Characterization of Branched Polymers by Size Exclusion Chromatography Coupled with Multiangle Light Scattering Detector. I. Size Exclusion Chromatography Elution Behavior of Branched Polymers

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ABSTRACT: The elution behavior of branched macromolecules during their separation by size exclusion chromatography (SEC) was studied. The elution behavior of branched polymers was investigated using samples of randomly branched polystyrene and star branched poly(benzyl methacrylate) of different levels of branching by means of a SEC chromatograph coupled with a multiangle light scattering detector. Abnormal SEC elution behavior was found to be typical for highly branched polymers. After a normal elution at small elution volumes the molar mass and root mean square radius of the eluting molecules increased with increasing elution volume. Several SEC experiments were carried out to find explanation for this effect and SEC separation was compared with the separation by thermal field flow fractionation. © 2001 John Wiley & Sons, Inc. J Appl Polym Sci 81: 1588–1594, 2001

Key words: size exclusion chromatography; field flow fractionation; light scattering; branching

INTRODUCTION

Branched polymers are of a great scientific and practical interest. Their detailed characterization is a great challenge in polymer analysis. Size exclusion chromatography (SEC) coupled with a multiangle light scattering (MALS) detector is recognized as one of the most powerful techniques for the investigation of branched polymers.[1,2] The reason for this is the ability of SEC–MALS to determine the molar mass and root mean square (RMS) radius for narrow polymer fractions eluting from the SEC separation. Then information about the polymer chain structure can be gained from the relation between the molar mass and size. This study of the SEC elution behavior of branched macromolecules was carried out as part of an extensive study of the application of SEC–MALS for the characterization of branched polymers.

EXPERIMENTAL

A chromatograph was used that consisted of a 600 Waters pump, a 717 autosampler (Waters, Mil-

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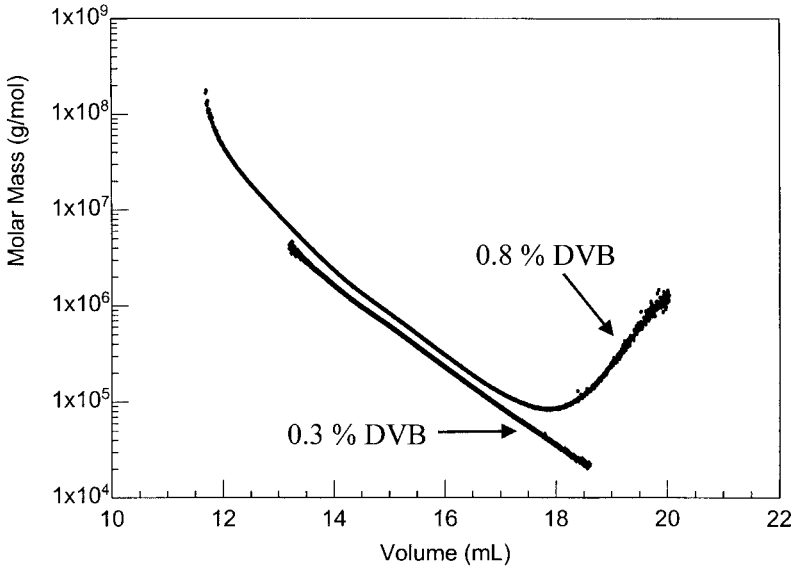

Figure 1 The molar mass versus the elution volume plots of branched PS samples containing different amounts of DVB.

ford, MA), a laser photometer miniDAWN® (Wyatt Technology Corporation, Santa Barbara, CA), and a 410 differential refractometer (Waters). ASTRA software (Wyatt Technology Corporation) was used for data collection and processing. Two Waters 300 × 7.8 mm Styragel HR 5E mixed columns were used for separation. Tetrahydrofuran (THF) at a flow rate of 1 mL/min was used as a mobile phase. The calibration of the miniDAWN photometer was carried out by p.a. grade toluene and normalization with a polystyrene (PS) standard of 20,000 g/mol molar mass. The samples were injected as solutions in the mobile phase, and 100 μL of 0.1–0.2% (w/v) solutions were injected. The measurements were carried out at room temperature.

