Polystyrene Stars on Agilent PLgel 5 µm MIXED-C using Gel Permeation Chromatography

Application Note

Materials Testing and Research, Polymers

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Introduction

Recently, there has been increasing interest in the synthesis of star-branched polymers due to their unusual flow and viscosity properties compared to linear analogues. 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.

Analysis of Polystyrene Stars

GPC/viscometry was used to analyze a series of star-branched polystyrenes that had been synthesized by a core first approach, giving theoretical 5-, 14- and 21-arm structures. Figure 1 shows a dual detection chromatogram of the 14-arm star-branched polystyrene.

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Conditions

Columns	2 × Agilent PLgel 5 µm MIXED-C, 7.5 × 300 mm (p/n PL1110-6500)
Eluent	THF
Flow rate	1 mL/min
Temp	40 °C
Detector	Agilent PL-GPC 220

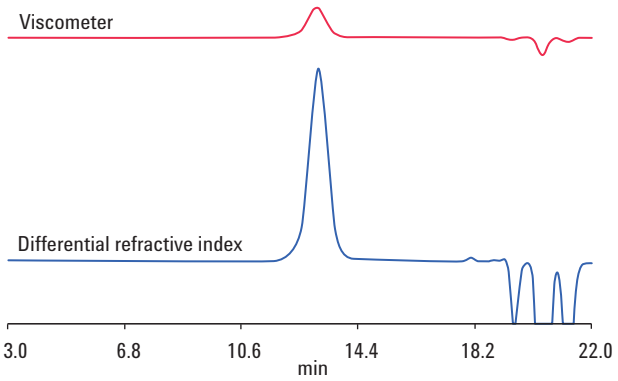

Figure 1 *A 14-star-branched polystyrene detected by viscometry and refractive index.*

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 polystyrene (PS) standards with narrow polydispersity (Figure 2).

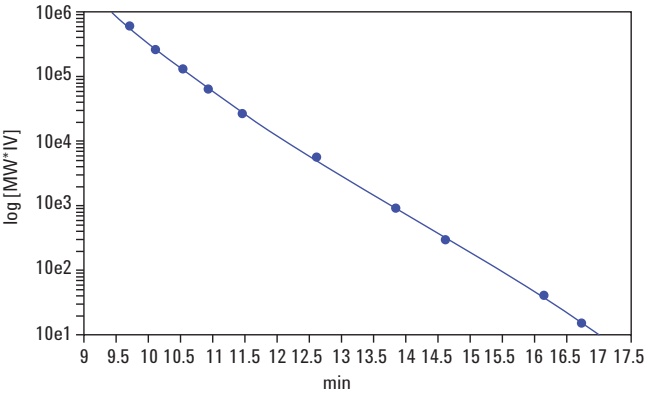

Figure 2 *Linear polystyrene standards produce a Universal Calibration curve.*

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 Intrinsic Viscosity for a 14-Star-Branched Polystyrene*

	Molecular weight averages/gmol^{-1}							
Polystyrene	**Mp**	**Mn**	**Mw**	**Mz**	**Mz+1**	**Mv**	**PD**	**IVw**
5-arm	56,120	10,460	64,856	98,594	134,877	46,292	6.20	0.28
14-arm	27,436	26,812	29,310	32,425	36,542	28,687	1.10	0.10
21-arm	149,752	111,377	157,884	201,225	256,977	141,293	1.42	0.21

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 results 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.

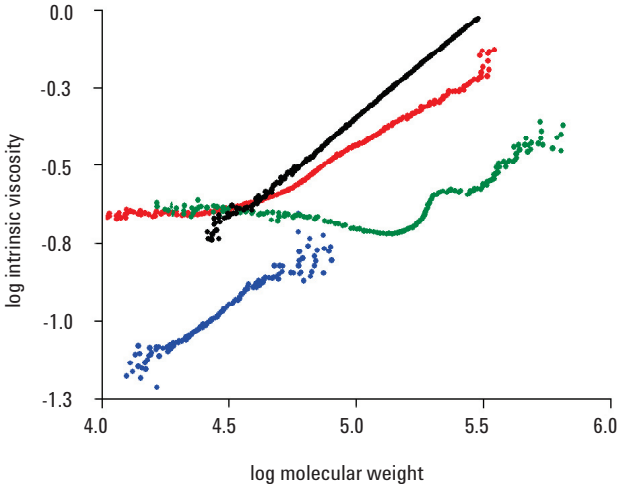

Figure 3 *Overlaid Mark-Houwink plots for the linear PS (black) and the 5-arm (red), 14-arm (blue) and 21-arm (green) star-branched polymers.*

