A new model for rapid evaluation of the degree of long-chain branching in polymers

Yongsok Seo* and Kwang Ung Kim
Polymer Processing Laboratory, Korea Institute of Science and Technology, PO Box 131, Cheongryang, Seoul, Korea

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A new model is proposed for rapid evaluation of the degree of long-chain branching in polymers, which correlates the intrinsic viscosity and the molecular weight. Intrinsic viscosity is expressed as a simple inverse tangent function of molecular weight. The model is based on the observation of rheological behaviour of polymer melts and solutions. It can describe the intrinsic viscosity behaviour over a wider range than the Mark–Houwink equation. This model does not use trial and error procedure to decide the threshold molecular weight where the intrinsic viscosity starts to deviate from the Mark–Houwink relation. Calculation by the proposed model of the long-chain branching frequency of low density polyethylene shows good agreement with experimental results in the literature.

(Keywords: intrinsic viscosity; inverse tangent function; long-chain branching frequency)

INTRODUCTION

The degree of long-chain branching, along with molecular weight and chemical composition, is one of the fundamental parameters needed to fully describe polymer structure and melt-processing properties[1]. Over the years its importance has become increasingly apparent. Since the fundamental work of Zimm and Stockmayer[2], the influence of long-chain branching on polymer properties has been studied extensively[3]. Long-chain branching can be determined experimentally by gel-permeation chromatography (g.p.c.) and combined methods. The basis for all g.p.c.-related methods is the universal retention volume–hydrodynamic volume relation (universal calibration) proposed by Grubisic *et al.*[4]. However, branched molecules have a smaller hydrodynamic volume than linear molecules and thus will elute in g.p.c. with lower molecular weight linear molecules. So its true molecular weight distribution (*MWD*) is different from that of the linear molecules[5]. Specifically, the g.p.c.–viscometry method which has been most widely used has the problem of establishing the intrinsic viscosity–molecular weight relationship suitable for a particular branched resin.

The most prevailing relationship between the intrinsic viscosity and the molecular weight is the simple Mark–Houwink equation, which presents the intrinsic viscosity as a power-law function of molecular weight. However, intrinsic viscosity behaviour departs seriously from the Mark–Houwink equation at both low and very high molecular weights[1]. Also, the behaviour of branched polymers does not always follow the relation. One approach to solve this problem of the Mark–Houwink equation is the Ram–Miltz procedure, 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, M_0 is not an intrinsic property of the polymer. It can be markedly different from the same polymer prepared by different synthetic methods. Also, its determination by numerical trial and error procedure requires tedious computer iteration.

For more accurate and reliable analysis, we need a new model that can express the behaviour of polymer solutions and from which we can obtain the long-chain branching number more easily. The purpose of this paper is to report a simple general model which can depict the behaviour of intrinsic viscosity for both linear and branched polymers over a very wide range of molecular weight. We apply this model to the characterization of branched polymers and investigate its accuracy and applicability.

THEORETICAL CONSIDERATIONS

The viscosity of a dilute polymer solution depends on the nature of the polymer and the solvent, the concentration of the polymer, its average molecular mass and molecular mass distribution, the temperature and the rate of deformation[1]. The most important characteristic quantity in a very dilute solution under low deformation rate is the intrinsic viscosity (the limiting viscosity number), $[\eta]$ defined as:

$$[\eta] = \lim_{\substack{c \to 0 \\ G \to 0}} \frac{\eta_{1,2} - \eta_1}{\eta_1 c} \tag{1}$$

where η_1 and $\eta_{1,2}$ are the respective viscosities of the pure solvent and the solution, c is the concentration, and G

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*To whom correspondence should be addressed. Present address: Department of Chemistry, University of Wisconsin, 1101 University Avenue, Madison, WI 53706, USA

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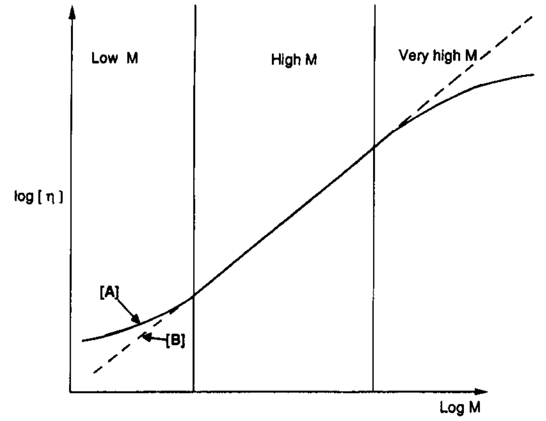

