

Time of Flight SIMS and MALDI Studies of the Surface Chemistry of PolySiloxanes and Biodegradable Polyesters: Quantitation

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*ASMS/NIST Workshop on
Polymer Mass Spectrometry* December 9/10 2004

Acknowledgements

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Quantitative ToF-SIMS and MALDI of Polymer Surfaces Outline

- ☞ Quantifying Amounts
 - ☞ PDMS Impurities in Contact Lens (SIMS)
 - ☞ Depth Profiles of Polymer Blends (SIMS)
- ☞ Quantifying Polymer Mw
 - ☞ PDMS MW mixtures in PMMA (MALDI)
 - ☞ Kinetics of PDMS polymerization (MALDI/SIMS)
- ☞ Quantifying Kinetics of Reactions (SIMS)
 - ☞ Degradation Kinetics of Biodegradable Materials
 - ☞ Simultaneous Drug Release/Degradation Kinetics

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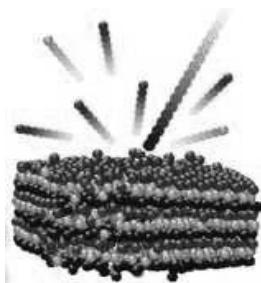
Research Themes

- Quantitative Analysis
 - Precision
 - Accuracy
 - LOQ, LOD, etc.
 - Sensitivity
- In-Depth Analysis
- Sampling Depth
- Low Temperature Angle Dependent XPS
- Polymer Surface Chemistry
 - Low Surface Energy (Si, F)
 - Structure/Property
 - Surface Structure
 - → **Reactivity** ←
- Link to Applications
 - Microelectronics
 - Tissue Engineering
 - Coatings
 - **Anti Corrosion**
 - **Minimal Fouling**

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Time-of-Flight Secondary Ion Mass Spectrometry



- Provides information at the top-most few atomic layers
- Very high sensitivity to detect species with very low concentration
- Imaging capabilities with spatial resolution ca. $2\mu\text{m}$ (Cs^+ primary ion gun)
- Sample surface chemistry preserved under static condition

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Bioadhesion and Bioabhesion to Polymers

- Low Surface Energy Materials: “Minimal Biological Adhesion”
 - Fluoropolymers
 - Siloxanes (PDMS Silicone™)
 - Polyethylene Oxide/Glycol (PEO/PEG)
 - Perfluoropolyethers
- “Bio-Active” Polymer Surfaces:
 - Rearrangement/Segregation
 - Degradation
 - Biological Recognition/Specificity at Surfaces

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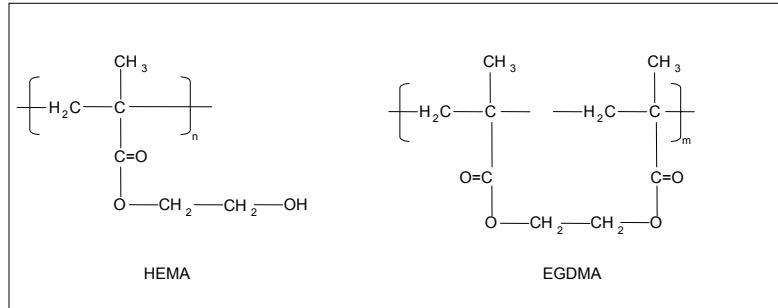
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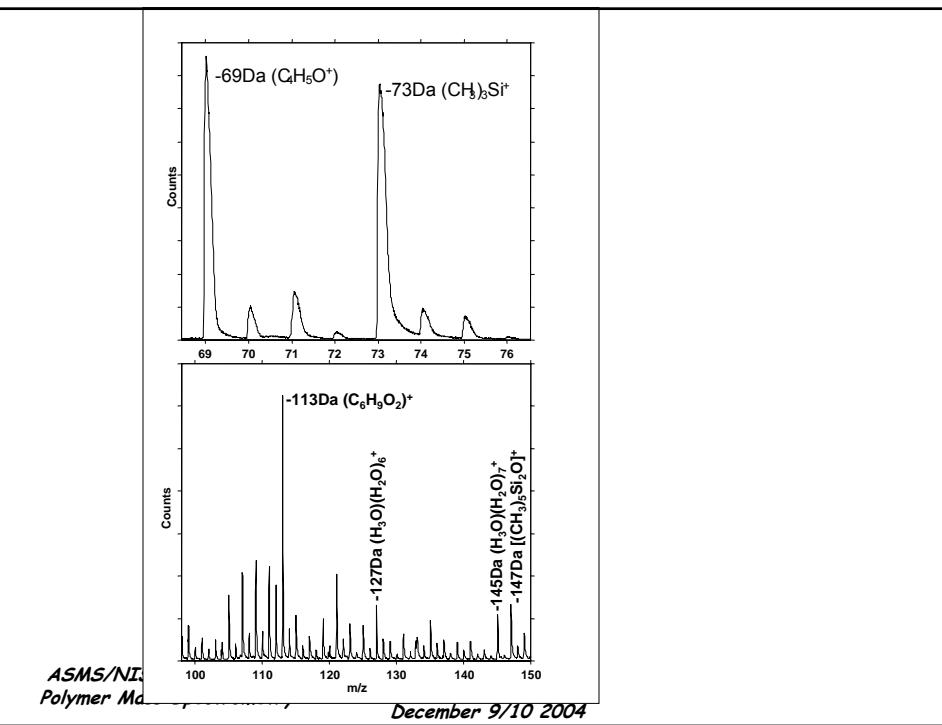
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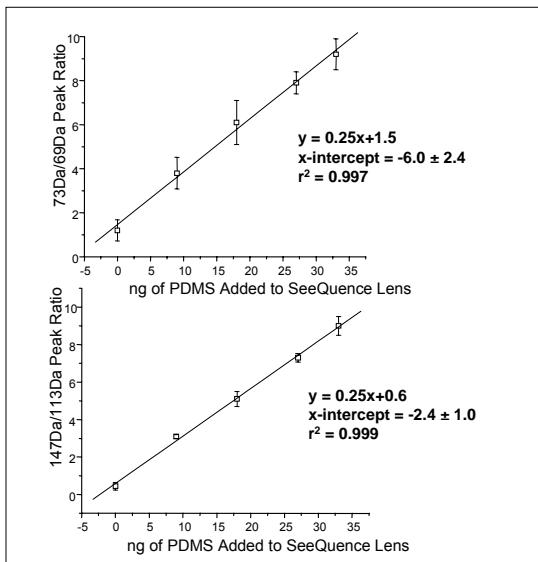
Analysis of Commercial Contact Lens Systems by XPS and SIMS



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Standard Additions



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PDMS Quantification

Area of a PDMS molecule $\approx 50\text{\AA}^2 = 5 \times 10^{-15} \text{ cm}^2$

Area of SeeQuence® lens segment = 0.283 cm^2

$2.4\text{ng PDMS} = 6.23 \times 10^{-12} \text{ mol PDMS}$

$6.23 \times 10^{-12} \text{ mol PDMS} = 3.75 \times 10^{12} \text{ molecules of PDMS}$

$3.75 \times 10^{12} \times 5 \times 10^{-15} \text{ cm}^2 = 0.02 \text{ cm}^2 \equiv \text{Area occupied by PDMS}$

$$(0.02 \text{ cm}^2 / 0.283 \text{ cm}^2) * 100 =$$

$6.6\% \pm 2.8\%$ monolayer coverage of PDMS

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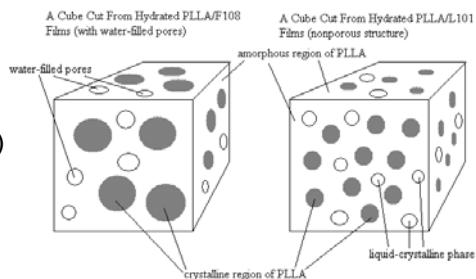
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PLLA/Pluronic® Blend model

- PLLA: crystalline region + amorphous region
- Blend: a third region in the hydrated film
 - Water-filled pores (F108/PLLA)
 - A liquid-crystalline phase (L101/PLLA)
- P104/PLLA blends: between these two extremes
- Presence of Pluronic® in PLLA
 - Changes of the structure of the PLLA matrix ->
 - Changes of the degradation rate->
 - Changes of the drug-release rate from the matrix



