APPLICATION NOTE

AN1005: Identifying short-chain branched polymers with conformational analysis

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Introduction

Polymer branching is an important molecular parameter since it affects various macroscopic polymer properties such as crystallinity, melting temperature, toughness, ductility, and optical clarity.1-2 Two types of branching are recognized: long-chain branching (LCB) wherein the molar mass of the branches is greater than the entanglement molar mass, and short-chain branching (SCB) wherein the molar mass of the branches is smaller than the entanglement molar mass.

Size-exclusion chromatography with multi-angle light scattering (SEC-MALS), alone or in conjunction with a viscometer (SEC-MALS-IV) is often used to characterize LCB in macromolecules. Branching analysis is typically conducted through the examination of:

- **Conformation plots**: Log-log plots of the rms radius (radius of gyration, R_g) versus molar mass (M), or
- **Mark-Houwink-Sakurada (MHS) plots**: Log-log plots of the intrinsic viscosity ($[\eta]$) versus M.

These plots have characteristic slopes of known value for a linear polymer in a thermodynamically good solvent: 0.58 for a conformation plot and 0.5 for a MHS plot. Polymers with LCB will exhibit a lower slope than the linear analog, since branching reduces R_g and $[\eta]$ at the same M value as the linear polymer. The difference in slope between a linear polymer and a branched polymer can be seen in Figure 1.

The conformation plot can readily be constructed by SEC-MALS analysis, and there are many literature conformation values for comparison. However, it can only be produced if the polymer has $R_g > 10$ nm. The MHS plot, which can be produced for polymers with $R_g < 10$ nm, requires a differential viscometer and SEC-MALS-IV.

While Figure 1 showcases the easily discernable difference between linear polymers and polymers with LCB, what about polymers with short-chain branching?

A simple means of distinguishing between LCB and SCB would be of great value to polymer scientists. The following analysis of branched silicones reveals the telltale characteristics of polymers with SCB.

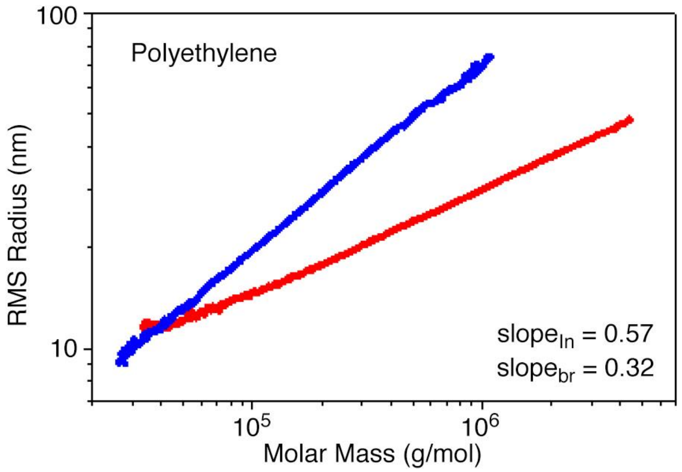

Figure 1. Linear and LCB polyethylene in a conformation plot. The linear polymer exhibits a slope close to 0.58, which is the value for a linear polymer in a thermodynamically good solvent. The branched polymer exhibits a slope less than 0.58.

Materials and Methods

A polystyrene standard from NIST was used (Standard Reference Material® 706a) for system validation. Three separate lots of branched silicone polymers were dissolved in THF for analysis. The samples were each measured twice by SEC-MALS. The instrument setup consisted of an Agilent 1100 pump and autosampler with two PLgel Mixed-C 300 × 7.5 mm columns for chromatographic separation. The detection system consisted of a DAWN® MALS detector and an Optilab® differential refractometer plumbed in series. Data acquisition and analysis were performed using ASTRA® software.

Discussion

The branches in polymers with SCB create a dense structure with lower intrinsic viscosities and radii than linear polymers of the same molecular weight. However, their overall conformation remains similar to the linear analog due to the short branch lengths. As a result, measurements of two polymers, one with and one without SCB, will produce parallel conformation plots or MHS plots. This phenomenon has been seen in previous studies of branched polyethylene polymers and poly(p-methylstyrene) comb polymers.[3-5]

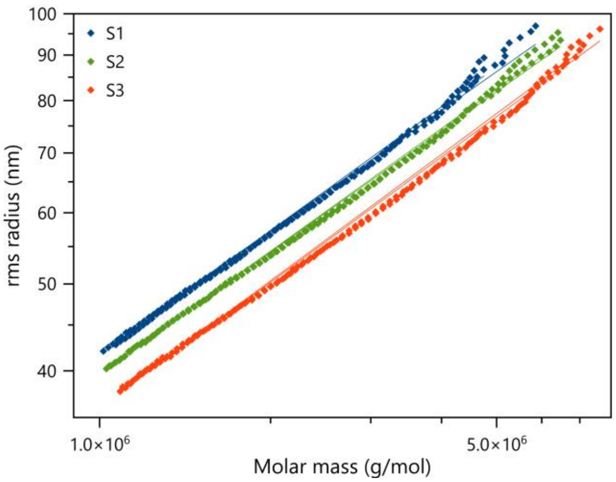

Figure 2. Conformation plot of three silicone polymers with both SCB and LCB, two replicates each.

Polymers may possess both SCB and LCB. In these cases, the branched polymer conformation or MHS slope is lower than that of the linear analog, and the plot is shifted down in size or intrinsic viscosity. This is seen in Figure 2, where silicone polymers with a fixed amount of LCB and increasing amounts of SCB have slopes lower than 0.58 in the conformation plot. As the amount of SCB increases, the [η] at a given molar mass decreases, while the slopes remain parallel with each other.

Conclusions

Light scattering and viscometry, implemented as SEC-MALS and SEC-MALS-IV, can effectively and rapidly characterize branching in polymers through conformation plots and Mark-Houwink-Sakurada plots. In both of these methods, polymers with LCB will exhibit lower slopes than the corresponding linear polymer, and these slopes will differ depending on the extent of LCB. Polymers containing only SCB will exhibit conformation or MHS plots parallel to those of their linear analogs, shifted down in R_g or [η].

If polymers possess both SCB and LCB, then their slopes will be less than the linear analog slope, and the plot will be shifted down relative to non-SCB analogs. Hence SEC-MALS and SEC-MALS-IV are essential tools for analyzing such polymers.

References

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