# Analysis of Star Polymers Using the Agilent 1260 Infinity Multi-Detector GPC/SEC System

## Application Note

Material testing


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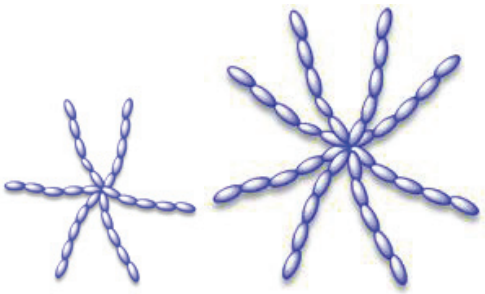
### Abstract

This Application Note demonstrates the use of the Agilent 1260 Infinity Multi-Detector GPC/SEC System for the analysis of star polymers. Accurate molecular weights are calculated through the use of a Light Scattering detector and a viscometer is used to determine the number of arms. The excellent stability and sensitivity enable subtle differences in molecular density that occur between stars with differing numbers of arms to be distinguished.

Star

Verified for Agilent
**1260 Infinity II LC**
**GPC/SEC System**

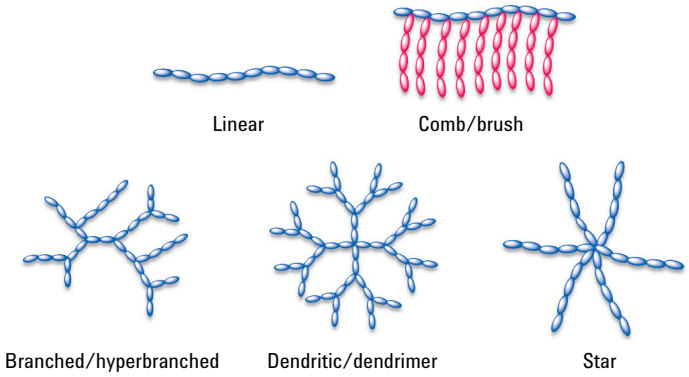
Agilent Technologies

## Introduction

Non-linear polymers can provide a range of desirable properties over their linear counterparts, such as increased solubility, low solution viscosities, modified melt rheologies, and high levels of terminal functionality, leading to an increase in applications such as coatings, resins, flow improvers/viscosity modifiers, and drug delivery vehicles.

A range of non-linear architectures exist including branched/hyperbranched, comb/brush, dendritic/dendrimers, and stars. The density of non-linear polymers can vary across the volume of each structure depending on the type of branching architecture, and the level of branching can change depending on length of polymer chain. This makes it essential to have a technique that can separate by size while determining density in order to have a full picture of the polymer topology.

GPC/SEC is the most common method to analyze polymers, and the technique can be expanded by the use of advanced detectors to provide accurate molecular weights and measure the average functionality (number of arms) of star polymers. This Application Note describes the determination of branching levels in star polymers using the 1260 Infinity Multi-Detector GPC/SEC System.




## Experimental

### Instrumentation and software

- Agilent 1260 Infinity Standard Degasser (G1322A)
- Agilent 1260 Infinity Isocratic Pump (G1310B)
- Agilent 1260 Infinity Standard Autosampler (G1329B)
- Agilent 1260 Infinity Thermostatted Column Compartment (G1316A)
- Agilent 1260 Infinity GPC/SEC Multi-Detector Suite (G7800A)
- Agilent 1260 Infinity MDS RID (G7801A)
- Agilent 1260 Infinity MDS Viscometer (G7802A)
- Agilent 1260 Infinity MDS Light Scattering (G7803A)
- Agilent GPC/SEC Software (G7850AA)
- Agilent GPC/SEC Multi-Detector Upgrade (G7852AA)
- Agilent GPC/SEC Instrument Control (G7854AA)

All detectors were plumbed in series, Light Scattering to Refractive Index, Detector to Viscometer.

### Column set and calibrants

- 3 × PLgel 5 µm Mixed-C, 7.5 × 300 mm (PL1110-6500)
- PS nominal Mp 100k (PL2013-5001)
- EasiVial PS-H 4 mL (PL2010-0200)

### Samples

In the case of star polymers, branching is controlled by the number of arms around a central core. There are two methods for the synthesis of stars, arm first and core first. The core first approach uses a multifunctional initiator as the central core, from which polymer chains are grown from the initiating sites. The number of arms per star is controlled by the number of initiation sites per core.