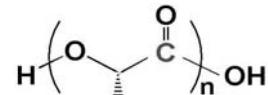
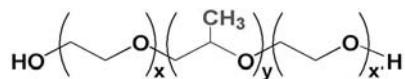
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Biocompatibility

- Pluronic® surfactants
 - Clinical uses
 - FDA approved marketed drugs (Geriplex® FS Liquid)
- PLLA
 - FDA approved
 - Biocompatible degradation product: lactic acid
 - Uses in medical area



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Justifications

- Importance of Surface Study
 - Surface Segregation: Due to the Difference of Surface Energies in components
 - Surface Chemistry Affects:
 - Degradation Kinetics -> Drug Release Rates
 - Drug activities
 - Cell Adhesion to the Implanted Devices
 - Interlayer Adhesion
 - Mechanical Properties
- Quantification of the surface concentration

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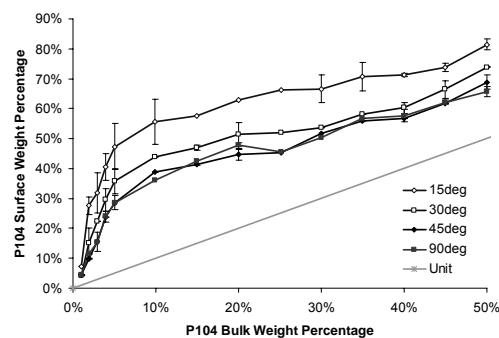
Samples Prepared

Name	PLLA	9901	9802	9703	9604	
PLLA%	100%	99%	98%	97%	96%	
Name	9505	9010	8515	8020	7525	
PLLA%	95%	90%	85%	80%	75%	
Name	7030	6535	6040	5545	5050	P104
PLLA%	70%	65%	60%	55%	50%	0%

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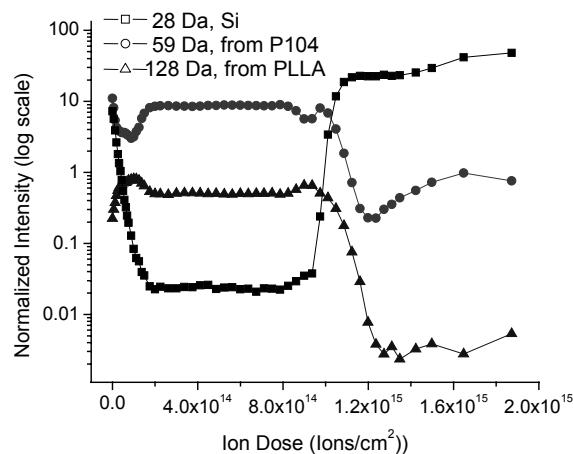
Blend XPS Results

- 1-5wt% P104 blends:
the sharp slope; the
10-50wt% blends: less
sharp slope
- A relatively
homogenous region
from 73Å to 103Å
- No points on the unit
line



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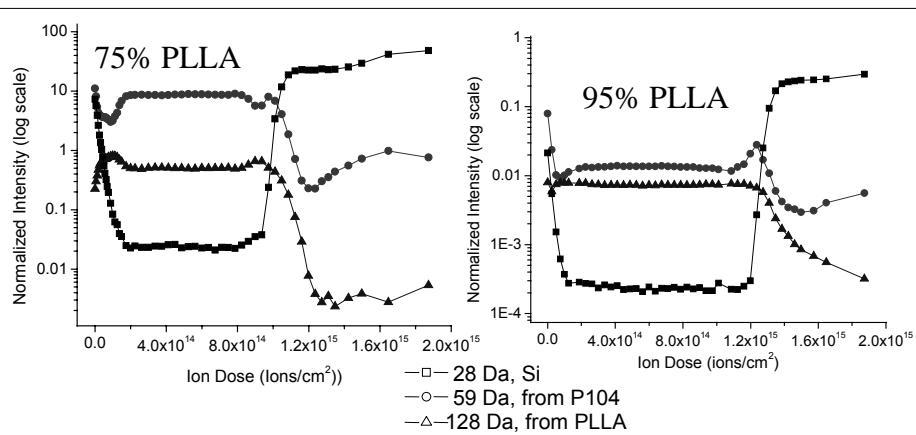
TOF-SIMS Depth Profiling



75% PLLA in bulk
Sample thickness:
6200 Å
59 Dalton: $(PO+H)^+$
and $(EO+CH_3)^+$
fragments from P104
128 Dalton: $(2LA-O)^+$
fragment from PLLA
The Intensity:
normalized to the
total ion intensity

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TOF-SIMS Depth Profiling



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TOF-SIMS Depth Profiling

- A depletion zone
 - 75% PLLA blends: Deeper (~730 Å, calculated)
 - 5% PLLA blends: Shallower (~ 267 Å, calculated)
- No interaction between the air surface and the interface
- A stable mixture between the air surface and the interface
- To compare to the XPS data
 - Limit to the topmost 100 Å
 - XPS results: need to be deconvoluted
- Identical Trends

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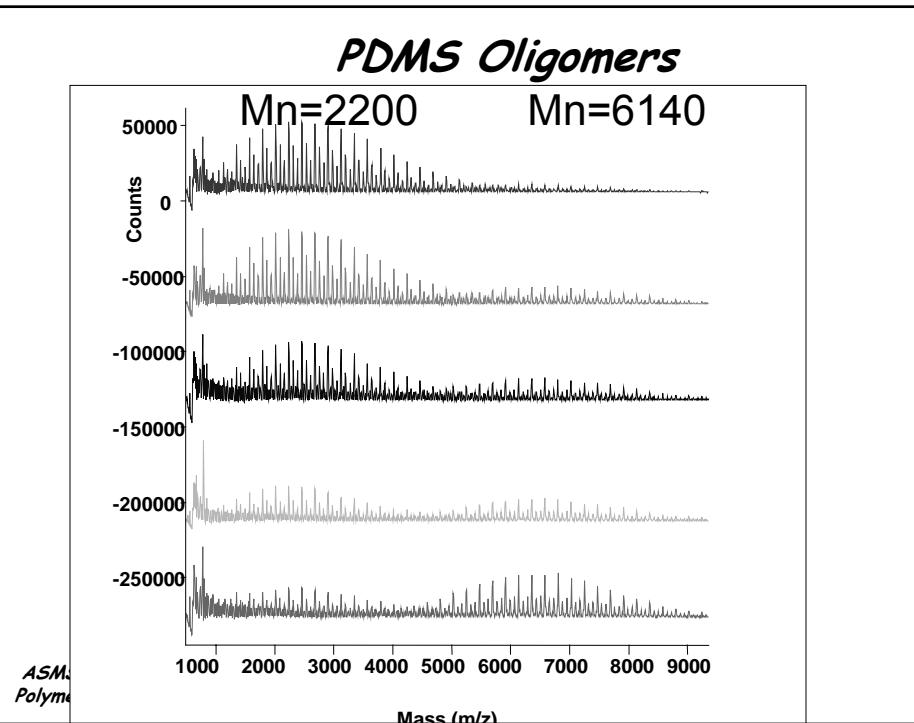
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Quantification of Mixtures of PDMS Oligomer Distributions in PMMA matrix

- Mixtures of Low PDI (< 1.1) Oligomer distributions
- PMMA Matrix
- Quantification using integration of all oligomer ions
- Summation to get integrated intensity
- Plot versus Monomer moles

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Quantification of Mixtures of PDMS Oligomer Distributions in PMMA matrix

Name	V ₆₁₄₀ /V ₂₂₀₀ (uL)	M ₆₁₄₀ /M ₂₂₀₀ (Theoretical)	I _{1/2k} /I _{1/6k} (Calculated)
Sample 1	50/10	5.0	4.72 ± 0.86
Sample 2	40/20	2.0	2.11 ± 0.23
Sample 3	30/30	1.0	0.97 ± 0.05
Sample 4	20/40	0.5	0.55 ± 0.04
Sample 5	10/50	0.2	0.21 ± 0.03
Sample 6	0/60	0.0	0.00 ± 0.00

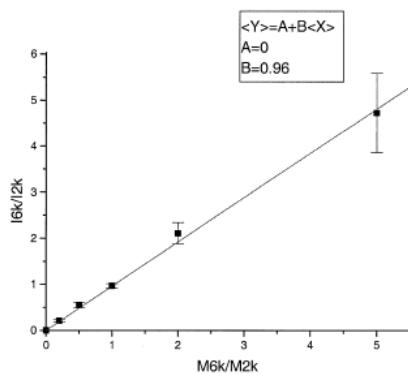


Figure 4. Plot of relative ion intensities ratios versus the weight ratios of polydimethylsiloxane.

