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Fractionation of Linear Polyethylene with Gel Permeation Chromatography. Part III*

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Summary

Many commercial linear polyethylenes have very broad distributions of molecular weight. The high molecular weight fractions often extend beyond the highest molecular weight calibration standard of GPC. For this reason the reliability of information obtainable from GPC has been examined with attention to the average molecular weights. Calibration range is a serious limitation for the accurate determination of the weight-average and the higher averages of molecular weight. Uncertainty in the baseline at the high molecular weight region, however, does not produce a significant error. With a four-column GPC having 10^3 to 10^7 Å nominal capacity, improved resolution is needed in the high molecular weight range. In order to examine the resolution and to improve the calibration, a polyethylene standard of ca. 3–4 million molecular weight is required. With the present limitation of GPC the greatest amount of information can be obtained by examining and intercomparing the cumulative distribution curves. With this representation ca. 95% or more of the cumulative weight range is free from uncertainty in calibration and resolution. A question is raised as to whether melt index is precisely a function of the weight-average molecular weight. This question is pertinent when significantly different molecular weight distributions are involved. GPC offers an opportunity to resolve the question.

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INTRODUCTION

In the first paper of this series (*1*), the usefulness of gel permeation chromatography (GPC) was examined as a tool for fractionating linear polyethylenes. The conclusions of practical importance were (a) two column GPC (10^4 and 10^6 Å) exhibits resolution comparable to extractive-column fractionation, (b) unmatched rapidity of GPC operation, (c) need for improving resolution at high molecular weights, and (d) necessity of using polyethylene fractions as the calibration standards. The questions of resolution and calibration are quite general ones with many fractionation techniques. Progress has been made along these lines with GPC; however, improvements continue almost indefinitely. For the practical utilization of GPC, therefore, one has to accept the best means available at a given time.

In the second paper (*2*), a four-column GPC having 10^3 to 10^7 Å nominal capacity was accepted as the practical instrument. The calibration was based on polystyrene rather than polyethylene standards. Although the latter are ideal for obtaining absolute molecular weights, the relative molecular weights based on polystyrene are quite adequate for comparing one distribution to another. The usefulness of GPC was proven by demonstrating reliable reproductibility.

One selected sample was run (*2*) with four different GPC units having a similar capacity. The results showed excellent reproducibility, provided sufficient care was taken in calibration and other operations. At the same time, reproducibility on a single instrument was checked and found satisfactory by making consecutive runs of a number of samples. The work not only demonstrated reproducibility but provided a control sample to be used in the future for ensuring reproducible performance of GPC.

In these earlier papers (*1*), (*2*), examples of fractionation curves were presented to show that GPC could reveal interesting details of molecular weight distribution. In this paper, an examination on the confidence limits of the information obtained from GPC fractionation is continued. Further examples of fractionation results are discussed.

RESULTS

Calculation of Moments and Average Molecular Weights

In this section, calculations of moments and average molecular weights are reviewed with respect to the confidence limits of the

