

# Relationships between Molecular Weight, Solution Viscosity, and Melt Index for Narrow Distribution, High Pressure Polyethylene Whole Polymers. Fast $\bar{M}_n$ Determinations

GEORGE A. MORTIMER, GREG W. DAUES, and  
WILLIAM F. HAMNER, *Plastics Division, Monsanto Chemical Company,  
Texas City, Texas*

## Synopsis

Melt and solution viscosity properties of laboratory-prepared batch polymerized high pressure polyethylene have been found to correlate well with molecular weight. These polymers have narrow and nearly constant molecular weight distributions and contain essentially no long-chain branches. Short-chain branching was found to have little or no effect on the relationships. Polyethylene made in the same reactor having long-chain branches had melt and solution viscosity properties which deviated seriously from these relationships. The deviations serve as a semiquantitative measure of long-chain branching. When long-chain branching is absent, the correlations serve as rapid methods of determining  $\bar{M}_n$  for narrow-distribution polymers.

## INTRODUCTION

In connection with the studies of this laboratory, an investigation of the relationships between the number-average molecular weight and other properties of high pressure polyethylene was undertaken. In contradistinction to other similar studies, the samples used in this investigation were laboratory-prepared by batch polymerization under known and well-defined conditions. For this reason, it was possible to obtain more than the normal amount of information from a study of the molecular and flow properties of the samples. Furthermore, it was possible to develop two correlations from which  $\bar{M}_n$  can be rapidly determined for such samples.

## EXPERIMENTAL

### Sample Preparation

Polymerizations were conducted in a 240-cc. high pressure vessel which contained an internal agitator.<sup>1</sup> Most runs were made at constant pressure and temperature under conditions where kinetic steady state was achieved. Pressures ranged from 20,000 to 30,000 psi. Temperature varied from 130 to 200°C. The initiators used were di-*tert*-butyl peroxide, ethyl nitrate,<sup>2</sup> and acetone oxime. Various types and amounts of chain-

transfer agents were used, ranging from none to an amount sufficient to appear as end-groups on approximately 80% of the polymer molecules.

All polymerizations were terminated at about 10% conversion by rapidly reducing pressure. Polymer which blew out with the ethylene was caught in a screened container. Both the polymer remaining in the reactor and that which blew out were dissolved in hot xylene and precipitated together with cold methanol. The sample was suction-filtered and dried overnight in a vacuum oven at 80°C. In no instance was any polymer formed that was not completely soluble in boiling xylene.

### Evaluation Procedure

Intrinsic viscosities and number-average molecular weights were obtained in *p*-xylene at 105°C. as previously described in a communication from this laboratory.<sup>3</sup> Melt indexes were measured by a modification of ASTM method D-1238-57T. Because of the small amount of polymer available from each polymerization, the melt indexer weight was not placed on the plunger until after the 5-min. warm-up period. For each sample, three consecutive test strands were taken. The arithmetic average of the three test strand melt indexes, which generally agreed within 1%, was used as the melt index for the sample.

Additional evaluations were performed for some samples. Weight-average molecular weights were determined from light-scattering measurements.<sup>3</sup> Short-chain branching was estimated from densities<sup>1</sup> and melting points.<sup>4</sup>

### Sample Characteristics

The density range of the samples included in this study was 0.924–0.945. The melting points of the samples with the highest densities were 118.5–119.5°C. Molecular weight distributions, defined here as  $\bar{M}_w/\bar{M}_n$ , were consistently 2.0–2.2. Because of the narrowness of the distribution,  $\bar{M}_w$  data could only be obtained for the high molecular weight samples.

## RESULTS

Excellent correlations were found between number-average molecular weight  $\bar{M}_n$ , melt index MI, and intrinsic viscosity  $[\eta]$ . These correlations, shown in Figures 1 and 2, are sufficiently precise that we have used them as routine methods for  $\bar{M}_n$  measurement for narrow-distribution batch-type polymers. The MI method is particularly advantageous in that the measurement is both quick and simple. For both correlations, the standard deviation of points about the line is close to the standard deviation of the osmotic  $\bar{M}_n$  measurement.

