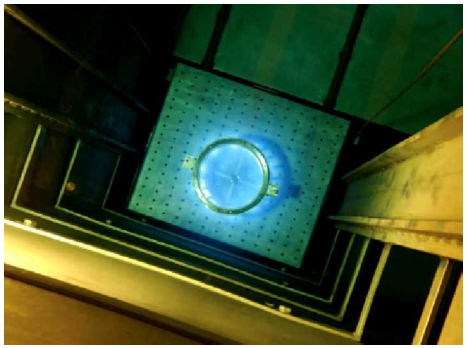
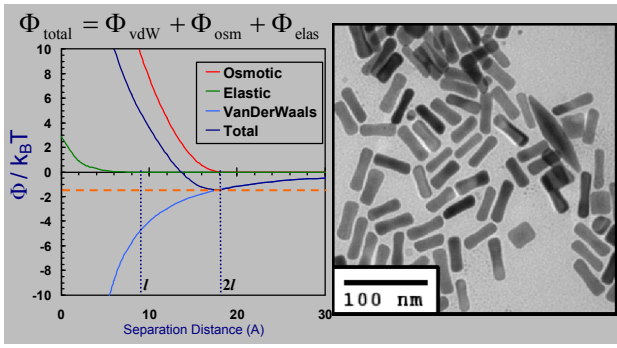
SAND2012-4810P

Exceptional service in the national interest

Sandia National Laboratories





Materials: Synthesis, Characterization, Processing, and Determination of End of Life

Gregory Von White II, PhD.

R&D S&E Chemical Engineer Candidate, Org. 1821

U.S. DEPARTMENT OF ENERGY | NNSA

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  - South East Alliance for Graduate Education and the Professoriate (SEAGEP) for fellowship funding
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  - Dr. Roger L. Clough
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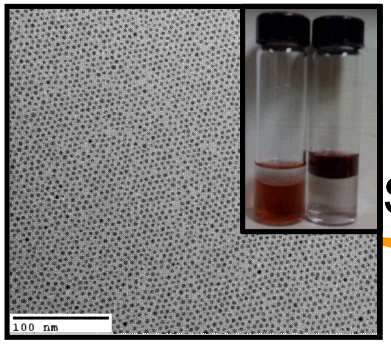
  - Cody Washburn
  - Patti Sawyer, John Schroeder, Derek Wichhart, Michael White, Don Bradley, Ray Boucher, Bradley Hance, Thu Doan, Don Hanson, Maryla Wasiolek

Outline

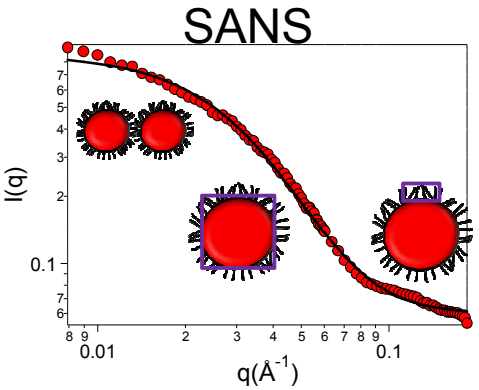


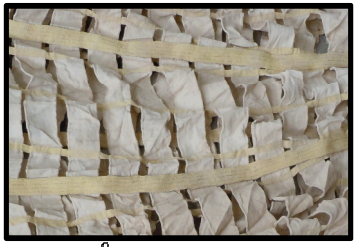
Synthesis

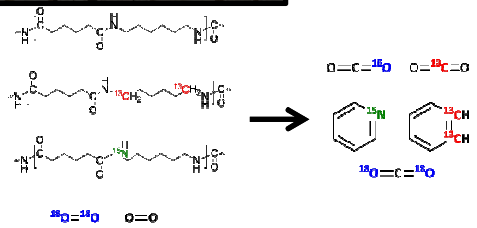
Characterization

Processing

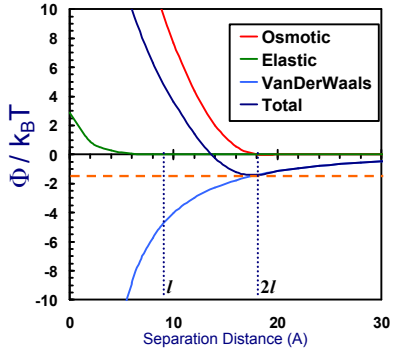
Aging

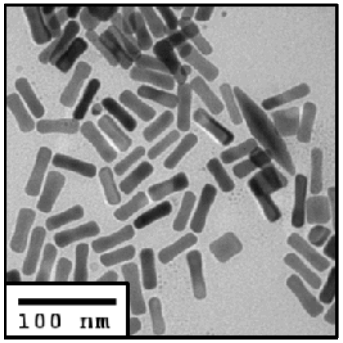






$$\Phi_{total} = \Phi_{vdW} + \Phi_{osm} + \Phi_{elas}$$





Understanding Materials to Aid in Design, Application, and Development of Lifetime Predictions

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

Sandia National Laboratories

O-rings

Nuclear Power Plant Cable Insulation

Aircraft Wire Insulation

Textiles/Fibers

Protective Clothing

Polymer Aging - Approaches/Goals

Sandia National Laboratories

Macroscopic level

Physical Properties

Tensile Property

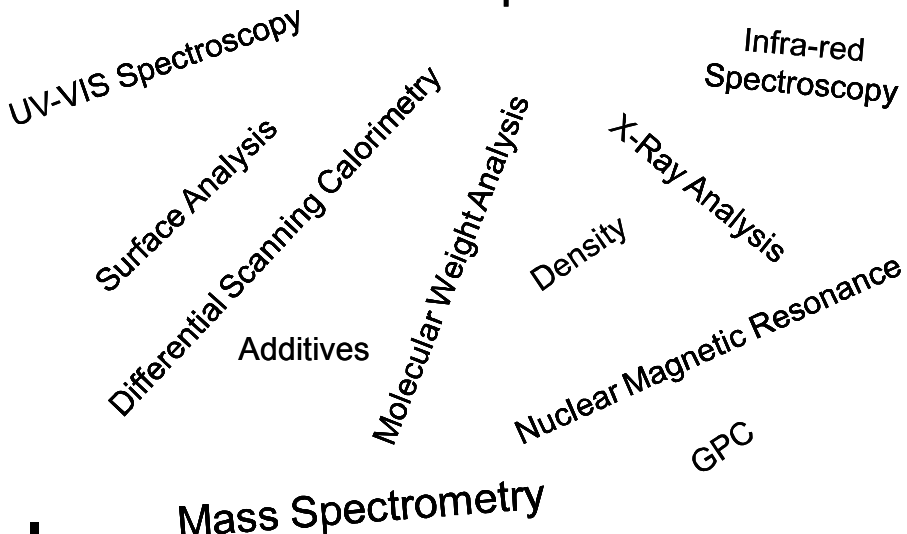
Permeation

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

Polymer Aging - Approaches/Goals

Sandia National Laboratories

Macroscopic level

Physical Properties

Tensile Property

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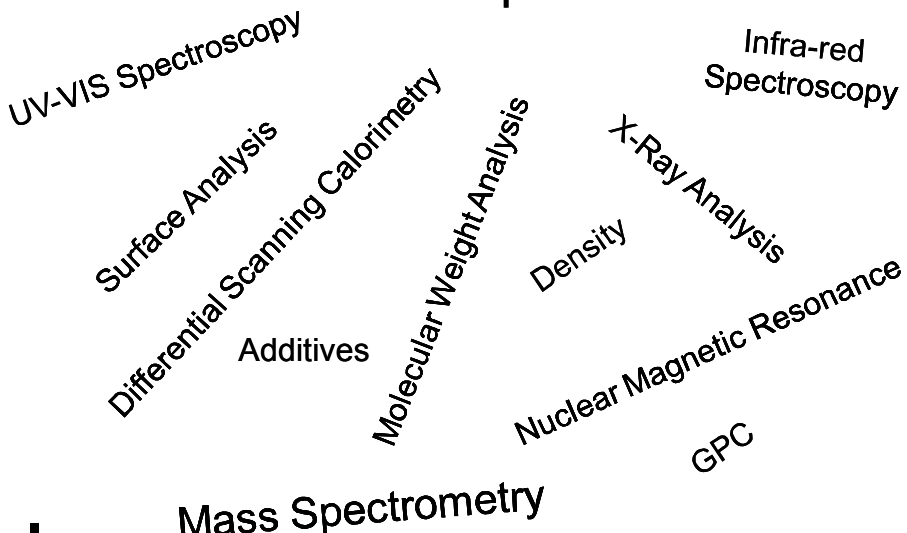
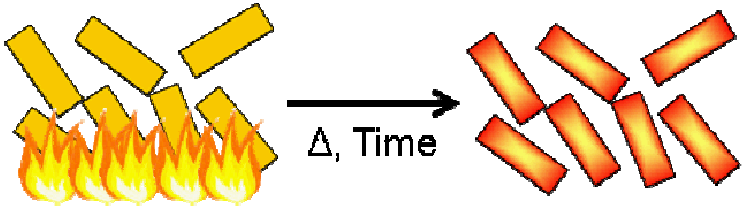


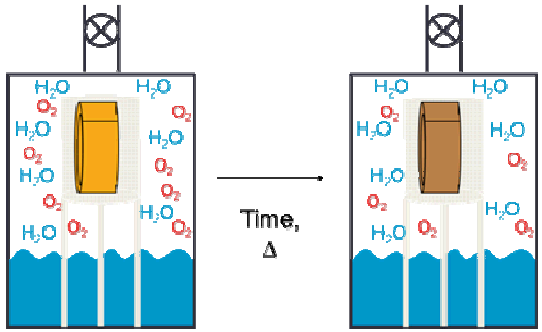
Goals

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

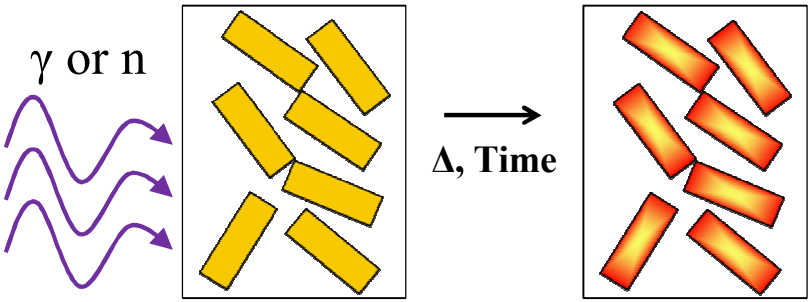
Methodologies



Thermal-Oxidative Aging

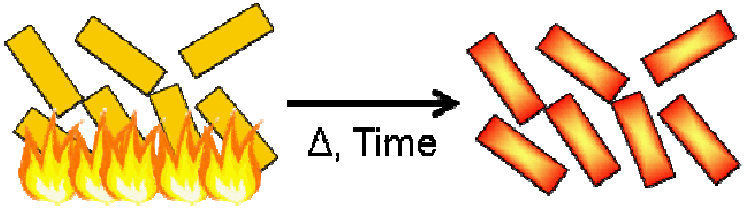


Humidity Aging

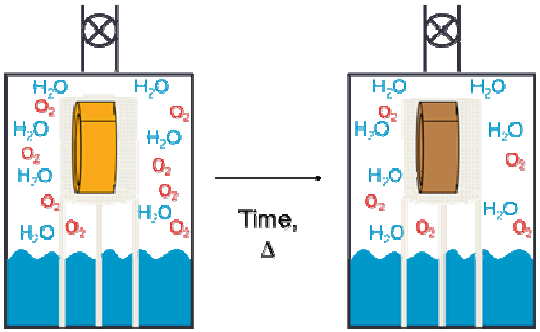


Radiation Aging

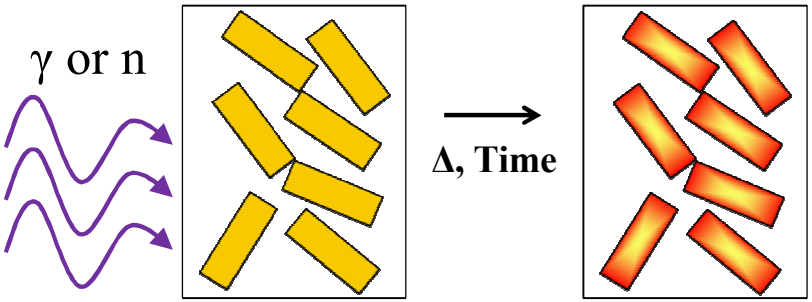
Methodologies



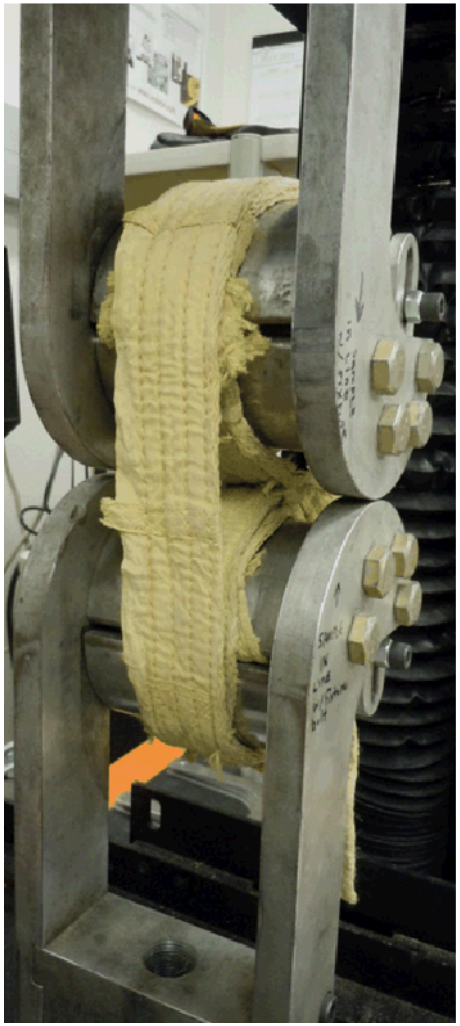
Thermal-Oxidative Aging



Humidity Aging

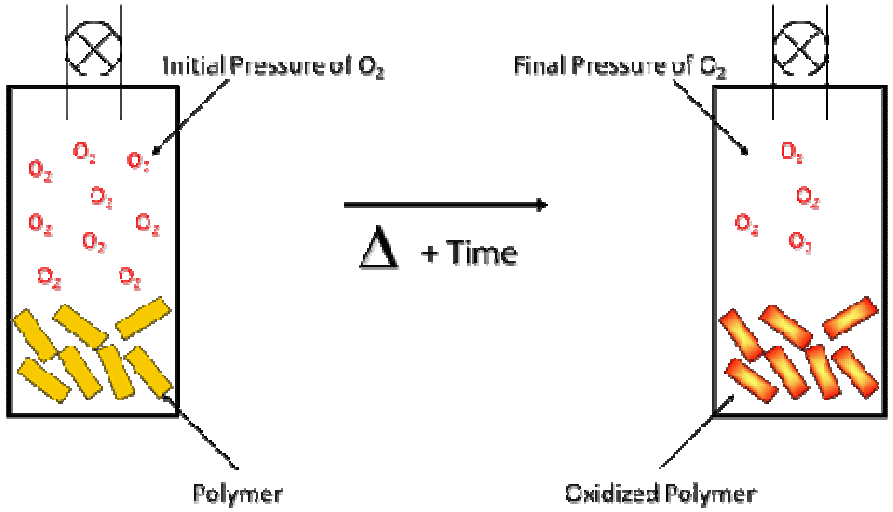


Radiation Aging



Tensile Testing

Methodologies



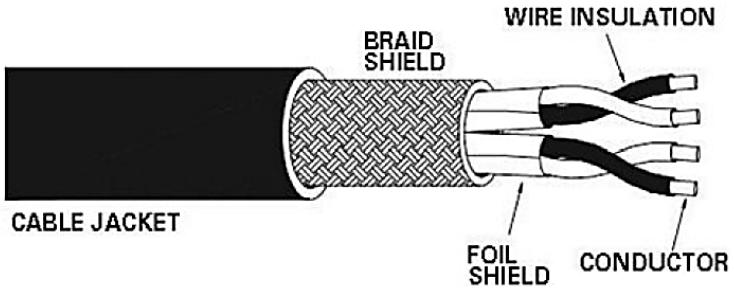
Oxygen Consumption

Sandia National Laboratories

Nuclear Power Plant Cable Insulations

DEVELOPING LIFETIME PREDICTIONS FOR ORGANIC MATERIALS

Power Plant Cables



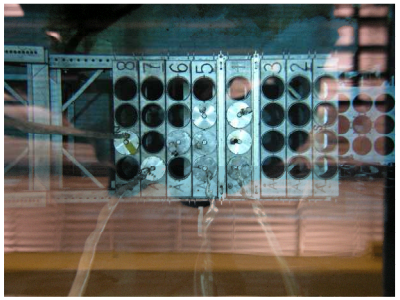
Hashemian, Nuclear Technology 2011, vol. 176, 414-429

Nuclear Power Plant Cable Insulation

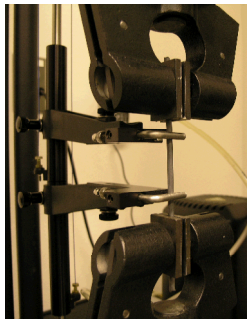
One of the 5 critical concerns for license renewal of US Nuclear Power Plants (NPPs)

IEEE 383-1974: ~50 Mrad (500 kGy) in 40 years at 50 °C

Sample Prep

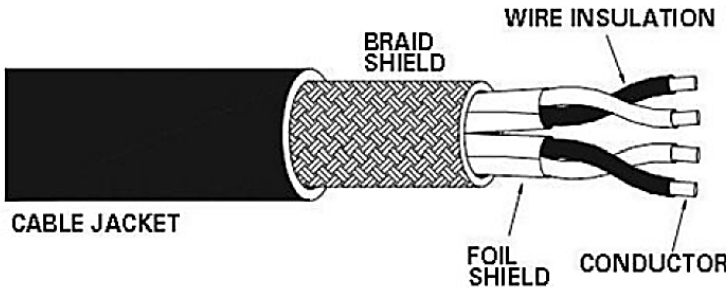


Aging



Tensile Testing

Power Plant Cables



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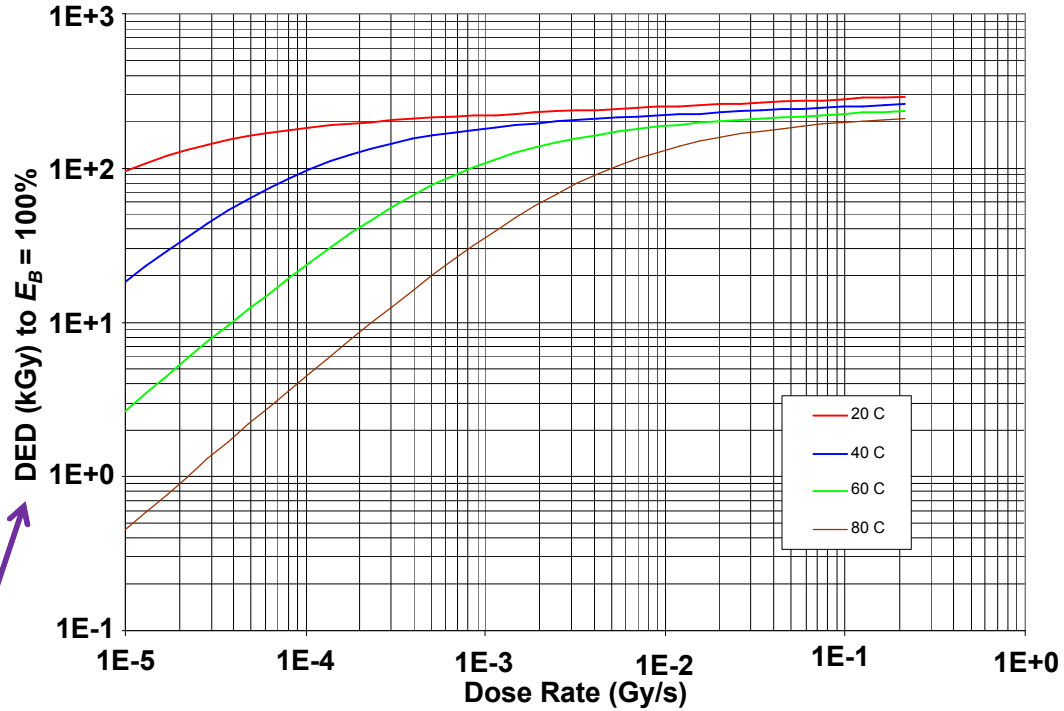


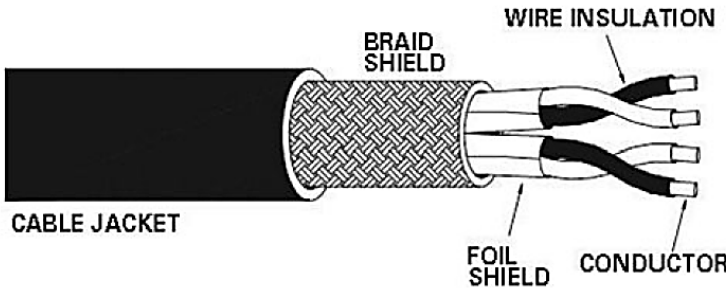
Figure taken from a collaborative (NRC/DOE/EPRI) document ***in progress*** to be published later in 2012 – NUREG 6923, "Expert Panel Report on Proactive Materials Degradation Assessment"

Dose-to-Equivalent Damage = DED

DED is assumed to be E_B = 100%

(IEEE Standards Define End-of-Life when a cable achieves E_B = *50%)*

Power Plant Cables



Hashemian, Nuclear Technology 2011, vol. 176, 414-429

Nuclear Power Plant Cable Insulation

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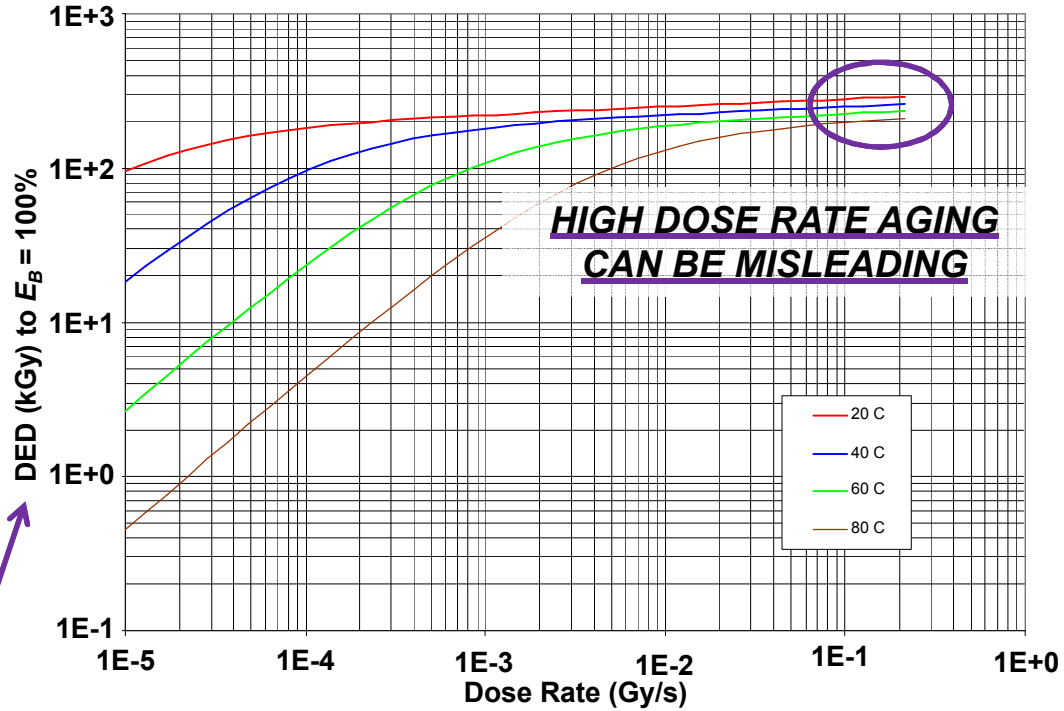

