Characterization of Model Branched Polymers by Multi-Detector SEC in Good and Theta Solvents

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Abstract: Well-defined linear and branched polystyrenes with complex architectures (regular combs and centipedes) were characterized via on-line size exclusion chromatography (SEC), in the good solvent tetrahydrofuran and the theta solvent trans-decalin, in order to measure their radii of gyration (R_g), hydrodynamic radii (R_H), and intrinsic viscosities. Various measures of the sizes of these macromolecules were plotted as a function of the retention volume (V_R) in order to examine the validity of different universal calibration strategies for SEC. Hydrodynamic-based calibration curves were found to be universal, whereas a plot of log R_g versus V_R did not yield universal curves in either solvent. These findings are consistent with previously published data for linear and branched polymers in thermodynamically good solvents. In addition, good solvent data were used to

derive values of the epsilon parameter relating radius of gyration-based and intrinsic viscosity-based chain shrinkage factors. Values of about 0.9 were found for both regular combs and centipedes.

INTRODUCTION

Size exclusion chromatography (SEC) has proven to be a valuable tool for characterization of polymers since its inception in the 1960s.[1] Conventional SEC employs calibration with linear standards, most commonly narrow molecular weight distribution (MWD) polystyrene (PS) standards since materials covering an extremely broad range of molecular weights may be purchased from commercial vendors. Conventional calibration curves thus generated are strictly valid only for linear PS and will generate erroneous results if applied to other linear polymers or to branched polymers, including PS. An important breakthrough in SEC calibration was the discovery by Grubisic et al. that SEC separates on the basis of hydrodynamic volume.[2] These researchers demonstrated that data plotted in the form of log ([η]M) versus V_R, where [η] is intrinsic viscosity, M is molecular weight, and V_R is retention volume, fell on a single curve for different polymer types and for different branched architectures and copolymers. Thus, if data on intrinsic viscosities are available for polymers being analyzed, the PS standard calibration can be converted to a universal calibration curve that will give accurate molecular weights. SEC universal calibration is important and widely used but somewhat controversial. Theory and simulations assume a thermodynamic separation principle for SEC based on the fact that hydrodynamic factors have little effect on molecular separation. Thus, most theories use the radius of gyration R_g as the relevant size parameter. However, recent work by Sun et al. and Teraoka have shown that the hydrodynamic radius (R_H) correlates better with elution behavior of branched molecules than does R_g.[3,4]

The use of on-line viscometers and on-line light-scattering detection has become popular in recent years, spurred by advances in instrumentation and computer interfacing.[5–7] The use of the viscosity detector facilitates universal calibration, and light-scattering detection can be used to directly measure the molecular weight of eluting fractions (calibration of the SEC is not required). Furthermore, whereas classical characterization of dilute solution properties required fractionation in order to obtain narrow molecular weight fractions with which to explore solution properties, the combination of light scattering and viscometry with SEC allows for the various fractions of a polydisperse sample to be characterized in a single injection.[8,9]

Recent developments have led to two-angle light-scattering (TALS) detectors (15° and 90°) capable of performing both static and dynamic light-scattering measurements on-line.[10,11] This advance in on-line measurements has allowed for improved characterization of polymers by investigating a number of different parameters. The ρ-ratio ($\rho = R_g/R_H$) provides information on the shape and conformation of linear and branched polymers in solution, in both good and theta solvents.[11] In terms of branched polymers, the g parameter[12] is defined as the ratio of the radius of gyration of the branched molecule to that of the linear molecule of the corresponding molecular weight.

$$g = \frac{\langle R_g^2 \rangle_b}{\langle R_g^2 \rangle_l} \tag{1}$$

The g parameter will always have values <1 for a branched polymer, reflecting the smaller dimensions of branched species. In a similar manner, the g′ contraction parameter is defined as the ratio of the intrinsic viscosity of a branched molecule to that of the linear molecule of the corresponding molecular weight.[9,13]

$$g' = \frac{[\eta]_b}{[\eta]_l} \tag{2}$$

These two branching parameters are related by a factor ε:

$$g' = g^\varepsilon \tag{3}$$

Zimm and Kilb predicted the value of ε to be $1/2$ for star polymers,[14] but there is still much debate about the value of ε for different branched architectures and whether the parameter is universal for all branched polymers.[13] A knowledge of the value of ε is of practical importance since R_g is often difficult to measure for branched polymers due to their smaller sizes and the corresponding lack of angular dependence of the scattering intensity. The intrinsic viscosity, however, can be measured accurately down to very low molecular weights, but a knowledge of the dependence of g′ on structure is not developed quantitatively as it is for g. Another important point is that the calculations used to derive the g branching parameter are based on the Gaussian coil approximation, which is closely approximated under theta solvent conditions.[12] However, very few SEC experiments are run under theta conditions, where polymer adsorption on the stationary phase would be a problem, but instead are nearly always carried out under good solvent conditions.[15,16]

In this study, R_g, R_H, and intrinsic viscosity data were generated via multi-detector SEC for regular comb and centipede polystyrenes in both a thermodynamically good solvent (tetrahydrofuran, THF) and a theta solvent (trans-decalin). These data allow a comparison of the various

methods for generating SEC universal calibration curves. In addition, these data are used in deriving the value of the ε parameter for these model multibranched polymers and in computing values of universal dilute solution parameters.

