

Characterization of Branched Polyethylene Fractions from the Elution Column*

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Synopsis

Fractions from several elution column runs on samples of up to 6 g. of a well-characterized high-pressure polyethylene were analyzed by absolute molecular weight methods and several other techniques. The M_n and M_w integral distribution curves are free from any reversal, as was the viscosity distribution curve. Fractions with M_w as high as 8×10^6 were recovered, more than 20 times higher than the original sample's M_w . The polydispersity of the fractions increases from $M_w/M_n = 1.5$ or less in the low molecular weight fractions to a nearly constant value of 4.5-5.0 in fractions above 60% cumulative sample weight. Nonetheless, refractionation on the elution column shows that the fractions are narrowly distributed in terms of solubility, while GPC analysis reveals that the fractions have an extremely narrow size distribution. It is concluded from the combined results that long-chain branching plays an important role in determining the equilibrium solubility and, further, that long-chain branching increases the polymer solubility. Sample calculations are provided, which illustrate the effect of fraction polydispersity on calculated original sample molecular weights and the fit of the fractionation results to several model distribution functions.

INTRODUCTION

As a result of a detailed study of elution column variables it has been possible to fractionate a well-characterized high-pressure polyethylene sample in moderate quantity¹ and to obtain a distribution curve that is highly reproducible and free from any reversals. This has opened the way to answering important questions concerning the influence of long-chain branching or, possibly, of other molecular parameters, on the solubility of branched polyethylene.

Although frequent references have been made to the expected influence of long-chain branching on polymer solubility, there is little experimental indication of the magnitude of the effect or even of whether long-chain branching increases or decreases the solubility of the polymer. Judged by the wide range of viscosities represented in the distribution curve of the

* This paper is assigned No. TP432 in the series of papers approved for publication by the U. S. Army Natick Laboratories.

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sample used in this work, fractionation appears to proceed mainly on the basis of molecular weight. In fact, Guillet and his co-workers² have presented evidence, based on refractionation and sedimentation patterns, that branched polyethylene fractions obtained by column elution are quite sharp. This suggests the absence of any factors that seriously interfere with resolution. On the other hand, Schuurmans³ found very large heterogeneities by absolute molecular weight measurements of the fractions from a standard two-stage fractional precipitation. It is not clear whether this difference in results is due to the greater efficiency of column elution, to individual sample differences, or to still other factors. However, the occurrence of such large-order polydispersity would have a marked effect on all aspects of the molecular characterization of branched polyethylene fractions.

In this paper fractions from efficient 4 and 6 g. elution column runs have been analyzed by absolute molecular-weight methods to give a direct assessment of fraction polydispersity. When combined with the analyses from refractionation and gel permeation chromatography, the results provide considerable insight into the factors controlling the polymer solubility and molecular weight resolution, besides instructive conclusions on the related problems of calculating average molecular weights or deriving molecular weight distributions from the fractionation data.

EXPERIMENTAL

Samples

The properties of the linear and the branched polyethylene samples used in this work, designated PE-85 and PE-76, respectively, have been described previously.^{1,4} In the discussion that follows references are made to the fractionation runs from which the fractions of PE-76 were derived. The corresponding elution conditions for these runs were summarized by Traskos et al.¹ in their Table I. The numerical designation of linear fractions is used only to differentiate between separate runs.

Viscometry

Viscosity measurements were made at 105°C. on 0.1% *p*-xylene solutions of the fractions with a spiral capillary Ubbelohde type of viscometer. Solutions were clarified by filtration at 105°C. with Gelman Metricel Alpha 6 (0.45 μ) membrane filters (Gelman Instrument Co., Ann Arbor, Mich.) and a modified Millipore stainless-steel microsyringe holder, as previously described.¹

Light Scattering

α -Chloronaphthalene at 126°C. was chosen as the solvent for light-scattering measurements, to take advantage of the high refractive-index increment in this solvent compared with those of tetralin and *p*-xylene.^{4,5}