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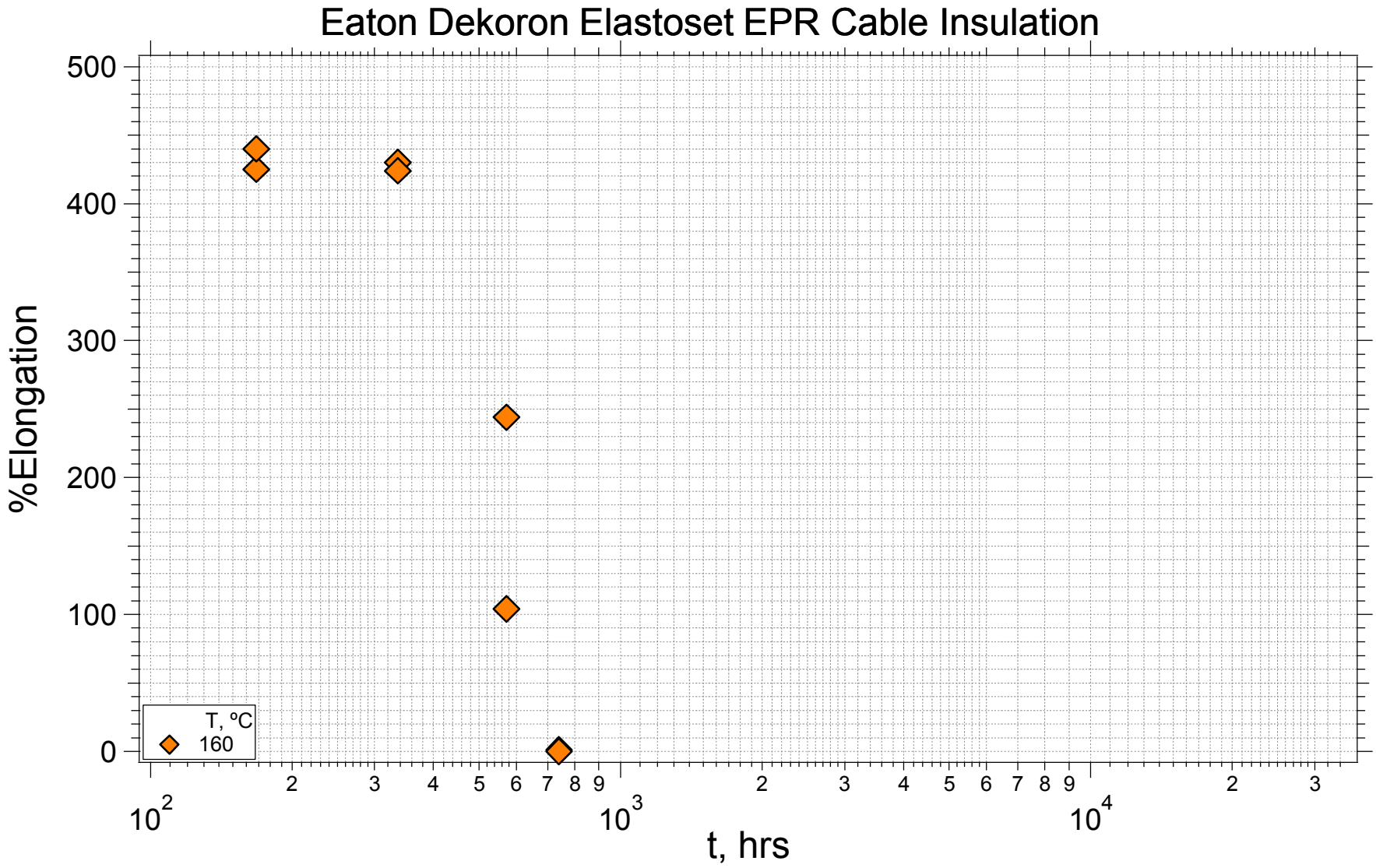
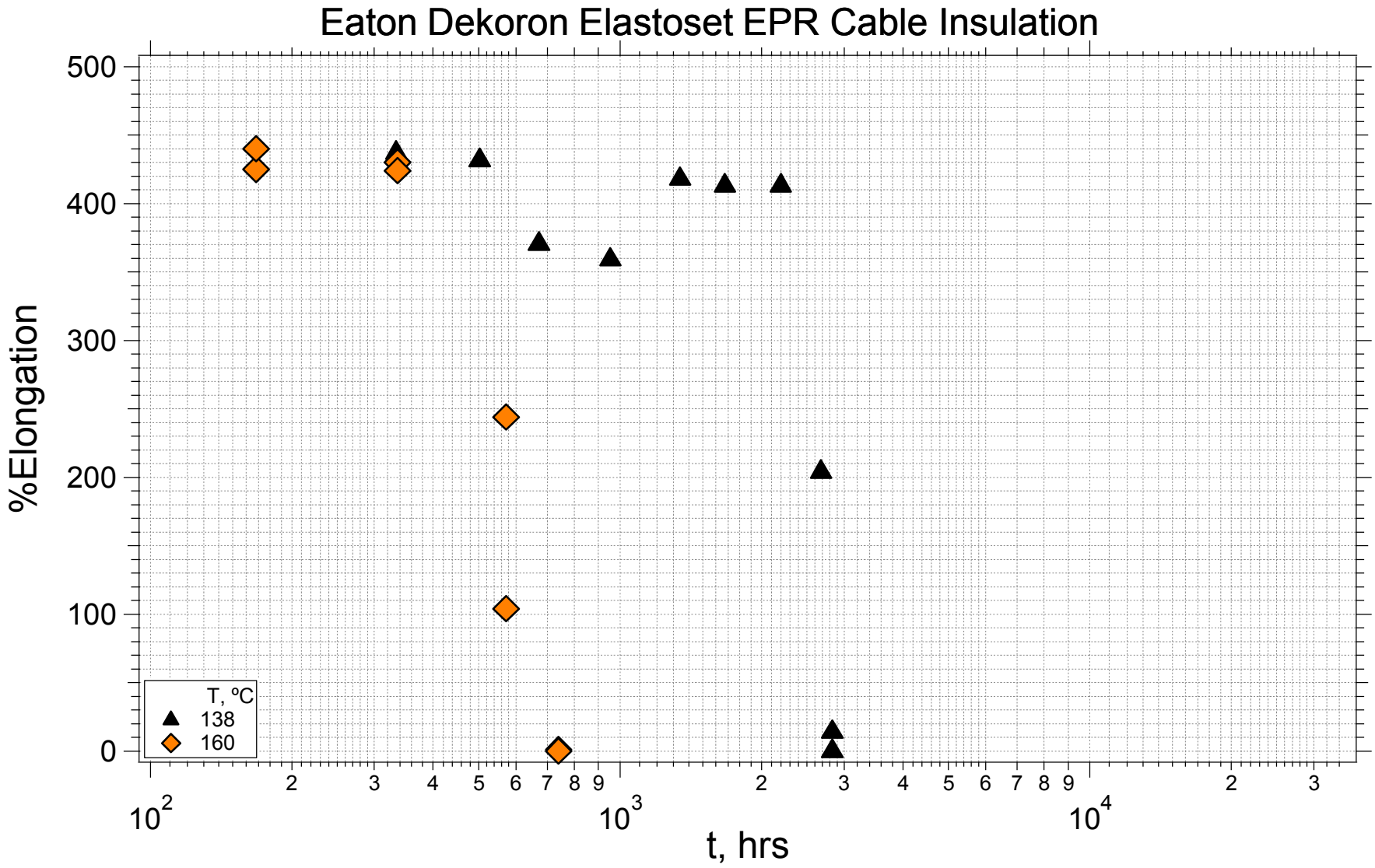
Tensile Properties – Thermal Aging



Tensile Properties – Thermal Aging



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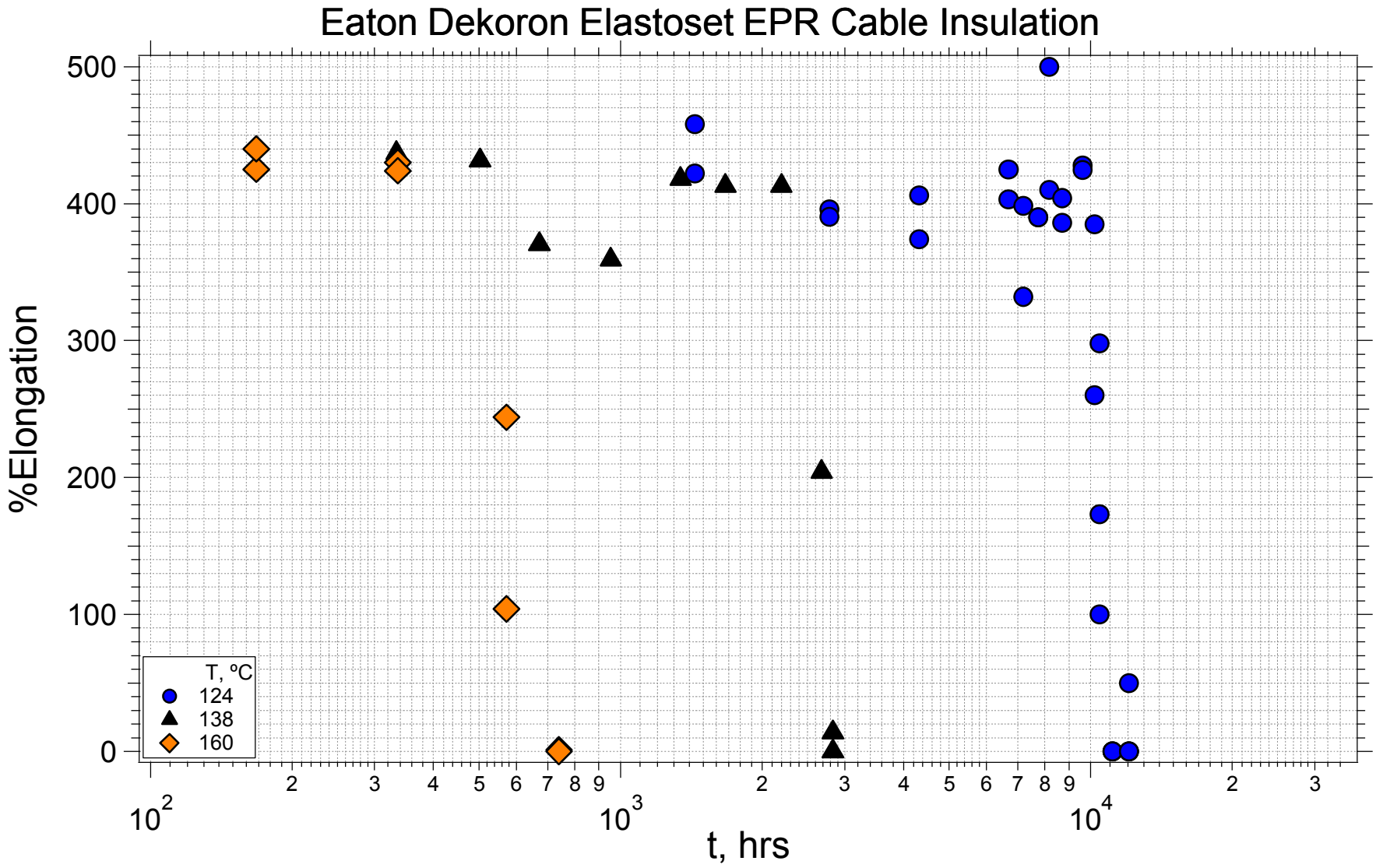
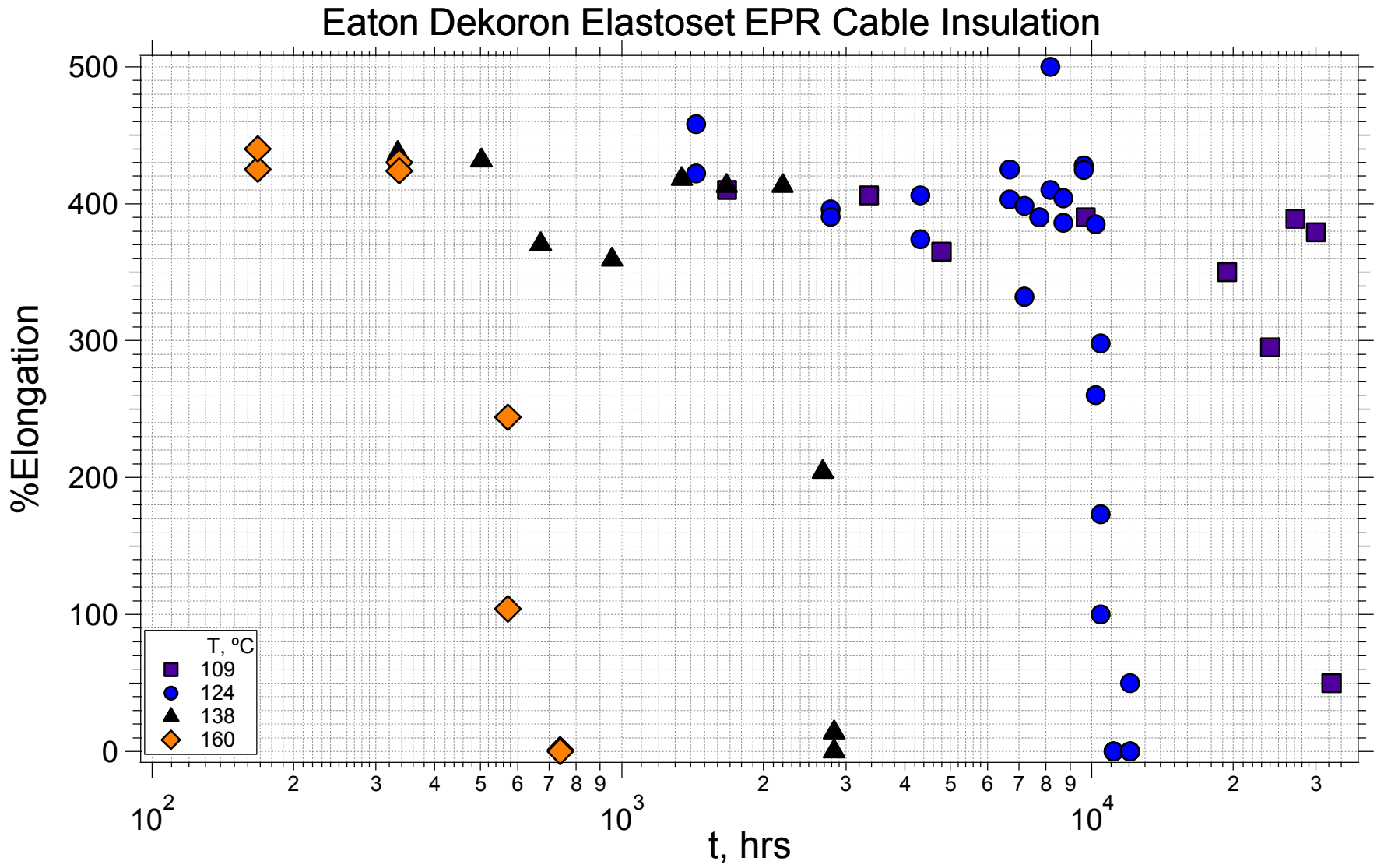


Tensile Properties – Thermal Aging



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.

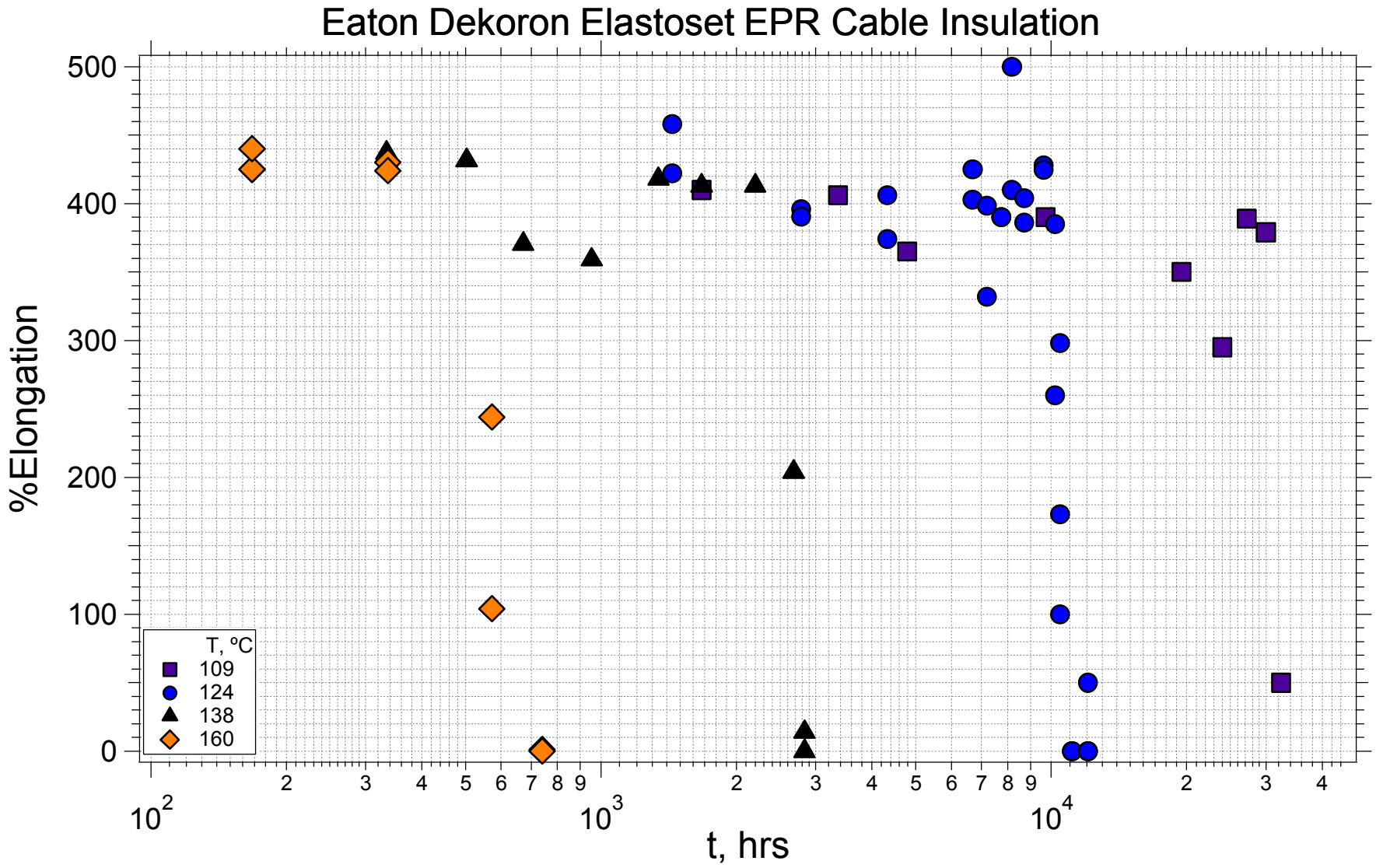
Arrhenius equation:

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

Empirical equation

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

Time-Temperature Superposition



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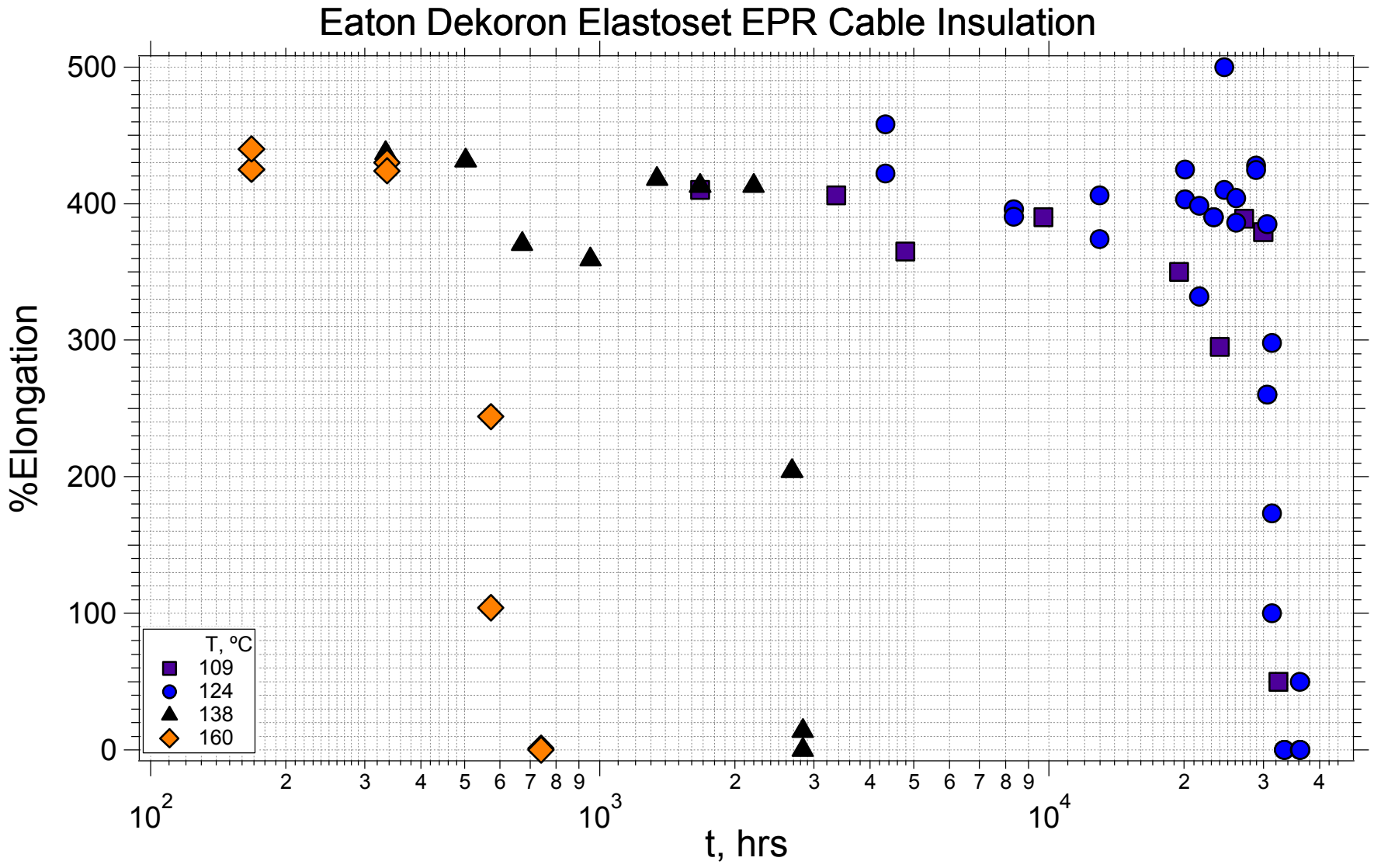

