

# Gel Permeation Chromatography of Polyethylene.

## II. Rapid Evaluation of Long-Chain Branching and Molecular Weight Distribution

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### Synopsis

A comparison is made of two methods by which one may derive molecular weight distribution and degree of long-chain branching using only the measured solution viscosity of a branched polyethylene whole polymer and its GPC trace. These are (a) Drott and Mendelson method and (b) Ram and Miltz procedure. In each case, the purpose of the method is to devise a means by which one may establish a relationship between solution viscosity and molecular weight for use in conjunction with the GPC universal calibration relationship of Benoit et al. The effectiveness of these theoretical approaches is evaluated by comparison with the true  $D$  and degree of long-chain branching data obtained using our complete iterative analysis method. Such a detailed comparison using low, moderate, and highly branched resins leads to a conclusion that both the techniques provide very good MWD and branching data and, further, that they may be considered interchangeable for most resins. For highly branched resins, the Ram and Miltz method, which is slightly more sensitive to the presence of a high degree of long-chain branching, is preferred. In practice, the Drott and Mendelson method has the advantage of using less computer time and providing a direct measure of degree of long-chain branching, and thus is likely to be used most frequently.

### INTRODUCTION

Over the past few years, gel permeation chromatography (GPC) has established itself as the most powerful analytical tool available to the polymer chemist. This technique provides the cornerstone of our polyethylene structure studies and has been used extensively, with considerable attention being paid to both the practical operation of the instrument and the details of data analysis. Some aspects of this work have been reported previously,<sup>1,2</sup> particularly concerning the importance of effective GPC calibration.

Through GPC, one obtains a molecular separation based on size (hydrodynamic volume), and the resultant separation is displayed on a chart as a weight distribution, which may be converted to a molecular weight distribution by a suitable calibration method. In the analysis of low-density polyethylenes, the nature of the separation (by size) presents both a distinct problem and an opportunity. This is because almost all low-density polyethylenes exhibit long-chain branches which exert a strong influence on molecular size. Thus, the weight distribution provided by GPC is influenced by both long-chain branching and molecular weight, making molecular weight calibration very difficult. The

dual dependence of GPC separation on molecular weight and LCB does, however, provide the opportunity for obtaining information as to the degree of LCB present in a particular resin as well as its molecular weight and molecular weight distribution (MWD).

The means by which one might resolve the problem of separating out the two effects due to molecular weight and LCB was provided by Benoit et al.<sup>4</sup> He demonstrated that the GPC elution volume can be related to a hydrodynamic volume parameter  $M[\eta]$ , i.e., GPC calibration in terms of  $[\eta]M$  applies to all polymer systems and provides a universal calibration for a particular instrument. When applied to a branched polymer like polyethylene, if one knows the solution viscosity of the molecular species eluting at any particular point, one may simply determine its molecular weight, allowing one to construct a MWD curve. Further, a knowledge of the actual solution viscosity in relation to the solution viscosity which would be exhibited by a linear species of the same molecular weight provides a measure of the degree of LCB.<sup>5</sup>

The great potential of the GPC technique for the analysis of branched polyethylenes can thus be appreciated, for it is only through a knowledge of both MWD and degree of LCB that one can hope to understand the complex behavior of these materials. Because of this, considerable effort has been expended in these and other laboratories to establish practical methods of applying the universal calibration concept of Benoit to the GPC analysis of polyethylenes.

The calibration of the GPC in terms of  $[\eta]M$ , i.e., establishing a universal calibration, is readily achieved using *linear* polymer standards because the relationship between solution viscosity and molecular weight is normally well defined and known in terms of the Mark-Houwink equation  $[\eta] = KM^\alpha$ . The problem in the analysis of branched polymers finally becomes the problem of determining the value of the solution viscosity at each molecular weight level for the material being analyzed.

Several approaches are possible and have been tried for establishing the solution viscosity-molecular weight relationship for a particular branched resin. They break down into two categories, one involving the measurement of the viscosity values at differing molecular weight levels,<sup>1,6,7</sup> and the second approach attempting 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 whole polymer.<sup>8,9,10</sup> The former approach presents considerable practical difficulty, while the problems associated with the latter type of method are those concerning the effectiveness of the theoretical definition of the solution viscosity-molecular weight relationship for real branched resins.

