Evaluation of Different Branching Functions Used in the Determination of Random Branching by GPC

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Synopsis

Three branching functions are evaluated for use in the measurement of random branching by GPC. Initial evaluations of the functions $g^{1/2}$, $g^{3/2}$, and h^3 were made by computer simulations of GPC experiments using published data of lightly and highly randomly branched polymers. Actual GPC experiments were then performed on characterized samples of lightly and highly branched styrene–divinylbenzene copolymers. The results indicate that h^3 adequately predicts branching and molecular weight at all branching densities, while $g^{1/2}$ is accurate only for lightly branched polymers and $g^{3/2}$ is accurate only for highly branched polymers. A means for predicting the M–$[\eta]$ curve for branched polymers from the M–$[\eta]$ calibration curve for linear polymer is proposed.

INTRODUCTION

In a previous report,[1] a method was discussed for the measurement of random branching by a combination of GPC and $[\eta]$ measurements. This method required some prior knowledge of the branching structure being studied (i.e., it was assumed that random branching in the sample was light) and has found widespread application in the analysis of polymers. However, the original branching method has been found to generate unrealistic results when measuring branching in highly branched polymers. Consequently, work was undertaken to modify the branching method so that it could accurately analyze branching at all branching densities. This was done by evaluating several mathematical functions describing branching to find the one most suitable. This paper discusses modifications made to permit the determination of branching in randomly branched polymers of all branching densities, whether lightly or highly branched. Data generated using characterized branched styrene–divinylbenzene copolymers of widely differing branching densities are given in support of the conclusions drawn.

EXPERIMENTAL

The GPC experiments of the characterized styrene–divinylbenzene samples have been previously described,[2] as has the characterization of these samples.[3] The computer calculations were done using a method which has also been discussed in an earlier paper.[1]

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DISCUSSION

This article is presented as an addition to an earlier publication. The reader is urged to refer to the earlier report[1] for a full explanation of the pertinent derivations used in the development of the basic equations used.

The Branching Parameter g

Branching in a polymer molecule has been mathematically described as a function of the number of branch points it contains. This mathematical function is called g. There are several points of view regarding the determination of g by intrinsic viscosity measurements. For lightly randomly branched polymers[4] and star branched polymers,

$$\frac{[\eta]b}{[\eta]l} = g^{1/2} \tag{1}$$

is usually used, while for highly randomly branched polymers,

$$\frac{[\eta]b}{[\eta]l} = g^{3/2} \tag{2}$$

is preferred. A more general mathematical expression,[5] suitable for both lightly and highly branched systems, is h^3; h^3 was derived as a function of g but is of a different mathematical nature than either $g^{1/2}$ or $g^{3/2}$. Thus,

$$\frac{[\eta]b}{[\eta]l} = h^3 \tag{3}$$

is also used in the literature.

In the original published GPC branching method,[1] eq. (1) was used, and the whole series of equations developed were based upon eq. (1). For the purposes of this study, eqs. (2) and (3) were each used in the same manner as was done with eq. (1), and two new complete sets of branching and molecular weight equations were developed. The characterized samples which were evaluated were then analyzed as many as three separate times so that the different results could be compared. By comparing the calculated branching and molecular weight results to the actual values, decisions could be made as to which of the three branching functions were best suited for calculating branching.

Branching Parameters from $\bar{\lambda}$

The objective of the branching method is to calculate an average branching density, $\bar{\lambda}$. After establishing a model for the randomly branched structure, certain branching parameters describing this model and, hence, branching, can be expressed as functions of $\bar{\lambda}$. In a previous publication,[1] a model was proposed which has been recently observed to be unsuitable for highly branched systems. Therefore, corrections to this model were made and are presented here.