### Chromatographic conditions

Table 1. Chromatographic parameters used for GPC/SEC.

| Parameters | Conditions |
|---|---|
| Eluent | Tetrahydrofuran (stabilized with 250 ppm BHT) |
| TCC temperature | 35 °C |
| Detectors temperature | 35 °C |
| Injection volume | 100 µL |
| Flow rate | 1.0 mL/min |
| Run time | 35 minutes |
| Detection | Refractive Index at 660 nm<br>Viscometer Inlet Pressure<br>Viscometer Differential Pressure<br>Light Scattering 15° at 660 nm<br>Light Scattering 90° at 660 nm |

To achieve full control over the amount of arms and to keep the length of the arms consistent, controlled/living radical polymerization techniques (LRP) were employed in the synthesis. Two multi-initiating cores, with both five and eight initiating sites were used, with the molecular weights of the resulting stars controlled by the ratio of core to arms. Samples were dissolved over a period of 3 hours in eluent at nominally 2.0 mg/mL.

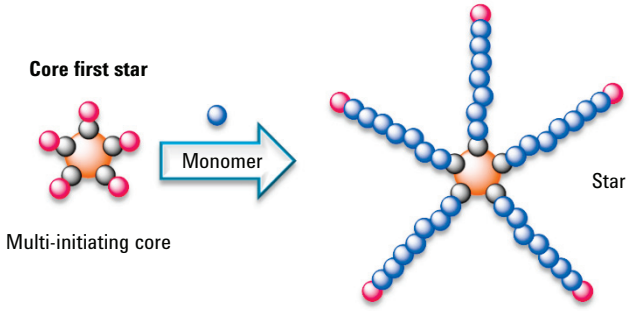
## Calibration Standards

The 1260 Infinity Multi-Detector GPC/SEC System, featuring Refractive Index, Viscometer and dual angle Light Scattering detectors was calibrated using a single polystyrene narrow standard of 113,300 g/mol$^{-1}$.

Although not required for this study, the column was calibrated with PS-H EasiVials to highlight difference between conventional and advanced data.

## Results and Discussion

A range of core-first stars were synthesized utilizing living radical polymerization from multi-initiating cores with both 5-arm and 8-arm initiating sites. The ratio of monomer to core was varied in order to provide two distinct molecular weight polymers for both the 5 arm and 8 arm initiators (5-arm Low, 5-arm High, 8-arm Low, and 8-arm High).



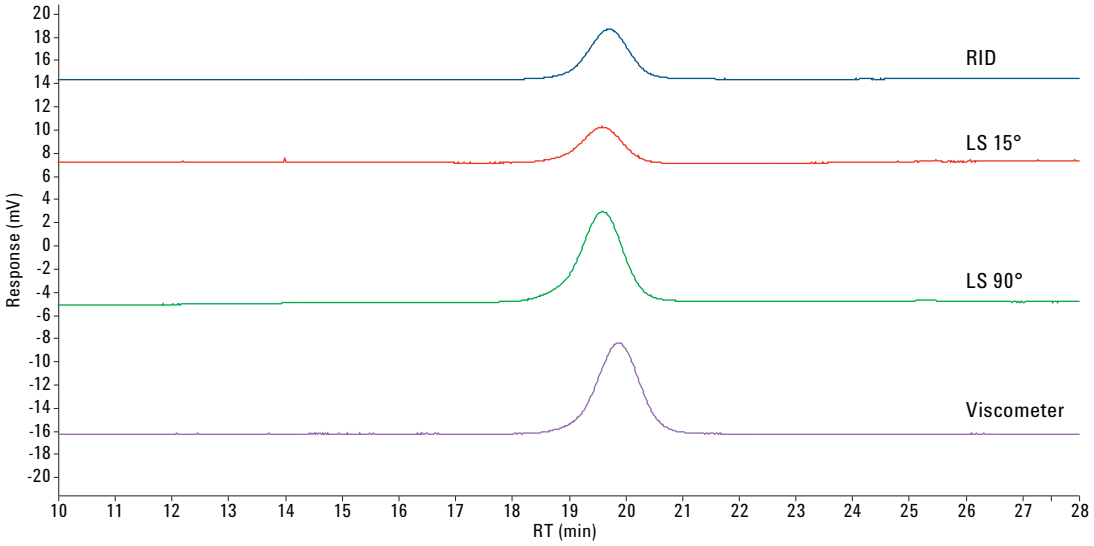




Figure 1. Raw data chromatogram showing RID, LS 15° and 90°, and Viscometer responses to 5-arm Low star.