Figure 1 The Mark–Houwink relation for a given polymer in solution: A (——), real intrinsic viscosity; B (- -), prediction by the Mark–Houwink relation

is the shear gradient. The intrinsic viscosity is related to the dimension of the isolated polymer molecule and it can be presented as a function of molecular weight by the Mark–Houwink relation, which can be derived theoretically:

$$[\eta] = KM^{\alpha} \tag{2}$$

where M is the molecular weight, and K and α are constants[1]. However, a plot of $\log[\eta]$ *versus* $\log M$ for many polymer solutions shows deviation from the linear relationship at both low and very high molecular weights (*Figure 1*). In the low molecular weight region, it is common to find $\alpha \approx 0.5$ for flexible chains despite the use of good solvents. The failure of the Mark–Houwink relationship to predict behaviour at low molecular weight is a consequence of the non-Gaussian character of short flexible chains, and at very high molecular weight is due to hydrodynamic interaction[7]. So, when applying data reported in the literature to the Mark–Houwink relationship, attention must be given to the nature of the calibration. Also, as mentioned above, the dilute solution properties of branched polymers differ from those of linear polymers of the same composition. The effect of branching is to increase the segment density within the molecular coil. Thus a branched molecule occupies a smaller volume and has a lower intrinsic viscosity than a similar linear molecule of the same molecular weight. For the characterization of branched polymers using the universal calibration, therefore, higher order terms of log M should be adopted to correct for the lower viscosity of branched polymers[8].

Figure 2 shows the plot of $\log[\eta]$ *versus* $\log M$ of a long-chain branched low density polyethylene (LDPE) sample. From *Figures 1* and *2*, we can see that curves of $\log[\eta]$ *versus* $\log M$ have a sigmoidal shape. From rheological considerations, we have already proposed the following empirical equation[9] for shear viscosity, η:

$$\log \eta = C_1 \tan^{-1}(\log \lambda_r \dot{\gamma}) + C_2 \tag{3}$$

where $\dot{\gamma}$ is the shear rate, λ_r is the relaxation time constant, and both C_1 and C_2 are constants. This model for the shear viscosity was proposed to describe the non-linear behaviour of polymer melts and solutions with few parameters and applied to the first normal stress coefficient prediction using Wagner's relationship. Its prediction was compared with the published experimental data of polymer melts and solutions[9]. Its non-linear form was shown to correlate the model very well with experimental data over many decades of shear rate. This model has some additional merits when compared to the finite relaxation time series approach of Wagner, i.e. it has fewer parameters and it does not show any numerical artefacts in the prediction of the first normal stress coefficient function. The proposed model also fits the elongational viscosity very well. The current model is quite compact in its form and useful for simple modelling and simulation (see ref. 9 for details).

From molecular theory it is known that the relaxation time is proportional to the molecular weight of the polymer in ideal solutions (it scales with the first power of the molecular weight up to some characteristic molecular weight, after which it scales with the cubic (or, more precisely, 3.4) power)[10]. Therefore, when the deformation rate is so low that its effects are negligible and the solution concentration is very dilute, we can expect a relationship between $\log[\eta]$ and $\log M$ to be as follows:

$$\log[\eta] = m_1 \tan^{-1}[\log(M/m_2)] + m_3 \tag{4}$$

provided that a linear relationship exists between the intrinsic viscosity and the shear viscosity. In equation (4), m_1, m_2 and m_3 are fitting parameters: parameter m_1 is the span of intrinsic viscosity values at the limit of high and low molecular weight multiplied by $(2/\pi)$; parameter m_2 is the amount of horizontal shift of the inverse tangent function curve and m_3 is the amount of vertical shift. These parameters appear because the centre of the viscosity function is not at the origin. As shown later, equation (4) is actually so versatile that it is applicable to a wider range of molecular weight than expected owing to its non-linear nature and sigmoidal shape of the inverse tangent function.

