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International Journal of Polymer Analysis and Characterization

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713646643>

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To cite this Article Jackson, Christian(1996) 'On the Accuracy of Molecular Weight and Radius of Gyration Measured by Right-Angle Light Scattering with SEC-Viscometry', *International Journal of Polymer Analysis and Characterization*, 2: 4, 425 – 437

To link to this Article: DOI: 10.1080/10236669608033360

URL: <http://dx.doi.org/10.1080/10236669608033360>

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On the Accuracy of Molecular Weight and Radius of Gyration Measured by Right-Angle Light Scattering with SEC-Viscometry

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(Received October 16, 1995; in final form January 25, 1996)

The use of a right-angle light scattering detector with a size exclusion chromatograph equipped with an online viscometer provides a convenient method of estimating polymer molecular weight distribution. The 90° scattered intensity provides an initial estimate of the molecular weight at each elution slice. This value is then improved using an estimate of the light-scattering asymmetry based on the measured intrinsic viscosity in order to determine the 0° scattering intensity required to obtain the true molecular weight. In addition, an estimate of the radius of gyration can be obtained. In this paper the accuracy of the method is examined for different linear polymers and also for branched polymers. In most cases molecular weights within 2% of the true values can be obtained up to 1×10^6 g/mol. Errors are about 5% for molecular weights of 2×10^6 g/mol and rapidly increase for higher molecular weights. The errors in the radius of gyration estimated using this method are higher (~ 10%); however, the viscometric radius is determined with high accuracy.

KEY WORDS Polymer characterization, size exclusion chromatography, light scattering, viscometry, molecular weight, molecular weight distribution, radius of gyration.

INTRODUCTION

The molecular weight of a polymer in dilute solution can be determined by measuring the excess light scattered at a range of angles relative to the incident light beam for different concentrations using Zimm's double extrapolation method, to zero angle and to zero concentration [1,2]. When light scattering is combined with size exclusion chromatography (SEC) the concentration of the polymer solution as it elutes from the columns through the light-scattering detector measurement cell is generally so low that concentration effects are negligible so that the polymer concentration can be assumed to be zero, and the extrapolation to zero concentration is not required (Appendix 1). The extrapolation of the scattered intensity to 0° is still required in order to correct for the variation of the scattered intensity with angle θ caused by interference between light scattered from different segments of the same polymer molecule. This variation is described by the particle scattering

function $P(\theta)$, which is solely a function of the radius of gyration R_G at low angles for a given wavelength [2]. Measurement of the scattered intensity at low angles can be difficult because small amounts of dust and other particles in the solution can scatter as much light as the polymer molecules and can distort the results. One method to avoid this problem is to measure the light scattered at right angles to the incident beam and correct for the scattering asymmetry using an estimate of the radius of gyration based on the intrinsic viscosity $[\eta]$ and molecular weight M and a known form of the particle scattering function [3]. The estimated radius of gyration and the scattering function are used to calculate the 0° scattered intensity and thus the molecular weight.

Recently, light scattering was combined with SEC to estimate the molecular weight and radius of gyration at each fraction of the molecular weight distribution using a right-angle light scattering (RALS) detector and an online viscometer [4,5]. Accurate molecular weights were obtained up to 1×10^6 g/mol, although it was anticipated that errors would increase at higher molecular weights. In this paper the accuracy of this method is investigated by applying the algorithm to calculated right-angle scattered intensities for linear and branched molecules over the molecular weight range 1×10^3 to 10×10^6 g/mol. The precision of the method is not discussed, although it should be noted that the iterative algorithm described below requires precise initial data and is sensitive to noise and baseline setting errors at the peak edges for high-molecular-weight materials. Discussion of the accuracy of other SEC-light scattering methods, such as low-angle light scattering and multiangle light scattering can be found in refs [6–10].

BACKGROUND

The SEC-Visc-RALS method is based upon estimating the polymer radius of gyration from measurements of the intrinsic viscosity and the molecular weight. The relationship between the intrinsic viscosity and the radius of gyration of a polymer in solution has been the subject of numerous theoretical and experimental studies. Both properties provide a measure of the average size of the polymer molecule in solution. However, although the average size values obtained are very similar, the properties measured are quite different; the radius of gyration measures the mean square distance of each segment of the polymer chain from the center of mass, whereas the intrinsic viscosity gives an effective hydrodynamic radius for the polymer in shear flow.

Under Θ conditions, the radius of gyration and intrinsic viscosity are found to obey a nearly universal relationship described by the Flory-Fox relationship [11]

$$R_G^3 = \left(\frac{[\eta] M}{\sqrt{6} \phi_\Theta} \right) \quad (1)$$

where ϕ_Θ is the Flory viscosity constant with experimental and theoretical values found in the range of 2.0 – 2.7×10^{23} mol⁻¹ [12]. Both the intrinsic viscosity and the radius of gyration scale with the square root of the molecular weight and so the equation is accurate over a wide molecular weight range.