### $[\eta]$ - $\bar{M}_n$ Correlation

The curve shown in Figure 1 is described by the equation

$$[\eta] = 7.63 \times 10^{-4} \bar{M}_n^{0.69} \quad (1)$$

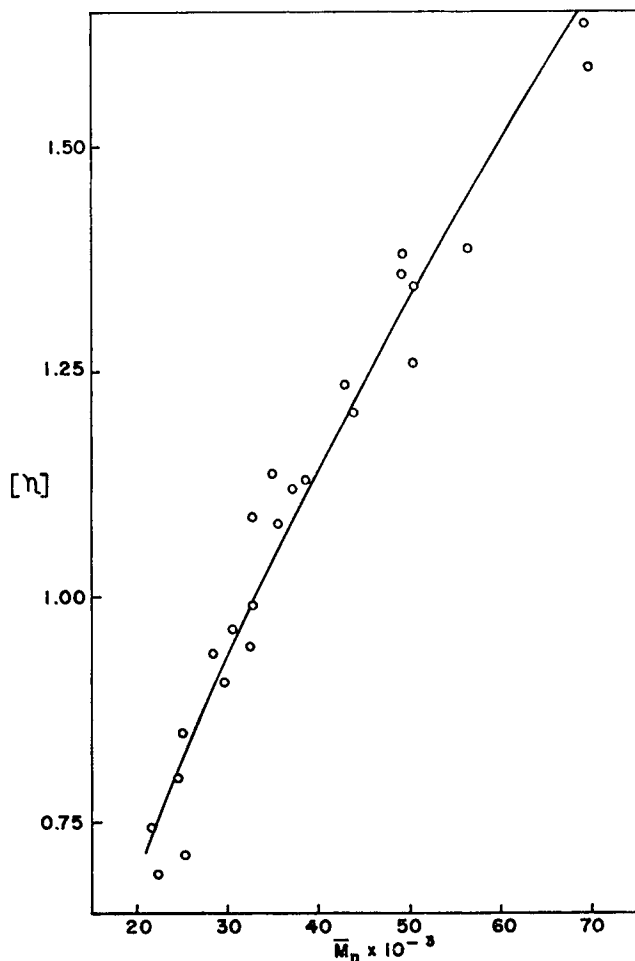


Fig. 1. Intrinsic viscosity-number-average molecular weight correlation.

in which the exponent has a standard deviation of  $\pm 0.03$ . It is of interest that the value of  $0.69 \pm 0.03$  is within experimental error of the exponents given by Tung,<sup>5</sup> Chiang,<sup>9</sup> and Atkins et al.<sup>10</sup> for linear polyethylene fractions. It therefore seems that the slope of the log-log plot is only slightly dependent on short-chain branching. Long-chain branching, as will be discussed later, does have a pronounced effect on  $[\eta]$ . The greater incidence of long branching in the high molecular weight portions of many commercial high pressure polyethylenes has been blamed for the "tailing off" of the  $[\eta]-\bar{M}_n$  curve often observed.<sup>6</sup> Our samples did not tail off.

The literature reveals considerable discussion as to whether  $[\eta]$  should correlate with  $\bar{M}_n^{5-8}$  or  $\bar{M}_w$ .<sup>9-13</sup> The arguments in no way diminish the usefulness of our correlation for determining  $\bar{M}_n$  (or  $\bar{M}_w$ ) for samples of constant distribution.

