Characterization of Branched Polymers by A4F-MALS

Long chain branching strongly affects rheological, mechanical and other properties of polymer materials. The basic principle of the characterization of branching is given by the fact that branching *reduces* molecular size, *e.g.*, at a given molar mass the molecular size *decreases* with an *increasing* degree of branching.

The relation between the root mean square (RMS) radius and molar mass (called the "conformation plot") enables the branching to be detected and is the basis of further branching calculations. The characterization of branching by means of the conformation plot is based on the assumption of almost monodisperse fractions eluting from a separation system. This means that an efficient analytical separation technique is crucial for accurate branching characterization.

The conformation plots of many branched polymers show a noticeable upswing in the region of lower molar masses. The upswing is that typical that it can be used as the evidence of the existence of branched molecules. However, it makes further branching calculations uncertain—or even impossible. The upswing on the conformation plot is a virtual artifact and does not exist in reality, *i.e.* there are no molecules in the sample that would have RMS radii this large at molar masses *below* 10^5 g/mol (see Figure 1).

The upswing is simply a consequence of poor separation of branched macromolecules by SEC due to the entanglement of branched molecules in the interstitial pores of the column packing. Poor SEC separation results in significantly increased polydispersity of elution volume slices, especially at higher elution times. In the case of polydispersity within elution slices, the DAWN multi-angle light scattering (MALS) detector determines the slice weight-average and z-average moments, respectively.

Since the z-average is more sensitive to the presence of high-molar-mass fractions than the weight-average, the conformation plot slopes upward. The A4F separation takes place in an empty channel where entanglement effect is totally eliminated.

The results prove that AF4 is a more efficient separation technique for branched polymers than traditionally-used SEC. In contrast to SEC-MALS, A4F-MALS provides linear conformation plots with no virtual upswings, which allow accurate characterization of branched polymers.

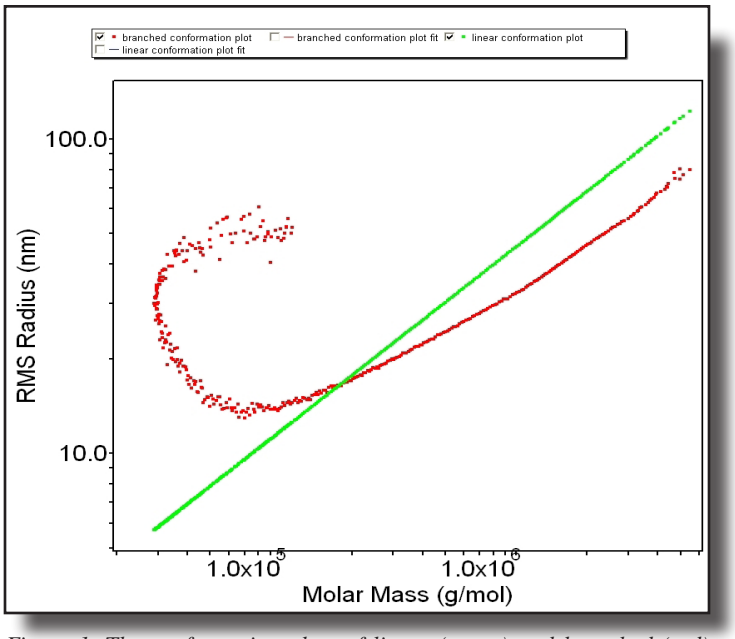

Figure 1. The conformation plots of linear (green) and branched (red) polystyrene obtained by SEC-MALS. The cross point and upswing on the plot of branched sample are the consequence of poor SEC separation.

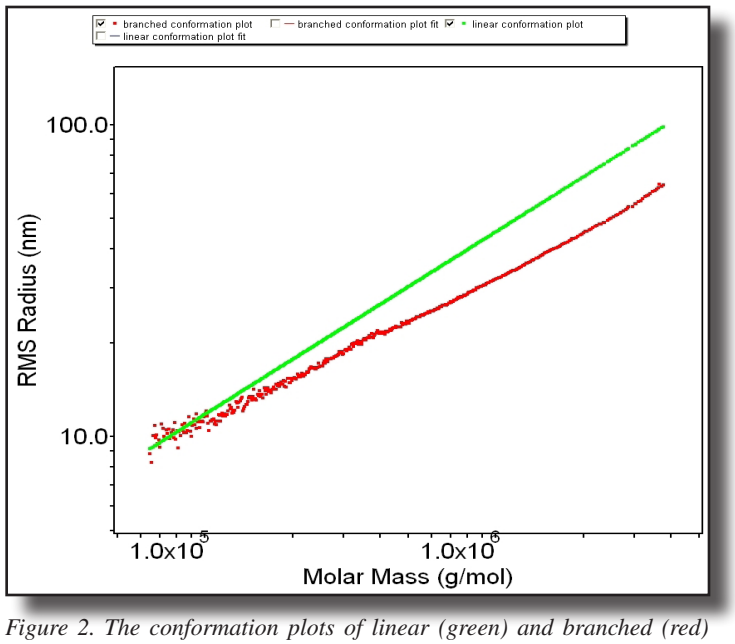

Figure 2. The conformation plots of linear (green) and branched (red) polystyrene obtained by A4F-MALS. The comparison with Figure 1 confirms that A4F provides superior separation of branched molecules giving linear conformation plot with no upward shift.

S. Podzimek, T. Vlcek, C. Johann: *J. Appl. Polym. Sci.* **81**, 1588 (2001).

This note graciously submitted by Stepan Podzimek, Synpo Research, Pardubice, Czech Republic.

Wyatt Technology CORPORATION
6300 Hollister Avenue • Santa Barbara, CA 93117
TEL (805) 681-9009 • FAX (805) 681-0123
E-mail: info@wyatt.com • URL http://www.wyatt.com