The uncertainties possible when using any of the theoretical approaches dictated that our initial application of the universal calibration concept be through a method using direct solution viscosity measurement of the various molecular weight species from a parent resin. The technique involves an initial preparative fractionation, followed by GPC and solution viscosity determinations on the resulting fractions, from which one may derive the molecular weight of each of the fractions and allow the direct construction of a molecular weight calibration curve for the parent resin. The calculations have been computerized with the inclusion of an iterative section in the program to correct for the polydispersity of the fractions. The details have been reported earlier,<sup>1</sup> and this has become

known as our standard iterative analysis method for the derivation of molecular weights, molecular weight distribution, and degree of LCB. The results are unambiguous but the method is time consuming and needs considerable experimental equipment.

In the studies described below, an attempt is made to evaluate the effectiveness of the more rapid methods of Ram and Miltz (R & M) and Drott and Mendelson (D & M) in providing realistic MWD and degree of LCB data.

### THEORETICAL RELATIONSHIPS BETWEEN SOLUTION VISCOSITY AND MOLECULAR WEIGHT FOR BRANCHED POLYMERS

As indicated in the Introduction, in the absence of a means of directly determining the solution viscosity of the various molecular weight branched species in a resin, one must find a means of defining the relationship between solution viscosity and molecular weight for any particular resin in order to use the universal calibration. Such a definition has been attempted using two different approaches. One involves the use of a theoretical relationship between degree of LCB and solution viscosity from which one may derive the solution viscosity-molecular weight relationship. This method has been described by Drott and Mendelson<sup>8</sup> and by Shida and Cote.<sup>9</sup> The second method<sup>10</sup> makes no assumption as to the relationship between degree of LCB and solution viscosity and molecular weight value. Both choose the numerical values of their expressions by an iteration procedure using the conditions that the final computed solution viscosity of the whole polymer equals the experimentally measured value.

The two approaches are outlined in the following paragraphs.

#### Ram and Miltz Procedure

For linear polyethylenes, the solution viscosity-molecular weight relationship is expressed by the Mark-Houwink equation  $[\eta]_{lin} = KM^\alpha$ , where  $K$  and  $\alpha$  are constants for a given solvent at a particular temperature. No such simple relationship is possible for the long chain-branched polyethylenes.

An approach to a derivation of the solution viscosity-molecular weight relationship for branched polyethylenes has been suggested by Ram and Miltz. In their method, the formulation of a Mark-Houwink-type relationship for a branched polymer is assumed to be described by a polynomial expression as in

$$\ln [\eta] = \ln K + \alpha \ln M + b \ln^2 M + c \ln^3 M$$

where  $\alpha$  and  $K$  have the same significance and values that qualify for a linear polymer. The parameters  $b$  and  $c$  for each branched polyethylene under consideration are varied in such a way that the computed solution viscosity of the whole polymer equals the measured value. With the aid of this expression the GPC data for the branched LDPE is interpreted to determine its molecular weight distribution.

The method takes advantage of the experience and information gathered in the past on the branched polyethylenes of varying degrees of long-chain branching. It has been observed that the different long chain-branched poly-

ethylenes all behave as linear polyethylenes below the molecular weight level of  $5 \times 10^3$  and up to this threshold value (say,  $M_0$ ) can be represented by the simple Mark-Houwink relationship:

$$\ln [\eta]_{\text{TCB}}^{140} = \ln K + \alpha \ln M \quad \text{for } M < M_0 = 5 \times 10^3$$

where  $K = 3.95 \times 10^{-4}$  and  $\alpha = 0.726$ . Above this molecular weight level, the solution viscosity-molecular weight relationship is expressed by the polynomial referred to earlier, viz.,

$$\ln [\eta] = \ln K + \alpha \ln M + b \ln^2 M + c \ln^3 M \quad \text{for } M \geq M_0 = 5 \times 10^3$$

The GPC data of the whole polymer are handled with the aid of this polynomial expression for solution viscosity based on the fact that this viscosity is made up of the contributions from each species, and thus

$$[\eta]_{\text{total}} = \Sigma W_i [\eta]_i$$

In applying this to the GPC curve, we have the weight fraction of species  $i$ ,

$$W_i = h_i / \Sigma h_i$$

where  $h_i$  is the height of the GPC curve at the corresponding count number (elution volume).

