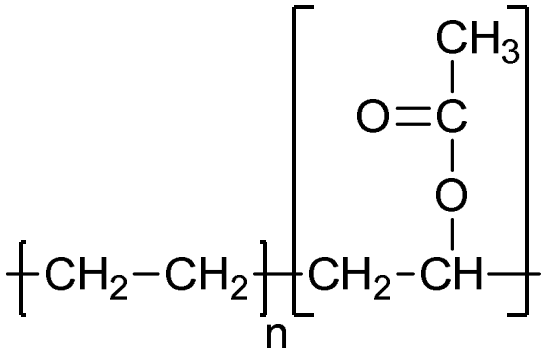
A representative water mass spectrum from oxidation of unlabeled nylon 6.6



Water mass spectrum from oxidation of unlabeled nylon 6.6 in an ^{18}O enriched environment

poly(ethylene co-vinyl acetate)

- EVA is employed as an adhesive material in various applications
- Acetic acid outgassing and reduced physical strength concerns exist
- Elucidation of the degradation chemistries is complex due to water formation. The degradation chemistries are said to be auto-catalytic, i.e. water is a thermal-oxidative degradation species that induces hydrolytic degradation.
- Fundamental understanding of the degradation mechanisms is critical to providing insight into physical property changes



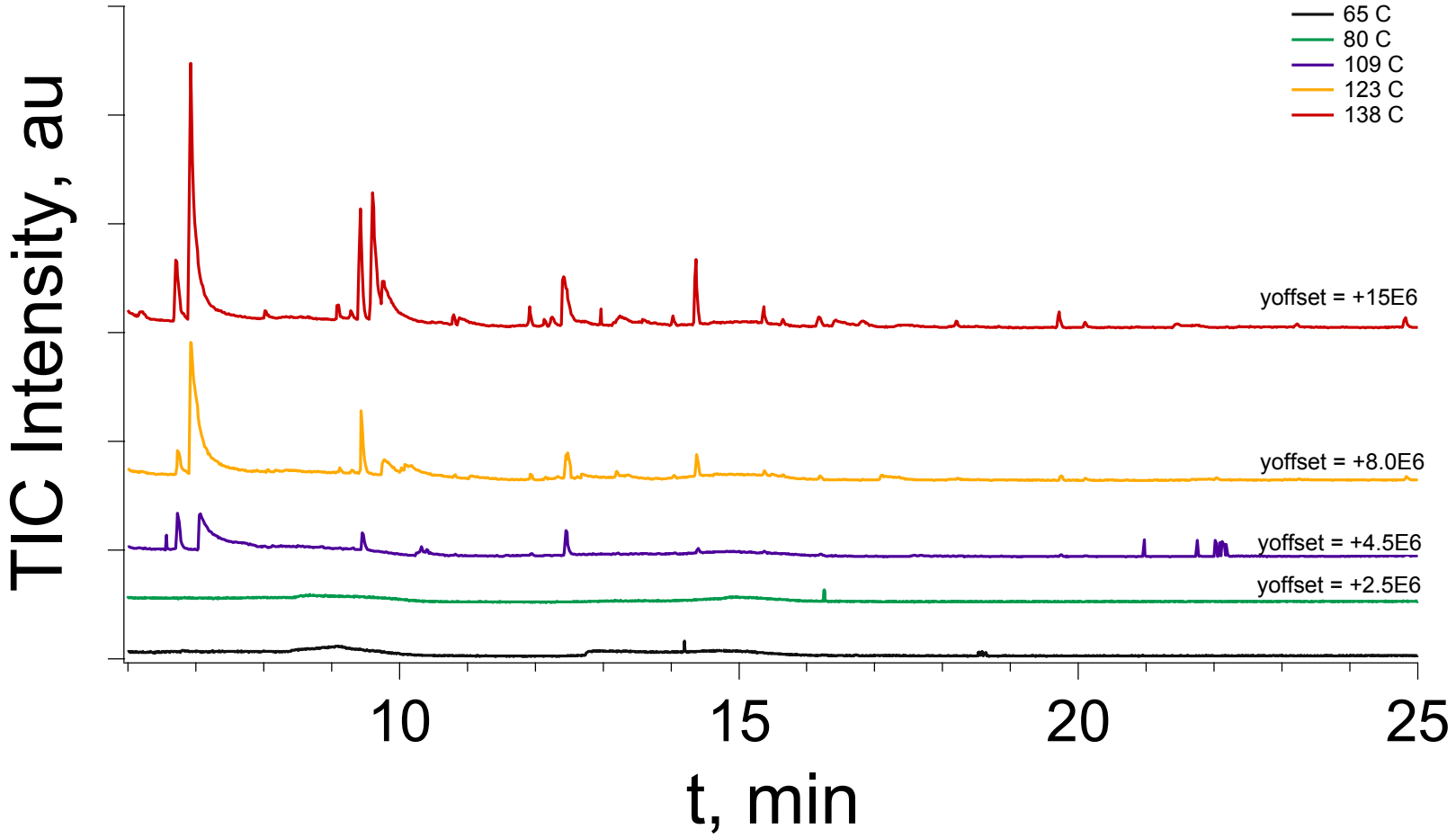
Objectives

- Outgassing, cryo-GC/MS
  - Identify outgassing species over time
  - Ensure degradation products are representative of performance environment by comparing products and product distributions at varying temperatures. This will aid in mechanism elucidation at relevant environmental conditions.
- Physical Properties
  - Identify changes in tensile strength/elongation by performing accelerated aging experiments on EVA films
- Correlate changes in physical properties to degradation species formation

Outgassing Study

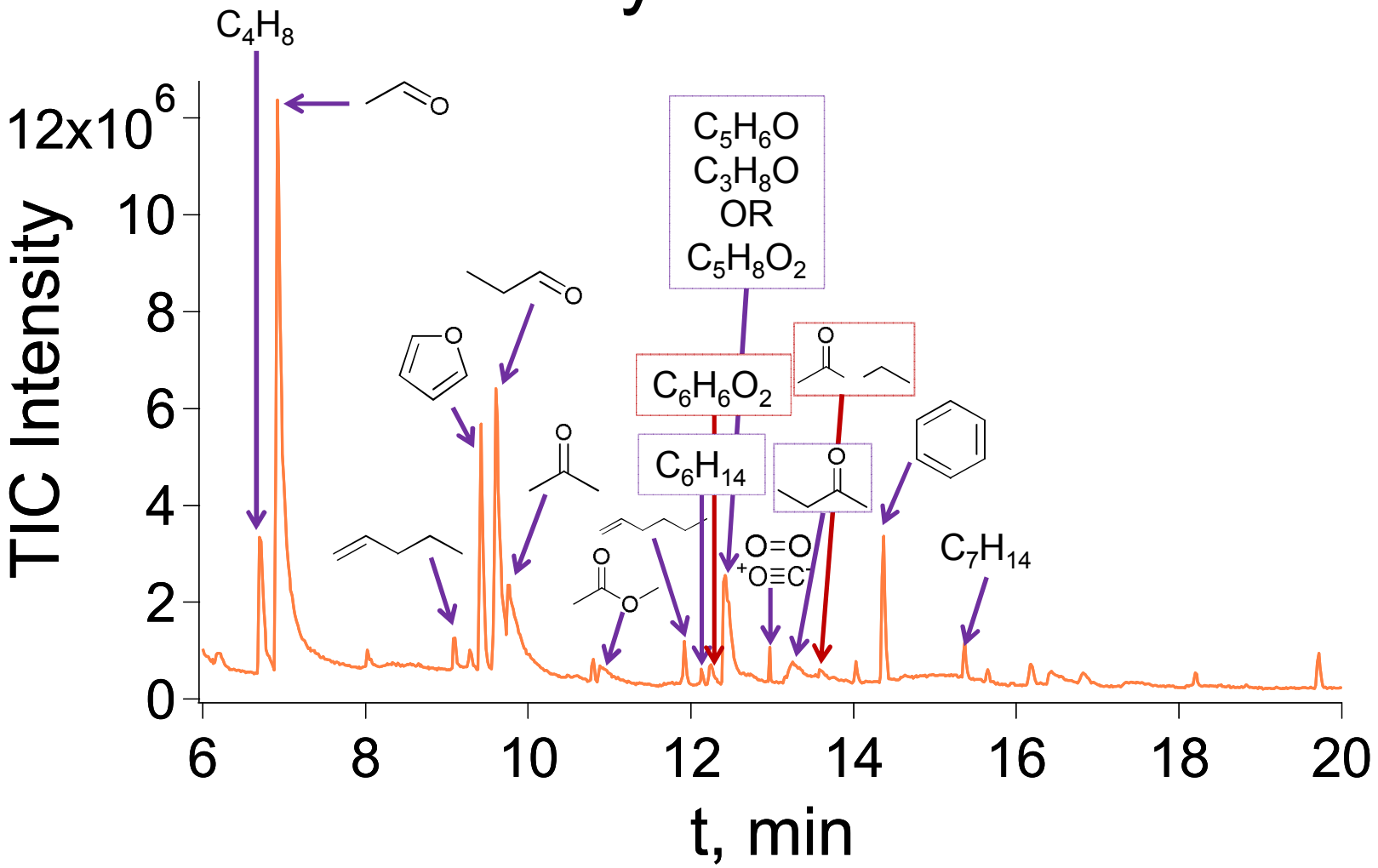
- EVA specimens (40.5 ± 0.3 mg) have been subjected to thermal-oxidative aging in 5 cm^3 stainless steel vials at 25°C, 40°C, 65 °C, 80 °C, 123 °C, and 138 °C
- Current samples have been aged to 84 days
- Mass spectral data results were collected for samples aged at 40 and 60 days

Outgassing Study, 40 Days



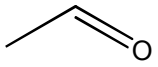
As the aging temperature increases, more degradation species are formed and the concentration of the products increases

Preliminary Outgassing Data
40 Days at 138 °C

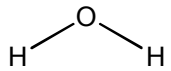


Preliminary mass spectral data analysis has identified a few volatile degradation species. Water, carbon monoxide, and an acetic acid based species (acetaldehyde) have also been identified

m

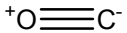


C_4H_8
M_W 56
RT 6.73

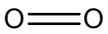


acetaldehyde
C_2H_4O
M_W 44
RT 6.97

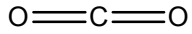
water
H_2O
M_W 18
RT 7.35 to 9.35



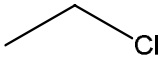
carbon monoxide
CO
M_W 28
RT 7.35 to 9.35



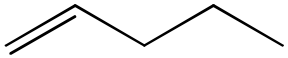
oxygen
O_2
M_W 32
RT 7.35 to 9.35



carbon dioxide
CO_2
M_W 44
RT 7.35 to 9.35

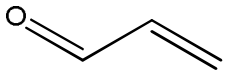


ethyl chloride
C_2H_5Cl
M_W 64
RT 8.06



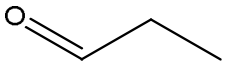
1-pentene
C_5H_{10}
M_W 70
RT 9.1

???
RT 9.29

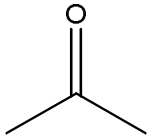


furan
C_4H_4O
M_W 68
RT 9.43

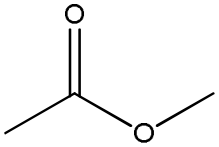
2-propenal
C_3H_4O
M_W 56
RT 9.59



propanal
C_3H_6O
M_W 58
RT 9.69

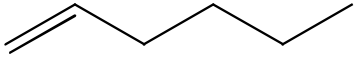


acetone
C_3H_6O
M_W 58
RT 9.84



methyl acetate
$C_3H_6O_2$
M_W 74
RT 10.87

water
carbon monoxide
RT 11.75



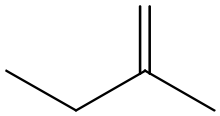
1-hexene
C_6H_{12}
M_W 84
RT 11.92

hexane ???
C_6H_{14}
M_W 86
RT 12.14

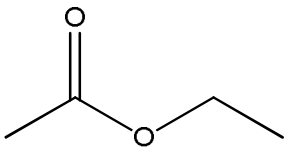
$C_4H_6O_2$
M_W 86
RT 12.25

C_4H_8O
M_W 73
OR...
$C_5H_8O_2$
M_W 100
RT 12.41

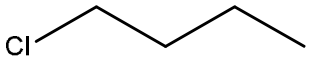
carbon monoxide
oxygen
RT 12.97



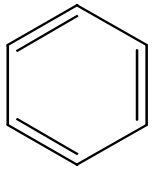
2-butanone
C_4H_8O
M_W 72
RT 13.27



ethyl acetate
$C_4H_8O_2$
M_W 88
RT 13.62



1-chloro-butane
C_4H_9Cl
M_W 92
RT 14.03



benzene
C_6H_6
M_W 78
RT 14.37

C_7H_{14}
M_W 98
RT 15.37

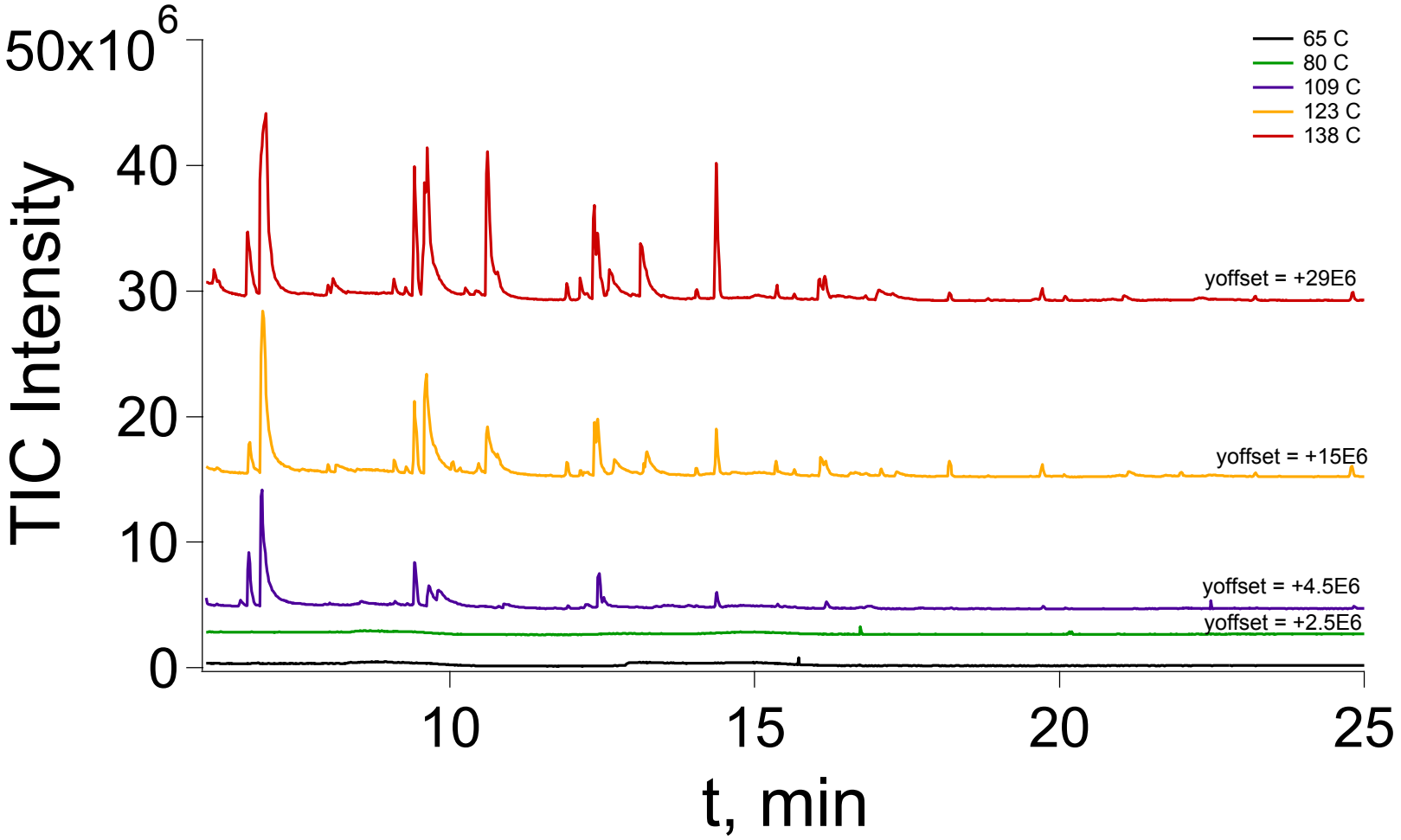
C_8H_{16}
M_W 112
RT 16.17

C_8H_{16}
M_W 112
RT 16.8

???
RT 16.3 to 26

water (18)
carbon monoxide (28)
oxygen (32)
carbon dioxide (44)
RT 20 to 51 & spike at 27