EXPERIMENTAL SECTION

Synthesis

The centipede and comb polymers used in this study were synthesized using anionic polymerization. The centipede polystyrene samples were previously prepared by Iatrou et al.,[17] while the comb polystyrene was previously synthesized by Nakamura et al.[10] A detailed account of the synthesis has been described in these articles and is summarized in Figures 1 and 2. The linear polystyrene sample used in this study was a commercial sample obtained from Aldrich with a reported weight-average molecular weight of 280,000.

Characterization

SEC investigation of the samples under good solvent conditions was performed in HPLC grade THF (obtained from Fisher Scientific) at a flow rate of 1 mL/min. 100 mL injections of polymer solutions with
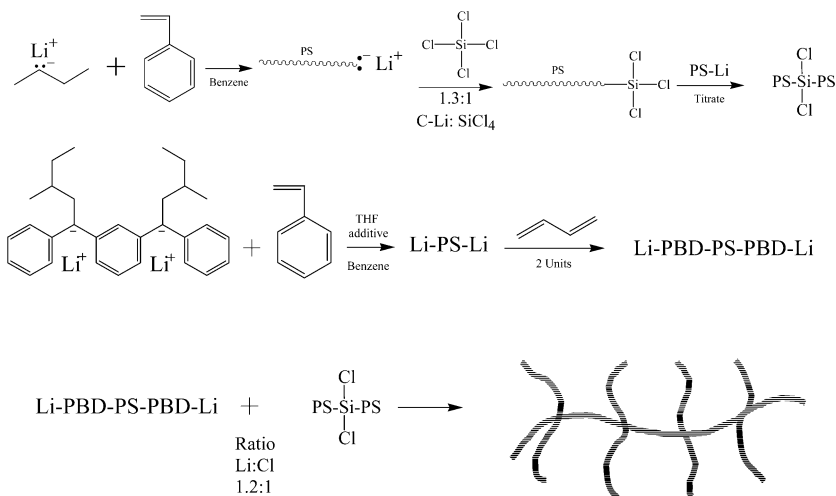
Figure 1. Polystyrene centipede synthesis. Notice that each regularly spaced branch point bears two branches.
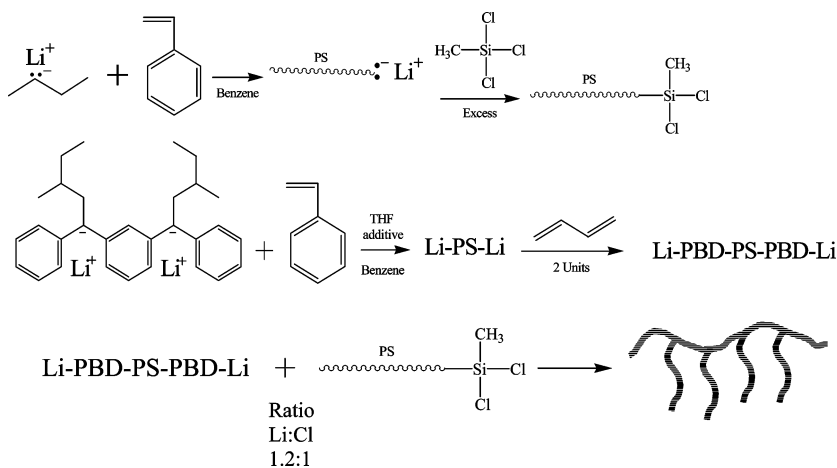
Figure 2. Polystyrene comb synthesis. Notice that each regularly spaced branch point bears one branch.

concentrations of about 1 mg/mL were used. The SEC unit was a Polymer Laboratories (PL) GPC-120 equipped with two PL-Gel 10 micron mixed B columns. Incorporated in the SEC was a Precision Detectors PD-2040 two-angle light-scattering detector for performing static (15° and 90°) and dynamic (90°) light-scattering (DLS) measurements. The system was also equipped with a Viscotek differential viscometer. The system was run at a reduced flow rate (0.5 mL/min) and higher concentration (10 mg/mL) to obtain a better signal-to-noise ratio for the DLS measurements. All of the measurements for THF were performed at 40°C. The light-scattering detectors were calibrated with a low polydispersity 50,000 molecular weight polystyrene standard. The refractive index increment (dn/dc) value used was $0.184 \, cm^3 g^{-1}$, measured on a Wyatt Optilab DSP detector at a wavelength of 690 nm and temperature of 40°C.

