

A New Method for Rapid Evaluation of Long-Chain Branching in Polymers

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Synopsis

A new method for rapid evaluation of long-chain branching (LCB) in polymers was developed. The crude GPC chromatogram and the measured value of intrinsic viscosity of the whole polymer are the only data required. By using trial and error in combination with graphic analysis, the threshold value M_0 and average molecular weights \bar{M}_w and \bar{M}_n , as well as LCB can be simultaneously evaluated. The advantage of this method lies in avoiding predetermination of the M_0 for a given resin. The results obtained by this method for NBS Branched Polyethylene Standard Reference Material SRM 1476 and for a branched *cis*-1,4-polybutadiene sample were in good agreement with those given by the conventional Ram-Miltz method.

INTRODUCTION

Since the framework of Zimm and Stockmayer,¹ the influence of long-chain branching (LCB) on polymer properties has been extensively studied. LCB of a real polymer can be determined by GPC-viscometry, GPC-low-angle laser-light scattering (LALLS), and GPC-sedimentation methods.²⁻¹⁵ The basis for all GPC-related methods is the universal retention volume-hydrodynamic volume relation (universal calibration) proposed by Benoit et al.¹⁶ Branched molecules have smaller hydrodynamic volume and hence will elute in GPC with lower molecular weight linear molecules.

Particularly, the GPC-viscometry method was widely used, and its problem lies in establishing the solution viscosity-molecular weight relationship suitable for a particular branched resin. Several approaches are possible and have been tried on purpose. They may break down into two categories as proposed by Wild et al.⁴ One involving the measurement of the viscosity values at differing molecular weight levels presents considerable practical difficulty. The second attempted to establish a theoretical relationship between solution viscosity and molecular weight, which may be quantified by reference to the measured solution viscosity of the unknown polymer; the problems then concern the effectiveness of the theoretical definition of the solution viscosity-molecular weight relationship for real branched resins.

One of the widely used theoretical approaches is the well known Ram-Miltz procedure,³ which is based on the assumption that the relationship between the intrinsic viscosity and molecular weight for a branched polymer can be described by a polynomial expression when the molecular weight is above a certain threshold value M_0 . However, the shortcomings for the Ram-Miltz

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method may stem from the fact that the threshold value M_0 , beyond which the branch occurs, may be markedly different for the same polymer prepared by different synthetic methods¹⁷ and from the practical difficulty in determination of the M_0 . The aim of this work is to develop a procedure by which LCB and M_0 for a particular resin can be simultaneously evaluated. This work is also based on the polynomial expression proposed by Ram and Miltz; meanwhile trial and error in combination with graphic analysis was used. The evaluated results by this method for NBS Branched Polyethylene Standard Reference Material SRM 1476 and for a branched *cis*-1,4,-polybutadiene sample will be compared with those obtained by the Ram-Miltz procedure.

THEORY

For linear polymers, the solution viscosity-molecular weight relationship is expressed by the Mark-Houwink equation

$$[\eta]_{\text{lin}} = KM^\alpha \quad (1)$$

where K and α are constants for a given solvent at a particular temperature and the subscript lin denotes linear polymer. A branched polymer obeys eq. (1) (under the same condition) only up to a certain threshold value M_0 :

$$\ln[\eta]_{\text{br}} = \ln K + \alpha \ln M \quad \text{for } M \leq M_0 \quad (2)$$

where subscript br denotes branched polymer. Beyond the M_0 the curve can be described by a polynomial expression, according to Ram and Miltz,³

$$\ln[\eta]_{\text{br}} = \ln K + \alpha \ln M + b \ln^2 M + c \ln^3 M \quad \text{for } M > M_0 \quad (3)$$