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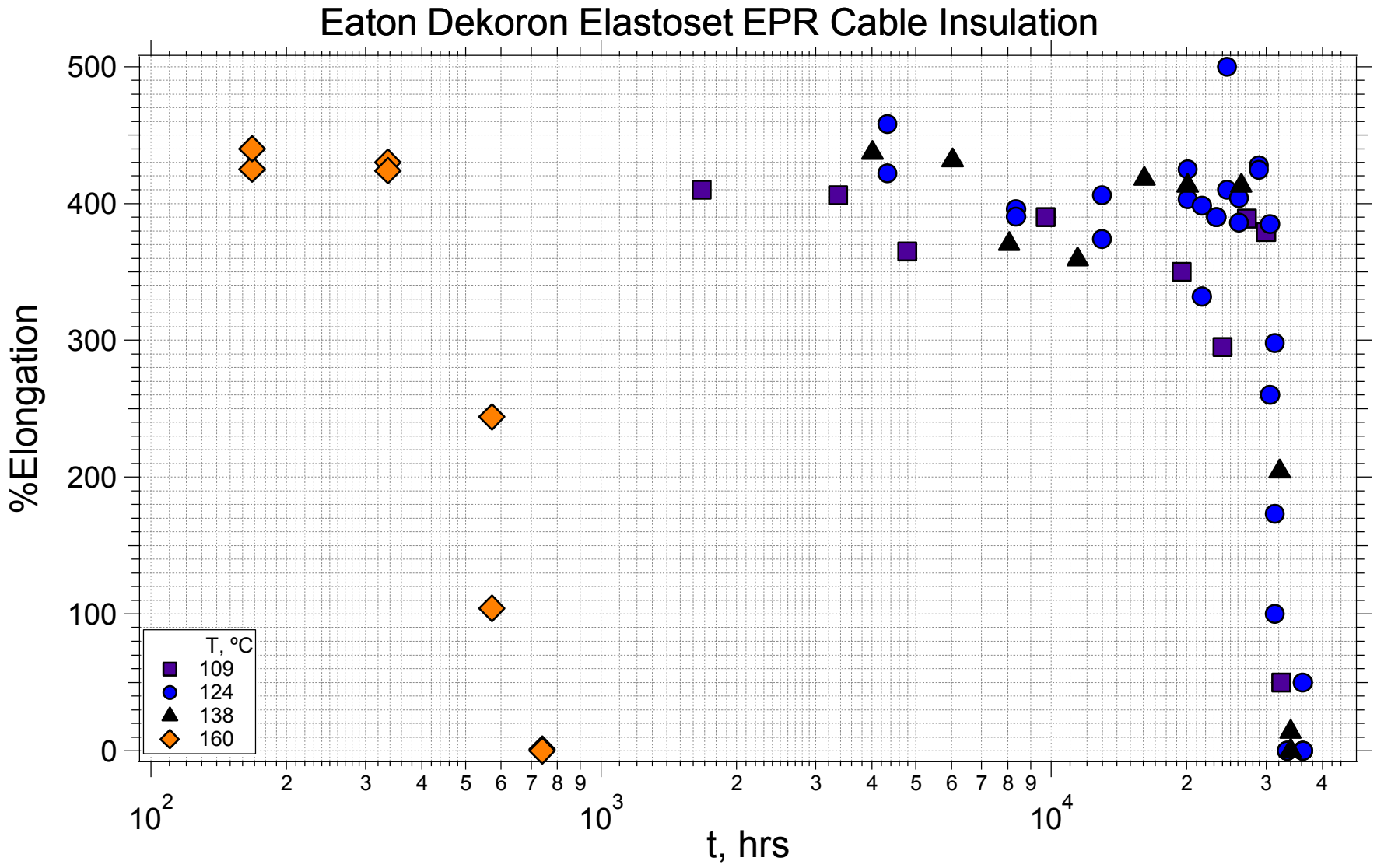

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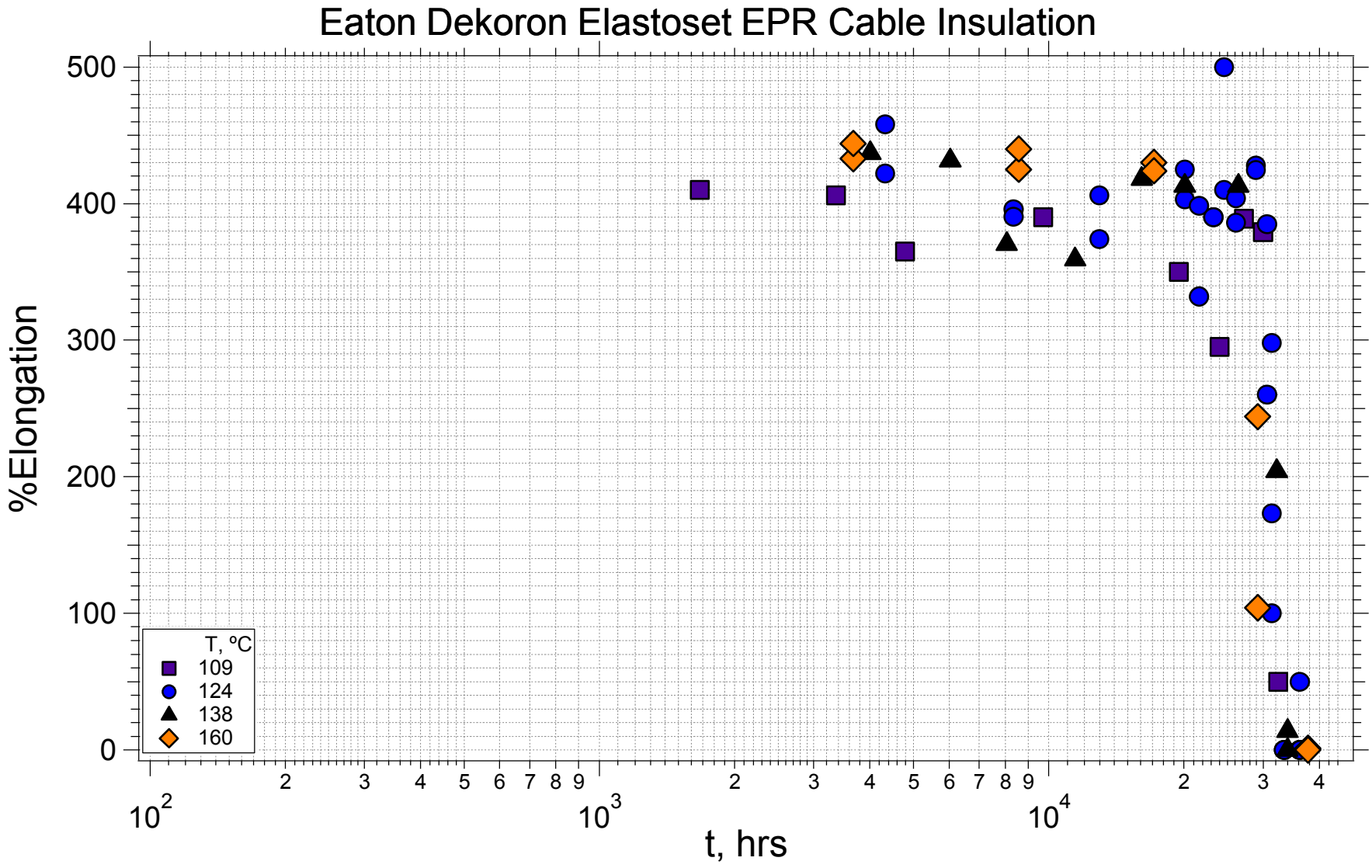
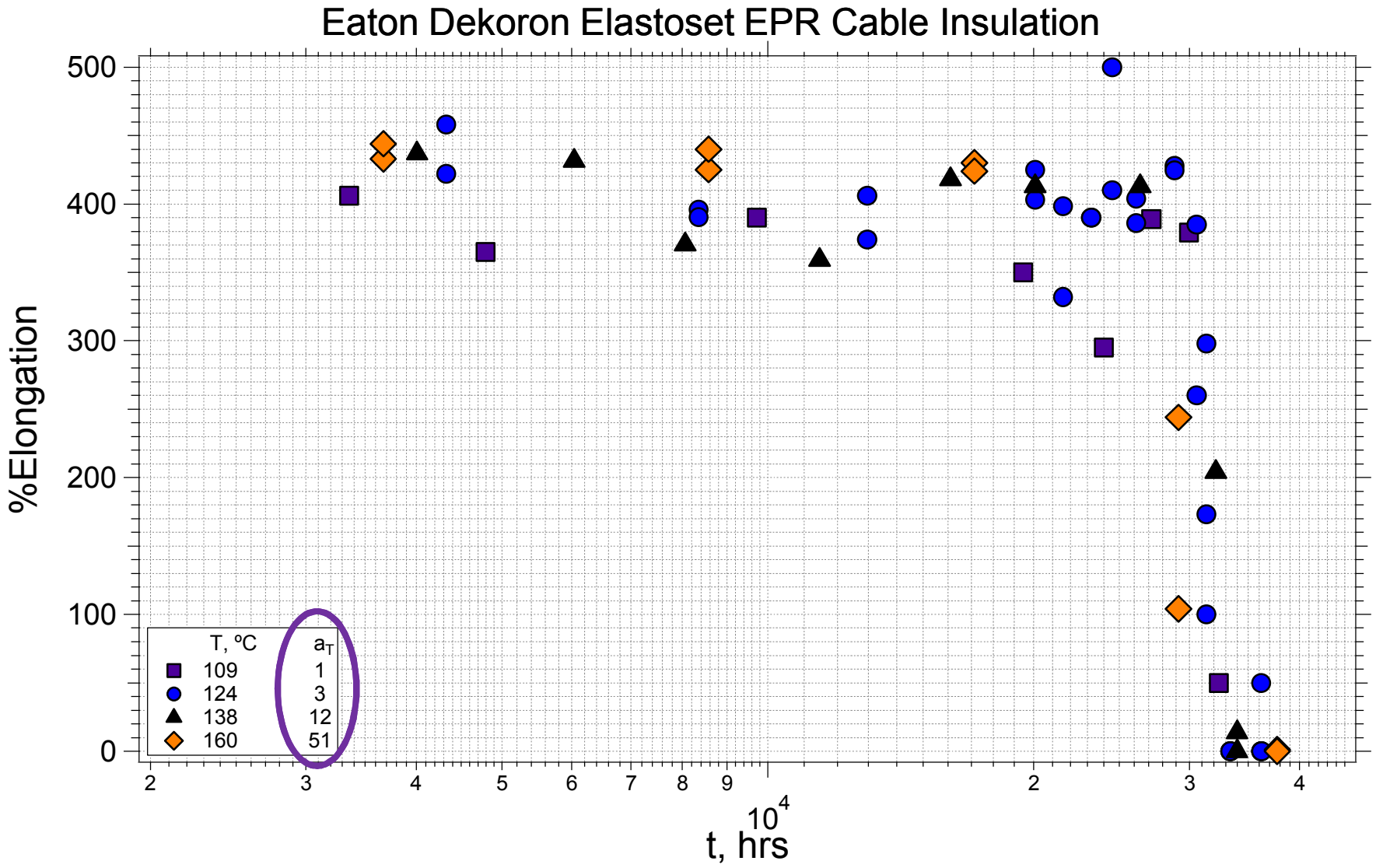


Arrhenius Plot



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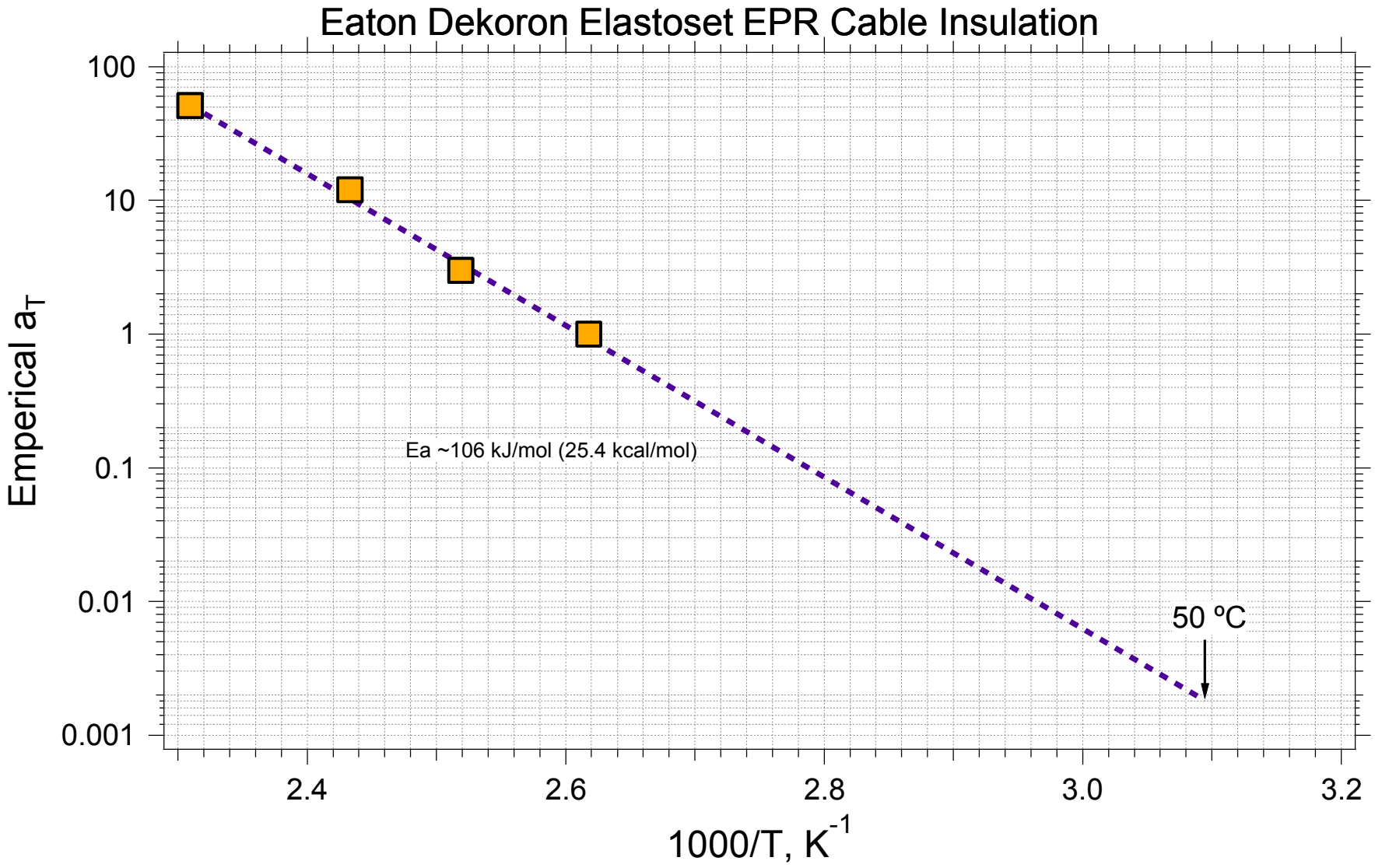
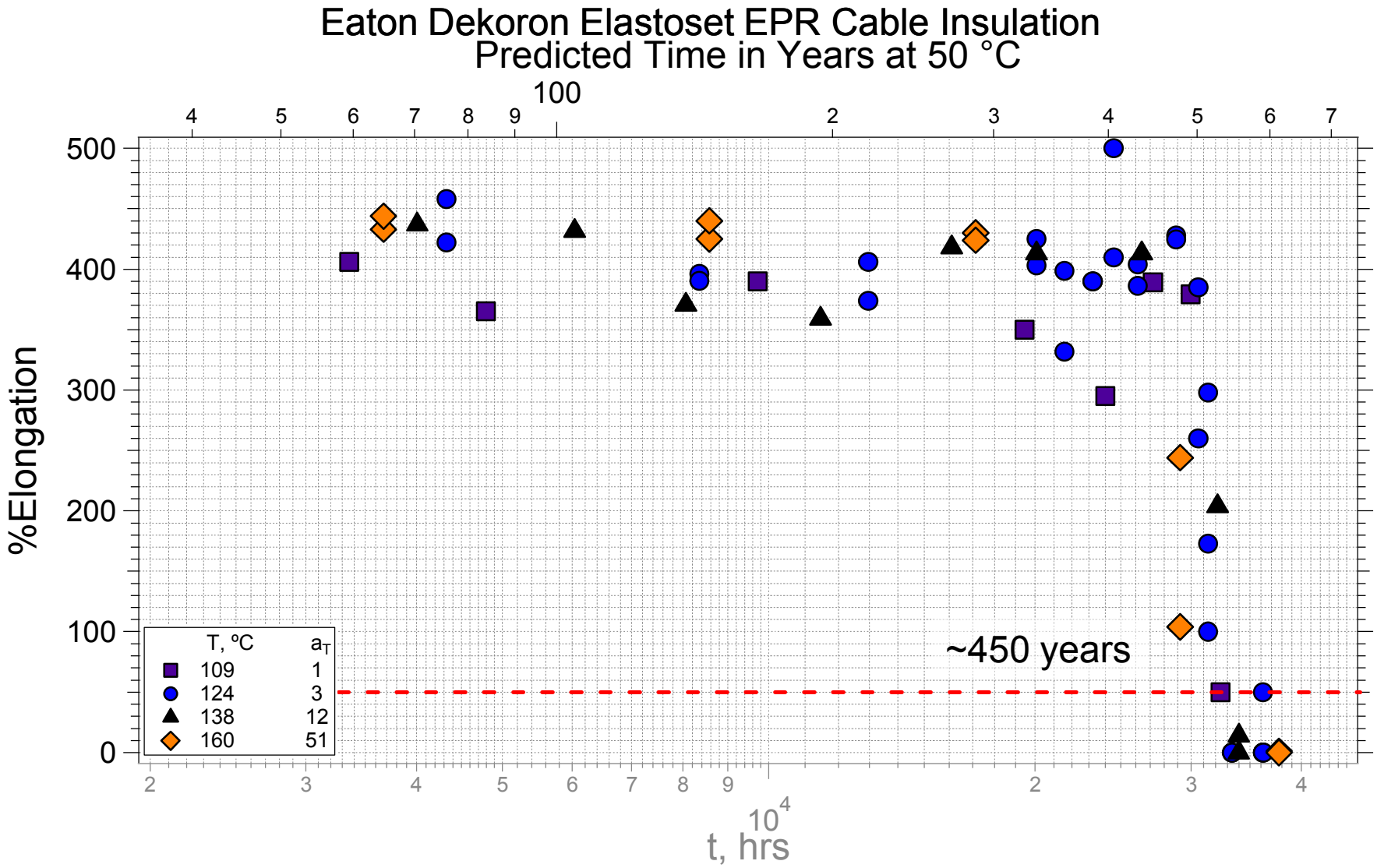
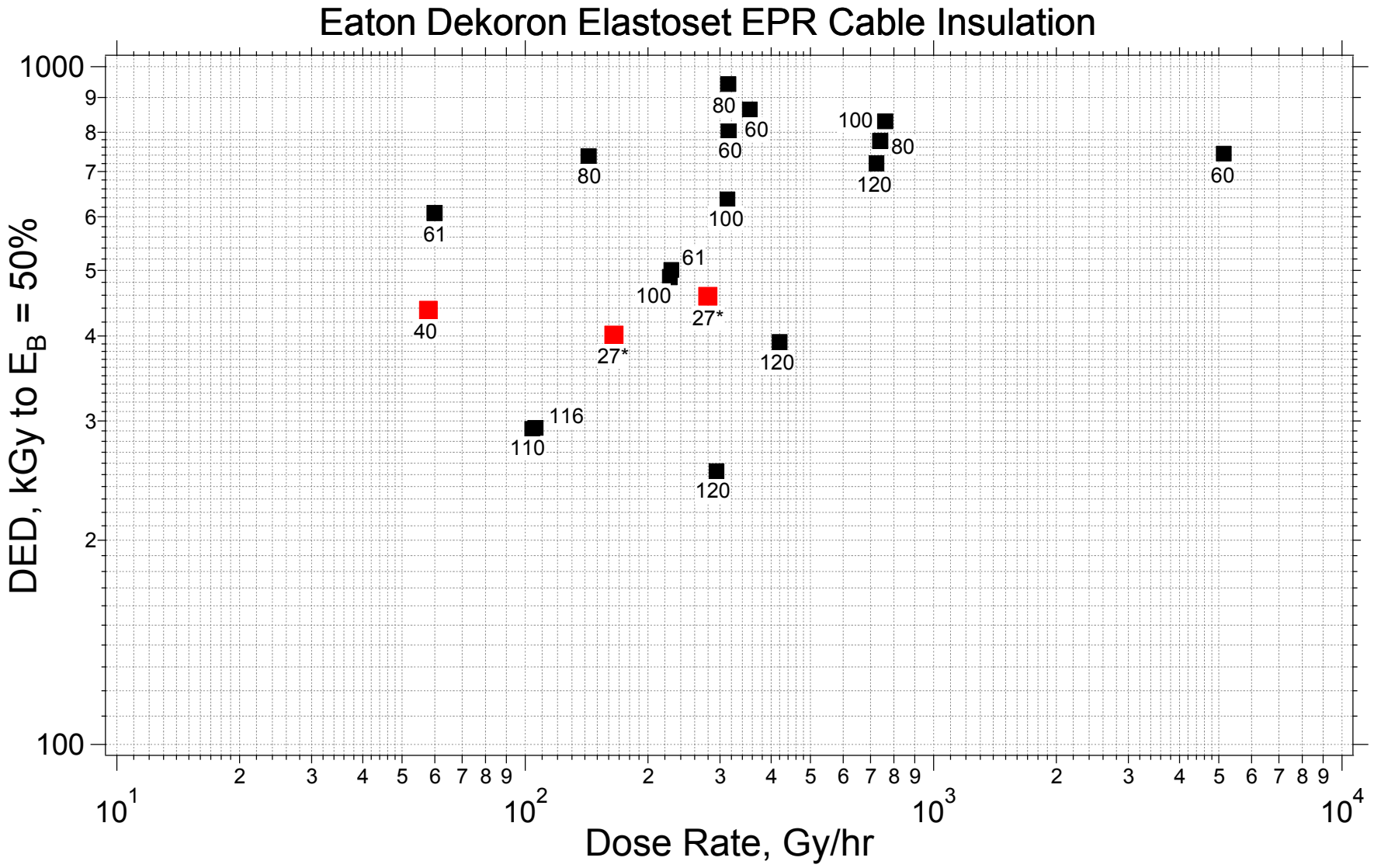