A MiniStar HPLC pump (Knauer, Berlin, Germany) with a pulse dampener, a T-100 Thermal FFF channel (FFFractionation, LLC, Salt Lake City, UT), a DAWN DSP detector (Wyatt Technology Corporation), and an Optilab 903 (Wyatt Technology Corporation) detector with a P10 cell were used for thermal field flow fractionation (FFF). The amount injected was 200 μL of 0.22% solution in THF.

Samples of randomly branched PS were prepared by radical solution polymerization of 50% solutions of styrene/divinylbenzene (DVB) mixtures in toluene. The polymerization reactions were carried out in glass sealed vials using azobisisobutyronitrile (0.1% to styrene) as an initiator at 80°C. The reaction time was 8 h. The polymer was precipitated with petroleum ether with a yield of about 30%. Star branched poly(benzyl methacrylate) (PBZMA) samples were prepared by group transfer polymerization.[3] The branched fractions were isolated by precipitation with petroleum ether.

RESULTS AND DISCUSSION

Figures 1 and 2 compare the molar mass versus the elution volume and RMS radius versus the elution volume plots of randomly branched PS samples with different extents of branching (i.e., containing different amounts of DVB). The figures show that the highly branched sample had abnormal SEC elution behavior: after the normal decrease of the molar mass or RMS radius with increasing elution volume, both plots curved up. This effect was more pronounced in the RMS radius versus the volume plot and resulted in a typical curvature of RMS radius versus the molar mass plot as seen in Figure 3. Figure 4 contrasts the RMS radius versus the molar mass plots of linear and highly branched PS samples. The plot of branched PS crosses that of the linear sample. The position of the crossing point was found to be related to the amount of branching and shifted toward higher RMS radii with an increasing level of branching. A comparison of the plots of randomly branched and star branched samples (Fig. 5) showed that randomly branched samples had a

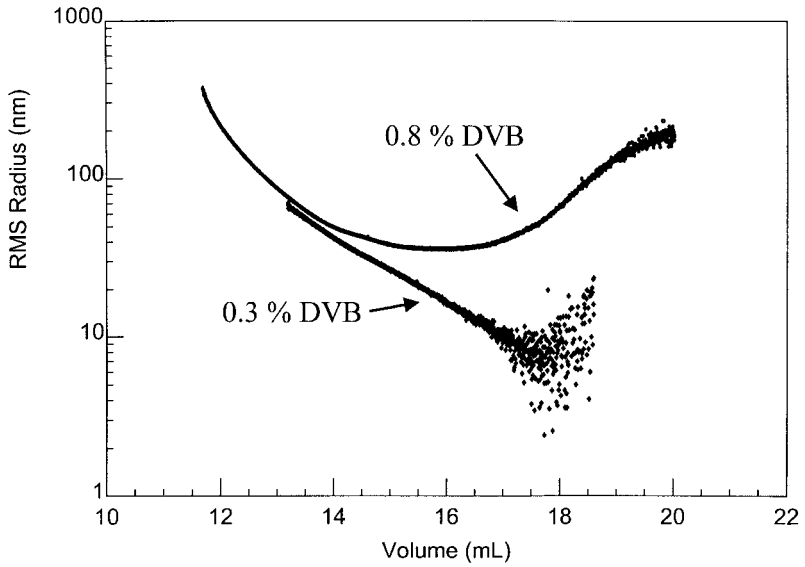

Figure 2 The RMS radius versus the elution volume plots of branched PS containing different amounts of DVB.

significantly higher tendency toward abnormal behavior.