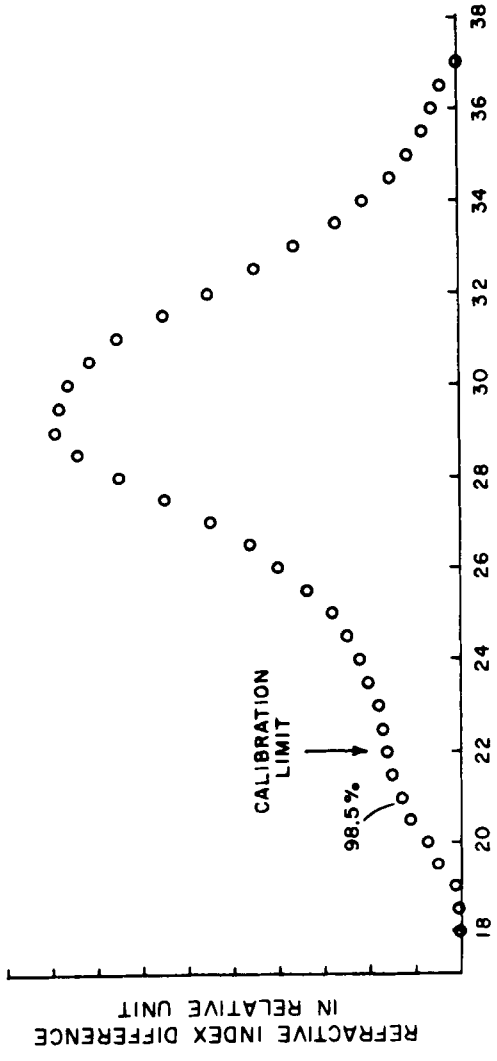

FIG. 1. A typical chromatogram of linear polyethylene. Solvent: trichlorobenzene. Temperature: 137°C. Columns: 7×10^4, 3×10^5, 10^6, and 10^3. Solution concentration: 0.5%. Injection time, 130 sec. Flow rate: 1 cc/min.

results. Specific attention is paid to the higher moments, where errors might arise from uncertainties in baseline and calibration.

A typical GPC trace of 0.4 melt index resin is reproduced in Fig. 1. The points in the curve are the input data for computer calculation (*3*). The computer outputs are shown in Fig. 2, as Curves a, b, c, d, and e. These five curves represent the following quantities:

$$Q_0 = \int \frac{1}{A_i}\left(\frac{dW_i}{dA_i}\right) dA_i = \int \left(\frac{dW_i}{dA_i}\right) d \ln A_i \quad (1)$$

(Curve a)

$$Q_1 = \int \left(\frac{dW_i}{dA_i}\right) dA_i = \int A_i \left(\frac{dW_i}{dA_i}\right) d \ln A_i \quad (2)$$

(Curve b)

$$Q_2 = \int A_i \left(\frac{dW_i}{dA_i}\right) dA_i = \int A_i^2 \left(\frac{dW_i}{dA_i}\right) d \ln A_i \quad (3)$$

(Curve c)

$$Q_3 = \int A_i^2 \left(\frac{dW_i}{dA_i}\right) dA_i = \int A_i^3 \left(\frac{dW_i}{dA_i}\right) d \ln A_i \quad (4)$$

(Curve d)

$$Q_4 = \int A_i^3 \left(\frac{dW_i}{dA_i}\right) dA_i = \int A_i^4 \left(\frac{dW_i}{dA_i}\right) d \ln A_i \quad (5)$$

(Curve e)

where Ai is the relative chain length based on polystyrene standards and (dW_i/dA_i) is obtained from the cumulative distribution curve as the derivative of cumulative fraction with respect to A_i. On these

TABLE 1

Moments and Average Chain Length

Quantity	Computer integration	Possible range of value resulting from baseline error (hand calculation)
Q_0	1.59×10^{-3}	Negligible
Q_1	1.01	Negligible
Q_2	8.95×10^{3}	Negligible
Q_3	4.77×10^{8}	$4.52–4.85 \times 10^{8}$
Q_4	4.82×10^{13}	$4.32–5.30 \times 10^{13}$
$\bar{A}_n$	6.3×10^{2}	Negligible
$\bar{A}_w$	8.9×10^{3}	Negligible
$\bar{A}_z$	5.3×10^{4}	$5.05–5.4 \times 10^{4}$
$\bar{A}_{z+1}$	1.01×10^{5}	$0.96–1.09 \times 10^{5}$