Thermal-Oxidative Prediction



Gamma Irradiation + Thermal Effects



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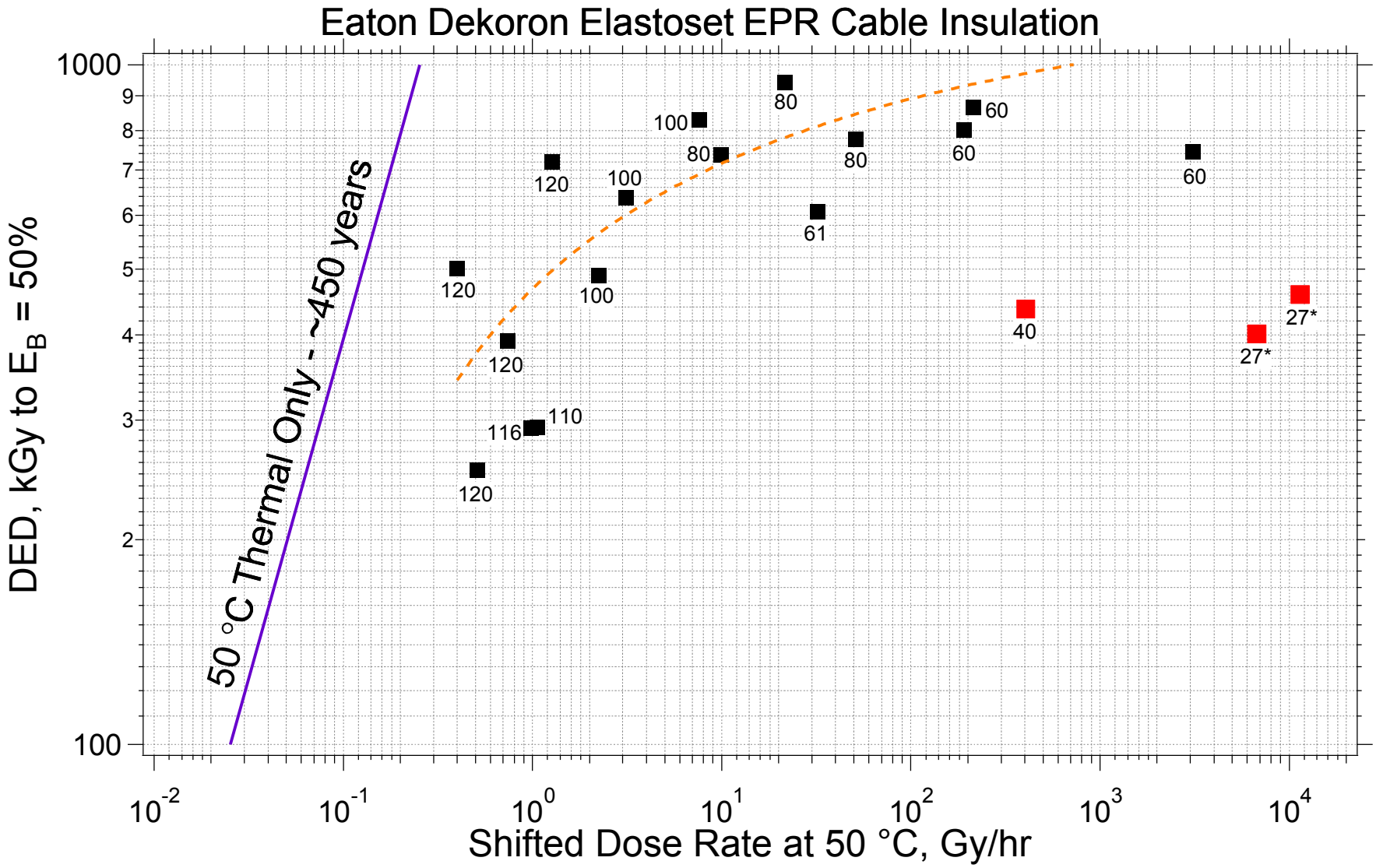


Inverse Temperature Effects

Ongoing NPP Cable Research

Sandia National Laboratories

- Investigate Inverse Temperature Effects at varying low dose-rates and low temperatures for EPR and XLPO materials
  - Experiments are planned out through FY15
- Validate predictive models
  - Received a ~30 year old SiR cable from Argentina, CNEA (environmental conditions include gamma irradiation at elevated temperatures)
- New interest in submerged cables…

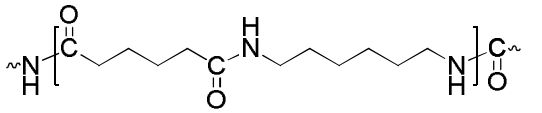
Sandia National Laboratories

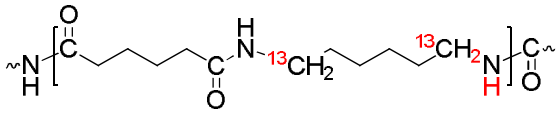
A Basis for Detecting and Mitigating Aging

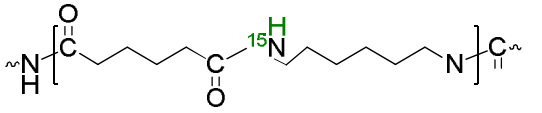
UNDERSTANDING UNDERLYING AGING MECHANISMS

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

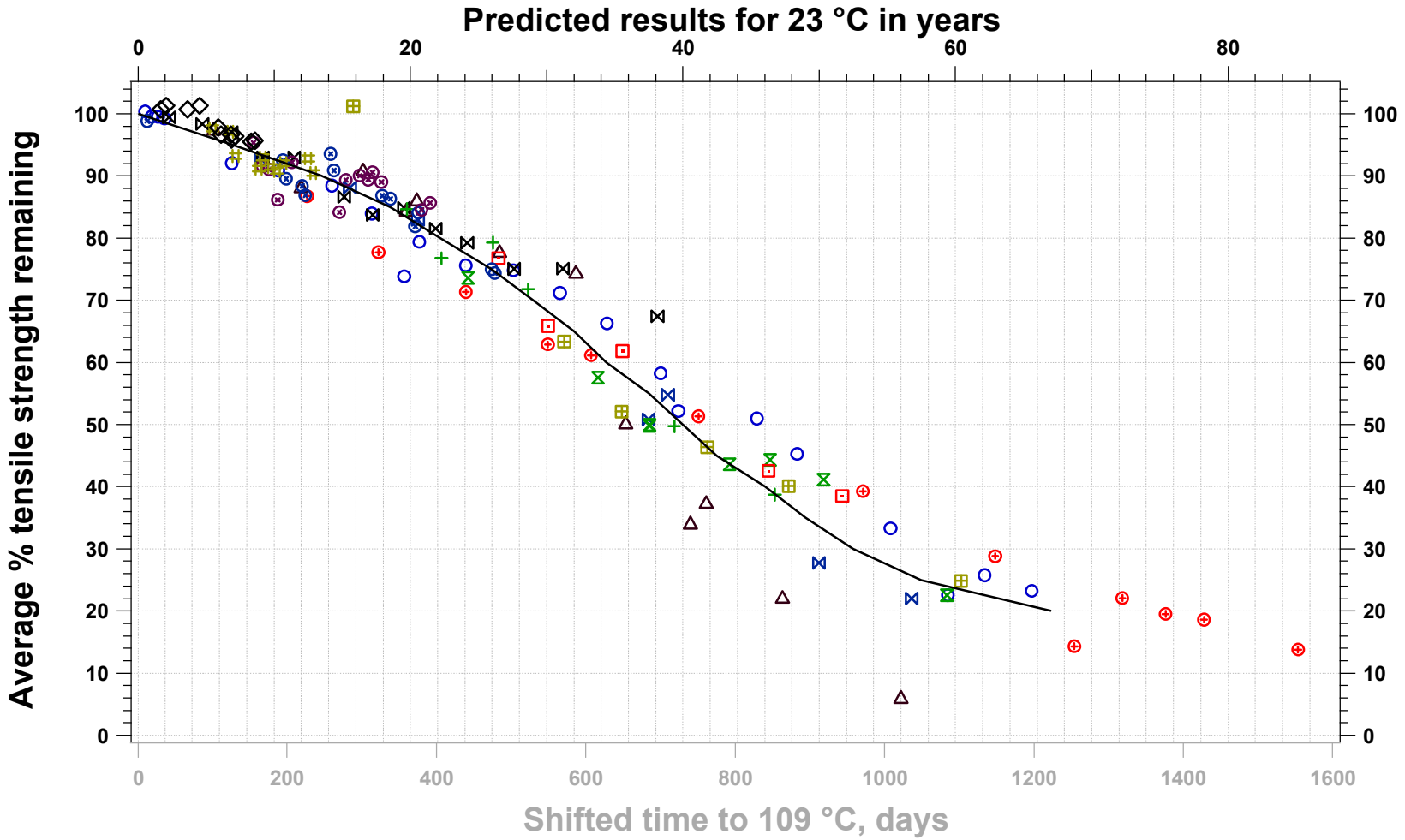






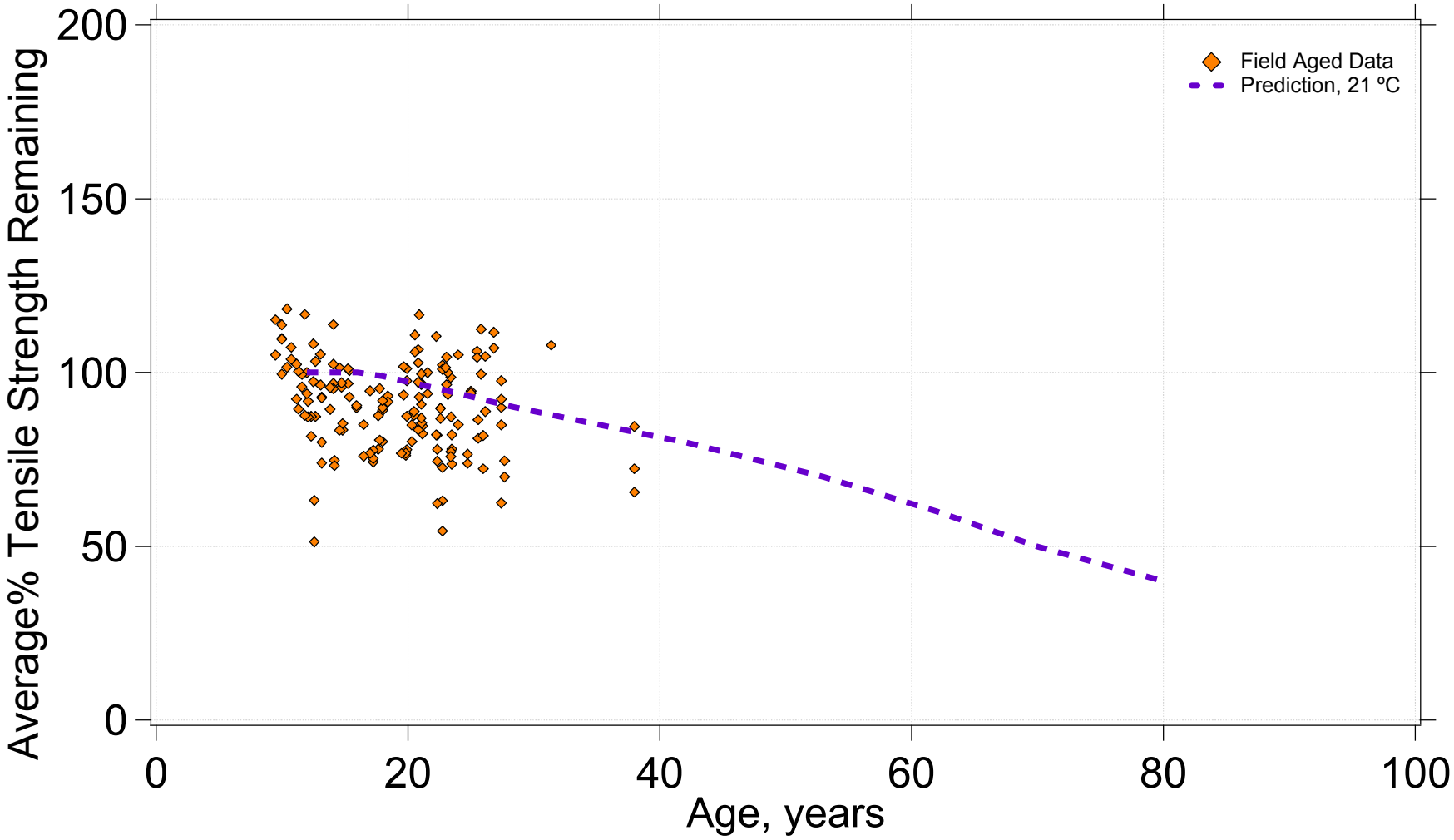
Karstens *Makromol Chem.* **1989**, 190, 3033-3053.
Groning et al. *J. Appl. Polym. Sci.* **2002**, 86, 3396-3407.
Shamey et al. *Rev. Prog. Color* **2003**, 33, 93-107.
Bernstein et al. *Polym. Degrad. Stab.* **2005**, 88, 480-488.
Bernstein et al. *Polym. Degrad. Stab.* **2010**, 95, 1471-1479.
Smith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

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



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Sandia National Laboratories

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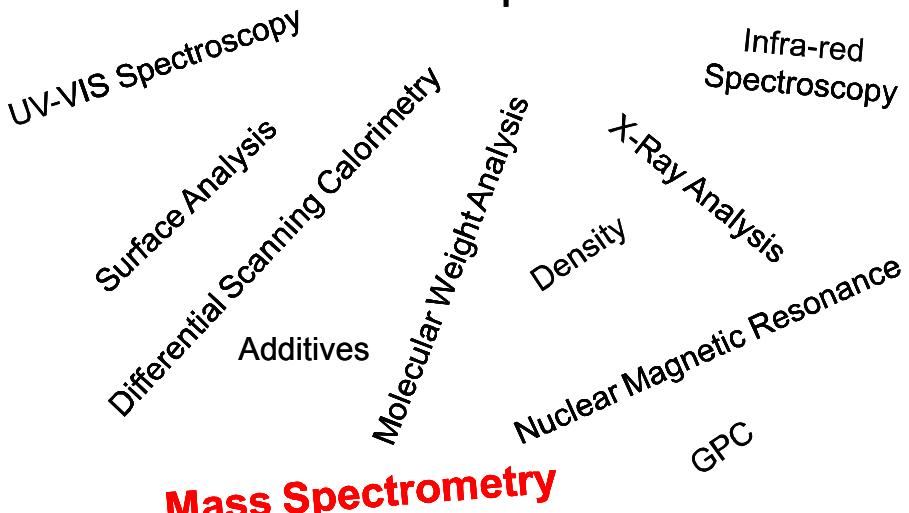

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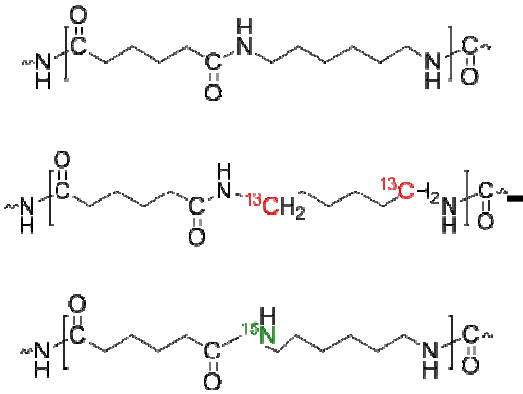
Methodologies

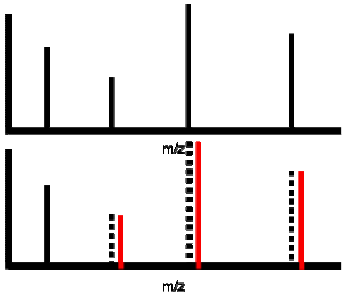


Isotopically labeled and unlabeled nylon 6.6 were aged in 5 cm^3 stainless steel vessels between 1 and 243 days at 109 °C and 138 °C

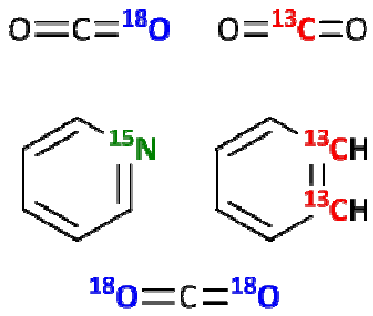
Cryo-GC/MS

Identify degradation

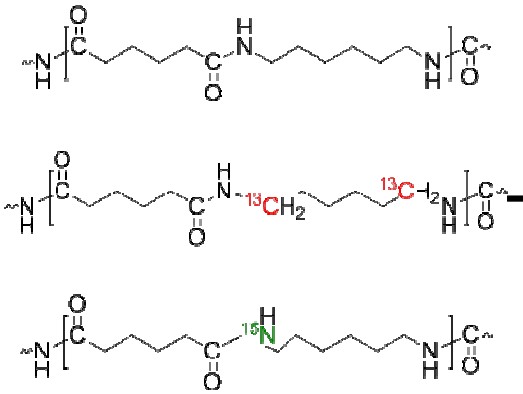
Monitor mass spectra for shifts



Use mass shifts to determine degradation



Methodologies

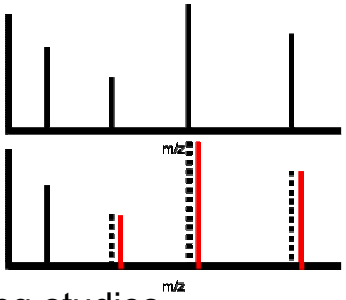


Isotopically labeled and unlabeled nylon 6.6 were aged in 5 cm^3 stainless steel vessels between 1 and 243 days at 109 °C and 138 °C

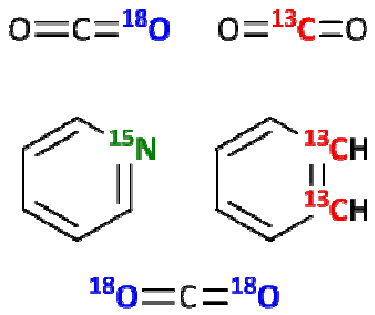
Cryo-GC/MS

Identify degradation

Monitor mass spectra for shifts

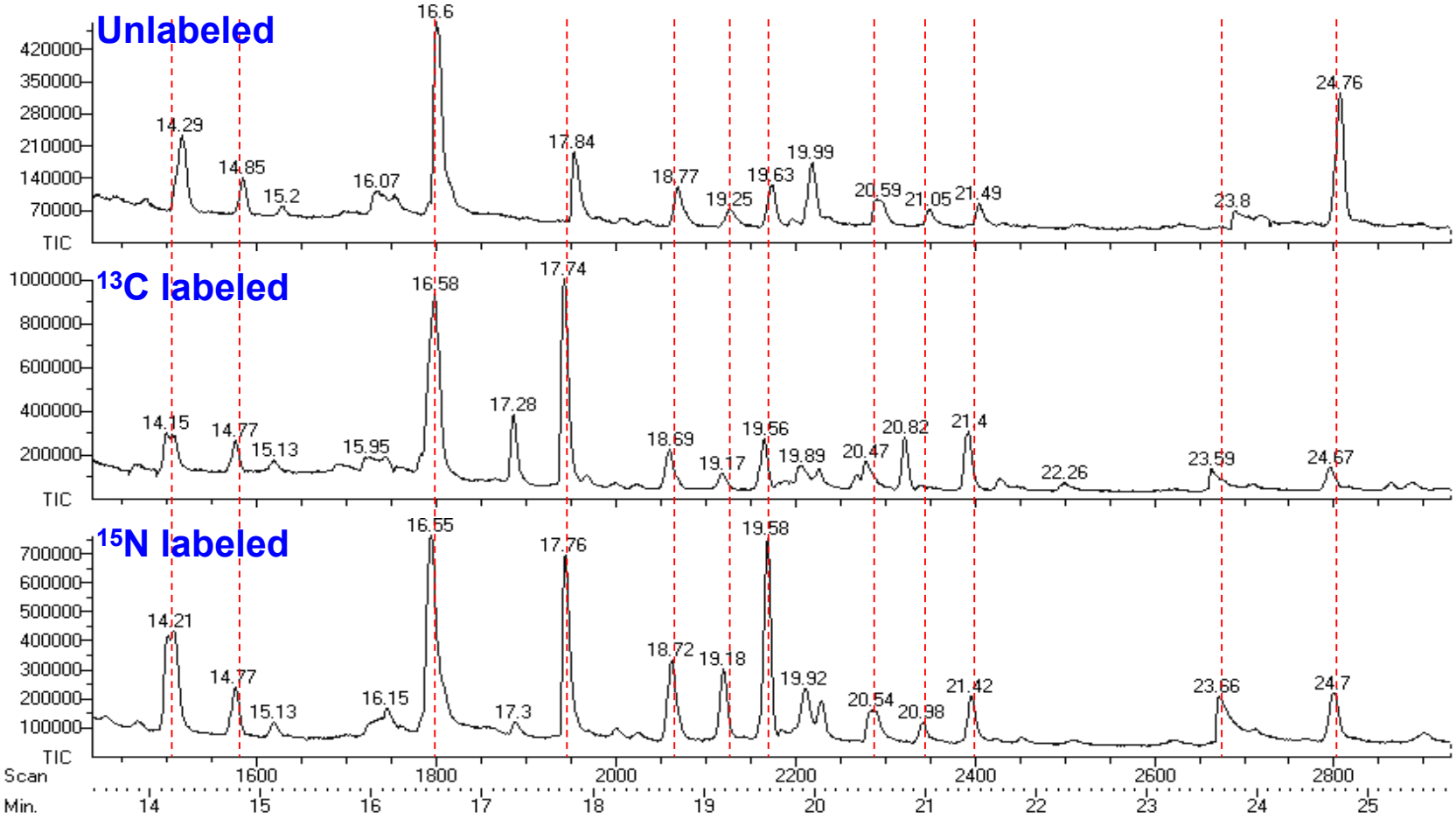


Use mass shifts to determine degradation



Caveat: It is critical to employ ***well characterized*** polymers in your aging studies

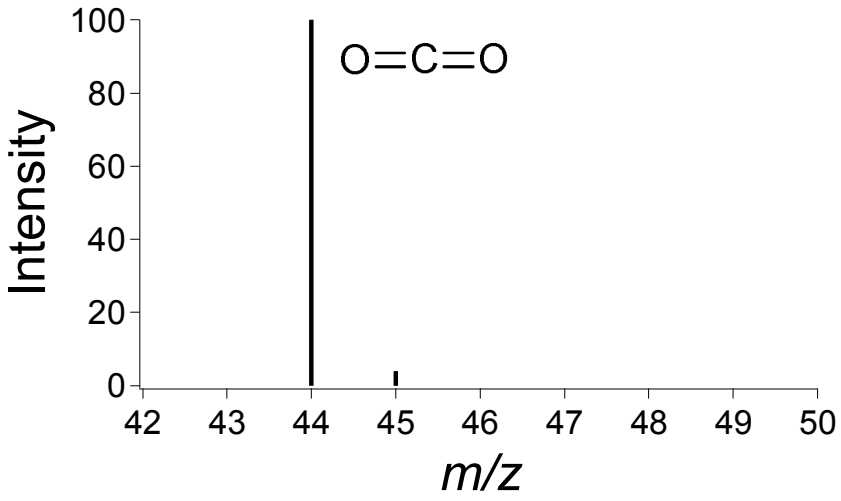
Selected region of TIC for the three nylons tested

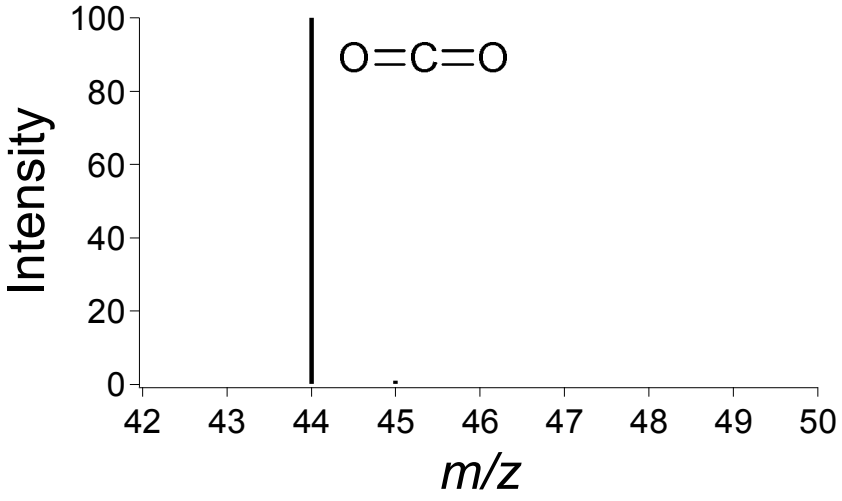


Nylon degradation follows similar mechanism for all variants.
Chromatograms show high reproducibility.