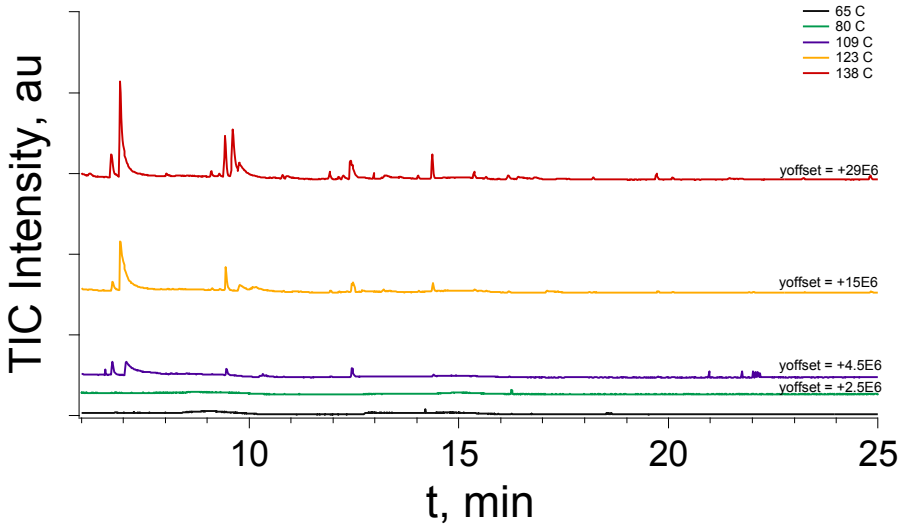
Outgassing Study, 60 Days



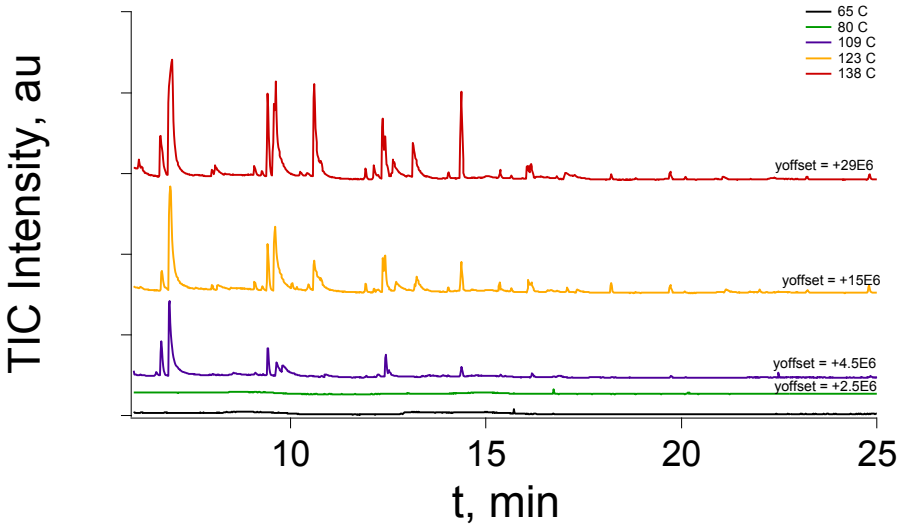
As the aging temperature increases, more degradation species are formed and the concentration of the products increases.

Outgassing Study

40 Days

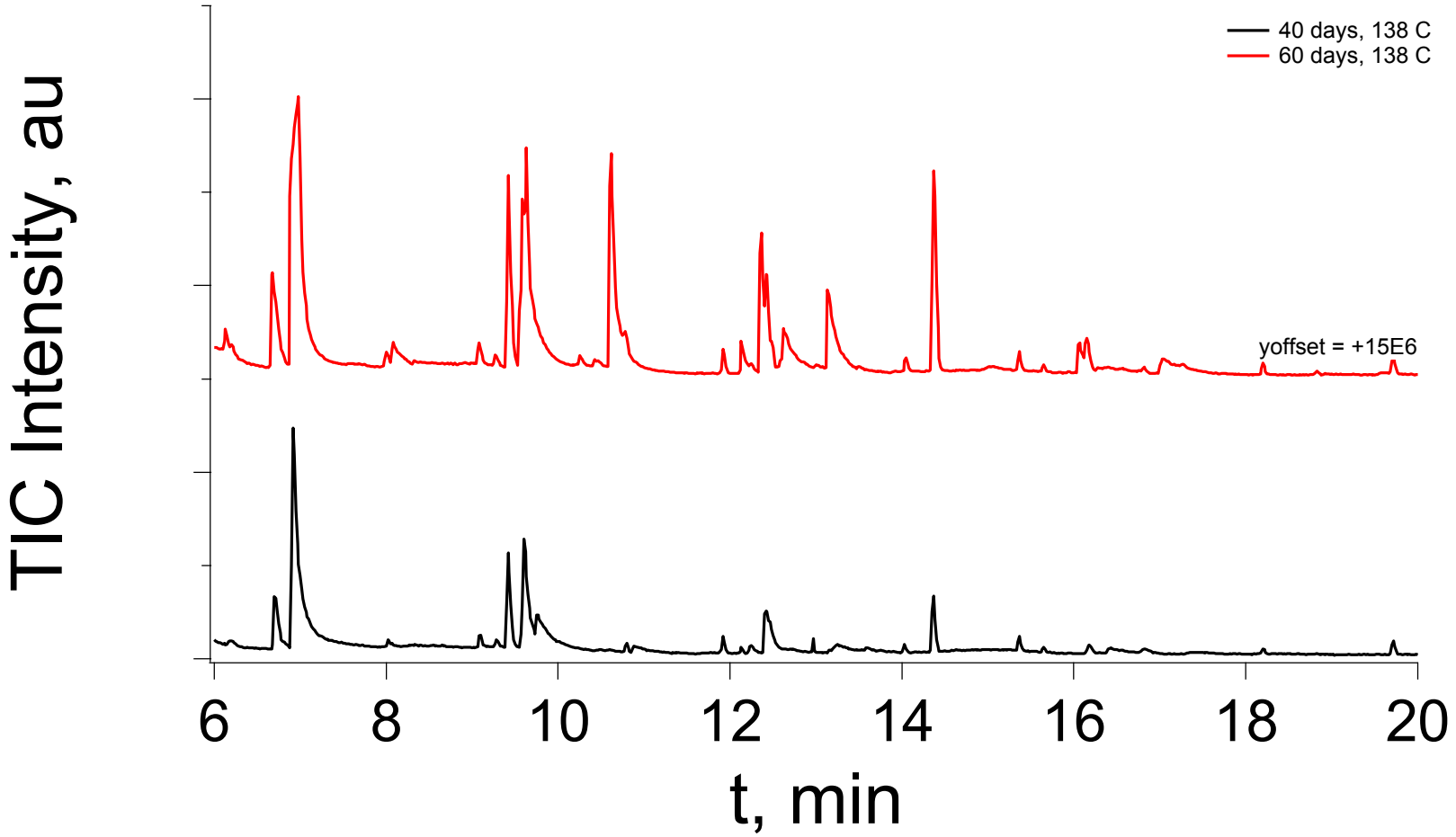


60 Days

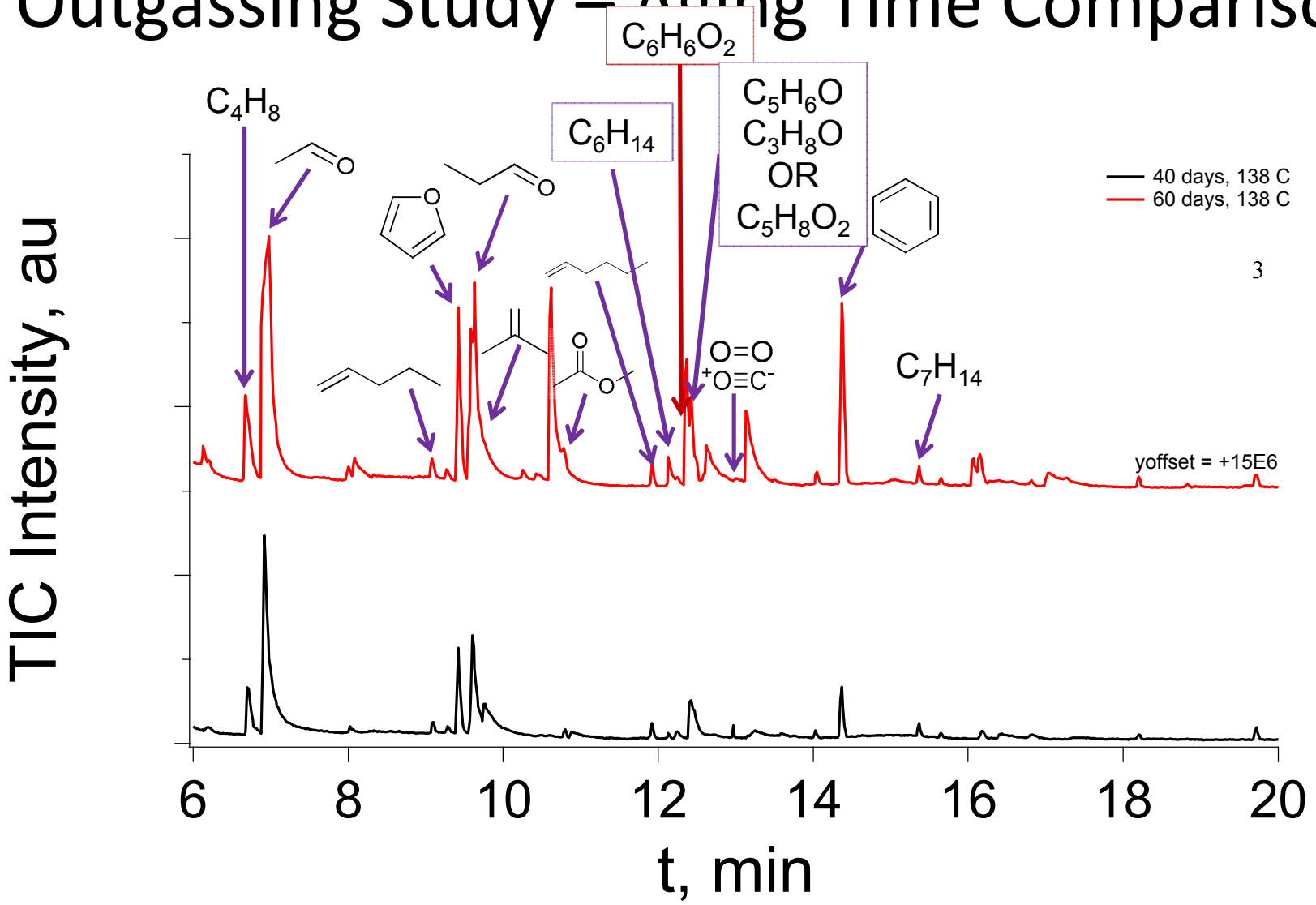


As the aging time and temperature increases, more degradation species are formed and the concentration of the products increases.

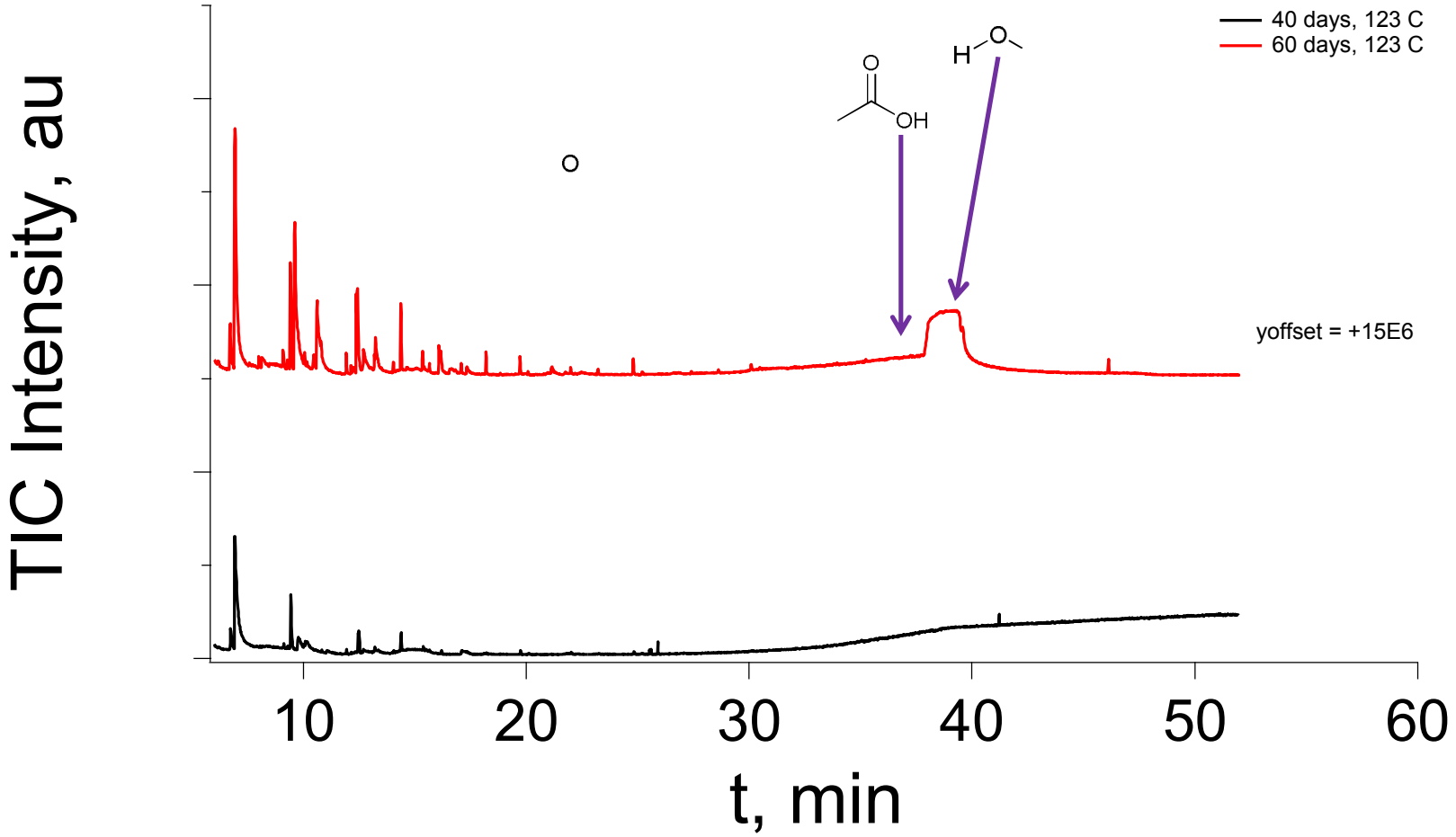
Outgassing Study – Aging Time Comparison