The filtering system used in preparing solutions for viscometry also proved suitable for the rapid ultraclarification of solutions for light scattering. However, it was found that the Metrical Alpha 6 filters discolored and embrittled in α -chloronaphthalene at 125°C., in some cases imparting considerable turbidity to the solutions. Microporous membranes of various other types were tried. Selas Flotronics metal membrane filters (Selas Corp. of America, Spring House, Pa.) were found to be somewhat less efficient than the organic membrane filters of equivalently rated pore size and, further, appeared to react with the α -chloronaphthalene to produce a hazy suspension. With proper conditioning Millipore HA Filters (Millipore Filter Corp., Bedford, Mass.), 0.45 μ , proved usable. These filters also discolored but appeared to swell somewhat, and after 6 hr. of conditioning at 126°C. in α -chloronaphthalene, while restrained in the filter holder, gave very clear, dust-free solutions. However, it was necessary to limit the contact time of solutions to only a few minutes, to avoid discoloration of the solutions. The excellent filtering characteristics of the swollen membrane persisted for 2 or 3 days. After that time the gradually decreasing filtration rate became too slow for practical use.

The α -chloronaphthalene as received was yellowish and hazy. Vacuum distillation was not successful in completely removing the impurities, but overnight contact with silica gel, followed by membrane filtration, resulted in dissymmetry ratios I_{45}/I_{135} that were always less than 1.02.

Light-scattering determinations were carried out in the Sofica light-scattering instrument (Mechrolab Division of Hewlett Packard) with vertically polarized light of wavelength 4360 Å. The instrument constant was established from a Zimm plot^{1,4} of sample PE-85 with use of the value 0.192 cm.³/g. for the refractive index increment⁴ of polyethylene. Light-

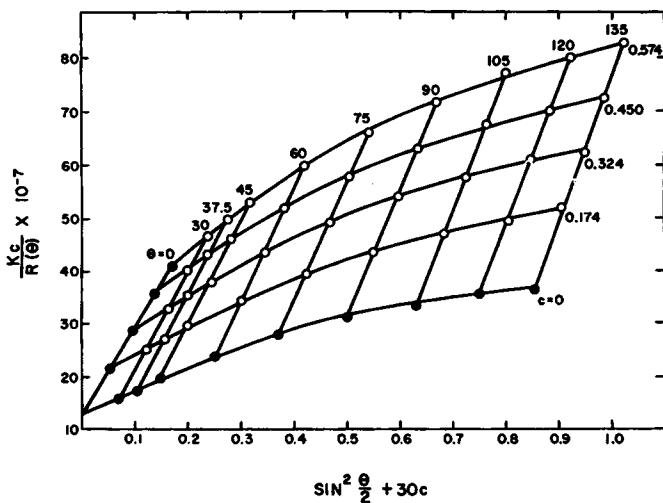


Fig. 1. Zimm plot, PE-76 fraction, $M_w = 8.1 \times 10^5$.

scattering measurements of solutions of each polyethylene fraction at three or four concentrations were made. The required amount of sample was dissolved in about 5 ml. of solvent and filtered into a clean 20 mm. o.d. light-scattering cell. Intensities were determined over the angular range 30–150° at no less than three different rotated cell positions, to minimize the effect of imperfections in the glass cell. A representative Zimm plot for a fraction of 8.1×10^5 weight-average molecular weight from PE-76 is shown in Figure 1. The plot is normal and, in particular, is free of the severe downward curvature at low angles in the zero-concentration limiting curve, which has been observed when microgel is present in high-pressure polyethylene samples.⁵⁻⁷

Osmometry

A high-speed membrane osmometer (Mechrolab, Model 502) was used to determine number-average molecular weights. Osmotic pressures were measured at 110°C. in *o*-dichlorobenzene with gel cellophane membranes (ARRO Laboratories), type 300 for $M_n > 1 \times 10^6$ and type 450 for $M_n < 1 \times 10^6$. To avoid the release of troublesome air bubbles in the cell, all solvent was degassed at 110°C. under vacuum before use, and solutions were made only with hot, degassed solvent. The membrane was also degassed in the solvent under vacuum at 105°C. for no longer than 45 min. before being clamped in the instrument. Longer incubation of the unclamped membrane greatly increased the equilibrium response time. Degassed solvent and solution were maintained at 115°C. in an oil bath prior to use and were introduced to the instrument from a heated hypodermic syringe. No antioxidant was used.

