Hydrolytic Degradation of Polylactide and Production of Water-Soluble Hydrolyzate Species

Richard Cairncross
Drexel University
Chemical & Biological Engineering
Philadelphia, PA 19104
cairncross@drexel.edu

Shri Ramaswamy, Danielle Wojdyla & Ulrike Tschirner
University of Minnesota
Bioproducts & Biosystems Engineering
St. Paul, MN 55108
shri@umn.edu

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- ***NatureWorks***, LLC

Drexel UNIVERSITY

CSREES EDUCATION RESEARCH USDA EXTENSION

IREE Initiative for Renewable Energy and the Environment

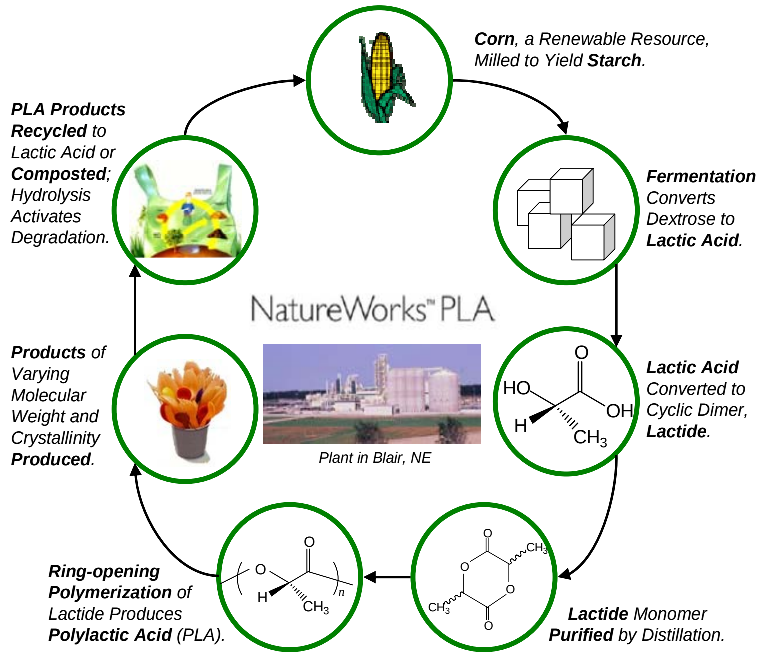
NatureWorks LLC

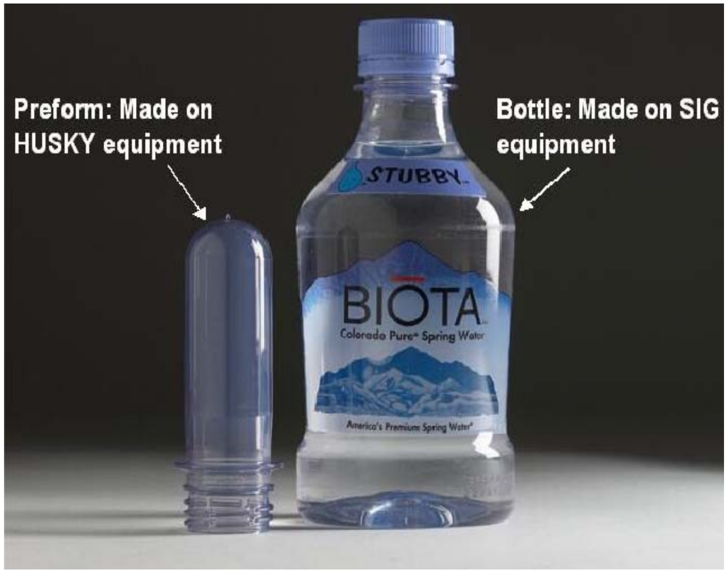
Polylactide (PLA)

- **Polylactide (PLA)** is an *aliphatic polyester* polymer derived from lactic acid. Controlled **stereochemistry** of lactides allows flexibility to control physical and mechanical properties.

- **Applications of PLA:**
- Textile fibers
- Rigid thermoforms
- Food and beverage containers
- Biocompatible medical devices

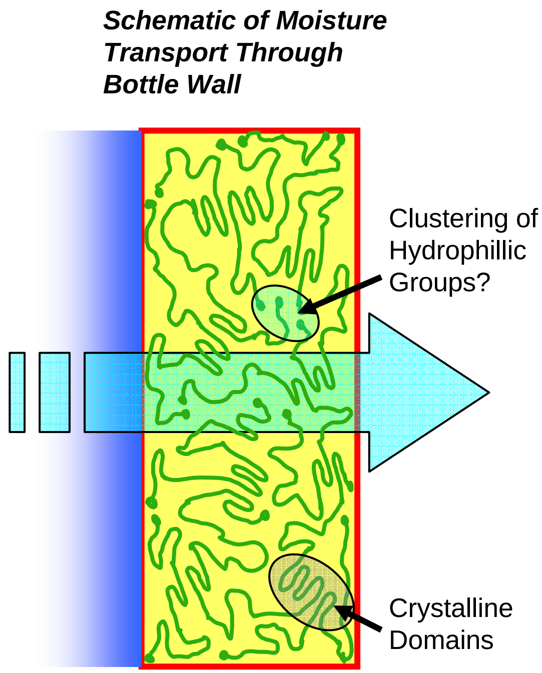
Conceptual Cycle for PLA from the Farm to a Commodity Plastic and Composting Back to Soil

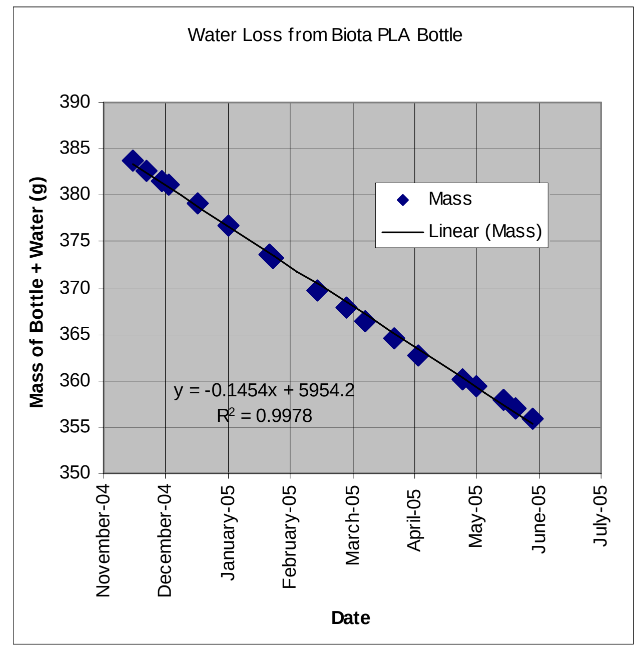




A Critical Property Limiting PLA Applications is Moisture Permeation

- **Why is Moisture Sorption/Transport in PLA Important?**



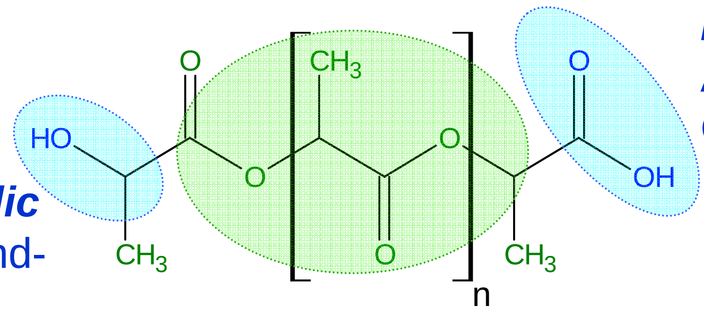


Commercial PLA water bottle buckles due to water loss after storage in warehouse for several months!