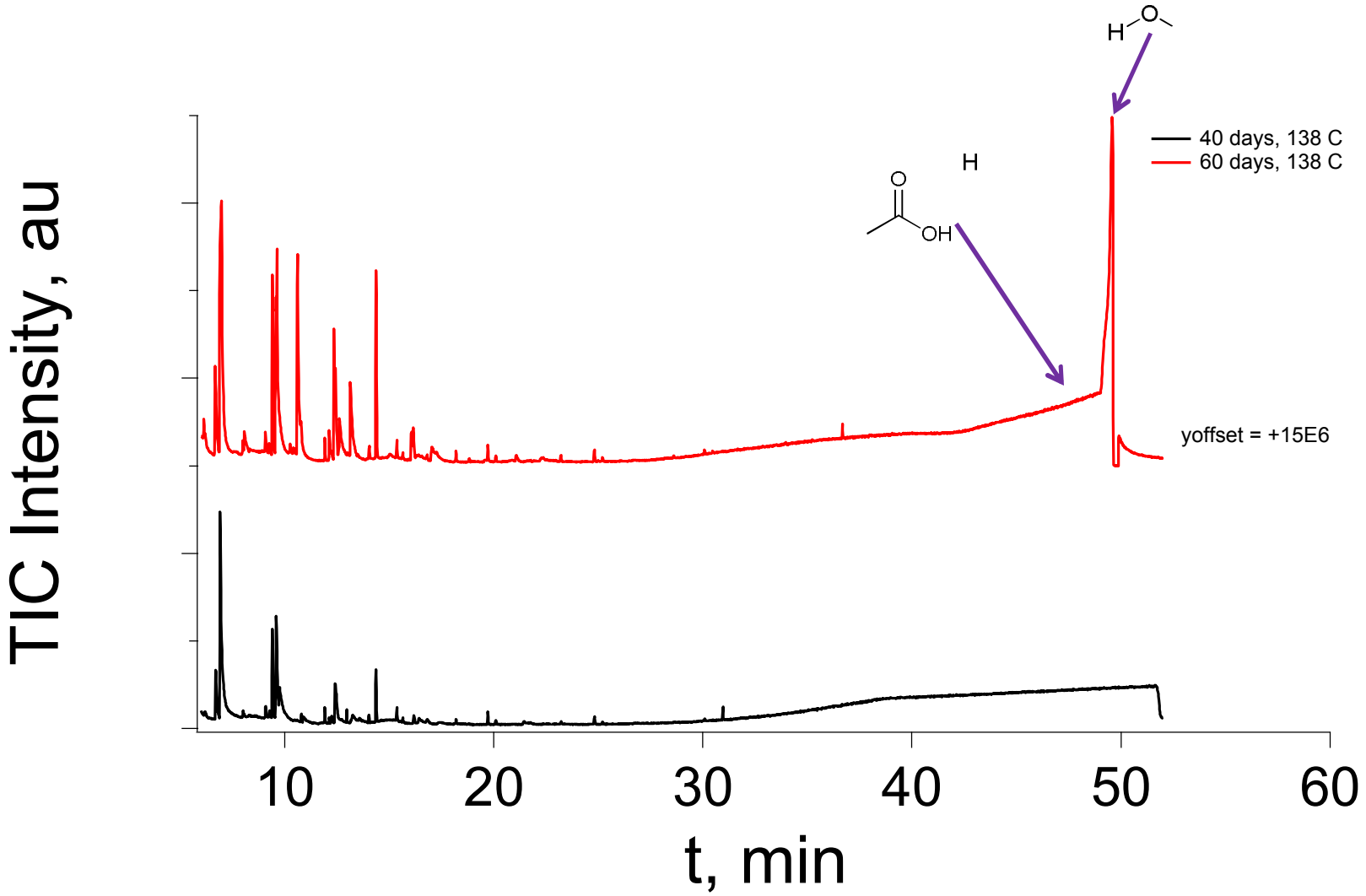
Outgassing Study – Aging Time Comparison



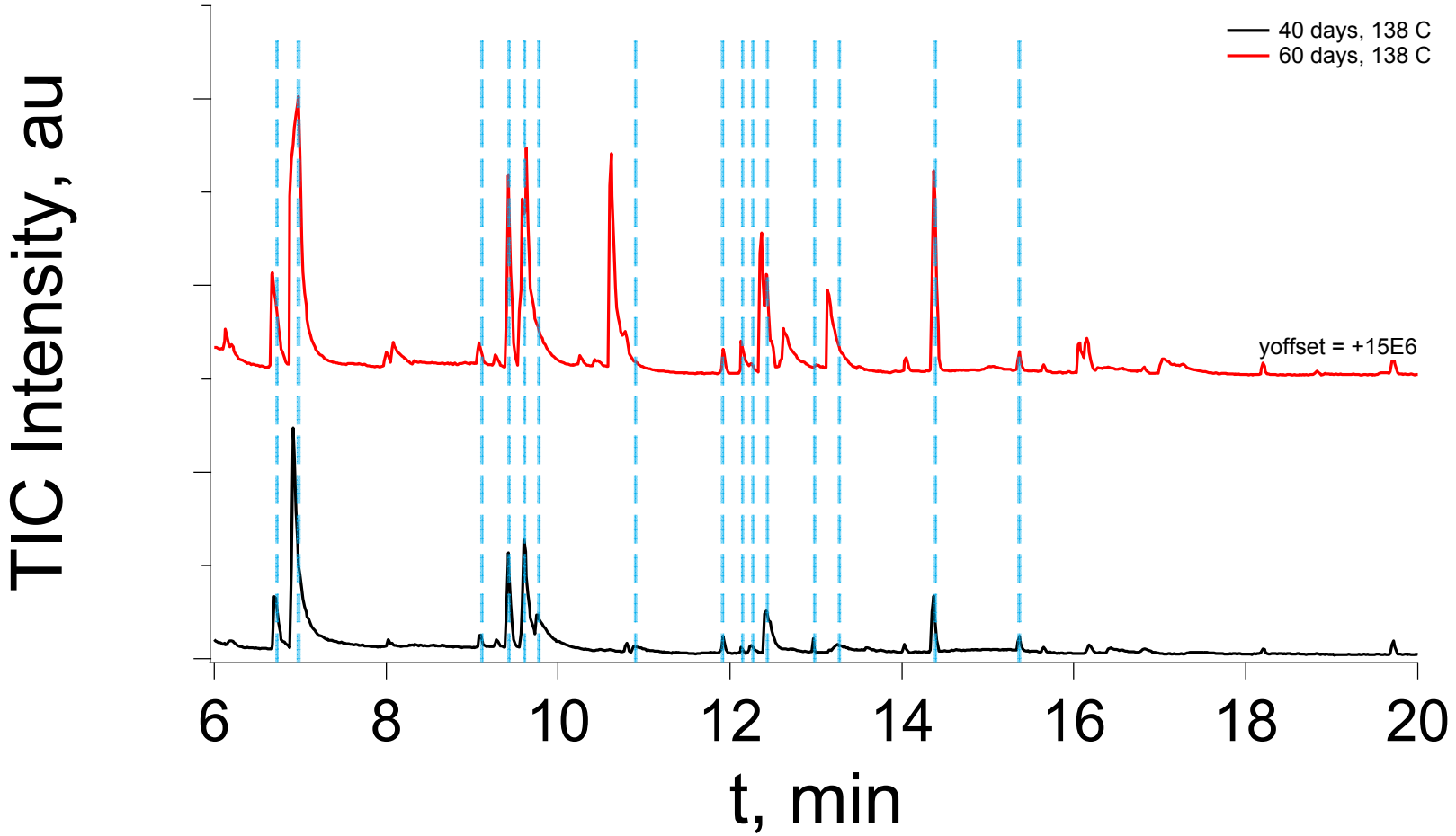
Outgassing Study – Aging Time Comparison



Outgassing Study – Aging Time Comparison



Outgassing Study – Aging Time Comparison

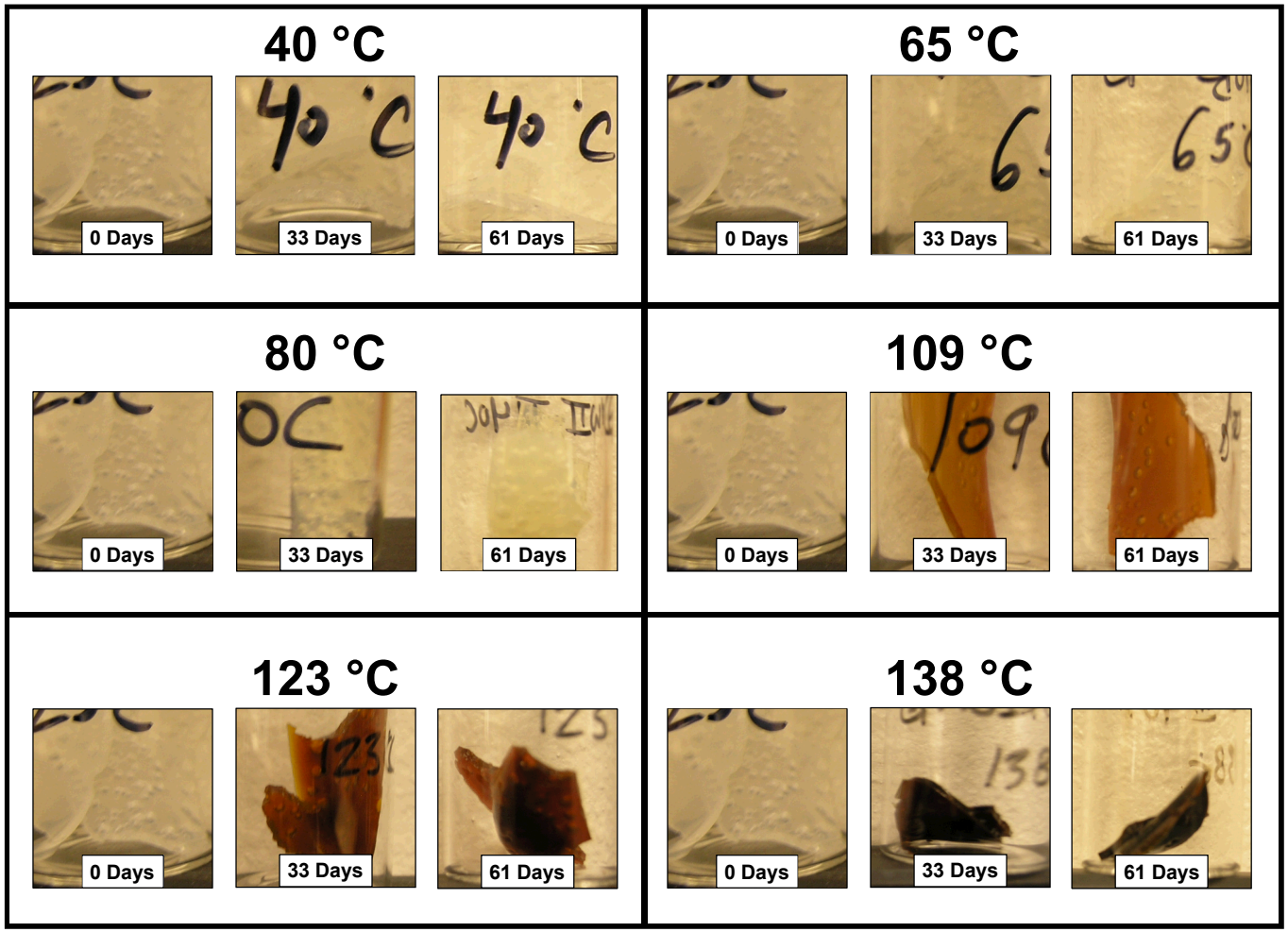


Yellowing Study

- Yellowing of organic materials which age under thermal-oxidative conditions can often be correlated to physical properties

- EVA specimens aged at varying temperatures are photographed as a function of time. Pulling samples from ovens affords the opportunity to acquire DSC and FTIR samples at the same aging times. We have collected these specimens for future analysis at 33 and 61 days of aging. The current samples have aged to 68 days.

Yellowing Study



EVA yellows and then turns brown with increasing aging time and temperature

Conclusions

- As the aging time and temperature increases, more degradation species are formed and the concentration of the products increases—the degradation chemistries seem to remain constant from 40 °C to 138 °C. Mass spectral analysis at longer aging times will confirm this.

- Several degradation species have been identified, including water, carbon monoxide, benzene, and acetic acid. Future work will include correlating the products formed to changes in physical properties

- EVA yellows and then turns brown with increasing aging time and temperature

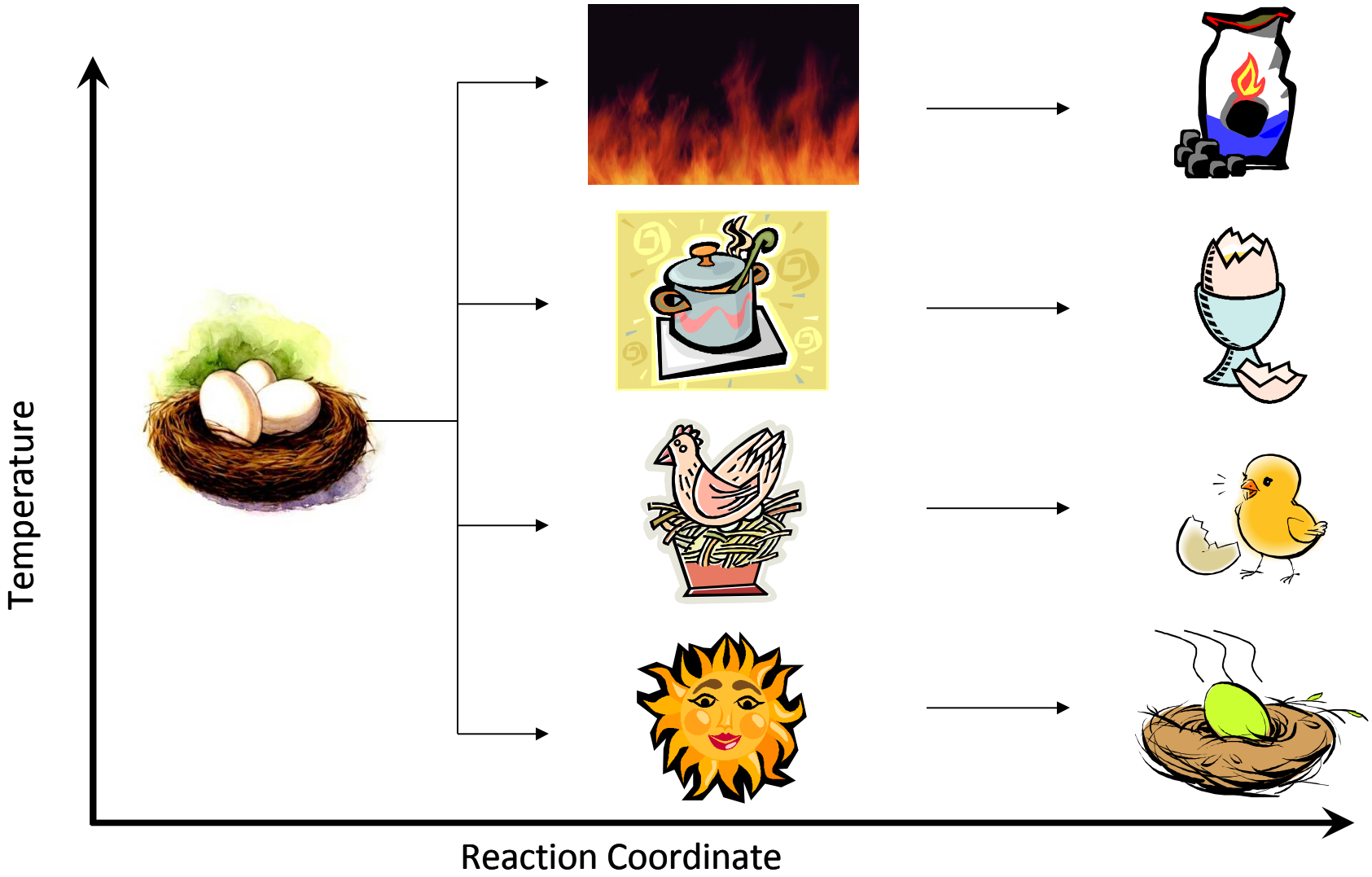
Deception!

