Analysis of Fragile Ultra-High Molar Mass Polymers by Hydrodynamic Chromatography

Amandaa K. Brewer

October 22, 2015
Particle size and shape of polymers and colloids with a molar mass $> 10^6 \text{ g/mol}$.

**Particle size and shape play a role in:**
- Environmental and quality control concerns
- Development of new materials
- Control of material processing
- End-use properties
Ultra-High Molar Mass Polymers and Colloids

Particle size and shape of polymers and colloids with a molar mass > 10^6 g/mol.

Particle size and shape play a role in:
- Environmental and quality control concerns
- Development of new materials
- Control of material processing
- End-use properties

Methodology and Limitations:
- Sieving
- Sedimentation
- Microscopy
- Laser Diffractions
- Cost
- Speed
- Complexity
- Accuracy
- Resolution

String-of-pearl Colloidal Silica

SNOWTEX® ST-PS-M
- Nissan Chemical Industries

SiO₂ in water

Particle Size (via TEM)
- “Pearl” Diameter: 18-25 nm
- “String” Length: 80-150 nm

Particle Shape (via TEM)
- String-of-pearl colloidal silica

Morphology applications
- Protein complexes
- Vesicles
- Bacteria
- Synthetic polymers
- Biopolymers

End-use Properties
- Fracture toughness
- Polish Retention
Multi-Detector Size Exclusion Chromatography

Columns
Multi-Detector Size Exclusion Chromatography

- Multi-Angle Light Scattering (MALS)
- Quasi-Elastic Light Scattering (QELS)

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Multi-Detector Size Exclusion Chromatography

Multi-Angle Light Scattering (MALS)

Quasi-Elastic Light Scattering (QELS)

Differential Refractometry (DRI)

Differential Viscometry (VISC)

Columns

MALS

QELS

VISC + MALS + DRI

DRI + MALS

$R_G$

$R_H$

$R_\eta$

$M$
## Multi-Detector Size Exclusion Chromatography (SEC/RI/MALS)

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<tr>
<th>Method</th>
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# Multi-Detector Size Exclusion Chromatography

**SEC/RI/MALS**

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![Graph](image)

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Multi-Detector Size Exclusion Chromatography

**SEC Limitations**

- Possible degradation due to flow rate limitations, leading to a skewed molar mass distribution.

- Extremely long analysis times for ultra high molar mass polymers (> 2 hrs per injection.)
Multi-Detector Size Exclusion Chromatography

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**Possible Solutions**

- A gentler technique such as hydrodynamic chromatography or field-flow fractionation
- Less degradation of samples
- Faster analysis times.
Hydrodynamic Chromatography

HDC/ RI / MALS/ QELS/ VISc

• A solution-based separation method
  • Open tube
  • Packed (Non-porous beads)
• Separation is due to parabolic (Poiseuille) flow profile in an open tube channel.

Hydrodynamic Chromatography

HDC/ RI / MALS/ QELS/ VISC

- Analytes are sampled in a size-dependent manner

Hydrodynamic Chromatography

HDC/ RI / MALS/ QELS/ VISC

- Analytes are sampled in a size-dependent manner
- Small particles sample region close to the walls, where the flow is stagnant
- Large particles remain nearer to center where the flow is faster

Hydrodynamic Chromatography

**Advantages of HDC**
- Low-cost (depending on detectors)
- Relatively Fast
- Characterize based on molar mass or particle size
- Ideal for particles/polymers with $M > 10^6$ g/mol

**Major Disadvantage of HDC**
- Non-absolute nature (calibrant-relative)
  - Solution: absolute detection methods
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Multi-Detector Hydrodynamic Chromatography

HDC/ RI / MALS/ QELS/ VI SC

\[ \text{RI} \propto c \]
\[ \text{MALS} \propto M \times c \]

Multi-Detector Hydrodynamic Chromatography

HDC/ RI / MALS/ QELS/ VISC

Detector response ($V$)

Retention volume (mL)

RI \propto c

MALS \propto M \times c

Polymeric Radii

**MALS $\rightarrow R_G$**

Root mean square distance of an array of atoms from their common center of mass

$$R_G = \left[ \left( \frac{1}{n+1} \sum_i (r_i - R_{cm})^2 \right) \right]^{1/2}$$

- $n =$ number of bond in polymer backbone
- $r_i =$ location of an individual atom or group of atoms
- $R_{cm} =$ the location of the center of mass
**Polymeric Radii**

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### QELS → $R_H$
Radius of an equivalent hard sphere that has the same translational diffusion coefficient ($D_T$) as a macromolecule.

$$R_H = \frac{k_B T}{6\pi \eta_s D_T}$$

- $k_B$ = Boltzman’s Constant
- $\eta_s$ = Viscosity of the solvent
- $D_T$ = Translational Diffusion Coefficient
Polymeric Radii

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**VISC → $R_\eta$**
Radius of a solid sphere that increases the fluid viscosity by the same amount as does the macromolecule or particle.

\[
R_\eta = \left( \frac{3[\eta]M}{10\pi N_A} \right)^{1/3}
\]

- $[\eta]$ = Intrinsic viscosity
- $M$ = Molar mass
- $N_A$ = Avogadro’s number
**Multi-Detector Hydrodynamic Chromatography**

**Dimensionless Ratio**

**Dimensionless Ratios**

**VISC/MALS:** \( R_{\eta,w}/R_{G,z} \)

Provides information about the structure or compactness

**MALS/QELS:** \( \rho \equiv R_{G,z}/R_{H,z} \)

Provides information about the shape
## Dimensionless Ratios

**VISC/MALS:** $R_{\eta,w}/R_{G,z}$  

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<td>1.67-3.66</td>
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<tr>
<td>2.0-3.5</td>
<td>Non-overlapping beads on a random coil</td>
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Strings-of-pearls with varying degrees of polymerization (2 to 5) plus a large number of unattached “pearls”.

Conclusions

Multi-detector HDC was successfully used to determine the size, shape, and structure/compactness of particles varying in molar mass, size, shape, and structure as a function of the elution profile.

HDC provides accurate and complete characterization of molar mass, size, shape, and structure for fragile particle assemblies where SEC fails, in a fraction of the time needed by methods such as TEM.
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- Department of Chemistry and Biochemistry Florida State University
- Striegel Research Group
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