PLA bottle loses about 1 g water/week

Mechanics of Moisture Transport in PLA

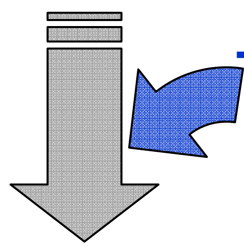
Hydrophilic Alcohol End-Group



Hydrophilic Acid End-Group

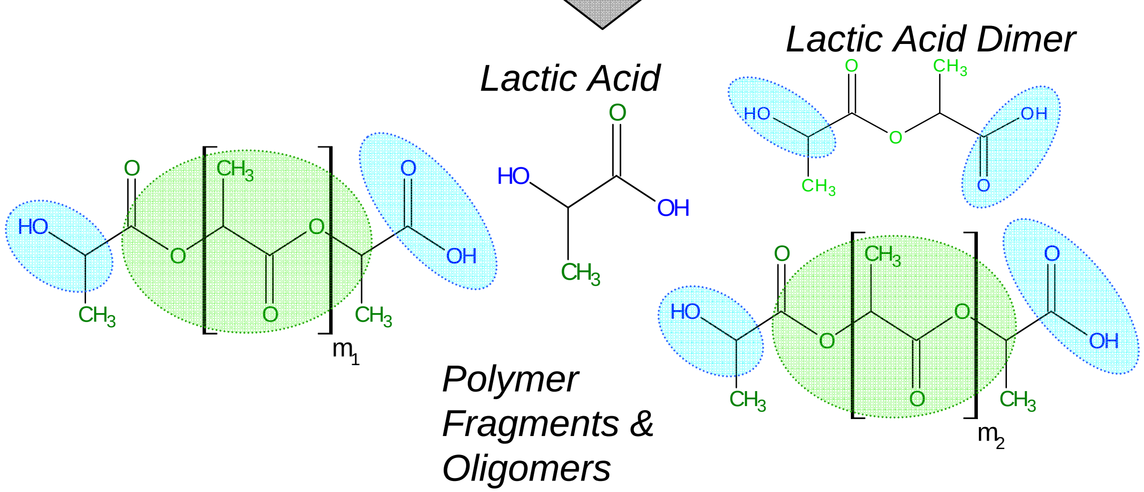
Hydrophobic Chain of Ester Linkages

Hydrolysis degrades PLA



+ H2O

scission of ester bonds with water



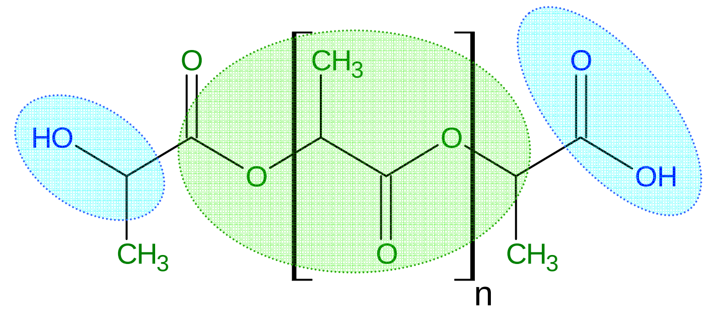
High MW PLA is Moderately Hydrophobic (absorbs 0.5-1% water)

Hypothesis:

Hydrophilic end groups critical for moisture sorption and transport:

- end groups excluded from crystalline regions of PLA
- # end groups increases with degradation

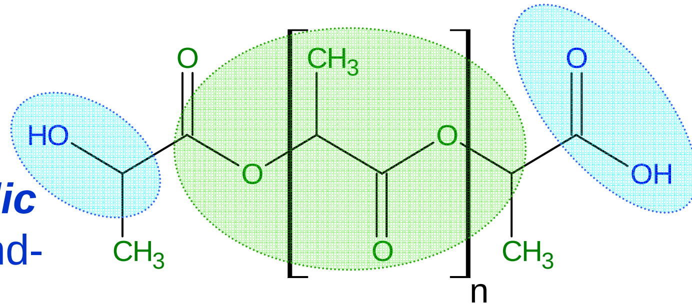
Hypothesis: *Hydrophilic end groups* critical for moisture sorption and transport



- Observations **Consistent** with Hypothesis
  - Sorption insensitive to crystallinity
  - Sorption increases with degradation
- Observations **Inconsistent** with Hypothesis
  - Low MW PEP-PLA block co-polymer absorbs only 30% less moisture
  - Sorption in Low MW PLA insensitive to end group composition (similar sorption to high MW PLA)

Degradation in PLA

Hydrophilic Alcohol End-Group



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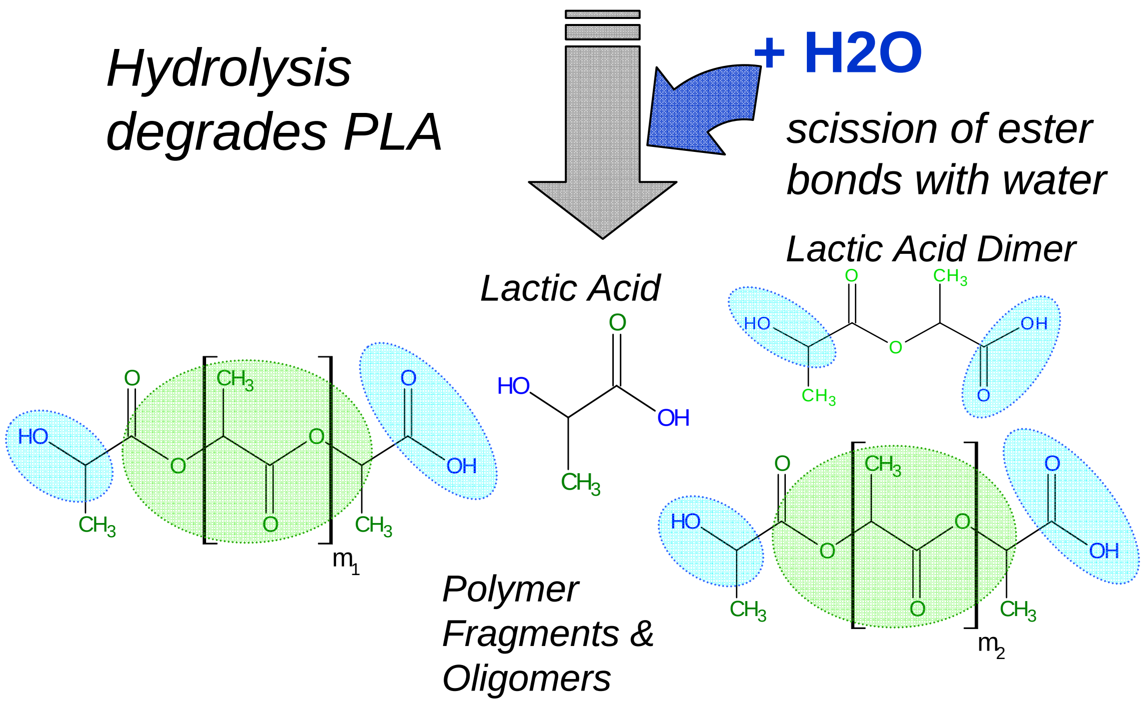