If equation (4) is applicable both to linear polymer solutions and branched polymer solutions, we can use it for branched polymer characterization as well. In branched polymer characterization, the long-chain branching frequency is one of the most important factors. The estimation of the long-chain branching frequency in LDPE has been achieved by many workers. However, large discordances in the reported results are observed, proceeding mainly from the various assumptions admitted *a priori*. In every case, the starting point is the structure

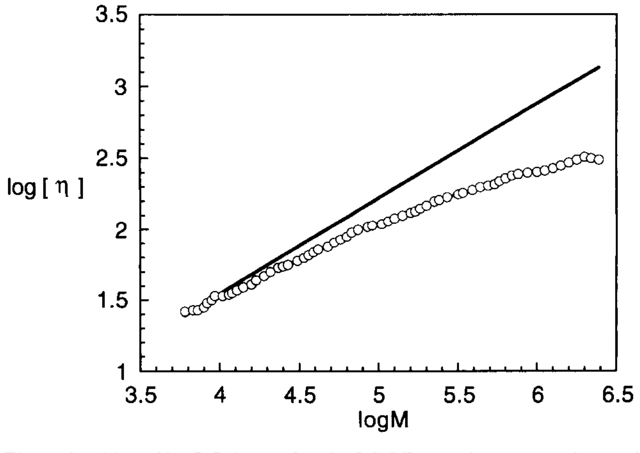

Figure 2 Plot of log[η]–log M for the LDPE sample: ○, experimental viscosity; ——, the Mark–Houwink relation for linear polyethylene from ref. 4

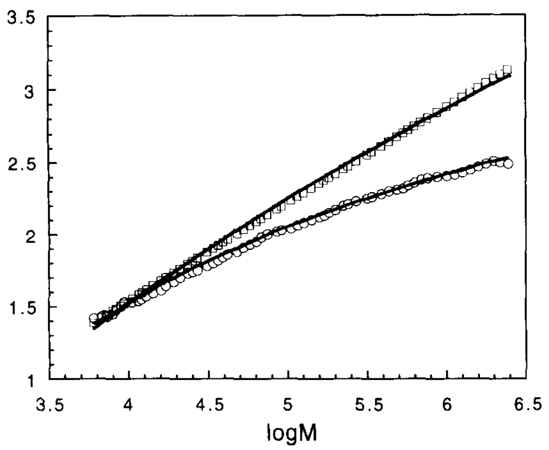

Figure 3 Correlation of the current model for intrinsic viscosity of linear polyethylene presented as following the Mark–Houwink relation (□) and long-chain branched polyethylene (○). Model parameters are presented in *Table 1*

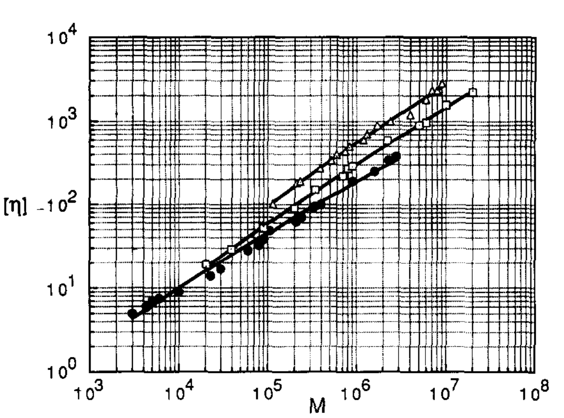

Figure 4 Molecular weight dependence of intrinsic viscosity (dl g^{-1}): □, experimental data from ref. 15 for solutions of polystyrene in tetrahydrofuran at 25°C; ●, experimental data from ref. 16 for solutions of poly (methyl methacrylate) in benzene at 30°C; △, experimental data from ref. 17 for solutions of poly(D-β-hydroxybutyrate) in chloroform at 30°C; ——, the current model. Parameter values are presented in *Table 1*

parameter g' defined as:

$$g' = \frac{[\eta]_b}{[\eta]_L} < 1 \tag{5}$$

where $[\eta]_b$ is the intrinsic viscosity of the branched species and $[\eta]_L$ is that of the linear species with the same molecular weight M_b. Let us assume that $[\eta]_b$ and $[\eta]_L$ follow the relationship represented as equation (4). It is then necessary to assume a relationship between g' and the ratio g of the mean square radius of gyration $\langle R_G^2 \rangle$ of the same species:

$$g = \frac{\langle R_G^2 \rangle_b}{\langle R_G^2 \rangle_L} \tag{6}$$

g and g' are interrelated by:

$$g' = g^x \tag{7}$$

where the exponent x is dependent on the type of branches and has a value between 0.5 and 1.5 (refs 2,11–14). For randomly branched polymers, x is 0.5, the theoretical value of Zimm and Kilb[11]. In case of LDPE[3], x is known to be 1.2 ± 0.2. Finally, the number of branches per macromolecule, n, is obtained by one of the Zimm–Stockmayer relationships[2]; the two most often encountered are:

$$g = \left[\left(1 + \frac{n}{7}\right)^{1/2} + \frac{4n}{9\pi}\right]^{-1/2} \tag{8}$$

$$g = \frac{6}{n}\left\{\frac{1}{2}\left(\frac{2+n}{n}\right)^{1/2} \ln\left[\frac{(2+n)^{1/2} + n^{1/2}}{(2+n)^{1/2} - n^{1/2}}\right] - 1\right\} \tag{9}$$