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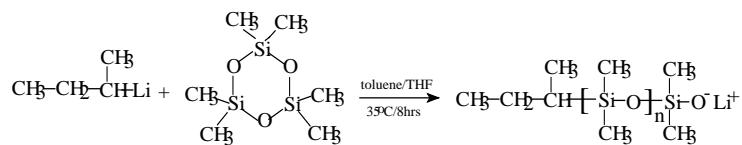
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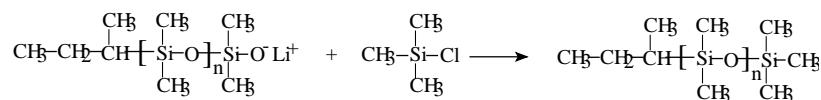
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Anionic Ring Opening Synthesis of Narrow Mw PDMS

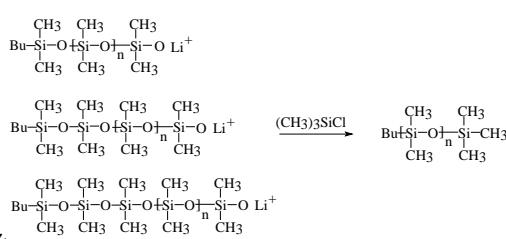
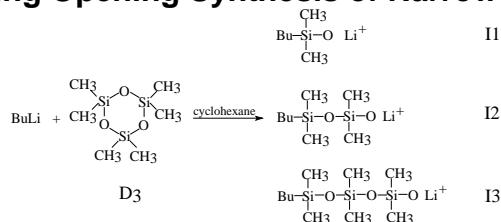


D3



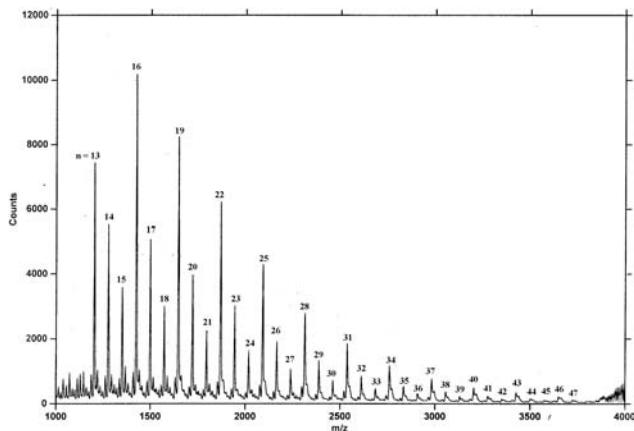
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Anionic Ring Opening Synthesis of Narrow Mw PDMS



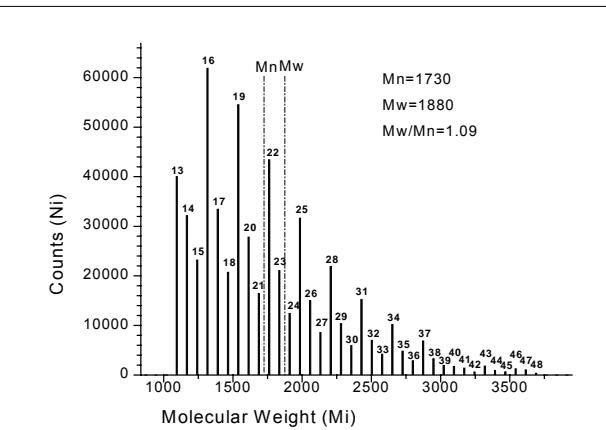
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ToF-SIMS of PDMS Oligomer Distribution Mw=2200 Mn/Mw = 1.05



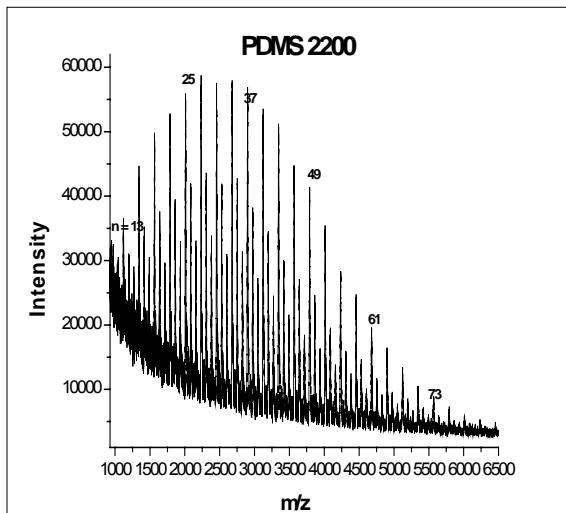
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Quantitative Data from Molecular Weight Distribution



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MALDI Molecular Weight Distribution

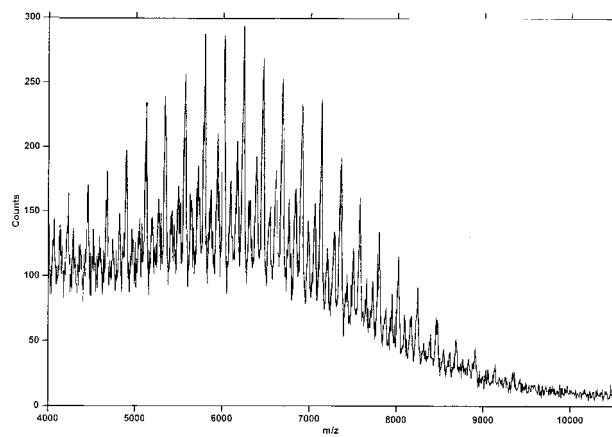


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ToF-SIMS of PDMS Oligomer Distribution

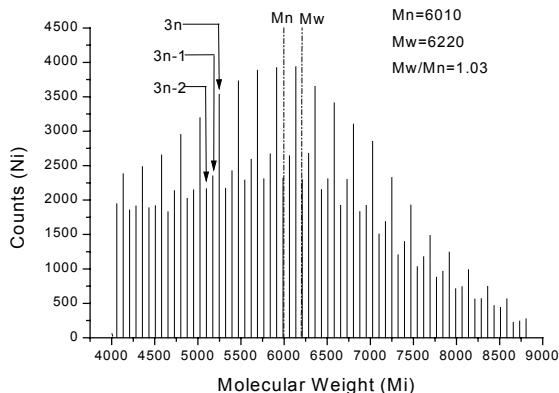
$M_w=6140$ $M_n/M_w = 1.07$



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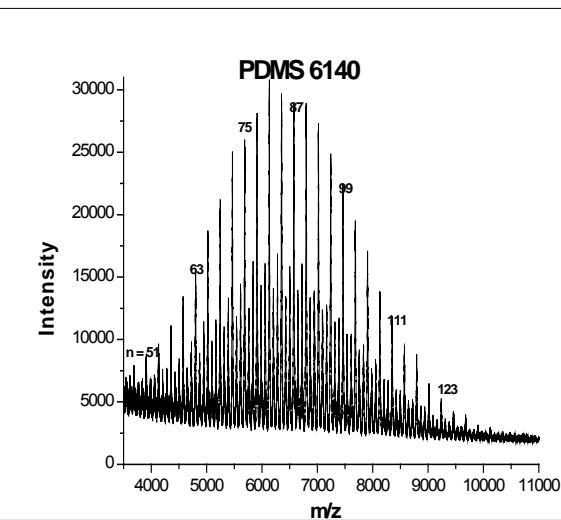
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Quantitative Data from Molecular Weight Distribution



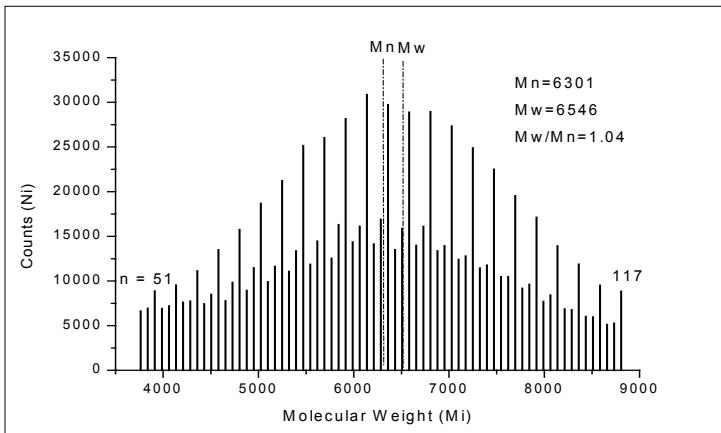
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MALDI Molecular Weight Distribution