Degradation of PLA

- Why is Degradation important?
- Controlled Degradability of PLA Products
  - Minimize degradation during use
  - Maximize degradation during waste management (composting)
- Degradation is coupled to moisture sorption/transport

Experimental Methods for Monitoring Degradation of PLA

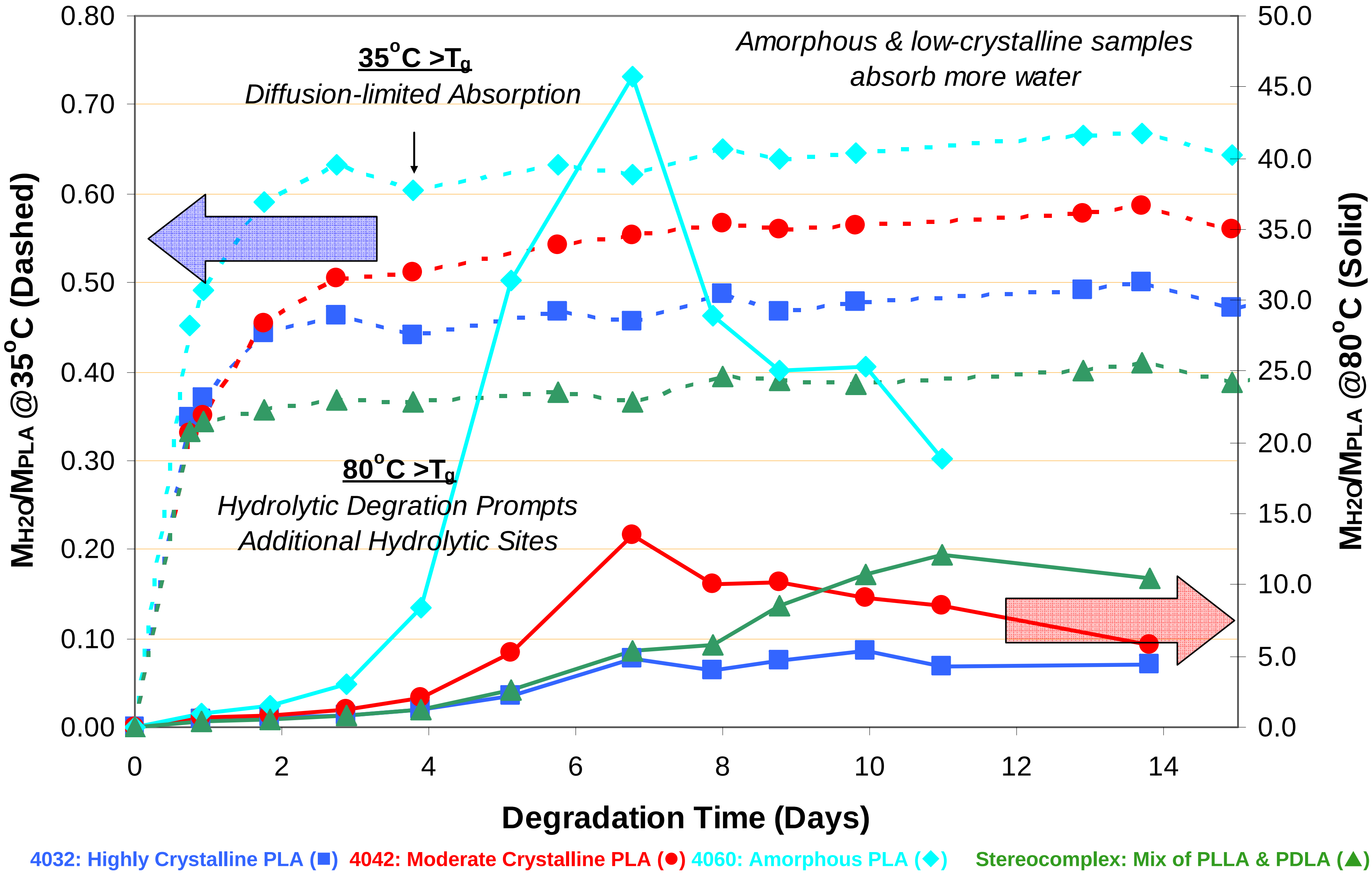
- Controlled Temp & RH
- Analysis
  - **Weighing**
  - **Acid/Base Titration**
  - **HPLC & GPC**
  - **NMR (with D_2O)**
  - **Sorption Experiments**
  - **Thermal Mechanical Properties**