The values of K and α are obtainable from the literature (or experimentally) for the linear polymer under predetermined conditions (solvent and temperature); the still unknown constants b and c have to be calculated. Assuming continuation of the curve at $M = M_0$, we have

$$\ln K + \alpha \ln M_0 = \ln K + \alpha \ln M_0 + b \ln^2 M_0 + c \ln^3 M_0 \quad (4)$$

$$c = -b/\ln M_0 \quad (5)$$

Obviously, the sum of the two last terms of eq. (3) is negative. Substituting eq. (5) into eq. (3), we get

$$\ln[\eta]_{\text{br}} = \ln K + \alpha \ln M + b \ln^2 M (1 - \ln M / \ln M_0) \quad \text{for } M > M_0 \quad (6)$$

As one deals with whole (unfractionated) polymers, the contributions of each species to the intrinsic viscosity and the overall average molecular weights should be taken into account. Thus,

$$[\eta]_{\text{total}} = \sum W_i [\eta]_i \quad (7)$$

$$\bar{M}_w = \sum W_i M_i \quad (8)$$

$$\bar{M}_n = 1 / \sum (W_i / M_i) \quad (9)$$

where W_i represents the weight fraction of species i and can be obtained from the GPC curve. In the case for the species i , eq. (6) becomes

$$\ln[\eta]_{\text{br},i} = \ln K + \alpha \ln M_i + b \ln^2 M_i (1 - \ln M_i / \ln M_0) \text{ for } M_i > M_0 \quad (10)$$

For a given fraction i in GPC chromatogram, the relationship between the molecular weights of linear and branched polymers should conform with the universal calibration, i.e.,

$$[\eta]_{\text{lin},i} M_{\text{lin},i} = [\eta]_{\text{br},i} M_{\text{br},i} \quad (11)$$

or

$$\ln[\eta]_{\text{br},i} = \ln K + (1 + \alpha) \ln M_{\text{lin},i} - \ln M_{\text{br},i} \quad (12)$$

Combining (10) and (12), we have

$$\ln M_{\text{br},i} = \frac{\ln M_{\text{lin},i}}{1 - [b/(1 + \alpha)] \ln M_{\text{br},i} (\ln M_{\text{br},i} / \ln M_0 - 1)} \text{ for } M_{\text{br},i} > M_0 \quad (13)$$

Equation (13) gives the relationship between the molecular weights of linear and branched molecules of the fraction i in the GPC chromatogram.

Using eq. (1), eq. (10) can be written as

$$\ln[\eta]_{\text{br},i} = \ln[\eta]_{\text{lin},i} + b \ln^2 M_i (1 - \ln M_i / \ln M_0) \text{ for } M_i > M_0 \quad (14)$$

Equation (14) is the correlation between the intrinsic viscosities of branched polymer and corresponding linear polymer with the same molecular weight. From eq. (14), we find the branching degree for species i ,

$$G_i = ([\eta]_{\text{br},i} / [\eta]_{\text{lin},i})_M = \exp[b \ln^2 M_i (1 - \ln M_i / \ln M_0)] \text{ for } M_i > M_0 \quad (15)$$

The branching degree G for the whole polymer

$$G = \sum W_i G_i \quad (16)$$

On the other hand, the branching degree g expressed in terms of parameters of macromolecule coil dimensions of branched and linear polymer of the same molecular weight

$$g = (\langle r^2 \rangle_{\text{br}} / \langle r^2 \rangle_{\text{lin}})_M \quad (17)$$

where $\langle r^2 \rangle$ is the mean square end-to-end distance of the macromolecule and subscript M denotes with the same molecular weight. The branching degrees G and g are interrelated by

$$G = g^\epsilon \quad (18)$$

where ϵ is the exponent dependent on the type of branches and its value is between 0.5 and 1.5.^{1,18-20} For randomly branched polymers, $\epsilon = 0.5$, the theoretical value of Zimm and Kilb,¹⁸ is used. We then have

$$G = g^{1/2} \quad (19)$$

Zimm and Stockmayer¹ have shown that the branching degree g is related with the number of branch points per molecule, n_b , by the theoretical equation below for the trifunctional branch point with reference to a polydisperse polymer,

$$g = \frac{6}{n_b} \left\{ \left(\frac{2 + n_b}{4n_b} \right)^{1/2} \ln \left[\frac{(2 + n_b)^{1/2} + n_b^{1/2}}{(2 + n_b)^{1/2} - n_b^{1/2}} \right] - 1 \right\} \quad (20)$$