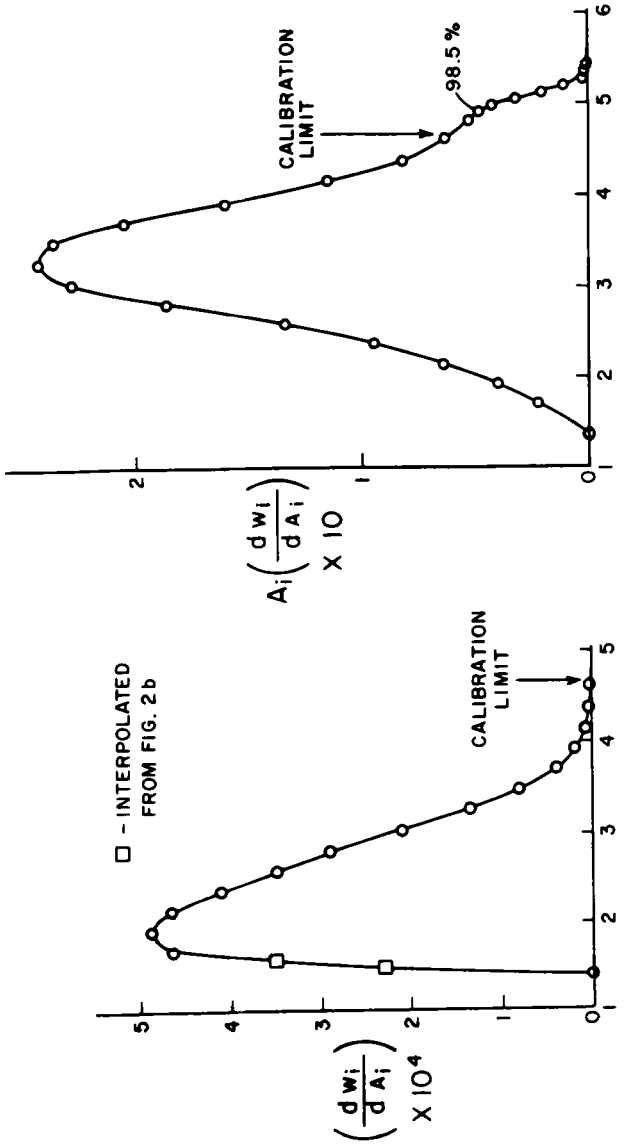

FIG. 2a and **2b.** Moments, percentages shown are cumulative weight fractions. Fig. 2a is based on Eq. (1) and Fig. 2b on Eq. (2).

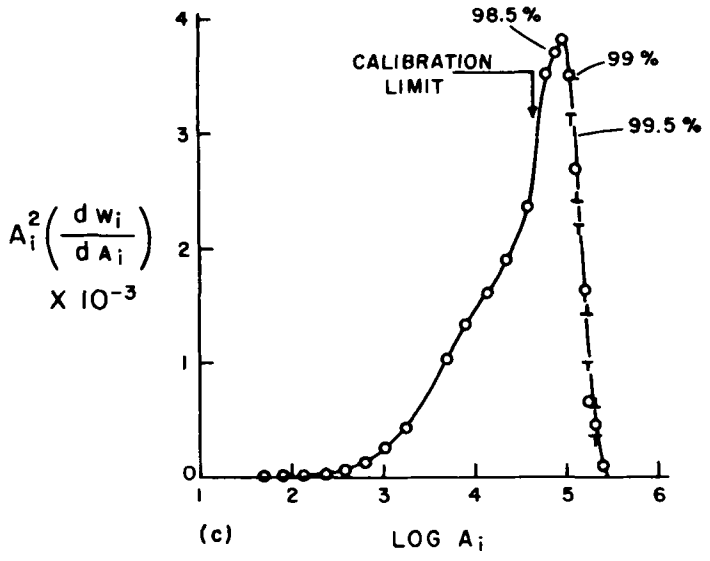

FIG. 2c. Based on Eq. (3).

curves, computer outputs are shown with circles. Except for the nine points at the highest molecular weight, every third point from the computer output is shown.

Hand calculation is also performed in the high molecular weight range, independent of the computer calculation. The input data for this calculation are taken by drawing as low and as high a baseline as possible to assess the errors involved in drawing the baseline. A graphical differentiation is used to obtain (dW_i/dA_i). The maximum (⊥) and minimum (T) values are shown in the graph with the symbols indicated. The results of the computer integration according to Eqs. (1)–(5) are given in Table 1, together with the limits of error in baseline drawing. Average values of chain lengths, Eqs. (6)–(9), are also listed.