But it was revealed by Lecacheux *et al.*[8] that the results are not very different with regard to the expected precision. When n is greater than 5, the following approximate equation is also accurate within 3% error:

$$g = \frac{3}{2}\left(\frac{\pi}{n}\right)^{1/2} - \frac{5}{2n} \tag{10}$$

RESULTS AND DISCUSSION

Experimental measurements of intrinsic viscosity of linear and branched polyethylenes were reported by Lecacheux *et al.*[8]. *Figure 3* shows the fitting of the intrinsic viscosity of linear polyethylene and branched polyethylene using equation (4). The current model correlates very well with both. It also agrees well with the Mark–Houwink relationship for linear polyethylene. *Figures 4* and *5* show fittings of the current model to other experimental data reported in the literature. The sigmoidal nature of the inverse tangent function in equation (4) shows very smooth fittings even at low molecular weight. As shown in the figures of references 15–18, the Mark–Houwink equation could not cover the entire molecular weight range in these figures. All constant values, m_1, m_2 and m_3, of the curves are presented in *Table 1*.

Figure 6 shows the g' calculation by the current model and the calculated results of Lecacheux *et al.* using the Mark–Houwink equation for the linear polymer and a third-degree polynomial regression for the branched polymers. The agreement is quite satisfactory, although small deviations occur at very high molecular weight. These may be due to the loss of sensitivity inherent in the molecular size detectors for the experiment, as well as to the logarithmic relation, since we used the following

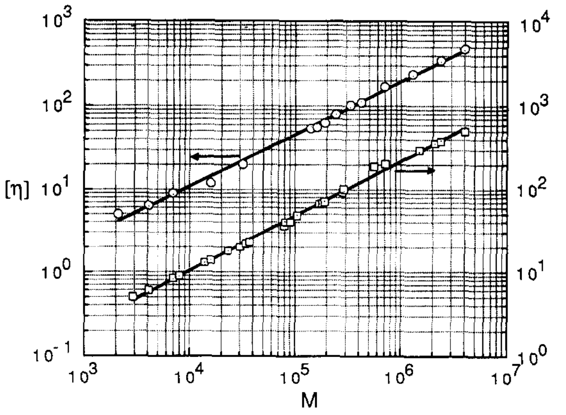

Figure 5 Molecular weight dependence of intrinsic viscosity (dl g^{-1}): ○, experimental points from ref. 18 for solutions of polystyrene in CCl_4 at 25°C; □, experimental points from ref. 18 for solutions of polystyrene in $CHCl_3$ at 25°C; ——, the current model predictions. Parameter values are presented in *Table 1*

Table 1 Parameter values for the inverse tangent model: $\log[\eta] = m_1 \tan^{-1}[\log(M/m_2)] + m_3$

Curve fitting	m_1	m_2	m_3
Figure 3, □	0.1562	1.945	−5.032 53
Figure 3, ○	0.1456	6.1747	−2.424 53
Figure 4, □	0.0866	13.976	−2.1968
Figure 4, ●	0.1190	10.893	−1.9572
Figure 4, △	0.1065	8.9178	−2.8143
Figure 5, ○	0.0047	342.137	−1.457 06
Figure 5, □	0.0084	179.5447	−1.644

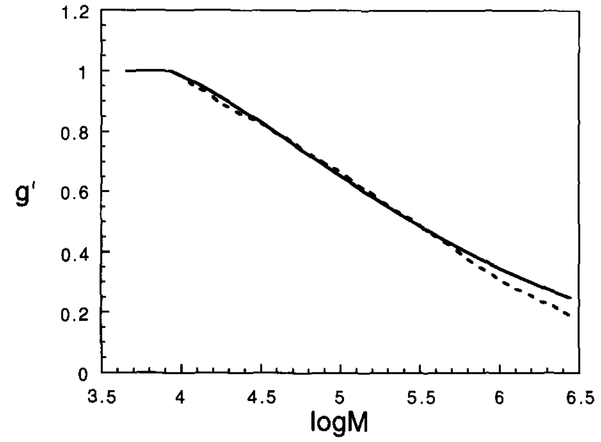

Figure 6 Plot of structure parameter g' *versus* molecular weight: – – –, calculation by Lecacheux *et al.*[8] using a third-degree polynomial regression; ——, the current model

equation for g' calculation:

$$\log g' = \log[\eta]_b - \log[\eta]_L \tag{11}$$

from equation (9).