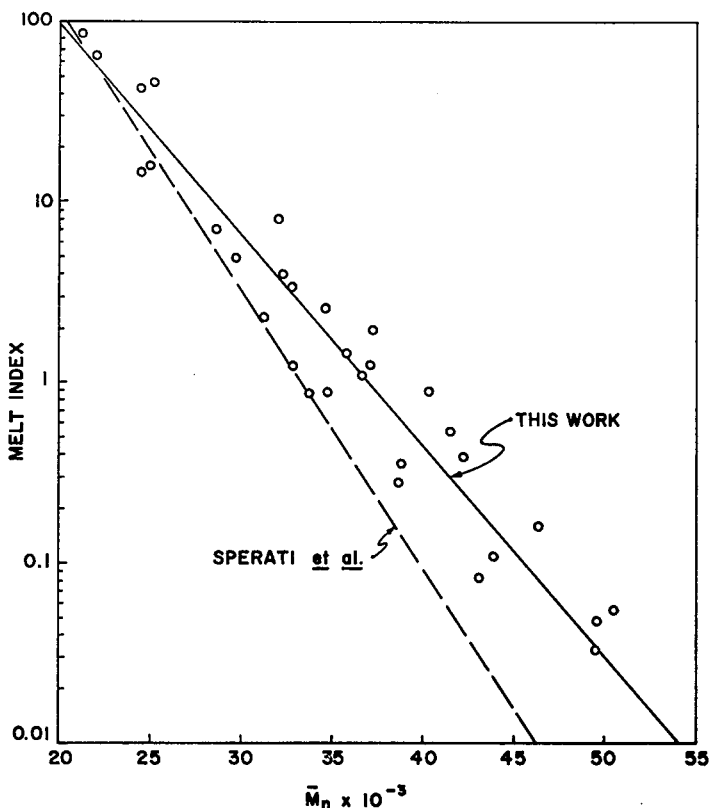


Fig. 2. Melt index-number-average molecular weight correlation.

### MI- $\bar{M}_n$ Correlation

The line given in Figure 2 is described by the equation

$$\bar{M}_n = 37,000 - 8610 \log \text{MI} \quad (2)$$

which gives the  $\bar{M}_n$  with a standard deviation of  $\pm 2200$ . This line is different from that of Sperati et al.,<sup>16</sup> especially at high molecular weights. It is probably more nearly correct since the square of the correlation coefficient,  $r^2$ , is 0.94 for our 32 samples and only 0.85 for their 14 samples. There seems to be no *a priori* reason for this correlation to be linear, in fact one would expect the relationship to have the form  $\log M = A + B \log \text{MI}$ . The latter form could neither be supported nor challenged from the data because of the narrow limits of  $\log \bar{M}_n$  covered in this work. For correlation purposes, eq. (2) was used.

It is apparently well established that melt viscosity, of which melt index is a form, is related to  $\bar{M}_w$  rather than  $\bar{M}_n$ .<sup>13-15</sup> However, when  $\bar{M}_w/\bar{M}_n$  is constant, as it is for our samples, the melt index correlates with  $\bar{M}_n$  also. The correlation with  $\bar{M}_n$  is the one shown in Figure 2. The MI determination of  $\bar{M}_n$  is preferred over the  $[\eta]$  method because of the speed

and simplicity and has been used in this laboratory for two years. During this period, no change in the correlation has been detected.

Although an effect of short-chain branching on melt viscosity was once claimed,<sup>15</sup> this claim was retracted when it was found that a direct correlation existed between the amounts of short and long branches in the polyethylenes used.<sup>17,18</sup> The long-chain branching was shown to be the con-

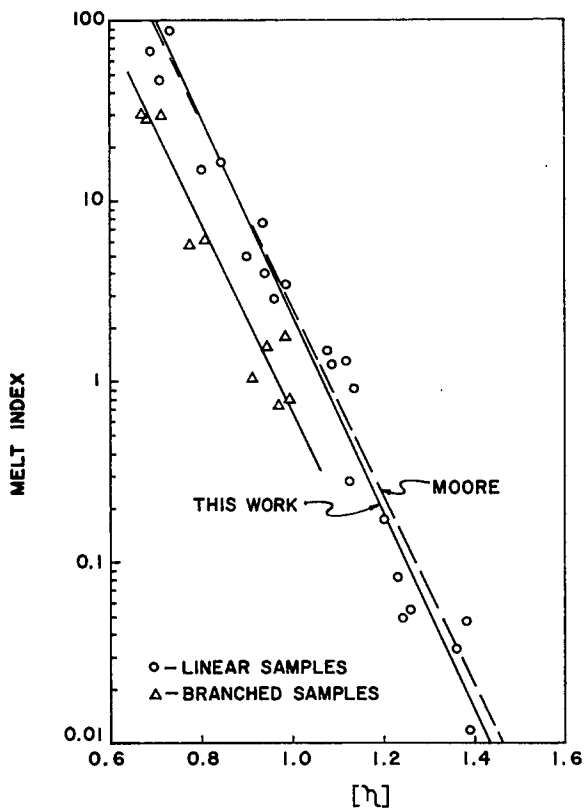


Fig. 3. Melt index-intrinsic viscosity correlation.

