Effect of Molecular Weight Distribution on Melt Flow Properties of Low-Pressure Polyethylene

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Synopsis

A series of low-pressure Ziegler polyethylene samples has been fractionated by the sand column technique. The molecular weight distributions have been determined by the Schulz-Dinglinger approximation. The number-average, weight-average, and z-average molecular weights have been calculated from the fractionation data for each sample by the method of summation. Melt indexes and melt flow ratios have been determined by standard techniques. The melt index is found to be related to the reciprocal of the fifth power of the weight-average molecular weight, and the melt flow ratio is proportional to the z-average molecular weight.

INTRODUCTION

One of the most important laboratory scale tests performed during the manufacture and subsequent fabrication of polyethylene resins, is the measurement of the melt index (I_2). Coupled with this, though perhaps not used to the same extent, is the measurement of the flow ratio, I_{10}/I_2, which gives a good indication of the shear sensitivity of the resin. I_2, determined by an ASTM method, measures the quantity of molten resin extruded through a tubular die under a load of 2.16 kg., moving in a vertical metal cylinder. I_{10}, though not listed as an ASTM procedure, is generally accepted as being standard, in so far as it is a modification of the I_2 test, incorporating a 10 kg. load in place of the 2.16 kg. load. A good indication of the processibility of a resin can be obtained from measurements of the melt index and flow ratio. Thus a knowledge of the variables which influence these properties could lead to an improvement in the functionality of a resin.

For many years it has been quite tacitly assumed that the melt index of low-pressure polyethylene is directly related to the weight-average molecular weight, $\bar{M}_w$, and that the flow ratio is proportional to the breadth of the molecular weight distribution, $\bar{M}_w/\bar{M}_n$. There is a certain justification for the former assumption, since melt index is a form of melt viscosity, and Peticolas and Watkins[1] have shown that the melt viscosity of high-pressure polyethylene is proportional to approximately the third power of the weight-average molecular weight. Mortimer, Daues, and Hamner,[2] however, have shown that for many high-pressure polyethylenes, the melt

index is related to a power of the number-average molecular weight. On the other hand, no measurements of the flow ratio have been reported in the literature.

This paper describes the fractionation and calculation of the three average molecular weights ($\bar{M}_n$, $\bar{M}_w$, and $\bar{M}_z$) of a series of commercial and experimental Zeigler polyethylene samples. Melt indexes and flow ratios have been measured. Two relationships, involving the flow properties and the molecular weight data, have been derived.

EXPERIMENTAL

A modified version of the sand column described by Francis, Cooke, and Elliott[3] was used for fractionating the polymers. Reagent grade p-xylene (Eastman Organic Chemicals) was the solvent and technical grade 2-butoxyethanol (The Dow Chemical Company) the nonsolvent. Reagent grade methanol (Nichols Chemical Company, Limited) served as the precipitant during the recovery of the fractions. Redistilled butyl acetate (Fisher Scientific Company) was used as the heating liquid, and a temperature of 125°C. was maintained on the column.

The experimental procedure of Francis et al.[3] was followed with a few minor alterations. The solvent–nonsolvent mixtures required to yield about 10 fractions of approximately equal size, were determined from trial experiments. The charge of polyethylene on the column was usually 1.5 g.

The fractions were dried in a vacuum oven at 60°C. and weighed. Specific viscosity measurements were made on 0.1 g./dl. solutions of the polymers in tetralin at 130°C. with the use of a modified Ubbelohde viscometer. The viscosity-average molecular weights of the fractions were calculated from their inherent viscosities $\{\eta\}$ by using the relationship[4] found by Tung:

$$\{\eta\} = 5.10 \times 10^{-4} M^{0.725} \tag{1}$$

The melt index (I_2) of each sample was determined by ASTM method D1238-52T and the I_{10} by a modification of this procedure, a 10 kg. being used in place of the standard 2.16 kg. weight.