In a good solvent excluded volume interactions between different parts of the polymer chain must be considered and they cause the value of both the radius of gyration and intrinsic viscosity to be larger. The value of the viscosity constant can be modified to account

for excluded volume effects, for example, using the model of Ptitsyn and Eizner [13,14] where

$$\phi = (1 - 2.63\varepsilon + 2.86\varepsilon^2) \phi_{\theta} \quad (2)$$

and

$$\varepsilon = \frac{2a-1}{3} \quad (3)$$

where a is the Mark-Houwink exponent. This gives a lower value for the viscosity function than in the Θ system, that is, the intrinsic viscosity is lower for a given radius of gyration than it is in the Θ system. However, modifications of the value of ϕ do not account for the experimental data. In a good solvent the radius of gyration of a flexible polymer generally scales with $M^{3/5}$. If the Flory-Fox relation held then the intrinsic viscosity should scale as $M^{4/5}$. In practice the molecular weight exponent for the intrinsic viscosity is rarely this high but is generally in the range 0.60–0.75. As a result the modified Flory-Fox relationship becomes increasingly inaccurate as molecular weight increases because the viscometric radius does not increase with molecular weight as fast as the radius of gyration does. This deviation between the scaling behavior of the two radii measurements does not appear to be universal; the differences are specific to a given polymer-solvent system and appear to depend on the effect of details of the chain structure on the hydrodynamic interaction and possibly the extent of partial draining of solvent through the polymer domain [15–19].

In the following discussion it should be kept in mind that the accuracy of the results produced by SEC-Visc-RALS algorithm depend on the accuracy of the theoretical understanding of the dilute solution properties of polymers. It is the deviation of these properties from “universal” behavior that lead to errors in the results.

METHODOLOGY

The basic algorithm for estimating molecular weight and radius of gyration from the SEC-Visc-RALS experiment is as follows:

Step 1. For the i^{th} -elution slice of the chromatogram, the intrinsic viscosity $[\eta]$, and initial molecular weight estimate M_{initial} are measured, where the initial molecular weight is determined from the normalized scattered intensity at 90° , $R(\theta = 90^\circ)$, by

$$M_{\text{initial}} = \frac{R(\theta = 90^\circ)}{K^* c_i} \quad (4)$$

where K^* is an optical constant for the polymer-solvent scattering system and c_i is the concentration of the polymer solution at the i th slice.

Step 2. The radius of gyration is estimated using some form of the Flory-Fox relationship (Equation (1)).

Step 3. The estimate of the radius of gyration is used to calculate the value of the particle scattering function at 90° . The particle scattering function for a Gaussian coil is given by the Debye function

$$P(\theta) = \frac{2}{x^2}(e^{-x} - (1-x)) \quad (5)$$

where

$$x = 16\pi^2 \left(\frac{\langle R_G^2 \rangle}{\lambda_s^2} \right) \sin^2(\theta/2) \quad (6)$$

where θ is the angle with respect to the incident beam and λ_s is the wavelength of the incident light in the solvent $\lambda_s = \lambda_0/n$, and λ_0 is the wavelength *in vacuo* and n is the solvent refractive index.

The value of $P(\theta)$ at 90° is then used to estimate the scattered intensity at 0° using

$$R(\theta = 0^\circ) = \frac{R(\theta = 90^\circ)}{P(\theta = 90^\circ)} \quad (7)$$

A revised estimate of molecular weight based on the estimated zero degree scattered intensity can then be determined

$$M = \frac{R(\theta = 0^\circ)}{K^* c_i} \quad (8)$$

Step 4. In general, the initial estimate of the radius of gyration will be less than the true value because the initial estimate of molecular weight will be less than the true molecular weight. As a result, the molecular weight in Equation (8) will be an underestimate of the true value. This error can be minimized by repeating steps 2 and 3 using the new estimate of molecular weight from Equation (8) instead of the initial estimate from Equation (4). The molecular weight can be recalculated in such an iterative fashion until the value is judged satisfactory, for example when the algorithm no longer significantly changes the calculated values.

This algorithm was applied to three polymers, polystyrene, polybutadiene and poly(octadecyl methacrylate), which were modeled using relationships between radius of gyration and intrinsic viscosity with molecular weight determined in our laboratory [20,21]. These values are listed in Table I. A discussion of the precision of these values can be found in ref [20]. Values for polystyrene were used for most of the calculations, polybutadiene was used as a model of a more flexible chain, and poly(octadecyl methacrylate) was used as a model chain with bulky side groups. All values are in tetrahydrofuran at 30 C.

TABLE I

Coefficients in the relationships between molecular weight and intrinsic viscosity and radius of gyration used in this study.

Polymer	Coefficients in $[\eta] = K M^a$		Coefficients in $R_g = K' M^v$	
	K (dL/g) $\times 10^4$	a	K' (nm) $\times 10^2$	v
Polystyrene	1.14	0.716	1.12	0.60
Polybutadiene	2.52	0.727	1.60	0.60
Poly(octadecyl methacrylate)	0.16	0.783	0.39	0.65

The methodology used was to calculate the radius of gyration and the intrinsic viscosity for a given molecular weight, from the coefficients given in Table I. The scattered intensity is calculated from the radius of gyration and used to give the initial estimate of molecular weight. The algorithm described above was then applied to this estimate and the final values were compared with the true values. The laser wavelength was taken as 633 nm and the refractive index of THF was 1.404. A calculation example is given in Appendix 2.