trolling factor.<sup>18</sup> We concur. Ethylene copolymers of propylene, butene-1, and octene-1<sup>19</sup> (which have additional methyl, ethyl, and *n*-hexyl short branches) were found to obey the  $\bar{M}_n$ -log MI correlation, indicating that, within the limits of short-chain branching and shear rates studied, the amount and type of short branches had no observable effect on melt viscosity.

#### $[\eta]$ -MI Correlation

Our data, covering four orders of magnitude of MI, are shown in Figure 3. The solid line represents the correlation.

$$[\eta] = 1.064 - 0.183 \log MI \quad (3)$$

which has a squared correlation coefficient,  $r^2$ , of 0.96.

Perhaps the most significant point to be made regarding this correlation is its consistency with the data of Moore<sup>17</sup> and the corroboration of his conclusions. Moore makes a strong point that samples from his source "F" did not contain a high molecular weight tail. By implication, then, they are of relatively narrow distribution for commercial polymers and probably contain few, if any, long-chain branches. The dotted line in Figure 3 is Moore's line for F-type polymers. Within experimental error, the two lines are identical. Variations in short-chain branching had no observable effect on this correlation.

### Effect of Long-Chain Branching on the Correlations

The correlations described in the preceding sections hold only for "linear" samples. The word linear will be used here to denote polymers which contain only short-chain branching, which was shown to have no observable effect on the correlations at the levels encountered in this study. The word branching will be understood here to mean long-chain branching. Because of the deviations from the correlations caused by the presence of branching, it is suspected that workers who have concluded that there is no correlation between MI,  $[\eta]$ , and  $\bar{M}_n$  have studied samples which varied widely in long-chain branching.<sup>20</sup>

In order to assess the effect of long-chain branches on the correlations established in this study, a new series of samples was studied which were

TABLE I  
Examples of Polyethylene in Which Long-Chain Branching Was Expected

Sample no.	MI	$[\eta]$	$\bar{M}_n$	$\bar{M}_w$	$\bar{n}_w$	$\left( \frac{\log \text{v.b.i.}}{c} \right)$
5	1.5	0.95	57,200	175,000	9.5	2.56
6	1.7	0.99	70,000	182,000	13.9	4.12
9	1.0	0.92	48,000	—	6.3	1.32
10	0.75	1.00	46,400	129,000	3.5	1.00
12	0.71	0.98	60,700	—	9.8	2.65
16	28.0	0.72	24,600	50,600	0.9	-0.03
22	5.6	0.78	33,600	—	4.2	0.34
24	27.0	0.69	23,800	—	1.0	-0.11
29	5.9	0.82	31,400	—	2.1	0.10
34	28.0	0.68	24,600	—	1.7	-0.03

prepared by polymerization in the same equipment, but generally at conditions outside the limits cited in the Experimental section. The conditions were chosen in order to favor long-chain branching. Data on some of these samples are given in Table I. For comparison, the same information on some of the polymers cited in previous sections are given in Table II.

TABLE II  
Examples of Polyethylenes in Which No Long-Chain Branching Was Expected

Sample no.	MI	$[\eta]$	$\bar{M}_n$	$\bar{M}_w$	$\bar{n}_w$	$\log \left( \frac{\text{v.b.i.}}{c} \right)$
102	0.0116	1.39	56,600	121,000	0.4	0.34
120	0.056	1.26	50,500	—	0.7	0.32
124	—	1.586	70,000	147,000	0.6	—
129	0.107	1.21	43,900	—	0.0	-0.28
132	3.4	0.99	32,900	—	0.0	0.04
140	3.94	0.945	32,300	—	0.4	0.04
147	64.0	0.693	22,100	—	0.2	-0.06
158	4.86	0.905	29,800	—	0.3	-0.16