Gel Permeation Chromatography

A number of samples were analyzed by GPC through the services of Waters Associates, Framingham, Mass. The results were obtained at different times with different sets of columns. The runs were made at a concentration of $1/4\%$ or $1/8\%$ in trichlorobenzene at 135°C. with a flow rate of 1 cm.³/min. and a series of four columns of different pore sizes, such as 10^7 , 10^6 , 8×10^5 , and 10^3 Å.

RESULTS AND DISCUSSION

Quality of the Fractionation

In a previous paper¹ it was shown that by appropriate selection of fractionation conditions it was possible to achieve the fractionation of samples of a branched polyethylene, leading to integral distribution curves as a function of reduced specific viscosity, which were free of any reversals or other abnormalities. However, in the case of branched polyethylene viscosity data alone provide only limited information with which to assess the effectiveness of the fractionation, since the viscosity depends on the

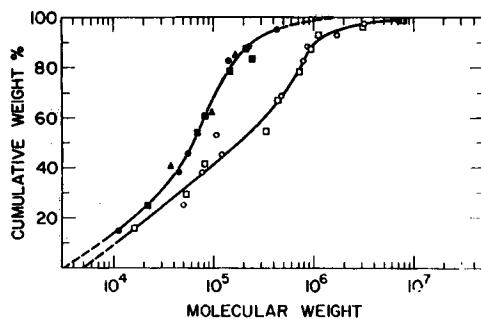


Fig. 2. Number-average and weight-average molecular weight distribution curves for PE-76: (black points) M_n results; (white points) M_w results.

degree of branching as well as on the molecular weight. From the several 4 and 6 g. runs in which the viscosity data indicated efficient fractionation alternate fractions were subjected to detailed molecular characterization. The weight-average molecular weight M_w integral distribution curve, based on two runs, and the number-average molecular weight M_n integral distribution curve, based on combined data for three runs on PE-76, are presented in Figure 2. The approximate M_w and M_n integral distribution curves for PE-85, based on more limited data, appear in Figure 3. The method of Schulz and Dinglinger,⁸ in which a given fraction is plotted at the cumulative weight of the previous fractions plus one-half the fraction weight, has been used to take account of the effect of fraction polydispersity.

For PE-76 there is reasonable agreement between the data from the different runs, which have been combined to obtain the M_w and M_n integral weight distribution curves. In accord with the previously reported viscosity distribution curves these molecular weight distribution curves are also free from any abnormal upward curvature or reversals. Moreover, the span of molecular weights covered by the fractions suggests that efficient resolution has been obtained. For example, in the M_w integral distribution curve about 10% of the sample has a molecular weight above

TABLE I
Comparison of Absolute Molecular Weight Values and Fractionation
Results, PE-76

	Absolute values		Fractionation values	
	Kokle et al. ⁴	This work	Average ^a	Maximum
$M_w (\times 10^{-5})$	3.0 ^b	3.7	4.8	79.0
$M_n (\times 10^{-5})$	0.266 ^c	0.247	0.244	4.3
$[\eta]$, dl./g.	0.95 ^d			4.6

^a Calculated by summation over the smoothed M_w and M_n integral distributions.

^b Light scattering.

^c Osmometry.

^d Converted from value in α -chloronaphthalene at 125°C.

1×10^6 , yet even over this region the distribution is represented in considerable detail.

The quality of the resolution obtained is displayed more clearly in terms of the comparisons in Table I. This table lists two sets of molecular weight values for PE-76, those of Kokle et al.⁴ in the second column and, in the third, those determined in the present work. These average sample values may be compared with the maximum M_w and M_n values obtained in the fractions, listed in the last column. The maximum M_w is about 8×10^6 , fully 21 times higher than the corresponding value in column 3. The maximum M_n of 4.3×10^5 is limited by the sensitivity of the osmometer but is about 17 times higher than the average value listed in column 3. It is interesting to note that the maximum $[\eta]$ is only some 5 times greater than the value for the original sample. This is indicative of the pronounced effect of long-chain branching in suppressing the increase in viscosity with increasing molecular weight that occurs in linear polymers.