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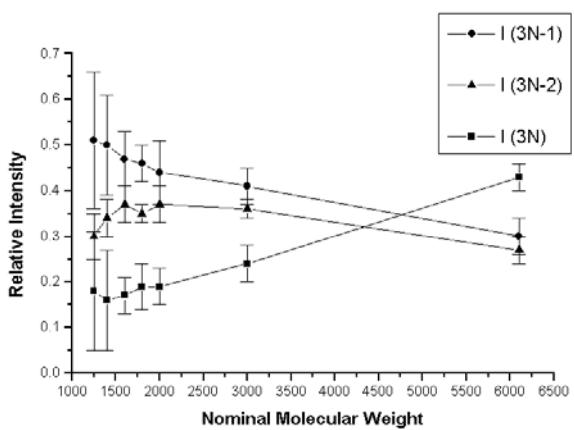
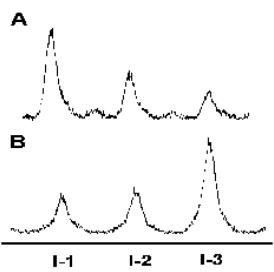
Quantitative Data from MALDI Molecular Weight Distribution



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Change in Branching with Mw



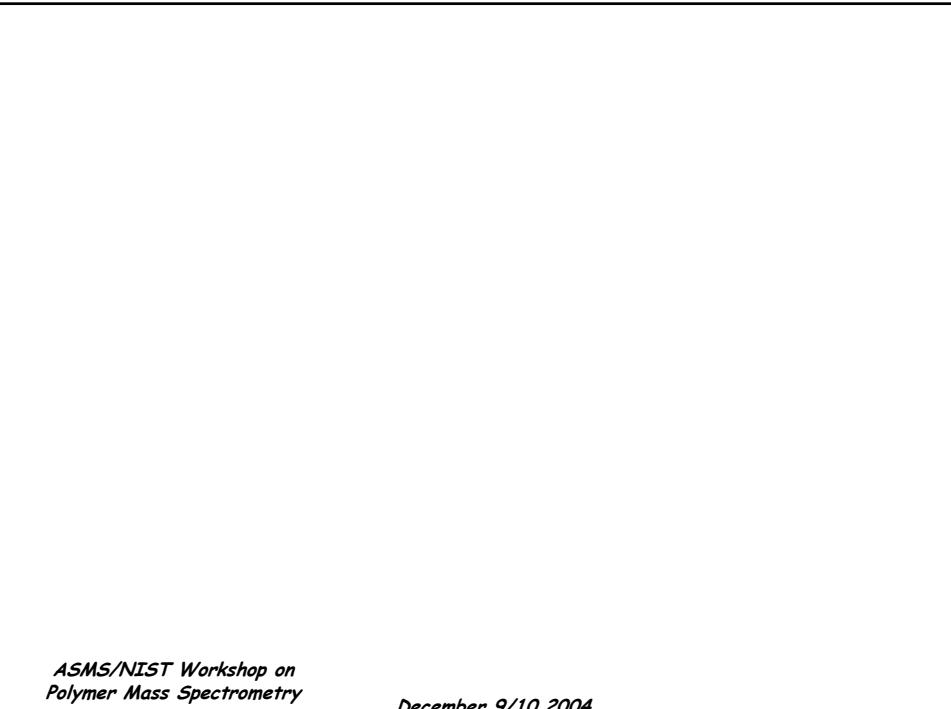
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pDMS Polymerization Kinetics Conclusions

- Kinetics can be followed by Quant MS
- Polymerization Conditions can be optimized
- Reaction Products directly probed
- Initiator Populations Very Sensitive to Impurities

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Introduction

➤ Polymeric Biomaterials

✓ Biodegradable Polymers

Uses: - Absorbable Sutures

- Drug Delivery Devices

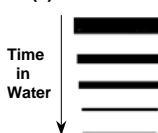
- Scaffolds for Tissue Engineering

✓ Stable Polymers

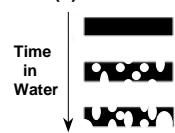
Uses: Joint & Tissue Replacements

➤ Schematic of Degradation Process

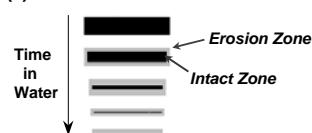
(a) Surface erosion



(b) Bulk erosion



(c) Erosion front formation



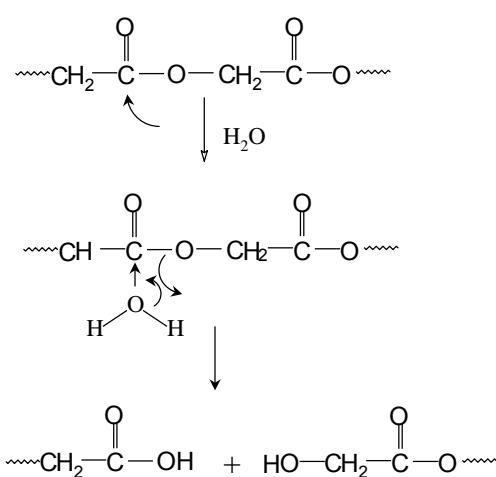
Desirable Application : Drug Delivery Systems

Desirable Application : Absorbable Sutures

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General ester hydrolysis mechanism



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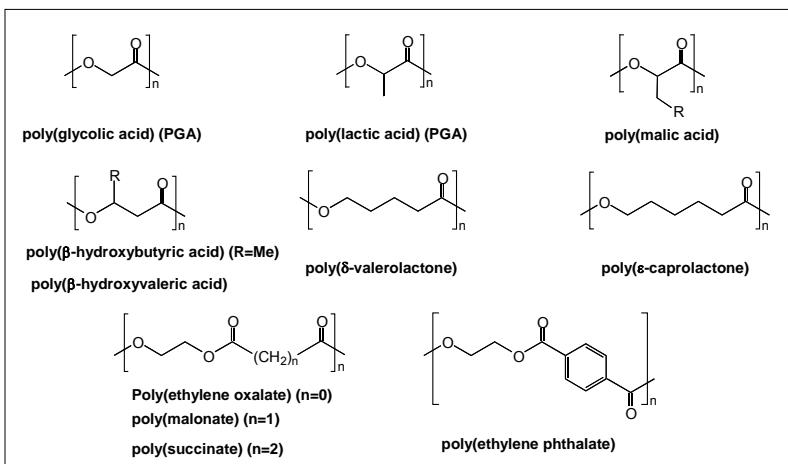
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Surface Erosion vs. Bulk Erosion Characterization for Biodegradable Polymers

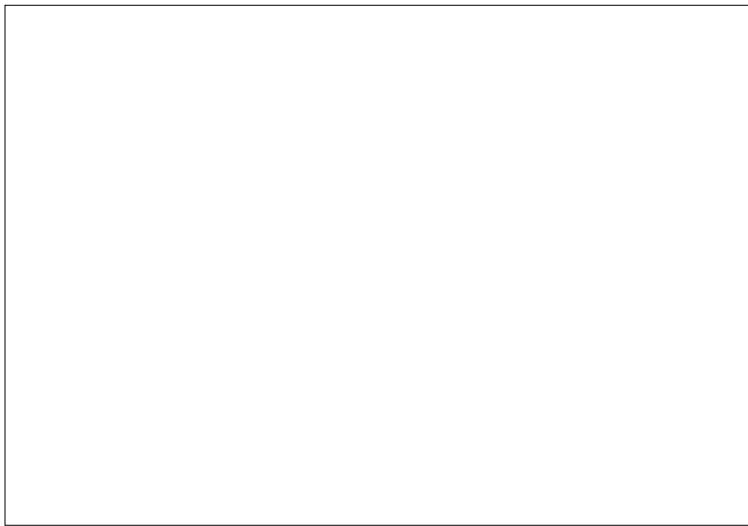
- **Surface:** Direct Contact Region with Physiological Environment
 - ❖ Dictate *in vivo* Performance of Material
- **Bulk Properties** → **Surface Properties**
 - Due to (1) Specific Molecular Orientation at the Surface
 - (2) Surface Specific Chemical Reactions
- **Surface Characterization: Essential Value**
 - ✓ Fundamental Understanding of Hydrolytic Surface Degradation Mechanism & Kinetics
 - ✓ Expanding into New Biodegradable Polymers