The SEC characterization of the samples under theta conditions was performed on the same instrument with a slightly different configuration. The theta conditions chosen were trans-decalin (TCI America) at 21–22°C, and the detectors were maintained at this temperature. The columns were heated separately in an Alltech 330 Column Heater to 110°C to obtain good solvent conditions preventing adsorption of the PS samples onto the columns. Trans-decalin has a high boiling point that allows for the higher temperatures to be maintained during the separation process to prevent adsorption.[18–20] This system was also run at a slower rate and higher polymer concentrations in order to obtain the DLS data. The detectors were also calibrated with the same polystyrene standard.

RESULTS AND DISCUSSION

Molecular characteristics of the polymers used in this study are presented in Table I. Using the chosen synthetic strategies, well-defined polymers with fixed spacing between branch points and fixed branch lengths were achieved. Also an advantage of the method is the ability to create samples that contain many species having different numbers of branch points, resulting from the final step-growth polymerization process that connects the backbone segments and side chains. Thus, in SEC the polymers are effectively fractionated according to their degrees of branching, with higher molecular weight polymers having larger numbers of branch points eluting first, followed by lower molecular weight polymers having fewer branch points. Thus, data on a variety of different branched species may be obtained in a single SEC experiment.

Radii of gyration for these polymers in THF and in trans-decalin at the theta temperature using multi-detector SEC and the instrumentation and methods described above have been previously reported by us.[21] In this work it was demonstrated that two-angle light scattering generates R_g and M values essentially identical to those generated using a sixteen-angle instrument. Furthermore, the power law exponents for linear PS in the two solvents exhibited their expected values, and branched specimens exhibited reduced radii of gyration relative to their linear counterparts.

Figure 3 shows a double logarithmic plot of the hydrodynamic radius versus the molecular weight for branched and linear PS samples in THF. The power law relationship for the linear sample falls within the range compiled by Fetters et al.[22] In this study we observed

$$R_H = 1.90 \times 10^{-2} \, M^{0.544} \tag{4}$$

compared with [22]

$$R_H = 1.44 \times 10^{-2} \, M^{0.561} \tag{5}$$

This agreement confirms the validity of the method, although it is clear that there is scatter in the data at the high and low molecular weight ends of the distributions, reflecting their lower concentrations. In general, the

Table I. Molecular characteristics of the branched polystyrenes

Polymer	M_{side}	M_{con}	r
CS25-35	35100	23100	1.52
g15-35	34400	15700	2.19
g40-25	28800	41200	0.70
g60-15	13500	57000	0.24

$r = (M_{side}/M_{con})$, CS = comb polymer, g = centipede polymer, $M_{con} = M_{connector}$.
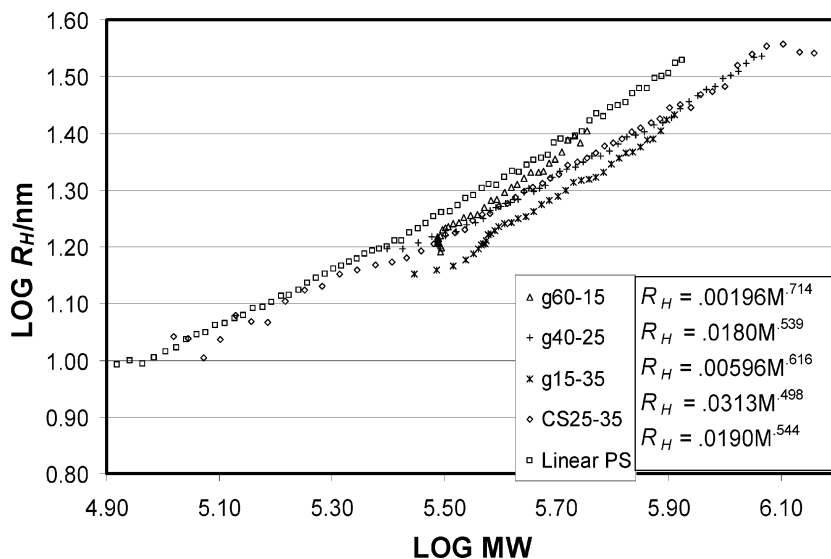
Figure 3. Comparison of the dependence of hydrodynamic radius on molecular weight range for different architectures in a good solvent (THF); g60-15 = △, g40-25 = +, g15-35 = *, CS25-35 = ◇, linear PS = □.

scatter is greater for on-line DLS data than for online static light scattering and intrinsic viscosity data.