Table I also lists in the fourth column the average molecular weight values calculated from the fractionation data. It should be stated that these average molecular weights were not obtained from a derived weight frequency distribution but by means of the direct summations $M_w = \sum_i w_i M_i$ and $M_n = 1/\sum_i (w_i/M_i)$ evaluated from the respective smoothed M_w and M_n integral distribution curves of Figure 2. The general accord between the calculated and absolute molecular weight values in Table I is evidence that the light-scattering and osmotic-pressure molecular weights of the fractions are reasonably accurate and consistent with the determination of the whole sample and that no serious losses or sample degradation have occurred in the process of carrying out the fractionation and analyses.

Considering the results in more detail, the calculated value $M_n = 24,400$ is in good agreement with the result $M_n = 24,700$ determined in the current work by osmometry, although both values are about 7% lower than those reported by Kokle et al.⁴ The difference could be related to the performance of the electronic osmometer as compared with the slower conventional osmometers used by these workers. On the other hand, it must be admitted that the agreement between the calculated and absolute values of M_n is in part fortuitous, since it depends on the arbitrary extrapolation represented by the dashed line in Figure 2, which leads to a molecular weight cutoff of about 3200.

Turning to the M_w values, the result $M_w = 480,000$ calculated from the fractionation data is about 30% higher than the $M_w = 370,000$ determined by light scattering in this work. In turn, the latter value is substantially above the result in column 2 reported by Kokle et al. Their M_w is undoubtedly depressed by the removal of about 2.5% of the sample during the clarification by high-temperature ultracentrifugation. Although the largest portion of the polymer removed was probably crosslinked gel, their analysis showed that a marked fractionation is produced in the supernatant by ultracentrifugation. It follows that part of the highest molecular weight species are also concentrated in the sedimented gel. This suggests that the

present-light scattering result might be more representative of M_w for PE-76. The appreciable difference between this value and that calculated from the fractionation data is believed due to the polydispersity of the fractions, as discussed later.

Ratio of Weight to Number-Average Molecular Weights in the Fractions

In the previous section the efficiency of fractionation and the resolution were examined primarily in terms of the absence of molecular weight reversals in the distribution curves and the range of molecular weights obtained

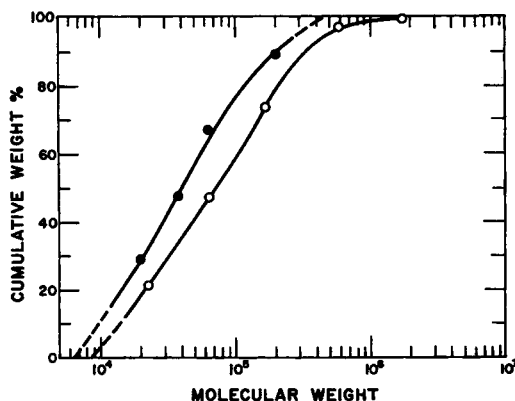


Fig. 3. Number-average and weight-average molecular weight distribution curves for PE-85: (●) M_n results; (○) M_w results.

in the fractions. However, the disparity between the M_w and M_n distributions in Figure 2 clearly indicates that the PE-76 fractions are appreciably polydisperse, and Figure 3 indicates that even the fractions from PE-85 are not exceptionally sharp.

