23rd International Symposium on Polymer Analysis and Characterization

Short course: Techniques for Polymer Analysis & Characterization

30 May 2010

Pohang University of Science and Technology
Pohang, Republic of Korea
Locations

Dining Facilities on Campus

D’medley (Buffet), 2F POSCO International Center
Phoenix (Chinese), 5F POSCO International Center
Wisdom (Cafeteria), 2F Jigok Community Center
Breakfast 08:30~10:30 / Lunch 11:50~13:20 / Dinner 18:00~19:00
Yeon-Ji (Korean), 1F Jigok Community Center
Lunch 13:00~15:00 / Dinner 16:00~20:00
Burger King, 1F Jigok Community Center
10:00~22:00
Oasis (Snack), 1F Student Union
Breakfast 08:00~10:00 / Lunch 11:30~15:00 / Dinner 16:00~19:30
Short Course: Techniques for Polymer Analysis & Characterization
Conference Room C&D, 2F POSCO International Center

Chair: Taihyun Chang/ Josef Janca

09:00-10:00  Registration

10:00-11:20  Advances in HPLC for Polymer Characterization
             Harald Pasch (Univ. of Stellenbosch)

11:20-11:30  Break

11:30-12:50  Advances in NMR Spectroscopy of Polymeric Materials
             H.N. Cheng (USDA)

12:50-14:30  Lunch

14:30-15:50  Tailored Synthesis and Characterization of Complex Polymers
             Jimmy Mays (Univ. of Tennessee)

15:50-16:00  Break

16:00-17:20  Principles and Applications of Continuous Online Polymerization Monitoring
             Wayne Reed (Tulane Univ.)/ Guy C. Berry (Carnegie Mellon Univ.)
ADVANCES IN HPLC FOR POLYMER CHARACTERIZATION

Harald Pasch
Univ. of Stellenbosch
Advances in HPLC for Polymer Characterization

Harald Pasch
SASOL Chair of Analytical Polymer Science
Department of Chemistry and Polymer Science,
University of Stellenbosch, South Africa

Molecular Heterogeneity of Complex Polymers

- **SEC**
  - but
  - direct correlation between $V_h$ and chain length (molar mass) only for linear homopolymers

- **LAC**
  - but
  - effects of molar mass, branching, functional groups?

- **LC-CC**
  - but
  - only for linear homopolymers with 0,1,2 endgroups
  - Effects of chemical composition and branching?

- **Topology Type Fractionation**?
  - size and chemical composition will contribute!
Molecular Heterogeneity of Complex Polymers

Molecular Heterogeneity of a Random Copolymer

distributions in composition and molar mass

Analysis of Distributions by Liquid Chromatography

Advantages of LC techniques

- simple, reproducible, precise
- adaptable to specific analysis problems
- high flexibility of technical setup

quantitative analysis of distributions

- molar mass
- chemical heterogeneity
- functionality
- architecture
Why Hyphenated Techniques?

Complex MMD/CCD distribution is distribution in (at least) two directions

⇒ requires separation in more than one direction

One separation step must be strictly in one direction (MMD or CCD/FTD)

⇒ separation with respect to MMD regardless of CCD/FTD

⇒ separation with respect to CCD/FTD regardless of MMD

⇒ chromatography at the critical point of adsorption!

---

Why Hyphenated Techniques?

First step must be

⇒ optimization of chromatographic separation:
  obtaining chemically or functionally homogeneous fractions

Second step ⇒ optimization of detection

⇒ determination of concentration in the eluate
⇒ determination of structural parameters

⇒ light scattering ($M_w$, molecular shape)
⇒ FTIR (chemical composition)
⇒ MALDI-TOF-MS (oligomer distributions, endgroups)
Liquid Chromatography of Polymers

HPLC, LAC: Enthalpy-driven

Separation with regard to chemical composition

SEC: Entropy-driven

Separation with regard to molecular size

Size of the spheres: hydrodynamic radii
Color of the spheres: different chemistry
Liquid Chromatography of Polymers

LC-CC: Compensation of entropic and enthalpic effects

Critical point of adsorption

Separation irrespective of molar mass

Elution Volume

Example:
- Column: Nucleosil Si 100
- Mobile phase: THF / Hexane 80:20
- PS
- PVAc
- PMMA
- Injection solvent
Why Coupled Techniques?

Schematic Protocol for 2D Separations
2D Chromatography - offline approach

„Orthogonal Chromatography“ (Balke, 1980)

„Chromatographic Cross-Fractionation“ (Glöckner, 1991)
2D Chromatography HPLC vs. SEC

1. Dimension: HPLC/LCCC
2. Dimension: GPC

Degasser Pump
Injector
HPLC Column

Data Processing
Detector

SEC Column
Waste

2D Chromatography – presentation of results

discontinuous and continuous

- a) intensity line diagram
- b) contour plot
- c) surface plot

Chemical Composition
Molar mass

a)
b)c)
Analysis of Oligomers

Functional Polyethylene Oxides

\[ \text{Alk(Ar)} - \text{OH} + \xrightarrow{\text{functional}} \xrightarrow{\text{primary reactions}} \text{Alk(Ar)} - (\text{OCH}_2\text{CH}_2)_n - \text{OH} \]

secondary reactions \hspace{1cm} additional functionality fractions

\[ \text{H} - (\text{OCH}_2\text{CH}_2)_n - \text{OH} \]

\[ \xrightarrow{\text{functional}} \xrightarrow{\text{primary reactions}} \text{Alk(Ar)} - (\text{OCH}_2\text{CH}_2)_n - \text{OAlk(Ar)} \]

\[ -(\text{OCH}_2\text{CH}_2)_n \]

↘ Molar mass distribution
↘ Functionality type distribution
↘ Amount of cyclics
Functional Polyethylene Oxides

Functionality separation by LC-CC
stationary phase: RP-18
mobile phase: MeOH-water 80:20

Oligomer Separation by LAC
stationary phase: Si
mobile phase: i-PrOH-water 88:12

\[ C_{n+2}H_{2n+1}O(CH_2CH_2O)_xH \]

Elution Volume (mL)

Detector Signal

Endgroup and oligomer separation by 2D-LC (LC-CC x LAC)

\[ C_{16}H_{33}O(CH_2CH_2O)_xH \]

Endgroup Length

Oligomer Length

4-8

9

10

11

12

13

14

15

16
Epoxy Resins - Advancement Process

\[
\text{BPA} + 2 \xrightarrow{[\text{KOH}]} \text{BPA} [\text{KOH}] - 2 \text{HCL}
\]

\[
k = 0, 2, 4, 6, ...
\]

Epoxy Resins

\[
\text{MMD}
\]

\[
\text{FTD}
\]

\[
\text{MAD}
\]
Epoxy Resins

LC of Epoxy Resins

SEC
(StyrageL, THF)

LC-CC
(Si, THF-Hexane)

Elution Volume [mL]

P1  P2  P3  P4

Retention Volume [mL]

Epoxy Resins

LC-CC of Epoxy Resins

stationary phase: Si
eluent: THF-Hexane
Identification of LC-CC Fractions by MALDI-TOF MS

Epoxy Resins

2D Chromatography LC-CC vs. SEC
### Epoxy Resins

<table>
<thead>
<tr>
<th>Structure</th>
<th>Amount</th>
<th>$M_n$</th>
<th>$M_w$</th>
<th>D</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>65</td>
<td>860</td>
<td>1.720</td>
<td>1.99</td>
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<tr>
<td>2</td>
<td>4</td>
<td>1.690</td>
<td>2.620</td>
<td>1.55</td>
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<tr>
<td></td>
<td></td>
<td>26</td>
<td>1.130</td>
<td>1.62</td>
</tr>
<tr>
<td>3</td>
<td>1</td>
<td>2.990</td>
<td>3.680</td>
<td>1.23</td>
</tr>
<tr>
<td></td>
<td>1</td>
<td>1.360</td>
<td>1.590</td>
<td>1.17</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>1.100</td>
<td>1.990</td>
<td>1.81</td>
</tr>
<tr>
<td>Total</td>
<td>All</td>
<td>100</td>
<td>953</td>
<td>1811</td>
</tr>
</tbody>
</table>
Analysis of Copolymers

Block Copolymers

-AAAAA-BBBB-    -AAAA-BBBBB-AAAAA-

- Total molar mass distribution
- Presence and quantity of homopolymers Poly-A and Poly-B
- Chemical Composition (ratio A/B)
- Molar mass of block A
- Molar mass of block B
LC-CC of Diblock Copolymers $A_nB_m$

\[ \Delta G_{AB} = \Sigma(n\Delta G_A + m\Delta G_B) \]

<table>
<thead>
<tr>
<th>critical point of homopolymer $A$</th>
<th>critical point of homopolymer $B$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\Delta G_A = 0$</td>
<td>$\Delta G_B = 0$</td>
</tr>
<tr>
<td>$\Delta G_{AB} = m_B\Delta G_B$</td>
<td>$\Delta G_{AB} = n_A\Delta G_A$</td>
</tr>
<tr>
<td>$K_{dAB} = K_{dB}$</td>
<td>$K_{dAB} = K_{dA}$</td>
</tr>
</tbody>
</table>

EO-PO Triblock Copolymers

PO block separation by LC-CC

PEO: chromatographically invisible
PPO: oligomer separation in LAC

stationary phase: RP-18
mobile phase: MeOH-water 86:14
EO-PO Triblock Copolymers

2D Chromatography LC-CC vs. SEC

Elution Volume (mL)

Critical Conditions for PMMA
silica gel, MEK-cyclohexane

Critical Conditions for PS
RP-18, THF-ACN

St-MMA Block Copolymers
LC-CC Analysis: Critical Conditions for PS

M&N Si-300-C18 + Si-1000-C18, THF - n-hexane 50:50

2D Chromatography LC-CC (PS) vs. SEC
St-MMA Block Copolymers

SEC and LC-CC of S/MMA Diblock ??? Copolymer

SEC indicates narrow MMD

LC-CC indicates some chemical heterogeneity

StSt -- MMAMMA Block Block Copolymers

2D-LC of S/MMA Diblock ??? Copolymer
Grafting of Polybutadiene with Methyl Methacrylate

Separation of the graft product by Gradient HPLC

Elution Volume (mL) vs. % Gradient

Vol % Gradient

Elution Volume (mL)
Grafting of Polybutadiene with Methyl Methacrylate

Separation of the graft product by 2D-LC

Quantitative analysis of the graft product components

<table>
<thead>
<tr>
<th>Reaction Time [h]</th>
<th>Component</th>
<th>$M_w$</th>
<th>Amount [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>PB</td>
<td>278.600</td>
<td>52</td>
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<tr>
<td></td>
<td>PB-g-PMMA</td>
<td>405.100</td>
<td>44</td>
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<tr>
<td></td>
<td>PMMA</td>
<td>33.400</td>
<td>1</td>
</tr>
<tr>
<td>4</td>
<td>PB</td>
<td>247.400</td>
<td>31</td>
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<tr>
<td></td>
<td>PB-g-PMMA</td>
<td>686.600</td>
<td>64</td>
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<tr>
<td></td>
<td>PMMA</td>
<td>32.600</td>
<td>4</td>
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</table>
16-Component Star Block Copolymer

Butadiene content
17, 39, 63, 78 wt.-%

Size Exclusion Chromatography
Gradient HPLC
silica gel, i-octane-THF
16-Component Star Block Copolymer

1st dimension Gradient-HPLC, 2nd dimension: SEC

3-D view

each trace represents a SEC chromatogram from a transfer injection
Multidimensional Chromatography: Ways to Hyphenation

Coupling with FTIR Spectroscopy
Universal LC-FTIR Coupling: Optics Module

IR beam

IR beam

IR-transparent Germanium disc

Deposited fraction

reflecting Al layer

Universal LC-FTIR Coupling: Presentation of results

Waterfall

Contour Plot

Wavenumbers (cm⁻¹)
Analysis of a Polymer Blend: SEC with RI Detection

![Graph showing elution volume vs. time with peaks labeled 1, 2, and 3.]

Analysis of a Polymer Blend: SEC-FTIR Coupling

![Graph showing time vs. wavenumbers with peaks labeled 1, 2, and 3.]

Additive

SAN

PMMA-b-PS
Analysis of a Polymer Blend: SEC-FTIR Coupling

High-Temperature HPLC Coupling with FTIR Spectroscopy
High-Temperature SEC
Polymer Labs Model PL GPC 220

Stationary phase:
Cross-linked PS

Mobile phase:
Trichlorobenzene

Temperature:
140 °C

Calibration: PS, PE

Detectors:
RI, ELSD, IR, LS, Vis

Separation by Chemical Heterogeneity

- Temperature Rising Elution Fractionation (TREF)
- Crystallization Analysis Fractionation (CRYSTAF)

分离与化学组成有关
Polymer Labs' High-Temperature Gradient HPLC System

- High-temperature gradient HPLC system
- Quaternary pump
- Automatic column switching
- RI and ELSD detectors
- Two arm robotic sample preparation platform
- Two x 96 well autosampler capability for continuous operation

Separation System for PE-PP Blends

- Column: Nucleosil 500
- Mobile phase: EGMBE-TCB
- T: 140°C
- Detector: ELSD
- Sample solvent: TCB

EP copolymer with 48% ethylene
HT-HPLC Separation of EVA Copolymers

- EVA 5% VA
- EVA 12% VA
- EVA 14% VA
- EVA 19% VA
- EVA 28% VA
- EVA 45% VA
- EVA 50% VA
- EVA 60% VA
- EVA 70% VA
- PVAc-St. 164KD
- PVAc-St. 32KD
- PE-St. 126KD

Stationary phase: silica gel
Mobile phase: gradient of decaline-cyclohexanone

High-Temperature HPLC Coupled to LC-Transform Interface

LC-Transform Series 300, LabConnections
Temperature of the transfer line: 150°C
Temperature of the Germanium disc: 152°C
Temperature of the nozzle: Gradient
Pressure: 30 mbar
HT-HPLC/FTIR Analysis of EVA Copolymers

![Graph showing elution volume (mL) vs. Gram Schmidt.]

- Model: Linear equation $y = A + Bx$
- $R^2 = 0.99139$
- $A = 0.44495 \pm 0.03758$
- $B = 0.07217 \pm 0.00224$

Relative Content of Vinyl Acetate
depicted by peak heights.

***Coupling with $^1$H-NMR Spectroscopy***
Analysis of the CCD of Styrene-Acrylate Random Copolymers

- Distributed in
  - Molar Mass
  - Chemical Composition
  - Amount of Homopolymers

- narrow CCD
  - homogeneous
  - monophase system

- broad CCD
  - heterogeneous
  - multiphase system

broadness of CCD is influenced by monomer reactivity, composition of the monomer feed and conversion.

Copolymer Composition as a Function of Conversion

Styrene - Ethyl Acrylate
\[ r_S/r_{EA} = 0.80/0.20 \]
Gradient HPLC of SEA Copolymers: Calibration with standards

Nucleosil RP-18
ACN/THF 90/10 to 0/100

Gradient HPLC of High Conversion SEA Copolymers

Nucleosil RP-18
ACN/THF 90/10 to 0/100
Off-line Spectra of SEA Copolymer and Mobile Phase

Copolymer SEA 40/60 in deuterated solvent

Solvent mixture THF/ACN 50/50 v/v

On-flow Coupling of HPLC and "H-NMR
On-Line Gradient HPLC-$^1$H-NMR: Experimental

**Instrument:** Varian UNITY INOVA™ 500 MHz

**HPLC-NMR Probe:** 60 µL flow cell, indirect detection probe with pulsed-field gradients (PFG)

**Sample Concentration:** 100 µL of 15 mg/mL = 1.5 mg

**NMR Sequence:** WET sequence of four selective SEDUCE pulses, four gradient pulses, followed by an additional delay and a composite read pulse; carbon decoupling during selective proton pulses using Waltz-16 decoupling


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On-Line Gradient HPLC-$^1$H-NMR: Contour plot of SEA 40.98

![Contour plot of SEA 40.98](image)

(ppm)
On-Line Gradient HPLC-$^1$H-NMR: On-line spectrum at peak max

On-Line Gradient HPLC-$^1$H-NMR: Comparison of calibrations
HPLC-NMR of Polymers: \(^1\)H-NMR of Oligostyrene

\(^1\)H-NMR of oligostyrene (500 MHz)
complex and difficult to interpret

Degree of polymerization ?
Endgroups ?
Stereochemistry ?