For the branched model, the radius of gyration and intrinsic viscosity were calculated by multiplying the linear values by the respective branching contraction factors g and g' [22,14]

$$\langle R_G^2 \rangle_{\text{branched}} = g \langle R_G^2 \rangle_{\text{linear}} \quad (9)$$

$$[\eta]_{\text{branched}} = g' [\eta]_{\text{linear}} \quad (10)$$

The relationship between the two branching factors was assumed to be

$$g' = g^\varepsilon \quad (11)$$

with $\varepsilon = 1$, i.e., $g' = g$.

RESULTS AND DISCUSSION

For the first series of calculations, polystyrene was used as the model and the expected scattered intensity at 90° was calculated from Equation (5). Then Equations (5) and (1) were used to correct for the scattering asymmetry. A value of $2.7 \times 10^{23} \text{ mol}^{-1}$ was used for the Flory viscosity constant [19]. Figure 1 shows the ratio of the estimated molecular weight to the true molecular weight for a range of molecular weights from 10^3 to 10^7 g/mol. Data are shown for the initial molecular weight estimate, based on the right-angle scattered intensity, and for values obtained using Θ solvent and good solvent values of the viscosity constant after ten iterations of the correction algorithm. With no asymmetry correction, the molecular weight is underestimated by 5% for a molecular weight of about 2.5×10^5 g/mol and the error increases rapidly for higher molecular weights. After three iterations, the molecular weight is underestimated by 5% at 8×10^5 g/mol. Further iterations of the algorithm produce no significant improvement in the result. The reason that the molecular weights are increasingly underestimated at higher molecular weights is that the viscometric size does not increase as rapidly with molecular weight as the radius of gyration for a polymer in a good solvent, so that the radius of gyration is increasingly underestimated by the Flory-Fox relationship. The first calculation used the Θ -point value for the viscosity constant. In the SEC experiment the polymer must be in a good solvent, to eliminate interactions with the column packing, and so will be in an expanded state. If we assume that the Mark-Houwink exponent for this system is unknown and assume a typical value of 0.725, we obtain $\varepsilon = 0.15$ and $\phi = 1.80 \times 10^{23} \text{ mol}^{-1}$. The result of using this modified value is also shown in Figure 1. The molecular weight can be estimated with an error less than 5% up to about 3×10^6 g/mol after ten iterations of the algorithm. Further iterations produce no improvement in the calculated value.