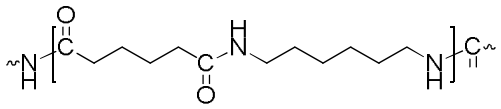
White et al. *Poly. Deg. Stab. In Press 2012*

Example: Carbon Dioxide





Mass spectrum of carbon dioxide from the NIST Spectral database



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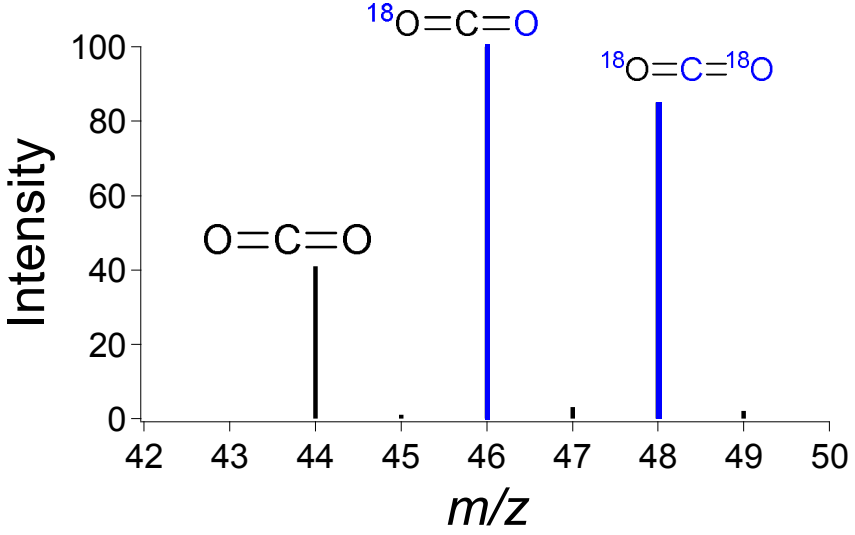
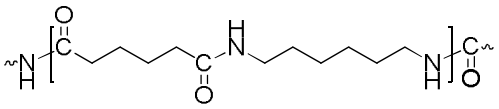
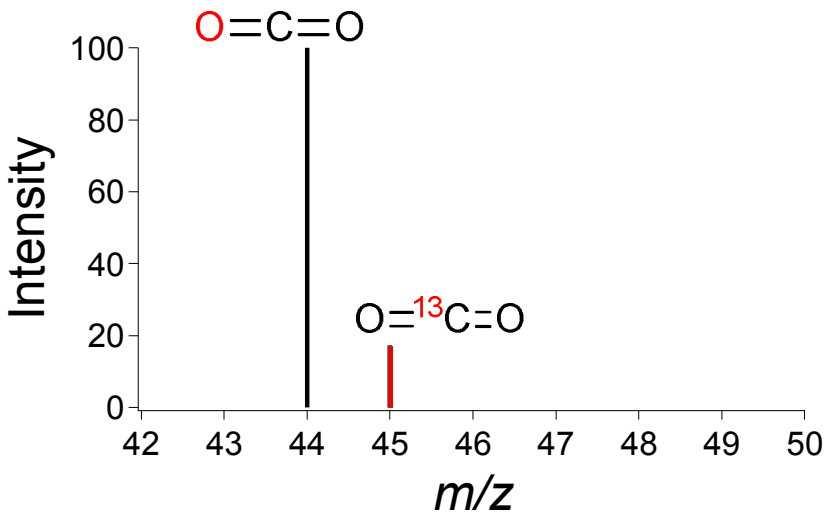
Example: Carbon Dioxide

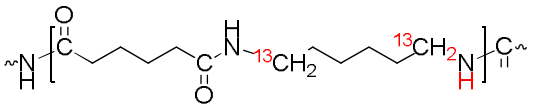


Carbon dioxide mass spectrum from oxidation of unlabeled nylon 6.6 in an ^{18}O enriched environment





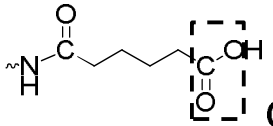
Carbon dioxide mass spectrum from oxidation of ^{13}C labele nylon 6.6 in an air environment



Quantitative Analysis of CO_2 Formation

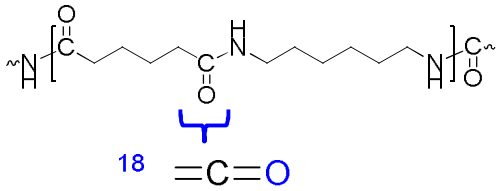
m/z	Assignment	Relative MS Intensity (%)	Functional Group
44	$CO_2^{+\bullet}$	17.6 ± 0.5	Chain End
46	$CO^{18}O^{+\bullet}$	42.3 ± 2.7	Amide Carbonyl
48	$C^{18}O^{18}O^{+\bullet}$	40.1 ± 3.3	Methylene

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



Chain End → Unlabeled CO_2

O=C=O



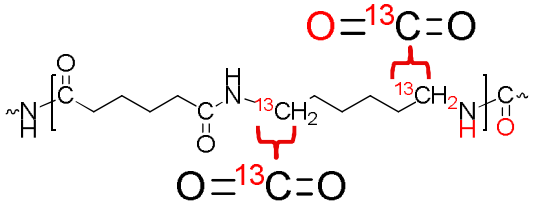
Amide Carbonyl → mono-labeled CO_2

Quantitative Analysis of CO_2 Formation

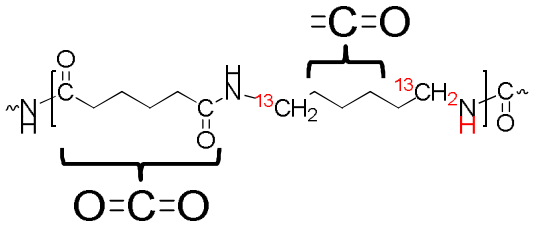
m/z	Assignment	Relative MS Intensity (%)	Functional Group
44	$CO_2^{+\bullet}$	17.6 ± 0.5	Chain End
46	$CO^{18}O^{+\bullet}$	42.3 ± 2.7	Amide Carbonyl
48	$C^{18}O^{18}O^{+\bullet}$	40.1 ± 3.3	Methylene

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

<u>CO_2 Products formed when aged in air</u>



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



Methylene → Unlabeled CO_2

O

Quantitative Analysis of CO_2 Formation

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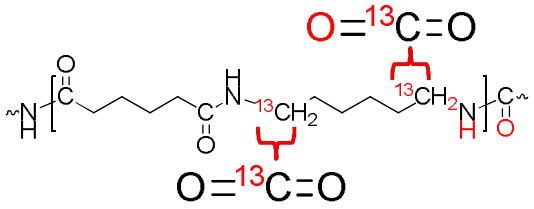
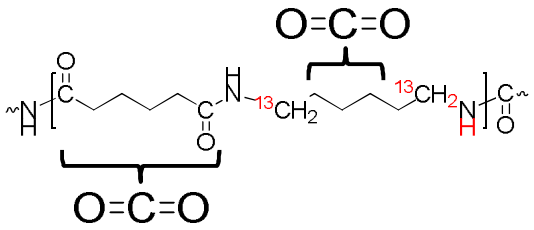
<u>CO_2 Products formed when aged in air</u>



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



Methylene → Unlabeled 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

Quantitative Analysis of CO_2 Formation

m/z	Assignment	Relative MS Intensity (%)	Functional Group
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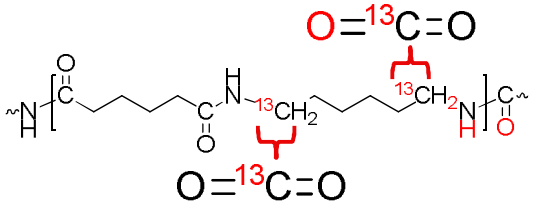
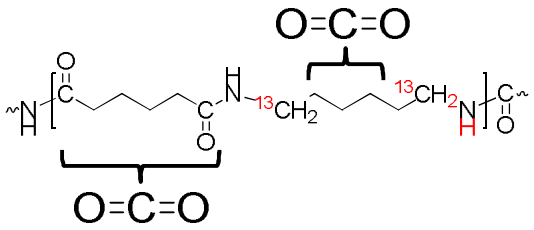
CO_2 Products formed when aged in air



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

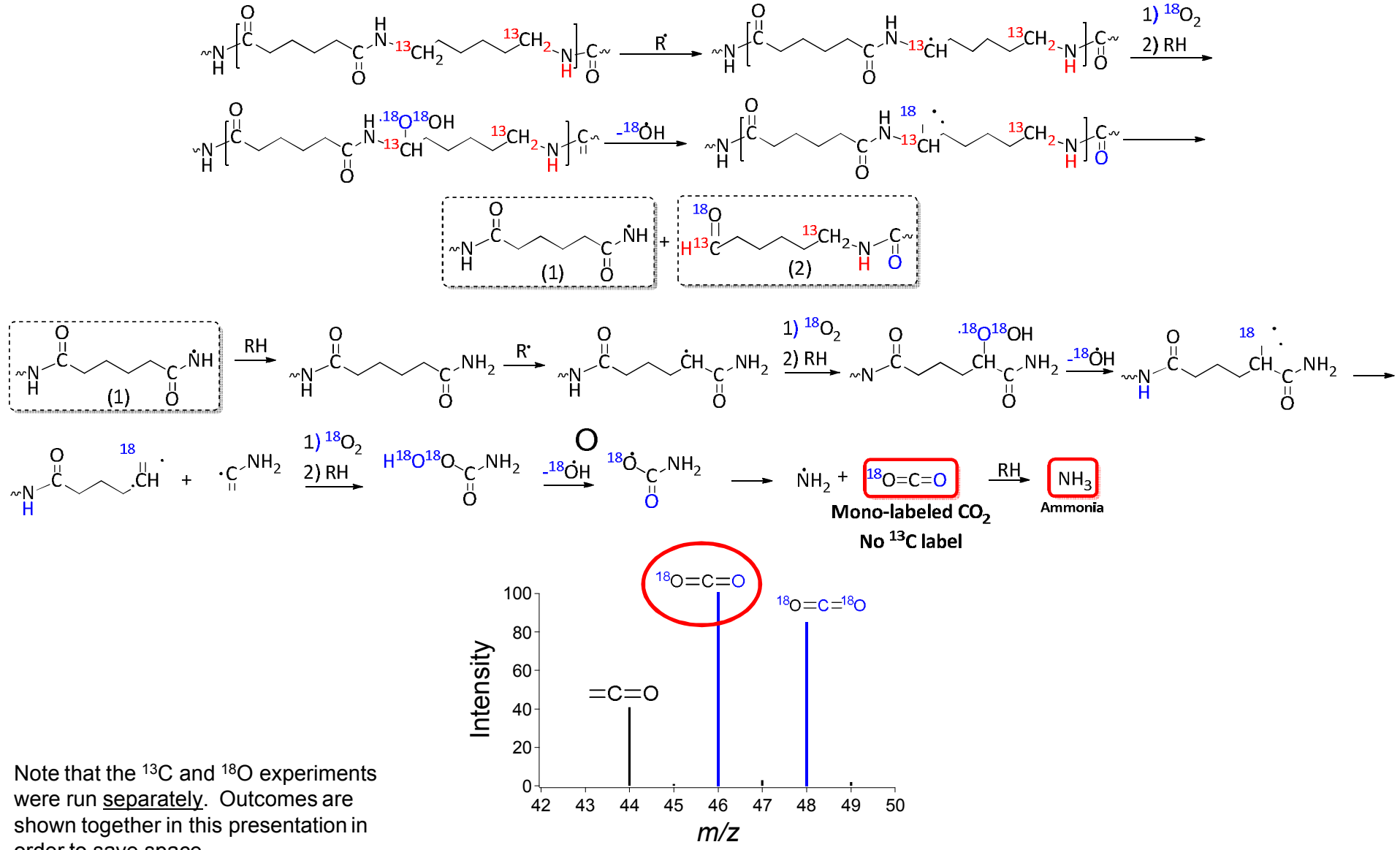


Methylene → Unlabeled CO_2

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

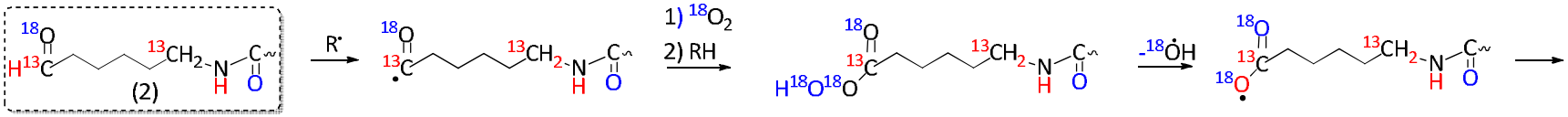
N-Vicinal methylene groups contribute 36% of CO_2 formed from the methylene groups. The other four types of methylene groups contribute an average of 16% each to the CO_2 formed from the methylene groups. **The most labile hydrogen in the nylon backbone is therefore in the *N*-Vicinal methylene group.**

Initiation at the N-Vicinal Methylene Group



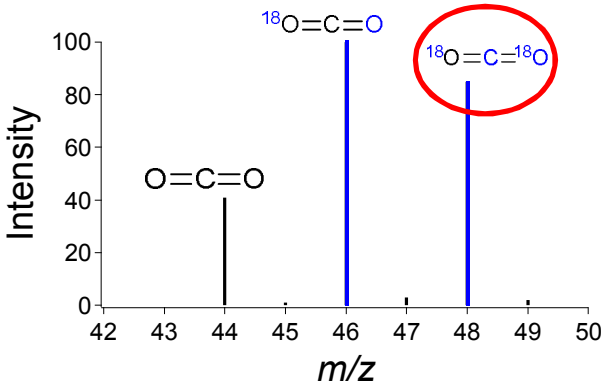
Note that the ^{13}C and ^{18}O experiments were run <u>separately</u>. Outcomes are shown together in this presentation in order to save space.

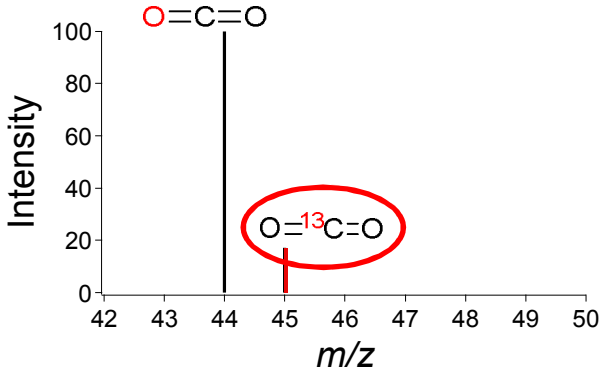
Initiation at the N-Vicinal Methylene Group



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

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





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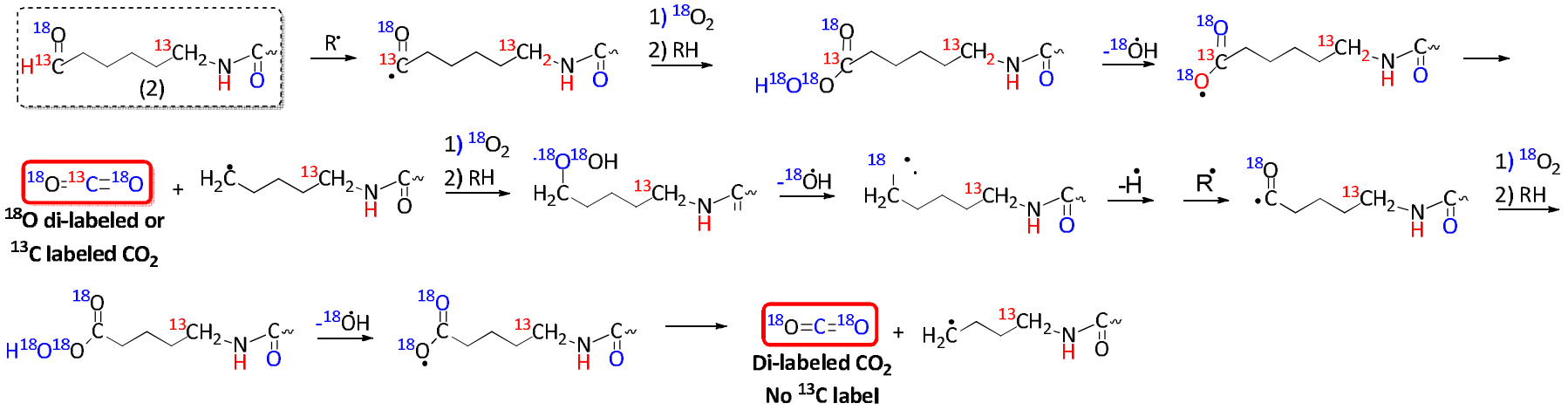
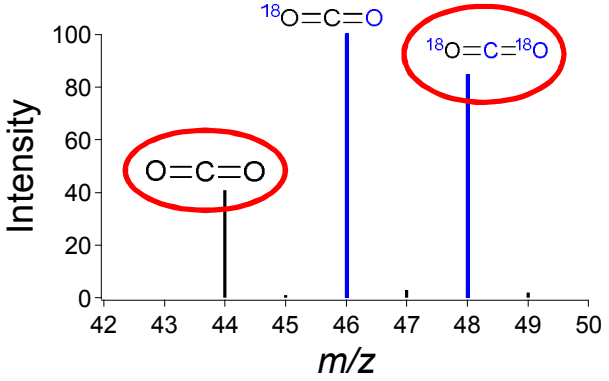
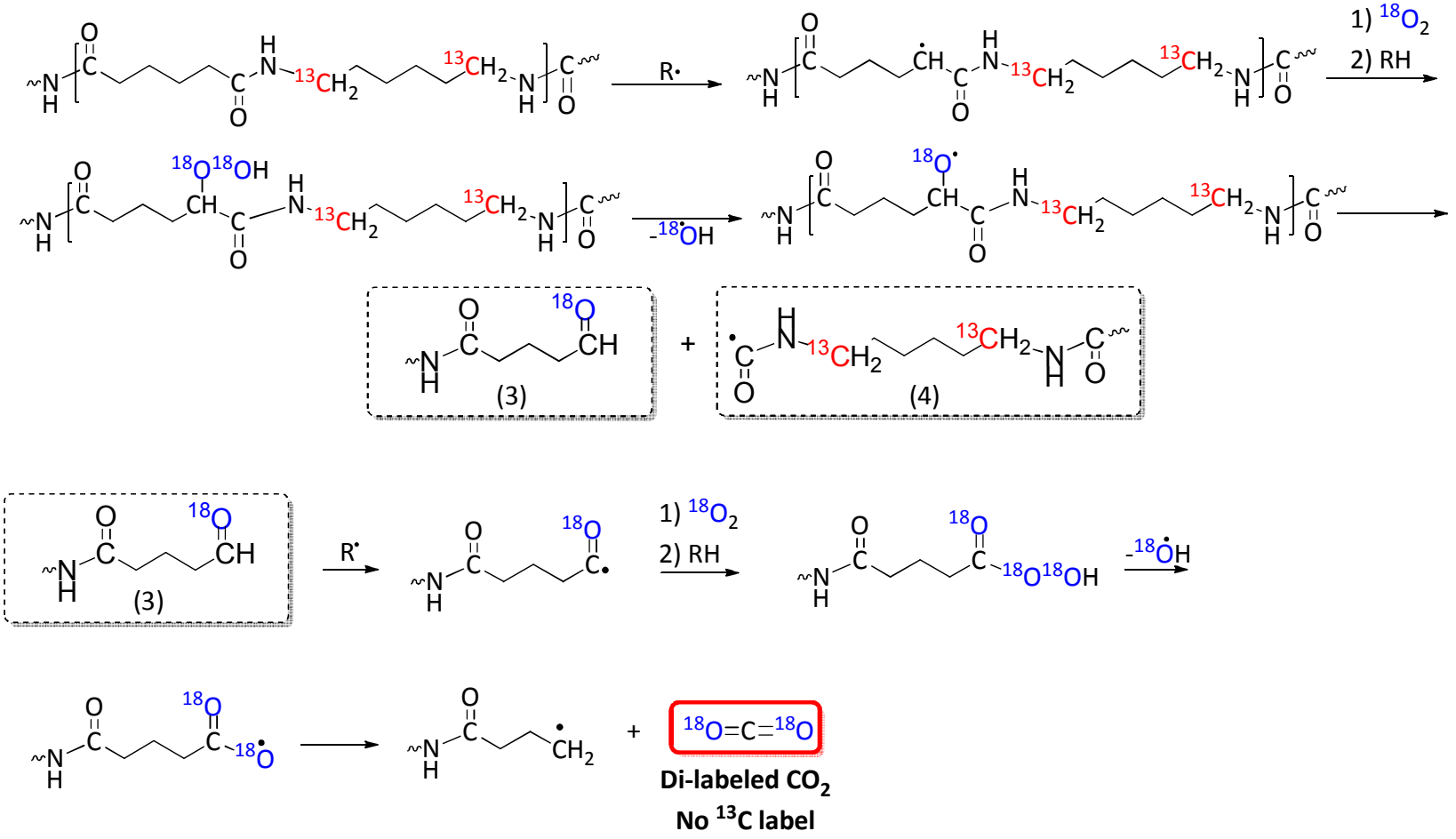
Initiation at the N-Vicinal Methylene Group