RESULTS AND DISCUSSION

The reproducibility of the fractionation technique was checked by carrying out repeated fractionations on two samples having a moderate difference in melt index (sample F, $I_2 = 0.860$; sample C, $I_2 = 0.545$). The results are summarized in Table I. The integral weight distributions were calculated by the Schulz-Dinglinger[5] method:

$$W_j = \sum_{i=j-1} w_i + \frac{1}{2} w_j \tag{2}$$

where W_j is the integral weight and w_j the weight of the jth fraction. From the distribution curves in Figure 1 it can be seen quite clearly that the duplicate determinations are in good agreement.
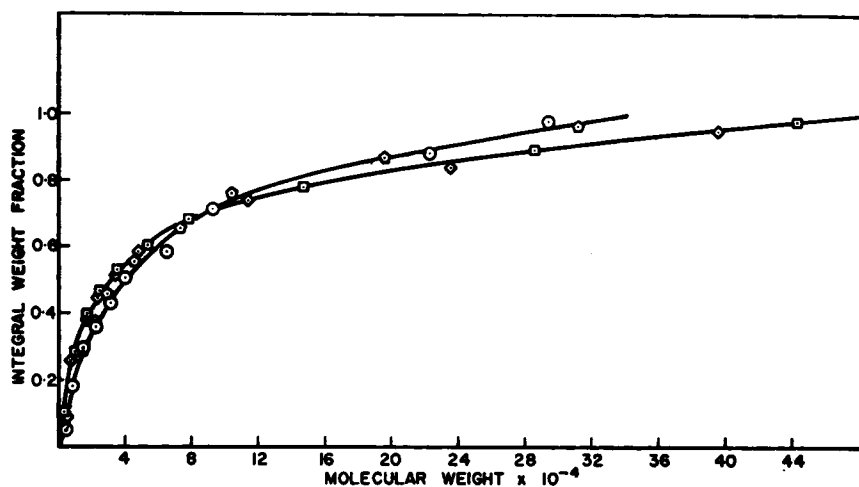
Fig. 1. Integral weight distribution curves demonstrating reproducibility from the fractionation column: (○) F(1); (◌) F(11); (▣) C(1); (◇) C(11).
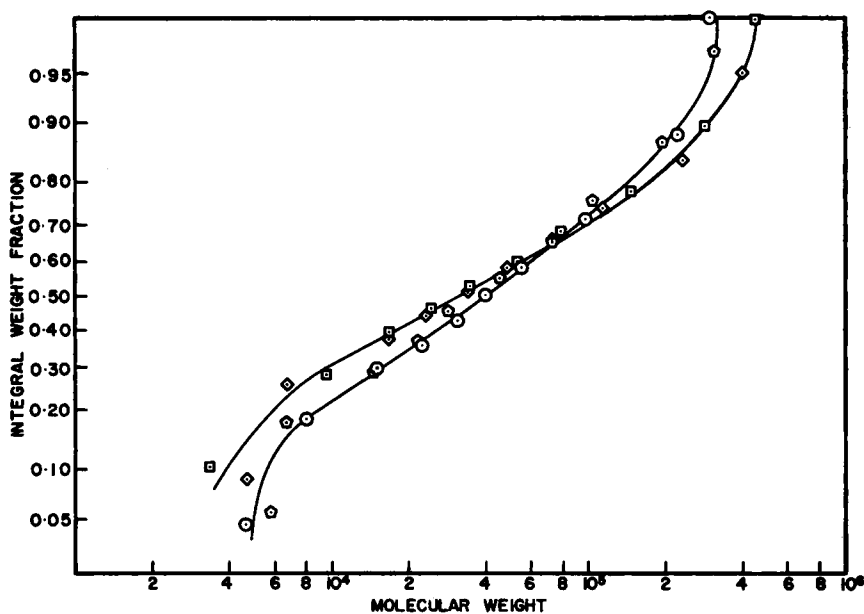

Fig. 2. Weight distribution curves plotted by Wesslau's method:[11] (○) F(1); (◌) F(11); (▣) C(1); (◇) C(11).

