Characterization of Ultralarge Polymers by Gel Permeation Chromatography: Challenges and Limitations

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Ultralarge versus ultrahigh molar mass key distinctions

- Ultralarge polymers defined as those having $R_g > \sim 150$ nm
- Extremely Ultralarge polymers defined as those having $R_g > 300$ nm
- Linear PS in THF $R_g$ of 300 nm corresponds to 24,000,000 g/mol (est.)
- Linear PS in THF of 15,000,000 g/mol* corresponds to $R_g$ of 230 nm
- Crosslinked PS nanoparticle having VSF of 2 and molecular weight of 24,000,000 g/mol has $R_g$ of $\sim 50$ nm

For linear chains….
Size, not molecular weight, governs the GPC separation
Synthetic polymers typically have broad size distributions
Finding ideal (or near ideal) GPC separation conditions is challenging for samples containing material having $R_g > 300$ nm

*Typically the highest MW PS standard available commercially
Key considerations for Ultralarge Polymers*

- Shear degradation and/or deformation
- Interchain association and/or aggregation
- Non-equilibrium transport between mobile phase and stationary phase
- Concentration polarization effect – lack of flow suppression in pores
- Hydrodynamically induced diffusion
- Stress-induced diffusion
- Multi-path effect
- Instrument limitations

Non-ideal GPC separation is manifested by late elution of ultralarge chains

A laser light scattering detector (e.g., MALLS or LALLS) is essential for detecting late elution

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Evaluation of GPC conditions with LS and narrow stds

Compare log M versus elution volume from light scattering (continuous points) to log M versus elution volume for narrow standards (discrete data points)

Ideal or near ideal GPC elution log M vs. elution volume plots are superimposable

Ultralarge polymer sample Late elution is clearly evident
Experimental

Sample preparation

• Solutions were prepared in mobile phase solvent (0.05 wt% NaN₃), and were filtered through a 0.45-μm nylon syringe filter prior to injection. Sample concentration was about 0.25C* to ensure that polymer chain entanglements were minimized.

Instruments

• Waters 2690 set at the optimum flow rate (0.2 – 1.0 ml/minute)
• Wyatt DAWN DSP MALLS + Wyatt Optilab rEX DRI detectors both operating at a wavelength of 632.8 nm at room temperature, or a Viscotek (Malvern) TDA 301 with LALLS and DRI detection.

Column set

• 2 Tosoh TSK-Gel GMPW. 7.5 mm i.d. x 300 mm, 17 μm particles at 25 °C
Defining a “standard” when none exist (1 of 2)

<table>
<thead>
<tr>
<th>MW (kg/mol)</th>
<th>R_g/ nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>MC 15</td>
<td>47.5</td>
</tr>
<tr>
<td>MC 400</td>
<td>146</td>
</tr>
<tr>
<td>MC 4000</td>
<td>277</td>
</tr>
</tbody>
</table>

Log $M_W$ versus elution volume plots are completely superimposable.
Defining a “standard” when none exist (2 of 2)

All samples have $R_g \sim 55$ nm and $MW \sim 300,000$ g/mol; compositions vary slightly.

Fractionation appears to be ideal (or near ideal). No late elution observed.

The 4000 series samples were chosen to define optimal separation conditions.
Evidence of non-ideal elution of ultralarge chains

Flowrate is 1.0 ml/minute

<table>
<thead>
<tr>
<th></th>
<th>$M_W$ (kg/mol)</th>
<th>$R_g$ (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>HPMC 2 4000</td>
<td>337</td>
<td>58.4</td>
</tr>
<tr>
<td>HPMC 2 220000</td>
<td>996</td>
<td>112</td>
</tr>
</tbody>
</table>

Red trace

Blue trace

Dow
Flow rate dependence of “standard” elution profiles

Molar Mass vs. volume

- MC- 4000
- MC 4000 FR 0.5
- MC 4000 FR0.2

Baseline shifts, S/N variation, flow rate accuracy produce slight differences in the chromatograms.
Flow rate dependence of ultralarge HPMC elution

Bulk $M_W$ measured by at each flow rate was the same – no shear degradation
Elution profile and log M versus elution volume is flow rate dependent
Ideal or near-ideal GPC elution observed for HPMC-2 220,000 at 0.2 ml/minute
Pay Attention to Deborah (Number)

\[ D_e = \tau \dot{\varepsilon} = \frac{C \eta R_g^3}{kT} k_1 \left( \frac{Q}{\pi r^2 d_p} \right) \]

De < 0.5: Random coil
De > 0.5: Coil to stretch transition

\[ R_{g,c} \text{ when } D_e \sim 0.5 \]

Fig. 5. Enlarged SEC region of the calibration curves for PS standards at different flow rates. Two 150 x 4.6 mm I.D. Acquity UPLC C18 columns connected in series. On the y-axes the molecular weights corresponding to the conditions where De ~ 0.5 are indicated for different flow rates (see text for more explanation).