## Molecular Weight Distribution

The majority of star polymers analyzed displayed narrow Gaussian peak distributions characteristic of polymers synthesized by living radical techniques. However, some high molecular weight shoulders were apparent on certain samples, indicative of star-star coupling. This is an undesired side-reaction during the synthesis which is easily detected when looking at the molecular weight distribution from GPC/SEC.

These key factors are obtained using conventional GPC however; an underestimation of the molecular weights is attained due to the star like architecture of the polymers. This applies to all stars, but the extra arms in the 8-arm star effect a more contracted hydrodynamic volume than in the 5-arm star. This is clearly seen using just the high molecular weight arm stars as example. Both the 5- and 8-arm high molecular weight stars had identical molecular weights targeted but looking at the elution volume this is not apparent, the 8-arm star elutes after the 5-arm star, indicating a lower molecular weight. The light scattering detector responds directly to molecular weight and therefore is not affected by this hydrodynamic change, thus the results from LS show near identical, much higher molecular weights (Table 2 and Figure 2).

Table 2. Molecular weight averages comparing conventional GPC to Triple GPC for the high molecular weight stars.

| | Molecular weight averages (g/mol$^{-1}$) | | | |
|---|---|---|---|---|
| Sample name | Mp | Mn | Mw | PD |
| 5-arm high (Conv) | 124,900 | 114,900 | 147,800 | 1.29 |
| 5-arm high (Triple) | 219,200 | 206,800 | 249,400 | 1.21 |
| 8-arm high (Conv) | 105,400 | 98,500 | 110,500 | 1.12 |
| 8-arm high (Triple) | 215,900 | 205,200 | 223,500 | 1.09 |

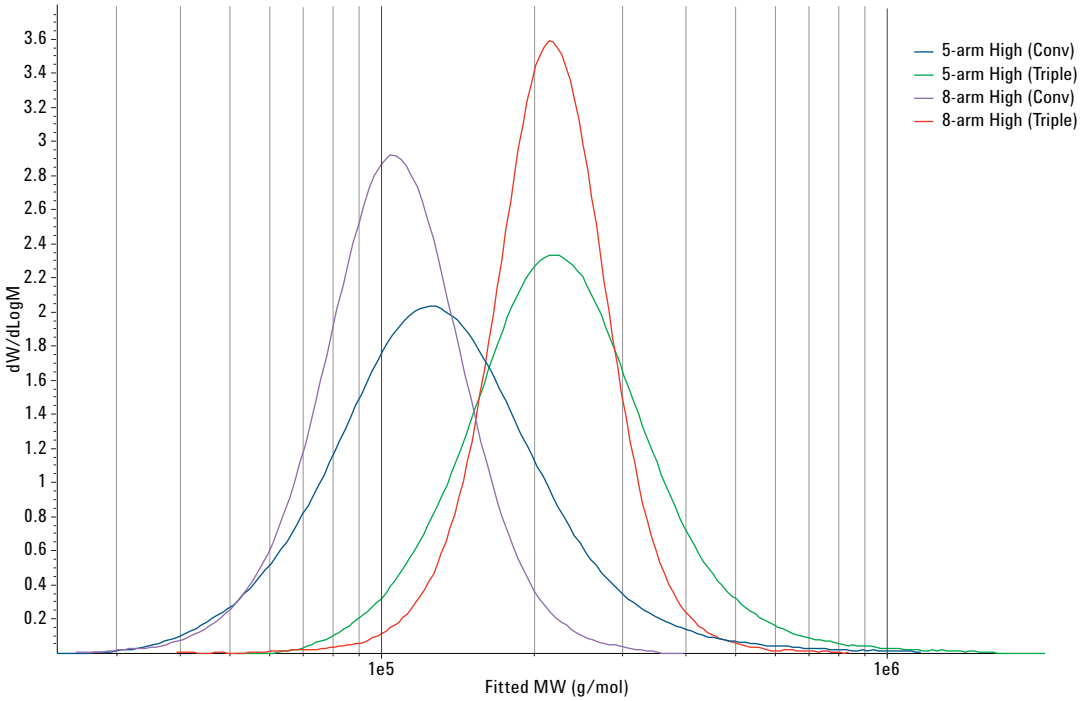



Figure 2. Overlaid Molecular Weight Distributions of the 5-arm and 8-arm High stars by Conventional and Triple GPC.

## Branching

Comparison of the intrinsic viscosity of a branched polymer and its linear analog over the same molecular weight range, (Figure 3) is used to obtain information on the contraction factor, *g'*.