The abnormal SEC behavior of branched polymers of various architectures and chemistries was reported by several authors[4–8] and explained in different ways. The following explanations of the abnormal SEC elution were reported in the literature: the presence of microgels,[4] adsorption,[5] large molecules spend too much time diffusing in and out of the column packing,[6] Argentinean bolas effect (i.e., entanglement of a part of the macromolecule in the column packing),[6,7] and sieving in the voids between packing spheres.[7] However, the retardation of branched molecules during SEC separation is a not yet a fully understood process. In order to get a better understanding and explanation of SEC abnormality, the following experiments were carried out using highly branched PS containing 0.8% DVB. Measurements at a low flow rate and at an elevated tem-

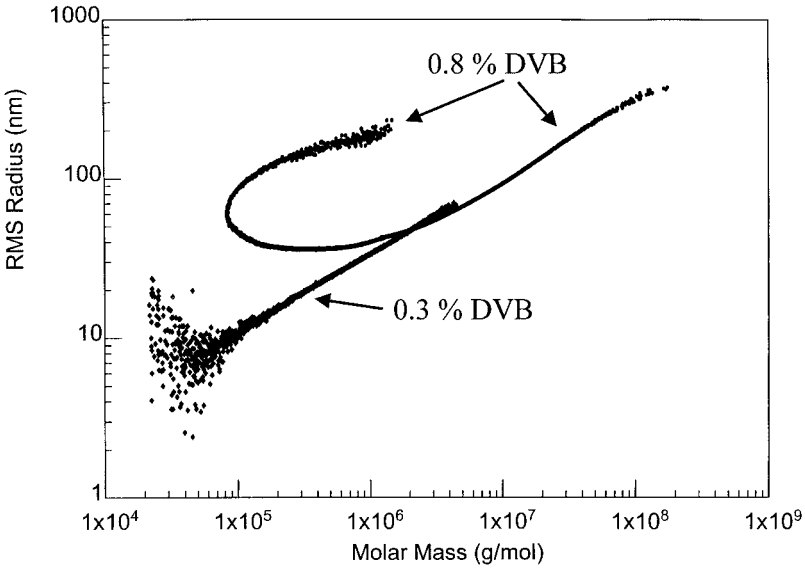

Figure 3 The RMS radius versus the molar mass plots of branched PS containing different amounts of DVB.

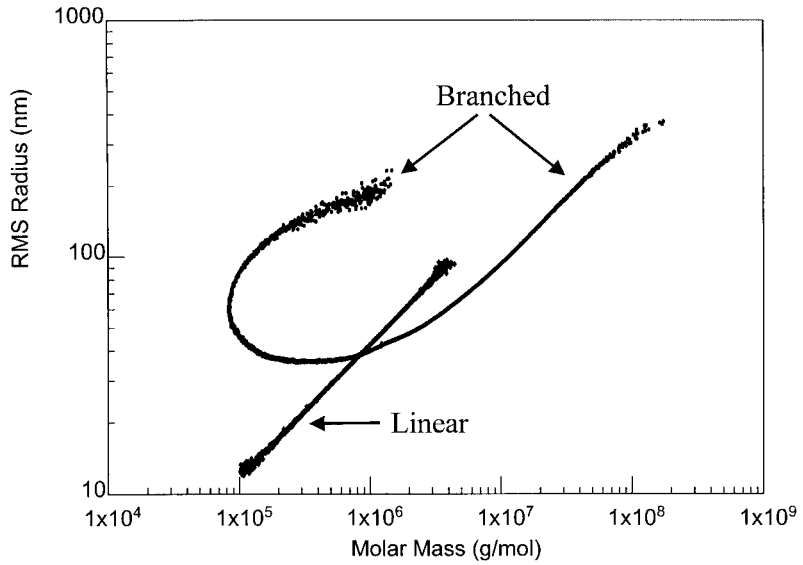

Figure 4 The RMS radius versus the molar mass plots of linear and highly branched PS determined by SEC–MALS.

perature of 60°C were made for the diffusion. An HPLC column (150 × 3.9 mm, 4 μm, C18) was connected between the injector and the SEC columns for the adsorption, sieving, and removing of microgels. The sample was centrifuged for 60 min at 100,000 × g prior to the analysis for microgel separation. An additional SEC column (Ultrastyragel 100 or 10^5 Å) was connected to a set of two Styragel HR 5E columns for adsorption, entanglement, and sieving. In addition, highly branched PS containing 0.8% DVB was analyzed by thermal FFF in order to see the effect of a quite different separation mechanism.