UV-Chromatogram in 100% ACN, flow rate gradient 1 - 2mL/min
Splitting of chromatographic peaks ????

HPLC-NMR of Polymers: HPLC of Oligostyrene
HPLC-NMR of Oligostyrene: Contour plot

HPLC-NMR on-flow-measurement (100% ACN), no lock signal!

- dimer
- trimer
- tetramer
- pentamer
- hexamer
- heptamer

HPLC-NMR of Oligostyrene: On-flow spectra of oligomers
HPLC-NMR of Oligostyrene: spectrum of monomer

HPLC-NMR of Oligostyrene: spectrum of dimer
HPLC-NMR of Oligostyrene: spectrum of trimer

Fraction of trimers:
1 chromatographic peak
2 $^1$H-NMR spectra
4 isomeric structures
Selected References

ADVANCES IN NMR SPECTROSCOPY OF POLYMERIC MATERIALS

H.N. Cheng

USDA
Advances in the NMR Spectroscopy of Polymeric Materials

H. N. Cheng
May 30, 2010

Product Development Scheme

<table>
<thead>
<tr>
<th>Raw Materials</th>
<th>Reaction or Process</th>
<th>Structure</th>
<th>Possible Improvements</th>
<th>Properties</th>
<th>Application Development</th>
<th>End Use</th>
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<tbody>
<tr>
<td>monomers plants</td>
<td>polymerization</td>
<td>composition</td>
<td>physical properties</td>
<td>rheology</td>
<td>fabrication processes</td>
<td>adhesives</td>
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<tr>
<td>microorganisms</td>
<td>extraction</td>
<td>tacitity</td>
<td>chemical properties</td>
<td>T_g / T_m</td>
<td>formulation</td>
<td>packaging</td>
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<td>film</td>
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<td>molecular</td>
<td>physical structure</td>
<td>impact</td>
<td>quality</td>
<td>specialties</td>
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<td>weight and</td>
<td></td>
<td>etc.</td>
<td>cost</td>
<td>etc.</td>
</tr>
<tr>
<td></td>
<td></td>
<td>distribution</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Monomers:
- styrene
- VC/VDC
- Sty/BuAc
- Sty/BD
- ethylene

Plant:
- Seaweeds
- alginate

Polymers:
- polystyrene
- copolymer
- SBR
- LDPE

NMR info:
- tacticity
- copolymer sequence
- branching
- rheology
- T_g / T_m
- crystallinity
- stiffness
- tensile
- impact

Rheology
Crystallinity
Stiffness
Tensile
Impact

NMR in Polymer Analysis

Information:
- stereochemistry (tacticity)
- regiochemistry
- copolymer sequence
- defect structure
- chain dynamics
- spin interactions
Stereochemistry of Vinyl Polymers

Stereselectivity

Isotactic

\[ \text{Isotactic} \]

\[ \begin{array}{cccccc}
\text{C} & \text{C} & \text{C} & \text{C} & \text{C} & \text{C} \\
\end{array} \]

Heterotactic

\[ \text{Heterotactic} \]

\[ \begin{array}{cccccc}
\text{C} & \text{C} & \text{C} & \text{C} & \text{C} & \text{C} \\
\end{array} \]

Syndiotactic

\[ \text{Syndiotactic} \]

\[ \begin{array}{cccccc}
\text{C} & \text{C} & \text{C} & \text{C} & \text{C} & \text{C} \\
\end{array} \]

Copolymer Sequence Placements

\[ \text{Triad } YXY; \text{ Pentad } XYXYX \]

\[ \text{Triad } XXY; \text{ Pentad } XXXYY \]

\[ ^{13}C \text{ NMR spectrum of vinyl chloride/vinylidene chloride copolymer (68.8 : 31.2).} \]
Assignments:

A = VC \(-\text{CH}_2\text{-CH(Cl)}\- \\
B = VDC \(-\text{CH}_2\text{-C(Cl)}_2\- \\

$^{13}$C NMR spectrum of vinyl chloride/vinylidene chloride copolymer (68.8 : 31.2).

Polymerization Model
Statistical Models for Polymerization

Chain End Control

— A B A [B] ... A

Bernoullian
1st Order Markovian
2nd Order Markovian

Catalytic-site Control

— A B A B ... A

Enantiomorphic-site

Polymerization Mechanism

Free Radical

Anionic

Cationic

Ziegler-Natta

Model

Bernoullian
1st order Markovian
(2nd order Markovian)

1st order Markovian
Coleman-Fox

Bernoullian
1st order Markovian

Bernoullian
1st order Markovian
2nd order Markovian
Enantiomorphic-site
First Order Markov

\[
\begin{align*}
- M_1' + M_1 & \quad \kappa_{11} \quad - M_1M_1' \\
- M_1' + M_2 & \quad \kappa_{12} \quad - M_1M_2' \\
- M_2' + M_1 & \quad \kappa_{21} \quad - M_2M_1' \\
- M_2' + M_2 & \quad \kappa_{22} \quad - M_2M_2'
\end{align*}
\]

Reactivity Ratios

\[
\begin{align*}
\lambda_1 &= \frac{\kappa_{11}}{\kappa_{12}} \\
\lambda_2 &= \frac{\kappa_{22}}{\kappa_{21}}
\end{align*}
\]

Reaction Probability

\[
\begin{align*}
P_{11} &= \frac{\kappa_{11} (-M_1) (M_1)}{\kappa_{11} (-M_1) (M_1) + \kappa_{12} (-M_1) (M_2)} = \frac{1}{1 + \frac{(M_2)}{(M_1)}/\lambda_1 (M_1)} \\
P_{21} &= \frac{\kappa_{21} (-M_2) (M_1)}{\kappa_{21} (-M_2) (M_1) + \kappa_{22} (-M_2) (M_2)} = \frac{1}{1 + \frac{(M_2)}{(M_1)}/\lambda_2 (M_2)} \\
P_{12} &= \frac{\kappa_{12} (-M_1) (M_2)}{\kappa_{12} (-M_1) (M_2) + \kappa_{11} (-M_1) (M_1)} = \frac{1}{1 + \frac{(M_1)}{(M_2)}/\lambda_1 (M_1)} \\
P_{22} &= \frac{\kappa_{22} (-M_2) (M_2)}{\kappa_{22} (-M_2) (M_2) + \kappa_{21} (-M_2) (M_1)} = \frac{1}{1 + \frac{(M_1)}{(M_2)}/\lambda_2 (M_2)}
\end{align*}
\]

Copolymer Types

<table>
<thead>
<tr>
<th>Alternating</th>
<th>Reactivity Ratio</th>
<th>Reaction Probability</th>
</tr>
</thead>
<tbody>
<tr>
<td>-AB(AB)_nAB-</td>
<td>(r_1r_2 = 0)</td>
<td>(P_{12} = 1)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(P_{21} = 1)</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Random</th>
<th>Reactivity Ratio</th>
<th>Reaction Probability</th>
</tr>
</thead>
<tbody>
<tr>
<td>-ABABAAABBA-</td>
<td>(r_1r_2 = 1)</td>
<td>(P_{12} + P_{21} = 1)</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Blocky</th>
<th>Reactivity Ratio</th>
<th>Reaction Probability</th>
</tr>
</thead>
<tbody>
<tr>
<td>-A(A)_nAB(B)_nB-</td>
<td>(r_1r_2 \gg 1)</td>
<td>(P_{12} = 0)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(P_{21} = 0)</td>
</tr>
</tbody>
</table>
Other Statistical Models

- 2nd order Markov and Coleman-Fox models
- Markovian/reversible propagation
- Complex participation
- E/Z model
- Bootstrap model
- Dual chain end/catalytic site control
- Consecutive multiple site model (generalized Coleman Fox)
- Multiple catalytic site model
- Perturbed models (compositional heterogeneity)
- Four-component models
  - Tetrapolymerization (4-component copolymer)
  - Regiorregular and stereoirregular homopolymers


Approaches to study $^{13}$C NMR spectrum of polymers

"Analytical" Approaches

Polymerization Model

Spectral Simulation or "Synthetic" Approaches
Common Routes

Analytical

\[ A_1 \] Observed Spectrum \[ \rightarrow \] \[ A_2 \] Spectral Analysis \[ \rightarrow \] \[ A_3 \] Composition Tacticity Sequence \[ \rightarrow \] \[ A_4 \] Statistical Model

Synthetic

\[ S_1 \]

NMR

Polymer/NMR Relationships

Polymer Microstructure

Polymerization Mechanism

Polystyrene

\[-(\text{CH}_2-\text{CH})-\]

[Graphical representation of Polystyrene spectra]
FIGURE 2. $^{13}C$ NMR spectra of the aliphatic carbons of atactic polystyrene (lower trace), syndiotactic polystyrene (middle trace), and isotactic polystyrene (upper trace), in 1,2,4-trichlorobenzene at ca. 115°C. The notation s* in the middle trace represents spinning side band.

<table>
<thead>
<tr>
<th>No</th>
<th>$^1H$ Shift</th>
<th>$^{13}C$ Shift</th>
<th>Steps 1–2</th>
<th>Step 3&lt;sup&gt;*b&lt;/sup&gt;</th>
<th>Steps 4–5&lt;sup&gt;*b&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1.53</td>
<td>46.79</td>
<td>mmm</td>
<td>mmm</td>
<td>mmm</td>
</tr>
<tr>
<td>2</td>
<td>1.46, 1.52</td>
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<td>mmm</td>
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<td>r</td>
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<td>mrrm</td>
</tr>
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<td>m(mrrm)x</td>
<td>m(mrrm)x</td>
</tr>
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<td>45.22</td>
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<td>44.84</td>
<td></td>
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<td>r(mmnnm)x</td>
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<td>r</td>
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<td>r</td>
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<td>mmmr</td>
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<td>mrrm</td>
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<td>mmmnr</td>
<td>mmmnr</td>
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<td>m(mmmm)m</td>
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<td>18</td>
<td>1.59</td>
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<td>42.73, 42.61</td>
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<td>mmmn</td>
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<td>42.52, 42.40</td>
<td>mmmmm</td>
<td>mmmmm</td>
<td>mmmmm</td>
</tr>
</tbody>
</table>

<sup>*a</sup>The 30 $^{13}C$ shift values given in this column are used in the simulated spectrum shown in Figure 8.

<sup>*b</sup>The symbol x denotes both m and r.
Figure 1. Curve deconvolution of the CH$_2$ carbon: top trace, observed spectrum; middle trace, fitted spectrum; lower trace, individual components.

Table 1. Assignments of backbone CH$_2$ carbon of atactic polystyrene: first-order Markovian probabilities and the observed versus calculated intensities

<table>
<thead>
<tr>
<th>No</th>
<th>$^{13}$C Shift</th>
<th>Assignment</th>
<th>Probability</th>
<th>Observed</th>
<th>Calculated ($P_n = 0.48$)</th>
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</thead>
<tbody>
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<tr>
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<td>46.5</td>
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<td>$2P_{rm}^2P_{nm}^2P_{rr}$</td>
<td>7.1</td>
<td>6.5</td>
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<td>3</td>
<td>46.2</td>
<td>rrrrr</td>
<td>$P_{rr}^4P_{mm}^2$</td>
<td>4.6</td>
<td>3.5</td>
</tr>
<tr>
<td>4</td>
<td>45.9</td>
<td>mmrrm</td>
<td>$P_{mm}^2P_{rm}^2P_{rr}$</td>
<td>4.9</td>
<td>3.2</td>
</tr>
<tr>
<td>5</td>
<td>45.4</td>
<td>mrrrr</td>
<td>$2P_{mm}^2P_{rr}^2$</td>
<td>6.6</td>
<td>7.0</td>
</tr>
<tr>
<td>6</td>
<td>45.2</td>
<td>mrrrr</td>
<td>$2P_{mm}^2P_{rr}^2$</td>
<td>6.6</td>
<td>7.0</td>
</tr>
<tr>
<td>7</td>
<td>44.9</td>
<td>mmrnm</td>
<td>$P_{mm}^4P_{rr}^2P_{nn}^2$</td>
<td>11.6</td>
<td>11.5</td>
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<tr>
<td>8</td>
<td>44.8</td>
<td>r(mmmnm)x</td>
<td>$2P_{rr}^2P_{mm}^2P_{nm}^2$</td>
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<td>3.2</td>
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<td>3.0</td>
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<td>mmrnm</td>
<td>$P_{mm}^4P_{rm}^2$</td>
<td>2.4</td>
<td>5.5</td>
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<tr>
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<td>2.5</td>
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<tr>
<td>13</td>
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<td>3.2</td>
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<tr>
<td>15</td>
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<td>rmrmr</td>
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<td>5.9</td>
<td>6.0</td>
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<tr>
<td>16</td>
<td>42.5</td>
<td>mmrmr</td>
<td>$P_{mm}^2P_{rm}^2P_{nr}$</td>
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</table>
Integrated Approaches

Analytical
- Observed Spectrum
- Spectral Analysis
- Composition Tacticity Sequence
- Statistical Model

Synthetic
- Simulated Spectrum
- Shift Rules
- Predicted Sequence
- Polymerization Simulation

NMR
- Polymer/NMR Relationships
- Polymer Microstructure
- Polymerization Mechanism

Presentation Scheme
Conversion heterogeneity

Styrene/methyl acrylate copolymer

Example of a High Conversion Copolymer:
* commercial VC/VDC copolymer (Buna)

<table>
<thead>
<tr>
<th>sequence</th>
<th>I(obsd)</th>
<th>B-model</th>
<th>M1 model</th>
<th>M2 model</th>
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</thead>
<tbody>
<tr>
<td>AAA</td>
<td>36.0</td>
<td>21.3</td>
<td>30.4</td>
<td>35.3</td>
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<tr>
<td>AAB</td>
<td>13.0</td>
<td>28.7</td>
<td>22.6</td>
<td>12.8</td>
</tr>
<tr>
<td>BAB</td>
<td>9.3</td>
<td>9.7</td>
<td>4.2</td>
<td>9.1</td>
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<tr>
<td>ABA</td>
<td>6.7</td>
<td>14.4</td>
<td>5.6</td>
<td>6.9</td>
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<tr>
<td>BBA</td>
<td>16.8</td>
<td>19.4</td>
<td>19.8</td>
<td>17.3</td>
</tr>
<tr>
<td>BBB</td>
<td>18.2</td>
<td>6.5</td>
<td>17.4</td>
<td>18.7</td>
</tr>
</tbody>
</table>

B model

\[ P_A = 0.597 \]

M1 model

\[ P_{AA} = 0.729 \]
\[ P_{BA} = 0.362 \]

M2 model

\[ P_{AAA} = 0.847 \]
\[ P_{AAB} = 0.444 \]
\[ P_{BAA} = 0.411 \]
\[ P_{BBA} = 0.316 \]

(Data from Schlothauer, et al, Polymer Bull., 13, 473 (1985))

---

Example of a High Conversion Copolymer:
* commercial VC/VDC copolymer (Buna)