The specific Mark-Houwink relationship is

$$[\eta]_i = KM_i^{(\alpha + b \ln M_i + c \ln^2 M_i)} \quad \text{for } M_i \geq M_0$$

i.e.,

$$[\eta]_i M_i = KM_i^{(1 + \alpha + b \ln M_i + c \ln^2 M_i)} \quad \text{for } M_i \geq M_0$$

The left-hand side of this expression is the molecular size of the species according to which it is separated in gel permeation and directly corresponds to the count number  $C_i$  at which it appears. Applying the universal calibration, it is now possible to use the crude chromatogram and the measured value of the solution viscosity of the whole polymer (both at the same temperature and in the same solvent) to obtain the best values of  $b$  and  $c$  by trial and error. In turn, the above viscosity-molecular weight relations yield the complete molecular weight data.

### Drott and Mendelson Procedure

This method, developed for characterizing long-chain branching and molecular weight distribution of branched whole polymers from GPC and intrinsic viscosity measurements, is an iterative computer program where the branching index  $\lambda$ , defined as the ratio

$$\frac{\text{number of branch points in the molecule}}{\text{molecular weight}}$$

is varied until the solution viscosity calculated using GPC data matches with the experimentally measured viscosity of the whole polymer. Using this value of  $\lambda$ , the raw GPC curve is interpreted to calculate the MWD for the whole polymer.

The basic equations and assumptions used in the LCB calculations are

(a) In the GPC, the universal calibration assumption, viz., that the separation

of molecules is controlled by their hydrodynamic volume, holds good for both linear and branched polyethylenes. That is,

$$[\eta]_{lin}M_{lin} = [\eta]_{br}M_{br}$$

(b) The viscosity ratio is

$$[\eta]_{br}/[\eta]_{lin} = g^{1/2}$$

where  $g$  is a function related to the number of branch points in a molecule. The specific function derived by Zimm and Stockmayer<sup>11</sup> for a trifunctional branch point with reference to a polydisperse polymer is

$$\langle g_3 \rangle = \frac{6}{\lambda M} \left[ 1/2 \left( \frac{2 + \lambda M}{\lambda M} \right)^{1/2} \ln \left( \frac{(2 + \lambda M)^{1/2} + (\lambda M)^{1/2}}{(2 + \lambda M)^{1/2} - (\lambda M)^{1/2}} \right) - 1 \right]$$

(c) The intrinsic viscosity of a branched whole polymer can be calculated from

$$[\eta]_{br} = \sum W_i [\eta]_{br_i} = K \sum W_i M_i^\alpha \cdot [g(\lambda M_i)]^{1/2}$$

where  $K$  and  $\alpha$  are Mark-Houwink constants and  $\lambda$  is the branching index defined earlier.

(d) The branching index  $\lambda$  is assumed to be independent of molecular weight for a given polymer. That is,  $\lambda$  is a constant for the whole spectrum of molecular weights that go to make up the whole polymer.

In the computer program,  $\lambda$  is varied until calculated and measured viscosities are in good agreement. To calculate the intrinsic viscosity, the branched calibration curve corresponding to the assumed value of  $\lambda$  must be obtained first. This is achieved through the use of the two functions

$$[\eta]_{br_i} = f(\lambda M_i)$$

and

$$[\eta]_{br_i} M_i = f(C)$$

which is the universal calibration where  $C$  is the elution volume.

Essentially, this leads to the branched calibration curve

$$C = f(M)$$

with which the GPC curve is interpreted to yield the molecular weight distribution of the whole polymer.

## EXPERIMENTAL

The only experimental data needed for the evaluation of MWD and degree of LCB by either of the above procedures are the measured solution viscosity, GPC trace, and calibration equation for the GPC columns in use.