Degradation of PLA Exposed to Humid Air

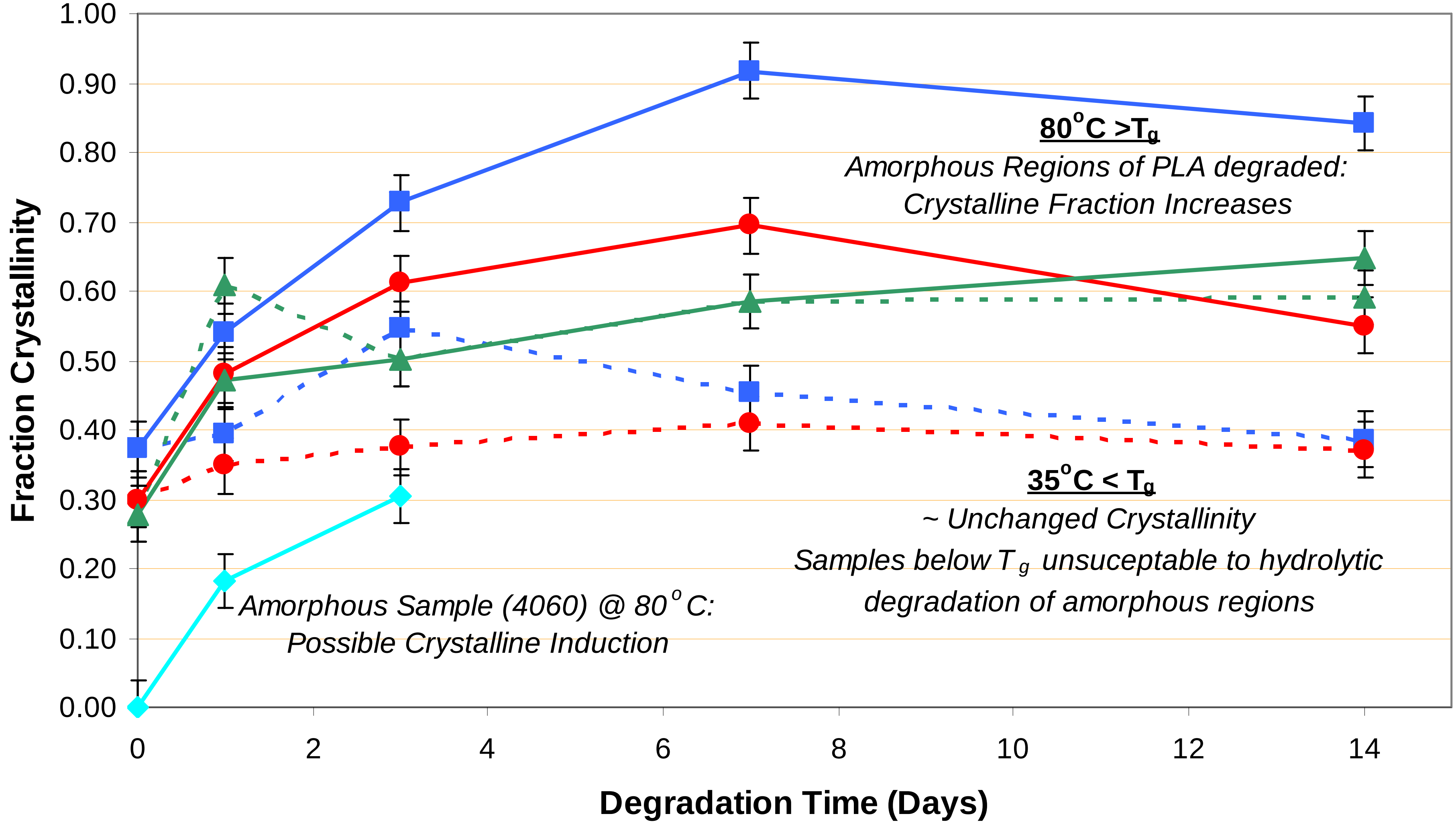
- Degradation of PLA in Controlled Environment
- Desiccator placed in oven at given temperature
- Water activity maintained via saturated salt solution in desiccator base
- Conditions studied:

  85% RH and 30^{o} C, 65^{o} C and 80^{o} C

Moisture Gain of PLA @ 85% Relative Humidity



Comparison of Changes in Crystallinity at 85%RH
Two Temperature Regimes



Degradation of PLA

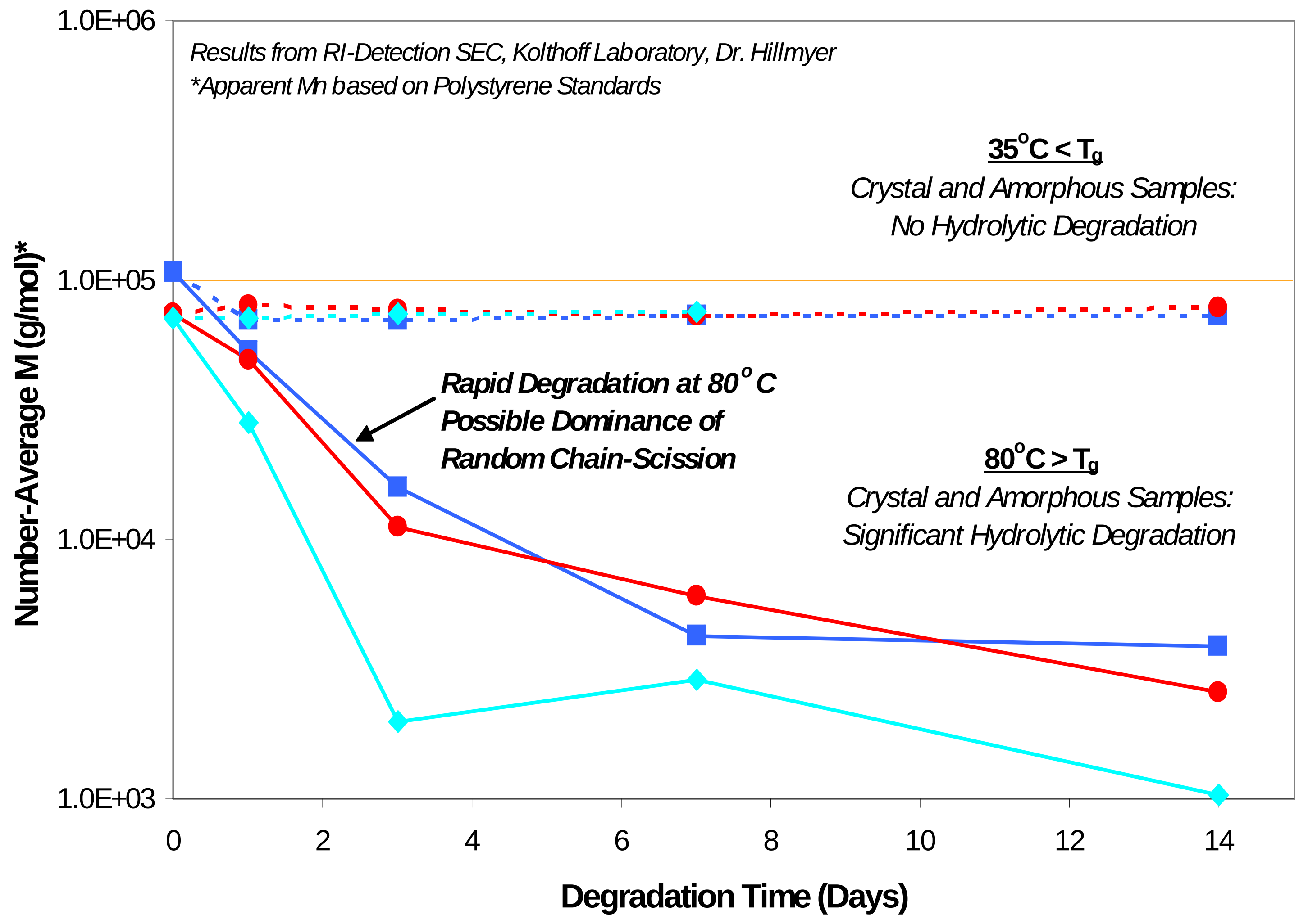
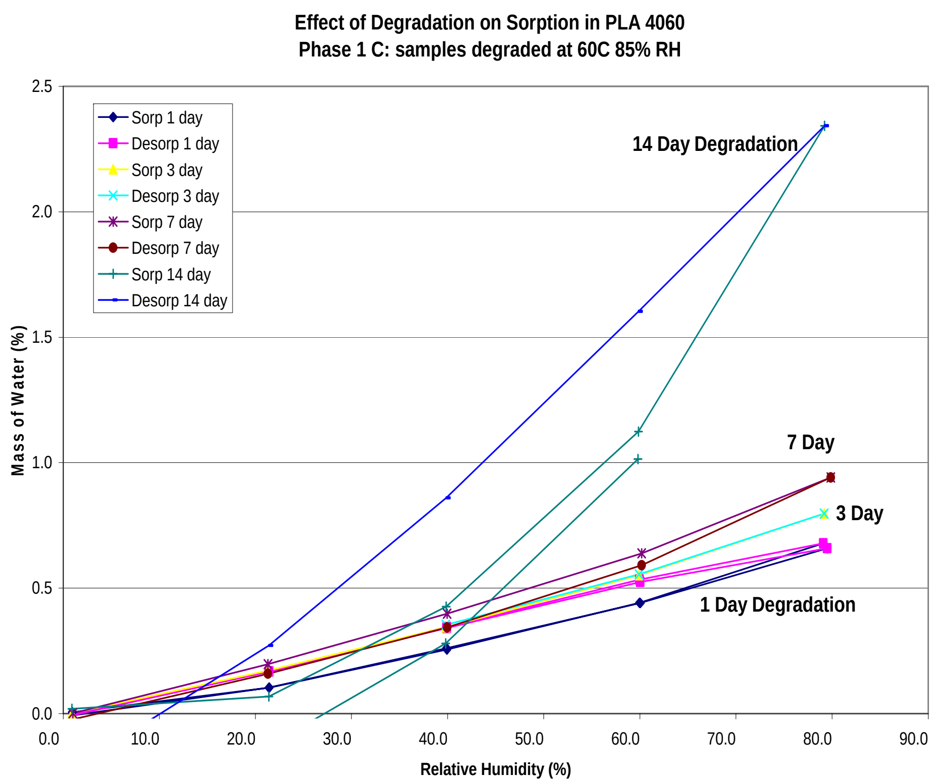