<table>
<thead>
<tr>
<th>sequence</th>
<th>I(obsd)</th>
<th>B-model</th>
<th>M1 model</th>
<th>M2 model</th>
</tr>
</thead>
<tbody>
<tr>
<td>AAA</td>
<td>36.0</td>
<td>21.3</td>
<td>30.4</td>
<td>35.3</td>
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<tr>
<td>AAB</td>
<td>13.0</td>
<td>28.7</td>
<td>22.6</td>
<td>12.8</td>
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<tr>
<td>BAB</td>
<td>9.3</td>
<td>9.7</td>
<td>4.2</td>
<td>9.1</td>
</tr>
<tr>
<td>ABA</td>
<td>6.7</td>
<td>14.4</td>
<td>5.6</td>
<td>6.9</td>
</tr>
<tr>
<td>BBA</td>
<td>16.8</td>
<td>19.4</td>
<td>19.8</td>
<td>17.3</td>
</tr>
<tr>
<td>BBB</td>
<td>18.2</td>
<td>6.5</td>
<td>17.4</td>
<td>18.7</td>
</tr>
</tbody>
</table>

\[ \text{Mean Deviation} = 8.8 \]

\[ P_A = 0.597 \]

M1 model

\[ P_{AA} = 0.729 \]
\[ P_{BA} = 0.362 \]

M2 model

\[ P_{AAA} = 0.847 \]
\[ P_{AAB} = 0.444 \]
\[ P_{BAA} = 0.411 \]
\[ P_{BBA} = 0.316 \]

(Data from Schlothauer, et al, Polymer Bull., 13, 473 (1985))
Previous Approaches


- NMR data
- Low conversion copolymers ----> reactivity ratios \( \{r_{ij}\} \) ----> high conversion NMR data

2. Perturbed Models


Combined Analytical/Synthetic Approach for High Conversion Polymers
NMR Analysis of Polymer Fractions

- Many polymers are structurally complex. NMR alone may not be able to provide a full description of the system.
- Fractionation, LC, or SEC, combined with NMR, may be used.
- More detailed information is usually available.
- A methodology is needed to extract the maximum information from the data.
- The same methodology can be used for the analysis of polymer mixtures.
Alginates

Microstructure of alginates (from Moe, et al. 1996):
(a) monomers, M = β-D-mannuronic acid, G = α-L-guluronic acid
(b) alginic acid, chain conformation
(c) alginic chain, block structure

SEC Chromatograms of Sodium Alginates

Retention Time (min.)

mAu

Protonal LFR
Na Algin
Manegel LMW
NMR Detection in “Stop-Flow” Mode

- Collect $^1$H spectrum in 240 \( \mu l \) windows
- Better spectral quality
- Discrete components

$^{13}$C NMR Spectrum of Na Alginate

Information:
- Monomer Composition
- Monomer Sequence

$C_{6M+G}$

$C_{1M+G}$
$^{13}$C NMR Spectrum of Na Alginate

$G = 41\%$

$G = 63\%$

$^{1}H$ SEC-NMR Spectrum of Alginate

- Stop-flow
- No solvent suppression
- ~1-15 $\mu$g. in cell
Table I. NMR analysis of whole (unfractionated) alginate samples

<table>
<thead>
<tr>
<th>Sequence</th>
<th>Protonal</th>
<th>NaAlginate</th>
<th>Manegel</th>
</tr>
</thead>
<tbody>
<tr>
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<td>$I_{\text{obsd}}$</td>
<td>$I_{\text{calc}}$ $^a$</td>
<td>$I_{\text{calc}}$ $^b$</td>
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<td>MM</td>
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<td>19.1</td>
<td>19.1</td>
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<tr>
<td>MG</td>
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<td>24.0</td>
<td>49.5</td>
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<td>GG</td>
<td>56.9</td>
<td>56.9</td>
<td>18.1</td>
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<td>MGM</td>
<td>5.9</td>
<td>2.1</td>
<td>8.8</td>
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<tr>
<td>GGM</td>
<td>6.4</td>
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</tr>
<tr>
<td>GGG</td>
<td>56.4</td>
<td>47.0</td>
<td>53.7</td>
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</table>

One-component $1^{\text{st}}$ order Markov model

- $P_{\text{GM}}$: 0.174
- $P_{\text{MG}}$: 0.386
- $\text{MD}^c$: 4.4

Two-component $1^{\text{st}}$ order Markov model

<table>
<thead>
<tr>
<th>Component 1</th>
<th>$P_{\text{GM}}$</th>
<th>0.004</th>
<th>0.006</th>
<th>0.004</th>
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<tbody>
<tr>
<td>$P_{\text{MG}}$</td>
<td>0.991</td>
<td>0.998</td>
<td>0.984</td>
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<tr>
<td>$w_1$</td>
<td>0.533</td>
<td>0.110</td>
<td>0.459</td>
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<table>
<thead>
<tr>
<th>Component 2</th>
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<th>0.774</th>
<th>0.678</th>
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<td>0.432</td>
<td>0.391</td>
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<tr>
<td>$w_2$</td>
<td>0.467</td>
<td>0.890</td>
<td>0.541</td>
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<tr>
<td>$\text{MD}^c$</td>
<td>0.9</td>
<td>0.3</td>
<td>0.5</td>
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</table>

1st Order Markovian Analysis

<table>
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<th>Sample</th>
<th>$P_{\text{GM}}$</th>
<th>$P_{\text{MG}}$</th>
<th>Characteristics</th>
<th>$P_{\text{GM}}$</th>
<th>$P_{\text{MG}}$</th>
<th>Characteristics</th>
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<tr>
<td>Protonal LFR</td>
<td>0.001</td>
<td>0.999</td>
<td>almost all G</td>
<td>0.64</td>
<td>0.36</td>
<td>high M, random</td>
</tr>
<tr>
<td>Na Alginate</td>
<td>0.004</td>
<td>0.996</td>
<td>almost all G</td>
<td>0.95</td>
<td>0.35</td>
<td>high M, alternating</td>
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<tr>
<td>ManegeL MW</td>
<td>0.006</td>
<td>0.994</td>
<td>almost all G</td>
<td>0.80</td>
<td>0.33</td>
<td>high M, alternating</td>
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</table>

- Component 1 corresponds to the enzymatic reaction of an enzyme that produces blocks of G.
- Component 2 corresponds to the reactions of enzyme(s) that produce random or alternating structures.
### SEC Fraction NMR Results

<table>
<thead>
<tr>
<th>Sample</th>
<th>Fr.</th>
<th>M&lt;sub&gt;W&lt;/sub&gt;</th>
<th>f&lt;sub&gt;M&lt;/sub&gt;</th>
<th>f&lt;sub&gt;G&lt;/sub&gt;</th>
<th>M/G</th>
<th>f&lt;sub&gt;NN&lt;/sub&gt;</th>
<th>f&lt;sub&gt;MG&lt;/sub&gt;</th>
<th>f&lt;sub&gt;GG&lt;/sub&gt;</th>
<th>f&lt;sub&gt;GM&lt;/sub&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>Protonal LFR</td>
<td>1</td>
<td>280</td>
<td>0.13</td>
<td>0.87</td>
<td>0.16</td>
<td>0.09</td>
<td>0.04</td>
<td>0.83</td>
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<tr>
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<td>0.81</td>
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<td>0.07</td>
<td>0.76</td>
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<td>0.22</td>
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<td>0.54</td>
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<td>Na Alginate</td>
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<td>0.39</td>
<td>0.14</td>
<td>0.38</td>
<td>0.09</td>
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<td></td>
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<td>0.46</td>
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<td>1.37</td>
<td>0.35</td>
<td>0.23</td>
<td>0.21</td>
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<tr>
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<td>0.20</td>
<td>0.26</td>
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<td>Manegel LMW</td>
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<td>0.78</td>
<td>0.28</td>
<td>0.156</td>
<td>0.06</td>
<td>0.78</td>
<td>0.00</td>
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<td>136</td>
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<td>0.77</td>
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<td>0.14</td>
<td>0.09</td>
<td>0.72</td>
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<tr>
<td></td>
<td>5</td>
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<td>0.38</td>
<td>0.62</td>
<td>0.62</td>
<td>0.24</td>
<td>0.14</td>
<td>0.49</td>
<td>0.12</td>
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</tbody>
</table>

### Table IV. Contributions of the components to each polymer

<table>
<thead>
<tr>
<th>Sample</th>
<th>Fr.</th>
<th>% polymer</th>
<th>w&lt;sub&gt;1&lt;/sub&gt;</th>
<th>w&lt;sub&gt;2&lt;/sub&gt;</th>
<th>% polym.* w&lt;sub&gt;1&lt;/sub&gt;</th>
<th>% polym.* w&lt;sub&gt;2&lt;/sub&gt;</th>
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<tbody>
<tr>
<td>Protonal LFR</td>
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<td>9.4</td>
<td>0.799</td>
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<td>7.51</td>
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<td>0.521</td>
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<tr>
<td>Component weight % from all fractions</td>
<td></td>
<td>60.97</td>
<td>39.03</td>
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<td>NaAlginate</td>
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<td>8.6</td>
<td>0.358</td>
<td>0.642</td>
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<td></td>
<td>2</td>
<td>20.0</td>
<td>0.348</td>
<td>0.652</td>
<td>6.96</td>
<td>13.04</td>
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<td></td>
<td>3</td>
<td>42.9</td>
<td>0.263</td>
<td>0.737</td>
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<td>0.759</td>
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<td>0.282</td>
<td>0.718</td>
<td>2.43</td>
<td>6.17</td>
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<tr>
<td>Component weight % from all fractions</td>
<td></td>
<td>28.55</td>
<td>71.45</td>
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<td>Manegel LMW</td>
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<td>0.250</td>
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<td>2</td>
<td>20.0</td>
<td>0.718</td>
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<td>5.64</td>
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<td></td>
<td>3</td>
<td>42.9</td>
<td>0.614</td>
<td>0.386</td>
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<td>0.455</td>
<td>10.85</td>
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<td>0.462</td>
<td>0.538</td>
<td>3.97</td>
<td>4.63</td>
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<tr>
<td>Component weight % from all fractions</td>
<td></td>
<td>61.97</td>
<td>38.03</td>
<td></td>
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<td></td>
</tr>
</tbody>
</table>

Alginate Results

- All samples can be described by a 2-component M1 model
  - Component 1 is G homopolymer
  - Component 2 is M/G copolymer, with a random to alternating tendency

- Correlation of structure with molecular weight
  - Second component increases as MW decreases
  - Less pronounced in high M polymer

- Implications for epimerization reaction
  - At least two separate enzymes that attack the alginate chains.
  - The first enzyme mostly converts M to blocks of G.
  - The second enzyme produces single M $\rightarrow$ G conversion or favors the formation of alternating MG units.
  - The components weights are different for different samples, reflecting different enzyme actions or different biological origins.

Presentation Scheme
4-component copolymerization

$M_1 = \text{cis-BD}\quad C = C$

$M_2 = \text{trans-BD}\quad C = C$

$M_3 = \text{vinyl-BD}\quad C - C$

$M_4 = \text{styrene}\quad C - C$

Statistical equations have been derived earlier:
### Table 1. Assignments of $^{13}$C NMR spectrum of SBR and the reaction probability expressions

<table>
<thead>
<tr>
<th>Peak Shift No.</th>
<th>Sequence</th>
<th>1st order Markovian probabilities</th>
</tr>
</thead>
<tbody>
<tr>
<td>C T V S</td>
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<td>C T V S</td>
</tr>
<tr>
<td>1</td>
<td>43.6-45.8</td>
<td>evC4</td>
</tr>
<tr>
<td>2</td>
<td>42.4-43.5</td>
<td>evC4</td>
</tr>
<tr>
<td>3</td>
<td>40.6-41.6</td>
<td>evC4</td>
</tr>
<tr>
<td>4</td>
<td>39.8-40.6</td>
<td>evC4</td>
</tr>
<tr>
<td>5</td>
<td>39.3-39.5</td>
<td>evC4</td>
</tr>
<tr>
<td>6</td>
<td>37.8-38.1</td>
<td>evC4</td>
</tr>
<tr>
<td>7</td>
<td>37.2-37.7</td>
<td>evC4</td>
</tr>
<tr>
<td>8</td>
<td>35.4-37.0</td>
<td>evC4</td>
</tr>
<tr>
<td>9</td>
<td>34.4-34.6</td>
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<tr>
<td>10</td>
<td>33.9-34.3</td>
<td>evC4</td>
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<td>11</td>
<td>32.7-33.0</td>
<td>evC4</td>
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<td>12</td>
<td>30.4-32.3</td>
<td>evC4</td>
</tr>
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<td>30.1</td>
<td>evC4</td>
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<td>16</td>
<td>24.9</td>
<td>evC4</td>
</tr>
<tr>
<td>Total</td>
<td></td>
<td></td>
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### Table 2. Analysis of $^{13}$C NMR data on SBR through four-component copolymerization model

<table>
<thead>
<tr>
<th>Peak No. (this work)</th>
<th>Peak No. (Jiao$^{22}$)</th>
<th>Sample (Fig. 2) ( \text{I}_{\text{calc}} )</th>
<th>Jiao Sample 1 ( \text{I}_{\text{calc}} )</th>
<th>Jiao Sample 3 ( \text{I}_{\text{calc}} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>33–35</td>
<td>14.6</td>
<td>16.2</td>
<td>19.2</td>
</tr>
<tr>
<td>2</td>
<td>30–32</td>
<td>0.7</td>
<td>0.8</td>
<td>5.1</td>
</tr>
<tr>
<td>3</td>
<td>26–29</td>
<td>4.2</td>
<td>4.2</td>
<td>8.6</td>
</tr>
<tr>
<td>4</td>
<td>24–25</td>
<td>5.1</td>
<td>6.1</td>
<td>7.9</td>
</tr>
<tr>
<td>5</td>
<td>21–23</td>
<td>1.0</td>
<td>1.2</td>
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<td>0</td>
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<td>7.9</td>
<td>11.4</td>
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<td>1.6</td>
<td>1.2</td>
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<td>7.1</td>
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<td>6.0</td>
<td>6.0</td>
<td>10.1</td>
</tr>
<tr>
<td>14</td>
<td>3–4</td>
<td>28.4</td>
<td>28.4</td>
<td>14.7</td>
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<td>0.6</td>
<td>1.3</td>
<td>1.7</td>
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<tr>
<td>16</td>
<td>1</td>
<td>0.7</td>
<td>1.7</td>
<td>2.0</td>
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Mean Dev. 0.7 0.9 0.9

For even more complex systems, replace probability models with realistic kinetic schemes.

<table>
<thead>
<tr>
<th>model</th>
<th>kinetic</th>
<th>chain</th>
<th>NMR</th>
<th>NMR</th>
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<tr>
<td>(kinetic scheme)</td>
<td>(probability)</td>
<td>generation</td>
<td>micro-structure</td>
<td>spectrum</td>
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</table>

Kinetic Scheme/Simulation Approaches:

We need:

1) a realistic reaction scheme
2) kinetic rate constants
3) a computer method to simulate polymerization
4) shift/structure correlations
5) conversion of the data to a predicted spectrum

Kinetic Scheme/Simulation Approaches:

We need:

1) a realistic reaction scheme
2) kinetic rate constants
3) a computer method to simulate polymerization
4) shift/structure correlations
5) conversion of the data to a predicted spectrum

Reaction Scheme

1. Initiator Decomposition
   \[ I_2 \rightarrow 2 I^* \quad \quad r_d = -k_d[I_2] \]

2. Reactions of the Initiator Radical

   a) Chain Initiation
      \[ I^* + E \rightarrow P_1^* \quad \quad r_s = k_s[I^*][E] \]

   b) Hydrogen Abstraction
      \[ I^* + P-H \rightarrow P^* + I-H \quad \quad r_h = k_h[I^*][P] \]

3. Chain Propagation
   \[ P^* + E \rightarrow P^* \quad \quad r_p = k_p[P^*][E] \]

4. Chain Termination

   a) by recombination
      \[ P^* + P^{**} \rightarrow P-P' \quad \quad r_{tr} = k_{t,r}[P^*]^2 \]

   b) by disproportionation
      \[ P^* + P^{**} \rightarrow P + P' \quad \quad r_{td} = k_{r,d}[P^*]^2 \]
5. Chain Transfer

a) to monomer
\[ \text{P}^* + \text{E} \rightarrow \text{P} + \text{P}_1^* \]
\[ \dot{r}_{\text{trm}} = k_{\text{tr},m}[\text{P}^*][\text{E}] \]

b) to transfer agent
\[ \text{P}^* + \text{X} + \text{E} \rightarrow \text{P} + \text{X} + \text{P}_1^* \]
\[ \dot{r}_{\text{trx}} = k_{\text{tr},x}[\text{P}^*][\text{X}] \]

c) to polymer (intermolecular)
\[ \text{P}^* + \text{P}' \rightarrow \text{P} + \text{P}'^* \]
\[ \dot{r}_{\text{trp}} = k_{\text{tr},p}[\text{P}^*][\text{P}'] \]

where \( \text{P}' \) is a different polymer chain, and \( [\text{P}'] \) is the concentration of ethylene units present in \( \text{P}' \). This rate is weighted by the length of the chains.

d) to polymer (intramolecular)
\[ \text{P}^* \rightarrow \text{P}^* \]
\[ \dot{r}_{\text{tri}} = k_{\text{tr},i}[\text{P}^*] \]
\[ \dot{r}_{\text{tri}'} = k_{\text{tr},i'}[\text{P}^*] \]

where \( i = 6 \) or 7, referring to the ring structure formed in the transition state. The rate constants \( k_{\text{tr},6} \) and \( k_{\text{tr},7} \), refer to the first intramolecular transfer event, and \( k_{\text{tr},6'} \) and \( k_{\text{tr},7'} \) refer to the second and the subsequent intramolecular transfers.