Recently, a number of authors[6-9] have been highly critical of the method of direct summation for expressing fractionation data.   Various distribution functions have been proposed, generally of logarithmic or exponential form, but they do not always fulfil the requirements of the polymer systems under examination.   In some cases, where more than one molecular weight

TABLE I
Data for Reproducibility of Fractionation Technique

Fraction no.	F(1)		F(11)		C(1)		C(11)	
	Wt. of fraction, g.	$M \times 10^{-3}$	Wt. of fraction, g.	$M \times 10^{-3}$	Wt. of fraction, g.	$M \times 10^{-3}$	Wt. of fraction, g.	$M \times 10^{-3}$
1	0.1440	4.63	0.1666	5.78	0.2917	3.34	0.2648	4.66
2	0.2610	8.02	0.1913	6.63	0.2085	9.55	0.2409	6.67
3	0.0891	14.84	0.1332	14.54	0.1164	16.63	0.1131	16.80
4	0.0943	22.44	0.1338	21.85	0.0840	24.25	0.0902	23.20
5	0.1243	30.80	0.1290	28.38	0.0977	34.43	0.1154	33.56
6	0.1070	39.37	0.1532	45.06	0.1057	53.19	0.1084	47.95
7	0.1276	54.54	0.1559	72.33	0.1230	77.59	0.1194	71.30
8	0.2702	97.88	0.1580	103.20	0.1523	146.00	0.1260	113.40
9	0.2381	220.30	0.1749	194.70	0.1779	285.00	0.1740	234.40
10	0.0565	293.30	0.1064	310.50	0.0568	444.00	0.1494	395.00
$\bar{M}_n \times 10^{-4}$	1.739		1.750		1.107		1.325	
$\bar{M}_w \times 10^{-4}$	7.709		7.472		8.734		9.224	
$\bar{M}_w/\bar{M}_n$	4.4		4.3		8.0		7.0	

TABLE II

Flow Properties and Molecular-Weight Averages for Low-Pressure Polyethylenes

Sample	I_2, dg./ min.	I_{10}, dg./ min.	I_{10}/I_2	$\bar{M}_n \times 10^{-4}$	$\bar{M}_w \times 10^{-4}$	$\bar{M}_z \times 10^{-5}$	$\bar{M}_w/\bar{M}_n$
A	0.610	10.80	17.7	1.05	9.17	3.08	8.7
B	0.401	6.36	15.9	1.02	9.467	2.85	9.3
C	0.545	7.38	13.5	1.20	9.00	2.50	7.5
D	0.529	8.49	16.0	1.33	9.05	2.88	6.8
E	0.958	14.26	14.9	0.928	7.98	2.39	8.6
F	0.860	8.89	10.3	1.75	7.47	1.77	4.3
G	0.950	9.89	10.4	1.28	8.09	1.96	6.3
H[a]	0.259	5.23	20.2	1.65	10.35	3.46	6.3
I	8.30	80.6	9.7	1.51	5.32	1.58	3.5
J[a]	0.201	3.81	19.9	2.00	9.97	3.59	5.0
K	5.73	61.0	10.6	1.39	5.52	1.86	4.0
L	6.25	72.8	11.6	1.41	6.21	1.97	4.4
M	6.83	71.4	10.5	1.50	5.12	1.41	3.4
N[a]	2.35	33.0	14.0	1.57	6.16	2.50	3.9
O[a]	2.31	30.8	13.3	1.33	6.34	2.20	4.26
P	2.69	26.7	9.92	1.82	7.03	1.72	3.86
Q	4.92	49.0	10.0	1.28	5.84	1.59	4.55
R[a]	5.42	60.0	11.1	1.356	5.728	2.12	4.22
S	0.872	15.64	17.9	1.351	9.253	3.05	6.85
T	0.137	7.35	53.6	0.175	17.44	9.509	100
U	0.042	1.25	29.8	0.374	17.06	5.041	46

[a] Copolymers.