The accuracy of $\bar{\lambda}$, and the resultant molecular weight and branching parameters based on $\bar{\lambda}$, are dependent on the use of the proper branching function, i.e., h^3, $g^{1/2}$, or $g^{3/2}$. Once $\bar{\lambda}$ is correctly identified, accurate molecular weight results are calculable.[1] $\bar{\lambda}$ also is useful in defining certain branching parameters for the sample, i.e., certain structural features of the branched molecule can be quan-
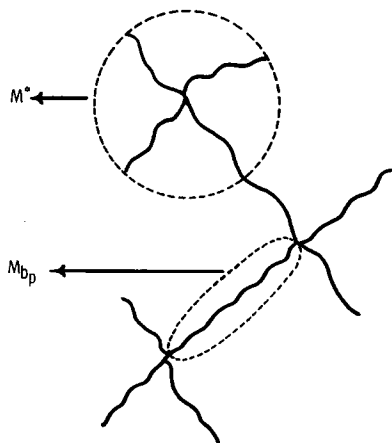
Fig. 1. Branching parameters M^* and $\overline{M}_{bp}$.

titatively described. These parameters are illustrated in Figure 1. For high molecular weights, the molecular weight interval between branch points ($\overline{M}_{bp}$) can be calculated if the branched molecule is assumed to be made up of segments of statistically equal length:[6]

$$M = \overline{M}_{bp} \cdot [(f - 1)m + 1] \tag{4}$$

For a highly branched molecule, where $m > 1$, eq. (4) reduces to the form

$$\overline{M}_{bp} = \frac{M}{(f - 1)m} \tag{5}$$

$\overline{M}_{bp}$ is related to $\overline{\lambda}$ by

$$\overline{M}_{bp} = \frac{1}{(f - 1)\overline{\lambda}} \tag{6}$$

Equation (6) can be applied only to highly branched molecules, but does allow the calculation of the molecular weight interval between branch points. For purposes of calculation, the randomly branched structure can be viewed statistically as a series of connected star-shaped segments joined together to form a dendritic configuration (i.e., assignment of a main chain backbone is impossible), each leg of the star being of $\overline{M}_{bp}/2$ molecular weight length. Then, M^*, which is the molecular weight of each star-shaped unit, is

$$M^* = \frac{f}{(f - 1)(2\overline{\lambda})} \tag{7}$$

where M^* represents a critical molecular weight in the sample. Since they contain one branch point, all molecules of molecular weight less than M^* can be regarded as linear in character. Thus, M^* represents the separation point of linear and branched molecules, i.e., the point on the Mark–Houwink, $[\eta]–M$, plot where the branched species first begins to deviate from the $[\eta]$–M plot for linear polymers.[1] The percentage of branched and linear species in the polymer is easily calculated from the GPC curve with a knowledge of M^*.

Thus, three branching parameters are calculable from $\overline{\lambda}$ which help characterize the polymer, especially if it has a broad molecular weight distribution: (a)

$\overline{M}_{bp}$, the molecular weight between branch points for the highly branched molecules in the distribution; (b) M^*, the lowest molecular weight species in the distribution that is branched; and (c) % branched, the percentage of the polymer that is branched.

Also, $\overline{\lambda}$ allows a generation of the log $[\eta]$–log M relationship of the sample. All these parameters should be viewed together to adequately compare branching in samples of different molecular weight and molecular weight distribution.

The "Universal Calibration" Parameter $M\,[\eta]$

It has recently been shown[2] that the GPC "universal" M–$[\eta]$ calibration curve for linear polymers is the same as the M–$[\eta]$ calibration curve of lightly branched polymers. However, at a given elution volume $M[\eta]$ for a highly branched polymer will be greater than $M[\eta]$ for linear polymer, apparently approaching a limit about two times greater at very high branching. That is, $M[\eta]$ for linear polymer does not function as a "universal" calibration curve for highly branched polymers. Thus, in order to accurately calculate molecular weights for branched polymers from GPC, a means must be available for converting calibration curves developed with linear standards to that of branched polymers. Since the deviation from $M[\eta]$ for linear polymer increases with branching, a correction of the following form is necessary:

$$(M[\eta])_b = (M[\eta])_1[2 - g^{1/2}] \tag{8}$$

where the boundary conditions

$$\lim_{g \to 1} (M[\eta])_b = (M[\eta])_1 \tag{9}$$

$$\lim_{g \to 0} (M[\eta])_b = 2(M[\eta])_1 \tag{10}$$

corresponding to linear polymer ($g \to 1$) and infinite branching ($g \to 0$), respectively, are qualitatively in agreement with the experimental evidence. The exponent $\frac{1}{2}$ is needed so that the g term in eq. (8) will not converge to a value of zero too rapidly. Equation (8) is empirical, but an equation of this form should aid in converting the polystyrene universal calibration to branched polymers.

