Branching Analysis of Star Polymers by SEC

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University of Paderborn:

- founded in 1972
- currently more than 20,000 students
- material science profile in chemistry, physics and mechanical engineering
Research Interests of Prof. Kucklings Working Group:

Controlled Radical Polymerization (NMRP, ATRP, RAFT)

Free Radical Polymerization and photo cross-linking / photo patterning

Smart Polymers

- Smart block copolymers for micro heterogeneous organocatalysis or pigment stabilization
- Smart nanohydrogels for targeted transport and controlled release systems
- Multisensitive phase separated hydrogel layers

Analytics
- NMR
- IR & UV/VIS
- SEC
- MS (MALDI, ESI-IMS)
- SPR

Receptor/Ligand modified (hydro)gels for sensor applications

Smart and biodegradable block copolymers for triggered release systems

Hydrogels for applications in biomedicine and as actuators and sensors in micro-system technology

enzyme
Induced Morphology Change in Star-Shaped Temperature-Responsive Block Copolymers:

**temperature-responsive block (LCST)**

**hydrophilic block**

**unimolecular colloidal nanoparticles:**
- small dimension (< 20 nm)
- spherical morphology

**T > T_c**

**T < T_c**

**hydrophilic shell**

**hydrophobic core**

**core-shell type nanoparticle**

Characterization of the obtained star (co)polymers:

- mean copolymer composition: $^1$H-NMR
- molecular weight: $^1$H-NMR, ESI-IMS-MS
  SEC (THF, CHCl$_3$, DMAc, HFIP)
- number of arms: viscosity (Kuhn-Mark-Houwink Plot)
SEC Setup for Branching Analysis

eluent: $N,N$-dimethylacetamide (DMAc)
flow: 1 ml/min
injection: manuel injection valve (100 µl, Knauer)
columns: PSS-GRAM (10\textsuperscript{4} Å, 10\textsuperscript{3} Å, 10\textsuperscript{2} Å)
column temp.: 50 ºC (Shimadzu CTO 6A)
detectors: Merck-Hitachi L3000 PDA
Waters RI 2410
PSS ETA 2010 viscosity detector
PSS SLD 7000 MALLS detector
Synthesis of Star Polymers

multifunctional initiator

<table>
<thead>
<tr>
<th>Sample</th>
<th>Initiator</th>
<th>ATRP catalyst</th>
<th>$M_{n,GPC}$ [g/mol]</th>
<th>D</th>
</tr>
</thead>
<tbody>
<tr>
<td>PS 4-arm</td>
<td>Penta-Br$_4$</td>
<td>Cu(I)Br / Me$_6$Tren</td>
<td>40.300</td>
<td>1.26</td>
</tr>
<tr>
<td>PNIPAAm 4-arm</td>
<td>Penta-Cl$_4$</td>
<td>Cu(I)Cl / Me$_6$Tren</td>
<td>70.000</td>
<td>1.13</td>
</tr>
<tr>
<td>PNIPAAm 7-arm</td>
<td>7-Cl-β-CD</td>
<td>Cu(I)Cl / Me$_6$Tren</td>
<td>149.800</td>
<td>1.11</td>
</tr>
<tr>
<td>PNIPAAm 14-arm</td>
<td>14-Cl-β-CD</td>
<td>Cu(I)Cl / Me$_6$Tren</td>
<td>155.000</td>
<td>1.17</td>
</tr>
<tr>
<td>PNIPAAm 21-arm</td>
<td>21-Cl-β-CD</td>
<td>Cu(I)Cl / Me$_6$Tren</td>
<td>250.000</td>
<td>1.25</td>
</tr>
</tbody>
</table>
Branching Analysis of Star Polymers

Kuhn-Mark-Houwink Plot

- standard calibration
- viscosity detector (universal calibration)
- MALLS detector (absolute method)
→ refractive index increment $dn/dc$ is required

\[
[\eta] = \lim_{c \to 0, G \to 0} \left( \frac{\eta_{\text{spez}}}{c} \right)
\]

\[
g' = \frac{[\eta]_{\text{branched}}}{[\eta]_{\text{linear}}}
\]

\[
g = (g')^{1/\varepsilon} \quad \text{with } \varepsilon = 0.5
\]

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

Refractive Index Increments in $N,N$-Dimethylacetamide

<table>
<thead>
<tr>
<th>Sample</th>
<th>Origin</th>
<th>$dn/dc$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Poly(styrene)</td>
<td>PSS Standard</td>
<td>0.15430 ± 0.0022</td>
</tr>
<tr>
<td>Poly(styrene)</td>
<td>Synthesized by FRP</td>
<td>0.15520 ± 0.0024</td>
</tr>
<tr>
<td>Poly(methylmethacrylat)</td>
<td>PSS Standard</td>
<td>0.05829 ± 0.0021</td>
</tr>
<tr>
<td>Poly(methylmethacrylat)</td>
<td>Synthesized by FRP</td>
<td>0.05737 ± 0.0006</td>
</tr>
<tr>
<td>Poly($N$-isopropylacrylamide)</td>
<td>Synthesized by ATRP</td>
<td>0.06497 ± 0.0013</td>
</tr>
<tr>
<td>Poly($N$-isopropylacrylamide) 14-arm star polymer</td>
<td>Synthesized by ATRP</td>
<td>0.06330 ± 0.0041</td>
</tr>
</tbody>
</table>

dn/dc-measurements of linear and star polymers in DMAc were performed with a refractometer Model 2010/540 (PSS, Mainz)
### Branching Analysis of Poly(styrene) Star Polymers