Pay Attention to Deborah (Number) and critical $R_g$

$$D_e = \tau\varepsilon = \frac{C \eta R_g^3}{kT} k_1 \left(\frac{Q}{\pi r^2 d_p}\right)$$

$R_{g,c}$ is the radius of gyration where $D_e = 0.5$ in GPC conditions used for cellulose ethers

<table>
<thead>
<tr>
<th>Flow rate (mL/min)</th>
<th>$R_{g,c}$ (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.0</td>
<td>169</td>
</tr>
<tr>
<td>0.5</td>
<td>213</td>
</tr>
<tr>
<td>0.2</td>
<td>290</td>
</tr>
</tbody>
</table>
## Molecular weight averages from GPC-MALLS

<table>
<thead>
<tr>
<th>Flow Rate mL/min</th>
<th>$M_N$ (kg/mol)</th>
<th>$M_W$ (kg/mol)</th>
<th>$M_W/M_N$</th>
<th>Wt% $&lt; R_{g,c}$</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>HPMC 3 100,000</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1.0</td>
<td>220</td>
<td>837</td>
<td>3.80</td>
<td>95</td>
</tr>
<tr>
<td>0.5</td>
<td>165</td>
<td>835</td>
<td>5.05</td>
<td>~100</td>
</tr>
<tr>
<td><strong>HPMC 3 250,000</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1.0</td>
<td>360</td>
<td>1,140</td>
<td>3.17</td>
<td>88</td>
</tr>
<tr>
<td>0.5</td>
<td>220</td>
<td>1,120</td>
<td>5.10</td>
<td>97</td>
</tr>
<tr>
<td><strong>0.2</strong></td>
<td>136</td>
<td>1,060</td>
<td>7.83</td>
<td>~100</td>
</tr>
<tr>
<td><strong>HPMC 2 220,000</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1.0</td>
<td>292</td>
<td>1,060</td>
<td>3.64</td>
<td>90</td>
</tr>
<tr>
<td>0.5</td>
<td>181</td>
<td>1,050</td>
<td>5.82</td>
<td>97</td>
</tr>
<tr>
<td><strong>0.2</strong></td>
<td>145</td>
<td>996</td>
<td>6.88</td>
<td>~100</td>
</tr>
</tbody>
</table>

Conditions highlighted in green yielded log M vs. volume plots that were superimposable with lower $M_W$ “standard”, and Wt% $< R_{g,c}$ was $\sim 100\%$.
Ultralarge polyethylene oxide samples

<table>
<thead>
<tr>
<th></th>
<th>$M_W$ (kg/mol)</th>
<th>$R_g,w$ (nm)*</th>
<th>Wt% &gt; 300 nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>PEO-1</td>
<td>1,000</td>
<td>67.7</td>
<td>0</td>
</tr>
<tr>
<td>PEO-2</td>
<td>1,750</td>
<td>93.8</td>
<td>0</td>
</tr>
<tr>
<td>PEO-3</td>
<td>2,500</td>
<td>115</td>
<td>NA</td>
</tr>
<tr>
<td>PEO-4</td>
<td>3,400</td>
<td>138</td>
<td>~2</td>
</tr>
<tr>
<td>PEO-5</td>
<td>5,700</td>
<td>187</td>
<td>2-8 estimate</td>
</tr>
<tr>
<td>PEO-6</td>
<td>7,000</td>
<td>210</td>
<td>~8</td>
</tr>
</tbody>
</table>

*Estimated from published conformation plot $R_g = 2.15 \times M_W^{0.583}$

*Macromolecules** 1991, 24, 5943-5947

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Flow rate dependence of elution – two different samples

<table>
<thead>
<tr>
<th></th>
<th>M_W kg/mol</th>
<th>Wt% &gt; 300nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>PEO 6</td>
<td>~7,000</td>
<td>~8</td>
</tr>
<tr>
<td>PEO 5</td>
<td>~5,800</td>
<td>2-8</td>
</tr>
</tbody>
</table>

PEO 6 M_W ~ 7,000 kg/mol (LALLS)
PEO 5 M_W ~ 5,800 kg/mol (LALLS)
Late elution of ultralarge polyethylene oxide

6 different samples all analyzed at a flow rate of 0.3 mL/min – $R_g, c = 253$ nm
TSK-Gel GMPW column, 17 µm particle size
Samples vary in $M_w (R_g)$ – significantly larger $R_g$ compared to HPMC

Late elution worsens as fraction of chains exceeding $R_g, c$ increases
Summary and Conclusions

- Systematic protocol for evaluating GPC conditions for ultralarge polymers has been developed
- Application of the protocol to commercial cellulose ether materials revealed that ideal (or near ideal) GPC conditions could be identified for all commercial grades
- Conditions corresponding to $D_e < 0.5$ for all chains were necessary for best GPC elution
- Ideal (or near ideal) conditions have not yet been identified for ultralarge polyethylene oxide having 1% or more of material exceeding 300 nm $R_g$
- Further increases in $R_{g,c}$ would appear to be necessary
  - Further flow rate reduction
  - Explore solvent viscosity – limited choices
  - Larger particle size (and pore size) mixed-bed packings – maintain flow suppression in pores
  - Larger radius columns
- Exploration of alternative separation mechanisms may be provide additional insight
Acknowledgments

Joe Kiefer
Danielle Dodge
Hongwei Shen
Later elution of polyethylene oxide

Light scattering ($90^\circ$) and DRI chromatograms at 0.5 and 0.2 ml/min

Log M vs. elution volume for PEO-1 superimposable with PEO narrow standards. Late elution of higher molar mass material was still observed for PEO-4 at the lowest practical flow rate of 0.2 ml/min.
Deborah Number and Deformation

\[ D_e = \tau \dot{\varepsilon} = \frac{C \eta R_g^3}{kT} k_1 \left( \frac{Q}{\pi r^2 d_p} \right) \]

Deborah number (De), which is the product of the longest relaxation time of the polymer, \( \tau \), and the strain rate of the flow, \( \dot{\varepsilon} \):

- De < 0.5: Random coil
- De > 0.5: Coil to stretch transition

0.3 < De < 1.0

De > 1.0