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Examples of Biodegradable Polyesters



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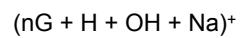
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Polyglycolic Acid Results

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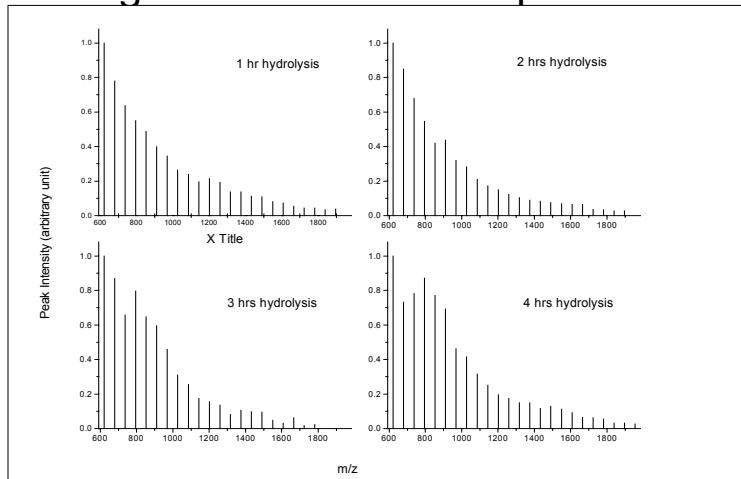
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Polyglyclic acid Results



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Plots of fragment peak intensities show
the oligomer molecular ion peak distribution



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Poly(ideitic Acid) Results

$(nL + 2H + Na)^+$

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Poly(glycolic acid lactic acid) copolymer

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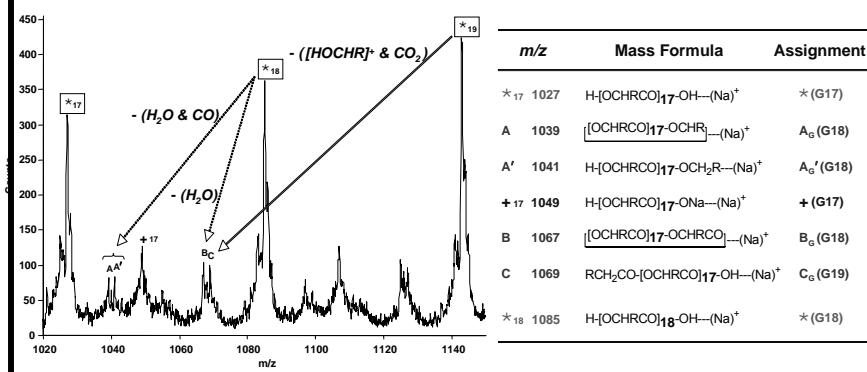
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Poly(glycolic acid lactic acid) copolymer

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Improving Quantitation by Integrating All Ion Formation Products: Possible Neutral Ion Dissociation and Fragmentation Pathways of Hydrolytic PGA Degradation Products

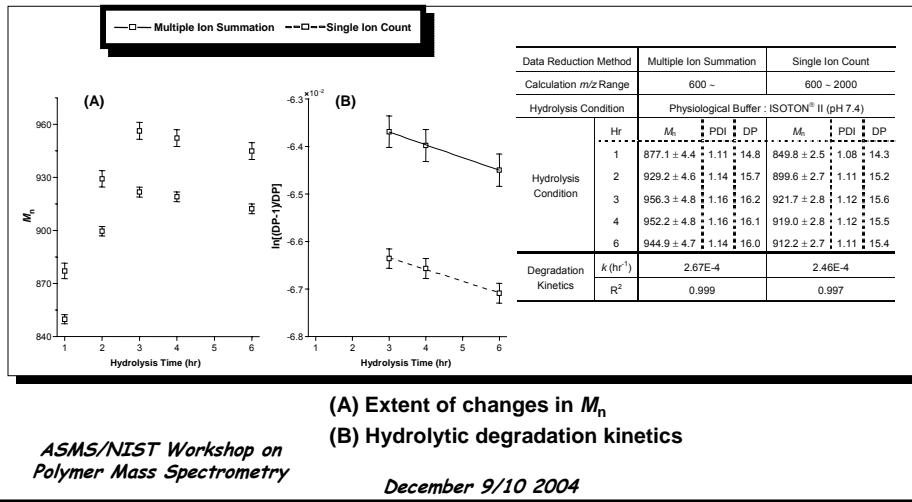


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Quantitative ToF-SIMS Results Depending on Data Reduction Methods

< Multiple Ion Summation vs. Single Ion Count >



Conclusions: Quantitative Methods

- Using Multiple Ion Summation Method, the Quality of MW Ave. Information about Polymer Biodegradation at the Surface has been Improved.
- This Method leads to a Better Data Reduction Method in Quantitative ToF-SIMS to Obtain Direct MW Information.
- This Present Work will be used as a Principal Tool for Surface Analysis of Biodegradable Polymers as a Function of Hydrolysis Treatment.

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Conclusions

- ✓ **Using ToF SIMS,**
 - : Direct Characterization of Hydrolytic Surface Degradation Mechanism & Kinetics of PGA ↵ in the Range of Hours
- ✓ **Using DSC,**
 - : Chain Scission of PGA ↵ Related to Increase of Crystallinity
- ✓ **From the combined ToF SIMS & DSC Results,**
 - Hydrolytic Degradation ↵ First in the Amorphous Region
 - Increase of Crystallinity ↵ partly Determine Rate of Degradation
 - Hydrolytic Degradation both at Surface and in Bulk
 ↳ pH Sensitive
- ✓ **Potential Application of This New Approach:** Simple, Fast, & Powerful
 - ↳ Screening Test of New Biodegradable Polymers
 - ↳ Degradation Kinetics Study of Biodegradable Polymers

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Conclusions

Hydrolysis products of biodegradable polymers can be observed as intact molecules with ToF SIMS over a wide range;

The data contained in ToF SIMS spectra, including molecular weight distribution of the hydrolysis products and molecular ion peak intensities, provides information to explore both reaction kinetics and mechanisms of the hydrolytic degradation of biodegradable polymers.

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Quantitative ToF-SIMS and MALDI of Polymer Surfaces

Outline

⇨ Quantifying Amounts

- ⇨ PDMS Impurities in Contact Lens (SIMS)
- ⇨ Depth Profiles of Polymer Blends (SIMS)

⇨ Quantifying Polymer Mw

- ⇨ PDMS MW mixtures in PMMA (MALDI)
- ⇨ Kinetics of PDMS polymerization (MALDI/SIMS)

⇨ Quantifying Kinetics of Reactions (SIMS)

- ⇨ Degradation Kinetics of Biodegradable Materials
- ⇨ Simultaneous Drug Release/Degradation Kinetics

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Application of the ToF-SIMS Method to Drug Delivery/Degradation Kinetics

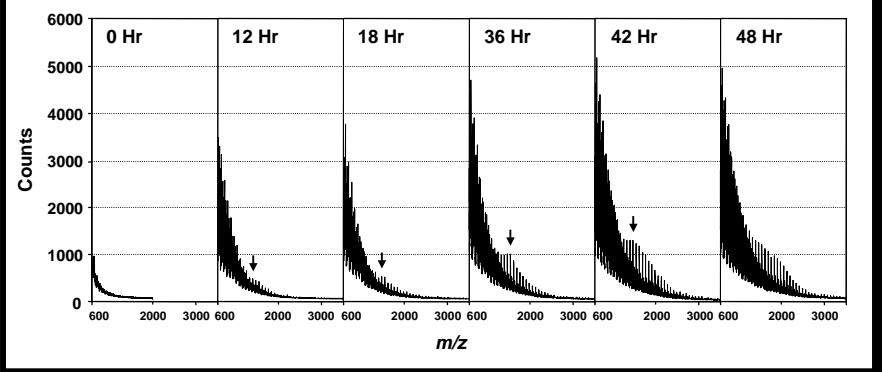
- PLLA biodegradable polyester used.
- Ph₃N used as an Insoluble Additive in aqueous buffer Media.
- Six different Blend Matrices of Ph₃N/PLLA analyzed.
(10:90 to 70:30 wt%)
- Degrade Blend Matrix (20:80 wt%) at two pHs (7.4 and 10.0) for different time intervals.