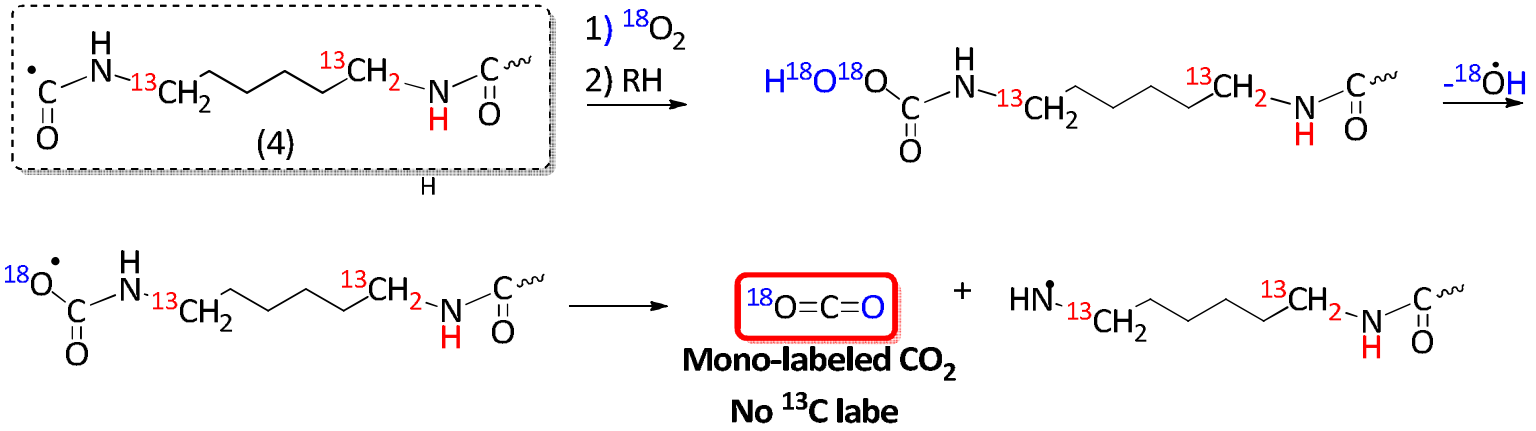


White et al. *Poly. Deg. Stab. In Press 2012*

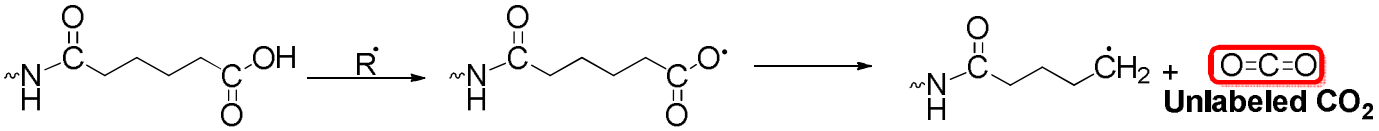
Initiation Adjacent to the Carbonyl Carbon

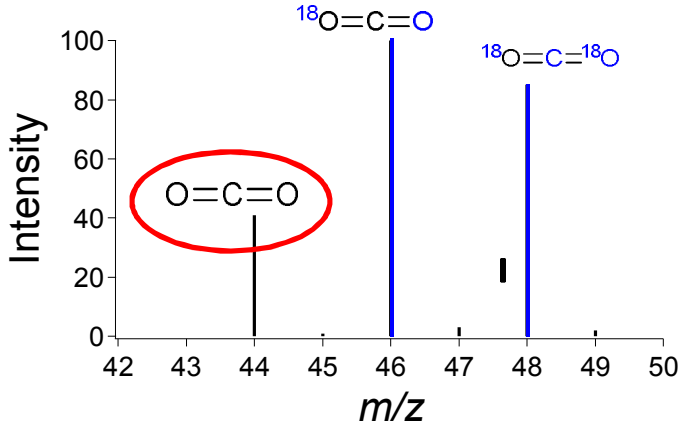


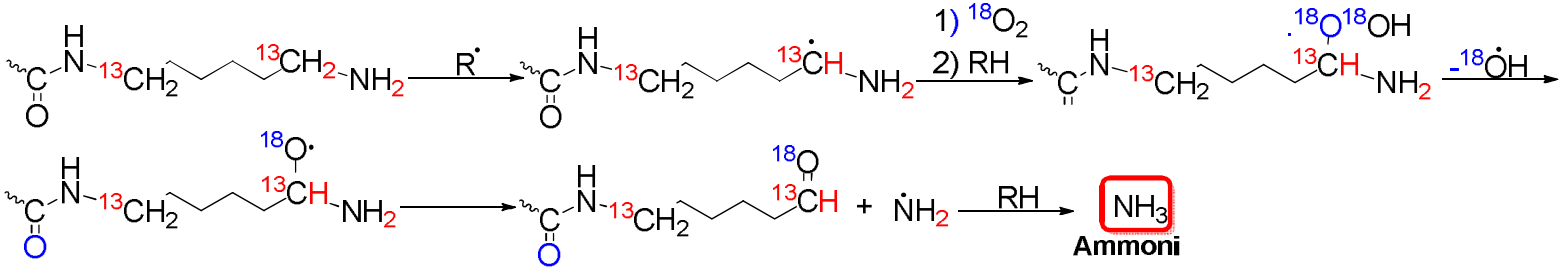
Initiation Adjacent to the Carbonyl Carbon



Degradation at the End Groups

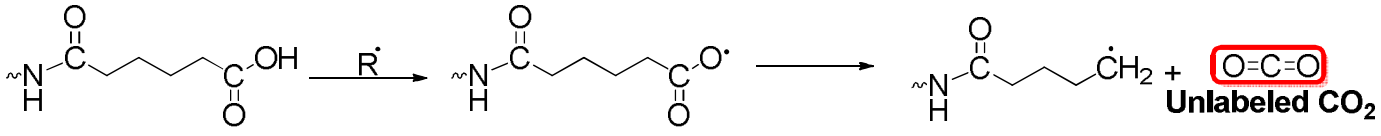


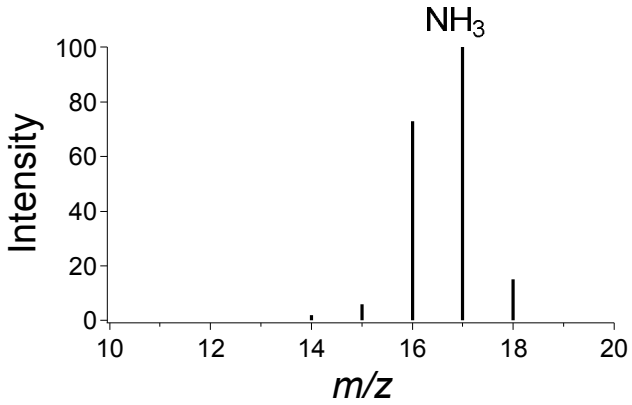


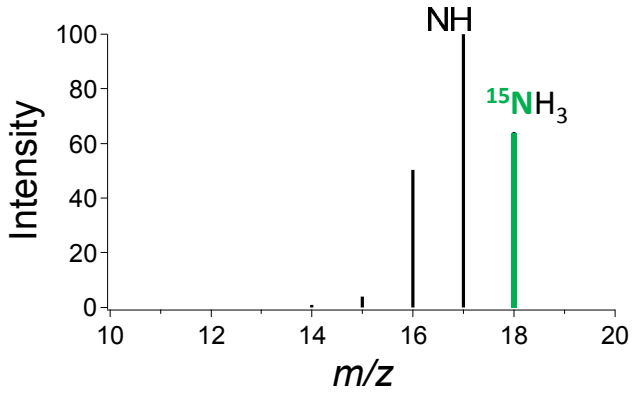


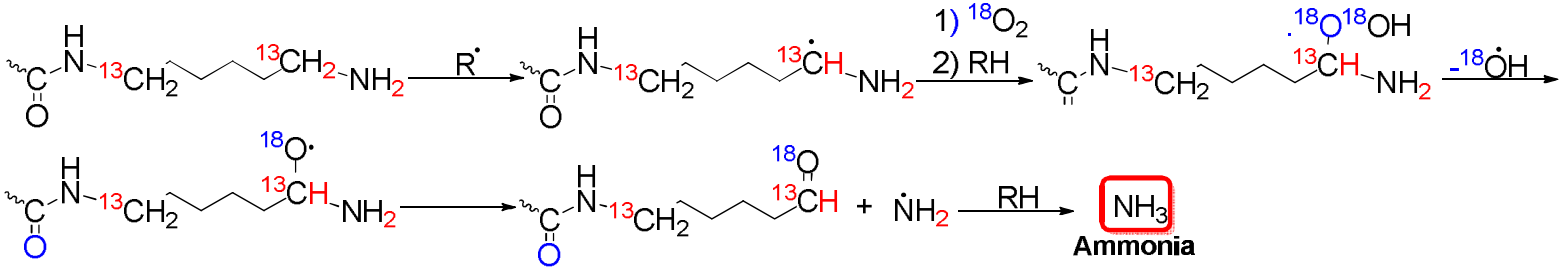
We observed NH_3 and $^{15}NH_3$ in aging experiments that employed ^{15}N labeled nylon 6.6 with relative mass spectral contributions of 46 ± 13 and 54 ± 12%, respectively. This is consistent with TOF-SIMS analysis of the neat ^{15}N labeled polymer (51.6% min atom ^{15}N) and the manufacturer's quality analysis (51.4% min atom ^{15}N), indicating that the ammonia product is indeed coming from nylon, and not from some nitrogen-containing impurity such as a solvent.

Degradation at the End Groups









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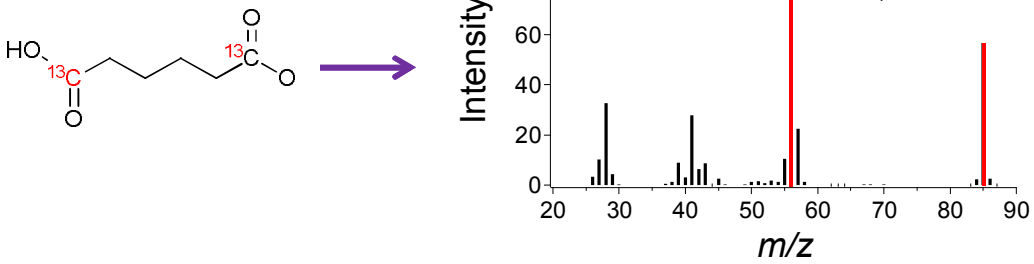
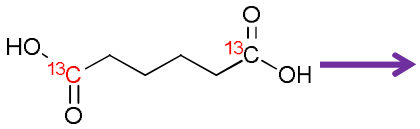
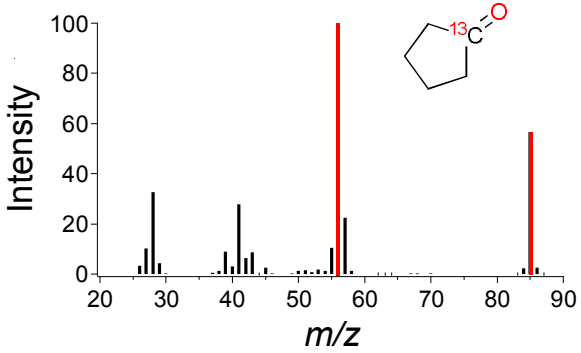
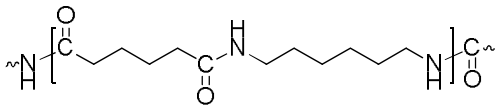
Cyclopentanone

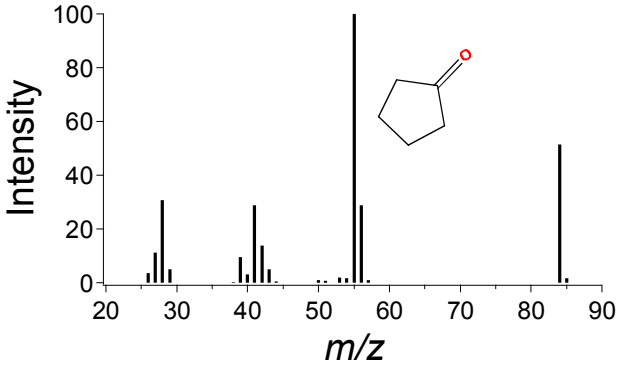


Cyclopentanone

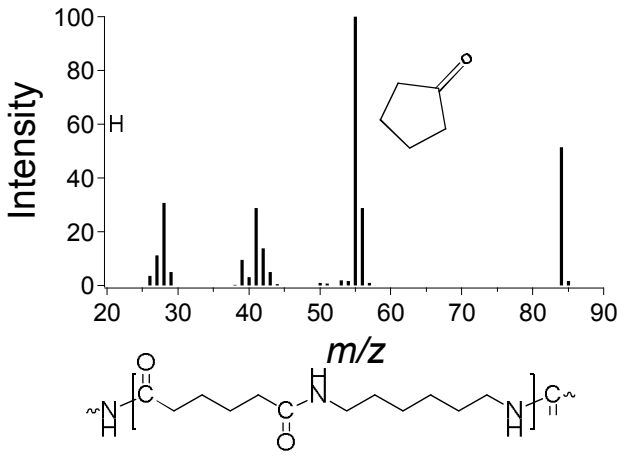


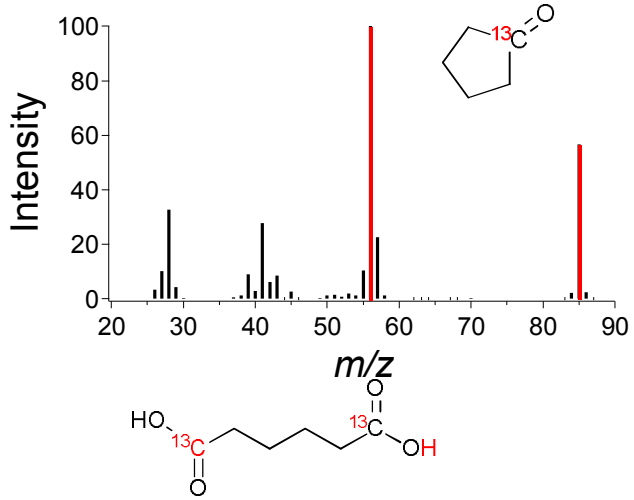


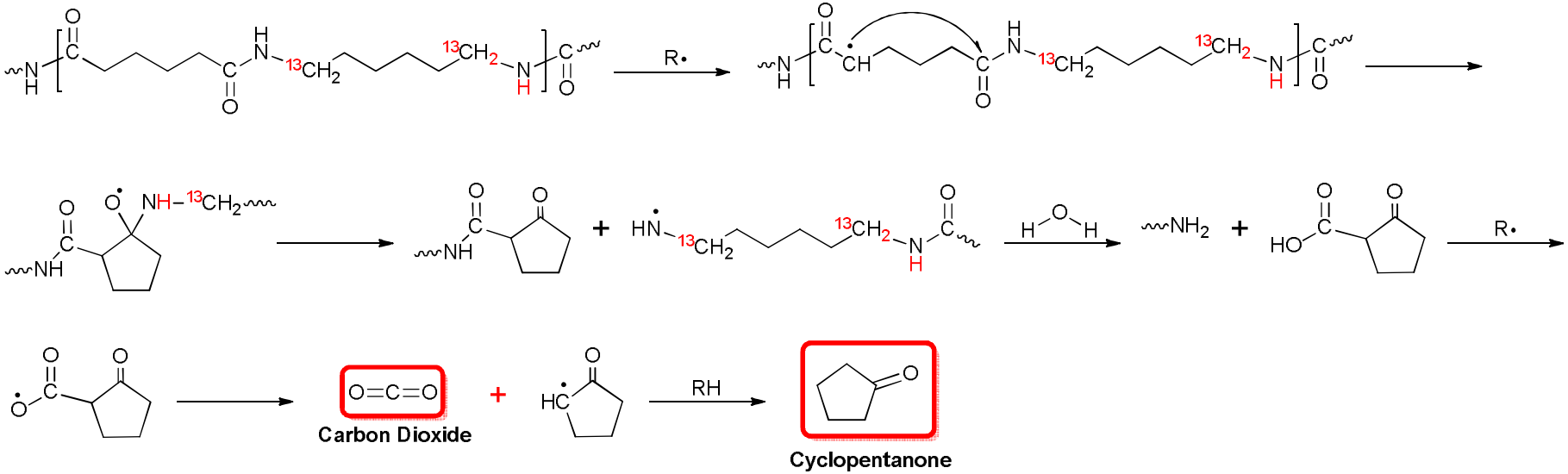




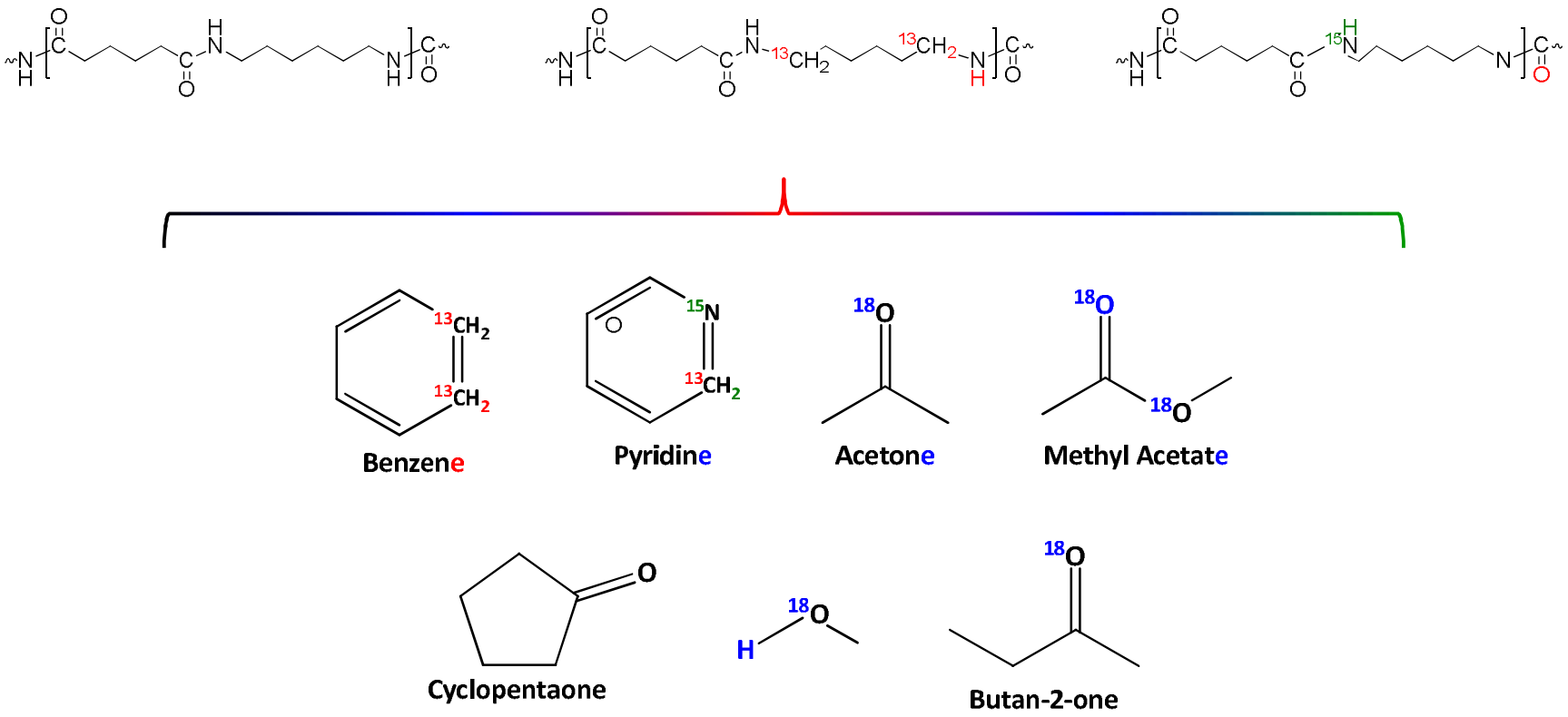
Cyclopentanone







Other Key Labeled Species Identified

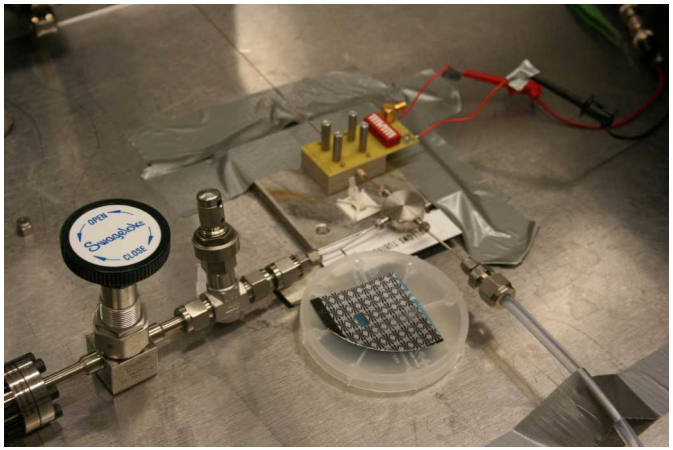


Conclusions

- 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, ammonia, and cyclopentanone
- We have identified and are proposing degradation mechanisms for other low molecular weight thermal-oxidative and hydrolytic degradation products

Future Development of this Research

- Other Degradation Pathways
  - Hydrolytic Degradation of Nylon
- Other Polymers
  - EVA
- Detecting Aging
  - Sensor Development (Effort led by Cody Washburn, 1821)



Photograph Courtesy of Cody Washburn

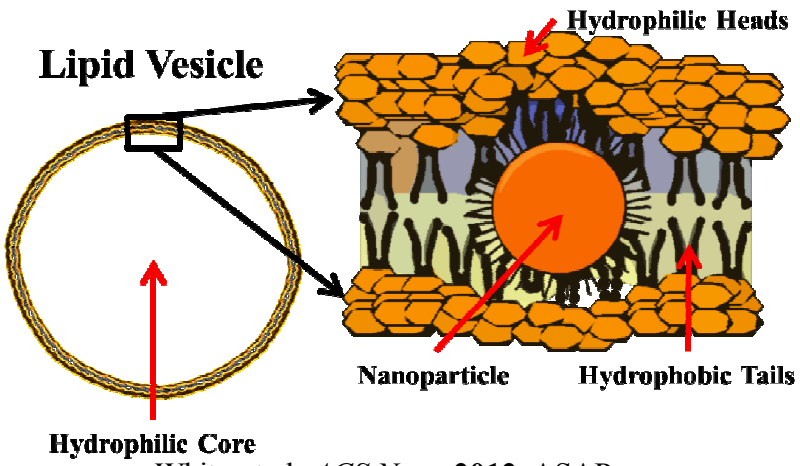
Sandia National Laboratories

The basis for up-scaling nanoparticle processing

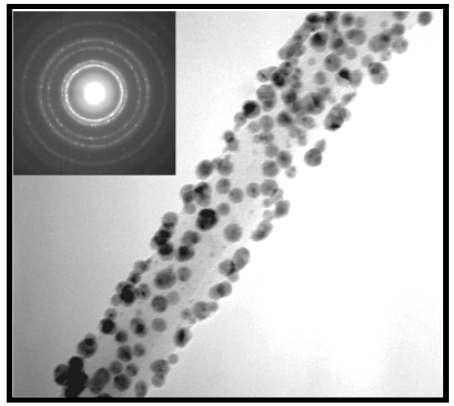
PREDICTING NANOPARTICLE DISPERSIBILITY IN SOLUTION

Nanomaterial Applications

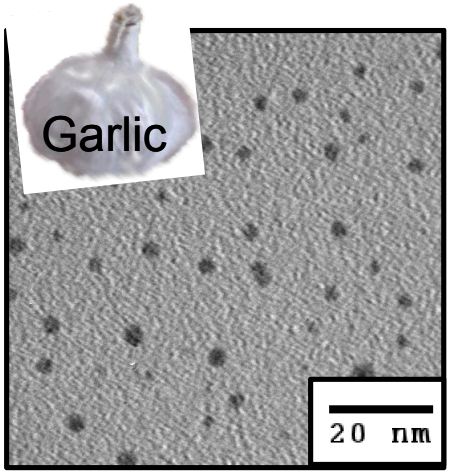
- Targeted Drug Delivery
- Optical/Chemical Sensors
- Biomedical Imaging
- Catalysts
- Electronic Devices
- Thin Film Applications