RESULTS

Evaluation of h^3, $g^{1/2}$, and $g^{3/2}$ by Computer-Simulated GPC Analyses of Previously Characterized Samples

An initial comparison of the three functions h^3, $g^{1/2}$, and $g^{3/2}$ was made using data published in the literature.[6,7] Examples of well-characterized branched samples of both high and light branching densities were found. It was the aim here to reanalyze the data published in the literature for whole, unfractionated samples in the manner proposed here. Basic to this work was the assumption that all the published data were correct. Computer-simulated GPC analyses of the samples were performed and then analyzed using the GPC branching method. Since the samples had previously been characterized for branching and molecular weight, the possible superiority of h^3 over $g^{1/2}$ and $g^{3/2}$ in predicting branching could be evaluated.

Results are shown in Table I (see ref. 1 for details of the procedures used). Characterization data for the samples were taken from the original publications. PS-1, the Thurmond–Zimm sample, was a lightly branched copolymer of styrene–divinylbenzene, while the three samples from the work of Salyer (EVA-15.4, EVA-48.5 and EVA-54.0) were highly branched copolymers of ethylene–vinyl acetate of different vinyl acetate contents. A comparison of the "GPC" results to the characterization data indicated that the $g^{1/2}$ function adequately described molecular weight and branching for the lightly branched Thurmond–Zimm sample, but that $g^{3/2}$ did not work (especially in predicting branching). Conversely, for the highly branched Salyer samples, $g^{3/2}$ was a much better indicator of molecular weight and branching than $g^{1/2}$. This supported the contention presented earlier regarding the inadequacy of $g^{1/2}$ for analyzing highly branched polymers, and indicated that an overestimation of branching occurred when $g^{1/2}$ was used. However, it was apparent that the h^3 function served as the best indicator of molecular weight for all the samples and adequately estimated branching at all branching densities. It can be concluded that the h^3 function suffices as a suitable function for generating accurate molecular weight results, regardless of the branching density of the sample, and provides good estimates of the branching parameter M^*.

One question that remained to be answered was whether, in actual GPC experiments, the universal calibration sufficed as a proper calibration for highly branched polymers. In these computer-simulated GPC analyses, there was no way of evaluating this aspect. Therefore, as a final analysis, actual GPC experiments of characterized samples of both lightly and highly branched polymers were performed. If the samples are characterized for branching and molecular weight, these analyses will provide (a) a final evaluation of h^3 and (b) data to determine whether corrections to the universal calibration curve are needed for branched polymers.

Evaluation of h^3 in Actual GPC Experiments on Previously Characterized Branched Samples

Samples of lightly and highly randomly branched polymers had been previously synthesized,[3] and fractions of these samples were extensively characterized as part of an analysis of the random branching in these samples. It was found that these fractions were fairly broad in molecular weight distribution. Thus, they were viewed in the context of this work as characterized whole polymers, suitable for analysis by this GPC method. Therefore, they each were analyzed in turn to evaluate the ability of h^3 in calculating both their molecular weight and branching.

Styrene–divinylbenzene copolymers were selected for use in actual GPC experiments and the subsequent calculation of branching because they had already been characterized in the conventional manner for molecular weight and branching. Characterization of the samples included ultracentrifuge, light scattering, osmometry, and viscometry. Results are summarized in Table II. It has been shown[3] that the 9A series (samples 9A, 9A5, 9A3, 9A1) obeyed $g^{0.65}$ (indicating it was lightly branched), while the 9B series (samples 9B3, 9B2-2, 9B2-1) followed $g^{1.41}$, i.e., it was highly branched.