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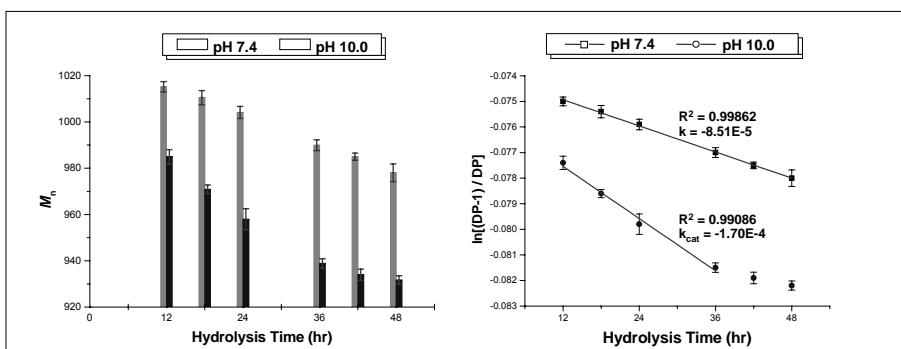
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MWD of Surface Hydrolytic Degradation Products of $\text{Ph}_3\text{N}/\text{PLLA}$ (20:80 wt%) Blend Matrices as a function of hydrolysis time



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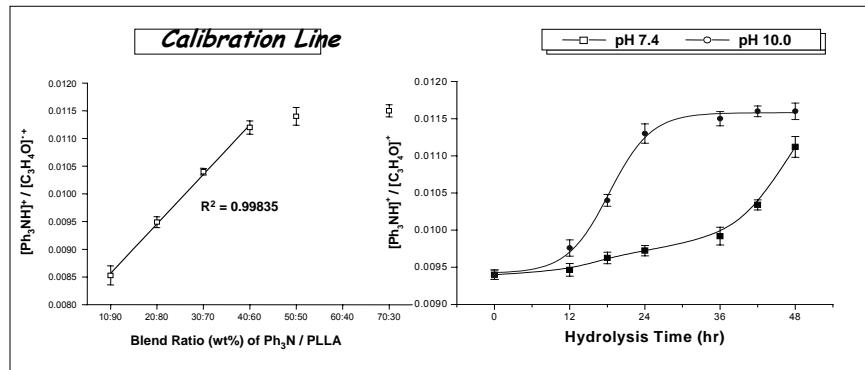
Hydrolytic Surface Degradation Kinetics of PLLA at the Surface of Blend Matrices ($\text{Ph}_3\text{N}/\text{PLLA} = 20:80$ wt%) Hydrolyzed in Two pH Buffer Systems



$$\text{Icon} \quad k_{\text{pH}10.0} = 2.00 \times k_{\text{pH}7.4}$$

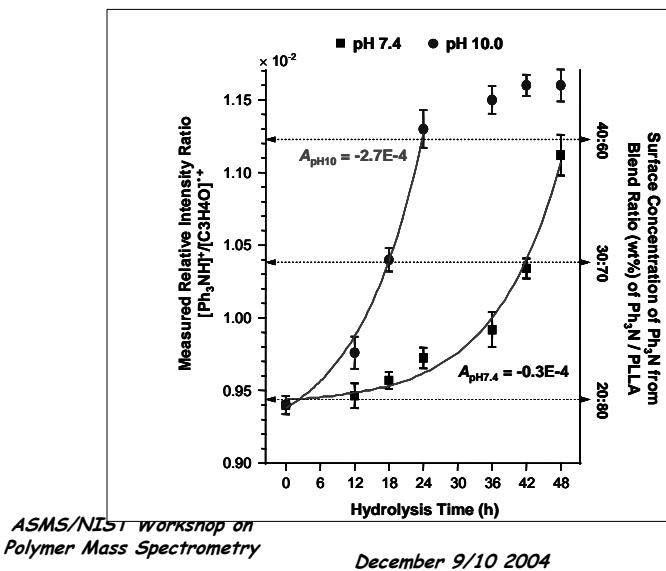
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Calibration Line and Resulting Release Profiles of Ph_3N^+ From Surface of Blend Matrices ($\text{Ph}_3\text{N}/\text{PLLA} = 20:80$ wt%) Hydrolyzed in Two pH Buffer Systems



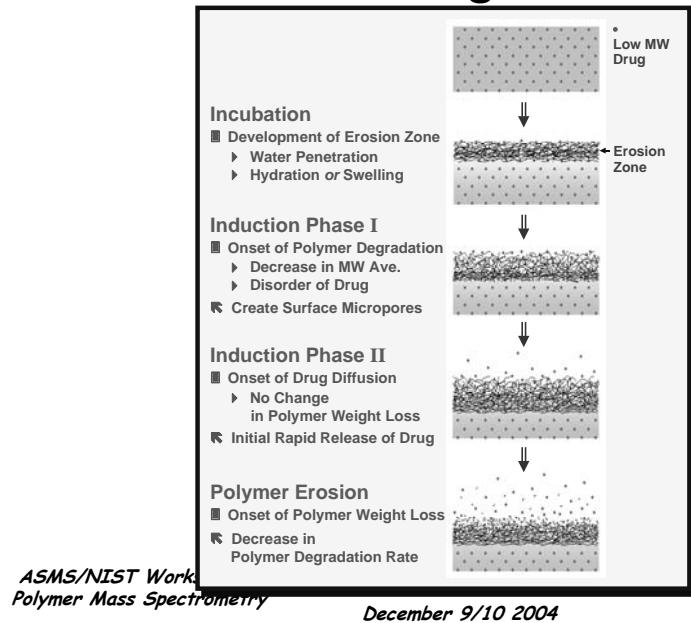
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Comparison of Changes in Surface Concentrations

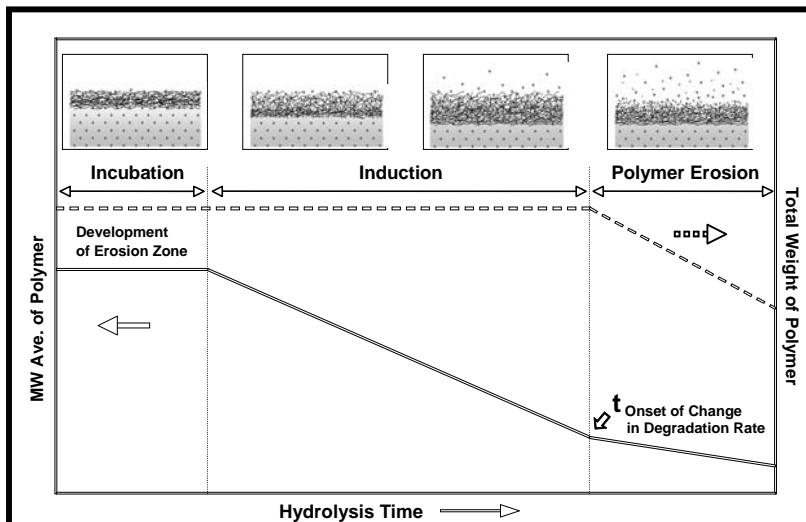


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Schematic of Drug Release Profile



Schematic at the Initial Stage of Bulk Erosion of Biodegradable Polymer Blend Matrices



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Conclusions: Drug Delivery

- The Initial Rapid Release of Drug is observed in the Induction Phase of Bulk Erosion of PLLA.
- The Environmental pH effects the Rate of Initial Drug Burst as Hydrolytic Polymer Degradation is pH Sensitive.
- The Relative Initial Burst of Drug Release in Basic Conditions is more than twice ($A_{\text{pH}10} \approx 9 \times A_{\text{pH}7.4}$) that of the corresponding Increase in Polymer Degradation Rate ($k_{\text{pH}10} \approx 2 \times k_{\text{pH}7.4}$).
- The Drug Release is related to but not *Singularly* dependent on Polymer Degradation Kinetics.