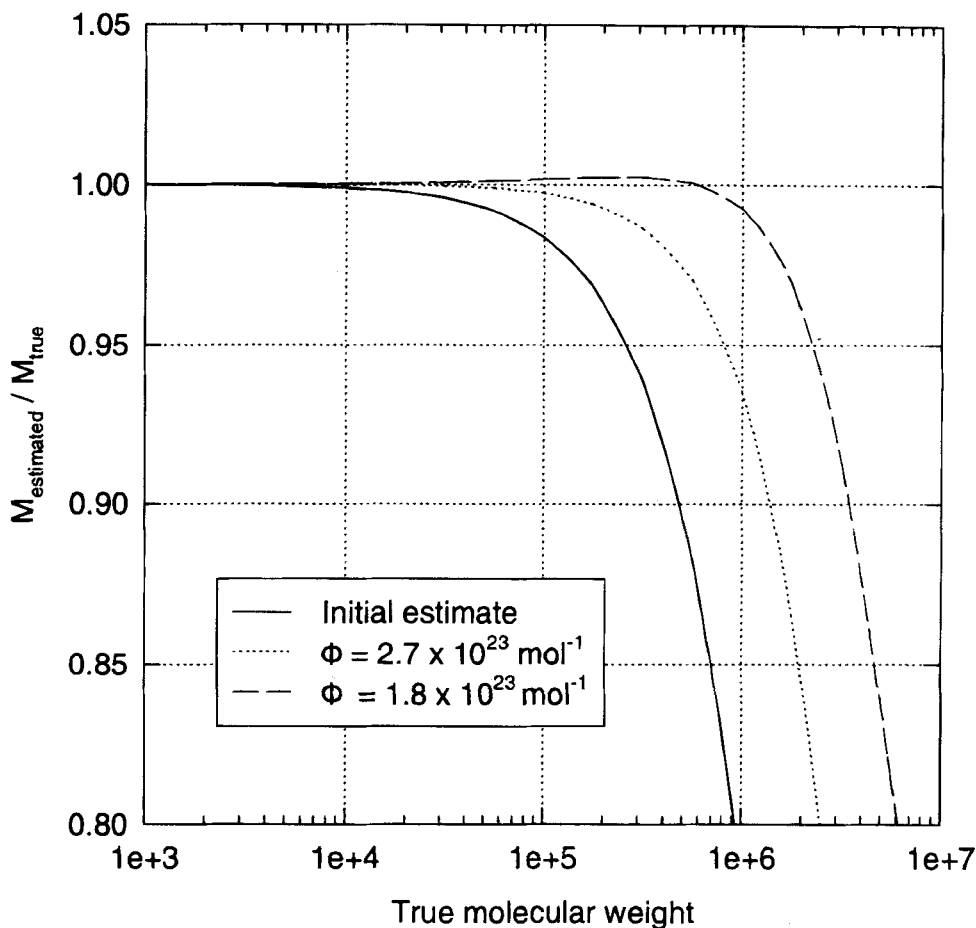


FIGURE 1 The ratio of the molecular weight estimated from right-angle scattering to the true molecular weight plotted against the true molecular weight for the model based on polystyrene. The initial estimate is from the right-angle intensity. The results from the iterative correction to the scattered intensity based on different values of ϕ are also shown for ten iterations.

A further refinement to the model is introduced by calculating the 90° scattered intensity using the particle scattering function for a polymer chain in a good solvent. The scattering functions for a polymer in Θ ($\epsilon = 0$) and good solvents ($\epsilon = 0.15$) at 90° are shown as a function of radius of gyration in Figure 2. The calculated values of the scattering functions are taken from ref [23]. The results obtained by using the good solvent scattering function to calculate the 90° scattered intensity, but still using the Debye relationship for the scattering function (Equation (5)) in the correction algorithm are shown in Figure 3. The error in molecular weight reaches 5% at 4×10^6 g/mol using ten iterations of the algorithm. However, for higher molecular weights, the direction of the error changes and for molecular weights above 1×10^7 g/mol the molecular weight is overestimated. This is because the slightly higher scattering at 90° for a given radius of gyration in a good solvent compared to a Θ solvent compensates, to some extent for the fact that the viscomet-

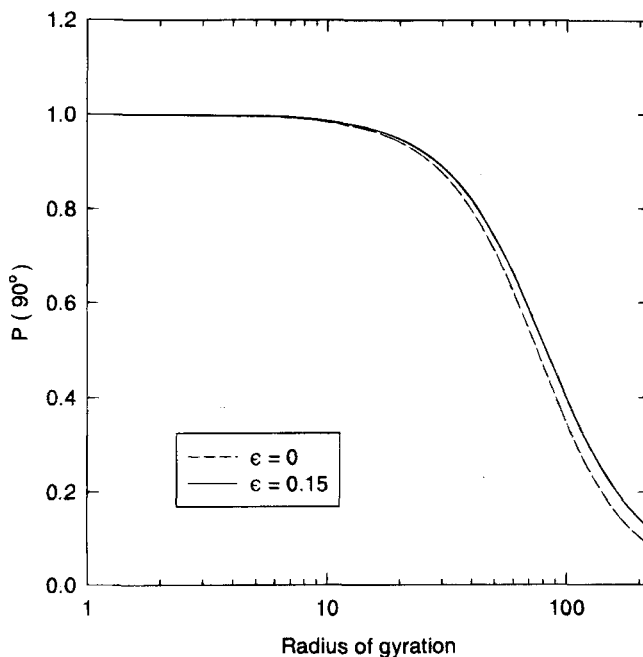


FIGURE 2 The value of the particle scattering function at 90° as a function of radius of gyration for an ideal chain (Θ conditions) and for a chain with excluded volume (good solvent conditions).

ric radius is not increasing as rapidly with molecular weight as the radius of gyration. There is thus some cancellation of errors at higher molecular weights.

Figure 4 shows the estimated values of the radius of gyration for the same calculation as in Figure 3 with $\phi = 1.80 \times 10^{23} \text{ mol}^{-1}$. It can be seen that errors in the estimated radius of gyration are larger than for molecular weight, however values within 10% of the true value are obtained above $2 \times 10^4 \text{ g/mol}$. This is not the case for the viscometric radius, defined as

$$R_V^3 = \frac{3[\eta]M}{10\pi N_A} \quad (12)$$

where N_A is Avogadro's number, which can be estimated within a few percent of the true value across the range up to $1 \times 10^7 \text{ g/mol}$ (Figure 5).

The effect of branching on the estimated molecular weight is shown in Figures 6, where the data are calculated for polystyrene with branching contraction factor g values of 0.9, 0.7 and 0.5, respectively. To calculate these data, the 90° scattered intensities and intrinsic viscosities are modified by g according to Equations (9) and (10). It can be seen that below molecular weights of about $2 \times 10^5 \text{ g/mol}$ branching has little effect on the results. Above $2 \times 10^5 \text{ g/mol}$ it causes the molecular weight estimate to be larger than the estimate for the linear polymer. The errors depend on the amount of branching, for small amounts of branching the accuracy of the molecular weight estimate is similar to the linear polymer, however, for highly branched materials it is significantly overestimated.