GPC curves of the samples in the 9A and 9B series were generated in the normal manner. The results of the GPC branching analyses using h^3 are shown

TABLE I
Branching Results by Computer-Simulated GPC Analysis

	PS-1[a]	EVA-15.4[b]	EVA-48.5[b]	EVA-54.0[b]
Actual				
$\overline{M}_w$	815,000	514,000	548,000	228,000
$\overline{M}_n$	—	33,500	23,100	18,400
M^*	360,000	60,000	20,000	21,000
$g^{1/2}$				
$\overline{M}_w$	783,000	489,000	382,000	153,000
$\overline{M}_n$	303,000	33,200	29,200	18,400
M^*	557,000	22,800	960	1,960
$g^{3/2}$				
$\overline{M}_w$	793,000	594,000	615,000	224,000
$\overline{M}_n$	300,000	32,300	24,300	16,800
$\overline{M}^*$	2,590,000	258,000	33,400	34,900
h^3				
$\overline{M}_w$	790,000	529,000	700,000	206,000
$\overline{M}_n$	301,000	36,800	24,200	17,200
M^*	474,000	67,700	14,300	9,600

[a] Reference 7.
[b] Reference 6.

TABLE II
Characterized Branched Samples Used in the GPC Experiments

Series	$[\eta]$	$\overline{M}_z$(UC)[a]	$\overline{M}_w$(UC)	$\overline{M}_w$(LS)[b]	$\overline{M}_n$(OP)[c]	M^*
9A	0.932	—	—	358,000	150,000	
9A1	1.305	—	—	572,000	348,000	
9A3	0.977	595,000	400,000	407,000	206,000	~200,000
9A5	0.456	139,000	88,200	88,400	67,000	
9B2-1	2.109	—	—	5,240,000	687,000	
9B2-2	1.201	—	—	2,230,000	322,000	~150,000
9B3	0.714	352,000	210,000	228,000	127,000	

[a] UC, ultracentrifuge.
[b] LS, light scattering.
[c] OP, osmotic pressure.

in Table III. Several variables were studied. The first step was to evaluate the proposed universal calibration correction scheme. This was done by first performing the branching analyses on these samples with eq. (8), i.e., using $(M[\eta]_b)$, and then repeating the analyses using $(M[\eta])_1$. In Figure 2, the values of $(M[\eta])_b$ calculated from eq. (8) for each elution volume are plotted. All of the 9A and 9B branched samples followed the same line. When compared to the actual linear $(M[\eta])_1$ calibration and the actual $(M[\eta])_b$ lines for the 9A and 9B series determined previously,[2] it was observed that eq. (8) overestimated $M[\eta]$ for lightly branched samples and underestimated $M[\eta]$ for highly branched samples. It is felt, nonetheless, that eq. (8) provides a reasonable means of correcting the linear universal calibration line for all branching densities. The results of Table III indicated that the molecular weight data for both the lightly branched samples and the highly branched samples were in good agreement with the characterization data in both cases. The reason for this is unknown, but it is felt that perhaps some internal compensations are occurring through the numerous it-

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TABLE III
GPC Evaluation of h^3 on Characterized Branched Polymers