$$\bar{A}_n = \frac{Q_1}{Q_0} \quad \text{or} \quad \frac{1}{Q_0} \quad \text{(number average)} \qquad (6)$$

$$\bar{A}_w = \frac{Q_2}{Q_1} \quad \text{or} \quad Q_2 \quad \text{(weight average)} \qquad (7)$$

$$\bar{A}_z = \frac{Q_3}{Q_2} \quad (z \text{ average}) \qquad (8)$$

$$\bar{A}_{z+1} = \frac{Q_4}{Q_3} \quad (z+1 \text{ average}) \qquad (9)$$

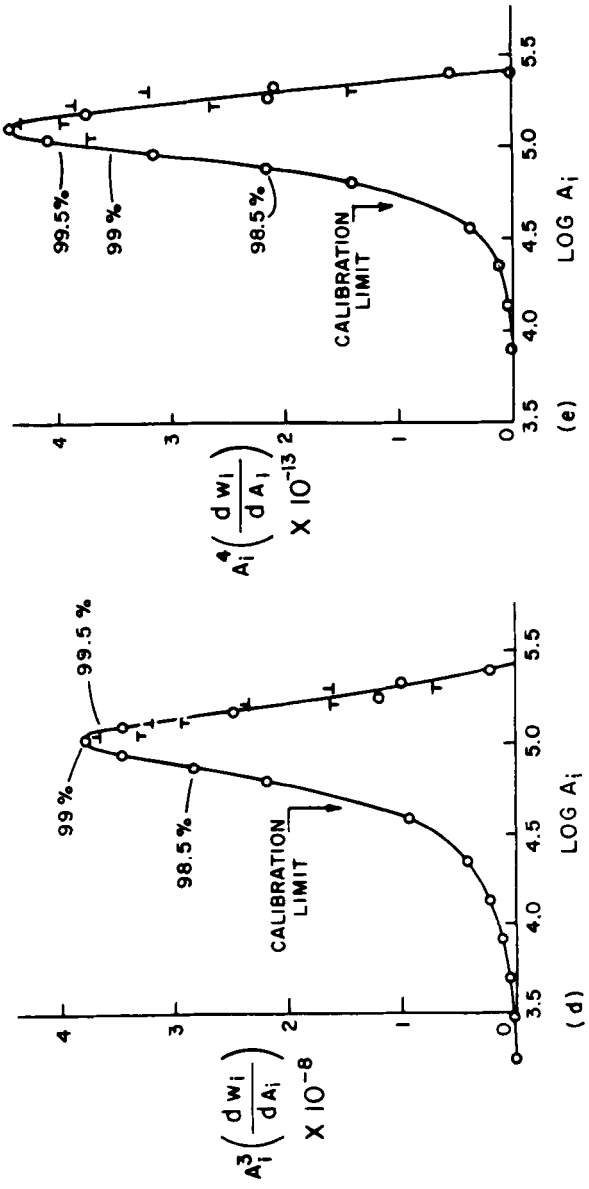

FIG. 2d and 2e. Fig. 2d is based on Eq. (4) and Fig. 2e on Eq. (5).

Conclusions from these results are:

(a) The computer outputs and the hand-calculated results are in good agreement.

(b) The errors arising from uncertainty in the base line are insignificant, even for the $(z + 1)$ average chain length.

(c) The highest molecular weight calibration standard, polystyrene of ca. 50,000 chain length, is not sufficient to provide reliable values for the weight-average molecular weight and the higher average chain length; a calibration standard having 250,000 chain length is required. This is approximately 3–4 million molecular weight polyethylene.

(d) Because the present calibration does not encompass the significant molecular weight range, $\bar{A}_w$, $\bar{A}_z$, and $\bar{A}_{z+1}$ are arbitrary values resulting from a particular data treatment. In this case, the treatment is based on the linear extrapolation of the calibration curve, i.e., a plot of logarithm of chain length versus GPC count.

(e) It appears that improved resolution is called for at the high molecular weight range. The shoulder at Count 21 in Fig. 1 may be one indication. Another is the change in the peak molecular weight from the Q_0 plot to the Q_4 plot (Fig. 2a–e and Table 2). This change becomes less and less from the lower moment to the higher moment, and behaves as if there is a cutoff at some point of the high molecular weight tail. The cut off may be real, but a lack of resolution is suspected.