The branching index $\bar{\lambda}$ is defined as

$$\bar{\lambda} = n_b / \bar{M}_w \quad (21)$$

COMPUTATION PROCEDURE

1. The molecular weight of linear polymer $M_{\text{lin},i}$ corresponding elution volume V_i in GPC chromatogram was obtained from the calibration. Taking $M_{\text{lin},i}$ as the initial value of $M_{\text{br},i}$ on the right-hand side of eq. (13) and giving a set of values (M_x, b_x) for M_0 and b in eq. (13), an improved estimate of $M_{\text{br},i}$ was obtained. If $M_{\text{br},i}$ (obtained) $\leq M_x$, let $M_{\text{br},i} = M_{\text{lin},i}$ and if $M_{\text{br},i}$ (obtained) $> M_x$, the $M_{\text{br},i}$ in turn was substituted on the right-hand side of eq. (13) to yield the new estimate. This procedure was repeated until two successive values of $M_{\text{br},i}$ relatively differed by less than 0.1%. Furthermore, the same was done for each V_i in the GPC chromatogram. A series of the last values of $M_{\text{br},i}$'s were thus obtained, and these were substituted into eq. (12) to calculate the values of $[\eta]_{\text{br},i}$'s [in the case of $M_{\text{br},i}$ (obtained) $\leq M_x$, the values of $M_{\text{br},i} = M_{\text{lin},i}$ were substituted into eq. (2) to obtain the values of $[\eta]_{\text{br},i}$] for each elution volume V_i . The values of all $[\eta]_{\text{br},i}$ then, through eq. (7), gave the average intrinsic viscosity of the whole polymer $[\eta]_{\text{total}}$ which was compared with the experimentally obtained value $[\eta]_{\text{exp}}$.

2. For the same value M_x given above for M_0 , giving a new value for b , repeated the procedure 1 until $[\eta]_{\text{total}}$ and $[\eta]_{\text{exp}}$ relatively differed by less than 0.1%. The last value b_x for b was one matched with the value M_x for M_0 . This matched pair for M_0 and b was denoted as (M_x, b_x) .

3. Giving a new value for M_0 , repeat the procedures 1 and 2 to yield a series of such matched pairs for M_0 and b which mean that $[\eta]_{\text{total}}$ thus obtained and $[\eta]_{\text{exp}}$ relatively differ by less than 0.1%.

4. The values (M_x, b_x) obtained by the procedure 3 were substituted into eqs. (15) and (16) to give a series of values for G . Plotting $\log G$ against $\log M_x$ (as shown in Fig. 1), $\log G$ slightly increased with increase of $\log M_x$ only up to a certain value of M_x beyond which $\log G$ increased more substantially with increase of $\log M_x$. This certain value of M_x was taken as the real value of M_0 . Repeating procedure 2 by using this real M_0 , the real value for b , matched with the real M_0 , was also obtained. The value G at $M_x = M_0$ in the $\log G$ - $\log M_x$ plot was taken as the real value of the branching degree for the polymer.

5. The values (M_x, b_x) obtained by the procedure were substituted into eq. (13) to give a series of values for $M_{br,i}$ corresponding to each V_i (in the case of $M_{br,i} \leq M_x$, then $M_{br,i} = M_{lin,i}$). These $M_{br,i}$'s were then substituted into eqs. (8) and (9) to yield two series of values for \bar{M}_w and \bar{M}_n , respectively. Plotting \bar{M}_w and \bar{M}_n against M_x (as shown in Fig. 2), the values \bar{M}_w and \bar{M}_n at $M_x = M_0$ were taken as the real values.