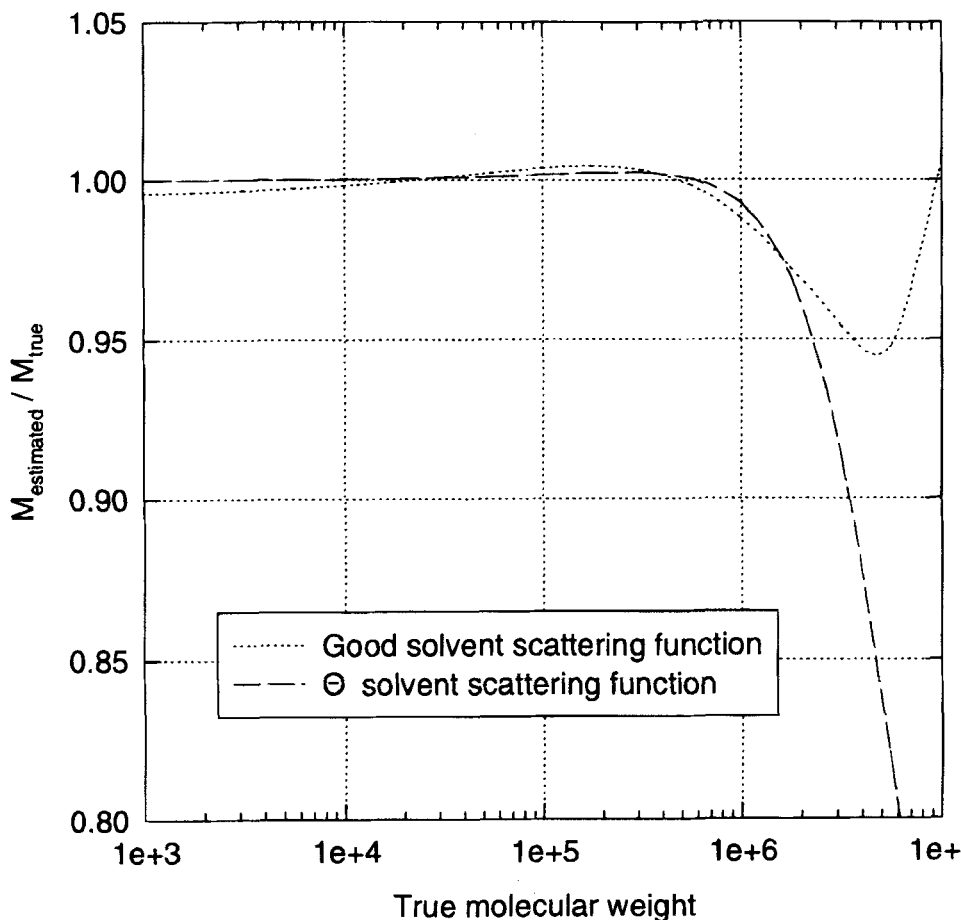


FIGURE 3 The ratio of estimated to true molecular weights with the light scattering intensity at 90° calculated from the particle scattering function for a good solvent for polystyrene.

The effect of the molecular weight per unit length of the chain on the accuracy of the molecular weight determination was studied using polybutadiene and poly(octadecyl methacrylate) as models. The molecular weight estimates are shown in Figure 7. The effect of the algorithm is very different at high molecular weights for the two cases; for polybutadiene the molecular weight is underestimated in the range 1×10^5 to 1×10^7 g/mol, but above this value it is overestimated. For poly(octadecyl methacrylate) the molecular weight is underestimated above 1×10^6 g/mol. However, in both cases the molecular weight is determined with an error less than 5% up to 1×10^6 g/mol, similar to polystyrene.

This indicates that this approach to measuring molecular weight becomes unpredictable at molecular weights above about 2×10^6 g/mol as the results depend on both the molecular weight and the relationship between the intrinsic viscosity and the radius of gyration for the polymer chain in solution.