Ratios of the succeeding average chain length also show the cutoff

TABLE 2

Peak Molecular Weight Corresponding to Each Moment and Ratios of Average Molecular Weight

Moment	Ratio of molecular weights	Peak chain length, A_i
Q_0		8.34×10^1
Q_1		1.8×10^3
Q_2		9.09×10^4
Q_3		1.08×10^5
Q_4		1.28×10^5
	$\bar{A}_w/\bar{A}_n$	14.2
	$\bar{A}_z/\bar{A}_w$	6.0
	$\bar{A}_{z+1}/\bar{A}_z$	1.9

TABLE 3

Melt Index and Average Chain Length

Group	Resins	Melt index	$\bar{A}_n \times 10^{-2}$	$\bar{A}_w \times 10^{-3}$	$\bar{A}_z \times 10^{-4}$	$\bar{A}_w/\bar{A}_n$
1	A	0.4	8.0	10.5	6.7	13.1
1	B	2.5	6.6	6.4	5.0	9.7
1	C	5	6.4	4.8	3.9	8.1
1	D	9	5.4	4.2	3.5	7.8
2	E	5	9.0	4.7	2.7	5.2
2	F	9	8.2	5.3	4.2	6.4
2	G	15	7.2	2.8	0.91	4.0

at the high molecular weight (Table 3). It appears that even the relative significance of the $(z + 1)$ average is very much in question.

(f) With the present state of the art, the moments and average molecular weights are merely arbitrary values, although they may be quite reproducibly determined. Any attempt to attach more than relative significance to these values requires extreme caution. This may not necessarily be true with polymers whose distribution is not extended to such high molecular weights as shown in this example. With linear high density polyethylenes, however, this example is not atypical.

Average Molecular Weights and Melt Index

In the preceding section, it has been shown that the average molecular weights determined by this technique are of relative significance only. They also provide a relative measure of polydispersity. In this section, the fractionation results on several resins are intercompared to see how much useful observation can be obtained. In Table 3 are values of average chain length for two groups of polyethylene having different melt indices. The basic difference between the two groups is in the polydispersity indicated by $\bar{A}_w/\bar{A}_n$.

With Group 1, there is a definite relation between the melt index trend and the average chain length trend. On the other hand, among the Group 2 samples the number-average chain length is the only one that shows a relationship with the melt index. By inspecting Group 1 and 2 together, however, it is evident that the melt index is not a function of number-average chain length. This is also a generally accepted observation. In Fig. 3, values of $\bar{A}_w$ are plotted against melt index. Evidently an approximate correlation is possible in this plot, as is

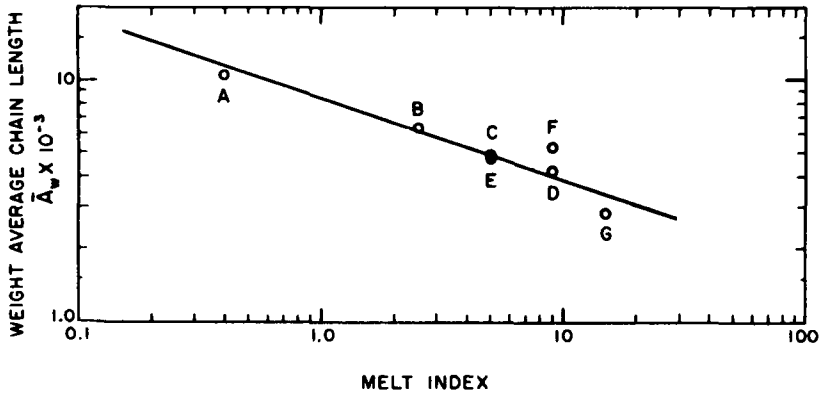

FIG. 3. Weight-average chain length and melt index.

illustrated by the straight line. From this straight line $\bar{A}_w$ value can be estimated for a given melt index. Such estimates of $\bar{A}_w$ are given in Table 4.

Whether melt index is *precisely* a function of $\bar{A}_w$ is not known. However, if we assume the correlation to be valid, errors in $\bar{A}_w$ of Resins F and G are far too excessive. Whether this is truly experimental error or not needs to be resolved.