Sample data provided by PSS

<table>
<thead>
<tr>
<th>Sample</th>
<th>Origin</th>
<th>$M_n$ [g/mol]</th>
<th>PD</th>
</tr>
</thead>
<tbody>
<tr>
<td>Poly(styrene) broad, linear</td>
<td>PSS</td>
<td>144.000</td>
<td>2.03</td>
</tr>
<tr>
<td>Poly(styrene) 3-arm star polymer</td>
<td>PSS</td>
<td>288.000</td>
<td>1.06</td>
</tr>
<tr>
<td>Poly(styrene) 8-arm star polymer</td>
<td>PSS</td>
<td>220.000</td>
<td>1.06</td>
</tr>
</tbody>
</table>

SEC results (universal calibration)

<table>
<thead>
<tr>
<th>Sample</th>
<th>Origin</th>
<th>$M_n$ [g/mol]</th>
<th>PD</th>
</tr>
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<tr>
<td>Poly(styrene) broad, linear</td>
<td>PSS</td>
<td>144.000</td>
<td>2.03</td>
</tr>
<tr>
<td>Poly(styrene) 3-arm star polymer</td>
<td>PSS</td>
<td>265.000</td>
<td>1.14</td>
</tr>
<tr>
<td>Poly(styrene) 4-arm star polymer</td>
<td>Synthesized by ATRP</td>
<td>40.300</td>
<td>1.26</td>
</tr>
<tr>
<td>Poly(styrene) 8-arm star polymer</td>
<td>PSS</td>
<td>216.000</td>
<td>1.07</td>
</tr>
</tbody>
</table>
Branching Analysis of Poly(styrene) Star Polymers

3-Arm PS star polymer (PSS)

4-Arm PS star polymer (Aw 152)

8-Arm PS star polymer (PSS)

Results:
- $\eta_{\text{spez}}$ (elution volume)
- $[\eta]$ (elution volume); not always linear
- Molar mass (elution volume) from universal calibration
Branching Analysis of Poly(styrene) Star Polymers

\([\eta]\) (elution volume)
Molar mass (elution volume)

\[ V_e = \text{const} \]

Kuhn-Mark-Houwink Plot

\([\eta]\) (molar mass)

\[
g' = \frac{[\eta]_{\text{branched}}}{[\eta]_{\text{linear}}} \quad g = (g')^{1/\varepsilon} \quad g = \frac{3f - 2}{f^2}
\]

<table>
<thead>
<tr>
<th>Sample</th>
<th>Average number of arms (f)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Poly(styrene) 3-arm star polymer</td>
<td>2.8</td>
</tr>
<tr>
<td>Poly(styrene) 4-arm star polymer</td>
<td>4.0</td>
</tr>
<tr>
<td>Poly(styrene) 8-arm star polymer</td>
<td>8.0</td>
</tr>
</tbody>
</table>
Branching Analysis of Poly(styrene) Star Polymers

- Three types of poly(styrene) star polymers: 3-arm, 4-arm, and 8-arm.
- Number of arms $f$ increases together with molar mass.
- Synthesis mechanism offers no convenient explanation.

Slope of the KMH plot lines is too small to provide a constant ratio for $g'$:

$$g' = \frac{[\eta]_{\text{branched}}}{[\eta]_{\text{linear}}}$$
Branching Analysis of Poly(N-isopropylacrylamide) Star Polymers

4-Arm Poly(NIPAAm) star polymer (MS 344-4)

7-Arm Poly(NIPAAm) star polymer (Aw 312)

14-Arm Poly(NIPAAm) star polymer (Aw 234)

21-Arm Poly(NIPAAm) star polymer (Aw 221)
# Branching Analysis of Poly(N-isopropylacrylamide) Star Polymers

The graph shows the relationship between the logarithm of the intrinsic viscosity ($\log [\eta]$) and the logarithm of the molecular weight ($\log M$) for different samples of Poly(N-isopropylacrylamide) star polymers. The equations for the linear fits are:

- **Broad linear Poly(NIPAAm)**: $y = -1.65638 + 0.68093 \times x$
- **4-Arm Poly(NIPAAm) star polymer (MS 344-4)**: $y = -0.47662 + 0.42752 \times x$

The calculated number of arms $f = 3.9$.

The table below summarizes the average number of arms $f$ and the $\alpha$-value for each sample:

<table>
<thead>
<tr>
<th>Sample</th>
<th>Average number of arms $f$</th>
<th>$\alpha$-value</th>
</tr>
</thead>
<tbody>
<tr>
<td>PNIPAAm 4-arm star polymer</td>
<td>3.8</td>
<td>0.43</td>
</tr>
<tr>
<td>PNIPAAm 7-arm star polymer</td>
<td>6.0</td>
<td>0.42</td>
</tr>
<tr>
<td>PNIPAAm 14-arm star polymer</td>
<td>14.5</td>
<td>0.27</td>
</tr>
<tr>
<td>PNIPAAm 21-arm star polymer</td>
<td>22.3</td>
<td>0.18</td>
</tr>
</tbody>
</table>
Branching Analysis of Poly(N-isopropylacrylamide) Star Polymers

number of arms $f$ increases together with molar mass
→ Synthesis mechanism offers no convenient explanation

Molecular weight distributions are monomodal and show no signs of star cross-coupling.
Summary
- branching analysis could be applied to synthesized star polymers based on poly(sytrene) or poly(N-isopropylacrylamide)
- average number of arms is consistent to the functionality of the ATRP initiator
- number of arms is not constant over the molecular weight range

Outlook
- optimization of the SEC system (especially with respect to the MALLS detector)
- analysis of star polymer samples with unknown number of arms
• 3- and 8-Arm Poly(styrene) star polymers (PSS)

• Linear Poly(styrene) (PSS)

• 4-Arm Poly(styrene) star polymer (Aw 152)