parameter is required, calculation of the results is time-consuming.[7,10] Sometimes the results obtained are inaccurate.[7,8] A typical example is the use of the logarithmic normal probability function proposed by Wesslau.[11]
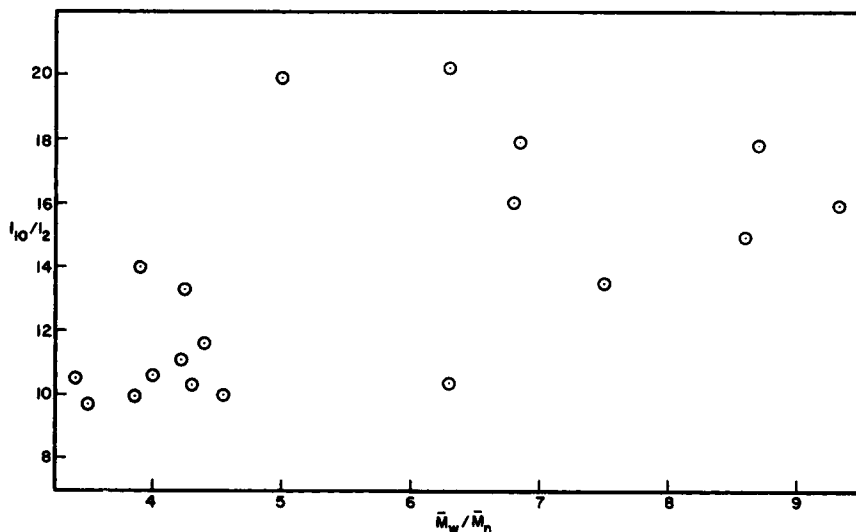

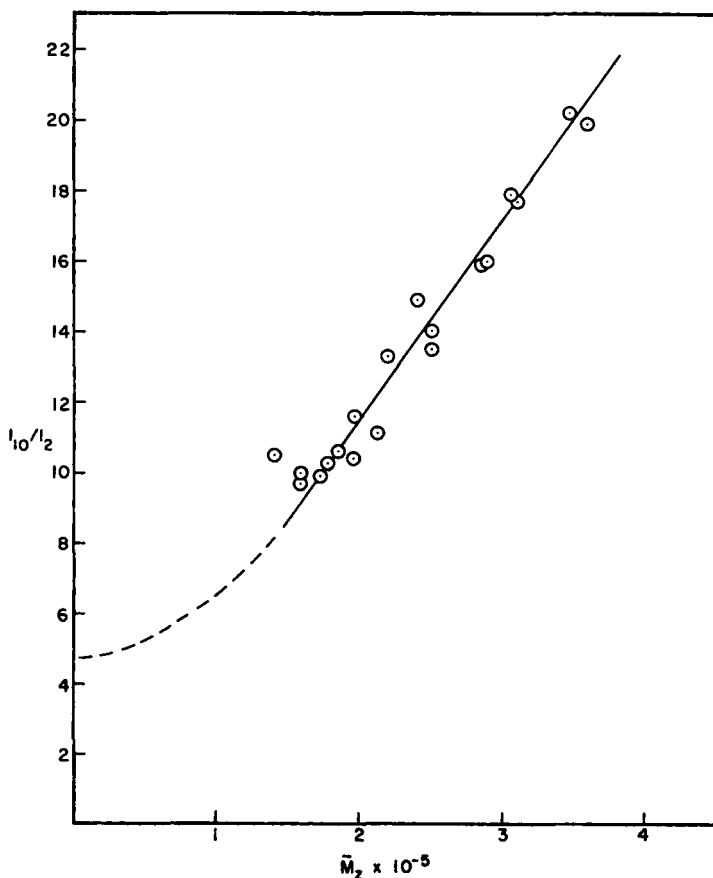Fig. 3. Variation of flow ratio with molecular weight distribution.

Fig. 4. Relationship between flow ratio and z-average molecular weight.