|	9A	9A1	9A3	9A5	9B2-1	9B2-2	9B3
$h^3 (M[\eta])_l$							
$\bar{M}_z$	729,000	977,000	613,000	136,000	27,400,000	18,500,000	283,000
$\bar{M}_w$	365,000	610,000	393,000	103,000	4,960,000	1,980,000	211,000
$\bar{M}_n$	171,000	353,000	254,000	75,000	775,000	347,000	159,000
M^*	220,000	228,000	164,000	310,000	202,000	120,000	199,000
$h^3 (M[\eta])_b$							
$\bar{M}_z$	737,000	988,000	619,000	136,000	29,500,000	20,300,000	284,000
$\bar{M}_w$	365,000	611,000	394,000	103,000	5,100,000	2,060,000	211,000
$\bar{M}_n$	171,000	352,000	254,000	75,700	766,000	343,000	159,000
M^*	239,000	251,000	180,000	315,000	245,000	143,000	210,000
Assumed linear							
$\bar{M}_z$	559,000	739,000	475,000	131,000	5,850,000	3,350,000	254,000
$\bar{M}_w$	319,000	516,000	338,000	101,000	2,040,000	838,000	197,000
$\bar{M}_n$	165,000	328,000	236,000	74,800	670,000	307,000	153,000
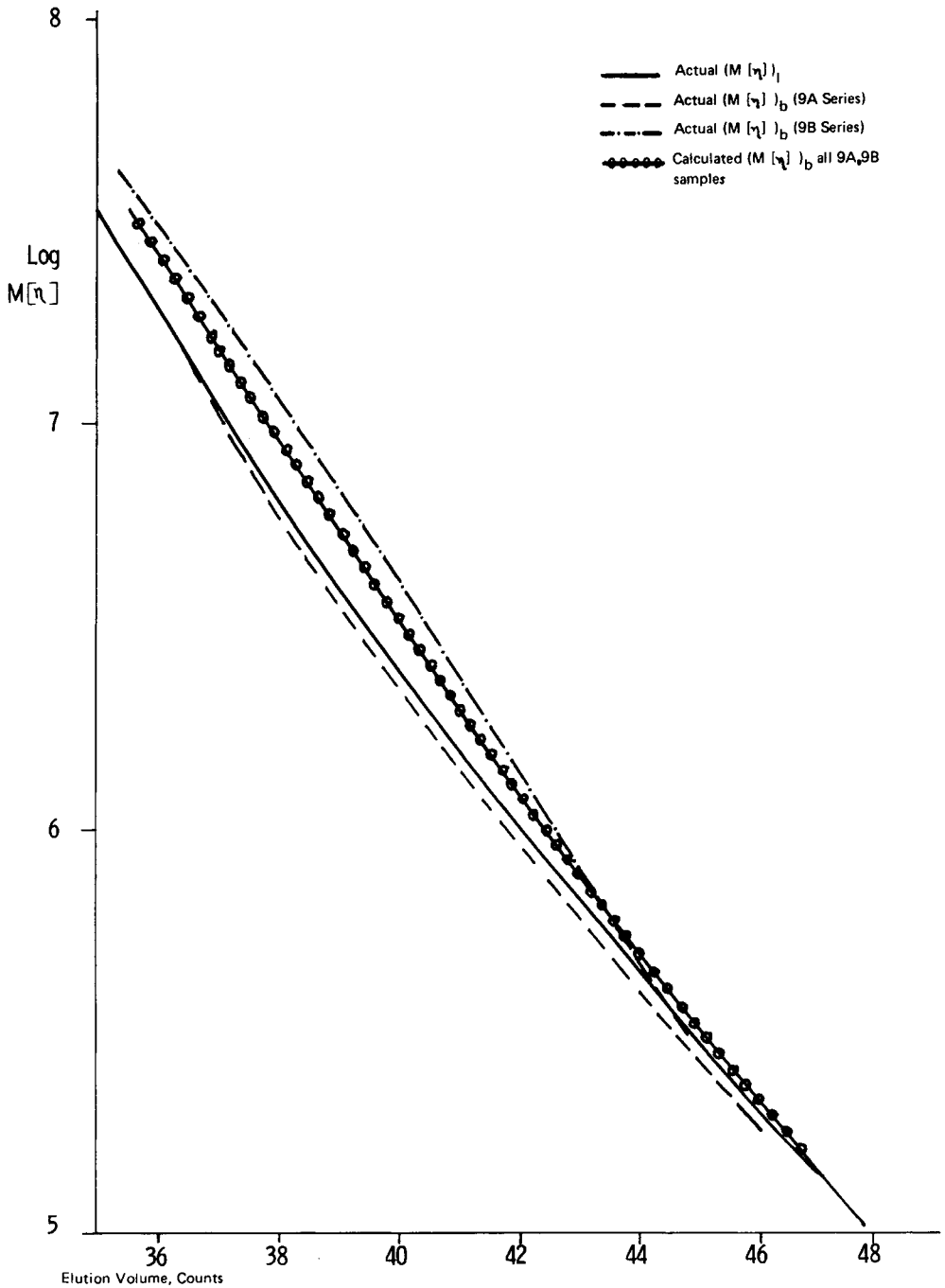
Fig. 2. Universal calibration for branched samples calculated from eq. (8).