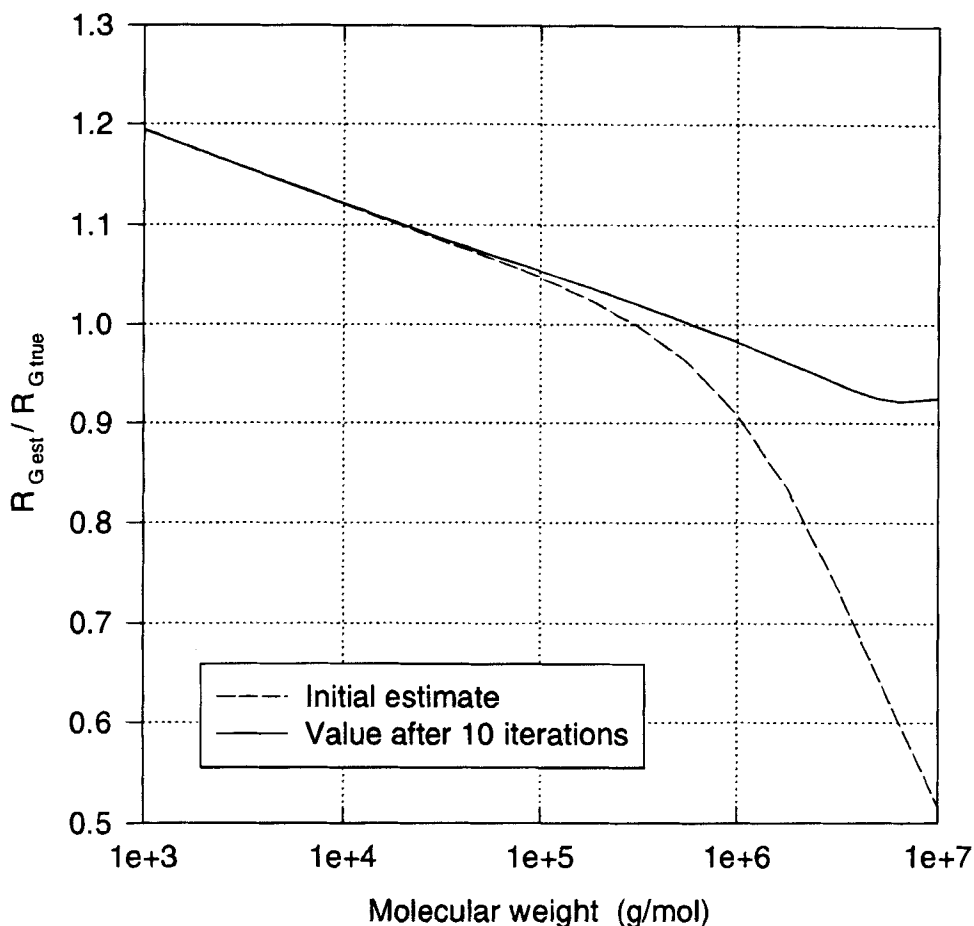


FIGURE 4 The ratio of the estimated to the true value of the radius of gyration plotted against the molecular weight for polystyrene. The initial estimate without any asymmetry correction and the effect of ten iterations of the correction algorithm are shown.

CONCLUSIONS

The accuracy of the SEC-Visc-RALS method has been investigated using models of different linear and branched polymers. For linear and branched random coil polymers the error in the estimated molecular weight is less than 5% up to about 2×10^6 g/mol. Above this value the molecular weight may be overestimated or underestimated significantly depending on the particular polymer. The estimated radius of gyration is less accurate with typical errors of 5%. However, the viscometric radius is estimated very accurately over the range studied. The effect of excluded volume on the light scattering angular function has little effect on the accuracy of the method and actually improves the results slightly.

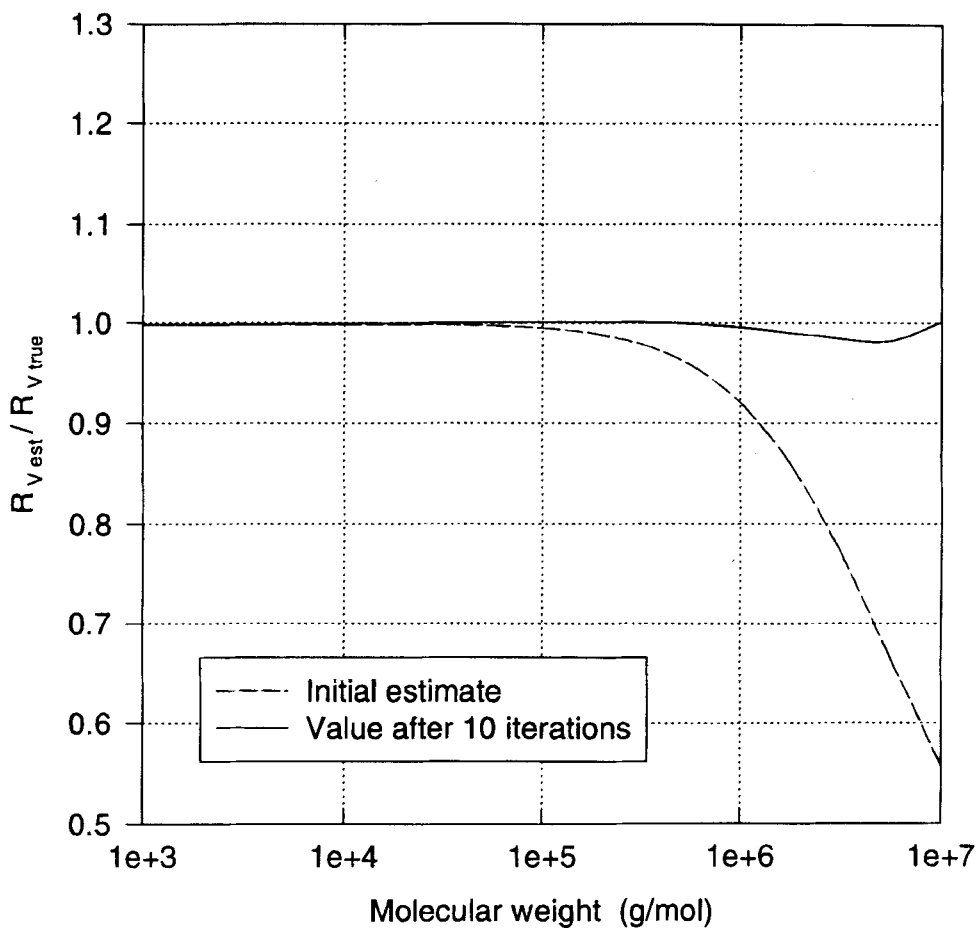


FIGURE 5 The ratio of the estimated to the true value of the viscometric radius plotted against the molecular weight for polystyrene. The initial estimate without any asymmetry correction and the effect of ten iterations of the correction algorithm are shown.