Conclusions derived from initial high temperature, short duration (even out to 1 year) accelerated aging can be misleading.

Chemistry / mechanisms must be understood.

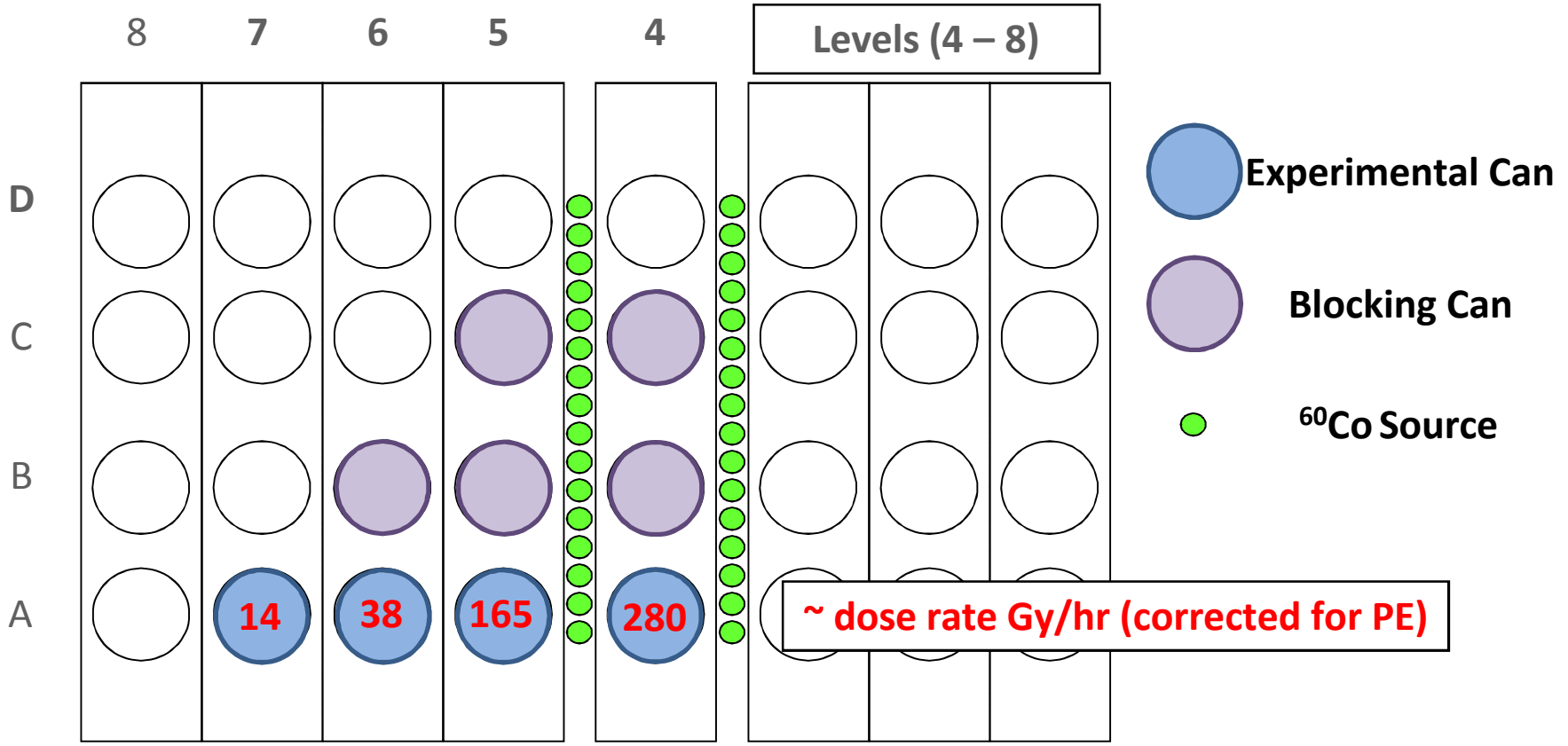
Results must be critically analyzed to identify and understand mechanism changes

‘Accelerated Aging’



LICA

Low Intensity Cobalt Array



Measured 02/15/2012

Time-Temperature Superposition

Does mechanism change as a function of temperature?

If same mechanism:

- same shape (log graph)
- should be constant acceleration (multiple)

1. Pick a reference temperature
2. Multiply the time at each temperature by the constant that gives the best overlap with the reference temperature data
3. Define that multiple as 'a_T' ($a_T = 1$ for ref. temp.)
4. Find a_T for each temperature

Plot $\log(a_T)$ vs $1/T$ linear if Arrhenius

Gillen, K. T.; Celina, M.; Clough, R. L.; Wise, J. *Trends in Polymer Science,* Extrapolation of Accelerated Aging Data -Arrhenius or Erroneous? 1997, *5*, 250-257.

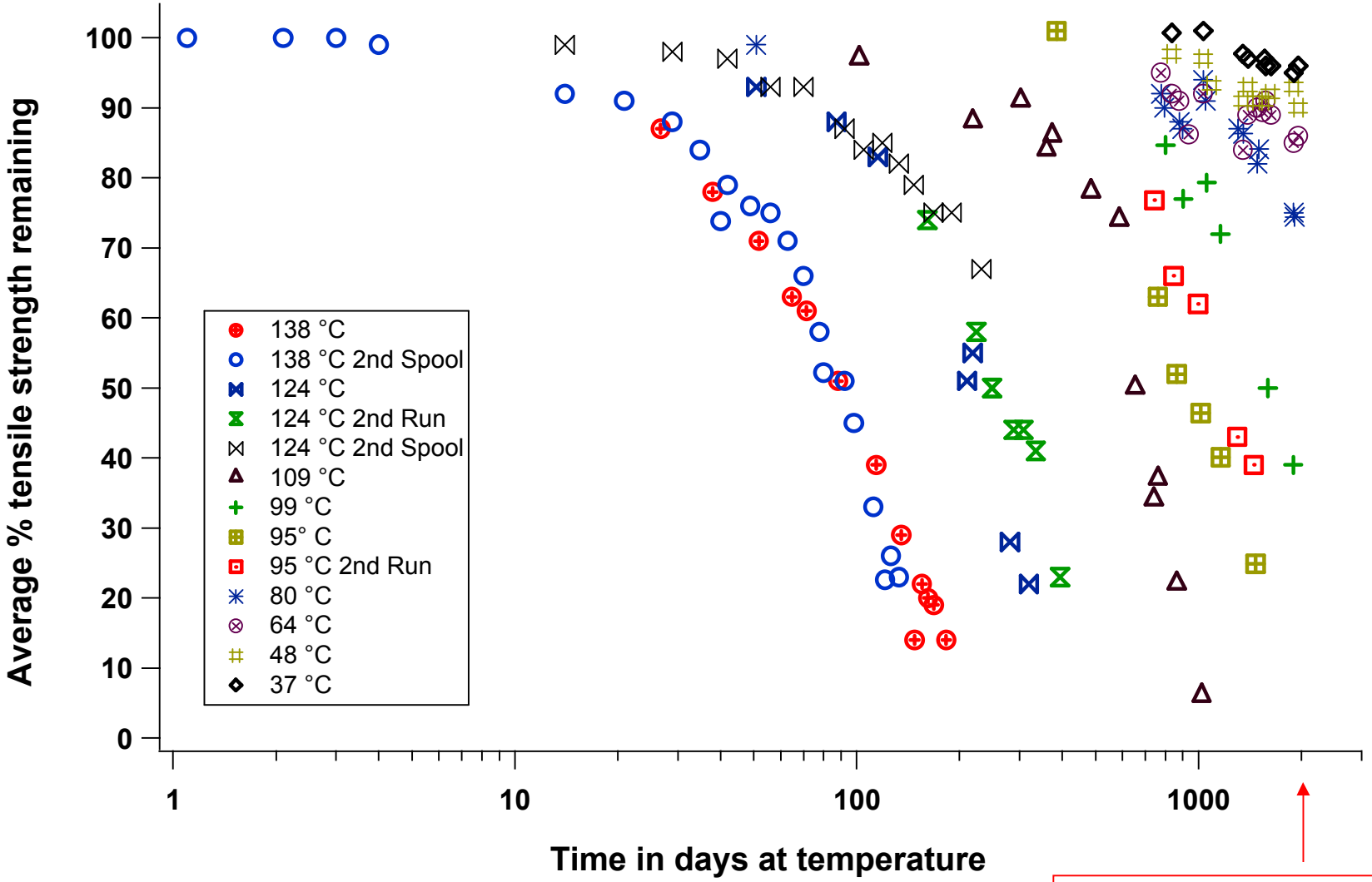
Arrhenius equation:

$k = Ae^{-Ea/RT}$

Empirical equation

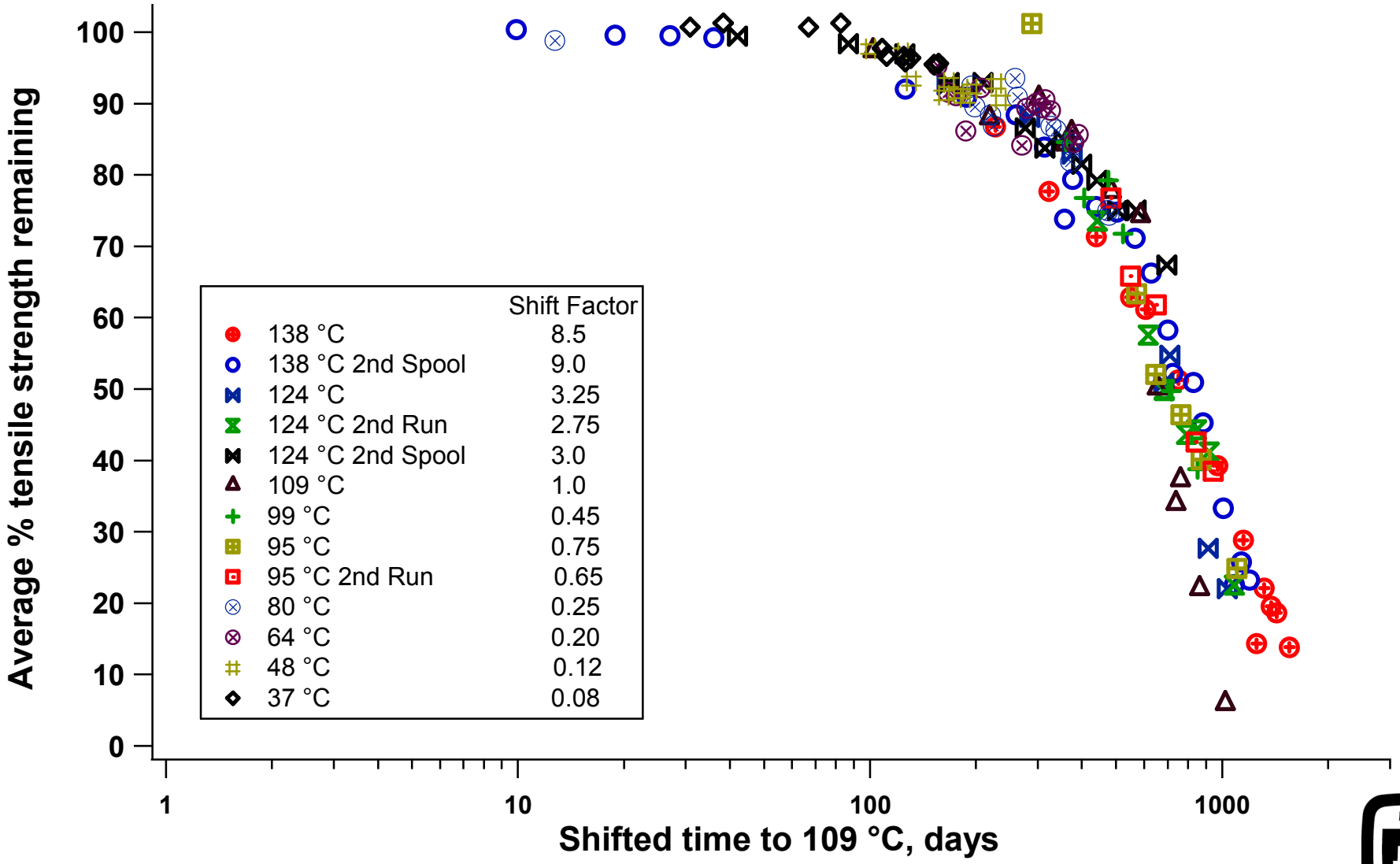
$\ln(k) = \ln(A) - Ea/RT$

Thermal-oxidative Aging: Nylon



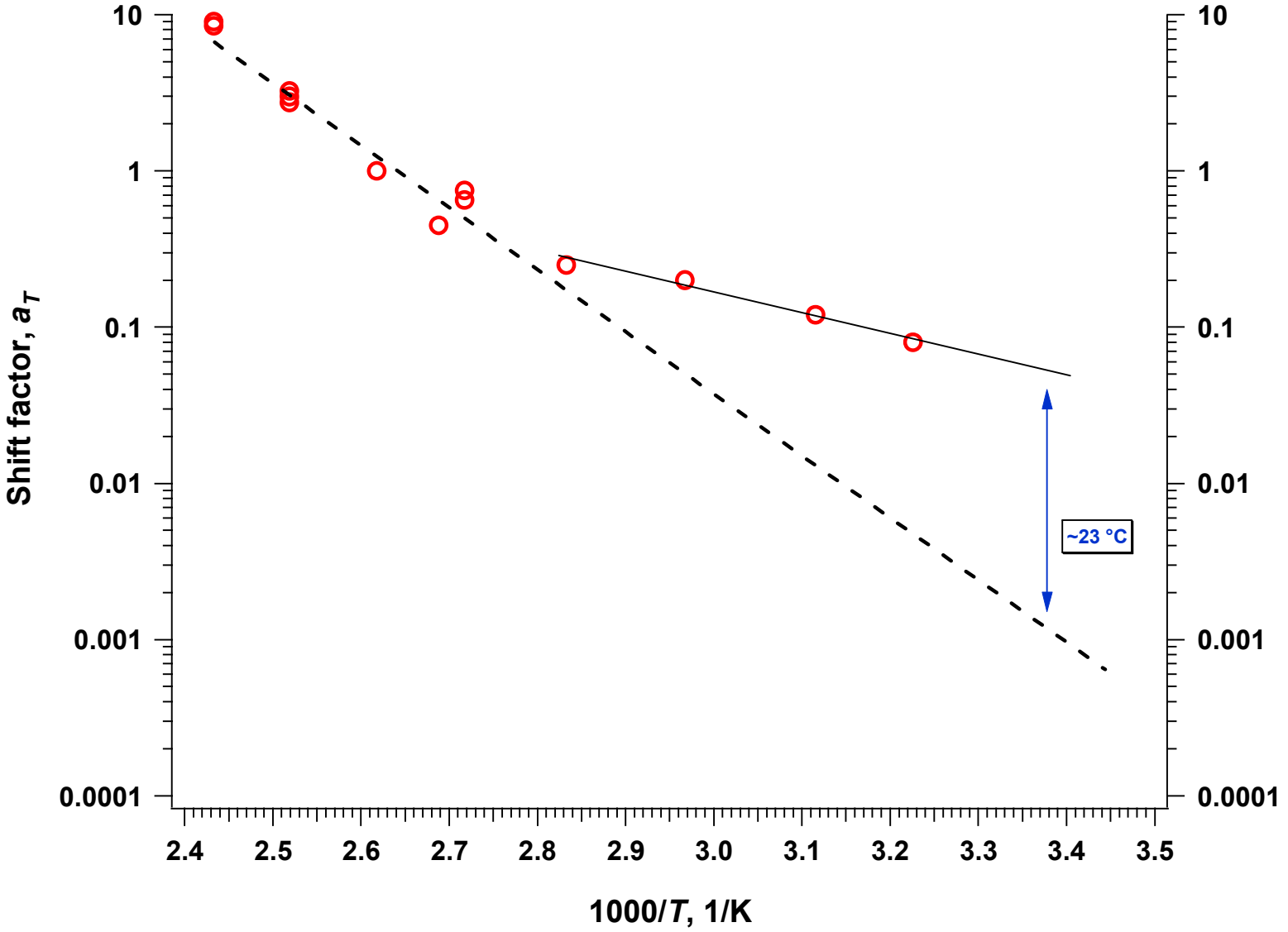
Bernstein, R.; Gillen, K. T. *Polymer Degradation and Stability, Nylon 6.6 accelerating aging studies: II. Long-term thermal-oxidative and hydrolysis results 2010, 95, 1471-1479.*