By using equations (7)–(10), we calculate the long-chain branching frequency λ ($= n/M$). *Figure 7* shows the calculated results. The agreement is again quite good. Using the same exponent value of 1.2, the λ value decreases continuously, and when the exponent is close to 1, it approaches a constant value. However, the λ value is in a reasonable range regardless of x value. Lecacheux *et al.*'s calculation shows no significant change of λ value with molecular weight, λ having a constant value of about 0.3×10^{-4} at high molecular weight[8]. Depending on the experimental conditions and data analysis, however, the trend can be varied as shown in *Figure 7*. When x is 0.5, which is the value for randomly branched polymers in the Zimm–Kilb model, λ increases with molecular weight rather than decreasing.

Recently, Jin and Guo[19] reported the long-chain branching frequency of polyethylene. Following the Ram–Miltz scheme[5], they used the Mark–Houwink relationship for the linear polymer and a third-order polynomial when the data deviated from the linear relationship with $\log M$, which requires numerical decision of the threshold molecular weight M_0, at which the intrinsic viscosity starts to deviate from the linear relationship. The current model does not need predetermination of M_0, which is a considerable advantage for correct λ estimation. The reported λ value was on the order of 10^{-4}, which is close to our value. However, when x is equal to 0.5, which was the value used by Jin and Guo, λ increases with molecular weight rather than decreasing, as shown in *Figure 7*. Jackson[14] also reported a λ value of 0.25×10^{-4}. The order of λ in other experimental data coincides with our result.

As Lecacheux *et al.* mentioned, it is certain that a particular calculation process can change the λ value. As shown in *Figure 7*, however, the order of magnitude in different cases remains the same. Therefore, the current model works well for branched polymer characterization as well as linear polymer characterization.

The current model can also be used for the *MWD* determination of branched polymers. For a given fraction i in a g.p.c. chromatogram, the relationship between the molecular weights of linear and branched polymers should conform with the universal calibration, i.e.:

$$[\eta]_{\mathrm{lin},i} M_{\mathrm{lin},i} = [\eta]_{\mathrm{br},i} M_{\mathrm{br},i} \tag{12}$$

since the product $[\eta]M$ of a polymer chain in solution is directly proportional to the hydrodynamic volume of the equivalent sphere[1]. Taking the logarithm of equation (12) gives:

$$\log M_{\mathrm{br},i} = \log[\eta]_{\mathrm{lin},i} - \log[\eta]_{\mathrm{br},i} + \log M_{\mathrm{lin},i} \tag{13}$$

Combining equations (4) and (13), we have:

$$\begin{aligned} \log M_{\mathrm{br},i} = {} & m_1' \tan^{-1}[\log(M_{\mathrm{lin},i}/m_2')] + m_3' \\ & - m_1 \tan^{-1}[\log(M_{\mathrm{br},i}/m_2)] \\ & - m_3 + \log M_{\mathrm{lin},i} \end{aligned} \tag{14}$$

For the first-order calculation we get:

$$\log M_{\mathrm{br},i} = \frac{(m_1'+1)\log M_{\mathrm{lin},i} + m_1' \log m_2' - m_1 \log m_2 + m_3' - m_3}{(m_1+1)} \tag{15}$$

For a more accurate calculation, $M_{\mathrm{br},i}$ obtained from equation (15) is inserted into equation (14) and the calculation is repeated three or four times until the value converges. The weight and number average molecular weights are calculated as follows:

$$\bar{M}_w = \sum (W_i M_{\mathrm{br},i}) \tag{16}$$

$$\bar{M}_n = 1/\sum (W_i / M_{\mathrm{br},i}) \tag{17}$$

where W_i is the weight fraction of i. As an example, the molecular weight distribution of polyethylene reported