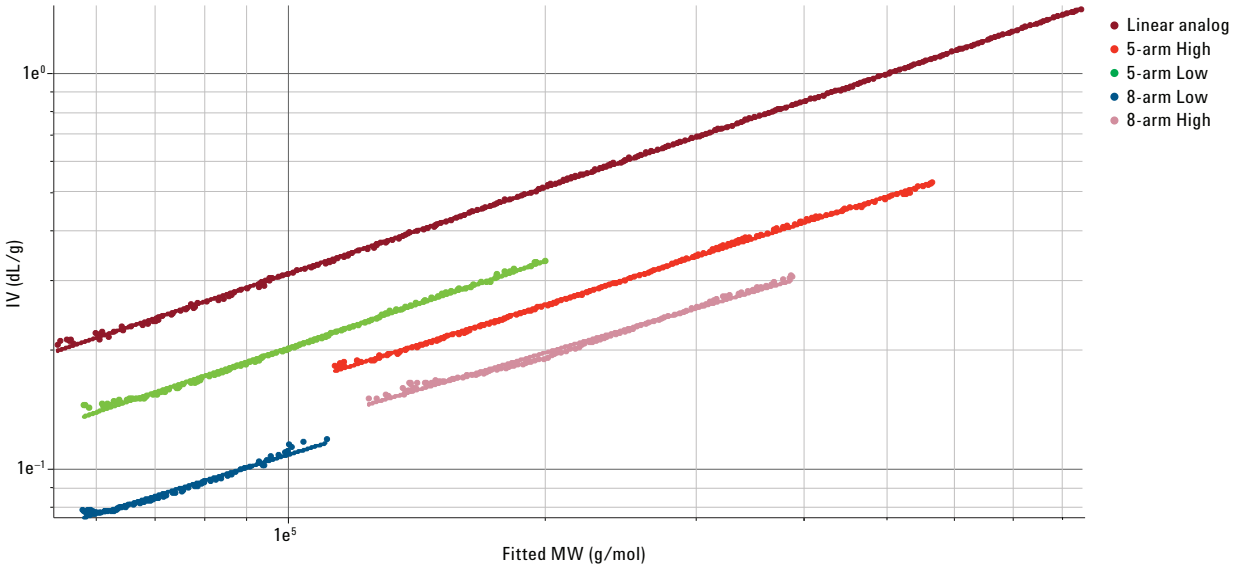



Figure 3. Mark-Houwink plot from Triple analysis showing all star polymers overlaid.

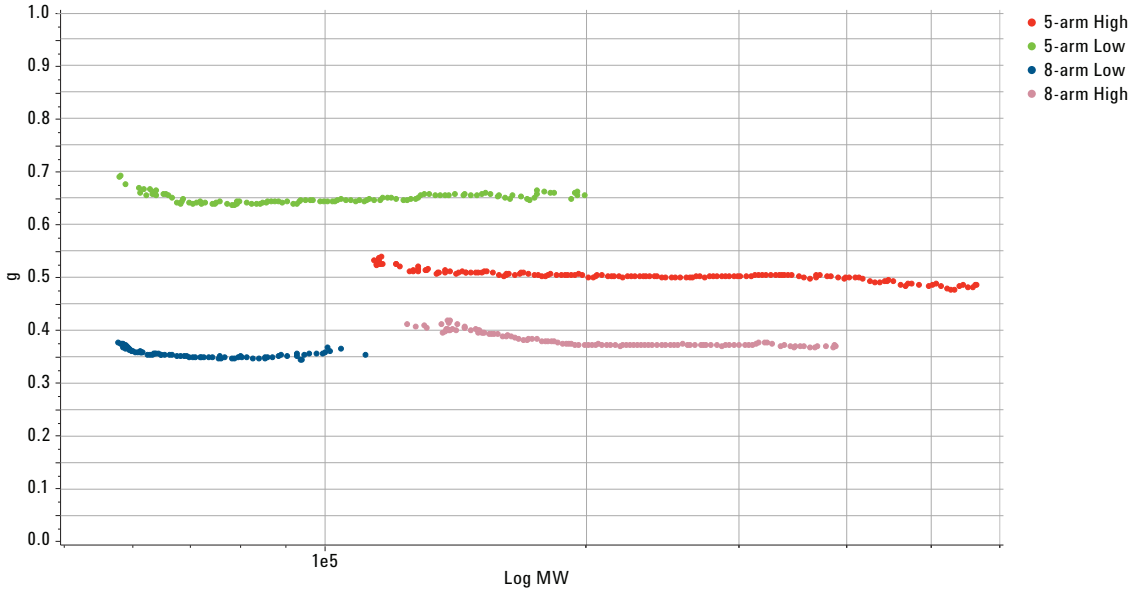



Figure 4. Branching contraction factors for all of the star polymers.