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Emerging Applications of ToF-SIMS of Polymer Surfaces

- ☞ Imaging of Polymer Surfaces
- ☞ Oligomeric Segments at Polymer Surfaces
- ☞ Reorganization of Oligomeric Segments after exposure to water

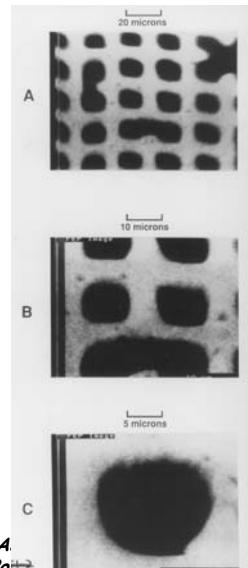
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ToF-SIMS Images of Teflon/Silicone Membrane

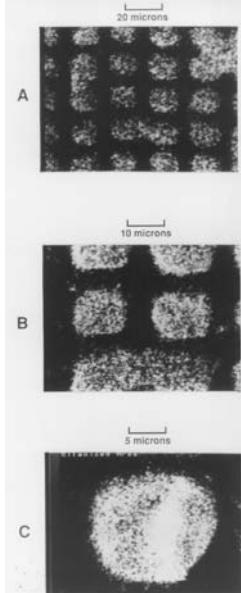
Fluorine based signals

Silicone based signals

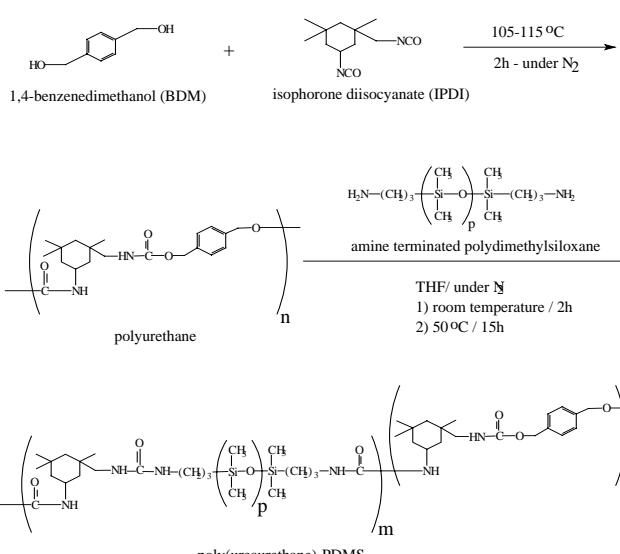


Proper Case for interpreting presence of different polymer membrane by complementary ToF SIMS images

Note: Where there is a dark region in teflon image, there is a light region in silicone images

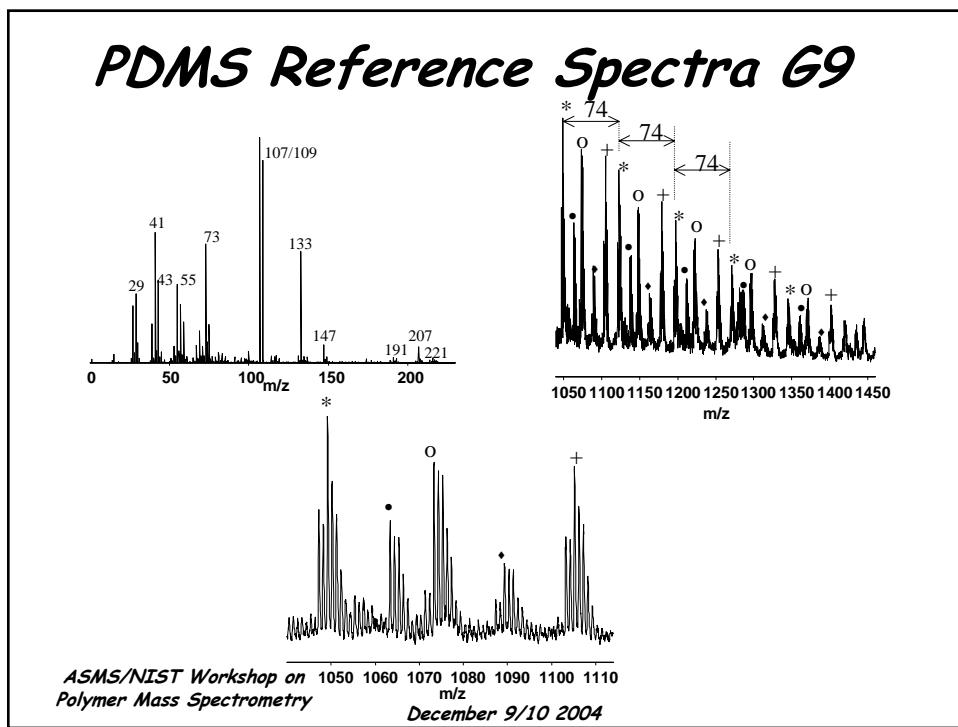
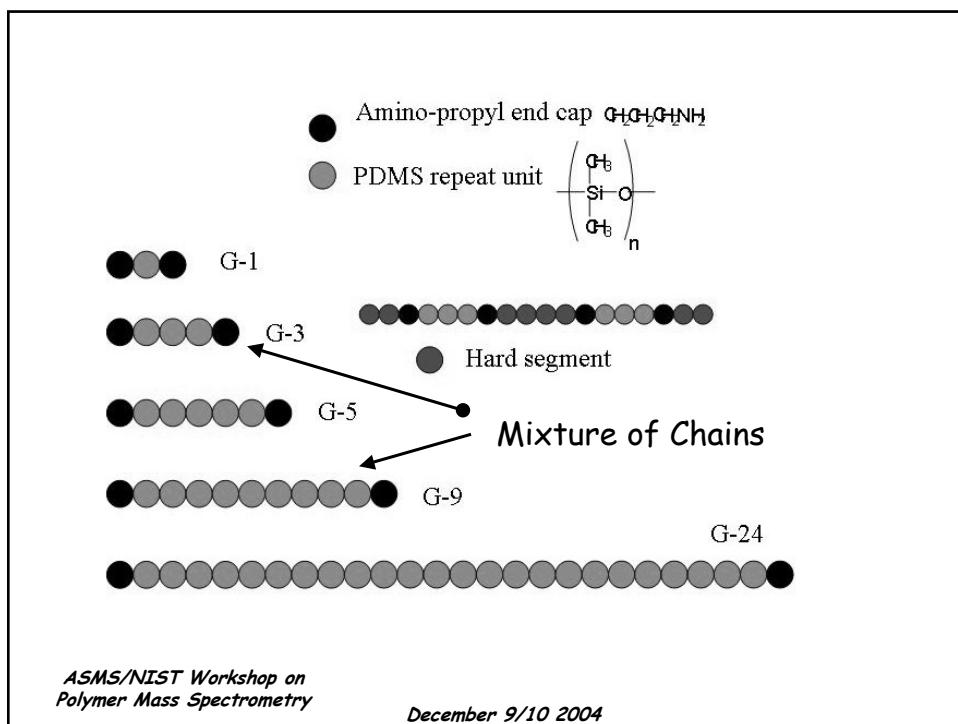


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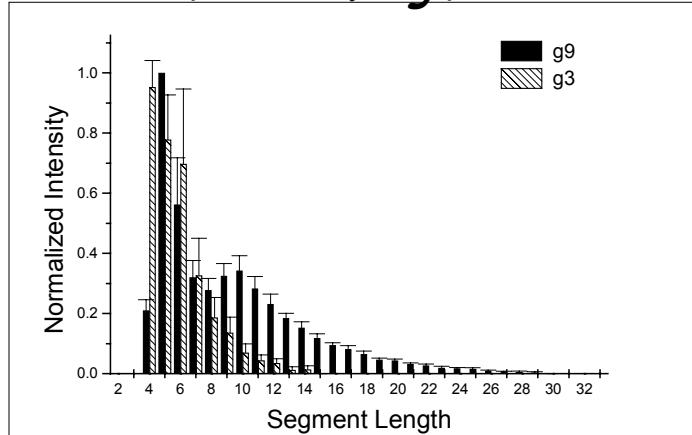


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*Apparent molecular weight distributions
Pure G-3 and G-9
-marked fragments