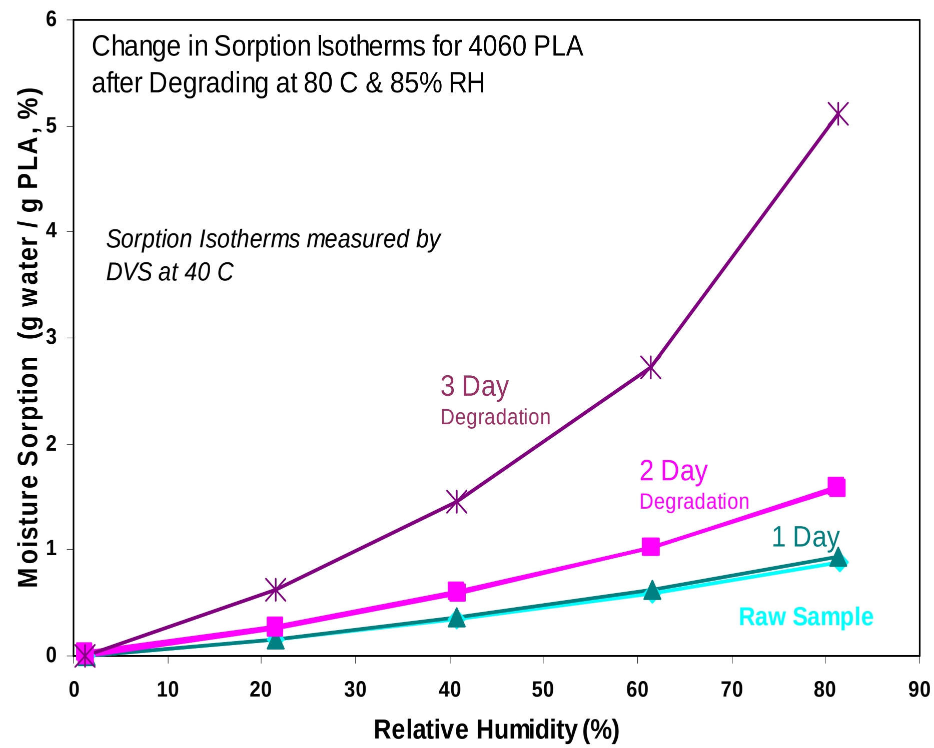
Figure 10*: Degradation of PLA exposed to 85% relative humidity. Changes in molecular weight measured by GPC.*