### Solution Viscosity

Theoretically, intrinsic viscosity,  $[\eta]$ , should be used in the above calculations, but in practice, inherent viscosity,

$$\{\eta\} = \frac{\ln \eta_{rel}}{\text{concn.}}$$

is used and considered equivalent to  $[\eta]$  for the relatively low-viscosity branched whole polymers. Determination of  $\{\eta\}$  is carried out in a 0.15% solution in TCB at 140°C, and the same solution is injected into the GPC. The accuracy of the solution viscosity value is important and so samples are usually run in duplicate and an automatic timer is now used for improved timing accuracy.

### GPC Calibration

The GPC column systems are not permanent and may vary in their operational characteristics over a period of time, finally needing replacement. It is therefore essential to devise a reliable and effective calibration procedure if one is to derive a long-range reproducibility comparable with that obtainable in successive runs. Initial calibration of the GPC is established using National Bureau of Standards SRM 1475 linear polyethylene whole polymer standard and high molecular weight linear polyethylene fractions from preparative fractionation of broad-MWD resins. The details of the technique are given in the previous paper.<sup>3</sup> Routine calibration is achieved directly using a secondary standard, a broad-MWD, homogenized linear polyethylene, with known MWD as derived as part of the initial calibration experiment.<sup>3</sup> The universal calibration is derived mathematically by combining the Mark-Houwink relationship for PE in TCB at 140°C,

$$[\eta] = 3.95 \times 10^{-4} M_v^{0.726}$$

with the linear polyethylene calibration equation. This is also outlined in the previous paper.<sup>3</sup>

### RESULTS AND DISCUSSION

Both the Ram and Miltz (R & M) and the Drott and Mendelson (D & M) methods of evaluating the raw GPC data were readily translated into appropriate computer programs. Each program incorporates a systematic search procedure in which changing values of  $b$  and  $c$  in the case of the R & M and  $\lambda$  in the D & M method were entered into the program loop. The set of values produces an initial calibration curve (count vs. molecular weight) in conjunction with the universal calibration from which an MWD is computed. This, in turn, is transposed into a viscosity distribution using the viscosity-molecular weight relationship from which the calibration curve was first obtained and an average value for  $[\eta]$  is calculated. A binary search procedure is used, which is terminated when  $[\eta]_{\text{computed}} = [\eta]_{\text{measured}}$  within less than 1%. The MWD data from this final loop are typed out, the MWD curve plotted out, and the various molecular weight

TABLE I  
Description of Resins

	MI	Density	Resin type
SRM 1476	1.2	0.931	tubular reactor, low conversion resin: low degree of LCB
LDPE A	2.8	0.924	autoclave reactor, high conversion resin: high degree of LCB

TABLE II  
Comparison of MWD Data for SRM 1476 Computed by Differing Methods

Technique	$M_n \times 10^{-4}$	$M_w \times 10^{-4}$	$R$	$[\eta]_{\text{meas}}$	$[\eta]_{\text{comp}}$	$g'$
Complete iterative analysis	2.19	8.47	3.87	0.85	1.33	0.64
Ram and Miltz	2.10	8.32	3.97	0.85	1.30	0.65
Drott and Mendelson	2.09	8.39	3.99	0.85	1.31	0.65

averages are calculated, together with a computed value for the solution viscosity that a linear polyethylene of the same MWD would exhibit ( $[\eta]_{lin}$ ). The ratio of measured viscosity to the linear viscosity is called  $g'$  (i.e.,  $g' = [\eta]_{br}/[\eta]_{lin}$ ), and this is taken as a measure of the degree of LCB. As the degree of branching increases, the measured  $[\eta]_{br}$  deviates further from the linear polyethylene value  $[\eta]_{lin}$  and  $g'$  becomes smaller.

As indicated in the Introduction, the objective of the present studies is to determine whether either the R & M or D & M methods provide MWD data which are more realistic than those derived using a linear polyethylene calibration with correction for branching. Further, we would like to establish to what extent the rapid methods produce data equivalent to that derived completely experimentally using our complete iterative analysis. To provide a direct test of the rapid method, it was decided to compare the actual data produced for two test resins (Table I). The first, SRM 1476, was chosen as a simple resin with a relatively low level of branching and a narrow, symmetric MWD. The second, LDPE A, has been included as an example of a resin with a high degree of branching and a broad irregularly shaped MWD. This LDPE A sample is one in which the molecular weight dependence of branching is expected to be difficult to define by any simple relationship. This material should, therefore, provide a good test of the effectiveness of the two rapid analytic methods.