EXPERIMENTAL

The National Bureau of Standards Linear Polyethylene Standard Reference Material SRM 1475 and Branched Polyethylene Standard Reference Material SRM 1476 were used. A branched *cis*-1,4-polybutadiene sample used was the same as that in a previous work.²¹

A Water 200 GPC was used. For SRM 1475 and SRM 1476, the apparatus was run at 135°C, with *o*-dichlorobenzene (DCB) as solvent, and was calibrated with the aid of narrow-distribution polystyrene standards. The universal calibration curve was constructed from the product $[\eta]M$ versus elution volume V .

The intrinsic viscosity of SRM 1475, SRM 1476, and polystyrene standards was measured on a Cannon-Ubbelohde viscometer at 135°C with DCB as solvent. The Mark-Houwink relationship was determined for polystyrene in DCB at 135°C,

$$[\eta] = 1.38 \times 10^{-4} \bar{M}_v^{0.700} \quad (20)$$

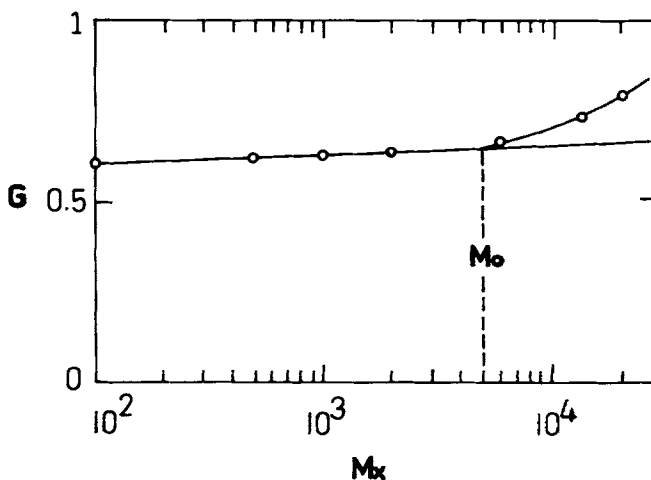
and for linear polyethylene in DCB at 135°C,

$$[\eta] = 5.48 \times 10^{-4} \bar{M}_v^{0.692} \quad (21)$$

The experimental details for branched *cis*-1,4-polybutadiene sample were described in the previous paper.²¹

TABLE I
 $M_x, b_x, G, \bar{M}_n,$ and \bar{M}_w for SRM 1476

M_x	20,000	13,500	6000	2000	1000	500	100
b_x	0.0172	0.0134	0.0087	0.0055	0.0042	0.0033	0.0019
G	0.79	0.73	0.68	0.64	0.63	0.62	0.61
\bar{M}_n	17,300	17,400	17,600	17,900	18,100	18,300	18,600
\bar{M}_w	86,900	85,700	84,200	83,400	83,000	82,800	82,500

Fig. 1. Plot of $\log G$ versus $\log M_x$.

RESULTS AND DISCUSSION

Calculated results for SRM 1476 branched material with SRM 1475 as linear reference material are listed in Table I. G is a function of M_x as shown in Figure 1. From Figure 1 it can be seen that $\log G$ tends to slightly and linearly increase with $\log M_x$ up to a value M_0 for M_x beyond which $\log G$ tends to substantially increase with $\log M_x$. We can find from Figure 1 that $M_0 = 5000$, and this value is considered as the threshold value. The value G at $M_x = M_0 = 5000$ in Figure 1 is taken as the real value of the branching degree G for SRM 1476. This real value G gives the value for the branching degree g by which the number of branch points per molecule n_b is then obtained through eq. (20). Moreover, the branch index $\bar{\lambda}$ is found through eq. (21). These branching parameters obtained are listed in Table II.

Both $\log \bar{M}_w$ versus $\log M_x$ and $\log \bar{M}_n$ versus $\log M_x$ are shown in Figure 2. It is noted that $\log \bar{M}_w$ tends to vary slightly and linearly increase with $\log M_x$, while $\log \bar{M}_n$ tends to vary slightly and linearly decrease with $\log M_x$. However, only those at $M_x = M_0 = 5000$ in Figure 2 give the real values for \bar{M}_w and \bar{M}_n , which are also listed in Table II.