6. β-Scission

This reaction produces vinyl chain ends:

\[ \text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}-\text{CH}_2- \rightarrow \text{CH}_2-\text{CH}_2^* + \text{CH}_2=\text{CH}_2-\text{CH}_2^- \]

\[ \dot{r}_\beta = k_\beta[\text{P}^*] \]
Table I. Reaction rate parameters for LDPE polymerization

<table>
<thead>
<tr>
<th>Reaction</th>
<th>$E_a$ (kJ/mol)</th>
<th>$k_0$ (s$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>initiator decomposition ($k_d$)</td>
<td>121.4</td>
<td>$7.0 \times 10^{12}$</td>
</tr>
<tr>
<td>initiation ($k_i$)</td>
<td>37.0</td>
<td>$7.3 \times 10^5$ m$^3$/mol-s</td>
</tr>
<tr>
<td>propagation ($k_p$)</td>
<td>37.0</td>
<td>$7.3 \times 10^5$ m$^3$/mol-s</td>
</tr>
<tr>
<td>termination ($k_{tr, r}$, $k_{tr, d}$)</td>
<td>3.0</td>
<td>$9.6 \times 10^5$ m$^3$/mol-s</td>
</tr>
<tr>
<td>intermolecular chain transfer:</td>
<td></td>
<td></td>
</tr>
<tr>
<td>to polymer ($k_{tr, p}$)</td>
<td>19.5</td>
<td>$1.75 \times 10^2$ m$^3$/mol-s</td>
</tr>
<tr>
<td>to chain transfer agent ($k_{tr, c}$)</td>
<td>19.5</td>
<td>$1.75 \times 10^2$ m$^3$/mol-s</td>
</tr>
<tr>
<td>intramolecular chain transfer:</td>
<td></td>
<td></td>
</tr>
<tr>
<td>6MI ($k_{tr, 6}$)</td>
<td>27.5</td>
<td>$2.5 \times 10^7$ s$^{-1}$</td>
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<td>7MI ($k_{tr, 7}$)</td>
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<td>$0.5 \times 10^7$ s$^{-1}$</td>
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<td>6MI' ($k_{tr, 6}'$)</td>
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<td>$20.0 \times 10^7$ s$^{-1}$</td>
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<tr>
<td>7MI' ($k_{tr, 7}'$)</td>
<td>27.5</td>
<td>$4.0 \times 10^7$ s$^{-1}$</td>
</tr>
<tr>
<td>$\beta$-scission (sec. radicals)</td>
<td>60.8</td>
<td>$1.0 \times 10^8$</td>
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</tbody>
</table>

*a* Values mostly taken from Feucht, et al.*a* and calculated from $k_0 = A \exp(-pAV^f/RT)$, where $p = 1700$ bar and $T = 500 K$.

---

Figure 1. Generation of short chain branching in LDPE for one and two backbiting events.
Observed spectrum of LDPE

Figure 1. $^{13}$C NMR Spectrum at 90 MHz of low-density polyethylene.

Predicted spectrum 1
Observed spectrum of LDPE

Figure 1. $^{13}$C NMR Spectrum at 90 MHz of low-density polyethylene.

Figure 2. Generation of short chain branching in LDPE for three backbiting events involving 6MI and 5MI only.
Predicted spectrum 2
Solution NMR Summary

- Many solution NMR techniques are being standardized and becoming routine.
- New approaches have been devised in several areas.
  - Analytical and Simulation approaches
  - Improved methodologies
    - Separation/NMR
    - 2D NMR
  - More sophisticated probability models
    - Multi-component copolymerization models
    - Kinetic modeling
  - Compositional heterogeneity
- Examples of NMR analysis are given for:
  - polystyrene tacticity
  - vinyl chloride/vinylidene chloride copolymer
  - alginates
  - low-density polyethylene

Solid State NMR

- Solution NMR spectra consist of a series of very sharp transitions, due to averaging of anisotropic NMR interactions by rapid random tumbling.
- In contrast, solid-state NMR spectra show broad lines, as the full effects of anisotropic or orientation-dependent interactions are observed in the spectrum.
  - Wideline NMR can provide a lot of information, e.g.,
    - % crystallinity, phase transitions, dynamics, etc.
- High-resolution solid NMR spectra can provide the same type of information that is available from corresponding solution NMR spectra, but a number of special techniques/equipment are needed
  - magic-angle spinning, cross polarization, high-power decoupling
  - 2D experiments, enhanced probe electronics, etc.
High Resolution Solid State NMR

- **Magic-angle spinning**
  - Rapid sample spinning at the magic angle w.r.t. $B_0$ (7 to 35 kHz)

- **Dilution**
  - Occurs naturally for many nuclei (e.g., $^{13}$C, 1.108% n.a.), and the dipolar interactions scales with $r^{-3}$. However, this only leads to “high-resolution” spectra if there are no heteronuclear dipolar interactions (e.g., with protons, fluorine).
  - Anisotropic chemical shielding can still broaden the spectra

- **Multiple-Pulse Sequences**
  - Pulse sequences can impose artificial motion on the spin operators. Good for $^1$H NMR spectra (e.g., CRAMPS -combined rotation and multiple pulse spectroscopy), and 2D NMR

- **Cross Polarization**
  - Polarization from abundant nuclei (e.g., $^1$H, $^{19}$F and $^{31}$P) can be transferred to rare nuclei ($^{13}$C, $^{15}$N, $^{29}$Si) to enhance s/n

---

**Example of Adamantane**

![Adamantane NMR Spectroscopy](image)
A practical example of solid NMR

- Pecan is a major crop in the US, with an annual production of 88,000 metric tons in 2008.
- Pecan shells are waste materials; their disposal is costly and may pose environmental problems.
- Pecan shells can be made into activated carbons
  - Remove metal ions and organic species in wastewater
  - Can potentially be used in sugar refining
  - Can potentially be used as a soil fertility agent
- Properties of pecan shell based activated carbon depend on the activation process
  - Effect of acid, oxygen level, phosphorus incorporation, etc.
  - Surface activity, porosity, oxidation, etc.
  - Better understanding is needed: Use NMR

Cheng, H.N. et al., Carbon, in press

NMR techniques used

<table>
<thead>
<tr>
<th>Techniques</th>
<th>Description</th>
<th>Information available for activated carbon</th>
</tr>
</thead>
<tbody>
<tr>
<td>CP-MAS</td>
<td>cross-polarization – magic angle spinning</td>
<td>chemical composition</td>
</tr>
<tr>
<td>SPE-MAS</td>
<td>single pulse excitation – magic angle spinning</td>
<td>quantitative $^{13}$C composition</td>
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<tr>
<td>DD-MAS</td>
<td>dipolar dephasing – magic angle spinning</td>
<td>observation of only aromatic quaternary carbons.</td>
</tr>
<tr>
<td>VCT</td>
<td>variable contact time (giving $T_{CH}$ and $T_{1p}^{H}$)</td>
<td>relative mobility and homogeneity</td>
</tr>
<tr>
<td>Relaxation</td>
<td>1. inversion recovery ($T_1$)</td>
<td>- mobility of carbon matrix</td>
</tr>
<tr>
<td></td>
<td>2. TD (time domain) expts for $T_1$ and $T_2$</td>
<td>- porosity of sample through water adsorption</td>
</tr>
</tbody>
</table>
Samples used

<table>
<thead>
<tr>
<th>Sample</th>
<th>Activation air flow rate</th>
<th>Nominal oxygen level (%)</th>
<th>Surface area (m²/g)</th>
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<tbody>
<tr>
<td>A</td>
<td>0</td>
<td>0</td>
<td>N/A</td>
</tr>
<tr>
<td>B</td>
<td>100 ml/min</td>
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<td>904</td>
</tr>
<tr>
<td>C</td>
<td>400 ml/min</td>
<td>7.6</td>
<td>895</td>
</tr>
<tr>
<td>D</td>
<td>2000 ml/min</td>
<td>14.0</td>
<td>915</td>
</tr>
</tbody>
</table>

Pecan shells were activated with phosphoric acid, and carbonized at 450°C for 4 hours with varying amounts of air flow.

Solid state CP-MAS and SPE-MAS
## Starting pecan shells

<table>
<thead>
<tr>
<th>Approximate Carbon Structure Type</th>
<th>Begin (ppm)</th>
<th>End (ppm)</th>
<th>Sample A – CP-MAS % intensity</th>
<th>Sample A – SPE-MAS % intensity</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbonyl C</td>
<td>210</td>
<td>190</td>
<td>2</td>
<td>1</td>
</tr>
<tr>
<td>Carboxyl C</td>
<td>190</td>
<td>165</td>
<td>6</td>
<td>6</td>
</tr>
<tr>
<td>Phenolic C</td>
<td>165</td>
<td>150</td>
<td>9</td>
<td>9</td>
</tr>
<tr>
<td>Substituted Aromatic C</td>
<td>150</td>
<td>140</td>
<td>5</td>
<td>6</td>
</tr>
<tr>
<td>Bridgehead+ Protonated Aromatic C</td>
<td>140</td>
<td>90</td>
<td>26</td>
<td>37</td>
</tr>
<tr>
<td>Aliphatic C</td>
<td>90</td>
<td>5</td>
<td>35 aliphatic C-O 16 aliphatic C-C</td>
<td>26 aliphatic C-O 16 aliphatic C-C</td>
</tr>
</tbody>
</table>

## CP-MAS of samples A-D

![CP-MAS spectra of samples A-D](image)
SPE-MAS of samples A-D

DD-MAS D2-array spectra and Gaussian/Lorentzian fit

For sample B
2-component fit of DD data

\[ M(\tau) = M_{0L} \exp(-\tau/T_L) + M_{0G} \exp(-0.5(\tau/T_G)^2) \]

<table>
<thead>
<tr>
<th>Definition</th>
<th>Parameter</th>
<th>Sample B</th>
<th>Sample C</th>
<th>Sample D</th>
</tr>
</thead>
<tbody>
<tr>
<td>Weakly Coupled C</td>
<td>( M_{0L} )</td>
<td>80.5</td>
<td>54.0</td>
<td>59.1</td>
</tr>
<tr>
<td>Strongly Coupled C</td>
<td>( M_{0G} )</td>
<td>48.3</td>
<td>61.2</td>
<td>59.8</td>
</tr>
<tr>
<td>Lorentzian Relaxation Time</td>
<td>( T_L ) ((\mu s))</td>
<td>599.6</td>
<td>598.2</td>
<td>599.6</td>
</tr>
<tr>
<td>Gaussian Relaxation Time</td>
<td>( T_G ) ((\mu s))</td>
<td>16.1</td>
<td>15.4</td>
<td>14.7</td>
</tr>
<tr>
<td>Fraction of Bridgehead C</td>
<td>( M_{0L}/(M_{0G}+M_{0L}) )</td>
<td>62 %</td>
<td>47 %</td>
<td>50 %</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Sample B</th>
<th>Sample C</th>
<th>Sample D</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>( F_{CO} )</td>
<td>1.1</td>
<td>2.0</td>
<td>1.3</td>
<td>Fraction of Carbonyl (%)</td>
</tr>
<tr>
<td>( F_{COO} )</td>
<td>5.6</td>
<td>8.3</td>
<td>9.2</td>
<td>Fraction of Carboxyl (%)</td>
</tr>
<tr>
<td>( F_P )</td>
<td>6.9</td>
<td>10.5</td>
<td>10.7</td>
<td>Fraction of phenolic carbon ((ar)-C-OH) (%)</td>
</tr>
<tr>
<td>( F_S )</td>
<td>9.6</td>
<td>10.9</td>
<td>9.9</td>
<td>Fraction of substituted aromatic carbon (%)</td>
</tr>
<tr>
<td>( F_{B+H} )</td>
<td>76.2</td>
<td>67.7</td>
<td>68.3</td>
<td>Fraction of combined bridgehead and protonated aromatic C (%)</td>
</tr>
<tr>
<td>( F_N )</td>
<td>64.1</td>
<td>53.2</td>
<td>54.6</td>
<td>Fraction of non-protonated aromatic carbon (%)</td>
</tr>
<tr>
<td>( F_C )</td>
<td>6.7</td>
<td>10.2</td>
<td>10.5</td>
<td>Fraction of sp^2 carbon present as carbonyl and carboxyl (%)</td>
</tr>
<tr>
<td>( F' )</td>
<td>92.7</td>
<td>89.1</td>
<td>88.9</td>
<td>Fraction of aromatic carbon (%)</td>
</tr>
<tr>
<td>( F_a )</td>
<td>99.3</td>
<td>99.3</td>
<td>99.4</td>
<td>Fraction of sp^2 carbon (aromatics and carboxyl/carbonyl) (%)</td>
</tr>
<tr>
<td>( F_{al} )</td>
<td>0.7</td>
<td>0.7</td>
<td>0.6</td>
<td>Fraction of sp^3 (aliphatic) carbon (%)</td>
</tr>
<tr>
<td>( F_{B} )</td>
<td>47.6</td>
<td>31.7</td>
<td>34.0</td>
<td>Fraction of bridgehead aromatic carbon (%)</td>
</tr>
<tr>
<td>( F_H )</td>
<td>28.6</td>
<td>35.9</td>
<td>34.3</td>
<td>Fraction of protonated aromatic carbon (%)</td>
</tr>
</tbody>
</table>
### Calculated structural parameters

<table>
<thead>
<tr>
<th>Molecular Parameter</th>
<th>Sample B</th>
<th>Sample C</th>
<th>Sample D</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\chi_b$</td>
<td>51</td>
<td>36</td>
<td>38</td>
<td>Mole fraction of bridgehead aromatic carbon (%)</td>
</tr>
<tr>
<td>C</td>
<td>25.6</td>
<td>17.8</td>
<td>18.9</td>
<td>Number of carbons per aromatic ring system</td>
</tr>
<tr>
<td># Ring Systems per 100 C</td>
<td>3.6</td>
<td>5.0</td>
<td>4.7</td>
<td>Number of aromatic ring systems per 100 carbons</td>
</tr>
<tr>
<td>Phenolic C per cluster</td>
<td>1.9</td>
<td>2.1</td>
<td>2.3</td>
<td>Number of phenolic carbons per aromatic ring system</td>
</tr>
<tr>
<td>Carboxyls per cluster</td>
<td>1.6</td>
<td>1.7</td>
<td>2.0</td>
<td>Number of carboxyl carbons per aromatic ring system</td>
</tr>
<tr>
<td>k/a per cluster</td>
<td>0.3</td>
<td>0.4</td>
<td>0.3</td>
<td>Number of ketone/aldehyde carbons per aromatic ring system</td>
</tr>
<tr>
<td>s+1</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>Average length of aliphatic substitutions on the aromatic ring system</td>
</tr>
</tbody>
</table>