The complete iterative analysis technique was undertaken on both LDPE A and SRM 1476 to provide comparison data. More than usual care was taken to assure that the experimental data were accurate, and all fractions derived from the gradient elution fractionation were included in the analysis. The resulting data represent the best we can do with our complete iterative analysis method, and the molecular weight and MWD data should approximate very closely the true values. These data are listed in Tables II and III, where they are compared with those derived using the R & M and D & M methods. In addition, data were obtained for LDPE using a calibration derived using SRM 1476, with MWD determined by the iterative analysis method, as the GPC standard.

TABLE III  
Comparison of MWD Data for LDPE A Computed by Differing Methods

Technique	$M_n \times 10^{-4}$	$M_w \times 10^{-4}$	$R$	$[\eta]_{\text{meas}}$	$[\eta]_{\text{comp}}$	$g'$
Complete iterative analysis	1.85	34.7	18.8	0.88	3.12	0.31
SRM 1476 Standard	1.69	19.1	11.3	0.88	2.16	0.45
Ram and Miltz	1.85	37.5	20.2	0.88	3.20	0.28
Drott and Mendelson	1.95	33.1	17.0	0.88	3.04	0.29

TABLE IV  
MWD and Branching Data for a Series of LDPE Resins Computed by Differing Methods

Resin	Iterative analysis				R & M method				D & M method				
	$M_n \times 10^{-4}$	$M_w \times 10^{-4}$	R	$g'$	$M_n \times 10^{-4}$	$M_w \times 10^{-4}$	R	$g'$	$M_n \times 10^{-4}$	$M_w \times 10^{-4}$	R	$g'$	$\lambda \times 10^4$
SRM 1476	2.19	8.47	3.87	0.64	2.10	8.32	3.97	0.65	2.09	8.39	3.99	0.65	0.25
LDPE I	2.01	11.9	5.92	0.52	2.03	11.0	5.43	0.54	2.04	11.1	5.42	0.54	0.63
LDPE II	2.41	11.8	4.98	0.50	2.22	11.4	5.12	0.53	2.25	11.4	5.07	0.53	0.73
LDPE III	1.98	6.89	3.48	0.69	1.88	7.57	4.02	0.65	1.88	7.61	4.04	0.65	0.50
LDPE IV	2.53	15.1	5.97	0.50	2.40	17.5	7.32	0.46	2.42	17.5	7.23	0.46	0.69
LDPE V	2.06	18.0	9.0	0.38	1.82	18.1	9.93	0.38	1.86	17.6	9.42	0.39	1.09
LDPE A	1.85	34.7	18.8	0.31	1.85	37.5	20.2	0.28	1.95	33.1	17.0	0.29	1.14



### Complete Iterative Method Versus SRM 1476 Standard

The SRM 1476 branched polyethylene standard MWD data were determined experimentally using the complete iterative method, and so the same data apply to both methods of analysis. Good agreement would be expected when applying the two methods of evaluation to any resin with a relatively low level of LCB. In the case of application to a highly branched resin like LDPE A, however, the use of the SRM 1476 standard calibration should considerably underestimate the level of LCB and hence the breadth of MWD. The data in Table II indicate that this is indeed the case and confirm that the use of the SRM 1476 calibration standard is not a good method for evaluating GPC data for highly branched resins.

### Ram and Miltz Versus Drott and Mendelson Method

The R & M method was proposed as a possible improvement over the D & M method inasmuch as it is not confined by the assumption of constant degree of LCB,  $\lambda$ , as a function of molecular weight. It is of interest to see if the former method is significantly better in practice. When applied to the low degree of LCB resin, SRM 1476, it is clear from the data in Table II that both methods lead to essentially the same answer. Surprisingly, the same is true in the case of the highly branched resin, LDPE A, with the only significant difference being noted in the value of the weight-average molecular weight  $M_w$ . It is observed that the R & M method results in a slightly higher  $M_w$  value than does the D & M method (see Table III).