### Branching and the $[\eta]$ - $\bar{M}_n$ Correlation

In all instances,  $[\eta]$  for the samples which were thought to be branched was lower than for the linear samples of the same  $\bar{M}_n$ , as expected. For each sample cited in the tables, the long-chain branching index,<sup>21,22</sup>  $\bar{n}_w$ , was calculated,  $g$  being obtained from the relationship<sup>23</sup>

$$g^{1/2} = [\eta]_b / [\eta]_l \quad (4)$$

and Figure 1 being used to obtain  $[\eta]_l$  from the osmotic  $\bar{M}_n$  of the samples. The subscripts,  $l$  and  $b$ , refer to linear and branched polymers respectively, and  $\bar{n}_w$  is defined as the weight-average number of trifunctional branch points per molecule. In this study, we ascribe only semiquantitative importance to  $\bar{n}_w$ , namely, the larger  $\bar{n}_w$ , the greater the amount of branching.

In Table II, data are cited only for linear samples whose  $[\eta]$  values fell on or below the correlation line. The purpose of doing this is to illustrate how much change in  $\bar{n}_w$  can be explained by scatter about the line (experimental error). From this study it is not possible to demonstrate that samples 120 and 124, for example, contain absolutely no long-chain branching. We do believe, however, that 0.7 is the maximum value of  $\bar{n}_w$  that we can ascribe to a linear sample of polyethylene. Higher values will be indicative of branching.

### Branching and the MI<sub>n</sub>- $\bar{M}$ Correlation

MI for samples which were thought to be branched was higher than for linear materials of the same  $\bar{M}_n$ , as expected. This effect has been used by Schreiber and Bagley<sup>14</sup> to define an index for long-chain branching, v.b.i., thus

$$\text{v.b.i.} = \eta_l / \eta_b \quad (5)$$

where  $\eta$  is the Newtonian melt viscosity of samples of the same  $\bar{M}_w$ . If we assume that MI is exactly inversely proportional to  $\eta$ , we can write

$$\text{v.b.i.} = c (\text{MI}_b / \text{MI}_l) \quad (6)$$

where  $c$  would be an empirical constant. In the tables, this index is expressed as  $\log (v.b.i./c)$  for convenience. A negative logarithm means that MI measured is smaller than  $MI_L$ . For linear samples, it would be expected that  $\log (v.b.i./c)$  would show roughly the same number of plus and minus values and the magnitudes of the plus and minus values would be roughly the same. This expectation is realized. However, inspection of the tables shows that the melt index method of estimating branching is not nearly as sensitive as the  $[\eta]$  method. Differentiation between branched and unbranched samples is not clear except for the most highly branched samples. The most likely reason for this result is that eq. (6) is only approximate.

### Branching and the $[\eta]$ -MI Correlation

The presence of branching altered the  $[\eta]$ -MI correlation also. The experimental points for samples containing long-chain branching lie to the left of the MI- $[\eta]$  line for linear polymer in Figure 3. The extent of displacement, however, did not appear to depend on  $\bar{n}_w$ . Apparently, for our samples, much of the decrease in  $[\eta]$  was offset by the increase in MI. The points for the long-chain branched samples are fit by a straight line having the equation.

$$[\eta] = 0.966 - 0.189 \log MI \quad (7)$$

and the points and line are shown in Figure 3. These results further substantiate the conclusions and data of Moore.<sup>17</sup> Our linear and branched materials show the behavior of samples from two of Moore's sources. Further work will be necessary to make clear the significance of the magnitude of the leftward displacement of the MI- $[\eta]$  correlation for branched samples, and the significance of the near-identity of the slopes for our two types of samples.

The authors gratefully acknowledge the helpful discussions of Dr. R. A. Mendelson, who also determined the  $\bar{M}_w$  values, and the osmometric  $\bar{M}_n$  values obtained by Dr. H. J. L. Schuurmans.