Part of the molecular weight data from a typical 4 g. run on PE-76 (run 6) are recorded in Table II, and corresponding data for PE-85 appear

TABLE II
Fractionation Results, PE-76 (4 g. run)

Fract. No.	Cumulative weight per cent	$M_w (\times 10^{-5})$	$M_n (\times 10^{-5})$	M_w/M_n	
				Direct	Curves
11	14.2		0.11		1.4
13	24.7	0.05			1.4
15	38.2	0.76	0.45	1.7	1.9
16	45.7	1.20	0.55	2.2	2.4
17	53.5	1.05			3.1
19	69.0	4.8			4.8
21	82.6	7.9	1.37	5.8	4.8
22	88.1	8.6	2.25	3.8	4.3

TABLE III
Fractionation Results, PE-85 (5 g. run)

Fract. no.	Cumulative weight per cent	$M_w (\times 10^{-5})$	$M_n (\times 10^{-5})$	M_w/M_n (curves)
11	21.4	0.225		1.5
12	29.0		0.20	1.6
14	47.3	0.66	0.38	1.7
17	66.8		0.74	1.9
20	73.6	1.72		1.9
23	88.3		2.06	1.9
25	97.5	5.9		

in Table III. As these tables show, there were very few fractions from which both M_n and M_w were determined for PE-76 and, in fact, only one such fraction for PE-85. Therefore, in order to assess the trend of the fraction polydispersity with molecular weight, values of M_w/M_n were also calculated from the smoothed distribution curves of Figures 2 and 3. Comparison of the two sets of values listed under the M_w/M_n heading of Table II indicates that, in general, there is reasonable correspondence between the estimated and directly measured M_w/M_n ratios for PE-76. This suggests that the values determined in this manner for PE-85 will also be reliable.

For PE-85 the M_w/M_n ratios in Table III appear to increase from about 1.5 to about 1.9. The polydispersity in these fractions is very much larger than the M_w/M_n values of 1.1 or 1.2 that have been reported in the literature as characteristic of fractions of linear polyethylene obtained by column elution.^{9,10} None of the reported values, however, were based on direct measurement of M_w and M_n but involve some approximation for estimating M_w , M_n , or the ratio M_w/M_n . Values of 1.1 or less are also predicted by various mathematical analyses of solution fractionation, even for samples of extremely high initial polydispersity.^{10,11} These calculations are usually based on a simplification of the equation governing the partitioning of species between the precipitated and supernatant phases. It has recently been shown¹² that these approximations yield incorrect results for several aspects of fractionation behavior and, in particular, tend to overestimate the fractionation efficiency. The more exact treatment appears to lead to fraction heterogeneities that are comparable to those reported here. On the other hand, since there was some reversal in the viscosity data for PE-85,¹ it is possible that somewhat more narrow fractions would be obtained under conditions completely free from any inversion in the fractionation.

Returning now to an examination of results from the PE-76 fractions, it is observed in Table II that below a 45% cumulative weight the M_w/M_n ratio is 1.5-2.0, equivalent to the values found with the linear polyethylene. The polydispersity ratio then increases rapidly with increasing

molecular weight and levels off to a value of 4.5–5.0. This behavior suggests that the heterogeneity of the lower molecular weight fractions is due primarily to the extremely high polydispersity of the sample, while the increasing heterogeneity that appears in the later fractions might reflect the expected increase in branching with increasing molecular weight.

Refractionation

A number of the fractions were refractionated on the elution column, to give some further insight into the nature of the sample polydispersity. Regardless of the size of the original fractions, samples of 0.12–0.15 g. were run on refractionation. The conditions were as close as possible to those used in the original fractionation in all respects, except that the volume per fraction was halved to allow more detailed analyses. Despite the care taken in setting up these runs, owing to the small size of the samples there were occasionally erratic results. Nonetheless, most of the refractionation results were consistent with the pattern described below.

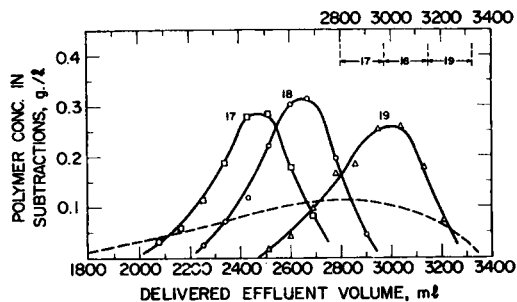


Fig. 4. Refractionation of three successive PE-76 fractions showing polymer concentration in subfractions versus elution volume: original range of elution volume indicated in upper right-hand corner; (---) fraction from inefficient run.