The tendency for R & M to give higher  $M_w$  values has been confirmed with other types of resin, but essentially it only occurs at high levels of LCB. In general, however, it is clear that both methods provide essentially the same MWD data. It is obvious also that either method is an improvement over the use of the SRM 1476, as both are sensitive to the differing levels of LCB present in the differing resins.

### R & M and D & M Methods Versus Complete Iterative Analysis Method

The final test of any rapid method is a check on how close the computed MWD and degree of LCB data are to actual data. In the present instance, we assume that our complete iterative analysis successfully approximates the true molecular weight values, and so a comparison has been made of the data from the complete analysis with those derived by the R & M and D & M methods. The data are compared in Tables II and III for SRM 1476 and LDPE A and in Table IV for a short series of differing resin types.

The results for LDPE A prove extremely encouraging, as can be seen in Table III. Both R & M and D & M methods give average molecular weight data which are in excellent agreement with those derived by the complete iterative method. The ability of both R & M and D & M methods to provide data which are very close to those produced by the complete iterative method is further illustrated by the data in Table IV. Here, the degree of LCB as indicated by  $g'$  is in good agreement among the three sets of data. Also, the  $\lambda$  values computed by the D & M method and shown in the last column of Table IV are, as one would expect, consistent with the variation of  $g'$ . Increasing  $\lambda$  corresponds to decreasing  $g'$ .

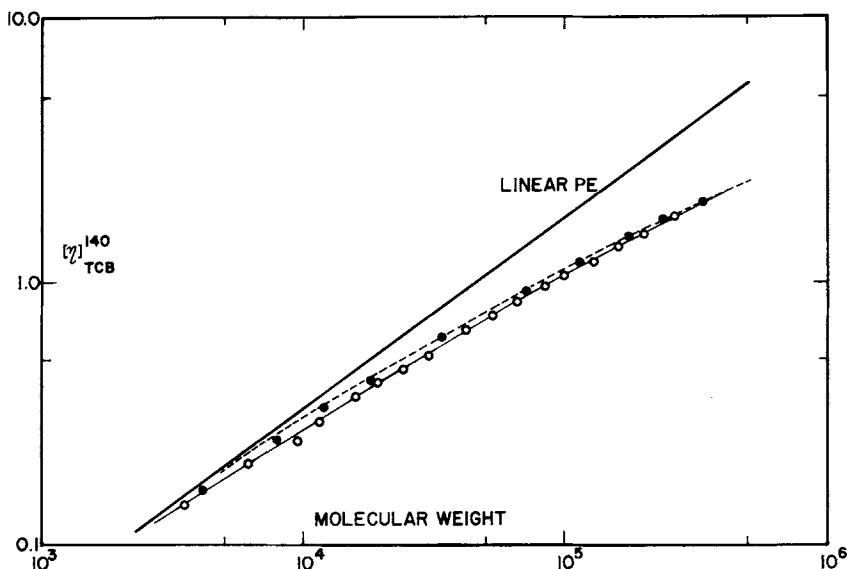


Fig. 1. Comparison of  $[\eta]$ - $M$  relationship for SRM 1476: (---) R & M; (●) D & M; (○) iterative.

The results so far presented suggest that either the R & M or D & M technique may be used to provide realistic MWD and degree of LCB data for most branched polyethylenes. However, the D & M method, in particular, has been criticized<sup>9</sup> from the point of view that its basic assumption (that the degree of LCB,  $\lambda$ , is constant as a function of molecular weight) is not always true in practice. To provide a more detailed comparison of the methods which may throw some light on this question, data have been expressed in terms of the solution viscosity-