erations present in the mathematical branching calculations. At any rate, it appears that the use of the universal calibration parameter $(M[\eta])_1$ could probably safely be used in most cases, but that eq. (8) should be used in the case of extreme branching.

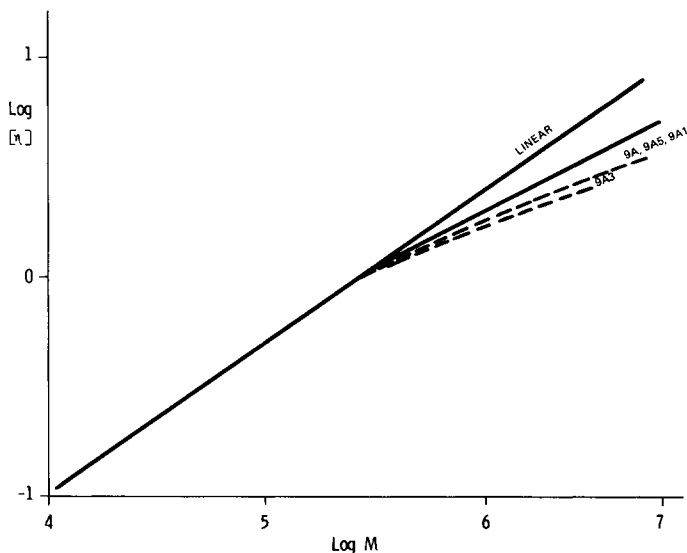Next, the effect upon the calculated molecular weight when branching is not

Fig. 3. Mark–Houwink relationship of lightly branched styrene–divinylbenzene copolymer, 9A series: (—) actual branched line; (- - -) calculated branched line.

considered was evaluated by (a) assuming the chromatograms of the samples were of linear polystyrene and (b) performing the usual molecular weight calculations. With the high molecular weight, highly branched 9B samples, very large errors in $\overline{M}_w$ resulted, but only small deviations in $\overline{M}_n$ were observed.

Finally, the calculated branching parameters were evaluated. As discussed previously, the calculated branching parameter M^* is related to the point on the $[\eta]$–M plot where the branched sample first begins to deviate from the relationship for linear polymer. Figures 3 and 4 show the actual $[\eta]$–M relationships for series A and B. A comparison of the two intersection points, i.e., the "true" M^* values, with the calculated M^* values indicates that the calculated M^* is somewhat higher. That is, branching is underestimated. The predicted $[\eta]$–M relationships are calculated from $\overline{\lambda}$ and are shown in Figures 3 and 4 as dotted lines. The $[\eta]$–M lines at high molecular weight indicate, on the other hand, an overestimation of branching. However, it can be generalized that the calculated branching parameter M^* does appear to be within 25% of the actual value and the calculated $[\eta]$–M lines are in reasonable agreement with the actual plots.

One last question remains to be commented on, i.e., whether the assumption that $\overline{\lambda}$ is a constant value over the entire molecular weight distribution is a valid one. The most direct way to evaluate the constancy of $\overline{\lambda}$ in the 9A and 9B series is to check its ability to accurately generate the $[\eta]$–M relationship for each of the two series. As pointed out above, reasonable agreement in the two $[\eta]$–M plots were obtained. For these samples, $\overline{\lambda}$ appears to be reasonably constant, since a large change in $\overline{\lambda}$ would have drastically altered the actual $[\eta]$–M line and less agreement would have been obtained.