### Effective overall $^1$H spin-lattice relaxation times ($T_1$)

<table>
<thead>
<tr>
<th>Sample</th>
<th>A</th>
<th>B</th>
<th>C</th>
<th>D</th>
</tr>
</thead>
<tbody>
<tr>
<td>$T_1$ (ms)</td>
<td>33 ± 7</td>
<td>23 ± 1</td>
<td>19 ± 2</td>
<td>16 ± 3</td>
</tr>
</tbody>
</table>

(from $^1$H-$^{13}$C-CP-MAS-prepared inversion recovery experiment)

(for sample B)
CP-MAS-VCT –relaxation fit (1-component)

<table>
<thead>
<tr>
<th>Sample</th>
<th>Carbon type</th>
<th>$T_{CH}$ ($\mu$s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>Carboxyl</td>
<td>294</td>
</tr>
<tr>
<td></td>
<td>Phenolic</td>
<td>269</td>
</tr>
<tr>
<td></td>
<td>Aromatic</td>
<td>238</td>
</tr>
<tr>
<td></td>
<td>Aromatic/Cellulose</td>
<td>185</td>
</tr>
<tr>
<td></td>
<td>Cellulose</td>
<td>81</td>
</tr>
<tr>
<td></td>
<td>Aliphatic</td>
<td>61</td>
</tr>
<tr>
<td>B</td>
<td>Aromatic</td>
<td>2530</td>
</tr>
<tr>
<td>C</td>
<td>Aromatic</td>
<td>4340</td>
</tr>
<tr>
<td>D</td>
<td>Aromatic</td>
<td>790</td>
</tr>
</tbody>
</table>
$^{31}$P SPE-MAS spectra

- Narrow component is most likely due to free phosphoric acid
- Broad component is likely to be alkyl (and dialkyl) phosphates
- Small peaks at -40 to -60 ppm, perhaps polyphosphates
- Phosphonates and phosphonic acid do not appear to be present

<table>
<thead>
<tr>
<th>Sample</th>
<th>Unbound (Narrow) (%P)</th>
<th>Bound (Broad) (%P)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>0</td>
<td>100</td>
</tr>
<tr>
<td>B</td>
<td>22.0</td>
<td>78.0</td>
</tr>
<tr>
<td>C</td>
<td>30.1</td>
<td>69.9</td>
</tr>
<tr>
<td>D</td>
<td>15.0</td>
<td>85.0</td>
</tr>
</tbody>
</table>
\(^1\)H NMR (TD low-resolution)

- FID signals varies with \(^1\)H spins present (mostly water here)
- Samples B-D are microporous and contain more water
  - Increasing pore volume, more adsorbed water expected
- Trend in porosity from FID intensity: D > B > C >> A

Comparison: Average pore volume and width from gas sorption measurements

<table>
<thead>
<tr>
<th>sample</th>
<th>air flow rate (mL/min)</th>
<th>average pore volume (mL/g)</th>
<th>average pore width (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>B</td>
<td>100</td>
<td>0.361</td>
<td>9.26</td>
</tr>
<tr>
<td>C</td>
<td>400</td>
<td>0.354</td>
<td>10.07</td>
</tr>
<tr>
<td>D</td>
<td>2000</td>
<td>0.368</td>
<td>8.52</td>
</tr>
</tbody>
</table>

- Gas sorption studies were carried out on a Nova® instrument (Quantachrome, Boynton Beach, FL)
- Samples were degassed and then brought to 77K when nitrogen was admitted in steps in the evacuated sample chamber
- Trend in porosity from gas sorption: D > B > C
ESR absorption spectra

![Graph showing ESR absorption spectra with peaks labeled for Illinois #6 coal, USDA A, USDA B, USDA C, and USDA D.]

ESR intensities, g factor and radical content

<table>
<thead>
<tr>
<th>sample</th>
<th>g value</th>
<th>intensity</th>
<th>radical content (10^{18} spins per gram)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Illinois #6 coal</td>
<td>2.0028</td>
<td>69.3</td>
<td>6.8</td>
</tr>
<tr>
<td>A</td>
<td>2.0018</td>
<td>5.8</td>
<td>0.6</td>
</tr>
<tr>
<td>B</td>
<td>2.0013</td>
<td>121.2</td>
<td>11.9</td>
</tr>
<tr>
<td>C</td>
<td>2.0039</td>
<td>129.3</td>
<td>12.7</td>
</tr>
<tr>
<td>D</td>
<td>2.0039</td>
<td>62.2</td>
<td>6.1</td>
</tr>
</tbody>
</table>

- g value increases with the number of heteroatoms present. Here increase in g value may be due to the oxidation of the carbon matrix and the formation of oxidized functional group.
- Radical content reaches a maximum at C, and then decreases at D, probably due to oxidation and/or reactions involving the radicals during carbonization at a very high oxygen flow rate.
Solid State NMR Summary

- The use of different NMR techniques and ESR gives complementary information on structure and dynamics of the polymeric system.
- For carbons, structural parameters available include mole fraction of bridgehead aromatic carbons, number of carbons per aromatic ring system, and number of phenolic carbons per aromatic ring system.
- The relaxation times are indicative of the relative mobility of different structural units.
- $^{31}$P NMR indicates the type of phosphorus-containing chemical species present.
- $^1$H NMR data on adsorbed water are shown to be consistent with the trends in the amount of pore volumes for different samples of activated carbons.
- ESR spectra showed the presence of π-type aromatic free radicals in the carbonized samples with a slight shift in g value with increasing oxidation.

Cheng, HN, et al., *Carbon*, in press

Acknowledgments

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  - Leo Kasehagen (now at Arkema)
  - Michael Roland (ex-Hercules)
  - Mark Bennett (ex-Hercules)
  - G. H. Lee (ex-Sunoco)
  - Thomas G. Neiss (now at GlaxoSmithKline)
- Solid State NMR
  - John Edwards (Process NMR)
  - Lynda Wartelle (USDA)
  - K. Thomas Klasson (USDA)
TAILORED SYNTHESIS AND CHARACTERIZATION OF COMPLEX POLYMERS

Jimmy Mays

Univ. of Tennessee
Molecular Characterization of Complex Polymers

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Knoxville, TN 37996
jimmymays@utk.edu

Categories of Complex Polymers

• Branched polymers (star, comb, dendrimers, randomly branched)
• Cyclic polymers
• Copolymers (blocky, random, branched)
• End-functionalized or telechelic polymers
• Stiff polymer chains (conformational studies)
For a review on synthesis of various polymer architectures see

Macromolecular architectures by living and controlled/living polymerizations

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Received 28 June 2006; revised in revised form 24 July 2006; accepted 27 July 2006

Molecular Weight Methods

Classical
- Absolute methods
  - end group analysis
  - colligative properties
  - light scattering
  - ultracentrifugation

Relative method
- solution viscosity

Fractionation methods
- Solvent/non-solvent fractionation
- SEC (GPC)

Advanced
- Absolute methods
  - MALDI-TOF MS
  - SEC with light scattering detection

Relative method
- SEC with viscosity detection

Fractionation method
- TGIC and multi-detector SEC
Synthesis of Model Star Polymers

This classic approach was first demonstrated using living anionic polymerization and chlorosilane linking chemistry by Morton et al. in 1962:
- this approach allows the "arms" to be sampled and characterized independently
- a small excess of arms is used to force the linking reaction to completion
- the star is isolated from excess arm by solvent/non-solvent fractionation (no SEC at the time!)
- Absolute molecular weight of the star should be 3x that of the arm for a 3-arm star, etc., i.e. this is proof of the star structure


The Evolution of Size Exclusion Chromatography (SEC)

- Unlike in HPLC (or interaction chromatography) no chemical attraction of the polymeric solute to the column is allowed.
- Solvent flow carries molecules from left to right; big ones come out first while small ones get detained in the pores.
- Polymer "hydrodynamic volume", not molecular weight, controls the order of elution.
Simple SEC

Conc sensitive detector only - DRI or UV most typically

DRI

V_e

log_{10}M

Average Molecular Weights and Polydispersity

Definition of molar mass averages

\[ M_n = \frac{\sum M_i N_i}{\sum N_i}, \quad M_w = \frac{\sum M_i^2 N_i}{\sum M_i N_i}, \quad M_z = \frac{\sum M_i^3 N_i}{\sum M_i^2 N_i}, \quad M_v = \left[ \frac{\sum M_i^{1+a} N_i}{\sum M_i N_i} \right]^{\frac{1}{a}} \]

Here \( a \) is the exponent in the Mark-Houwink equation which relates the intrinsic viscosity to molar mass.

The breadth of the molecular weight distribution (MWD) or polydispersity ratio (PDI) is usually taken as the ratio of \( M_w/M_n \), which would equal unity for a monodisperse polymer.
They were young when SEC was…

Compliments of Professor Paul Russo, Louisiana State University

Early Development of SEC

- Development of the technique: J. Moore, Dow Chemical Company (1962)
Conventional Calibration Requires Standard Samples

- **PROBLEM** - commercial narrow polydispersity standards are only readily available for polystyrene and a few other polymers and $V_h$ depends on type of polymer. PS equivalent MWs are often reported.

SEC of Branched Polymers

- Since the **hydrodynamic volume of branched polymer is smaller than the linear material having the same mass**, the density must be higher yielding a larger SEC retention volume, thus a lower apparent MW.
Universal Calibration

Grubisic, Rempp & Benoit, JPS Pt. B, 5, 753 (1967)

One of the most cited papers in polymer science.

Universal Calibration Equations

\[ [\eta]_A M_A = [\eta]_S M_S = f(V_e) \]

Universal Calibration
\( A = \) analyte; \( S = \) standard

\[ [\eta] = KM^a \]

Mark-Houwink Relation

\[ K_A M_A^{a_A+1} = K_S M_S^{a_S+1} \]

• must know Mark-Houwink parameters for both the standard and the analyte (very laborious and especially a problem with branched polymers)

• wouldn’t it be great if we could measure intrinsic viscosity online...
MW- and Size-Sensitive Detectors for SEC

• Beginning around 1980, molecular weight and size sensitive detectors for SEC became commercially available
• Detectors include viscosity detectors, which allow facile use of universal calibration and provide insight into branching
• Single-angle (LALLS) and multi-angle light scattering (MALLS) instruments, which allow measurement of absolute molecular weights and, for MALLS, the radius of gyration Rg

SEC with on-line Viscosity Detection

![Diagram of SEC with on-line Viscosity Detection]
SEC/MALLS

3D Plot - PBLG

Scattered intensity
(gives absolute MW)

V_e

(gives Rg)
By the mid-1990s SEC/MALLS/Vis was as reliable as much more tedious off-line measurements for measuring polymer molecular weights and sizes.

<table>
<thead>
<tr>
<th>Polymer</th>
<th>K (dL/g x 10^4)</th>
<th>a</th>
<th>r</th>
</tr>
</thead>
<tbody>
<tr>
<td>PI</td>
<td>1.57</td>
<td>0.731</td>
<td>0.9996</td>
</tr>
<tr>
<td>PB</td>
<td>2.52</td>
<td>0.727</td>
<td>0.9996</td>
</tr>
<tr>
<td>PIB</td>
<td>2.66</td>
<td>0.654</td>
<td>0.9992</td>
</tr>
<tr>
<td>PMMA</td>
<td>0.697</td>
<td>0.710</td>
<td>0.9992</td>
</tr>
<tr>
<td>PS</td>
<td>0.683</td>
<td>0.736</td>
<td>0.9997</td>
</tr>
<tr>
<td>POMA</td>
<td>0.190</td>
<td>0.783</td>
<td>0.9994</td>
</tr>
</tbody>
</table>

Evolution of Multi-Detector SEC

Table X  Radius of Gyration Scaling Coefficients

<table>
<thead>
<tr>
<th>Polymer</th>
<th>$R_g$ (nm x 10^6)</th>
<th>$\gamma$</th>
<th>$\rho$</th>
</tr>
</thead>
<tbody>
<tr>
<td>PI</td>
<td>1.32</td>
<td>0.909</td>
<td>0.9994</td>
</tr>
<tr>
<td>PB</td>
<td>1.60</td>
<td>0.987</td>
<td>0.9994</td>
</tr>
<tr>
<td>PIB</td>
<td>1.45</td>
<td>0.960</td>
<td>0.9971</td>
</tr>
<tr>
<td>PMMA</td>
<td>1.10</td>
<td>0.989</td>
<td>0.9992</td>
</tr>
<tr>
<td>PS</td>
<td>1.118</td>
<td>0.960</td>
<td>0.9988</td>
</tr>
<tr>
<td>POMDA</td>
<td>0.382</td>
<td>0.852</td>
<td>0.9998</td>
</tr>
</tbody>
</table>


Radius of Gyration of Branched Polymers

- Long chain branching can have a profound effect on polymer processing and properties even at very low levels that are hard to quantify via spectroscopy.
- As we saw earlier, branched polymers are smaller than their linear counterparts at a given molecular weight.
- A branching parameter $g$ has been defined

$$g = \frac{\left(\frac{R_g}{R_g}ight)_{\text{br}}}{\left(\frac{R_g}{R_g}ight)_{\text{l}}} < 1$$

- $g$ can be calculated theoretically for linear and branched chains of different architectures and degrees of branching.
- Thus, experimentally derived $g$ values can be used to estimate the degree of branching.
Effect of Branching on Hydrodynamic Properties

- Branching also affects hydrodynamic properties in solution.
- Another commonly used branching parameter is $g'$:
  \[ g' = \frac{[\eta]_{br}}{[\eta]_{lin}}M < 1 \]
- $g'$ is easier to measure, particularly at lower MW, but theory relating $g'$ to the branched architecture is not so well established.

Experimental Data on Randomly Branched Samples

- Randomly branched PMMAs were synthesized by copolymerization of MMA with small amounts of ethylene glycol dimethacrylate.
- At low MWs the data merge, suggesting that low MW samples contain little or no branching, as expected.
- Larger scatter in data at lower MW reflects larger errors in measuring $R_g$ for smaller macromolecules.

Experimental Data on Randomly Branched Samples

- Data for intrinsic viscosity are very high quality even at low MW.
- Clearly the extent of branching increases as MW increases.

**Figure 7** Mark-Houwink plot for R-3-4. The dashed line shows the Mark–Houwink relation for linear PMMA determined from the narrow-molecular-weight-distribution polymers.


---

**Figure 10** Plot of the radius of gyration branching factor $g$ and the intrinsic viscosity branching factor $g$ against log molecular weight for R-3-4.

**Limitation:** the Zimm-Stockmayer theory that relates $g$ to extent of branches was developed for polymers chains in theta solvents whereas SEC is almost always conducted in thermodynamically good solvents.

Can we carry out multi-detector SEC in a theta solvent???

- Would allow for simple and rapid studies of dilute solution properties, with better comparison to theory.
- We chose trans-decalin as the theta solvent for PS at about 21-22 °C. It has a high boiling point so it could be run through the SEC columns at 110 °C (good solvent conditions) to prevent adsorption of PS onto the columns.
- Viscosity and two-angle light scattering (TALS, also DLS at 90°) detectors were maintained at 21-22 °C.
- Failed with differential viscometer due to adsorption of polymer within viscometer.


Mₜ dependence of Rₜ for regularly branched PS in THF: open circles = TALS, filled circles = Nakamura et al. via MALLS

Two-angle light scattering has been shown to yield identical results to MALLS both theoretically and experimentally. Data at left are for linear and branched PS in the good solvent THF.

