Introduction

There has been increasing interest in the synthesis of star-branched polymers due to their unusual flow and viscosity properties compared to linear analogs. Star-branched polymers are constructed with several ‘arms’ radiating from a central core, either by preparing the individual arms and attaching them to a central molecule - the ‘arms first’ approach - or by growing the polymer arms from a central core - the ‘core first’ approach. Many commercial polymers can be constructed with a star-branched morphology relatively easily, but their characterization is still a challenge to the analytical chemist. Gel permeation chromatography (GPC) employing a concentration detector (typically a refractive index detector) combined with a viscometer can be used to measure not only the molecular weight of the materials but also to investigate the star-branched structure. The 390-MDS is ideal for this type of application since it was specifically designed to extract additional information from polymers by GPC.

A series of PS star-branched polymers was analyzed, which had been synthesized by a ‘core first’ approach giving theoretical 5-, 14- and 21-arm structures.
Materials and Methods

Conditions
Samples: Polystyrene star-branched polymers
Columns: 2 x Agilent PLgel 5 μm MIXED-C, 300 x 7.5 mm (part number PL1110-6500)
Eluent: THF
Flow Rate: 1.0 mL/min
Temperature: 40 °C
Detector Train: 390-MDS incorporating Viscometer and DRI
Detector Temp: All detectors set at 40 °C

Results and Discussion

Figure 1 shows the dual-detection chromatogram of the 14-arm polymer.

![Viscometer and refractive index detection of a 14-arm, star-branched polystyrene](image)

The universal calibration approach was used to calculate the molecular weight averages for the star-branched polymers. The universal calibration curve was generated using linear PS standards with narrow polydispersity and is shown in Figure 2.

![Universal calibration curve using polystyrene standards](image)

Based on this calibration, the molecular weight averages and weight average intrinsic viscosity (IVw) calculated for the PS star-branched polymers are given in Table 1.

Table 1. Molecular weight averages and weight average viscosities for star-branched polymers

<table>
<thead>
<tr>
<th>Sample</th>
<th>Molecular Weight Average (g.mol⁻¹)</th>
<th>PD</th>
<th>IVw</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Mp</td>
<td>Mn</td>
<td>Mw</td>
</tr>
<tr>
<td>5-arm</td>
<td>56,120</td>
<td>10,460</td>
<td>64,856</td>
</tr>
<tr>
<td>14-arm</td>
<td>27,436</td>
<td>26,812</td>
<td>29,310</td>
</tr>
<tr>
<td>21-arm</td>
<td>149,752</td>
<td>111,377</td>
<td>157,884</td>
</tr>
</tbody>
</table>

Mark-Houwink plots of log intrinsic viscosity as a function of log molecular weight were calculated for the PS star-branched polymers and for a broad PS material that was known to contain no branching. Figure 3 shows an overlay of the Mark-Houwink plots obtained, indicating that increasing the number of arms on the star-branched PS resulted in a decrease in intrinsic viscosity at any given molecular weight when compared to the broad linear PS. However, for the 21-arm star-branched polymer, the change in intrinsic viscosity relative to the linear PS varied strongly with the molecular weight.
Based on the linear regions in the Mark-Houwink plots for the stars, the intrinsic contraction factor \( g' \) was calculated as a function of molecular weight using Equation 1.

\[
g' = \frac{[\eta]_{\text{star}}}{[\eta]_{\text{linear}}} \quad \text{Equation 1}
\]

From the \( g' \) data, the radius of gyration contraction factor \( g \) was calculated using the empirical relationship in Equation 2

\[
g' = [a + (1-a)g^p]gb \quad \text{Equation 2}
\]

where \( a = 1.104 \), \( p = 7 \), and \( b = 0.906 \) (Weissmüller et al. 1997).

Figure 4 shows an overlay of \( g' \) plots for 5-, 14- and 21-arm star-branched polymers. Using the calculated \( g' \) values and the functionality \( f \) for the stars, the theoretical number of arms was calculated using the model in Equation 3, based on an assumption that the arms were ‘random’, that is, polydisperse in molecular weight (Burchard 1977, 1983).

\[
g = \frac{3f}{(f+1)^2} \quad \text{Equation 3}
\]

The variation in the functionality \( f \) with molecular weight provided valuable insight into the mechanism of the ‘core first’ approach used to synthesize the materials.
Conclusion

The results show that GPC employing refractive index and viscometry detectors in the 390-MDS can be used to investigate the structure of star-branched polymers, and provide valuable information on synthesis mechanisms used during their manufacture.

References