CONCLUSIONS

Proposed revisions to the original branching method include (a) changes from $g^{1/2}$ to h^3, (b) changes from $(M[\eta])_1$ to $(M[\eta])_b$, and (c) some redefinition of the branching parameters M^* and $\overline{M}_{bp}$. The experimental data shown here indicate
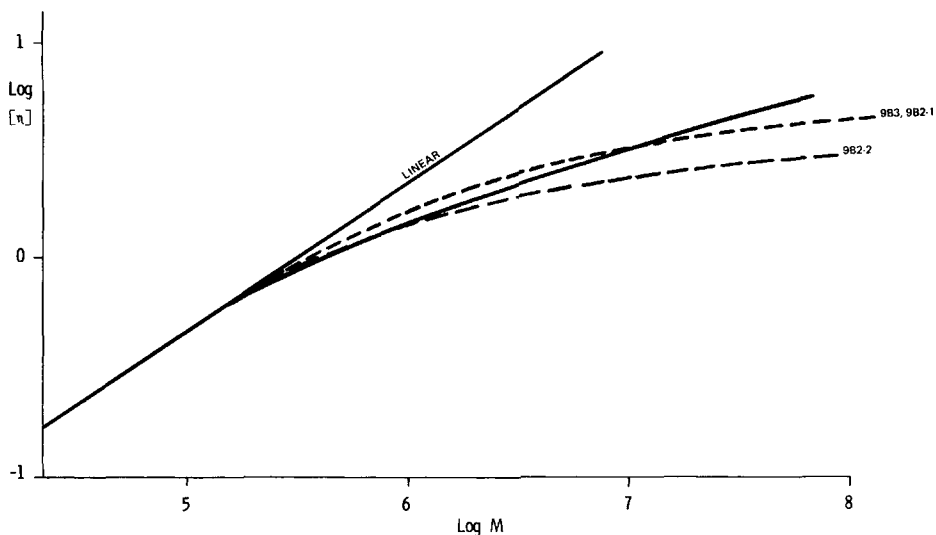
Fig. 4. Mark–Houwink relationship of highly branched styrene–divinylbenzene Copolymer, 9B series: (—) actual branched line; (- - -) calculated branched line.

that h^3 quantitatively predicts branching at all branching densities, while $g^{1/2}$ is accurate only for lightly randomly branched systems and $g^{3/2}$ is accurate only for highly randomly branched polymers. Although universal calibration works for linear and lightly branched polymers, corrections to the M–$[\eta]$ curve should be made to analyze GPC data for highly branched polymers. An expression for this correction is proposed.

The results verified the ability of the revised method based on h^3 to calculate $\overline{M}_w$ and $\overline{M}_n$ results accurately to within about ±5% for both highly and lightly randomly branched samples and also to furnish reasonable estimates of $\overline{M}_z$. The lowest molecular weight species in the broad molecular weight distribution samples that is essentially linear, defined as M^*, can be estimated only to within 25% of the actual value, and the molecular weight value is usually overestimated. The GPC analyses of characterized branched polystyrene samples revealed that when the chromatogram of a highly branched sample was analyzed as if it were a linear polymer, an underestimation of $\overline{M}_w$ by more than half the true value resulted, while $\overline{M}_n$ remained relatively unaffected (i.e., compared to the true $\overline{M}_n$). The calculated branching density, $\overline{\lambda}$, allowed the generation of log $[\eta]$–log M plots for the two branched polystyrene samples of broad molecular weight distribution which were in reasonable agreement with previously determined $[\eta]$–M relationships. The assumption that $\overline{\lambda}$ is a constant over the molecular weight distribution of the sample appears to be a reasonable one for these samples.

The revised GPC branching method provides a reliable method for the generation of accurate molecular weights for randomly branched polymers. Calculated branching parameters serve as adequate estimates and allow relative comparisons between samples. In light of the assumptions made as to the branching model being used, the method can only provide first-order approximations to branching, but it should be suitable when comparisons of many samples are requested. The usefulness of the method lies not in its ability to quantitatively describe the extent and type of branching, but rather in its ability

to generate meaningful molecular weight and branching results in a relatively short time.

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