Effect of Degradation on Sorption

Degradation at 60ºC



Degradation at 80ºC



Degradation Causes Rapid Rise in Sorption

– After Induction Period

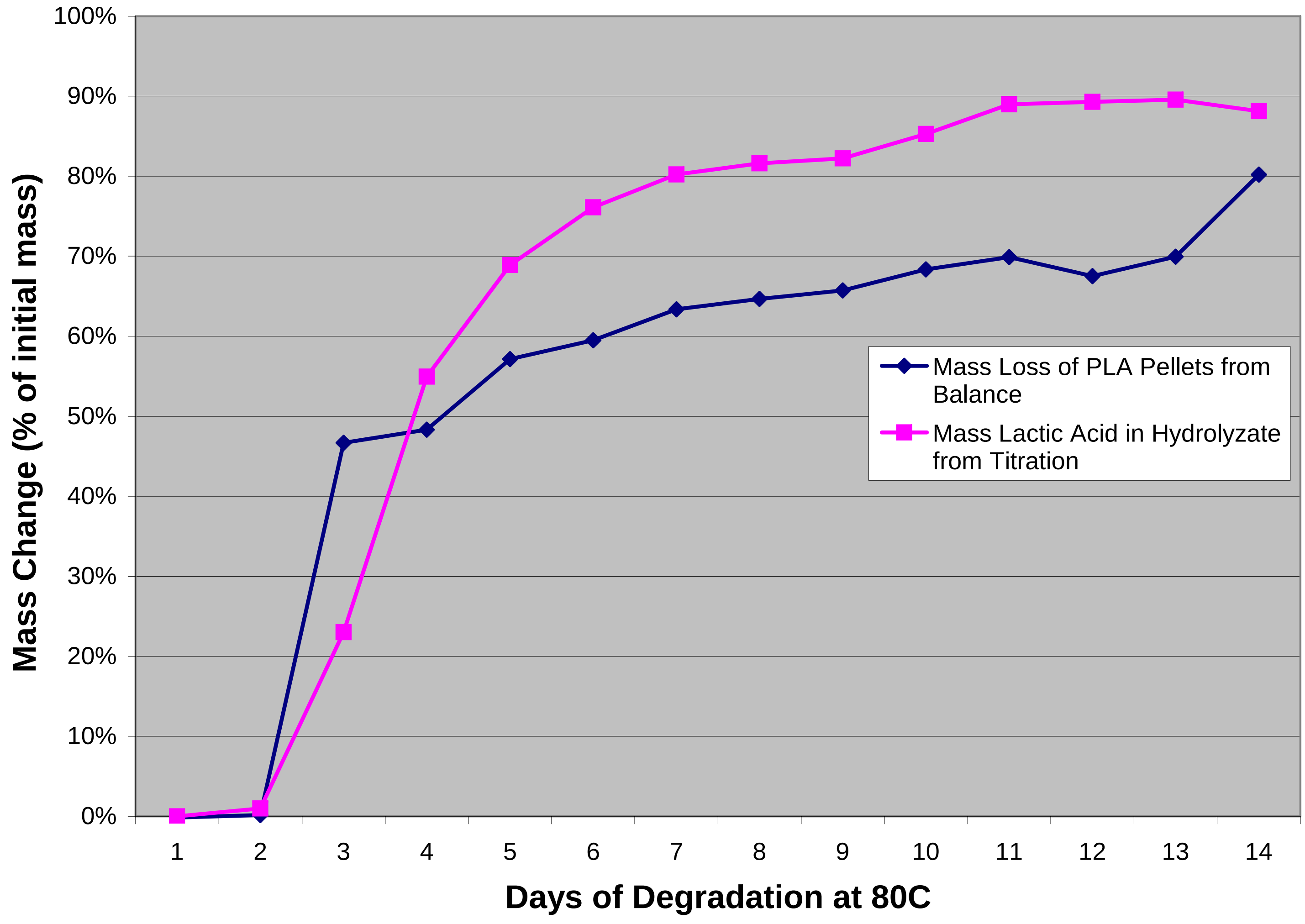
Degradation of PLA Immersed in Water

- Two time series of degradation experiments – varying degrees of degradation

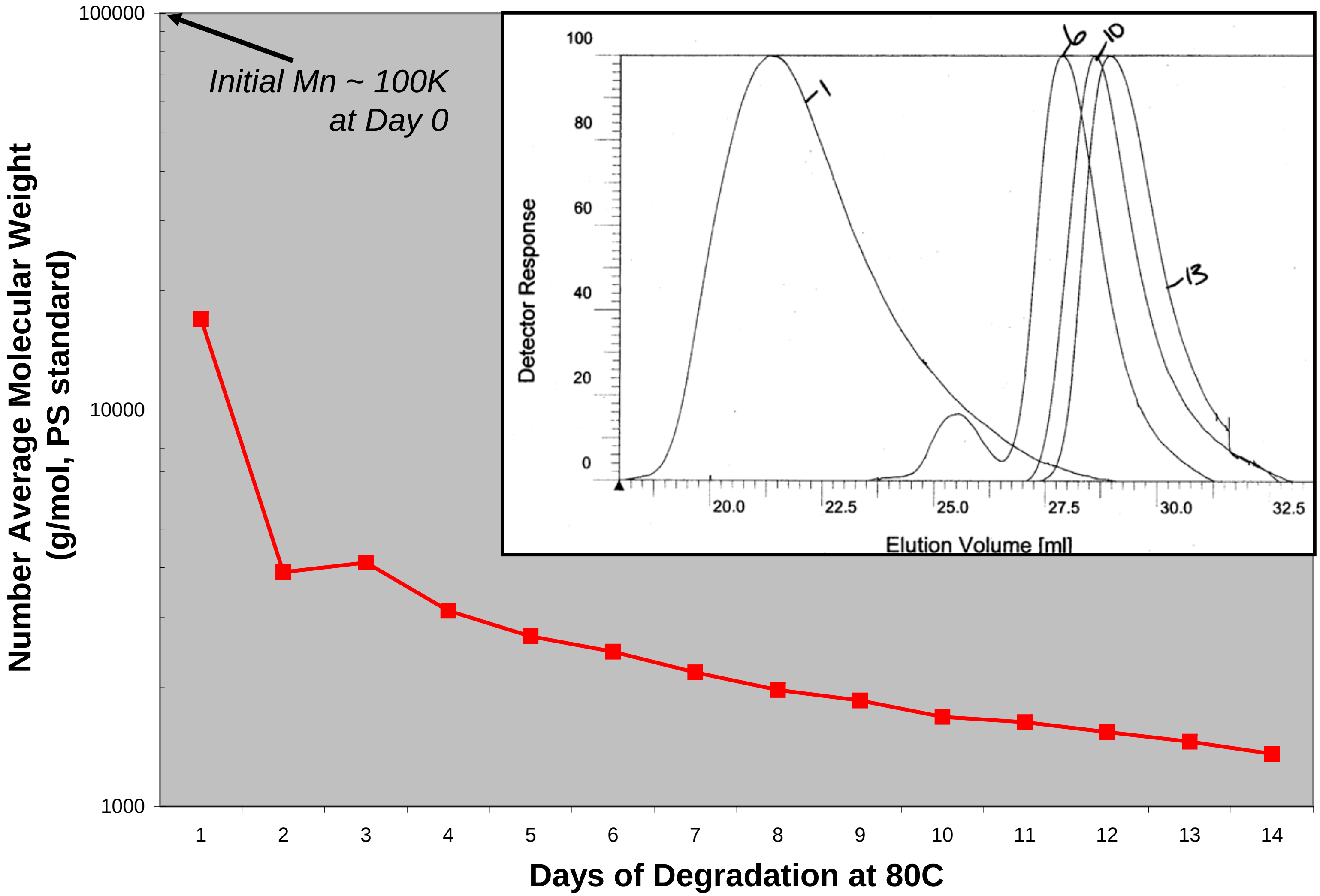
  deionized and deuterated water

- Analysis of the hydrolyzate containing the degraded products
  - **Weighing**
  - **Acid/Base Titration**
  - **HPLC & GPC**
  - **NMR (with D_2O)**