Thermal-oxidative Aging: Nylon Shifted Data



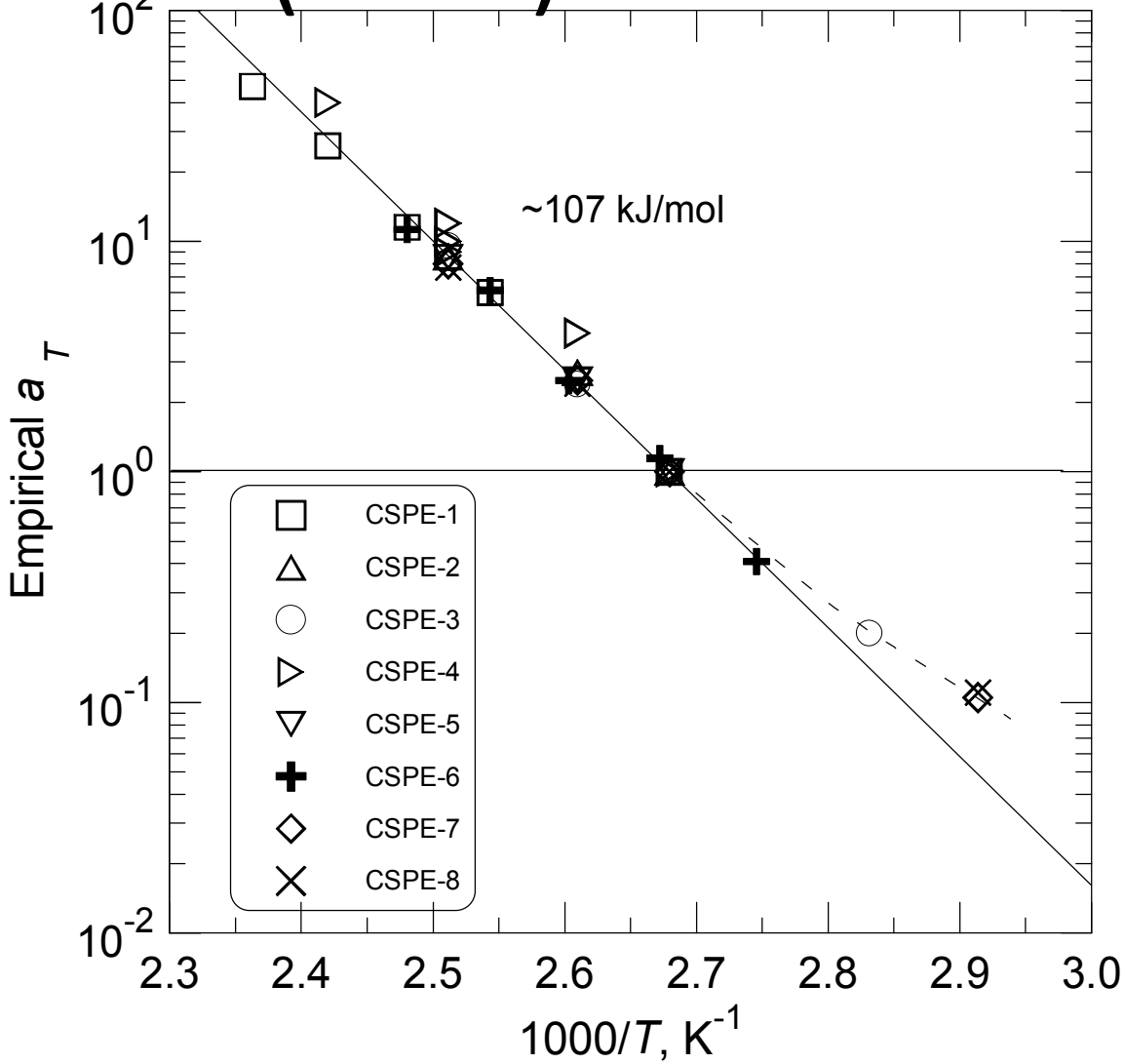
Bernstein, R.; Gillen, K. T. *Polymer Degradation and Stability, Nylon 6.6 accelerating aging studies: II. Long-term thermal-oxidative and hydrolysis results 2010, 95, 1471-1479.*

Thermal-oxidative Aging: Nylon Shift Factor Graph



Bernstein, R.; Gillen, K. T. *Polymer Degradation and Stability, Nylon 6.6 accelerating aging studies: II. Long-term thermal-oxidative and hydrolysis results 2010, 95, 1471-1479.*

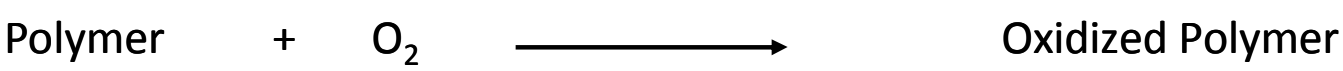
Hypalon (CSPE) Shift Factor Plot



Gillen, K. T.; Bernstein, R.; Celina, M. *Polymer Degradation and Stability,* Non-Arrhenius behavior for oxidative degradation of chlorosulfonated polyethylene materials 2005, *87*, 335-346.

Thermal Exposure

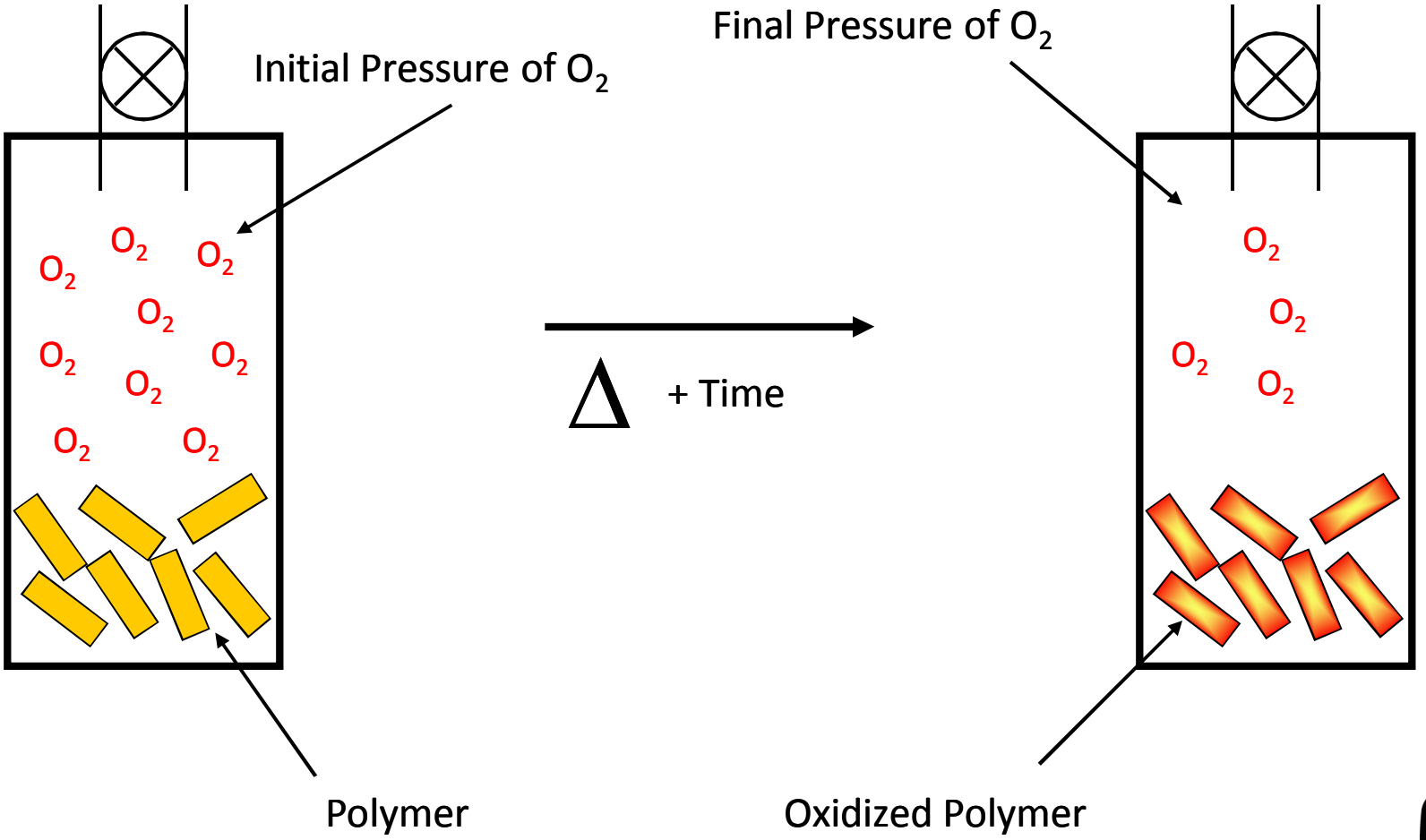
Thermal-Oxidation



Quantify amount of oxygen consumed

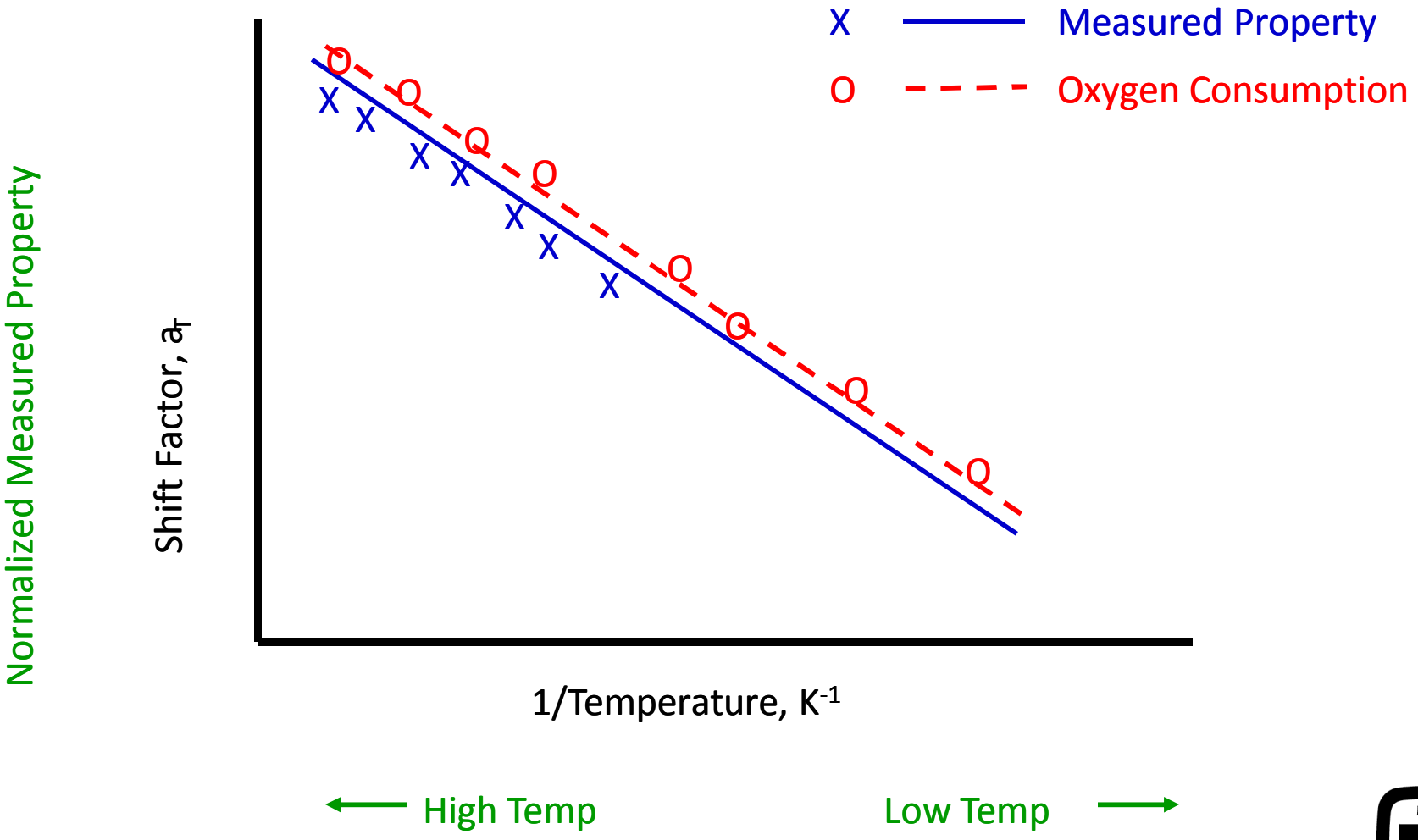
- Simple in theory
- Difficult in practice
- Amazingly sensitive