The elevated temperature or HPLC column had no effect on the sample of highly branched PS. Centrifugation of this sample removed a part of the highest molar mass fractions; however, an anomalous elution remained unchanged. The plot of the RMS radius against the molar mass was partly straightened at a low flow rate of 0.1 mL/min as demonstrated in Figure 6. The shape of the RMS radius versus the molar mass plot was

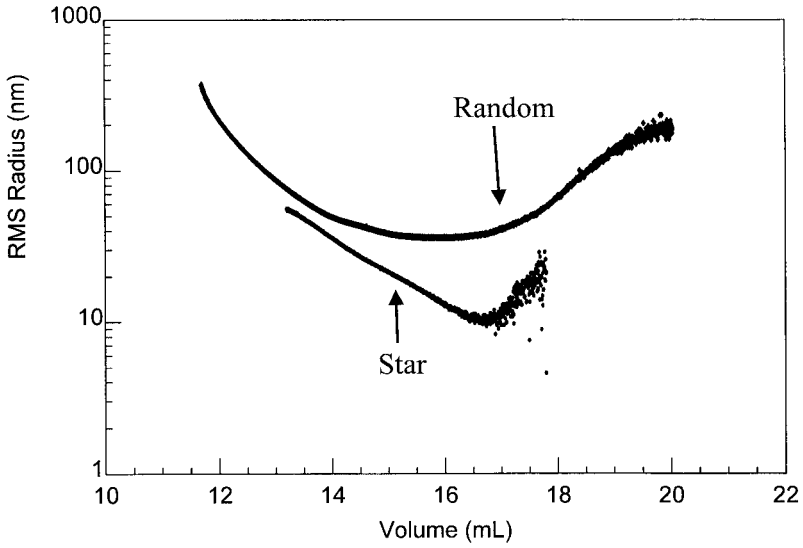

Figure 5 The RMS radius versus the elution volume plots of randomly branched PS and star branched PBZMA of comparable molar mass.

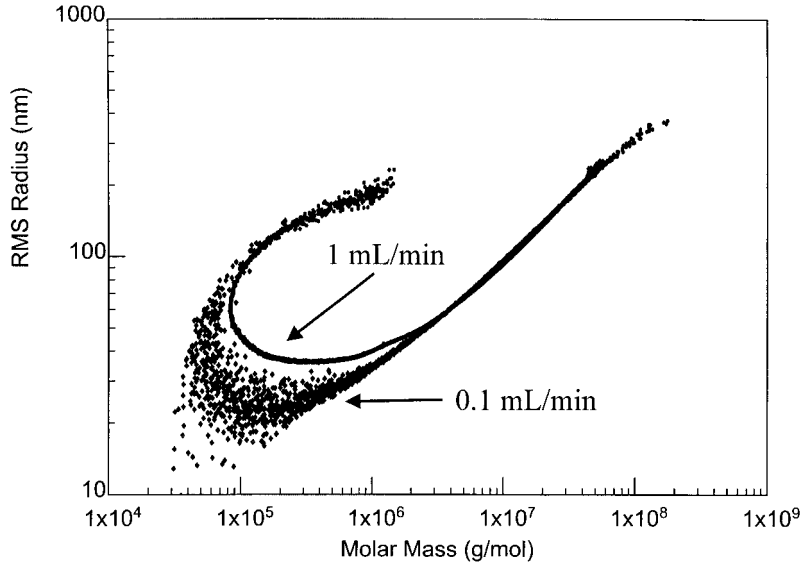

Figure 6 The effect of the flow rate on the RMS radius versus the molar mass plot of highly branched PS.

found to be sensitive to the SEC column system used for the separation, which can be seen in Figure 7.

An important finding was that the linear RMS radius versus the molar mass plot of the highly branched PS sample could be obtained by a thermal FFF–MALS technique as is demonstrated in Figure 8. The RMS radius versus the molar mass plots of highly branched PS determined by SEC–MALS and FFF–MALS overlapped in the region of RMS radii above about 70 nm. This proved good SEC separation in the region of large molecules.