Additionally, the level of functionality of star polymers can be modeled using the relationship which exists between *g* and number of arms (functionality). A choice of models exist for this in Agilent GPC/SEC Software, which vary, dependent on whether uniform or random architectures are obtained. LRP create stars of a regular structure, where both the number and length of arms is constant, therefore a Regular Star Branched Model was used (Figure 5).

From the functionality plots, it is observed that the results obtained are close to those expected from the number of initiation sites on the two cores. All of the stars have a flat profile, indicating that the length of arms is consistent across the molecular weight distribution – a key factor in the proof of a successful LRP. The 8-arm Low star polymer possesses a functionality of 8.0, which suggests that the polymerisation progressed from all eight initiation sites from the core. As more arms are targeted, steric crowding of the core can be a detrimental factor and often lower functionalities than expected are obtained due to this, therefore design of the initiator is key. Testing of the functionality is very difficult by methods other than GPC/SEC with Viscometry/Light Scattering. The 8-arm High star also displays a level of functionality close to its expected value at approximately 7.5. This, together with the deviation from linearity suggests that the polymerisation did not quite work perfectly. The functionality of the 5-arm Low is slightly lower than expected at approximately 4.0. However, the 5-arm High star displays a functionality of approximately 5.0, which again shows a high level of control over functionality.

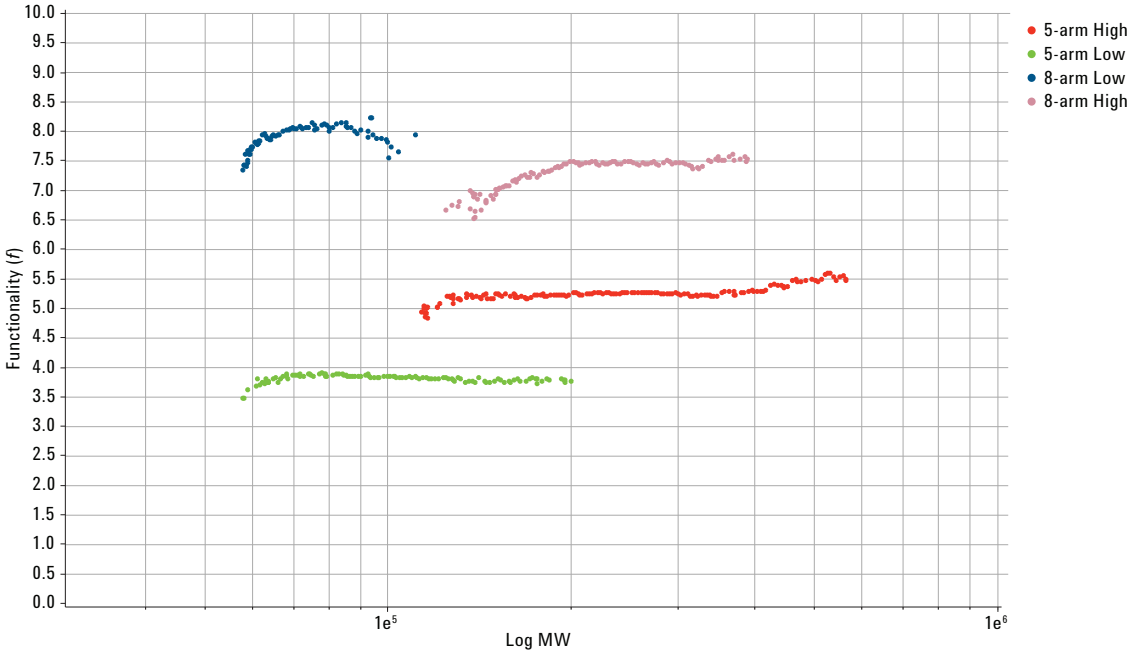



Figure 5. Plot to show functionality of the star polymers.

## Conclusions

The Agilent 1260 Infinity Multi-Detector GPC/SEC System provides an excellent tool to help characterize and understand advanced materials. A range of star polymers were analyzed and the true molecular weight and number of arms was calculated with excellent agreement with theoretical. This highlights the importance of not only characterizing the polymer but also validating the synthetic pathway.

The market-leading low dispersion advanced detectors provided critical data with excellent signal-noise without compromising the chromatography, especially important when using advanced detectors to look at narrowly disperse polymers.

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Published in the USA, May 1, 2016
5991-2887EN

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