Schematic of Oxuptake

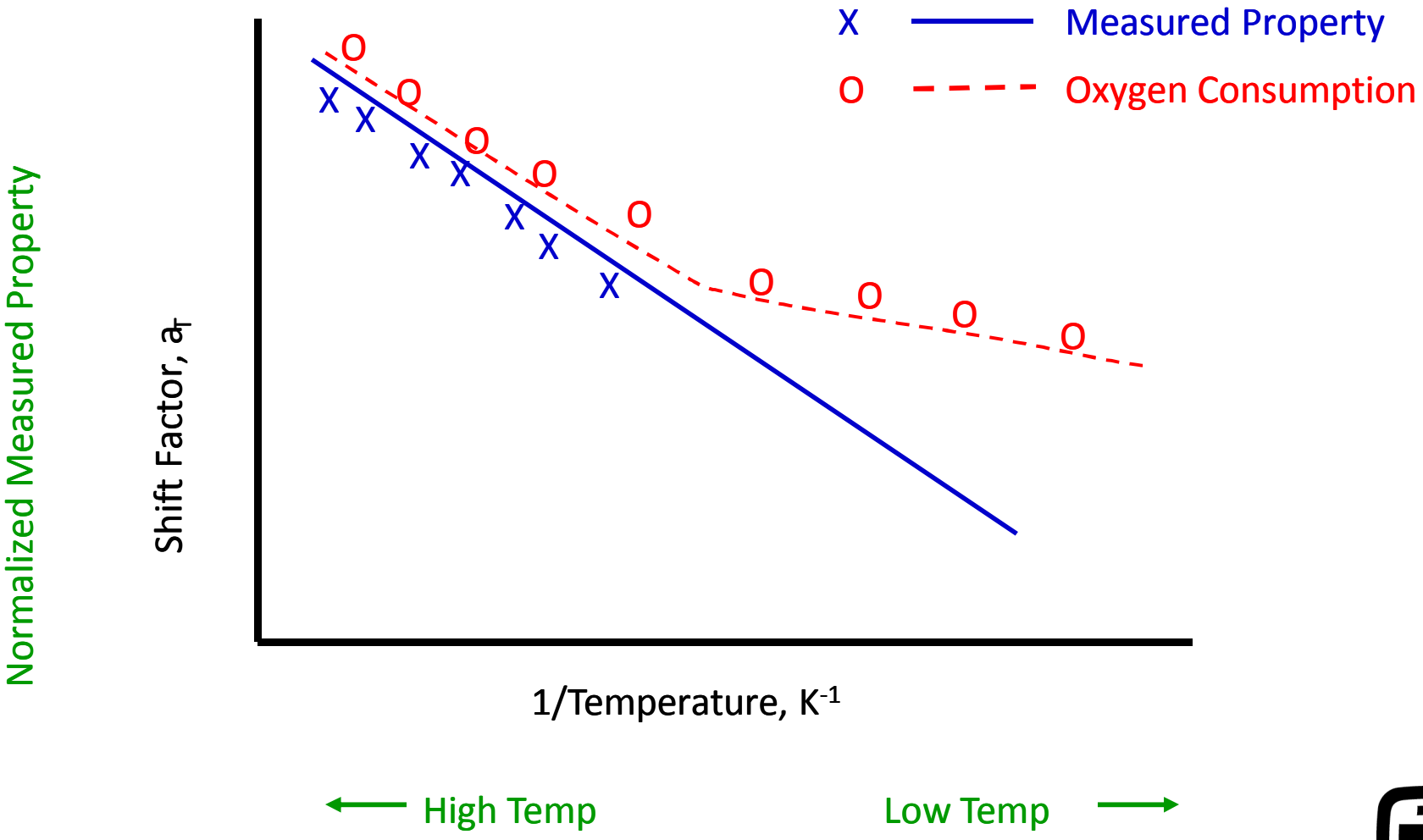


Oxygen Consumption

Enhanced Extrapolation ‘Good’



Enhanced Extrapolation ‘Bad’



DLO, Need to Know

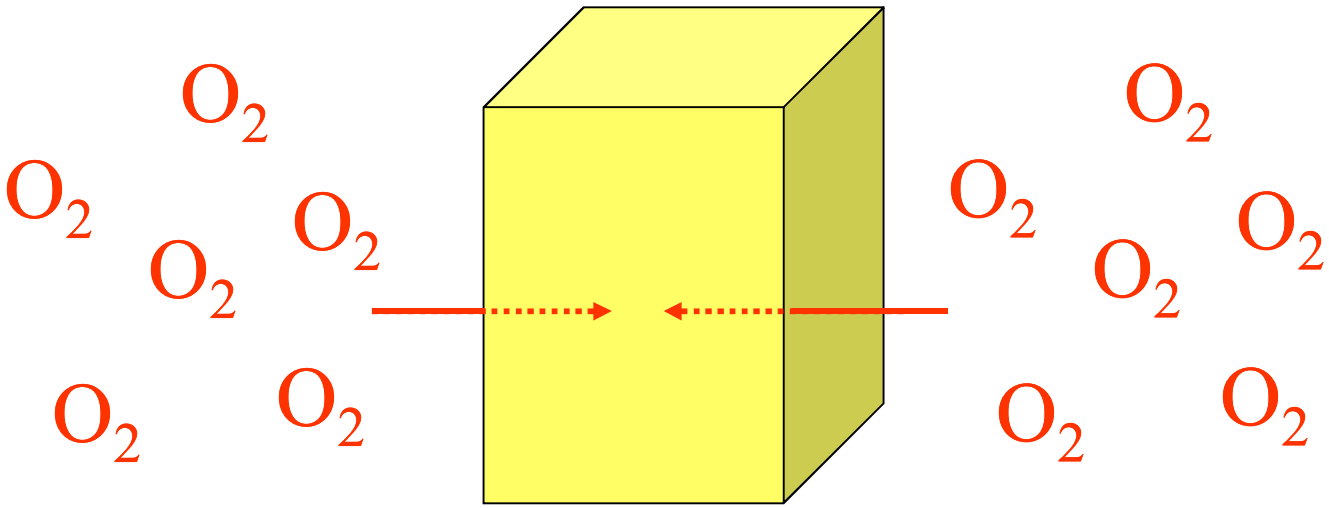
Diffusion Limited Oxidation (DLO) effects if oxygen dissolved in material used up faster by reaction than it can be replenished by diffusion from surrounding air atmosphere

Race between:
the oxygen consumption rate versus the oxygen diffusion rate

Therefore we need estimates of:

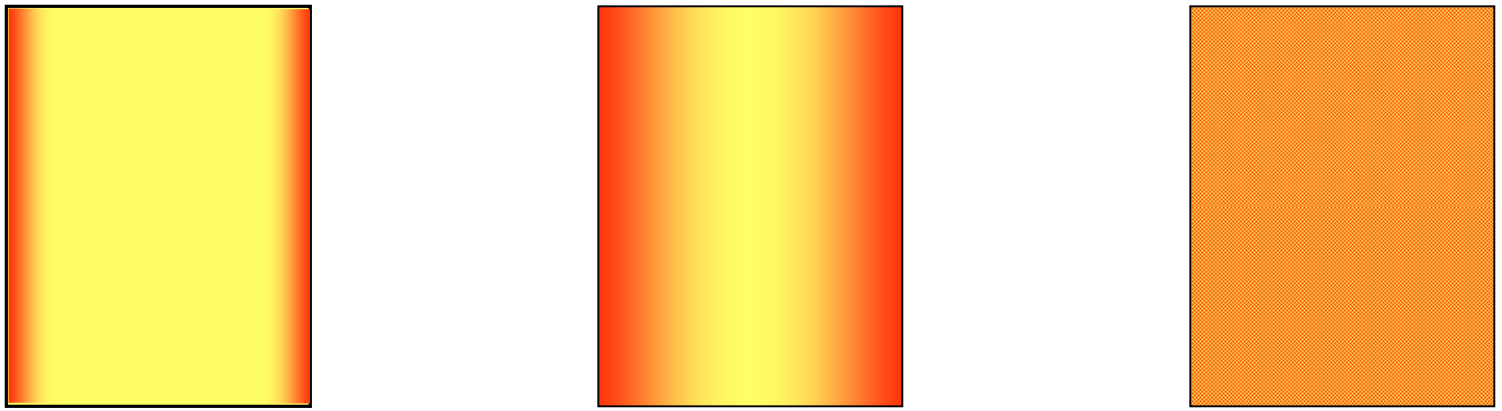
1. O_2 permeability versus aging temperature
2. O_2 consumption versus aging temperature

Diffusion-Limited Oxidation (DLO)



rxn rate > diffusion rate

rxn rate < diffusion rate



Heterogeneous

Homogeneous

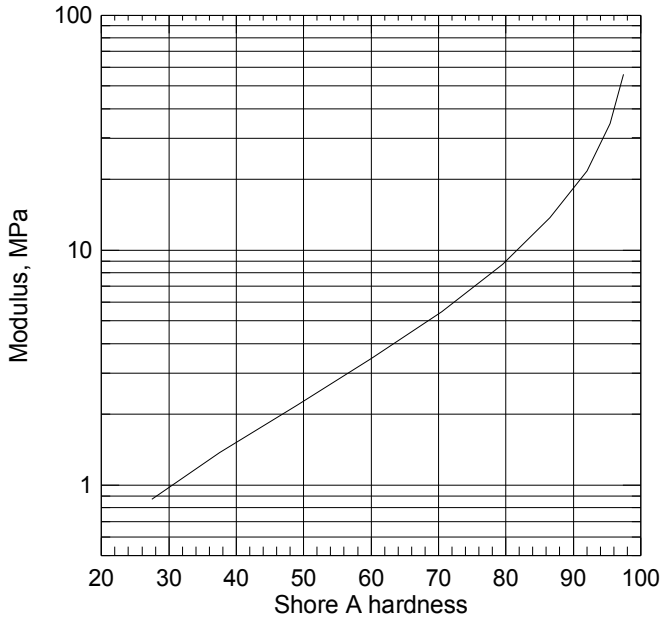
Modulus Profiling

Indentation technique ca. 50μm resolution

Measure of Inverse tensile compliance

Closely related to tensile modulus

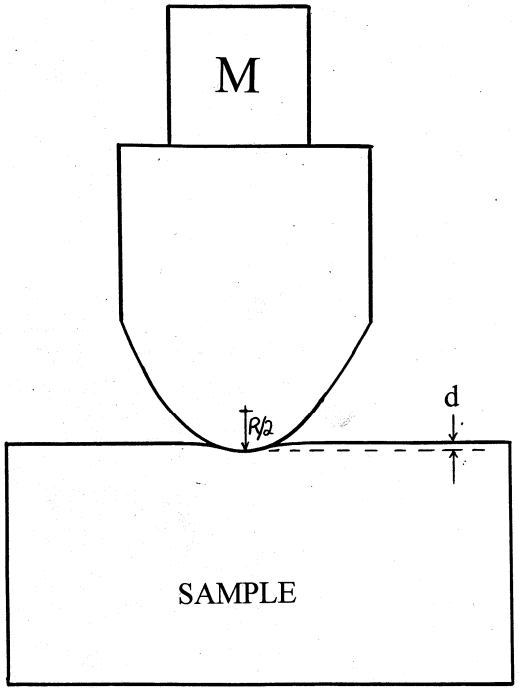
Modulus vs. Shore A



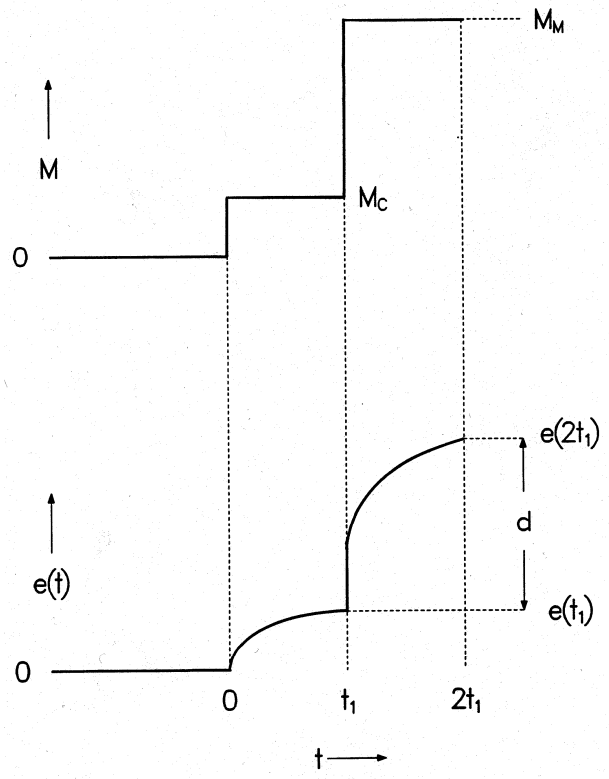
Excellent to examine ‘geneity’ of aging (heteo- or homo-) (DLO issues)

Schematic of Modulus Profile Experiment

Probe tip, sample and mass



Mass is applied in two steps



Gillen, K. T.; Clough, R. L.; Quintana, C. A. *Polym. Degrad. Stab., Modulus profiling of polymers 1987, 17, 31-47*

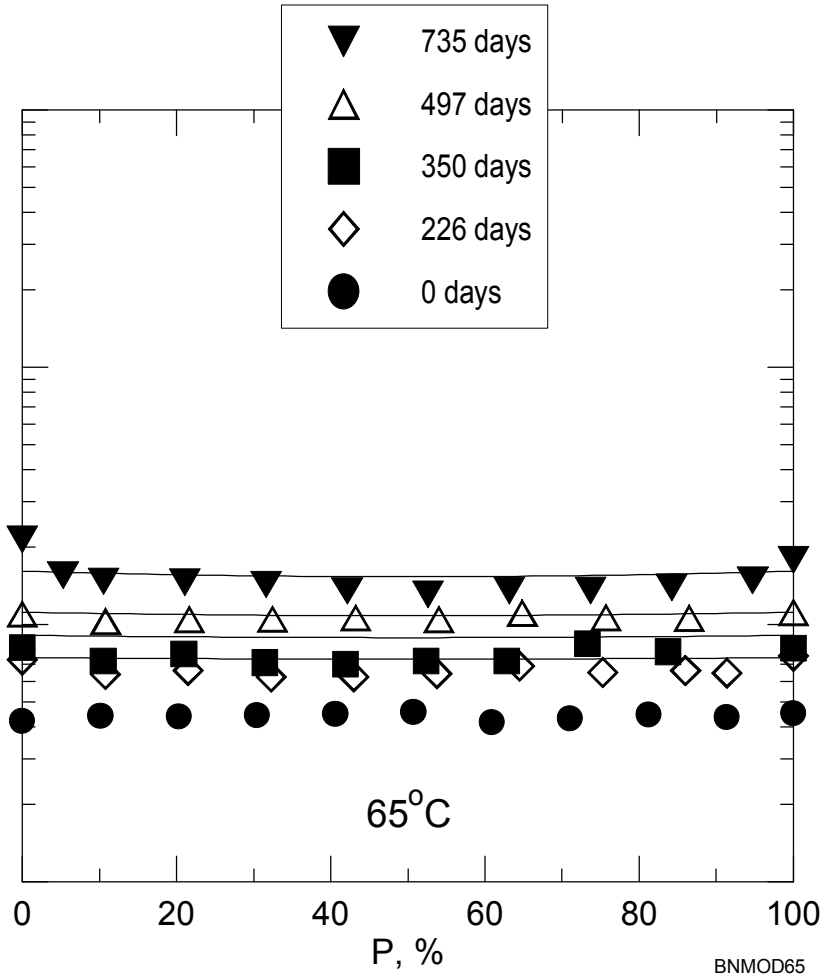
Modulus Profiler

Modulus Profiler Sample

Homogeneous Aging

Aging of a nitrile rubber at temperatures ranging from 65°C to 125°C

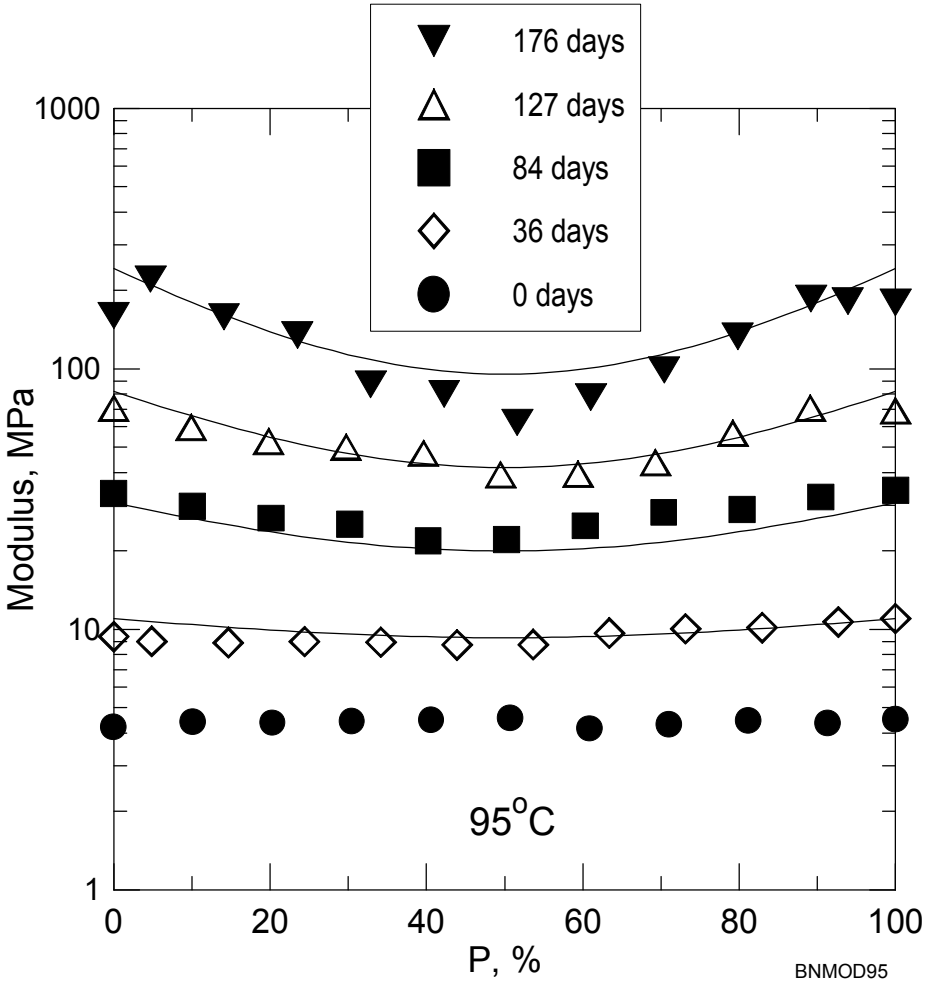
Modulus profiles of samples aged at 65°C indicate the presence of homogeneous aging