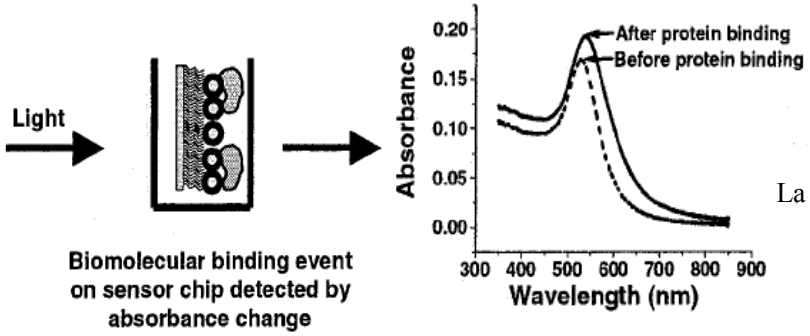
White et al. *ACS Nano* **2012**, ASAP



La Londe et al. *J. Mater. Res.*, **2005** Vol. 20, No. 11



White et al. *J. Nanomat.* **2012**, 730746, 1-12



Nath et al. *Anal. Chem.* **2002**, 74, 504-509

Total Interaction Energy Model

- Aim to predict nanoparticle dispersibility
  - Material type (Hamaker constant)
  - Nanoparticle size
  - Distance between nanoparticles
  - Solvent properties
  - Ligand length
  - Ligand solvation
  - Ligand surface coverage

$$\Phi_{osm} = \frac{4\pi R k_B T}{v_{sol}} \phi^2 \left(\frac{1}{2} - \chi\right)\left(l - \frac{h}{2}\right)^2 \qquad l < h < 2l$$

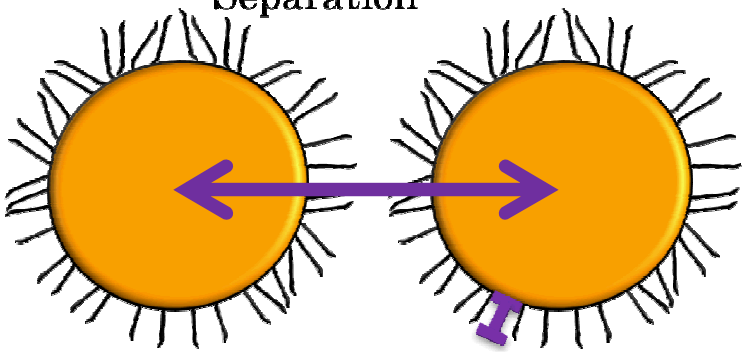
$$\Phi_{osm} = \frac{4\pi R k_B T}{v_{sol}} \phi^2 \left(\frac{1}{2} - \chi\right)\left[l\left(\frac{h}{2l} - \frac{1}{4}\right) - \ln\left(\frac{h}{l}\right)\right] \qquad h < l$$

h = Separation Distance

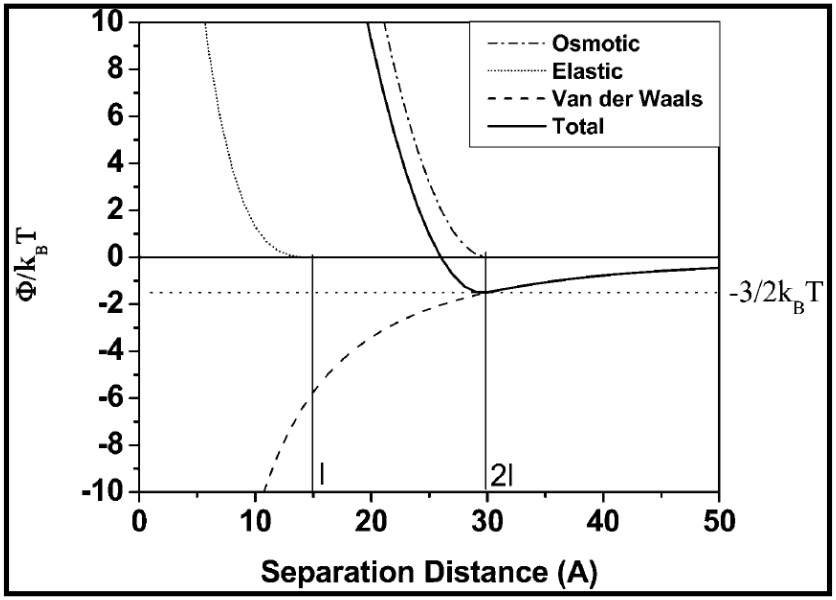
R = Particle Radius

l = Ligand Length

d = Center to Center Separation



Current interaction energy models assume constant ligand shell thickness and solvation, i.e. they over predict dispersibility

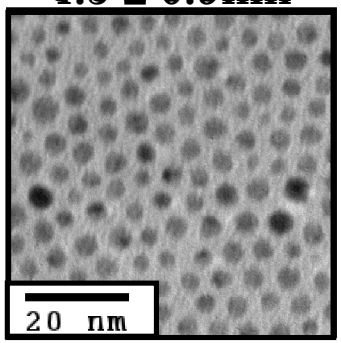


SANS IS THE ONLY WAY TO MEASURE THESE VALUES

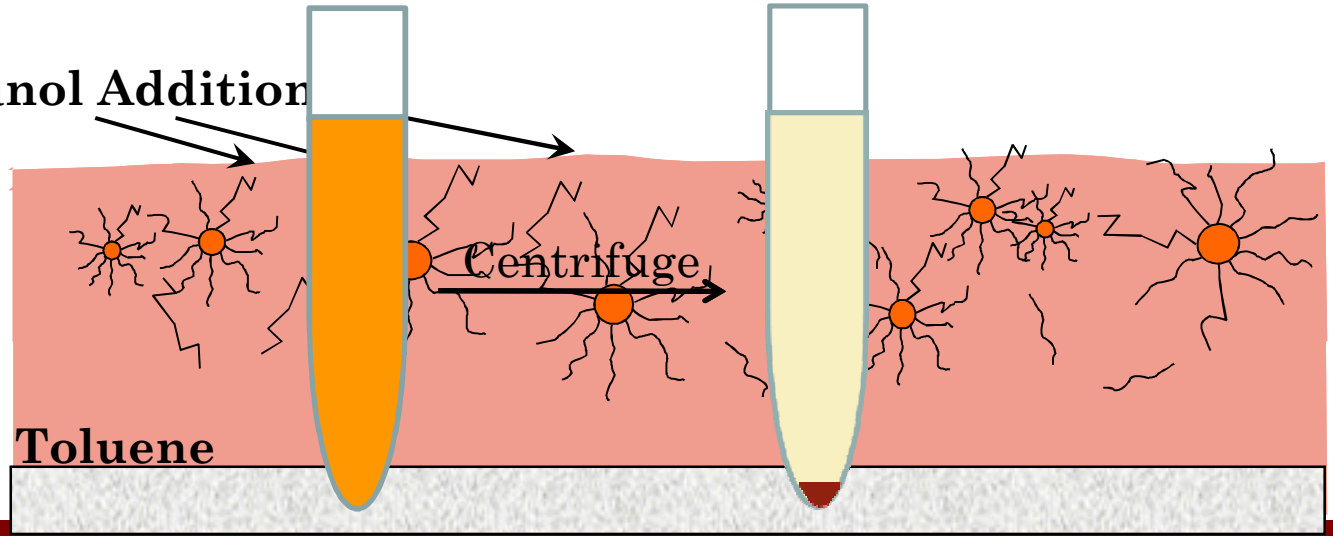
Anand et al. *Ind. Eng. Chem. Res.* **2008**, 47, 553-559

Traditional Processing

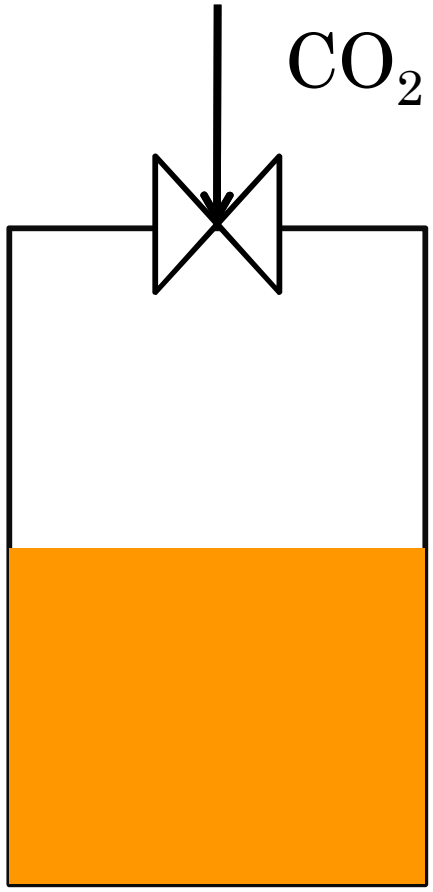
- Purification/Isolation
  - Removal of surfactants and excess ligands from dispersions which may impact final application ex. biocompatibility, altering phase behavior, etc.
- Size-selective fractionation
  - Solvent/anti-solvent system combined with recursive centrifugation to obtain monodisperse populations of nanoparticles



Dodecanethiol capped Gold nanoparticles



Gas-Expanded Liquids (GXLs)



n-hexane, d14

P (psi)	x, CO2	% Volume Expansion
0	0%	0

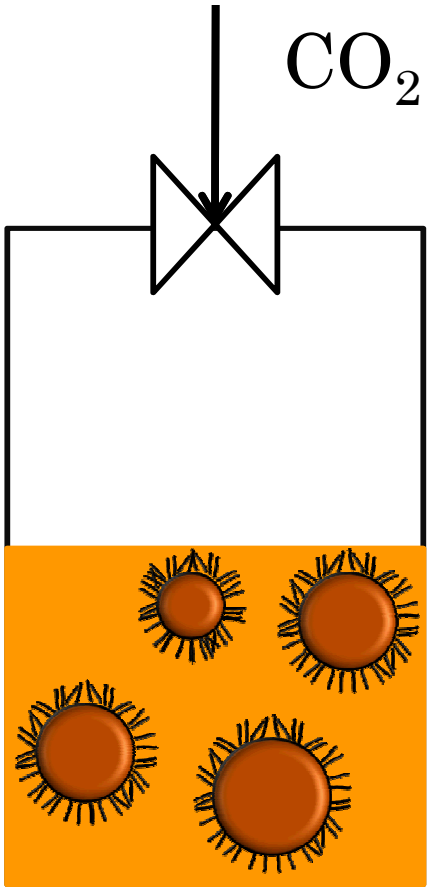
P (psi)	x, CO2	% Volume Expansion
407	36%	21%

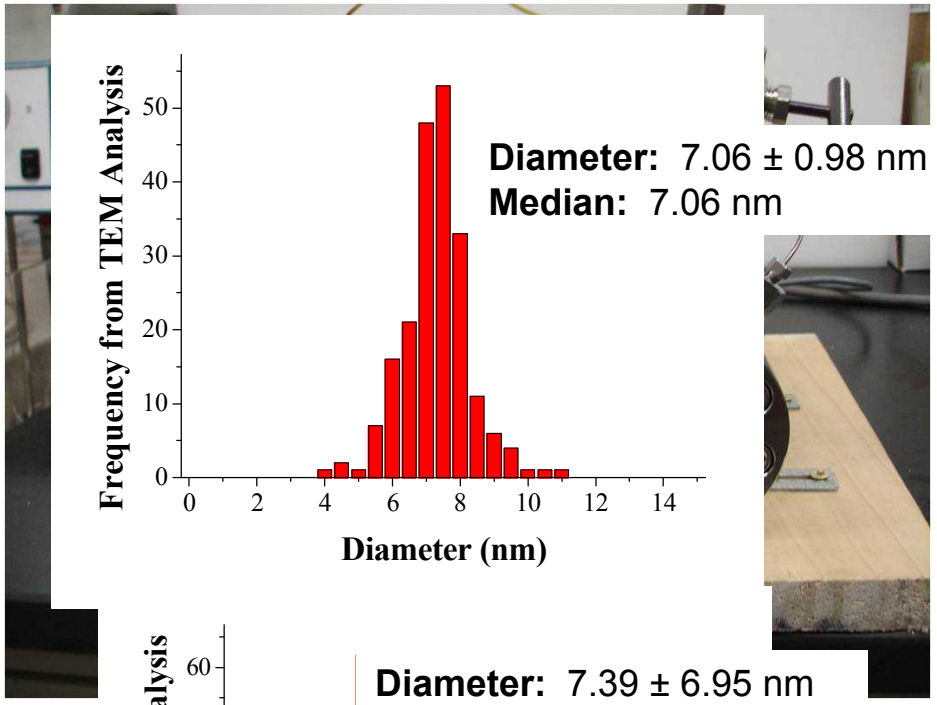
P (psi)	x, CO2	% Volume Expansion
717	81%	190%

Solvent properties change as a function CO_2 pressure

Volume fractions of *n*-hexane d14/CO_2 determined using the Patel-Teja Equation of state at 25°C

“Green” Processing with GXLs





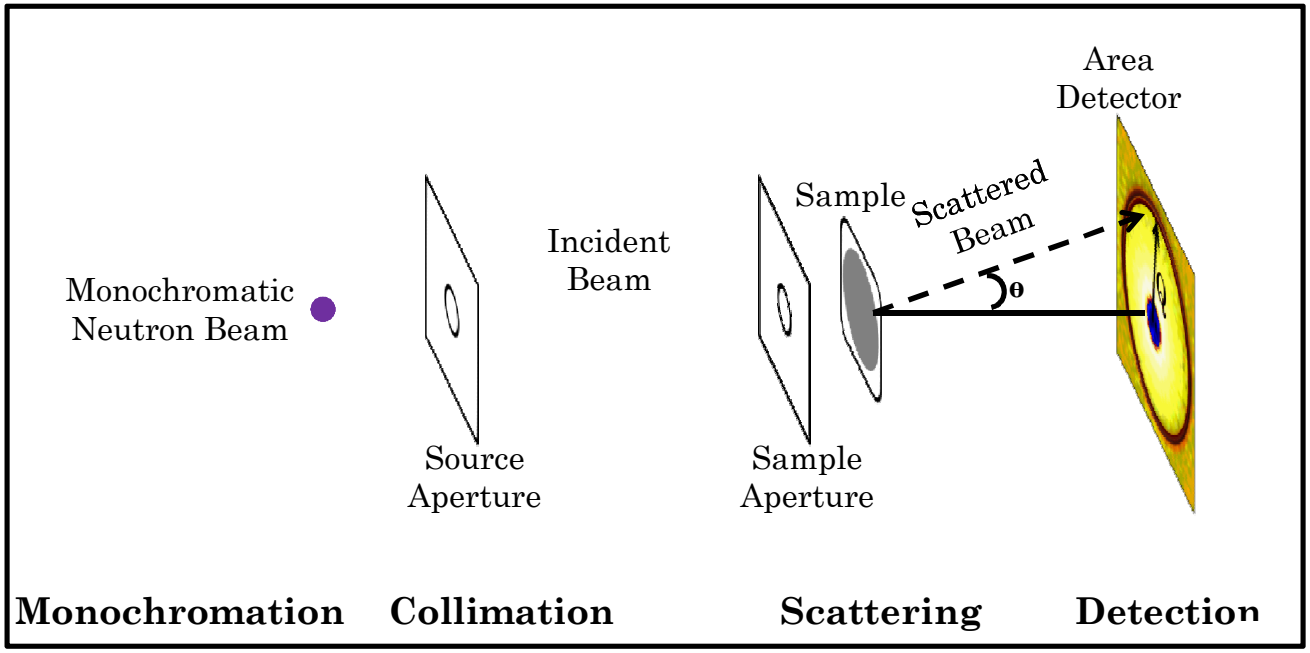
- Size
- Depo
- Com

n

Roberts et

852-22859

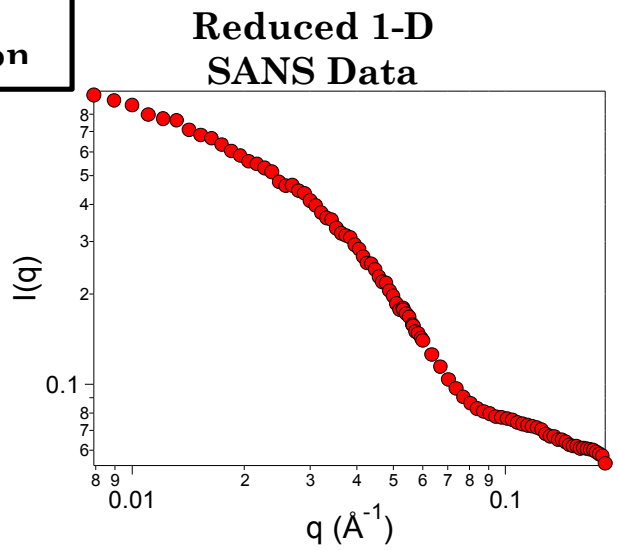
Small-Angle Neutron Scattering (SANS)



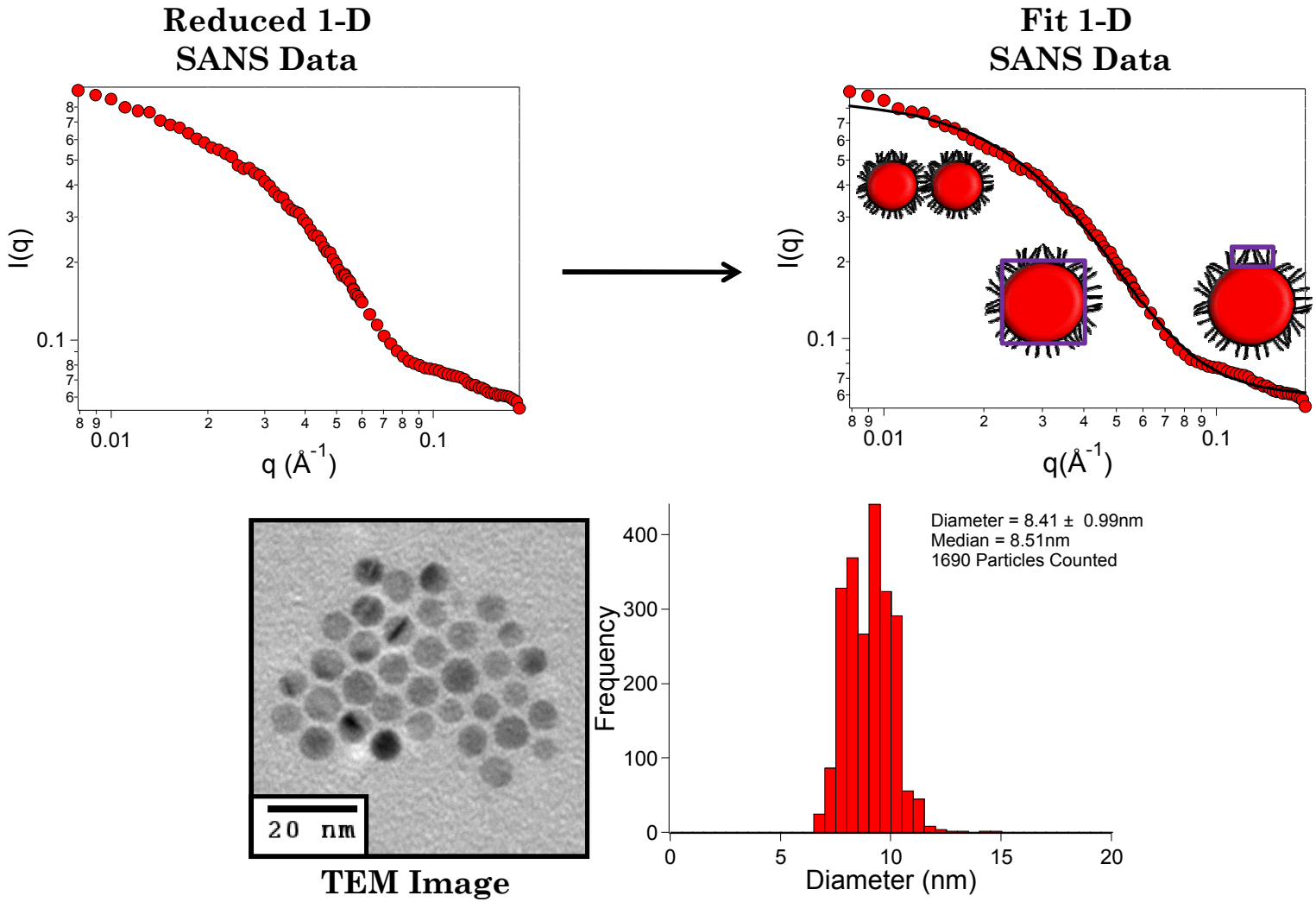
$$q = (4\pi/\lambda)\sin(\theta/2) \text{ in units of } Å^{-1}$$

and

$$I(q) = \varphi\, P(q)\, S(q)$$



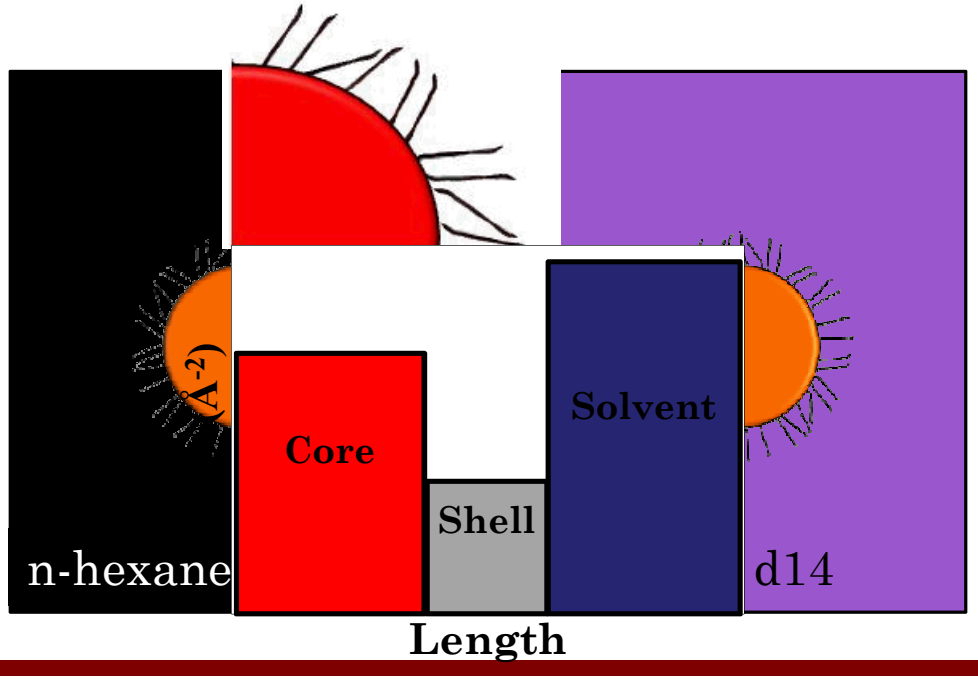
Small-Angle Neutron Scattering



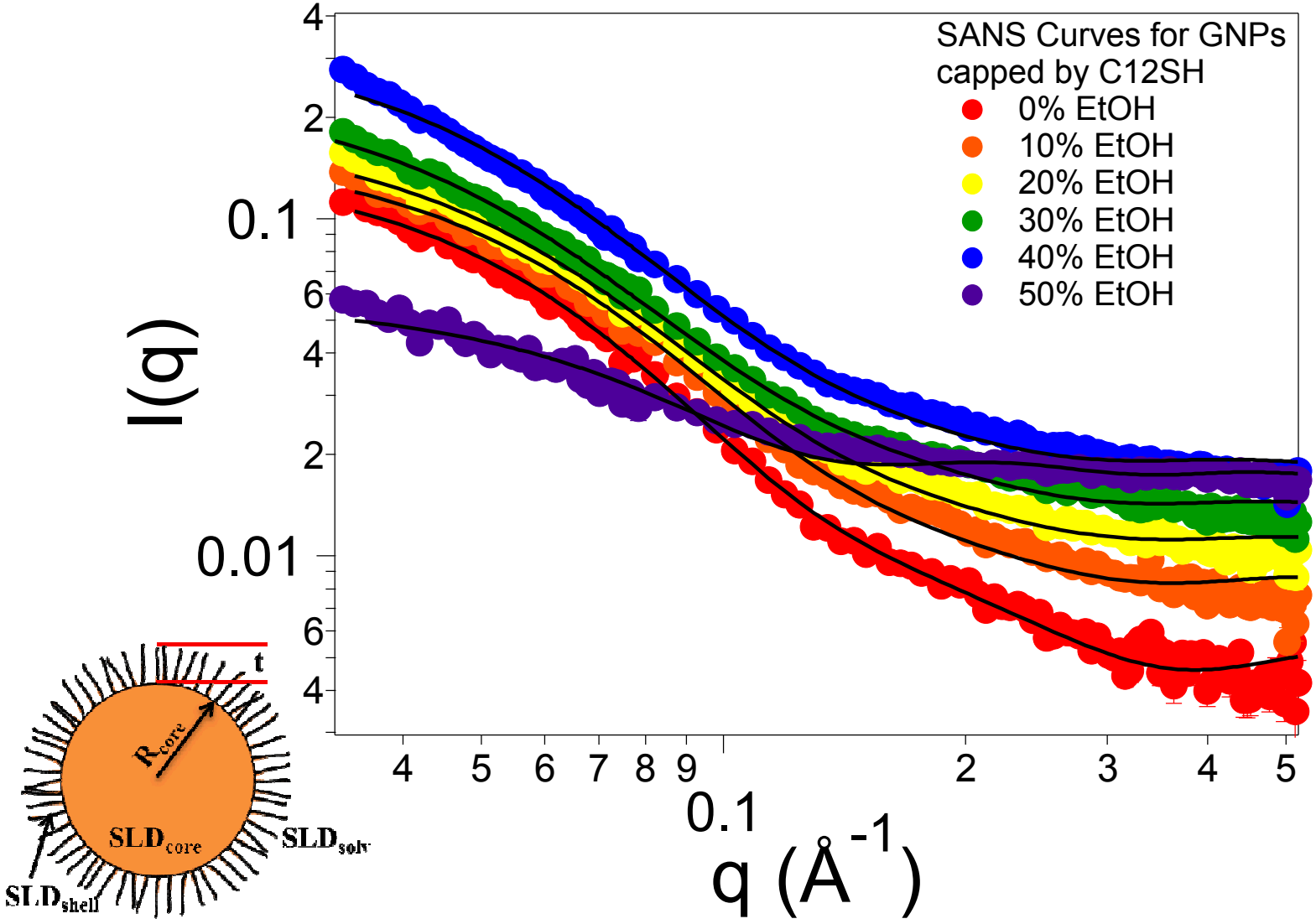
Small-Angle Neutron Scattering

- Scattering Length Density (SLD)
  - Dependent on atomic number/composition
  - Allows for great contrast between hydrogen and deuterium