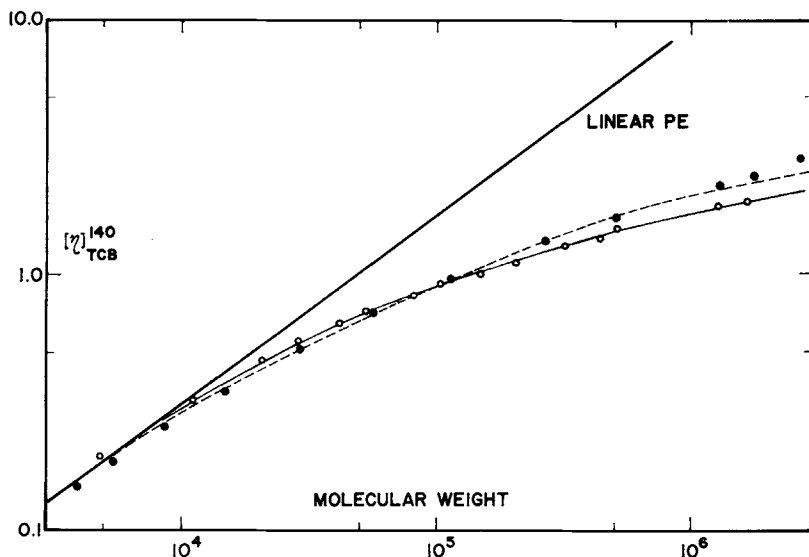


Fig. 2. Comparison of  $[\eta]$ - $M$  relationship for LDPE A: (---) R & M; (●) D & M; (○) iterative.

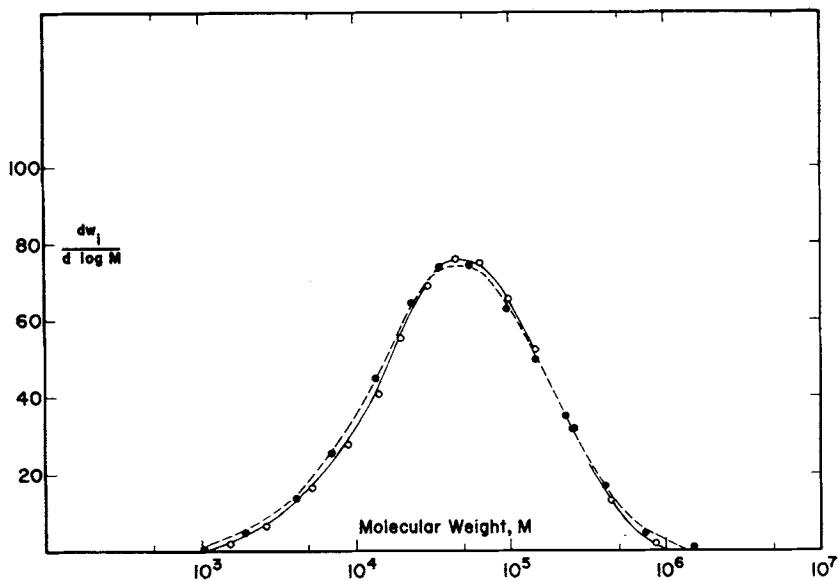


Fig. 3. Comparison of MWD curves for SRM 1476: (---) R & M; (●) D & M; (○) iterative.

molecular weight relationships (Figs. 1 and 2) and complete MWD curves (Figs. 3 and 4).

From the solution viscosity–molecular weight relationships, particularly those given in Figure 2, one is led to conclude the following:

(i) The data computed by both the R & M and D & M methods are practically identical. This is surprising in light of the quite different assumptions associated with the two methods.

(ii) The solution viscosity–molecular weight relationships obtained from the

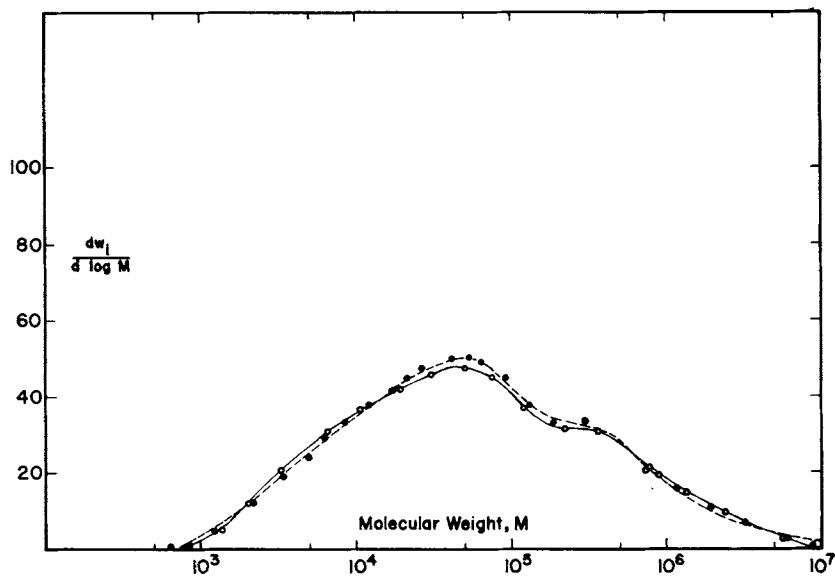


Fig. 4. Comparison of MWD curves for LDPE A: (---) R & M; (●) D & M; (○) iterative.