If a straight line is obtained when the fractionation results are expressed by this type of probability, then it can be stated quite categorically that the distribution of molecular weights, within the given polymer, must be of the form of this function.   If a curve results, then the function is not the correct one for the polymer system and cannot be used.   The fractionation data obtained in this work have been expressed by a number of these proposed functions, but in every case curved plots resulted.   Use of the Wesslau function[11] is demonstrated in Figure 2.   Similar curves were obtained by utilizing the expression proposed by Tung.[12]   Nevertheless, even though it is undesirable to calculate the molecular weight averages from these curves, they do show once more that good reproducibility has been attained from the fractionation column.   Booth and Beason[7] and Tung[8] have concluded that the method of direct summation is far better than many authors have supposed, and it is this method which has been used throughout this work.

Table II summarizes the fractionation results and the rheological data. $\bar{M}_n$, $\bar{M}_w$, and $\bar{M}_z$ have been calculated by summation by using eqs. (3)–(5):

$$\bar{M}_n = \sum w_i / \sum w_i / M_i \qquad (3)$$

$$\bar{M}_w = \sum w_i M_i / \sum w_i \qquad (4)$$

$$\bar{M}_z = \sum w_i M_i^2 / \sum w_i M_i \qquad (5)$$

where w_i is the weight and M_i the molecular weight of the ith fraction. A critical analysis of the use of these relationships for the calculation of the average molecular weights from fractionation data has been given by Tung.[8] The $\bar{M}_n$ values are probably high, and hence the subsequently derived $\bar{M}_w/\bar{M}_n$ ratios are probably low. The calculated z-average molecular weight values are possibly low due to lack of sensitivity in the high molecular weight region of the distribution. The use of $\bar{M}_z$ calculated from fractionation data is not favored by some authors because of the manner in which a power function of the molecular weight is involved. Extreme care has been taken in the solution viscosity measurements for
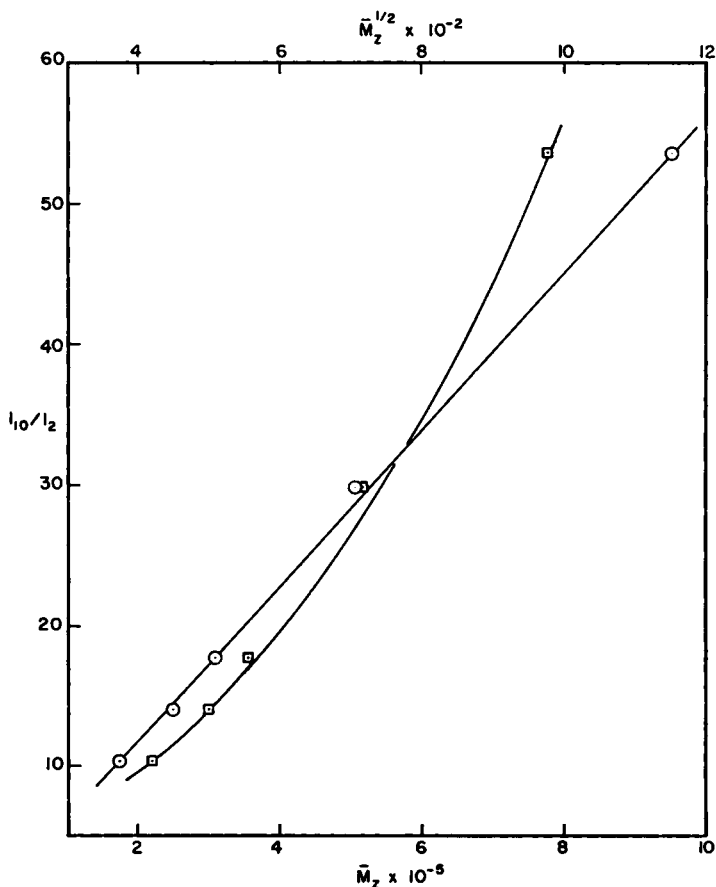
i . 5. Variation of I_{10}/I_2 with $\bar{M}_z$ compared to the variation of I_{10}/I_2 with $\bar{M}_z^{1/2}$: (⊙) $\bar{M}_z$ points; (⊡) $\bar{M}_z^{1/2}$ points.
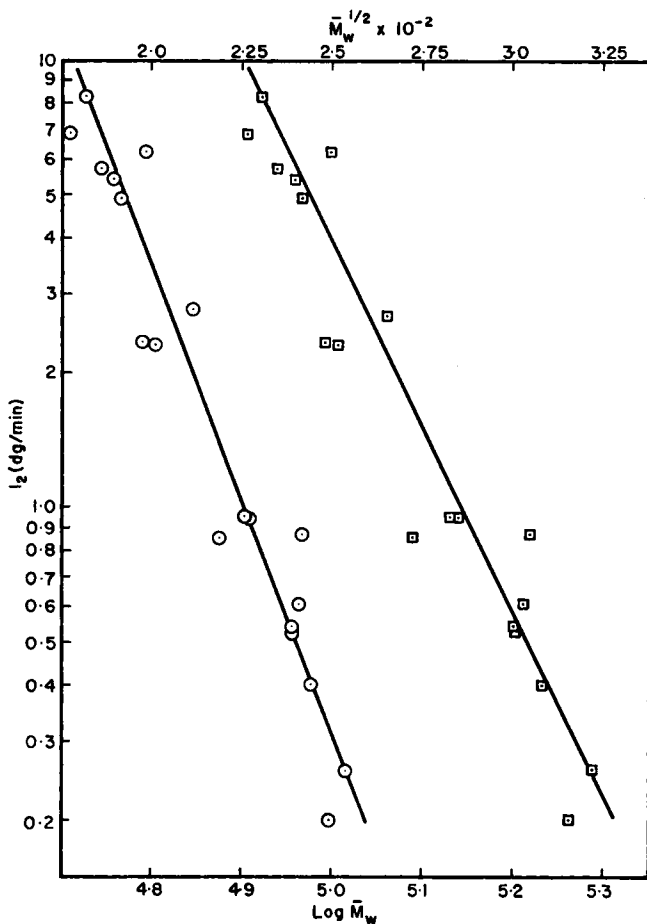
Fig. 6. Variation of log I_2 ($\odot$) with log $\bar{M}_w$; ($\square$) with $\bar{M}_w{}^{1/2}$.