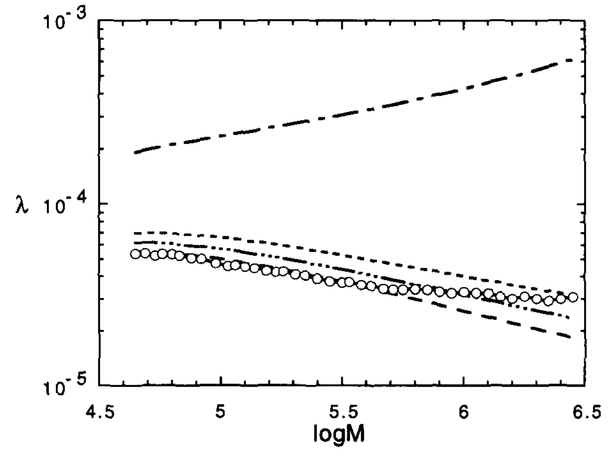

Figure 7 Plot of long-chain branching frequency λ *versus* molecular weight: ○, Lecacheux *et al.*'s calculation[8]. Lines represent the current model predictions for: – – –, $x = 1.2$; —— –, $x = 1.1$; ------, $x = 1.0$; — · —, $x = 0.5$

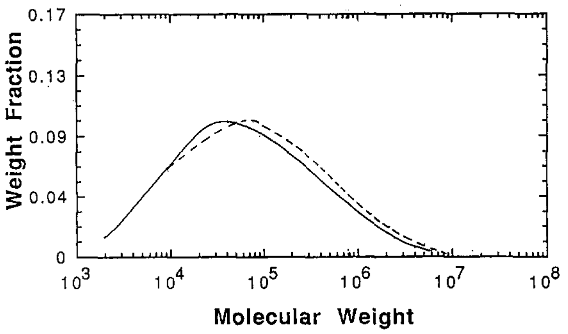

Figure 8 Molecular weight distribution of polyethylene (PE-76): —, Ram and Miltz calculation[5]; – –, the current model calculation

by Ram and Miltz[5] is recalculated as shown in *Figure 8*. Generally, the agreement with the third-order calculation is rather satisfactory. A slight deviation is observed in the high molecular weight portion. This deviation affects the calculated values of M_w but has very little effect on the value of M_n. Calculation of M_n by the proposed method yields 13 000, which is smaller than the third-degree calculation of Ram and Miltz but quite close to the measured value of 13 300. Even though M_w is not calculated because we do not have exact distribution data, we can see from *Figure 8* that the current model will give a higher M_w value than that obtained by the third-degree polynomial calculation.

From its explicit form, equation (4), two different shapes of the intrinsic viscosity behaviour can be described. The first is the approach of the lower part of the sigmoidal shape and the second is the approach of the upper part of the sigmoidal shape[20]. Generally, flexible chains with backbones of small diameter, permitting closer approach of the chain units and greater flexibility, follow the lower part of the sigmoidal shape, i.e. their approach to the power-law region takes place from above, with larger values of $[\eta]$ than those of the power law as shown in *Figure 1*. On the other hand, rigid chains with wider backbone diameters approach the power-law region from below, with smaller values of $[\eta]$ than those of the power law. The two different behaviours are explained by means of the interactions between the units of the chain[20]. Owing to its natural shape, equation (4) is flexible enough to fit both cases. This behaviour is related to the shifting of the curve inversion point. Depending on the m_2 value, approaches from both directions are possible.

CONCLUSION

Based on the rheological behaviour of polymers, we proposed a new equation having the form of an inverse tangent function of $\log M$ to correlate intrinsic viscosity. It is quite versatile, describing not only the intrinsic viscosity behaviour of both flexible and rigid chains but also the molecular weight distribution of branched polymers. Good agreement of intrinsic viscosity values between the proposed model and experimental data was observed for both linear and branched polymer solutions. Using the proposed model, long-chain branching frequency was calculated and found to be in good agreement with values reported by Lecacheux *et al.*

Compared to the conventional Ram–Miltz method for long-chain branching frequency calculation, the current model does not need predetermination of the threshold molecular weight M_0 for a given polymer, nor higher-order terms to compensate for the deviation from the linear relationship. Even though the long-chain branching frequency value is quite sensitive to the calculation process, its order of magnitude always remains in a reasonable range.

When used with g.p.c. chromatograms and the measured values of the intrinsic viscosity of the whole polymer, the current model will be useful for rapid and accurate evaluation of the long-chain branching frequency in polymers, as well as for proper evaluation of molecular weight distribution.

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