TABLE 4

Melt Index And Weight Average Chain Length

Resins	Melt index	$\bar{A}_w \times 10^{-3}$ (observed)	$\bar{A}_w \times 10^{-3}$ (estimated)
A	0.4	10.5	11.5
B	2.5	6.4	6.2
C	5	4.8	4.9
D	9	4.2	4.0
E	5	4.7	4.9
F	9	5.3	4.0
G	15	2.8	3.4

FRACTIONATION CURVES

In the preceeding section, average molecular weights and polydispersities of seven resins have been presented. Further, an approximate correlation has been observed between melt index and weight-

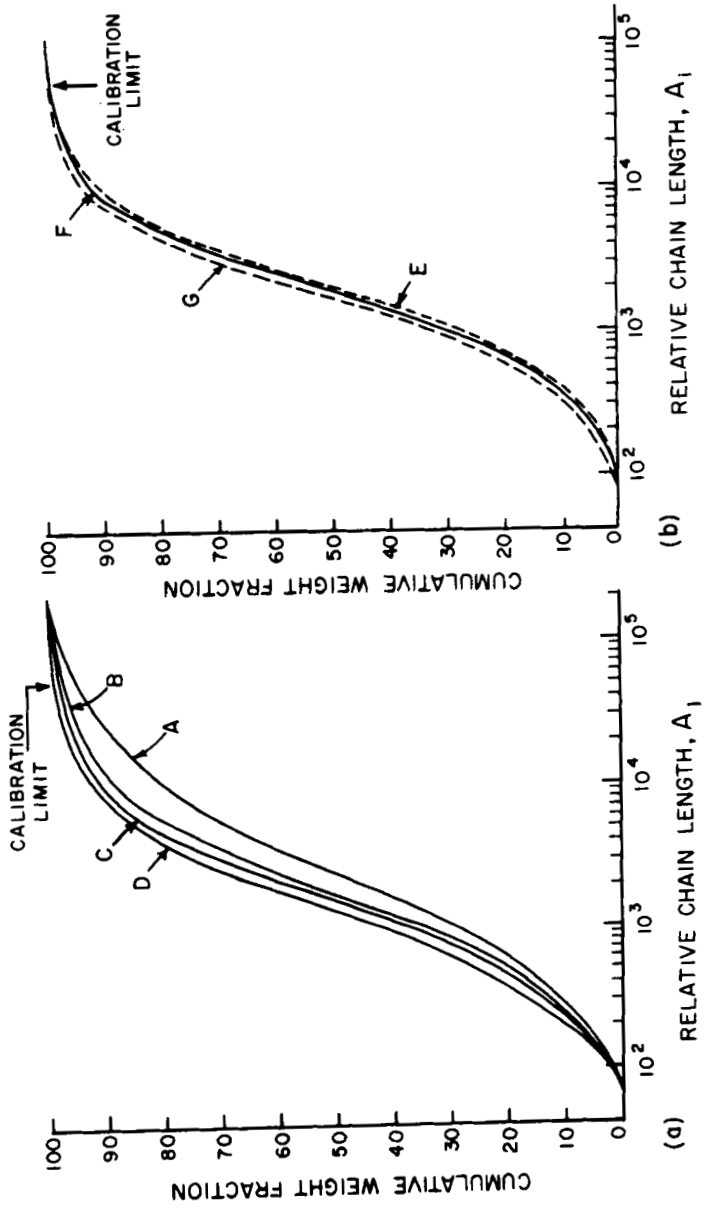

FIG. 4. Fractionation curves. (a) Resins A, B, C, and D. (b) Resins E, F, and G.

average molecular weight. The remaining question is whether GPC results have been exhaustively analyzed. In this section, the fraction curve itself is examined to see if any advantage is found in representing the result as a curve rather than as average molecular weights. In Fig. 4a, the fractionation curves of resins in Group 1 are shown in the cumulative form.

It is obvious that the chain length corresponding to a constant cumulative fraction follows a reverse order to that of melt index at practically all levels of cumulative fraction. Therefore, with this group, it is not surprising that melt index and any of the average chain lengths show the consistent trend previously noted. The fractionation curves of the Group 2 resins are presented in Fig. 4b. Compared to Group 1, this group has not only narrower distribution, but less spread among the curves at comparable melt indices. In particular, there is very little difference between the curves of Resins E and F in spite of the melt index difference of 5 and 9. This emphasizes an important need for performing the fractionation precisely.

The advantages in using the cumulative distribution curve rather than average molecular weights are (a) more detail in the molecular weight distribution may be seen, and (b) more emphasis is placed on the midportion of the curve where the data are relatively free from the uncertainty in calibration and resolution. Consequently, more than 95% of the curve in terms of the cumulative fraction can be used effectively.

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