Acknowledgments

I am grateful to Wallace Yau (Chevron Chemical Company), Steven Threefoot (DuPont) and the reviewers for many helpful comments on this manuscript.

APPENDIX 1

The error in the molecular weight caused by ignoring concentration effects can be determined by rewriting the light scattering equation

$$\frac{K^*c}{R(\theta)} = \frac{1}{M_{true}} + 2A_2c \quad (13)$$

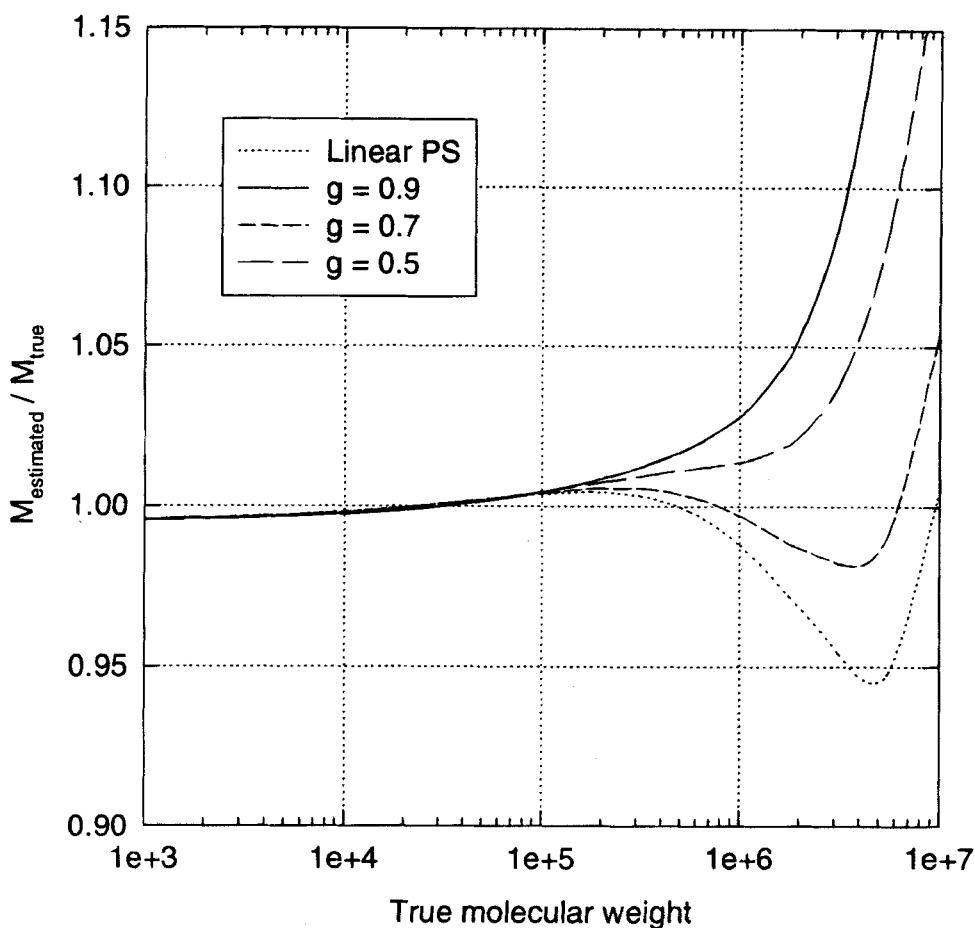


FIGURE 6 The effect of branching on the ratio of the estimated to the true molecular weight. The data were calculated with $g = 0.90, 0.70$ and 0.50 .

where A_2 is the second virial coefficient, in the form

$$\frac{M_{true}}{M_{estimate}} = 1 + M_{true} 2A_2c \quad (14)$$

The error increases linearly with increasing concentration and increasing molecular weight. However, for typical eluting concentrations of 5×10^{-5} g/mL, and a second virial coefficient on the order of 5×10^{-4} mol mL/g², the error at molecular weights of 1×10^6 g/mol is 5%. If the intrinsic viscosity of the polymer is measured during the experiment, this error can be minimized by estimating the second virial coefficient from the approximate relationship for a polymer in a good solvent [16]