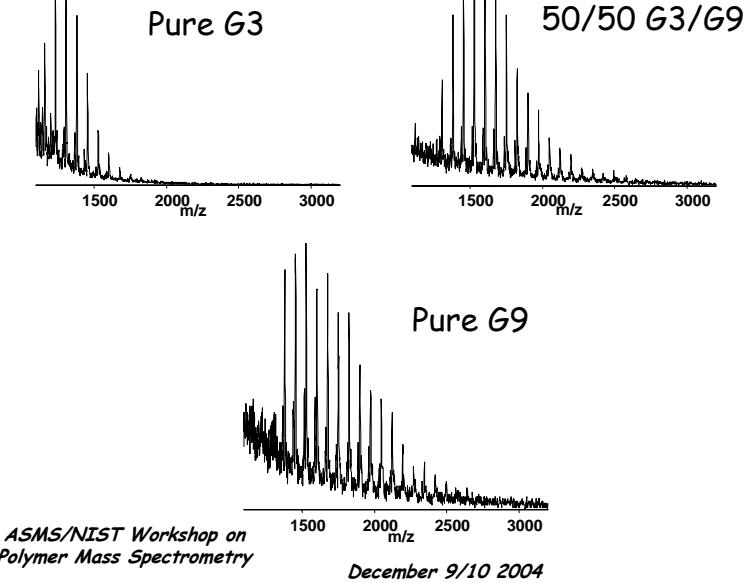
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*Apparent molecular weight distribution information
for high-mass range PDMS distributions*

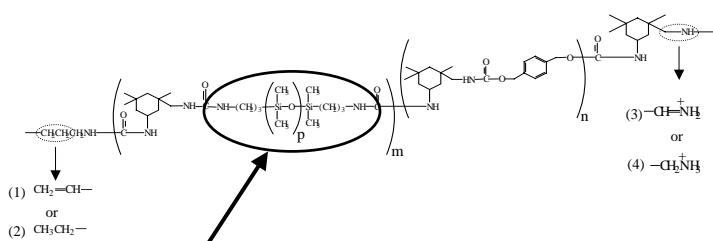
Sample	Structure (table 2)	Apparent M_n (1^{st} moment of distribution)	Apparent M_w (2^{nd} moment of distribution)	2^{nd} moment / 1^{st} moment (M_w / M_n)
G-9	*	856.57	995.11	1.16
G-9	o	827.68	1044.93	1.26
G-3	*	602.87	635.77	1.05
G-3	o	516.97	574.52	1.11

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High Mass Spectra of Agglomerates



Proposed Structure of Ions in High Mass Spectra of Agglomerate Thin Films

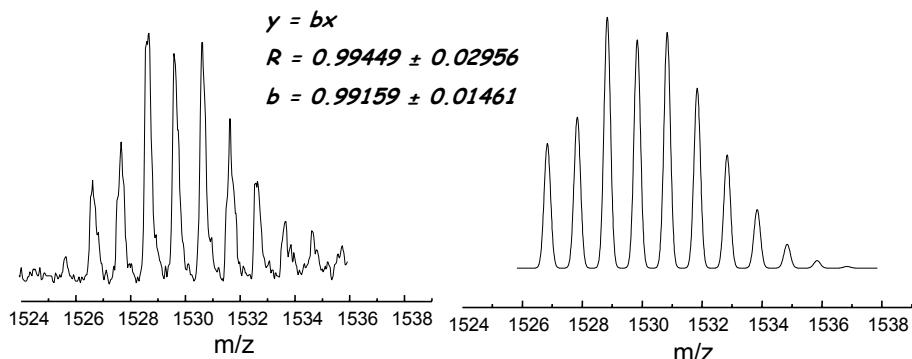


GX PDMS Block

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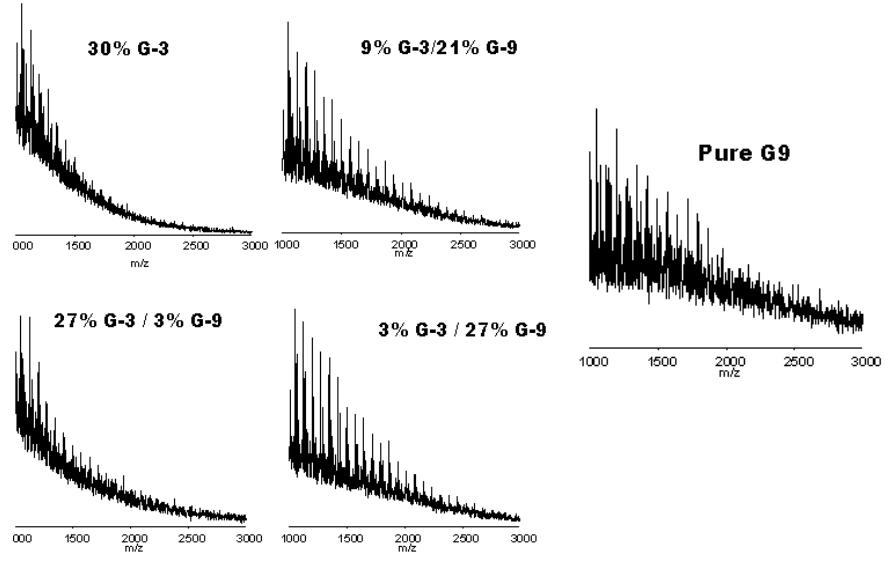
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Comparison of High Mass Isotope Distributions to Support Ion Structure Assignment



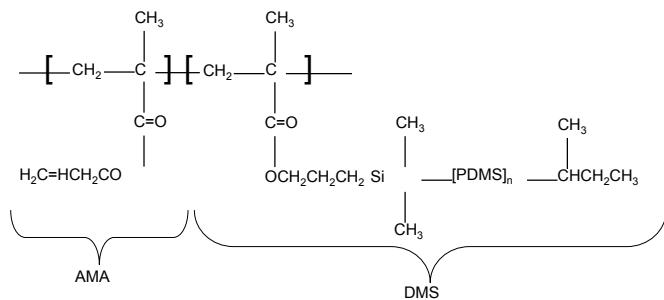
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Spectra from Thick/Complete Films



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AD Polymer System



Is it possible to perform low temperature SIMS analysis and obtain high mass fragmentation?

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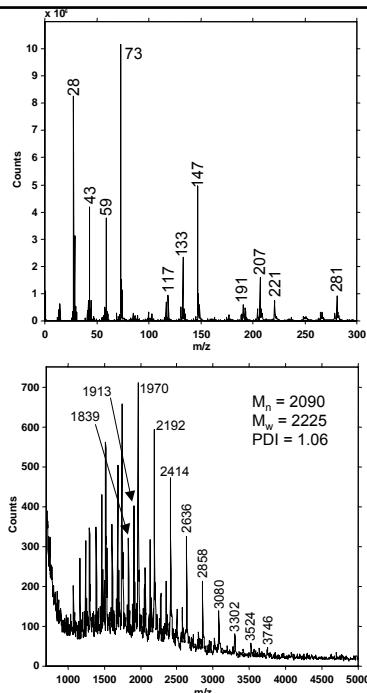
AD Copolymers

Polymer	PDMS Weight %	PDMS M_n	PDMS M_w/M_n
AD1	9	2170	1.13
AD2	16	2170	1.13
AD3	26	2170	1.13
AD4	5	3170	1.14
AD5	13	3170	1.14
AD6	21	3170	1.14
AD7	33	3170	1.14

M_n and M_w determined by GPC

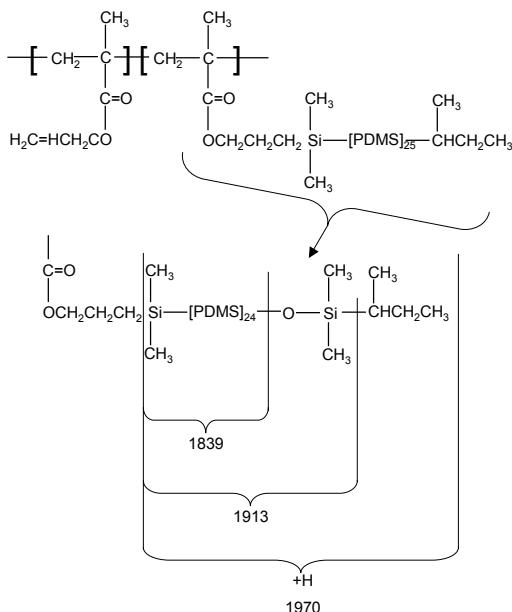
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SIMS Analysis
AD7 Polymer Series -
Dehydrated



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Conclusions

- Detailed Quantitative Approaches can yield in-depth structure which correlates with practical performance
- Quantitation can influence polymer synthesis and design
- New methods can evaluate reaction kinetics at surfaces
- Mass Spectrometry is ripe for development for quantitative analysis

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