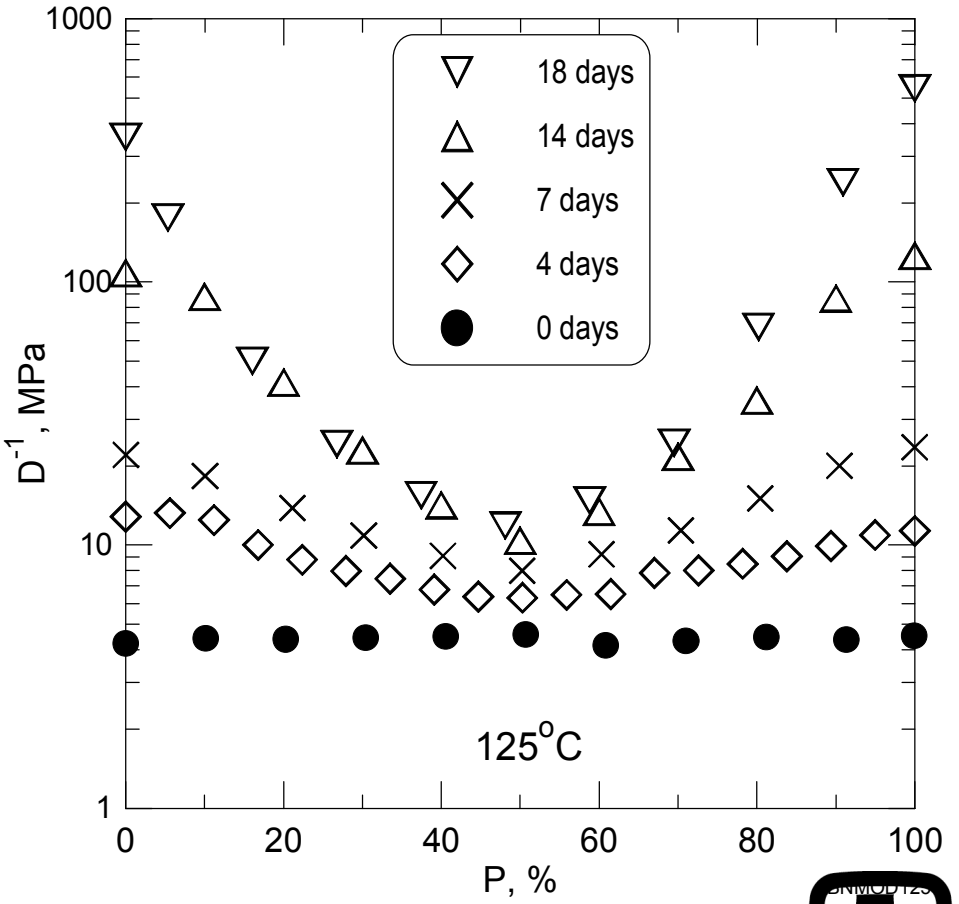


Wise, J.; Gillen, K. T.; Clough, R. L. *Polymer Degradation and Stability, An ultrasensitive technique for testing the Arrhenius extrapolation assumption for thermally aged elastomers 1995, 49, 403-418.*

Heterogeneous Aging

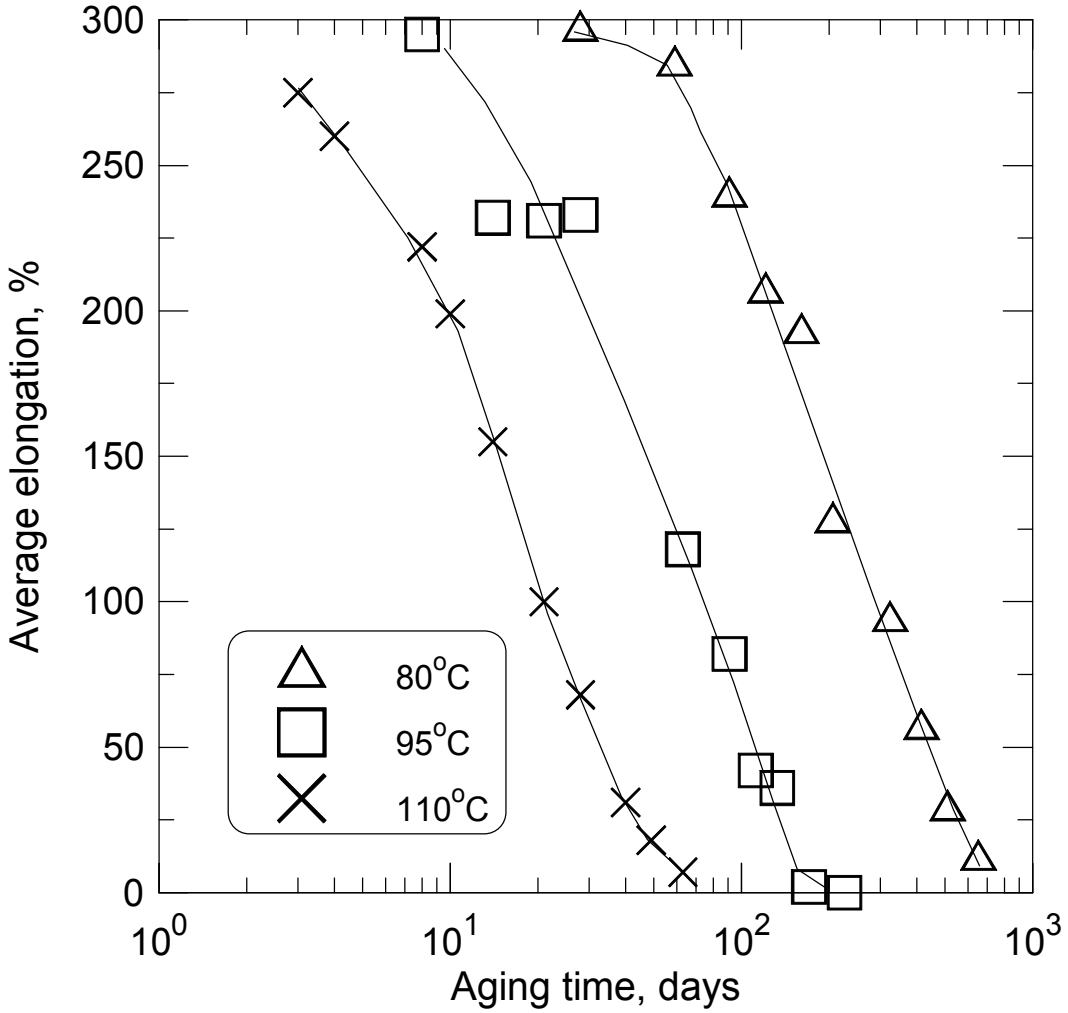
Modulus profiles for samples aged at 95°C show that diffusion-limited oxidation (DLO) is becoming important; at 125°C, DLO effects are very significant





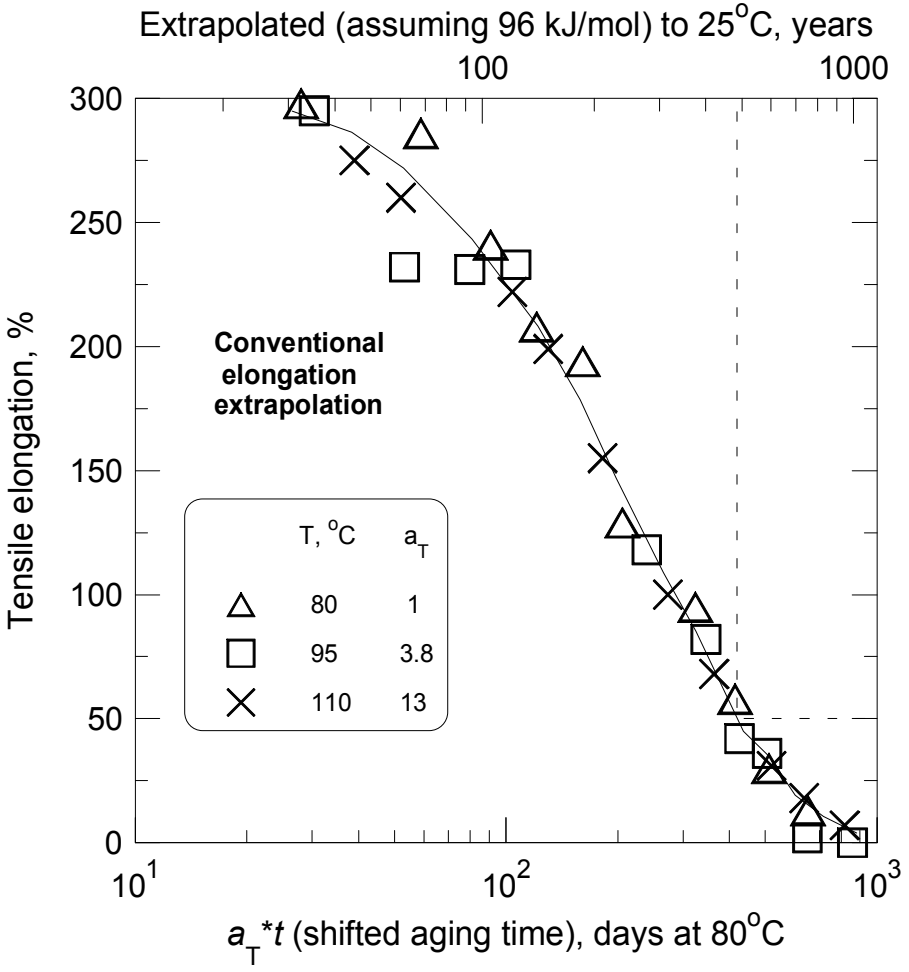
Wise, J.; Gillen, K. T.; Clough, R. L. *Polymer Degradation and Stability, An ultrasensitive technique for testing the Arrhenius extrapolation assumption for thermally aged elastomers 1995, 49, 403-418.*

Neoprene Cable Jacket



Gillen, K. T.; Bernstein, R.; Celina, M. *Polym. Degrad. Stab., Non-Arrhenius behavior for oxidative degradation of chlorosulfonated polyethylene materials 2005, 87, 335-346.*

Neoprene Cable Jacket



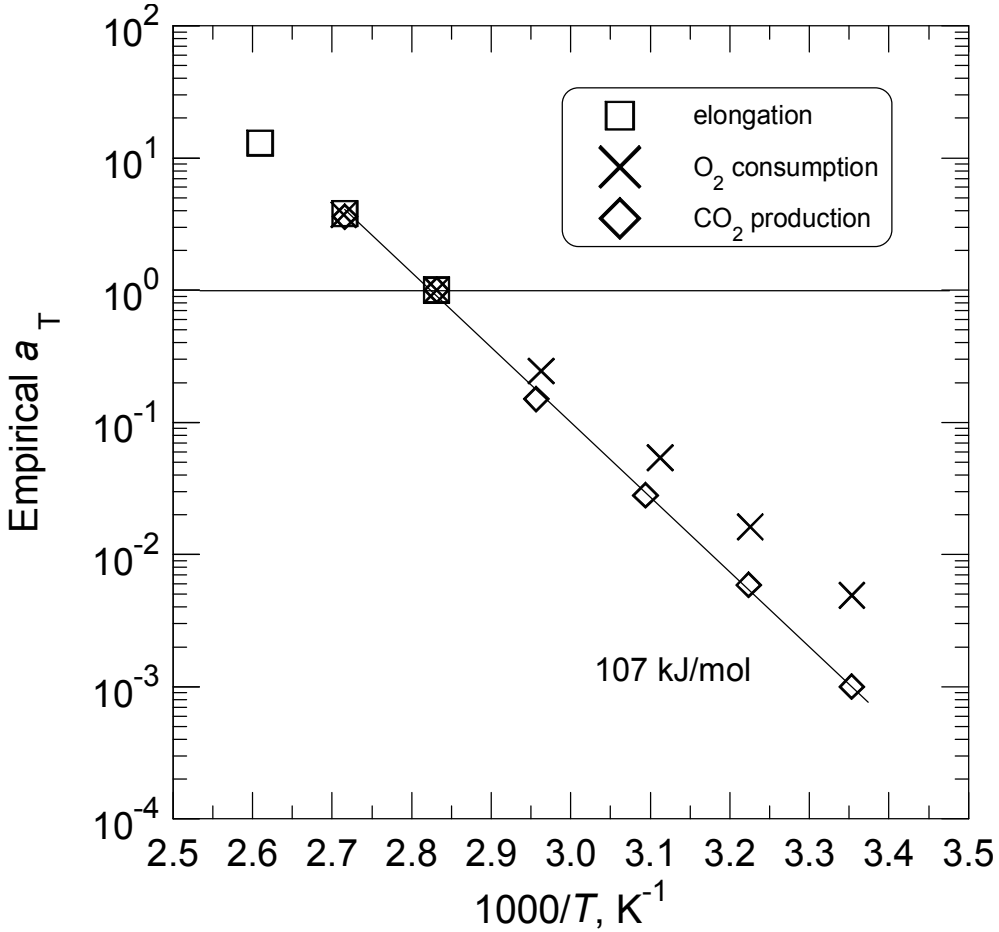
Using just the elongation data:

50% Elongation predicted ~480 years

Gillen, K. T.; Bernstein, R.; Celina, M. *Polym. Degrad. Stab., Non-Arrhenius behavior for oxidative degradation of chlorosulfonated polyethylene materials 2005, 87, 335-346.*