$M_w$ dependence of $R_g$ for linear PS in trans-decalin at 22°C: open circles = TALS, filled squares = Inagaki et al. (J. Phys. Chem., 70, 1718 (1966)), filled triangles = Fukuda et al. (JPS-Phys., 12, 871 (1974)), filled circles = Konishi et al. (Macromolecules, 24, 5614 (1991))

\[ R_g = 0.028 M^{0.5} \]

Data under theta conditions allow a direct comparison with Zimm-Stockmayer theory for relating $g$ to the branching architecture
Limitations in SEC analysis

1. SEC separates polymers by hydrodynamic size only
2. Hydrodynamic size decreases with chain branching

SEC vs. IC

Size Exclusion Chromatography

Interaction Chromatography
Temperature & Solvent Effect on HPLC Retention

Column: Nucleosil C18, 5 μm, 100 Å, 250 x 4.5 mm
Eluent: CH₂Cl₂/CH₃CN mixture, 0.5 mL/min

Eluent Effect (30.5°C)

Temperature Effect (57/43)

< Samples >

<table>
<thead>
<tr>
<th>PS</th>
<th>MW</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>2,500</td>
</tr>
<tr>
<td>2</td>
<td>12,000</td>
</tr>
<tr>
<td>3</td>
<td>29,000</td>
</tr>
<tr>
<td>4</td>
<td>165,000</td>
</tr>
<tr>
<td>5</td>
<td>502,000</td>
</tr>
<tr>
<td>6</td>
<td>1,800,000</td>
</tr>
</tbody>
</table>


Temperature gradient elution chromatography

Column: Nucleosil C18, 3 mm, 100Å, 50 x 4.6 mm
Eluent: CH₂Cl₂/CH₃CN = 57/43 (v/v), 0.7 mL/min

TGIC separation of polystyrene

1 C18 silica column, 100 Å, 250 x 4.5 mm, CH$_2$Cl$_2$/CH$_3$CN (57/43)

4 DVB columns, 10$^5$, 10$^4$, 10$^3$ Å, mixed, 250 x 10 mm, THF

9 PS standards: 2.0 k, 11.6 k, 30.7 k, 53.5 k, 114 k, 208 k, 502 k, 1090 k, 2890 k

Lee & Chang, Polymer 37 5747 (1996)

SEC and TGIC Characterization of Polystyrenes

\[
\text{Styrene} \xrightarrow{\text{Cyclohexane, 45 °C}} \text{PS1, PS2, PS3, PS4, PS5, PS6, PS7, PS8, PS9}
\]

Take out aliquots and terminate with i-propanol at different polymerization times.

\[
\text{T (°C)} \quad 5 \quad 10 \quad 15 \quad 20 \quad 25 \quad 30 \quad 35 \quad 40 \quad 45 \quad 50 \quad 55 \quad 60 \quad 65 \quad 70 \quad 75 \quad 80 \quad 85 \quad 90 \quad 95 \quad 100
\]

\[
\text{A$_260$ (a.u.)} \quad 0 \quad 0.5 \quad 1.0 \quad 1.5 \quad 2.0 \quad 2.5 \quad 3.0 \quad 3.5 \quad 4.0 \quad 4.5 \quad 5.0
\]

\[
\text{t$_R$ (min)} \quad 0 \quad 2 \quad 4 \quad 6 \quad 8 \quad 10 \quad 12 \quad 14 \quad 16 \quad 18 \quad 20 \quad 22 \quad 24 \quad 26 \quad 28 \quad 30 \quad 32
\]

\[
\text{M$_w$/M$_n$ = 1.005}
\]

\[
\text{M$_w$/M$_n$ = 1.05}
\]
**MWD of Polystyrenes by SEC and TGIC**

**SEC:** 2 x PL mixed C, THF

**TGIC:** 1 x Nucleosil C18 (100 Å),
CH₂Cl₂/CH₃CN 57/43 (v/v)

Poisson distribution: \[ W_i = \frac{i^\nu e^{-\nu}}{(\nu + 1)(i - 1)!} \]

<table>
<thead>
<tr>
<th>Poly'n time</th>
<th>M_w/M_n (M_w) SEC</th>
<th>M_w/M_n (M_w) TGIC</th>
<th>Poisson</th>
</tr>
</thead>
<tbody>
<tr>
<td>238s</td>
<td>1.08 (4.3k)</td>
<td>1.06 (4.0k)</td>
<td>1.02</td>
</tr>
<tr>
<td>888s</td>
<td>1.04 (21.3k)</td>
<td>1.02 (21.0k)</td>
<td>1.003</td>
</tr>
<tr>
<td>1626s</td>
<td>1.05 (35.0k)</td>
<td>1.02 (34.4k)</td>
<td>1.002</td>
</tr>
<tr>
<td>2296s</td>
<td>1.05 (42.9k)</td>
<td>1.01 (43.4k)</td>
<td>1.002</td>
</tr>
<tr>
<td>3098s</td>
<td>1.05 (50.3k)</td>
<td>1.008 (50.2k)</td>
<td>1.002</td>
</tr>
<tr>
<td>4220s</td>
<td>1.05 (56.0k)</td>
<td>1.006 (55.2k)</td>
<td>1.002</td>
</tr>
<tr>
<td>14345s</td>
<td>1.05 (62.0k)</td>
<td>1.005 (62.0k)</td>
<td>1.002</td>
</tr>
</tbody>
</table>

**Branched PS by linking with divinyl benzene**

Styrene + DVB \[ \rightarrow \] Higher Branched Species

**SEC**

2 x PL mixed C (300 x 7.5 mm)
Eluent: THF at 0.8 mL/min

**TGIC**

Nucleosil C18 250 x 4.6 mm (500 Å)
Eluent: CH₂Cl₂/CH₃CN = 57/43 (v/v)
Flow rate: 0.5 mL/min

**K. Lee, Kumho Petrochemical Ltd.**
**Synthesis of Symmetric H-PBd**

\[
s-\text{BuLi} + \text{Benzene} \xrightarrow{\text{RT}} \text{Li}^\bullet \]

\[
\begin{align*}
\text{Cl} & \quad \text{Si} & \quad \text{Cl} \\
\text{CH}_3 & & \\
\text{Cl} & \quad \text{Si} & \quad \text{Cl} \\
\text{CH}_3 & & \\
\end{align*}
\]

\[
\text{Li}^\bullet \xrightarrow{\text{Titr}} \text{Li}^\bullet \]

\[
\begin{align*}
& \quad \text{Si} \\
& \quad \text{CH}_3 \\
\end{align*}
\]

\[
\text{s-BuLi} \quad \text{Butadiene} \\
\]

\[
\begin{align*}
(\text{CH}_3)_2\text{SiCl}_2 & \xrightarrow{\text{s-BuLi}} \\
\end{align*}
\]

**GPC**

\[M_n=98\text{K}, \ PDI=1.03\]

**TGIC**

- 99K
- 86K
- 74K
- 125K
Synthesis of Asymmetric H-PBd

Comparison of conventional GPC with TGIC

Sample: Asymmetric H-shaped Polybutadiene

GPC

TGIC

Column: PL mixed - B 2EA and PL Mixed D
Eluent: THF
Flow rate: 1 mL/min
Precision detector PD-2040, low angle light Scattering at 15°.

Column: Kromasil C18 150×4.6 mm (i.d.), 5 μm, 300 A
Eluent: 1,4-dioxane
Flow rate: 0.5 mL/min
Detector: Wyatt miniDAWN (LS), shodex RI-101 (RI)
Sample: Asymmetric H-shaped Polybutadiene

**GPC**

- Column: PL mixed - C 2EA, 300×7.5 mm l.d., 5μm
- Eluent: THF
- Flow rate: 0.8mL/min
- Wyatt TREOS (LS), Younglin UV, Shodex RI-101

**TGIC**

- Column: Kromasil C_{18} 150×4.6 mm (l.d.), 5 μm, 300 Å
- Eluent: 1,4-dioxane
- Flow rate: 0.5 mL/min
- Detector: Wyatt miniDAWN (LS), shodex RI-101 (RI)

Matrix-Assisted Laser Desorption/Ionization Time of Flight Mass Spectrometry (MALDI-TOF MS)

Schematic of MALDI-TOF MS

The MALDI process
The TOF mass spectrum is a recording of the detector signal as a function of time.
The time of flight for a molecule of mass m and charge z to travel this distance is proportional to \((m/z)^{1/2}\).
This relationship, \(t \sim (m/z)^{1/2}\), can be used to calculate the ions mass.
Through calculation of the ions mass, conversion of the TOF mass spectrum to a conventional mass spectrum of mass-to-charge axis can be achieved.

Advantages and Limitations of MALDI-TOF MS

- Baseline separation of low MW polymers (<10K)
- Great mass accuracy for low MW polymers allows determination of end groups
- Limited separation at higher MWs
- Underestimates polydispersity especially for samples with PDI>1.2 (sampling issues, detector saturation issues).
- SEC-MALDI-TOF MS is useful with higher PDI samples
**Determination of numbers of repeat units and end group masses**

The observed mass of a singly charged copolymer chain in MALDI-TOF-MS is described by the following equation:

\[
m_{\text{obs}} = m_A \cdot n_A + m_{\text{ion}} + m_{\text{end}1} + m_{\text{end}2}
\]

where \(m_{\text{obs}}\) is the observed mass of a peak in the MALDI-TOF spectrum, \(M_A\) is the mass of the repeating unit, \(n_A\) is the number of repeat units, \(m_{\text{ion}}\) is the mass of the adduct ion, and \(m_{\text{end}1}\) and \(m_{\text{end}2}\) are the masses of the end groups.

MALDI spectrum of PS with two different types of end groups, yielding two series of peaks differing by 104.1 in mass.

**TGIC is also very useful in characterizing end-functionalized polymers**

**OH end-functional PS**

- sec-Butyl Li + Styrene
- i-propanol
- Ethylene oxide

**SEC:** 2 x PL-mixed B

<table>
<thead>
<tr>
<th>Fraction</th>
<th>PS,PS-OH 10K</th>
<th>PS,PS-OH 100K</th>
<th>PS,PS-OH 500K</th>
</tr>
</thead>
<tbody>
<tr>
<td>Peak</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(A_{260}) (a.u.)</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>(V_m) (mL)</th>
<th>10</th>
<th>11</th>
<th>12</th>
<th>13</th>
<th>14</th>
<th>15</th>
<th>16</th>
</tr>
</thead>
<tbody>
<tr>
<td>PS,PS-OH 10K</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>PS,PS-OH 100K</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>PS,PS-OH 500K</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
**NP- vs. RP-TGIC: Separation by a single -OH end group**

**NP-TGIC**
- Column: Nucleosil bare silica
- Column size: 100 Å pore, 250 x 2.1 mm
- Eluent: i-octane/THF = 55/45 (v/v)

**RP-TGIC**
- Column: Nucleosil C18 bonded silica
- Column size: 100 Å pore, 250 x 2.1 mm
- Eluent: CH₂Cl₂/CH₃CN = 57/43 (v/v)

*Lee et al. J. Chromatogr. A 910 51 (2001)*

---

**LCCC separation of Rings from Linear precursors**

**Synthetic scheme of Ring PS**

- Possible byproducts

*J. Roovers, NRC-Canada*
LCCC separation of Rings from Linear precursors

**SEC**
- Column: 2 x PL mixed-C
- Eluent: THF
- Column temperature: 40 °C

**LCCC for linear PS**
- Column: Nucleosil C18AB
- Eluent: CH₂Cl₂/CH₃CN=57/43
- Column temperature: 42 °C

Fractionation results by SEC & MALDI-TOF MS

**SEC**
- Δn (a.u.)
- tₚ (min)
- As-received Ring PS
- Fractionated Ring PS

**MALDI-TOF MS**
- Intensity (a.u.)
- m/z
- R17H (Ring PS)
- R17P (PS precursor)
Before and After LCCC Fractionation

Before

After

DP = 38

Cho et al. Macromolecules 34 7570 (2001)

Fractionation of individual blocks of BCP

MW

PS block length

Composition

PI rich

PS rich

Low MW

High MW

RP LC

PS block

PI block

PS block length

NPLC
Polymer Conformational Analysis

- From the measured sizes (Rg and [η]), conformational parameters like chain stiffness and the ratio Rg/Rh can be calculated for polymer coils.
- How about stiffer polymer chains? Use α-helical rodlike homopolypeptides to test validity of universal calibration in SEC (work of Paul Russo, LSU).
- Can SEC/Multi-angle Light Scattering arbitrate between disparate estimates of stiffness from dozens of previous attempts by other methods (P. Russo)?

Strategy

Severe test of universal calibration:
compare rods & coils
Combine $M_s$ from SEC/MALLS with [$\eta$] values
from literature Mark-Houwink relations.

Polymers Used

$[\text{CH}_2\text{-CH}]_x$  Polystyrene (expanded random coil)
Solvent: THF = tetrahydrofuran

$[\text{NH-CHR-C}]_x$  Homopolypeptides ( semiflexible rods)
$R = (\text{CH}_2)_2\text{COCH}_2$  PBLG = poly(benzylglutamate)
Solvent: DMF=dimethylformamide
$R = (\text{CH}_2)_2\text{CO}(\text{CH}_2)\text{CH}_3$  PBLG = poly(stearylglutamate)
Solvent: THF = tetrahydrofuran
Mark-Houwink Relations

\[ [\eta] = 0.011 \cdot M_w^{0.725} \] for PS

\[ [\eta] = 1.26 \cdot 10^{-5} \cdot M_w^{1.29} \] for PSLG

\[ [\eta] = 1.58 \cdot 10^{-5} \cdot M_w^{1.35} \] for PBLG

Universal Calibration Works for These Rods and Coils
Persistence Length $a_p$ from $R_g$

$$R_g^2 = \frac{L a_p}{3} - a_p^2 + \frac{2 a_p^3}{L} \left[ 1 - a_p \left( 1 - e^{-L/a_p} \right) \right]$$

Persistence length is the projection of an infinitely long chain on a tangent line drawn from one end. $a_p = \infty$ for true rod.

Persistence Length of Helical Polypeptides is Very Large

What the biggest polymers in our sample would look like at this $a_p$
Conclusions

• Multi-Detector SEC provides an accurate and facile means for characterizing polymer solution properties, such as Mark-Houwink coefficients and chain stiffness, in thermodynamically good solvents.
• Measurements on branched polymers can detect branching and provide insight into the level of branching across the molecular weight distribution.
• However, multidetector SEC has limitations in band broadening, resolution, and due to its size-based separation mechanism.
• TGIC and MALDI-TOF MS are powerful newer tools that provide deeper insight into polymer structure, particularly for complex polymers.

Acknowledgments

Co-workers and collaborators:
Taihyun Chang (Postech), C. Jackson (DuPont), K. Terao (Osaka Univ.), Y. Nakamura (Kyoto Univ.), Nikos Hadjichristidis Athens) and many great students and postdocs over the years.

Paul Russo (LSU)

Support and funding:
PRINCIPLES AND APPLICATIONS OF CONTINUOUS ONLINE POLYMERIZATION MONITORING

Wayne Reed

Tulane Univ.
Principles and applications of Automatic Continuous Online Monitoring of Polymerization reactions (ACOMP)

Wayne F. Reed and Alina M. Alb
Physics Department and PolyRMC
Tulane University
New Orleans, Louisiana, USA

http://tulane.edu/sse/polyRMC/
TULANE CENTER FOR POLYMER REACTION MONITORING AND CHARACTERIZATION: PolyRMC

Polymer 'born characterized'

Polymers with desired properties ‘on-command’

Accelerate R&D of new materials

Advanced characterization

Monitoring and control

Fundamental and applied research

• new polymeric materials
• drug delivery, other medical applications
• nanotechnology,
• new high performance materials and coatings,
• materials for optical and electronic purposes, etc.