The data for the branched polymers may also be fit by power laws. Clearly, these data fall below the line for the linear material, and this deviation is larger as the amount of mass in the polymer side chain is increased. Also, the centipede sample g40-25 curve coincides with the comb sample CS25-35 curve, reflecting the fact that, although one has a single branch at every branch point while the other has two branches at each branch point, each sample contains the same weight fraction of side chain.

These trends correlate well with the viscometry data (Figure 4). Again, the power law plot of the viscosity correlates well with data by Fetters and coworkers:

$$[\eta] = 1.21 \times 10^{-2} M^{0.718} \tag{6}$$

compared with [22]

$$[\eta] = 9.96 \times 10^{-3} M^{0.734} \tag{7}$$

As with the DLS data, the viscosity data for the branched polymers may also be well fit by power laws and the same branching trends are
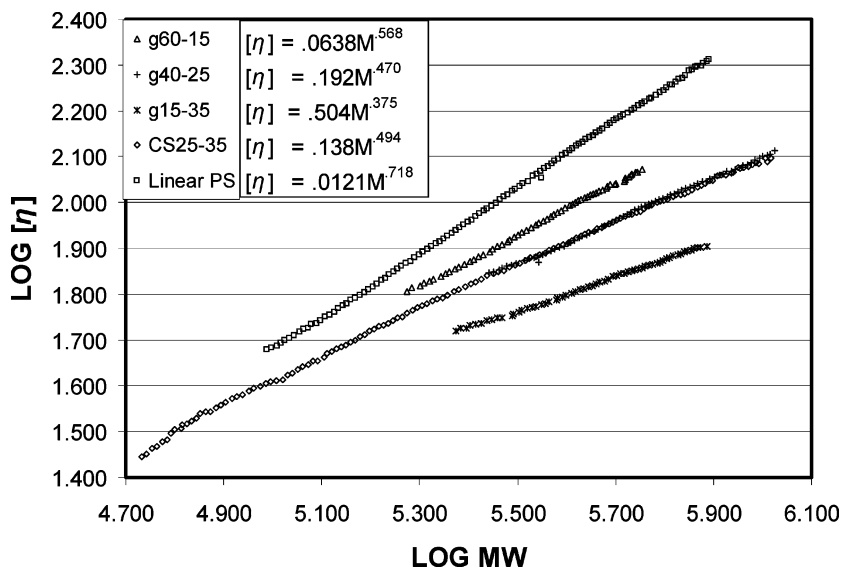
Figure 4. Dependence of intrinsic viscosity on molecular weight for different architectures in a good solvent (THF); g60 − 15 = △, g40-25 = +, g15-35 = *, CS25-35 = ◇, linear PS = □.

followed. For samples having a greater proportion of their mass in the side chain, the departure from the linear PS line increases, reflecting their smaller sizes. The data for the centipede sample g40-25 curve again coincide with that for the comb sample CS25-35, which has the same portion of its mass in the side chains. It is also obvious that the data obtained by on-line viscometry show less scatter than data obtained via DLS; nevertheless, the trends in the data are the same.

In Figure 5 the R_H data under theta conditions are summarized. It must be noted that we have assumed the theta temperature for the branched polymers to be the same as that for linear PS, and this assumption may not be strictly true, although differences would be expected to be small. The linear sample gives a power law relationship of

$$R_H = 4.09 \times 10^{-2} M^{0.451} \tag{8}$$

where the exponent is slightly smaller than the value of 1/2 expected in a theta solvent. The branched samples follow the same trends as in the good solvent. Unfortunately, we were unable to obtain reproducible viscometry data, apparently due to adsorption of the polymer on the capillary giving spurious data. A viscometer constructed of a different capillary material may provide a solution to this problem.
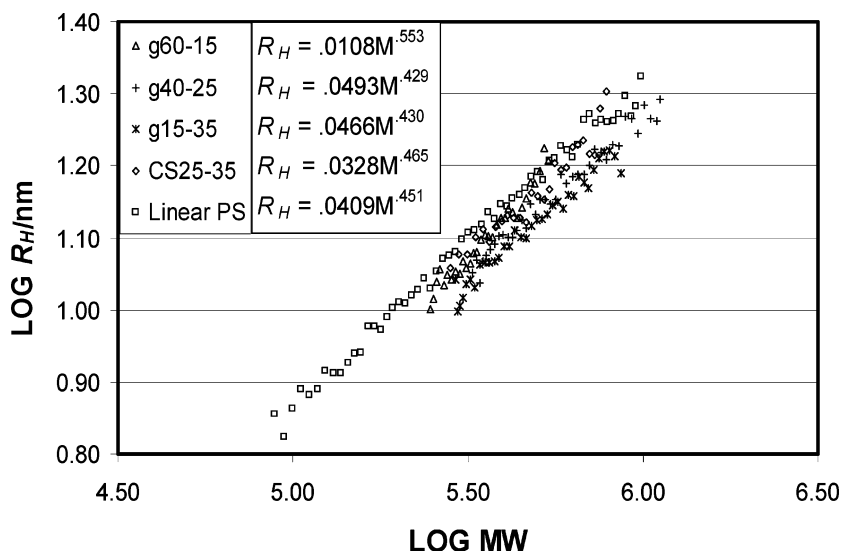
The chart legend contains:

- △ g60-15 $R_H = .0108M^{.553}$
- + g40-25 $R_H = .0493M^{.429}$
- * g15-35 $R_H = .0466M^{.430}$
- ◇ CS25-35 $R_H = .0328M^{.465}$
- □ Linear PS $R_H = .0409M^{.451}$

Y-axis: LOG R_H/nm, X-axis: LOG MW

Figure 5. Dependence of the hydrodynamic radius on molecular weight for different architectures in a theta solvent (trans-decalin); $g60 - 15 = \triangle$, $g40\text{-}25 = +$, g15-35 = *, CS25-35 = ◇, linear PS = □.

Since values of both g′ and g were obtained for the samples in the good solvent, THF, we can calculate the exponent ε for these comb and centipede samples. In Table II we summarize the values calculated for polymers having regularly spaced branch points in this study and compare them with values reported previously for combs having randomly spaced branch points.[13,23–25] We report a range of ε values because ε changes slightly as the molecular weight changes in our samples. Recall that the number of branch points increases as the molecular weight of the polymer increases for these polydisperse specimens. It is

Table II. ε values for regular and random combs and regular centipedes

Polymer	ε values	Reference
Regular comb	0.8–0.9	This work
Random comb	0.9–1.1	Hadjichristidis et al.[23]
Random comb	0.7–1.0	Roovers[24,25]
Random comb	0.95	Radke and Mueller[13]
Regular centipedes		
g60-15	0.7–1.0	This work
g40-25	0.8–0.9	This work
g15-35	0.8–0.9	This work

clear from Table II that a value of ε of approximately 0.9 is a good fit for all of these multibranched polymers. Interestingly, values of about 0.9 have also been determined for randomly branched poly(methyl methacrylate) in the good solvent THF.[9] Furthermore, our present results also find good agreement with theory reported by Berry, who suggested that as the fraction of monomer units in the backbone increases for a range of the number of branches per molecule ε tends towards unity.[26]

The availability of both thermodynamic and hydrodynamic parameters for the model branched polymers also allows us to compute various "universal ratios." The Φ parameter, also known as the Fox-Flory factor, has been shown to fluctuate with varying architecture.[26]

$$M[\eta] = 6^{3/2}\Phi R_g^3 \tag{9}$$

The Φ parameter is often called a universal constant, but in reality its value depends on architecture, local solvent conditions, and local structure.[27] In Figure 6, we plot the experimentally determined Φ values as a function of molecular weight of the polymer samples. We obtain a value for the linear material that corresponds with the literature value of $1.8 \times 10^{23}\,\text{mol}^{-1}$, which is for polymers in a good solvent, approximating the case of polystyrene in THF.[8] It is interesting that the curves of g40-25 and CS25-35 also coincide with one another, as they do in Figures 1–4. It is evident from the plots that Φ changes with the changing architectures of each sample and is not constant.
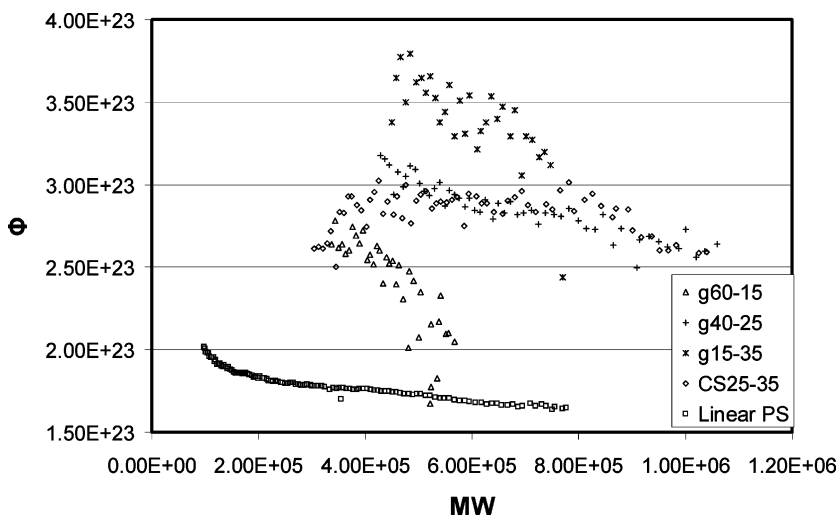