Degradation of PLA – Monitored by Mass Changes & Acid-Base Titration

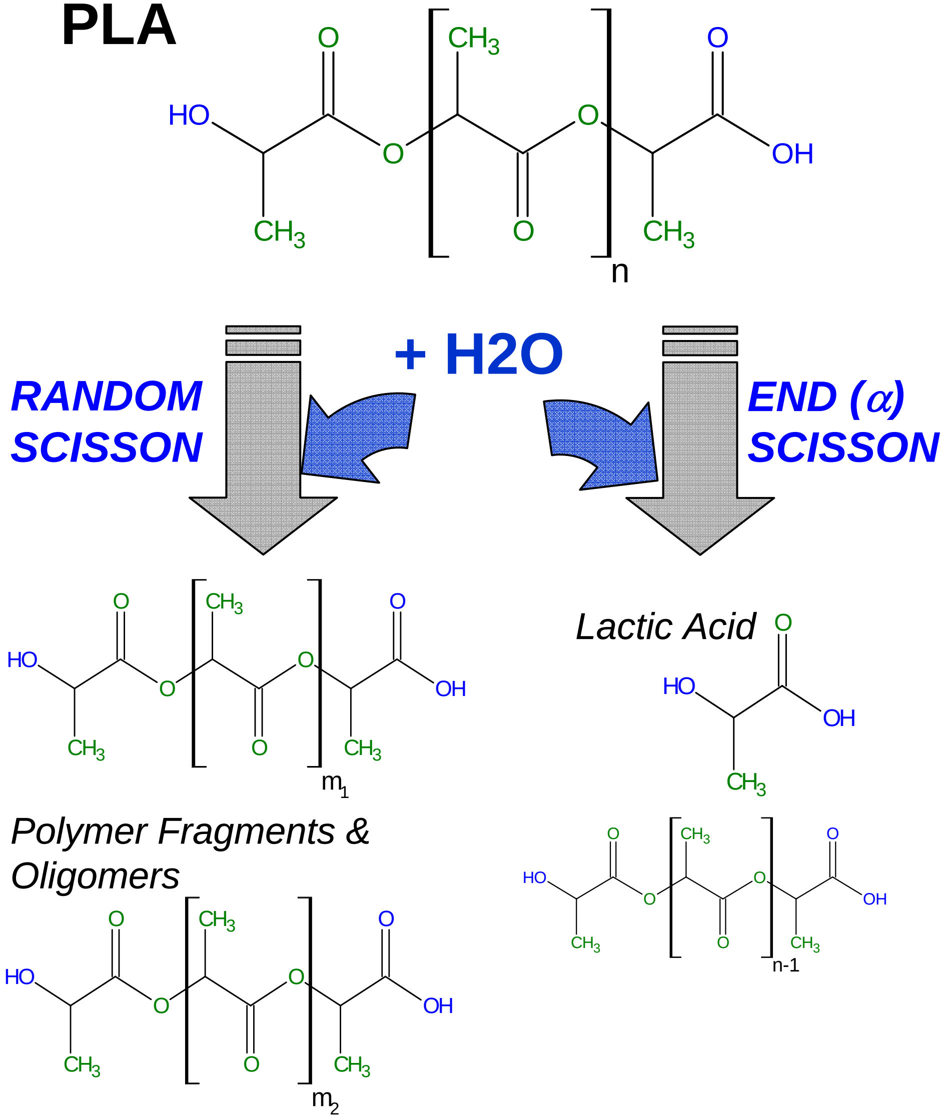


Change in PLA Molecular Weight (Mn) from GPC



Degradation Reactions in PLA

PLA



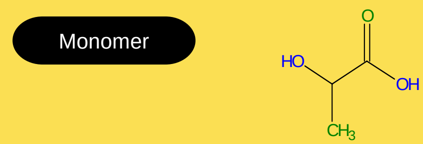
Hydrolysis degrades PLA

By scission of ester bonds with water

Functional Group Kinetics

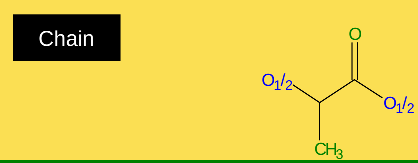
3 Functional Groups:

- Monomer = Lactic Acid (90 g/mol)



- End Group (81 g/mol)

- Chain Group (72 g/mol)



½ Oxygen Atom To Account For Sharing of Ester Bonds

Functional Group Kinetics for PLA Degradation

Functional Group Kinetics

3 Functional Groups:

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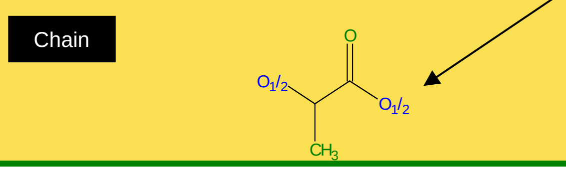
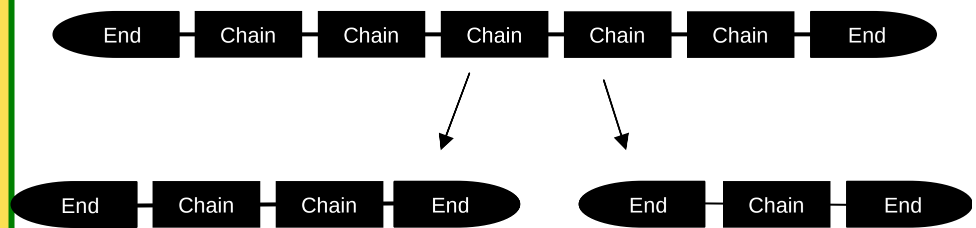


½ Oxygen Atom To Account For Sharing of Ester Bonds

Random Scission Reaction:



2 Chain + H_2O → 2 End

End Scission Reaction:

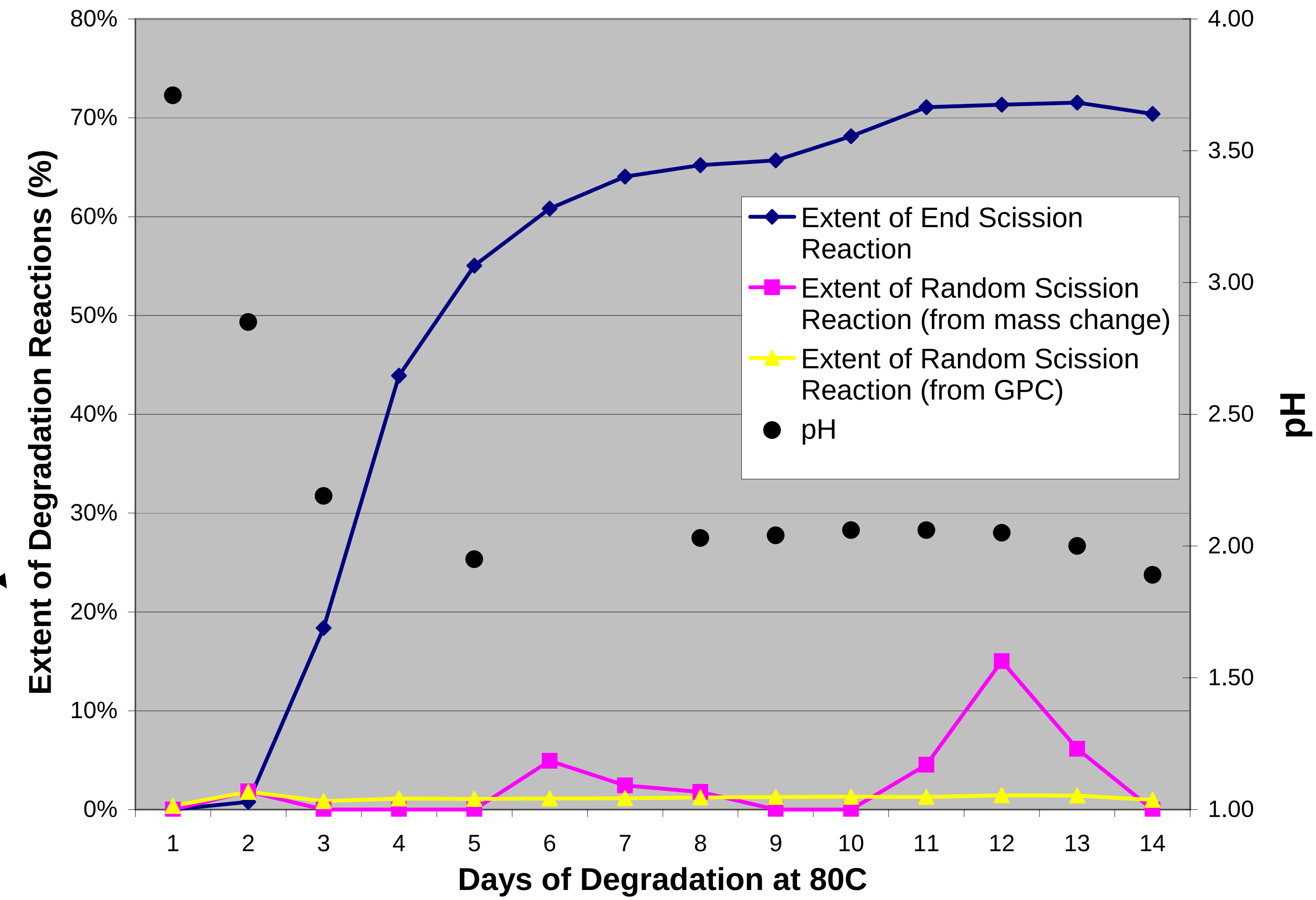
Chain + End + H_2O → End + Monomer

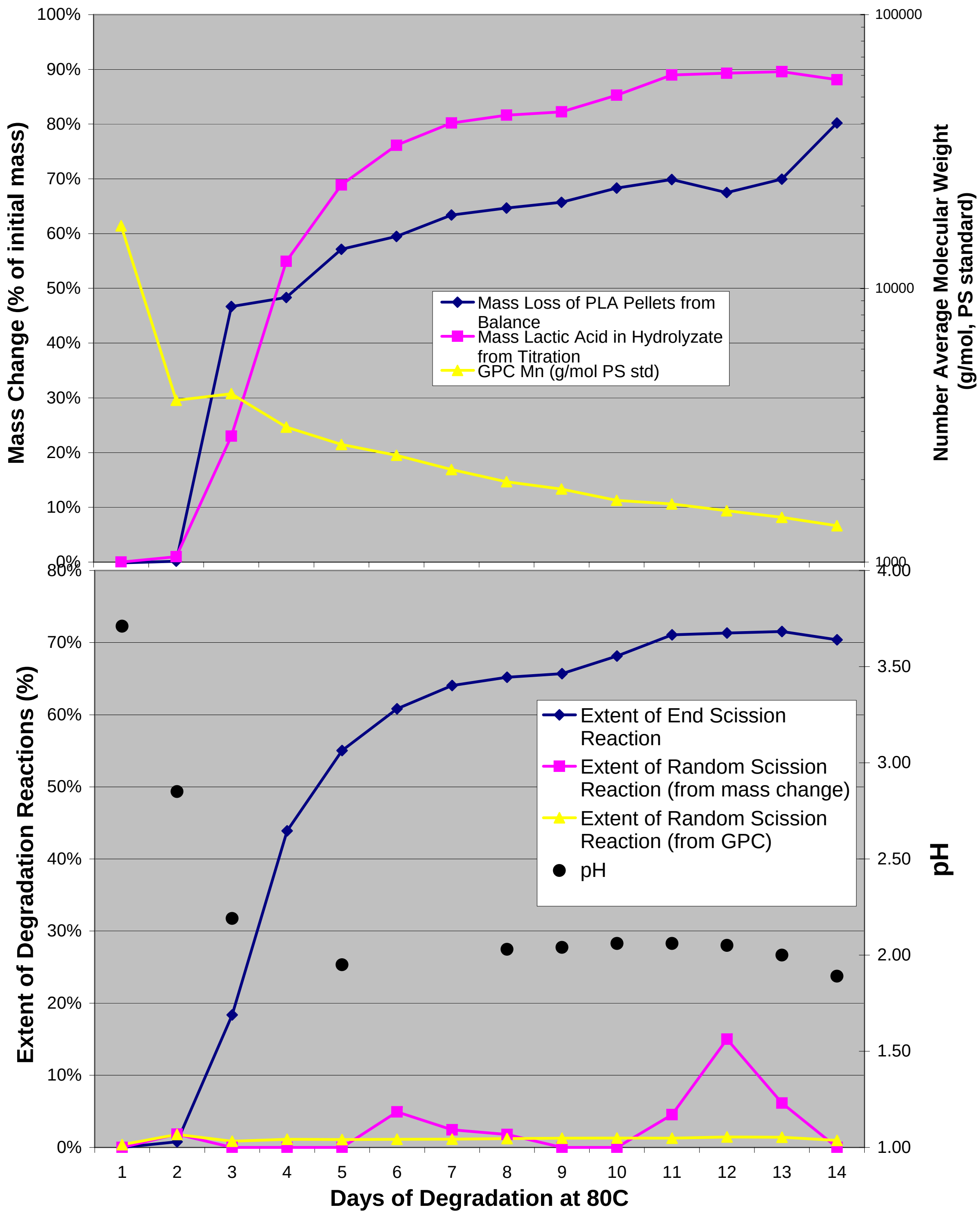
Molecular Weight:

$$M_n = \frac{72 \cdot n_C + 81 \cdot n_E}{n_E / 2}$$

Analysis of Extent of Random and End Scission Reactions

Extent of Reaction = % of Ester Bonds Cleaved





Degradation of PLA immersed in Water at 80ºC

- Random scission increases slightly the first two days - ~1% random scission sufficient to more than half the Mn
  - Falling MW without Soluble Products (lactic acid)
  - No change in polymer pellets mass until 2 days
- End Scission Dominates after the first 2 days
- Falling pH after 2 days
  →Rapid End Scission

Conclusions

- A Critical Property Limiting PLA Applications is Moisture Permeation
- Degradation is Coupled to Moisture Sorption/Transport
- PLA is Moderately Hydrophobic
- Hydrolytic Degradation creates additional hydrolytic sites causing rapid rise in sorption – After Induction Period
- Functional Group Kinetics of PLA degradation indicate that end group scission dominates after the first 2 days creating an autocatalytic effect
- Random scission, albeit small (~1%), very active in the first two days causing more than 50% decrease in Mn