Material	SLD ($Å^{-2}$)
Gold	4.50E-06
Dodecanethiol (C12SH)	-3.67E-07
1-Octadecanethiol (C18SH)	-3.49E-07
n-hexane, d14	6.14E-06
n-hexane	-5.71E-07
toluene, d8	5.66E-06

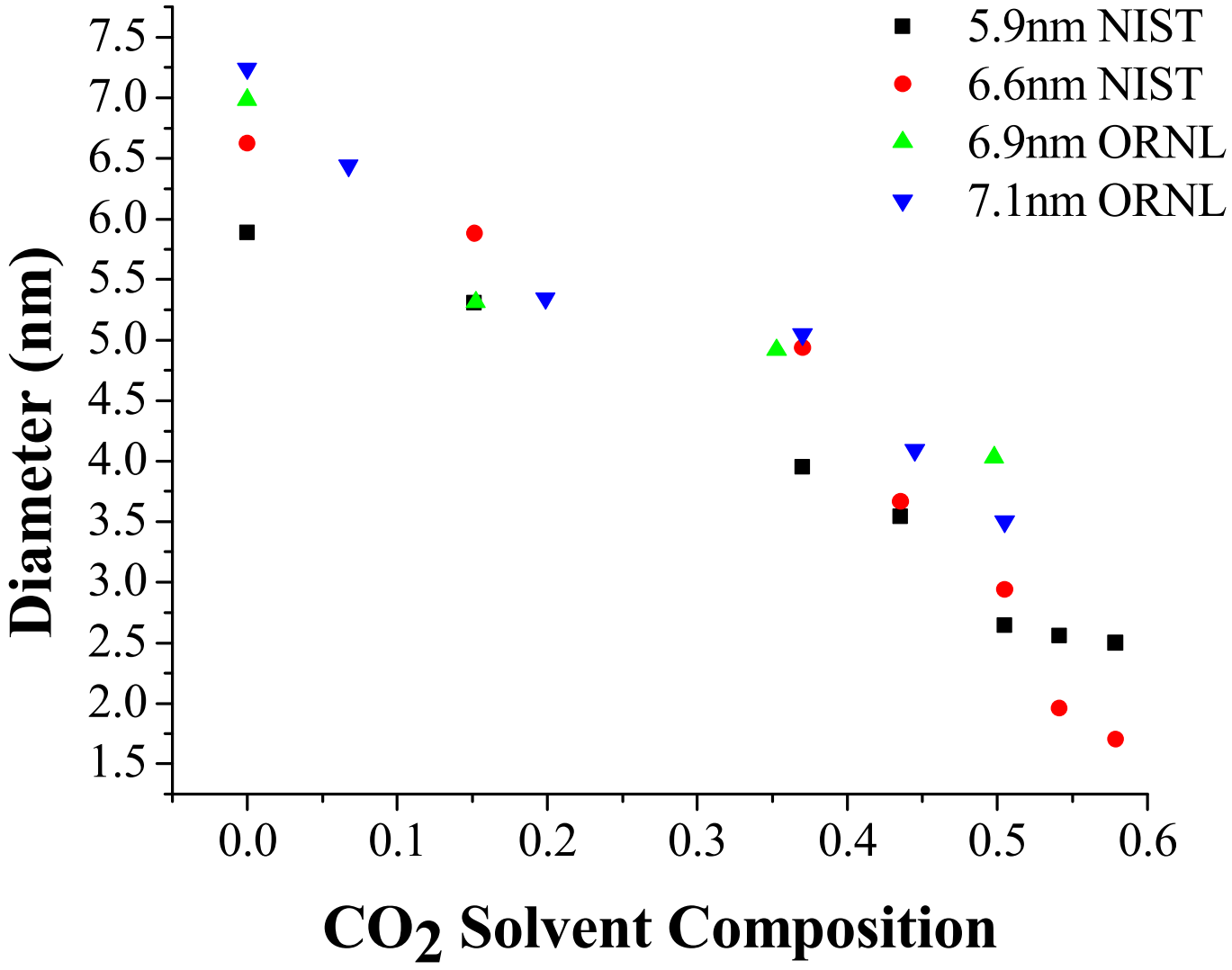


Core-Shell Fit of SANS Data

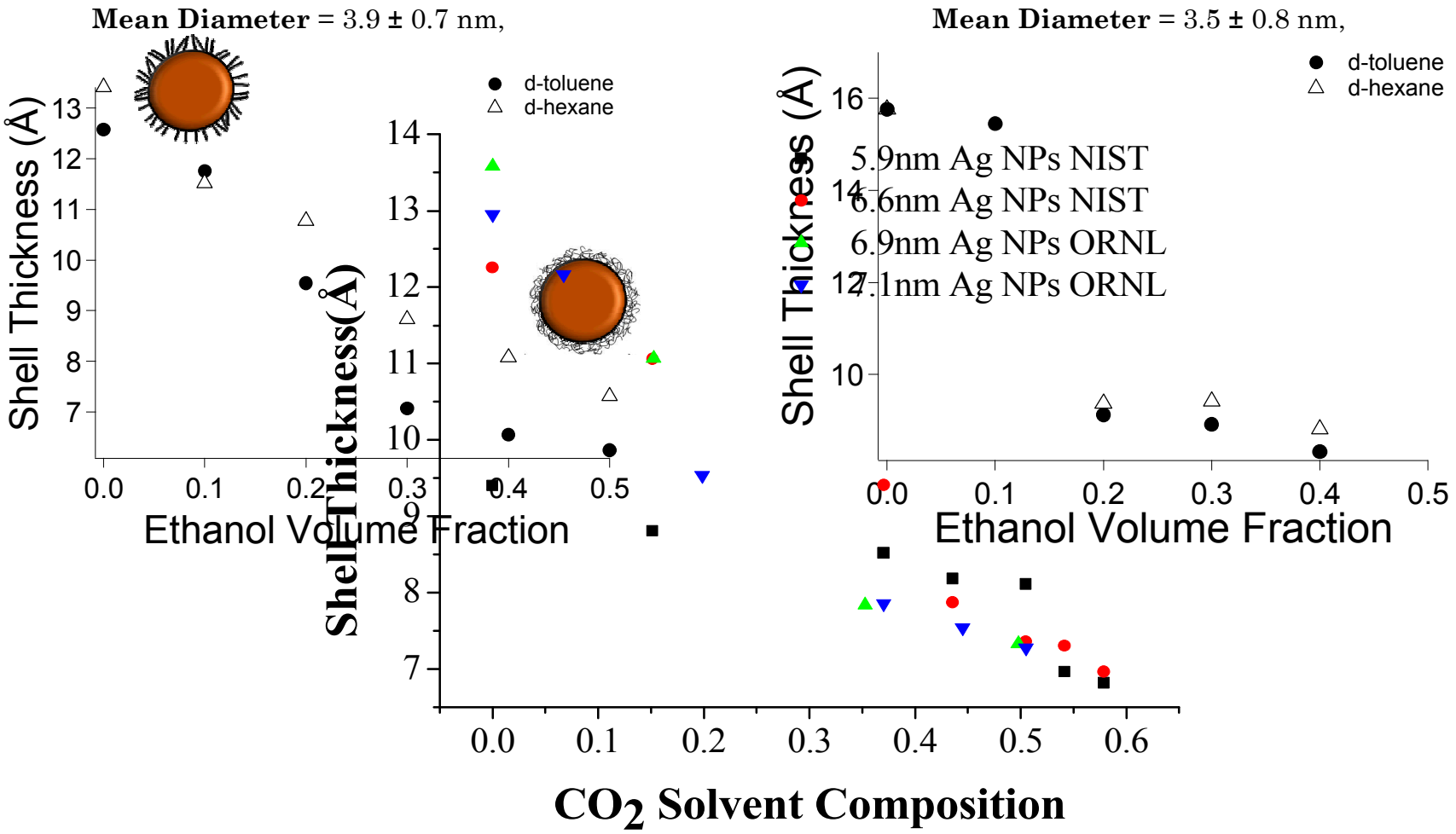


White et al. *J. Phys. Chem C.* 2011, 115, 18397-18405

Diameter of Dispersed Nanoparticles

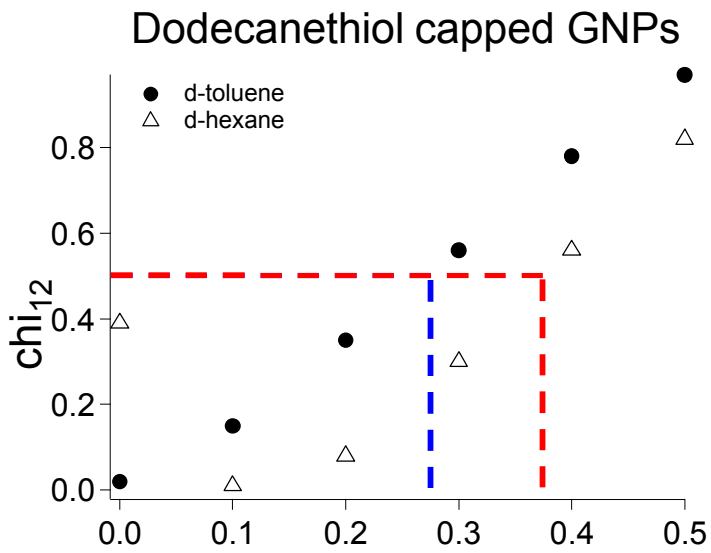


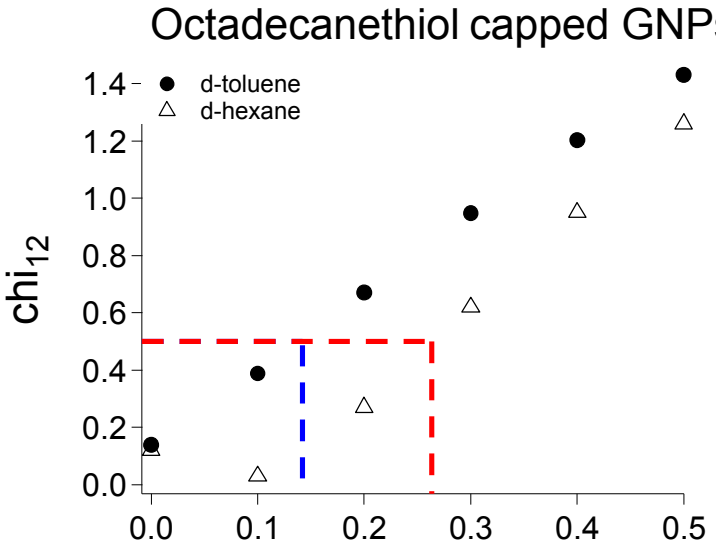
SHELL THICKNESS

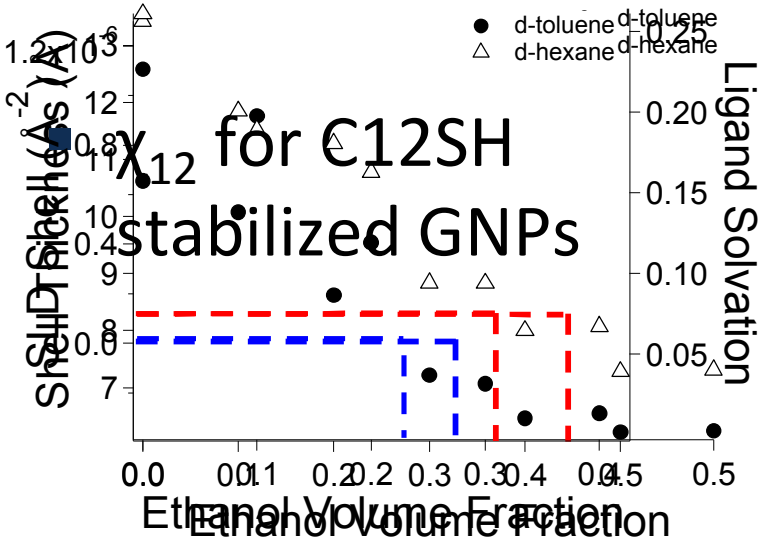


White et al. *J. Phys. Chem C.* 2010, 114, 16285-16291, White et al. *J. Phys. Chem C.* 2011, 115, 18397-18405

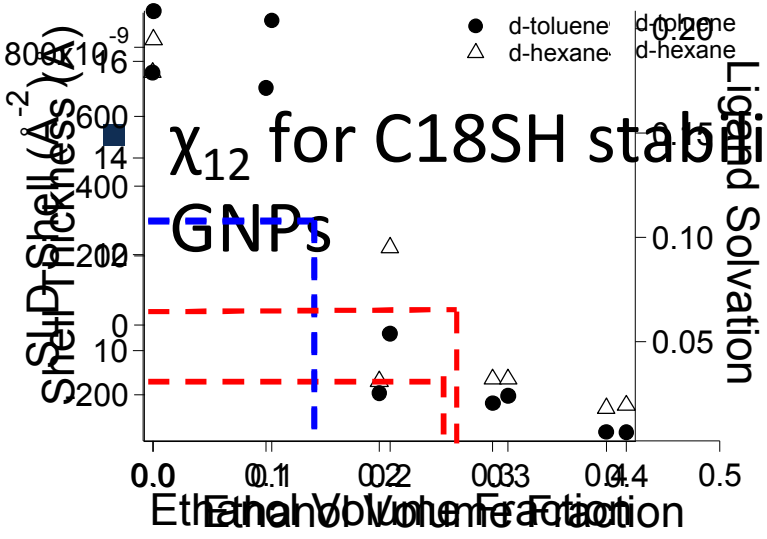
Flory-Huggins Interaction Parameters







χ_{12} for C12SH stabilized GNPs



χ_{12} for C18SH stabilized GNPs

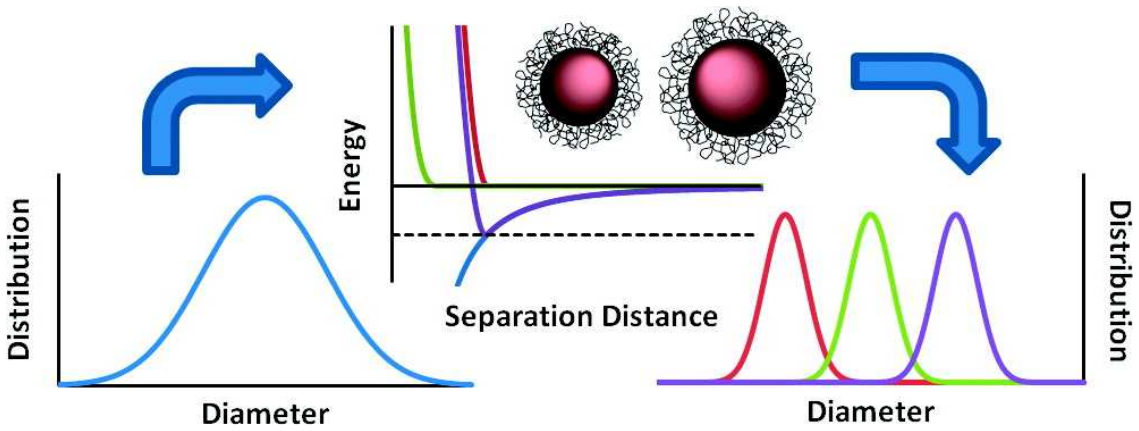
Curvature Effects at Ambient Pressure

Mean (nm)	ΔL (Å)	% Surface Coverage	Curvature ($Å^{-1}$)	%Ligand Solvation
5.9	2.6	60	0.339	26.9%
6.6	5.3	62	0.303	16.6%
6.9	6.3	55	0.290	18.7%
7.1	5.7	44	0.282	19.4%

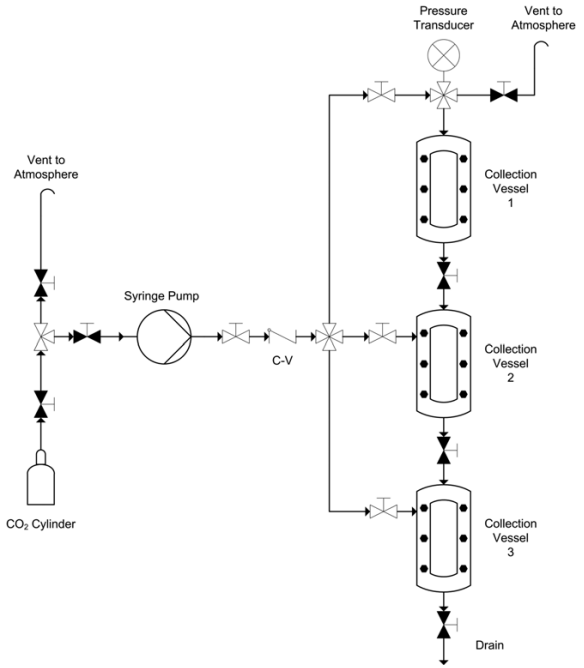
- Similar Surface Coverage, Varying Curvature
  - ↑ Curvature = ↑ Ligand Solvation
- Similar Curvature, Varying Surface Coverage
  - ↑ Surface Coverage = ↓ Ligand Solvation

White et al. *J. Phys. Chem C.* 2010, 114, 16285-16291

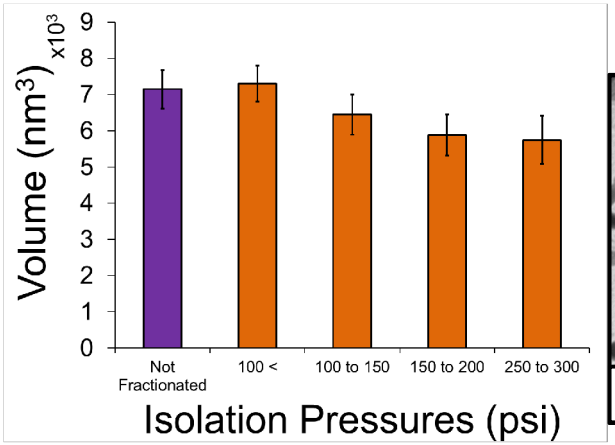
More Accurate Models and Extension to Non-Spherical Particles

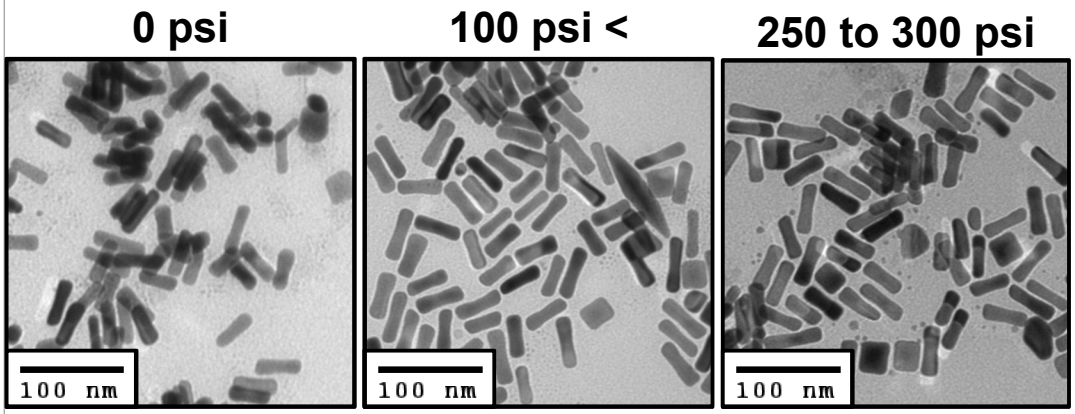


Saunders et al. *J. Phys. Chem. C* 2011, 115, 4603-4610



Saunders et al. Nanotechnology 2009,475605
Patent No.: US 2007/0243716, US2010/0323527





White et al. *Ind. Eng. Chem Res.* 2012, 51, 5181-5189

Future Directions

- Neutron Irradiation Effects to Organic Materials of Interest
- Development of Passive Sensors (nanocomposites) which Identify Aging
- Development of More Efficient Oxygen Consumption Measurements to Reduce Accelerated Aging Experiment Times

Thank you for your attention!

QUESTIONS?