Another important finding was that a very similar linear plot nearly overlaying that determined by thermal FFF–MALS was obtained by an experiment when the PS sample was first separated into four fractions of roughly identical size by multiple SEC analytical runs. Four fractions were collected from each run, and fractions from 10 runs were accumulated. The THF was evaporated

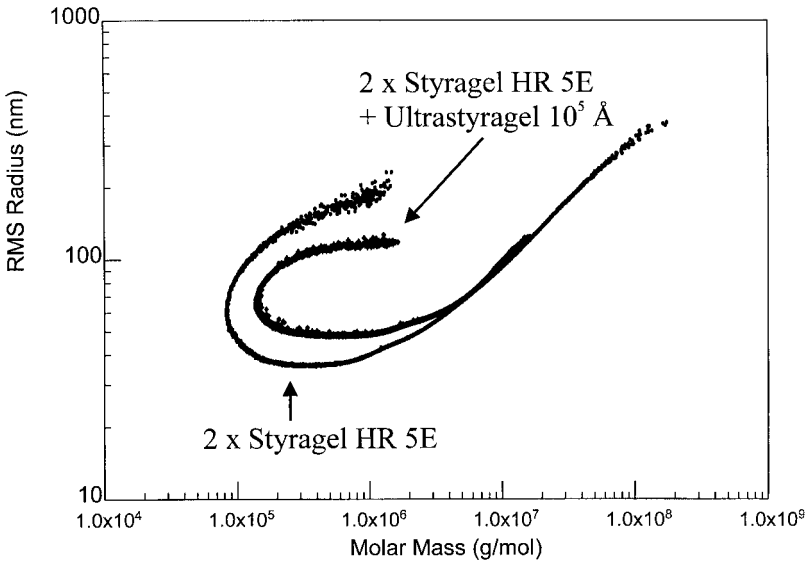

Figure 7 The effect of the type of SEC columns on the RMS radius versus the molar mass plot of highly branched PS.

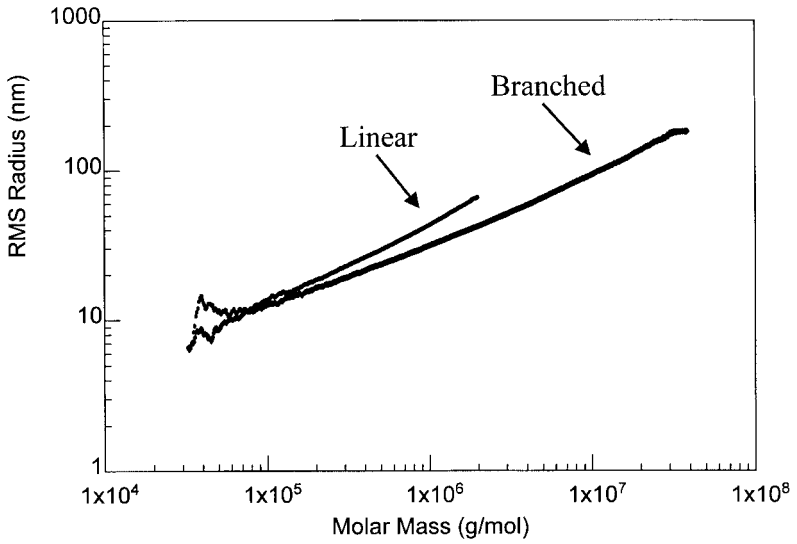

Figure 8 The RMS radius versus the molar mass plots of linear and highly branched PS determined by thermal FFF–MALS (cf. Fig. 4).

and the polymer was dissolved again in an amount of THF that gave an appropriate concentration for further SEC–MALS experiments. In spite of the curvature of particular plots, it was possible to construct a linear RMS radius versus the molar mass plot from linear segments of the three plots. This plot is depicted in Figure 9. A very similar result was obtained using fractions isolated by precipitation fractionation.

CONCLUSIONS

Retardation of large highly branched molecules was found during SEC separation. Because of the retardation, the large branched molecules coeluted together with normally eluting smaller molecules at the region of high elution volumes, which resulted in high polydispersity of the eluting fractions. Light scattering measures the *z* average of the RMS radius and the weight average of the molar mass. Because both quantities have different sensitivities to the presence of high molar mass fractions (the RMS radius *z* average being more sensitive), the RMS radius versus the molar mass plot shifts upward at regions of lower molar masses.