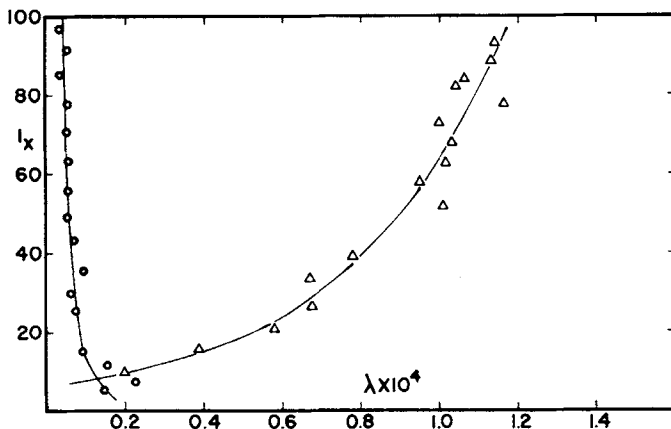


Fig. 5. Distribution of branching frequency within SRM 1476 (O) and LDPE A ( $\Delta$ ).

iterative analysis method do not agree very well with those from the R & M and D & M methods. This is in spite of good overall agreement of computed molecular weight averages. Differences are most apparent in the case of the highly branched resin LDPE A, in the higher molecular weight regions.

This latter observation is consistent with the view that in the case of LDPE A, the relative degree of LCB ( $g'$  or  $\lambda$ ) increases with increase in molecular weight. This, in turn, suggests that, although reasonable values for average molecular weight and degree of LCB are forthcoming from the rapid evaluation methods, they give no direct indication of the specific nature (i.e., degree of LCB) of the individual polymer species present in the whole polymer. This should not be surprising in light of the small amount of informational input to the computer when making the molecular weight calculations.

The inability of the D & M method to describe the individual polymer species can be further illustrated by the following interesting analysis conducted on the series of gradient elution fractions obtained from SRM 1476 and LDPE A. The GPC data, together with measured solution viscosity values, for each fraction were subjected to the D & M computer analysis. This provides individual values for the degree of LCB,  $\lambda$ , and those data have been plotted as a function of the cumulative weight per cent ( $I_x$ ), which represents a branching distribution for each of the resins (Fig. 5). The results clearly indicate that whereas SRM 1476 conforms quite well to the D & M assumption of constancy of  $\lambda$ , in the case of LDPE A  $\lambda$  is observed to vary considerably. For LDPE A,  $\lambda$  is much larger in the higher molecular weight region (at high  $I_x$ ) than at lower molecular weights.

## CONCLUSIONS

From the above detailed comparison of MWD and branching data obtained by the R & M and D & M approaches with those determined by the more complete method of Wild, Ranganath, and Ryle, it is concluded that the rapid methods provide an acceptable overall measure of MWD and degree of LCB for polyethylenes. Further, it is noted that both rapid methods give essentially the same computed data, and thus one would prefer the Drott and Mendelson

method over that of Ram and Miltz on the basis of the reduced computer time needed for the former method. A value of  $\lambda$  is also obtained directly as an average degree of LCB by the D & M method, which is an additional convenience. For routine analysis of branched polyethylene resins, the D & M method is preferable to the complete iterative analysis method, not only on the basis of the reduced time and effort needed, but also because the experimental simplicity of the D & M approach leads to extremely reliable and reproducible data. This, of course, assumes that the GPC calibration is properly derived and monitored. However, wherever it is the intent to pursue detailed branching structure studies for polyethylenes, the more detailed methods of analysis are essential as it is clear that the D & M assumption of constancy of  $\lambda$  within any particular resin is not true for many polyethylene types.

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