Figure 6. Dependence of the Fox-Flory factor Φ on molecular weight; g60 − 15 = △, g40-25 = +, g15-35 = *, CS25-35 = ◇, linear PS = □.

Table III. ρ values for regular and random combs and regular centipedes

Sample	ρ (trans-decalin)	ρ (THF)
Linear PS	1.13	1.32
CS25-35	1.15	1.04
g60-15	1.23	1.13
g40-25	1.15	1.04
g15-35	1.04	0.96

The ρ parameter is the ratio of the radius of gyration to the hydrodynamic radius and is expected to exhibit values of 1.2–1.5 for linear random coils and 0.775 for a hard sphere.[28] In Table III measured values of ρ for all the samples are compared in good and theta solvents. The values for linear PS are in the expected range, and as the relative amount of mass in the side chain of the branched polymers increases, ρ exhibits lower values, smaller than that for linear coils and approaching hard sphere behavior, which has been observed for highly branched species like many-armed stars.[29]

The Flory-Scheraga-Mandelkern β parameter

$$\beta = (M[\eta]/100)^{1/3}/6\pi \, R_H \qquad (10)$$

exhibits values that decrease slightly from the linear chain theta solvent value ($2.27 \times 10^6 \, \text{mol}^{-1/3}$) with improved solvent quality and branching. We find values of 2.0×10^6 for linear PS in THF and values of 1.8–1.9×10^6 for the regular combs and centipedes in THF. These values are close to the value of $\beta = 2.05 \times 10^6$ reported for many-armed stars in a theta solvent.[30]

In Figures 7–11 we use the various data obtained to construct "universal calibration curves." Figure 7 is a plot of the universal calibration curve based on hydrodynamic volume ($[\eta]M$) in THF for all the polymers used in this study. While there is some scatter in the data, this plot appears to be effective for reducing data for branched and linear polymers to a common calibration curve. In Figures 8 and 9, we compare, respectively, the plots of R_g and R_H versus V_R of the polymers in the good solvent THF. While neither plot is as good as the standard hydrodynamic calibration plot, clearly R_H does a much better job than R_g of reducing the data for linear and branched polymers to a common curve. In Figures 10 and 11, we plot R_g and R_H versus V_R under theta solvent conditions. The latter plot nicely reduces all the data to a single universal calibration curve, while the former plot fails to do so. Other recent work has shown that R_H correlates better with elution behavior
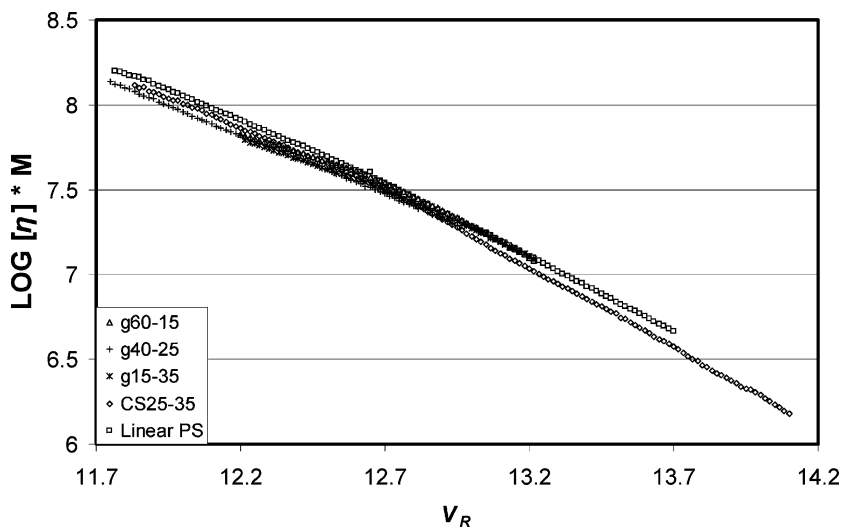
Figure 7. Traditional universal calibration of $[\eta] * M$ versus retention volume; $g60 - 15 = \triangle$, g40-25 $= +$, g15-35 $= *$, CS25-35 $= \Diamond$, linear PS $= \square$.
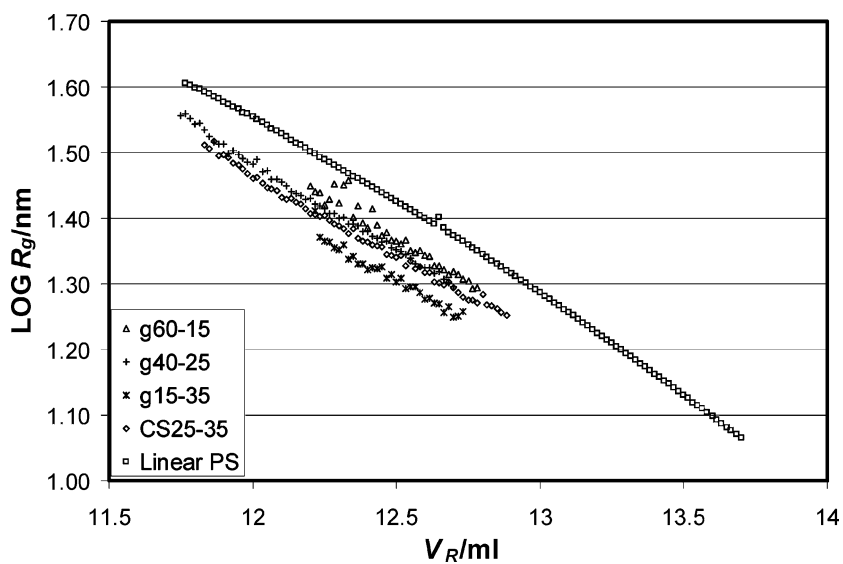