Because THF is a good solvent for PS, the retardation by adsorption in the crosslinked PS column packing is of low probability. Experiments

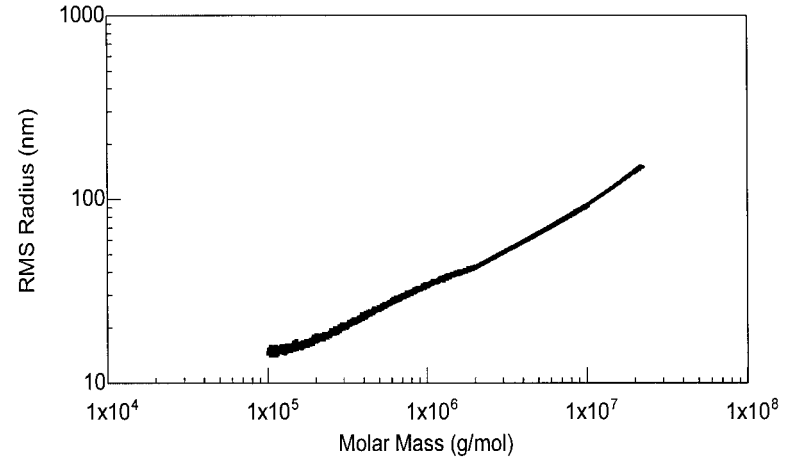

Figure 9 Linear sections of the RMS radius versus the molar mass plots of three fractions from four that were separated from highly branched PS by multiple SEC runs. The fraction with the highest molar mass is not shown.

with an HPLC column and sample centrifugation did not support the idea of extremely dense small particles (i.e., microgels).

The entanglement of large highly branched molecules in the column packing may explain the retardation. The large branched molecule may consist of several parts that may behave as separate molecules, penetrate into the column packing, and anchor the entire molecule. This idea is supported by a significant change of the shape of the RMS radius versus the molar mass plot due to connection of an additional 10^5 Å SEC column while a 100 Å column had only a minor effect. It suggests that the retardation takes place inside the column pores. More regular star branched molecules have less abnormal behavior, because more regular structures have lower possibility of entangling in the column packing. In the case of duplicate SEC–SEC separation the molecules retained during the first run were separated by the subsequent run. In the FFF separation there was no column packing and therefore no retardation.

SEC–MALS separated and characterized highly branched samples only in the high molar mass part of their molar mass distribution, but the SEC separation failed in the region of lower molar masses because of delayed elution of the large branched molecules. The characterization of highly branched samples can be improved by their separation into several fractions by either SEC or precipitation fractionation and subsequent SEC–MALS analysis of particular fractions. However, this is not convenient for routine work and therefore thermal FFF–MALS can be employed as an alternative powerful technique for the study and characterization of highly branched polymers.

REFERENCES

1. Wyatt, P. J. Anal Chim Acta 1993, 272, 1.
2. Podzimek, S. J Appl Polym Sci 1994, 54, 91.
3. Eastmond, G. C.; Webster, O. W. In New Methods of Polymer Synthesis; Ebdon, J. R., Ed.; Blackie Academic & Professional: Glasgow, 1993; Chap. 2, p 23.
4. Johann, C.; Kilz, P. J Appl Polym Sci Appl Polym Symp 1991, 48, 111.
5. Wintermantel, M.; Antonietti, M.; Schmidt, M. J Appl Polym Sci Appl Polym Symp 1993, 52, 91.
6. Frater, D. J.; Mays, J. W.; Jackson, C. J Polym Sci Part B: Polym Phys 1997, 35, 141.
7. Gerle, M.; Fischer, K.; Roos, S.; Müller, A. H. E.; Schmidt, M.; Sheiko, S. S.; Prokhorova, S.; Möller, M. Macromolecules 1999, 32, 2629.
8. Percec, V.; Ahn, C.-H.; Cho, W.-D.; Jamieson, A. M.; Kim, J.; Leman, T.; Schmidt, M.; Gerle, M.; Möller, M.; Prokhorova, S. A.; Sheiko, S. S.; Cheng, S. Z. D.; Zhang, A.; Ungar, G.; Yeardley, D. J. P. J Am Chem Soc 1998, 120, 8619.