Focus on industrially relevant R&D and problem solving

Resins, Paints, Coatings

Multi-detector SEC analysis:
Multi-angle Light Scattering, Viscometer, RI, UV detectors

http://tulane.edu/sse/polyRMC/
Why monitor polymerization reactions?

• Fundamental studies of polymerization kinetics and mechanisms

• Optimization of reactions at bench and pilot plant levels

• Full scale, *feedback control* of industrial reactors; more efficient use of energy, natural resources, plant and labor; higher quality products.
Energy consumption in the US polymer industry

The polymer industry is a major consumer of non-renewable resources. It is an ideal target for efficiency gains to reduce overall energy consumption and dependence on foreign oil.

• The US chemical industry is the 2\textsuperscript{nd} largest industrial consumer of energy.

### Energy consumption in the polymer manufacturing sectors

<table>
<thead>
<tr>
<th>Sector</th>
<th>NAICS</th>
<th>TBtu*</th>
<th>Barrels of crude oil equiv.</th>
<th>$ of crude oil equivalent @$50/barrel</th>
</tr>
</thead>
<tbody>
<tr>
<td>Plastics and Resins</td>
<td>32521</td>
<td>1,821</td>
<td>314 million</td>
<td>$15.7 billion</td>
</tr>
<tr>
<td>Synthetic Rubber</td>
<td>32521</td>
<td>57</td>
<td>10 million</td>
<td>$0.5 billion</td>
</tr>
<tr>
<td>Non-cellulosic organic fibers</td>
<td>32522</td>
<td>63</td>
<td>11 million</td>
<td>$0.6 billion</td>
</tr>
<tr>
<td>Petrochemicals**</td>
<td>32511</td>
<td>889</td>
<td>153 million</td>
<td>$7.6 billion</td>
</tr>
<tr>
<td><strong>Total Polymer sector</strong></td>
<td>2,830</td>
<td>488 million</td>
<td></td>
<td>$24.4 billion</td>
</tr>
</tbody>
</table>
Important characteristics of polymer products

- Molecular weight distributions and averages
- Dimensions, static and hydrodynamic
- Intrinsic viscosity
- Branching/ cross-linking
- Aggregated/microgel fraction of polymer
- Charged polymer linear charge density
- Copolymer composition
- Stimuli responsiveness of polymers
Important processes during polymerization reactions

• Kinetics

• Conversion of monomers

• Evolution of molecular weight distribution

• Evolution of intrinsic viscosity

• Charged polymers

• Composition drift and distribution

• Unexpected problems; premature reaction termination, microgelation, exotherms

• Heterogeneous phase changes; e.g. partitioning

• Onset and evolution of stimuli responsiveness of polymers
**Types of polymerization reactions**

**Chain growth polymerization**
- free radical
- controlled radical
- anionic, cationic, etc.
  e.g. vinyl monomers, acrylates, acrylamides, styrene

<table>
<thead>
<tr>
<th>Step-growth polymerization</th>
<th>Chain-growth polymerization</th>
</tr>
</thead>
<tbody>
<tr>
<td>Growth throughout matrix</td>
<td>Growth by addition of monomer only at one end of chain</td>
</tr>
<tr>
<td>Rapid loss of monomer early in the reaction</td>
<td>Some monomer remains even at long reaction times</td>
</tr>
<tr>
<td>Same mechanism throughout</td>
<td>Different mechanisms operate at different stages of reaction</td>
</tr>
<tr>
<td>Average molecular weight increases slowly at low conversion and high conversion is required to obtain high chain length</td>
<td>Molar mass of backbone chain increases rapidly at early stage and remains ~ the same throughout the polymerization</td>
</tr>
<tr>
<td>Ends remain active (no termination)</td>
<td>Chains not active after termination</td>
</tr>
<tr>
<td>No initiator necessary</td>
<td>Initiator required</td>
</tr>
</tbody>
</table>

**Step growth polymerization**
  e.g. polyesters, polyurethane, polysulfides, biopolymers (peptide bond)

**Post polymerization modification**; hydrolysis, PEGylation, quaternization, sulfonation, carboxylation, etc.
In free radical polymerization individual chains are initiated, propagate and terminate on the order of milliseconds, whereas the reaction that converts all monomer to polymer can last minutes or hours.
**Initiation**

a) Radical decomposition  
\[ I_2 \rightarrow 2I^* \]

b) Diffusion controlled production of first monomer radical  
\[ I^* + m \rightarrow R_1 \]

**Propagation**

\[ R_n + m \rightarrow R_{n+1} \]

**Termination**

\[ R_m + R_n \rightarrow P_m + P_n \] (disproportionation)

\[ R_m + R_n \rightarrow P_{m+n} \] (recombination)

*Individual polymer chains are formed by radical initiation, propagation, and termination, usually within milliseconds, whereas the entire reaction may require hours.*
A living type chain growth; *controlled free radical polymerization* (CRP)

Most radicals are thermoreversibly ‘capped’ and do not propagate (dormant). So actively propagating radical population is low and there is very little termination. When all monomer is used up, more monomer can be added later and the reaction will then resume, hence ‘living’

CRP includes

- Atom Transfer Radical Polymerization (ATRP)
- Reversible Addition Fragmentation Chain Transfer (RAFT)
- Nitroxide Mediate Polymerization (NMP)
Step growth polymerization reactions

There are two (or more) monomer units A, B, that can add to each other when in chains of arbitrary length


This leads to second order reaction kinetics and a continuously evolving mass distribution.
Homogeneous vs. heterogeneous phase polymerization

**Homogeneous phase** - with solvent - low viscosity and less exothermicity

- **in bulk** - very high viscosity with maximum use of reactor time since there is no dilution.

**Heterogeneous phase;**

e.g. emulsion polymerization - low viscosity and high molecular weight polymers, ease of handling, latex particles often used as product, water used instead of organic solvents

Other heterogeneous phase reactions include inverse emulsion polymerization, suspension, fluidized bed.
Batch, semi-batch and continuous reactors

**Batch reactor** - offers very little control over the reaction

- Reactants added at $t = 0$
- Volume $\sim$ constant during reaction

**Semi-batch reactor** - offers more control over MWD, kinetics, copolymer composition, etc.

- Some reactants added at $t = 0$, others flow in during reaction
- Volume increases during reaction

**Continuous reactor** - operates at a steady-state, continuously produces polymer

- Reaction at steady-state
- Volume $\sim$ constant
- Recovery of monomer, volatiles
- Reactant inflows
- Steady product stream output
Polymer architectures

Many types of architectures can be produced

\[ R_G \propto M^{1/3} - M^{1/2} \]

(a) Branched

(b) Star

(c) Comb

(d) Dendrimer
Types of copolymers

**Alternating copolymers**


**Random copolymers**


*(free radical polymerization)*

**Gradient copolymers** - composition changes along chain


*(living copolymerization)*

**Diblock copolymers**

Let us now look at:

• Methods for measuring polymer characteristics

• Methods to measure polymer characteristics during reactions

• Assessing reaction kinetics

• Applications
Polymer characteristics. Molecular weight

In linear polymers the individual polymer chains rarely have the exact same degree of polymerization and mass, and there is always a distribution around an average value.

The molecular weight distribution (MWD) relates the number of moles of each polymer species and the molar mass of that species.

** Measuring molecular weight

Different techniques measures different averages of MWD.

E.g. osmometry measures number average molar mass $M_n$, multi-angle light scattering measures weight average molar mass $M_w$, viscometry measures $M_v$, sedimentation offers $M_z$.

- The most common technique for measuring MWD: *size exclusion chromatography* (SEC).
Size exclusion chromatography. Setup

Based on separation by size:
- large particles (1) elute first, small particles (2) enter the columns pore gels and elute later (more volume to traverse)

Polymer absolute molecular weight based on direct measurements or approximate values based on the relationship between hydrodynamic volume and molecular weight of known species. **MWD by light scattering** provides an absolute determination of MWD, no calibration required.
Polymer characteristics. MWD

** Averages of the molecular weight distribution (MWD)

\[ M_n = \frac{\sum C_i}{\sum \frac{C_i}{M_i}} \]

\[ M_w = \frac{\sum M_i C_i}{\sum C_i} \]

\[ M_z = \frac{\sum M_i^2 C_i}{\sum M_i C_i} \]

\[ M_i = i \times m, \text{ } m = \text{monomer mass, also } C_i = N_i M_i, N_i = \# \text{ of polymers of mass } M_i \]
**Hydrodynamic radius \( R_H \) and radius of gyration \( R_G \)**

\[
R_G = \frac{\int \rho r^2 \, dV}{M}, \quad (R_G = \langle S^2 \rangle^{1/2})
\]

\[
R_H = \frac{k_B T}{6\pi \eta D}
\]

\begin{align*}
\{ & k_B = \text{Boltzmann's constant} \\
& T = \text{temp. in K} \\
& \eta = \text{solution viscosity} \\
& D = \text{self-diffusion coefficient (cm}^2/\text{s})
\end{align*}

\( R_H \) and \( R_G \) of a random coil polymer

(measured from polymer center of mass)

\[
R_G = 1.35R_H = \frac{\langle h^2 \rangle^{1/2}}{\sqrt{6}}
\]

Hollow sphere of radius \( R \):

\[
R = R_H = R_G
\]

Solid sphere of radius \( R \):

\[
R = R_H = \sqrt{\frac{5}{3}} R_G
\]
Measuring polymer characteristics

- Light scattering
- Viscosity
- Size exclusion chromatography (SEC)
- Combined measurements

Measuring monomer characteristics to determine conversion during reactions

- Spectroscopic identification of monomer concentrations; UV/visible/ Near Infra-Red (NIR), mid-IR, Raman scattering
- Refractive index identification of monomer concentrations. dn/dc of monomer vs. dn/dc of polymer in a given solvent
- Conductivity, for monitoring conversion of charged monomers
**Light Scattering Lexicon**

*Static Light Scattering* - single or multiple angle (*MALS*) measures total intensity of light scattered and can yield *molecular weight, virial coefficients, and radius of gyration.*

Depending on the type of data collection and analysis MALS can include Rayleigh, Rayleigh-Debye, Zimm, and Mie Scattering.

*Dynamic Light Scattering (DLS)* - autocorrelates scattered intensity fluctuations, usually to determine polymer and colloid diffusion coefficients, from which equivalent *hydrodynamic diameters* can be determined.

(Diffusing Wave Spectroscopy uses DLS for *concentrated* solutions)

*Electrophoretic Light Scattering* - Can make use of Doppler shifts and other features of light scattering from particles in directed motion under electric fields to obtain *electrophoretic mobility and zeta-potential.*
** Measuring polymer characteristics

** Static and Dynamic Light Scattering

• Static light scattering (e.g. ‘MALS’) measures the average total scattered intensity at any given scattering angle. It typically yields \( M_w \), \( A_2 \), and \( R_g \).

• Dynamic Light Scattering (DLS) autocorrelates the fluctuations in scattered intensity due to polymer diffusion. It typically measures polymer diffusion constants, which are then related to hydrodynamic size via the Stokes-Einstein equation.
Measuring polymer characteristics

** Typical light scattering experimental set-up for MALS and DLS

\[
q = \frac{4\pi n}{\lambda_t} \sin \left( \frac{\theta}{2} \right)
\]

\[
K_i = \frac{2\pi n}{\lambda_i}
\]

\[
K_f = \frac{2\pi n}{\lambda_f}
\]
**Rayleigh-Debye-Zimm Scattering** (for vertically polarized incident light)

- The size of such scatterers is typically >10nm
- Light is scattered preferentially in the forward direction
- Interactions are taken account of with the second virial coefficient $A_2$.

For $q < S^2 >^{1/2} < 1$, Zimm’s representation is used:

$$\frac{Kc}{R(c, q)} = \frac{1}{M_w} \left( 1 + \frac{q^2 < S^2 >_z}{3} \right) + 2A_2c$$
Measuring polymer characteristics. Zimm plot

For \( q<S^2>^{1/2} < 1 \), Zimm’s approximation

\[
\frac{Kc}{R(c, q)} = \frac{1}{M_w} \left( 1 + \frac{q^2 <S^2>_z}{3} \right) + 2A_2c
\]

allows \( M_w \), 2\text{nd} order virial coefficient, \( A_2 \) and radius of gyration, \( <S^2>_z \) to be determined:

![Graph showing Zimm plot with intercept and slope annotations](image-url)
**Continuous Zimm**

- $M_w$, $A_2$, and $<S^2>_z$ are determined based on Zimm equation (1 >> $2A_2cM_w$ >> $3A_3c^2M_w$ and $q^2<S^2> < 1$):

$$\frac{Kc}{I_R(c, q)} = \frac{1}{M_w} \left( 1 + \frac{q^2 < S^2 >_z}{3} \right) + 2A_2c$$

E.g.: poly(vinylbenzyl sulfonic acid)

\[
\begin{align*}
&\text{Solvent: 0.1M NaNO}_3 \\
&M_w = 2.2 \times 10^6 \text{g/mole} \\
&A_2 = 1.7 \times 10^{-3} \text{cm}^3 \text{mole/g}^2 \\
&A_3 = 0.09 \text{cm}^6 \text{mole/g}^3
\end{align*}
\]
Measuring polymer characteristics. Dimensions

R_g from SEC measurements: Effect of ionic strength for a charged polymer (VB)

R_h from DLS measurements: Effect of temperature on the particle size for a stimuli-sensitive copolymer
Polymer characteristics. Viscosity

The presence of particles in the solvent creates drag (frictional) forces, which is the origin of viscosity.

Total solution viscosity $\eta$:

$$\eta = \eta_s \left( 1 + [\eta]c + \kappa_H [\eta]^2 c^2 \right)$$

, $\kappa_H \sim 0.4$ for ideal coils

(Units: 1 Poise = 1 g/(cm-s))

Intrinsic viscosity of the polymer, $[\eta]$:

$$[\eta] = \lim_{c \to 0} \frac{\eta - \eta_{solvent}}{\eta_{solvent} c}$$

(Units: cm$^3$/g)

Flory relationship between $[\eta]$ and $R_G$ for ideal coils:

$$[\eta] = \frac{\Phi_v}{M} \left(\sqrt{6} R_G\right)^3$$

, $\Phi_v = 2.56 \times 10^{23}$
Measuring viscosity

Measurement principle for capillary viscometers: Poisseuille’s law for viscous flow

**Poisueille’s equation:**

\[ \eta = \frac{\pi R^4 \Delta P}{8LQ} \]

Average shear rate:

\[ \dot{\gamma}_{ave} = \frac{8Q}{3\pi R^3} \]

*Single capillary viscometer* measures pressure drop \( \Delta P \) across a capillary of radius \( R \) of length \( L \) with fluid flowing at rate \( Q \)

Differential Pressure Transducer (e.g. Validyne Corp.)