Figure 8. Universal calibration based on log radius of gyration versus retention volume in the good solvent (THF); $g60 - 15 = \triangle$, g40-25 $= +$, g15-35 $= *$, CS25-35 $= \Diamond$, linear PS $= \square$.
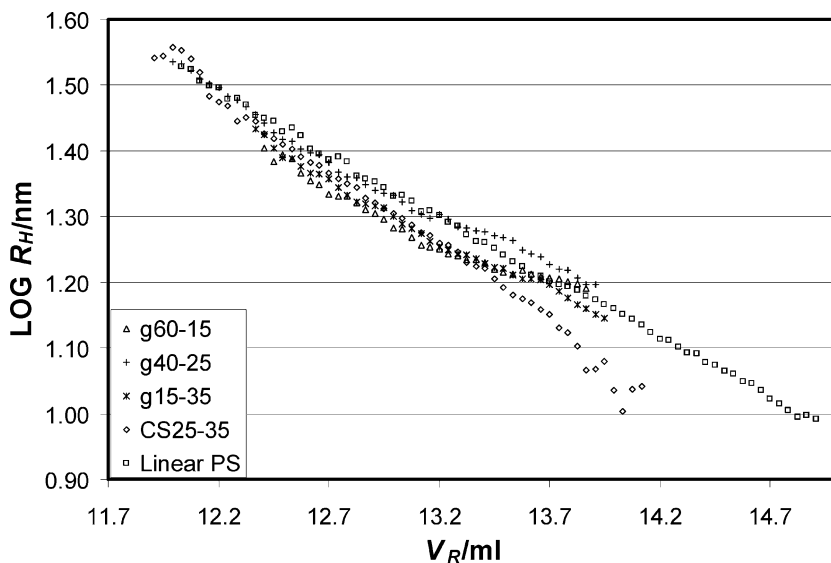
Figure 9. Universal calibration based on log hydrodynamic radius versus retention volume in the good solvent (THF); $g60 - 15 = \triangle$, $g40\text{-}25 = +$, $g15\text{-}35 = *$, $CS25\text{-}35 = \diamond$, linear PS $= \square$.