determining M_t, and the maximum error in $\bar{M}_z$, arising from the subsequent summation, is $\pm 2.5\%$. This does not significantly alter any of the results.

Figure 3 shows the result of plotting I_{10}/I_2 against $\bar{M}_w/\bar{M}_n$. There is a general tendency for the flow ratio to increase with the breadth of the distribution but there is no correlation. Figure 4, however, is a graph of I_{10}/I_2 plotted against $\bar{M}_z$. Though there is little scatter of the points, a direct relationship exists:

$$I_{10}/I_2 = 0.14 + 5.7 \times 10^{-5}\bar{M}_z \qquad (6)$$

One important aspect of eq. (6) is that there must be a lower limit of applicability, since I_{10}/I_2 can never fall below a value of 4.63 even for Newtonian flow. The lowest value measured in this work, 9.7, occurred at $\bar{M}_z = 1.58 \times 10^5$, hence not too much can be said about the lower limit. It is quite conceivable, however, that the line would approach an I_{10}/I_2 of

4.63 below this molecular weight, and the increased scatter in the lower molecular weight region suggests that the line has in fact already begun to curve towards the ordinate.

Because the z-average molecular weight range was narrow, it was possible to derive a second relationship from the experimental data, of the form:

$$I_{10}/I_2 \propto \bar{M}_z^{1/2} \tag{7}$$

Confirmation of the first-power molecular weight relationship, eq. (6), was brought about by the examination of two resins with very high flow ratios, sample T $(I_{10}/I_2 = 53.6)$ and sample U $(I_{10}/I_2 = 29.8)$. These samples were specially prepared experimental polymers. The result is demonstrated in Figure 5. The straight line obtained in the $\bar{M}_z$ plot and the curve obtained in the $\bar{M}_z^{1/2}$ plot, showed that the direct relationship of I_{10}/I_2 to $\bar{M}_z$ was correct. Inclusion of samples T and U in Figure 3, although agreeing with the general tendency of increasing I_{10}/I_2 with $\bar{M}_w/\bar{M}_n$, still did not lead to a conclusive relationship.

Figure 6 shows log I_2 plotted against log $\bar{M}_w$ and against $\bar{M}_w^{1/2}$. The straight lines obtained are described by the respective equations

$$\log I_2 = 24.505 - 5 \log \bar{M}_w \tag{8}$$

and

$$\log I_2 = 4.73 - 1.665 \times 10^{-2}\bar{M}_w^{1/2} \tag{9}$$

Either form seems to satisfy the data quite satisfactorily, and it is interesting to note that Mortimer, Daues, and Hamner[2] experienced a similar situation with high-pressure polyethylenes. The log I_2, half-power weight-average molecular weight relationship of eq. (9) seems to be in good agreement with the form put forward by Flory[13] for the melt viscosity of mixed polyesters of $\bar{M}_w < 10^4$. However, Flory's equation was shown not to have general applicability when polystyrenes and polyisobutylenes of higher molecular weights were studied.[13] In fact, these polymers followed the relationship:

$$\log \eta = A + 3.4 \log \bar{M}_w \tag{10}$$

where η is the melt viscosity and A is a constant. The melt viscosity studies of Peticolas and Watkins[1] on high-density polyethylenes confirmed this equation. The power relationship of melt index to weight-average molecular weight, as expressed by eq. (8), is more in keeping with the form of eq. (10), even though there is a small discrepancy in the value of the exponent. Hence, it is felt that in practice there is probably more justification for using eq. (8) and not eq. (9). There is a small degree of scatter in the experimental points of Figure 6, a few of them deviating quite markedly from the proposed relationship. In this respect, it is interesting to note that Peticolas and Watkins[1] showed that branched polymers did not fit the melt viscosity/$\bar{M}_w$ relationship which they found. Although no measurements have been made to demonstrate the presence of branching in

the polymer samples examined in this work, three of the samples showing deviation from the proposed relationship are copolymers and hence could quite conceivably exhibit some of the properties of a branched polymer.

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Résumé

On a étudié le fractionnement d'échantillons de polyéthylène basse pression suivant Ziegler par la technique à la colonne de sable. On a déterminé les distributions des poids moléculaires par l'approximation de Schulz-Dinglinger. On a calculé par la méthode d'addition le poids moléculaire moyen en nombre, en poids et en z-moyen, des données du fractionnement de chaque échantillon. Les indices à l'état fondu et le rapport de coulée à l'état fondu ont été déterminés par les techniques ordinaires. On a trouvé que l'indice à l'état fondu est proportionnel à l'inverse de la cinquième puissance du poids moléculaire moyen en poids et le rapport de coulée à l'état fondu est proportionnel au poids moléculaire z-moyen.

Zusammenfassung

Einige Proben eines nach Ziegler hergestellten Niederdruck-Polyäthylens wurde an einer Sandkolonne fraktioniert. Die Molekulargewichtsverteilung wurde nach der Methode von Schulz und Dinglinger bestimmt. Die Zahlen-, Gewichts- und z-Mittelwerte des Molekulargewichts wurden aus den Fraktionierungsdaten der einzelnen Proben nach der üblichen Methode berechnet. Der Schmelzindex und das Schmelzflussverhältnis wurden mit Hilfe der bekannten Technik bestimmt. Es wurde festgestellt, dass der Schmelzindex zum Reziprokwert der fünften Potenz des Gewichtsmittels des Molekulargewichts in Beziehung steht. Das Schmelzflussverhältnis ist dem z-Mittel des Molekulargewichts proportional.