### References

1. Mortimer, G. A., and W. F. Hamner, *J. Polymer Sci.*, to be published.
2. Mortimer, G. A., U. S. Pat. 2,920,067 (1960).
3. Mendelson, R. A., *J. Polymer Sci.*, **46**, 493 (1960).
4. Kohn, E., H. Medina, Jr., and J. V. Cavender, *J. Appl. Polymer Sci.*, **5**, 13 (1961).
5. Tung, L. H., *J. Polymer Sci.*, **24**, 333 (1957).
6. Trementozzi, Q. A., *J. Polymer Sci.*, **23**, 887 (1957).
7. Mussa, C., *J. Polymer Sci.*, **23**, 877 (1957).
8. Harris, I., *J. Polymer Sci.*, **8**, 353 (1952).
9. Chiang, R., *J. Polymer Sci.*, **36**, 91 (1959).
10. Atkins, J. T., L. T. Muus, C. W. Smith, and E. T. Pieski, *J. Am. Chem. Soc.*, **79**, 5089 (1957).
11. Trementozzi, Q. A., *J. Polymer Sci.*, **36**, 113 (1959).



12. Duch, E., and L. K uchler, *Z. Elektrochem.*, **60**, 218 (1956).
13. Busse, W. F., and R. Longworth, *J. Polymer Sci.*, **58**, 49 (1962).
14. Schreiber, H. P., and E. B. Bagley, *J. Polymer Sci.*, **58**, 29 (1962).
15. Peticolas, W. T., and J. M. Watkins, *J. Am. Chem. Soc.*, **79**, 5083 (1957).
16. Sperati, C. A., W. A. Franta, and H. W. Starkweather, Jr., *J. Am. Chem. Soc.*, **75**, 6127 (1953).
17. Moore, L. D., *J. Polymer Sci.*, **36**, 155 (1959).
18. Peticolas, W. L., *J. Polymer Sci.*, **58**, 1405 (1962).
19. Boghetich, L., G. A. Mortimer, and G. W. Daues, *J. Polymer Sci.*, **61**, 3 (1962).
20. Ashby, C. E., J. S. Reitenour, and C. F. Hammer, *J. Am. Chem. Soc.*, **79**, 5086 (1957).
21. Zimm, B. H., and W. H. Stockmayer, *J. Chem. Phys.*, **17**, 1301 (1949).
22. Billmeyer, F. W., Jr., *J. Am. Chem. Soc.*, **75**, 6118 (1953).
23. Zimm, B. H., and R. W. Kilb, *J. Polymer Sci.*, **37**, 19 (1959).

### R esum e

On a trouv e que les propri et es de viscosit e   l' tat fondu et en solution de poly thyl ne haute pression pr par e en s rie au laboratoire sont en accord avec le poids mol culaire. Ces polym res ont des distributions de poids mol culaire voisines et presque constantes et ne poss dent fondamentalement pas de longues ramifications. On a trouv e que les courtes ramifications n'avaient que peu ou pas d'effet sur les relations. Le poly thyl ne fabriqu  dans le m me r acteur mais   cha nes ramifi es longues a  t  fondu et les propri et es de viscosit e de la solution d vient fortement de ces m mes relations. Ces d viations servent de mesure semi-quantitative pour la ramification "longue cha ne." Lorsqu'il n'y a pas de ramifications "longue cha ne" les relations servent de m thodes rapides de d termination du  $\bar{M}_n$  pour des polym res   distribution voisine.

### Zusammenfassung

Schmelz- und L sungsviskosit t von laboratoriumsm ssig hergestelltem "batch"-polymerisierten Hochdruckpoly thylen stehen in guter Korrelation zum Molekulargewicht. Diese Polymeren haben enge und fast konstante Molekulargewichtsverteilungen und enthalten praktisch keine Langkettenverzweigungen. Kurzkettenverzweigung hat nur geringen oder gar keinen Einfluss auf die Beziehungen. Im selben Reaktor hergestelltes Poly thylen mit Langkettenverzweigungen zeigte in seinem Schmelz und L sungsviskosit tsverhalten betr chtliche Abweichungen von diesen Beziehungen. Die Abweichungen dienen als halbquantitatives Mass f r die Langkettenverzweigung. In Abwesenheit von Langkettenverzweigung k nnen die Beziehungen zur raschen  $\bar{M}_n$ -Bestimmung von Polymeren mit enger Verteilung herangezogen werden.

Received March 11, 1963