$$A_2 \approx \frac{[\eta]}{M} \quad (15)$$

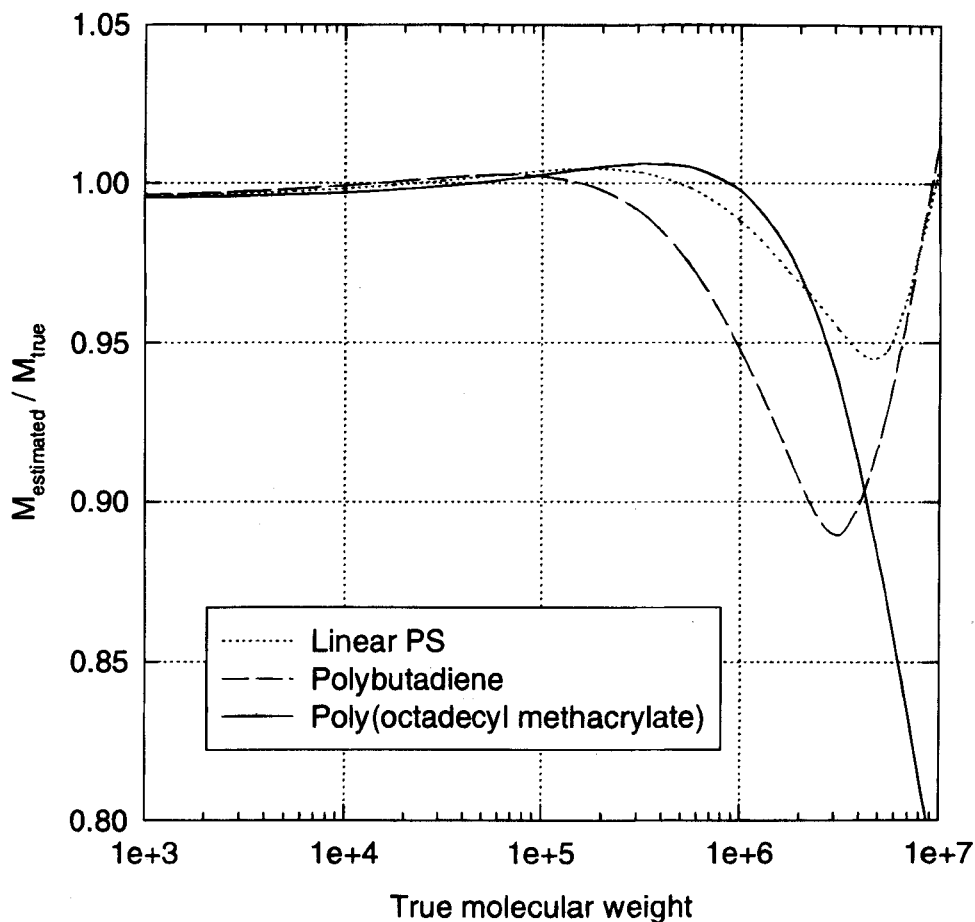


FIGURE 7 The ratio of estimated molecular weight to true molecular weight for polybutadiene and poly(octadecyl methacrylate), compared to polystyrene.

APPENDIX 2

Calculation Example

The effect of the algorithm can be seen by considering the calculation steps for polystyrene of molecular weight 1×10^5 and 1×10^6 g/mol with intrinsic viscosities of 0.433 and 2.254 dL/g and radii of gyration of 11.2 and 44.6 nm, respectively.

For a molecular weight of 1×10^5 g/mol, the calculation proceeds as follows.

Step 1: For the 100,000 case $P(\theta = 90^\circ)$ is 0.9839 so the initial molecular weight estimate will be 98,390.

Step 2: The radius of gyration is estimated at 10.02 nm using a value of $\phi = 1.73 \times 10^{23}$ (see below).

Step 3: The value of the particle scattering function is then estimated as $P(\theta = 90^\circ) = 0.9870$ leading to a revised molecular weight estimate of 99,680 g/mol.

Step 1 Iteration 2: We now repeat the calculation using this second estimate of molecular weight in the second iteration.

Step 2 Iteration 2: The radius of gyration estimate is now 10.06 nm.

Step 3 Iteration 2: The estimate of $P(\theta = 90^\circ)$ is now 0.9869 giving a third estimate of molecular weight of 99,690 g/mol.

In the case of a molecular weight of 1×10^6 g/mol the results are as follows.

Step 1: $P(\theta = 90^\circ)$ is 0.7845 so the initial molecular weight estimate will be 784,500 g/mol.

Step 2: The radius of gyration is estimated at 34.68 nm.

Step 3: The value of the particle scattering function is then estimated as $P(\theta = 90^\circ) = 0.8601$ leading to a revised molecular weight estimate of 912,000 g/mol.

Step 1 Iteration 2. The calculation is repeated using this second estimate of molecular weight.

Step 2 Iteration 2: The radius of gyration estimate is now 36.47 nm.

Step 3 Iteration 2: The estimate of $P(\theta = 90^\circ)$ is now 0.8471 giving a third estimate of molecular weight of 926,000 g/mol.

In both cases the first iteration produces the largest correction to the molecular weight estimate with subsequent iterations producing smaller corrections.

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