1 Poise = 1 g/(cm-s)
Polymer characteristics. Reduced viscosity

\[
\eta_r \equiv \frac{\eta - \eta_0}{\eta_0 c} = [\eta] + k[\eta]^2 c + O(c^2)
\]

\[
[\eta] = \lim_{c \to 0} \eta_{\text{red}}
\]

Solvent: 0.1M NaNO₃

\[[\eta] = 403 \text{ cm}^3/\text{g}\]

(poly(vinylbenzyl sulfonic acid))
Polymer characteristics. Intrinsic viscosity

** Intrinsic viscosity, $[\eta]$ relationship to $M$

$[\eta]$ measures the hydrodynamic volume per mass for a polymer:

$$[\eta] = \frac{V_H N_A}{M}$$

This leads to a Mark-Houwink relationship:

$$[\eta] = K M^\beta$$

For non-free draining coils and other structures:

$$V_H \propto R_G^3$$

$R_G$ vs. $M$ scaling offers information on the structure ($R_G \otimes R_H$):

$$R_G = aM^\alpha \rightarrow \beta = 3\alpha - 1$$

<table>
<thead>
<tr>
<th>Structure</th>
<th>$\alpha$</th>
<th>$\beta$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sphere</td>
<td>1/3</td>
<td>0</td>
</tr>
<tr>
<td>Ideal Random Coil</td>
<td>1/2</td>
<td>1/2</td>
</tr>
<tr>
<td>Random Coil with excluded volume</td>
<td>3/5</td>
<td>4/5</td>
</tr>
<tr>
<td>Rod</td>
<td>1</td>
<td>2</td>
</tr>
</tbody>
</table>
Measuring polymer characteristics: SEC

Raw SEC chromatogram: Each detector responds to a different polymer characteristic.

\[ \eta \propto M \]

\[ \text{RI} \propto C \]

\[ \text{Viscometer} \propto C \times [\eta] \]
E.g. Complete multi-detector SEC analysis of a polyacrylamide

\[ [\eta] = 0.028M^{0.69} \]

\[ R_g = 0.16M^{0.56} \]

\[ M_n = 83,000 \text{ g/Mole} \]
\[ M_w = 384,000 \text{ g/Mole} \]
\[ M_z = 1,030,000 \text{ g/Mole} \]

\[ <S^2>_{w}^{1/2} = 306 \text{ Ang.} \]
\[ <S^2>_{z} = 386 \]

\[ [\eta]_{w} = 177 \text{ cm}^3/\text{g} \]

PolyAcrylamide w/aqueous eluent
From SEC viscosity measurements: Mark - Houwink coefficients

E.g. $[\eta]$ vs. $M$ for copolymer samples in aqueous medium

$$[\eta] = KM^\beta$$
Polymer characteristics. Branching

Zimm-Stockmayer branching parameter:

\[ g = \frac{\langle S'^2 \rangle_{\text{branched}}}{\langle S'^2 \rangle_{\text{unbranched}}} < 1 \]

- g needs a model in order to be interpreted

* e.g. For star molecules with n branches:

\[ g = \frac{3n - 2}{n^2} \]

* e.g. For randomly branched polymers of n branches of functionality f:

\[ g = 3 \left( \frac{\pi}{2n(f - 1)(f - 2)} \right)^{1/2} - \frac{2(6 - f)}{n(f - 1)(f - 2)} \]

![Branching_Zimm_Stockmayer](image)
Polymer characteristics. Branching

- A related branching parameter is \( g' \), obtained from \([\eta]\):

\[
g' = \frac{[\eta]_{branched}}{[\eta]_{unbranched}} \quad , \quad g' = g^\varepsilon, \quad \varepsilon = 2 - \beta
\]

Contrasting elution behavior between a branched polymer and its linear analog
**Electrically charged polymers: *Polyelectrolytes***

Polyelectrolyte dimensions and electrostatic repulsion diminish with added salt; viscosity decreases, light scattering increases.
Measuring polyelectrolyte characteristics

E.g.: Sodium hyaluronate (HA). [NaCl] ramp at fixed polymer concentration

Effects of ionic strength on polyelectrolyte interactions and viscosity:

- light scattering increases as ionic strength shields the charges on the HA.
- viscosity drops as the shielding leads to a contraction in the coil size.

Sorci, Reed, Macromolecules 2002
**Concentration regimes** in polymer solutions

The overlap concentration $c^*$, is often approximated by $c^* \sim 1/\eta$
Concentration regimes in polymer solutions. High throughput screening of polymerization reactions

Signatures from polymerizing solutions in different conditions, with fits to theoretical forms.

Acrylamide polymerization

Drenski, Mignard, Alb, Reed, *J. Comb. Chem* 2004
Measuring polymer characteristics during reaction:

Automatic Continuous Online Monitoring of Polymerization reactions: ACOMP

ACOMP is normally a non-chromatographic method, although in certain applications its performance can be enhanced by addition of SEC
**Principle of ACOMP:**

- Continuously extract and dilute viscous reactor liquid producing a stream through the detectors so dilute that detector signals are dominated by the properties of single polymers, not their interactions.

ACOMP ‘front-end’:
*Extraction/dilution/conditioning*

- Reactor
- Solvent

ACOMP ‘back-end’:
*Detector train*

- Light scattering
- Viscometer
- Refractive index detector
- UV detector

Optional automatic SEC

- Detector train
- Auto-Injector/pump
Some complete ACOMP systems

A typical, custom built ACOMP at PolyRMC

Commercial ACOMP unit previously produced by Varian Inc. under license from Tulane University
ACOMP: Rapidly expanding applications

- Free radical homo- and copolymerization
- Step growth
- Controlled radical (co)polymerization (ATRP, NMP, RAFT) and other living types (ROMP)
- Batch, semi-batch, continuous, pressurized reactors
- Solvent, bulk (viscosity up to $10^6$ cP)
- Heterogeneous phase polymerization; free and controlled radical routes
- Grafting and cross-linking reactions, multiblock syntheses
- Predictive and feedback control of reactions
- Monitoring the evolution of stimuli responsiveness in tailored polymers
- Post-polymer modifications; e.g. hydrolysis, quaternization
- On the horizon: Extension to slurries, fluidized bed
Kinetics of polymerization and the Quasi-Steady State Approximation (QSSA), followed with ACOMP

Initiator decomposition: \([I_2] = [I_2]_0 \exp (-k_d t)\)

Radical concentration, \([R]\) \[\frac{d[R]}{dt} = 2Fk_d [I_2] - k_t [R]^2\]

\(F = \) fraction of radicals yielding propagating chains, ‘radical efficiency’

-For \([I_2]\) decomposition rate limited initiation:

\[\frac{d[m]}{dt} = -2Fk_d [I_2] - k_p[R][m] \approx -k_p [R] [m]\]  \(\) (long chain approximation)

The quasi-steady state approximation (QSSA): \(\frac{d[R]}{dt} = 0\)

\[\Rightarrow \quad [R] = \sqrt{\frac{2Fk_d[I_2]}{k_t}} \quad [m] = [m]_0 e^{-\kappa t}, \quad m(t) = m_0 \exp \left[\frac{2A k_p}{k_d} \left(e^{-k_d t/2} - 1\right)\right]\]

\(\kappa = k_p [R]\)

(expo-exponential monomer consumption)

If \([I_2](t) \approx [I_2]_0\) then

Kinetic chain length:

\[\nu = \frac{k_p [m]}{k_t [R]}\]

\[M_w(f) \cong M_{w0} \left(1 - \frac{f}{2}\right)\]

i.e. \(M_w\) decreases during the reactions
Typical ACOMP raw data

E.g. RAFT copolymerization of butyl acrylate (BA) and methyl methacrylate (MMA)
Comonomer concentrations

From continuously collected RI and UV signals

\[ V_{RI} = \left( \frac{dn}{dc_A} c_A + \frac{dn}{dc_B} c_B + \frac{dn}{dc_P} c_P \right) / CF \]

\[ V_{UV} = (\varepsilon_A c_A + \varepsilon_B c_B + \varepsilon_P c_P) l \]

Or, alternately, for charged monomers, from monitoring conductivity in aqueous medium

Comonomer concentrations
Monomer conversion

E.g. free radical polymerization of acrylamide. Conversion curves with first-order function fits

\[
V_{RI} = \left( \frac{dn}{dc_{mon}} c_{mon} + \frac{dn}{dc_{pol}} c_{pol} \right) / CF
\]

\[
V_{UV} = \left( \epsilon_{mon} c_{mon} + \epsilon_{pol} c_{pol} \right) l
\]

\[
c_{total} = c_{mon} + c_{pol}
\]

\[
[m] = [m]_0 e^{-\kappa t}
\]

\[
f = 1 - \frac{c_{mon}}{c_{total}} = 1 - \exp(\kappa t)
\]
Molecular weight in free radical polymerization

E.g. free radical polymerization of acrylamide. Conversion curves with first-order function fits

Kinetic chain length:

\[ \nu = \frac{k_p [m]}{k_t [R]} , \quad [m] = [m]_0 e^{-\kappa t} \]

Large circles are GPC data from aliquots withdrawn during the reaction.

\[ M_w(f) \approx M_{w0}(1 - \frac{f}{2}) \]

i.e. \( M_w \) decreases during the reactions

\[ T=60C \]

[Persulfate]/[AAm] (M/M)

Top to bottom: 0.006, 0.025, 0.1
Molecular weight in CRP vs. free radical polymerization
Radical transfer reactions

The radical is transferred to a monomer, another chain, solvent, or other molecule.

Generally, the effect of chain transfer is to shorten the chains.

Transfer of a radical to agent, S:

\[
R + S \xrightarrow{k_3} S^* + P
\]

\(S^*\) bears the transferred radical, \(P\) is the dead polymer chain left. \(S^*\) can initiate another propagating chain

\[
S^* + m \xrightarrow{k_4} R + S
\]

No loss of propagating free radical but rate of producing chains increases, since

\[
\frac{d[P]}{dt} = Yk_t[R]^2 + k_3[S][R]
\]

\((Y = 1\) for recombination dominates, and 2 for disproportionation).
Chain transfer in free radical polymerization

E.g. Free radical polymerization of acrylamide. Effect of alcohols used as chain transfer agents on the polymer molecular weight.

Increasing ethanol concentration:

\[ M_{n,\text{inst}} = \frac{k_p \langle m \rangle M_{\text{Aam}}}{Y k_1 [R] + k_{tr} [S]} \]
Chain transfer in emulsion polymerization

E.g. Free radical polymerization of methyl methacrylate (MMA). The effect of the transfer agent on the polymer molecular mass and reduced viscosity

\[
\begin{align*}
\text{MMA, 15\% solid content} \\
n\text{-dodecyl mercaptan added}
\end{align*}
\]
Chain transfer in living polymerization

E.g. Nitroxide mediated polymerization. Deviations in $M_w$ due to chain transfer
(NMP of butyl acrylate in butyl acetate with MONAMS/SG1)

\[ P_n - X \xrightarrow{k_{act}} P_n^\cdot + X \]

Monitoring the ‘livingness’ of controlled radical polymerization

Monitoring the transition from ‘living’-like behavior in the ‘controlled radical polymerization’ regime, to the non-controlled radical polymerization regime:

E.g. Polymerization of butyl acrylate (BA)

[BA]=2.08M, [AIBN]=2.42mM
T=70°C

Alb, Serelis, Reed, Macromolecules, 41, 2008
ACOMP and copolymerization: the copolymer is ‘born characterized’

Model independent:

- Average Bivariate Mass/Composition distribution
- Composition Drift
- Average viscosity distribution
- Reaction kinetics
- ‘Events’; e.g. microgelation due to composition drift

Model dependent:

- Reactivity ratios
- Average sequence length distributions
Copolymerization: Discrimination of comonomers of similar spectral characteristics

Random copolymer AABABAAABBAB , (40/60 BA/MMA)

Average extinction coefficient basis spectra for MMA, BA and the copolymer); computed comonomer concentration in detector train.

Average composition drift during MMA/BA free radical copolymerization reactions

(Alb, Enohnyaket, Head, Drenski, Reed, Reed, Macromolecules, 39, 2006)
Copolyelectrolytes

Unified understanding of copolyelectrolyte properties via monitoring of their synthesis and subsequent endproduct characterization

Large composition drift leads to bimodality


'Trivariate distribution': Mass, Composition, linear charge density ($\xi$)
- add conductivity monitoring

Counterion condensation: Composition dist. $\neq$ x dist.
Diblock copolymers by RAFT

E.g. RAFT copolymerization of MMA/BA

Light scattering and UV data agree well with theoretical predictions for a true diblock copolymer

\[ [\text{BA}]=0.08\text{M}; [\text{MMA}]=2.9\text{M}, T=70^\circ\text{C} \]

Alb, Reed, unpublished results
CRP ‘gradient’ copolymers by NMP

On average, each chain bears the composition profile corresponding to the composition drift.

ABBAABBABAAABBAAAAABAAAAA

**Styrene composition profile:**

\[
F_{\text{inst,Sty}} = \frac{d[\text{Sty}]}{d([\text{Sty}]+[\text{ba}])}
\]

Composition profile by ACOMP:

Mignard, LeBlanc, Bertin, Guerret, Reed, *Macromol.*, 37, 2004
Simultaneous continuous non-chromatographic and discrete chromatographic detection

Free radical polymerization of butyl acrylate with an initiator boost

ACOMP signals change as the reaction proceeds.

Automatic GPC data from several detectors follow the reaction progress.

Emulsion polymerization

- first simultaneous online monitoring of both polymer and particle properties

Raw data and analysis for free radical polymerization of MMA in emulsion at 70°C.

Left: polymer $M_w$ and $\eta_r$ vs. conversion; Right: particle size distribution and specific surface area

A. M Alb, W. F Reed, Macromolecules, 41, 2008
Different trends for $M_w$ as BA is added in one shot or continuously for NMP and for free radical polymerization reactions.
Predictive control through programmable reagent flow to the reactor (semi-batch)

- Free radical (co)polymerization

Detailed, quantitative reaction kinetics yielded by ACOMP allow for predictive control

• Control of conversion kinetics
• Control of molecular weight distribution
• Control of copolymer composition
Predictive control for free radical polymerization

Approach to quasi-steady state through monomer feed to the reactor

\[
[m](t) = [m]_0 \exp \left\{ - \left( \frac{\rho + \alpha V_0}{V_0} \right) t \right\} + \left( \frac{[m]' \rho}{\rho + \alpha V_0} \right) \left( 1 - \exp \left\{ - \left( \frac{\rho + \alpha V_0}{V_0} \right) t \right\} \right)
\]

\[
\frac{[m]' \rho}{\rho + \alpha V_0} < [m]_0
\]

‘Starved regime’

\[
\frac{[m]' \rho}{\rho + \alpha V_0} > [m]_0
\]

‘Flooded regime’

\[
\frac{[m]' \rho}{\rho + \alpha V_0} = [m]_0
\]

‘Isoreactive regime’

Approach Index, \( A \)

\[
A = \frac{(dm/dt)_{\text{reaction}}}{(dm/dt)_{\text{flow}}}
\]
Early results on predictive control of polymer $M_w$

*Use detailed knowledge of kinetics from ACOMP to control evolution of $M_w$*

*E.g.* Acrylamide free radical polymerization

In batch mode, $M_w$ decreases during conversion.
In semi-batch mode, $M_w$ is programmed
  - for constant $M_w$
  - for increasing $M_w$

---

Kreft, Reed, ?
Predictive control for free radical copolymerization

Control of composition drift for high drift comonomers VB and Am

High drift monomer pair

Styrene sulfonate, VB

\[ \text{SO}_3^- \]

Acrylamide, Am

\[ \text{H}_2\text{N-C}^-\text{CH}═\text{CH}_2 \]

Reactivity ratios

\[ r_{\text{VB}} = 2.14 \]

\[ r_{\text{Am}} = 0.18 \]

15% starting VB, 60c, \([V50]=0.002\text{M}\), and \([\text{Am}]+[\text{VB}]=0.360\text{M}\)
Predictive control for free radical polymerization in emulsion

E.g. Semi-batch free radical polymerization of methyl methacrylate in emulsion

The effect of the rate of monomer addition on reaction kinetics

(MMA polymerization at 70°C)
Predictive control for free radical polymerization in emulsion

The effect of the rate of monomer addition on $M_w$
Monitoring postpolymerization modifications

E.g. Postpolymerization production of a polyelectrolyte: NaOH hydrolysis of acrylamide to carboxylate.

Many modifications are possible: e.g.
- Hydrolysis
- Amination
- Grafting, cross-linking
- Huisgen cycloaddition, ‘Click reactions’

2nd generation ACOMP for determination of LCST

Measuring the onset of lower critical solution temperature with second generation ACOMP during copolymerization of NIPAM with styrene sulfonate.
Conclusions

Light scattering and other physical approaches are one way physicists contribute to interdisciplinary polymer science.

Automated, online, multi-detector methods provide massive data streams yielding rich, comprehensive characterization of equilibrium properties and non-equilibrium processes in polymer solutions for both fundamental and applied goals.