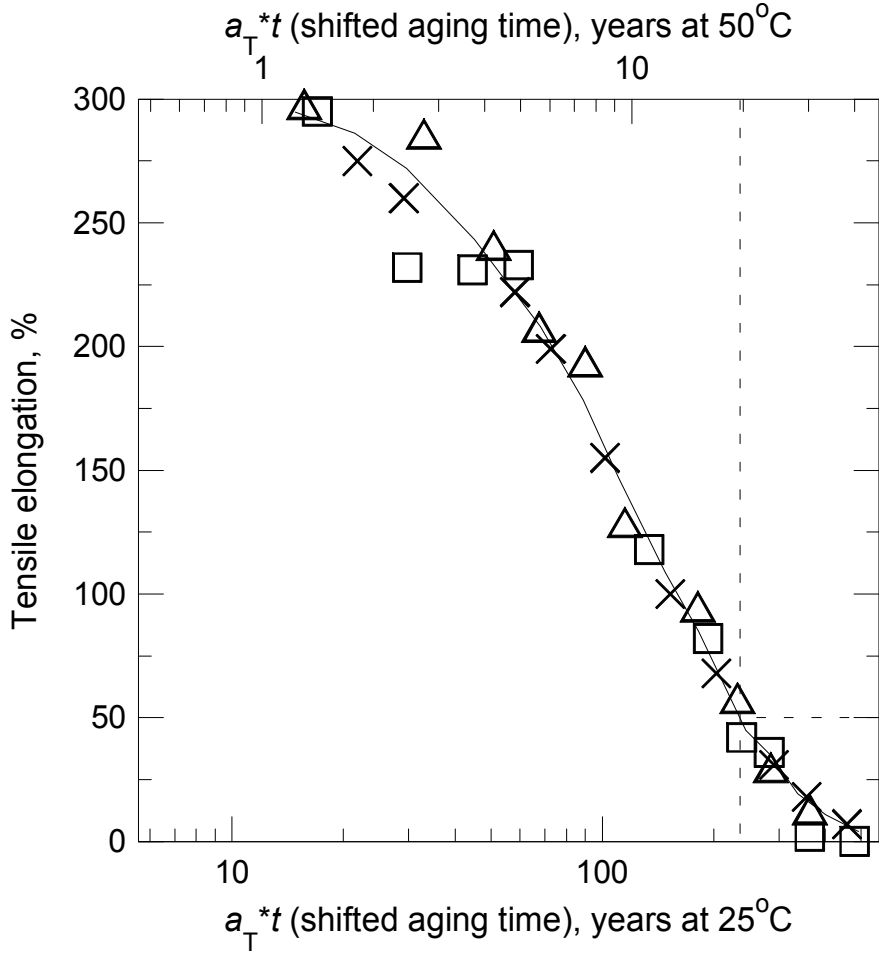
Validation

Using Oxygen Consumption Data



Gillen, K. T.; Bernstein, R.; Celina, M. *Polym. Degrad. Stab., Non-Arrhenius behavior for oxidative degradation of chlorosulfonated polyethylene materials 2005, 87, 335-346.*

Neoprene Cable Jacket



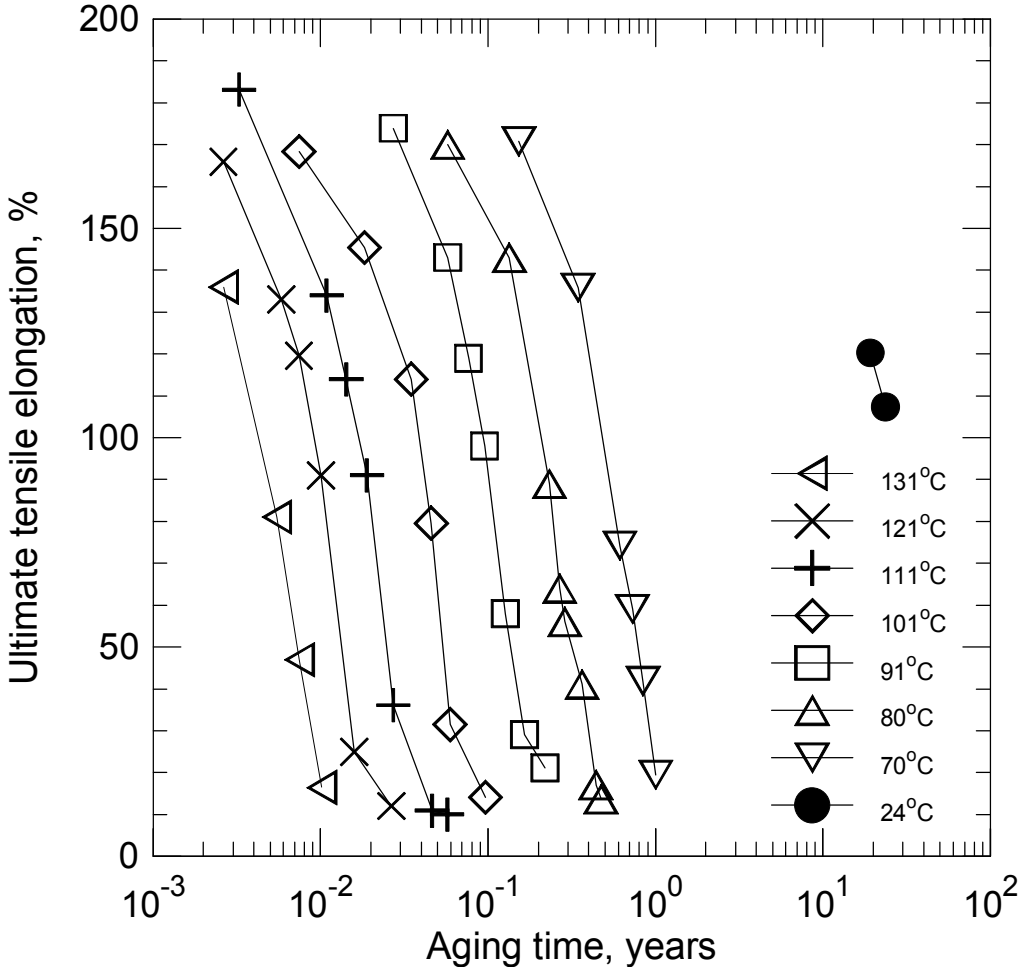
Prediction using the oxygen consumption data:

50% elongation predicted ~230 years

Approximately ½ the prediction from just the elongation

Gillen, K. T.; Bernstein, R.; Celina, M. *Polym. Degrad. Stab., Non-Arrhenius behavior for oxidative degradation of chlorosulfonated polyethylene materials 2005, 87, 335-346.*

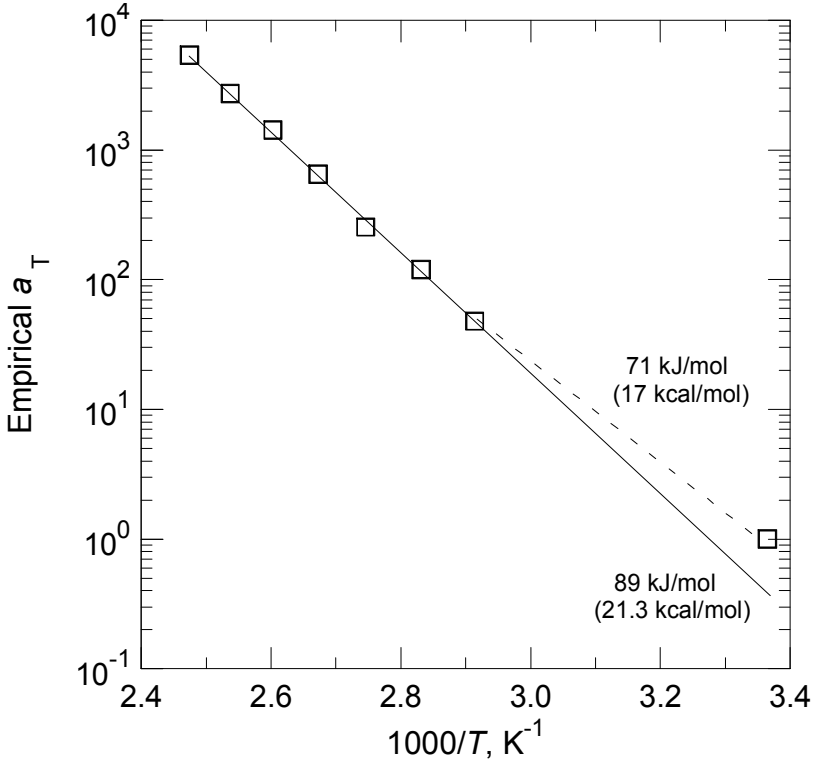
Neoprene (polychloroprene) Aging

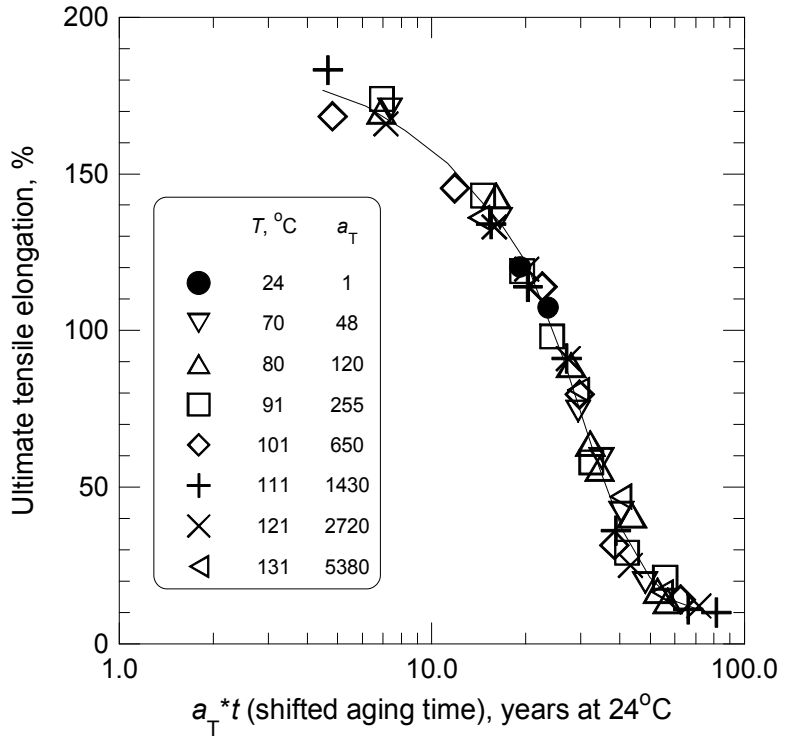


Gillen, K. T.; Bernstein, R.; Celina, M. *Polym. Degrad. Stab., Non-Arrhenius behavior for oxidative degradation of chlorosulfonated polyethylene materials 2005, 87, 335-346.*

Validation

Chloroprene rubber insulation:
Prediction versus 24 year old sample



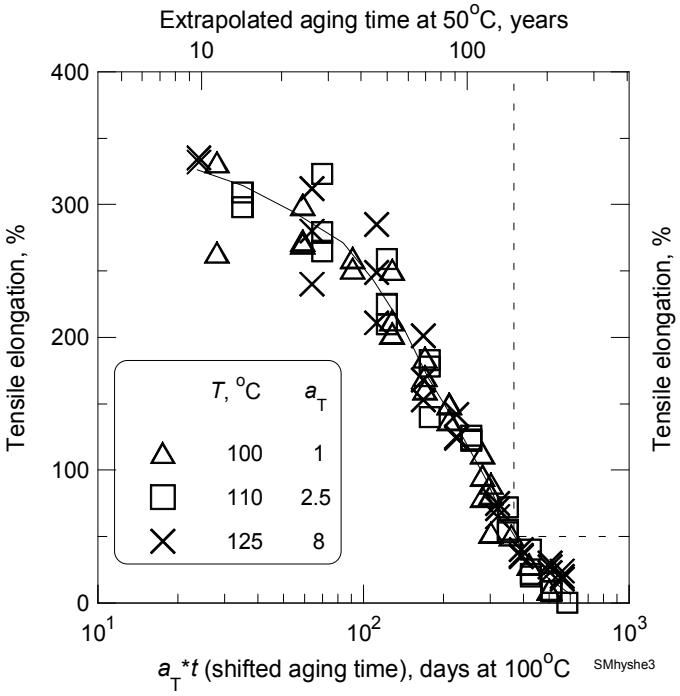


50% predicted to be ~93 years versus 37 years

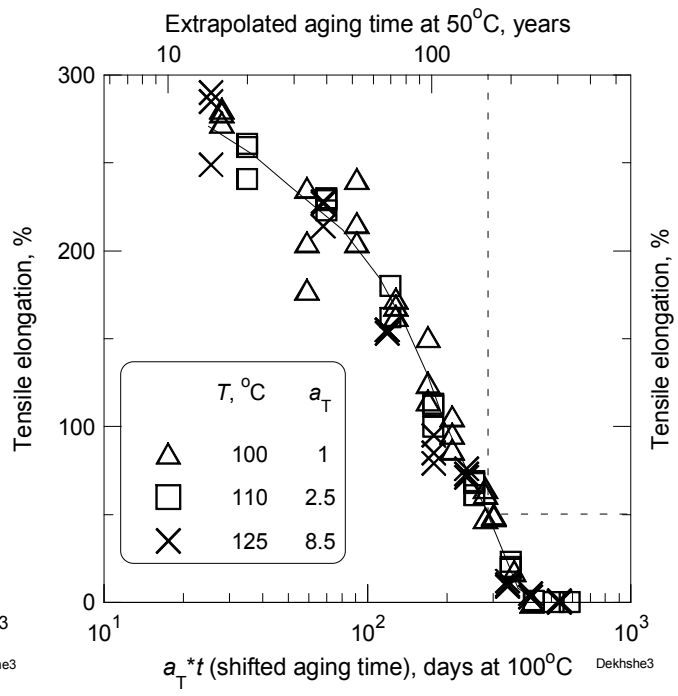
Gillen, K. T.; Bernstein, R.; Celina, M. *Polym. Degrad. Stab., Non-Arrhenius behavior for oxidative degradation of chlorosulfonated polyethylene materials 2005, 87, 335-346.*

Similar results for three additional hypalons

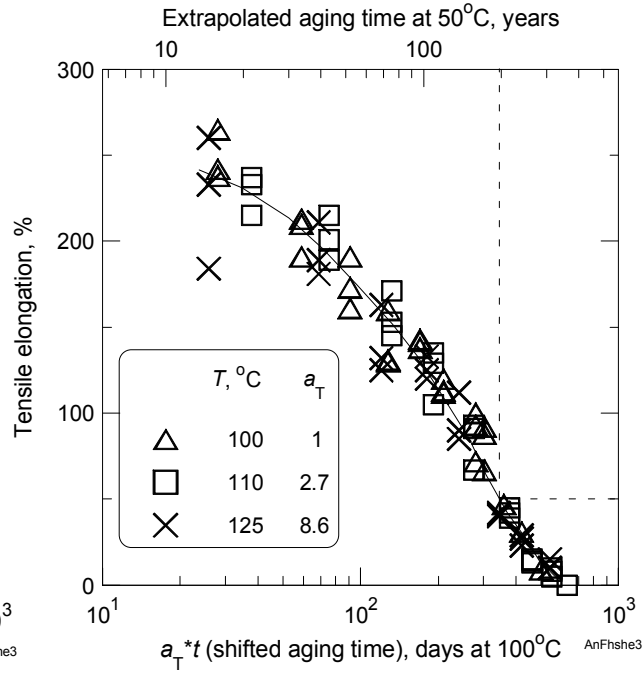
Samuel Moore jacket



Eaton Dekoron jacket



Anaconda Flameguard outer jacket



Predict 160 years at 50°C to reach 50% elongation

Predict 170 years at 50°C to reach 50% elongation

Predict 200 years at 50°C to reach 50% elongation

Results indicate generic behavior may hold for hypalon materials

Gillen, K. T.; Bernstein, R.; Celina, M. *Polymer Degradation and Stability,* Non-Arrhenius behavior for oxidative degradation of chlorosulfonated polyethylene materials 2005, *87*, 335-346.