Based on the linear regions in the Mark-Houwink plots for the stars, the intrinsic viscosity contraction factor for the stars, the intrinsic contraction factor g' was calculated as a function of molecular weight.

$$g' = \frac{[\eta]\ \text{star}}{[\eta]\ \text{linear}}$$

From the g′ data, the radius of gyration contraction factor g was calculated.

$$g' = [a + (1a)g^{p}]g^{b}$$

Where a = 1.104, p = 7 and b = 0.906 (Weissmuller & Burchard (1997) Polymer Internat. 44, 380).

Figure 4 shows an overlay of Rg contraction g plots. Using the calculated g values, the functionality f for the stars (the theoretical number of arms) was calculated using a model based on an assumption that the arms were random, that is, polydisperse in molecular weight. For random stars with f number of polydisperse arms:

$$g = \frac{3f}{(f+1)^{2}}$$

(Burchard (1983) Adv. Polym. Sci. 48, 1; Burchard (1997) Macromolecules 10, 919)

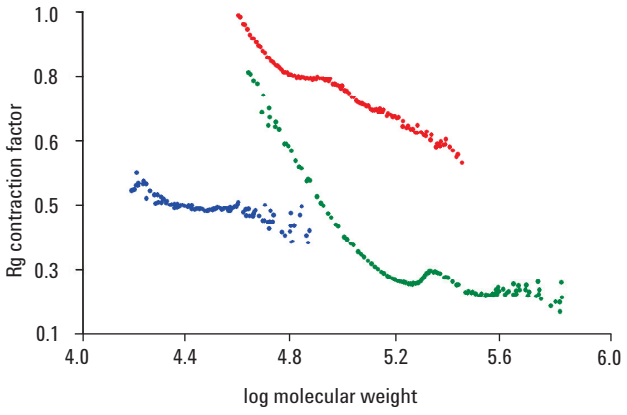

Figure 4. Rg contraction plots for the 5-arm (red), 14-arm (blue) and 21-arm (green) star-branched polymers.

Figure 5 shows an overlay of f for the stars as a function of the log molecular weight. The random model gave a prediction of the functionality f, the number of arms, which was in good agreement with the value expected from the synthesis. However, for all of the star-branched polymers, especially the 21-arm PS, the calculated value of f increased sharply with molecular weight, indicating that a considerable portion of the sample at low molecular weight contained components with fewer than expected arms.

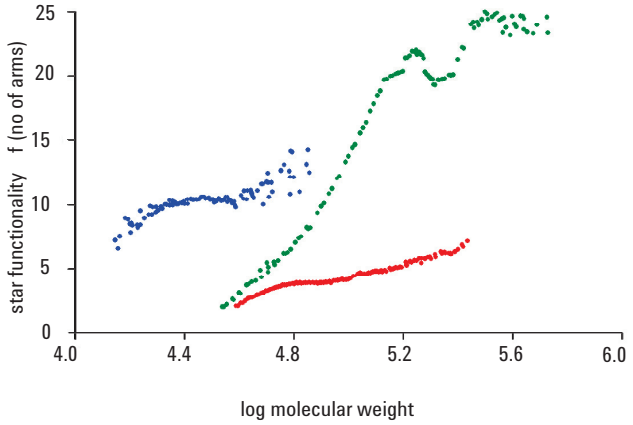

Figure 5. Functionality f plots for the 5-arm (red), 14-arm (blue) and 21-arm (green) star-branched polymers.

Conclusions

The results show that gel permeation chromatography employing refractive index and viscometry detectors can be used to investigate the structure of star-branched polymers. The variation in the functionality f (the number of arms on the polymers) with molecular weight gives valuable insight into the mechanism of the core first approach used to synthesize these materials.

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