Figure 10. Universal calibration based on log radius of gyration versus retention volume in the theta solvent (trans-decalin); $g60 - 15 = \triangle$, $g40\text{-}25 = +$, $g15\text{-}35 = *$, $CS25\text{-}35 = \diamond$, linear PS $= \square$.
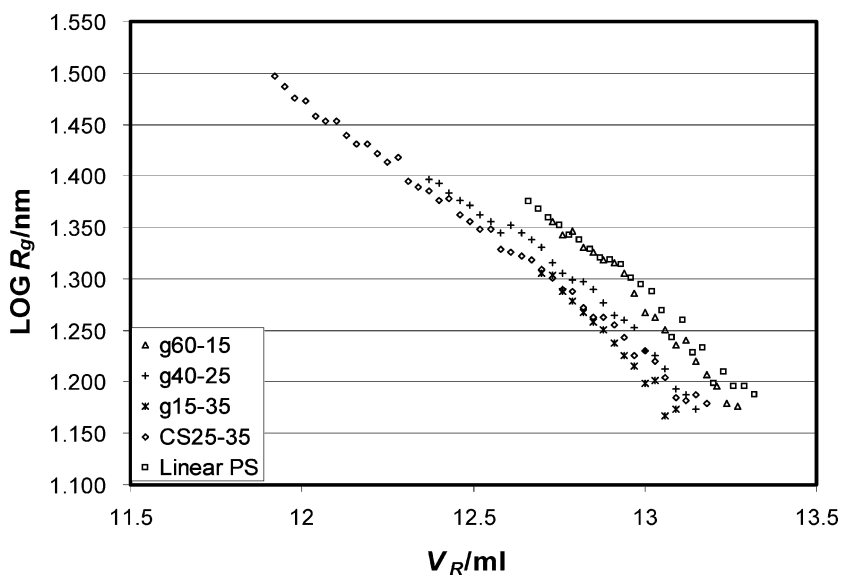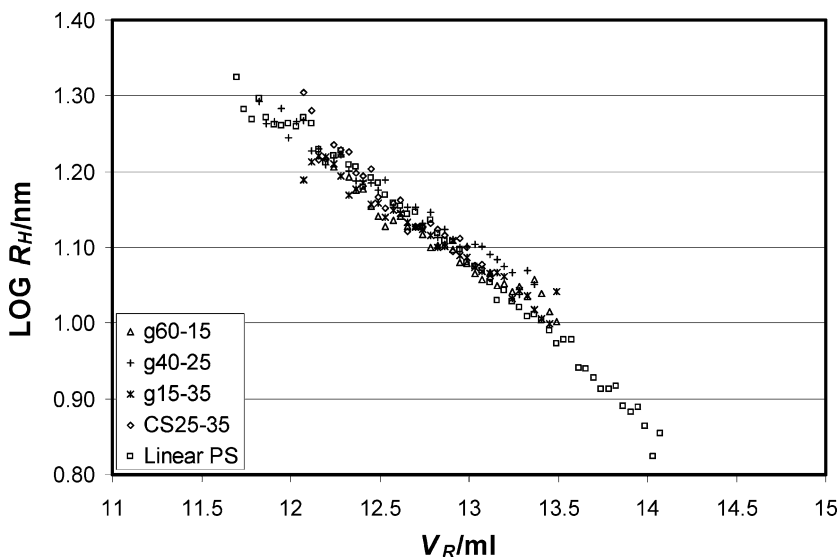
Figure 11. Universal calibration based on log hydrodynamic radius versus retention volume in the theta solvent (trans-decalin); $g60 - 15 = \triangle$, $g40\text{-}25 = +$, $g15\text{-}35 = {}^*$, $CS25\text{-}35 = \diamondsuit$, linear $PS = \square$.

of branched chains than does R_g.[3,4] Figures 9 and 11 match well with the theory proposed by Teraoka, but universal calibration by hydrodynamic volume is generally still a better choice for calibrating SEC, even in the case of branched molecules. A very noticeable feature of all the figures is that the same samples g40-25 and CS25-35 coincide in every instance.

CONCLUSIONS

SEC with on-line static and dynamic light-scattering and intrinsic viscosity detectors was used to probe the dilute solution properties of linear, regular comb, and regular centipede polystyrenes in both good and theta solvents. Measurements under theta conditions were made possible by choosing trans-decalin as a theta solvent. This solvent is a theta solvent for linear PS at room temperature, and its high boiling point allows the chromatography to be conducted at elevated temperatures where it becomes a good solvent for PS, avoiding adsorption of the polymer on the stationary phase. In this work, SEC with static and dynamic light-scattering detection, plus viscometry, has thus been shown to be a powerful technique for generating comprehensive dilute solution property data on polymers, even under theta conditions. The ε parameter

relating g and g′ was shown to have a value of about 0.9 for regular comb and regular centipede polystyrenes, in agreement with theory and data on random combs and certain randomly branched polymers. All dilute solution properties measured were found to be in agreement with theory and other experimental studies on branched polymer systems. It must be noted here that although our intrinsic viscosity studies failed under theta conditions, this is attributed to adsorption in the viscometer capillary rather than an inherent limitation of the technique. Generation of precise DLS data, using the present instrumentation, requires the use of reduced flow rates to enhance the signal-to-noise ratio in the correlation functions.

Traditional SEC universal calibration based on hydrodynamic volume is the best method at this time. The use of the hydrodynamic radius also gives fairly good universal calibrations, but radius of gyration is not a useful parameter for generating SEC universal calibration curves.

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