The values for M_0 , \bar{M}_w , \bar{M}_n , and the branching parameters for SRM 1476 obtained by Wild et al.⁴ using the Ram-Miltz approach are also listed in Table

TABLE II
The Values for M_0 , \bar{M}_n , \bar{M}_w , and Branching Parameters Obtained by
This Work and by Wild et al. for SRM 1476

	M_0	$\bar{M}_n \times 10^{-4}$	$\bar{M}_w \times 10^{-4}$	G	g	n_b	$\bar{\lambda} \times 10^4$
Wild ⁴	6000*	2.10	8.32	0.65	0.42	9.7	1.17
This work	5000	1.80	8.40	0.65	0.42	9.7	1.16

* This value for M_0 was predetermined.

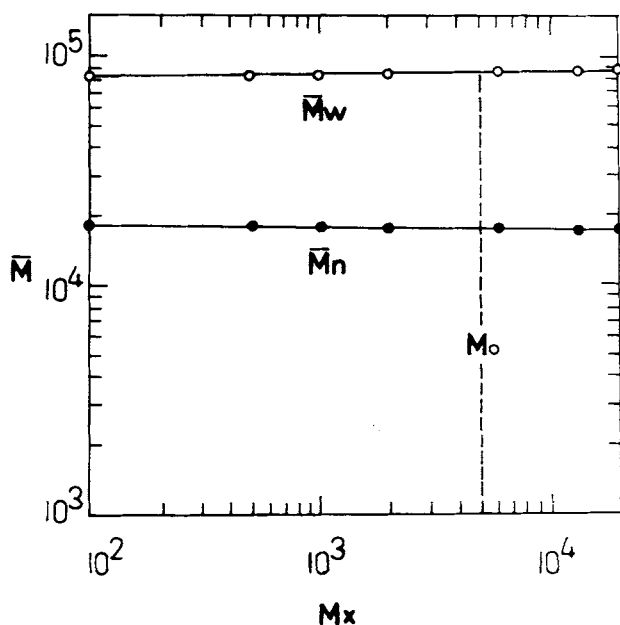


Fig. 2. Plots of $\log \bar{M}_w$ versus $\log M_x$ (O) and $\log \bar{M}_n$ vs. $\log M_x$ (●).

II. It can be seen that the results given by the Ram-Miltz approach and by the present method are in very good agreement.

The results for a branched *cis*-1,4-polybutadiene sample were also given by the present method and are compared in Table III with those obtained by using the Ram-Miltz method in our previous work.²¹ They are basically in agreement.

It will be seen from the above that the present method can be used in determination of LCB as well as the conventionally used Ram-Miltz method. Furthermore, our method has the advantage of avoiding predetermination of the threshold value M_0 for a particular resin. Thus, it will be more versatile for determination of LCB in polymers. The threshold value M_0 and average molecular weights \bar{M}_w and \bar{M}_n , as well as LCB for a polymer can be simultaneously evaluated. It must be pointed out that the influence of M_0 on \bar{M}_w and \bar{M}_n is only slight whereas that on branching degree G (i.e., on LCB) is rather remarkable. This means that it is very important to precisely determine the M_0 in characterizing branched polymers. However, to precisely determine the M_0

TABLE III
The Values for M_0 , \bar{M}_w , and Branching Parameters Obtained by This Work and the Previous Work for Branched *Cis*-1,4-Polybutadiene Sample

	$\bar{M}_0 \times 10^{-4}$	$\bar{M}_w \times 10^{-4}$	g	n_b	$\bar{\lambda} \times 10^4$
Previous work ²¹	120 ^a	76	0.91	0.46	0.6
This work	130	77	0.88	0.71	0.9

^a This value for M_0 was predetermined.

for a polymer is a laborious task, and sometimes may encounter considerable practical difficulty. Naturally, our method has no such problem.

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