The results obtained from three successive fractions of a 4 g. sample (run 3), each representing about 6% of the original sample, are plotted in Figure 4 as polymer concentration in the fractions against elution volume. The volume at which each fraction was eluted during the original run on the whole sample is indicated in the upper right-hand corner of this figure. Comparison of these values with the range of elution volume in the subfractions shows that on refractionation each of the three fractions was shifted to an earlier elution volume by about the same amount, 650–700 cm^3 . In addition, the 170–180 cm^3 volume increment over which each fraction was originally eluted has expanded on refractionation to 650–700 cm^3 . These shifts illustrate the marked influence that the distribution of molecular species and the higher polymer concentration during fractionation of the whole sample exert on the solubility behavior of the fractions.

Despite the pronounced redistribution of species that has occurred on refractionation and the very large molecular weight polydispersity of the

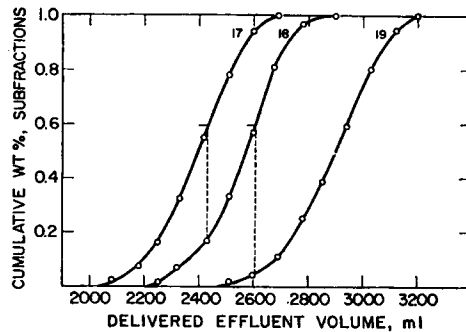


Fig. 5. Refractionation showing cumulative weight versus elution volume for three successive PE-76 fractions.

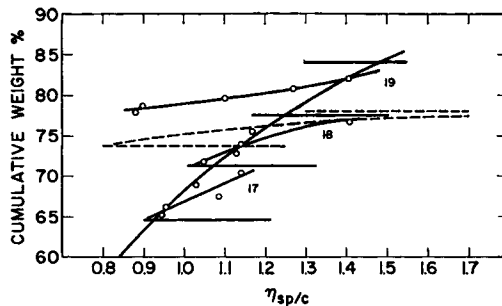


Fig. 6. Refractionation showing integral viscosity distributions in three successive PE-76 fractions: horizontal lines demarcate cumulative weight per cent range of each fraction on original distribution curve; dashed curve, results for fraction from an inefficient run.

fractions, the elution curves for these three fractions overlap to only a limited extent. The separation in the elution curves is even more clearly displayed when the results are plotted as an integral weight distribution curve, as in Figure 5. At a volume corresponding to a cumulative weight of 60% in fraction 17 only about 16% of fraction 18 has been eluted, and virtually none of fraction 19. The separation between fraction 17 and 19 appears to be virtually complete, although these fractions are separated by only 12% in cumulative weight and were taken from the portion of the integral distribution curve, which is changing very slowly in molecular weight. These results, along with the similar behavior in other fractions that have been rerun, suggest that the fractions are narrowly distributed in solubility despite the marked polydispersity in molecular weight.

The viscosity data obtained in the same refractionations appear in Figure 6. The viscosities for the subfractions of each sample are plotted on a cumulative weight basis, the original viscosity distribution curve being presented for reference. In fractions 17 and 18 there is good separation, since the first 60% of fraction 17 includes viscosities that are present in

only 14% of fraction 18. Unfortunately, the results for fraction 19 are completely erratic. The extent of the overlap with fraction 18 conflicts with the solubility separation between the same fractions evident in Figure 5, and the sum of the weighted specific viscosities of the subfractions is too low for the original viscosity of fraction 19. Although of lesser accuracy than the weight distribution curves in Figure 4, the viscosity data in Figure 6 suggest that the viscosities besides the solubilities are narrowly distributed in the fractions from an efficient elution run.

Evidence that the results obtained on refractionation offer a sensitive test of polydispersity is indicated by data on a fraction from an inefficient 10 g. run (run 8), in which there was poor resolution of the final 20% of the sample but no molecular weight reversal. This fraction amounts to about 4.5% of the original sample taken at 73% cumulative weight, which is below the region where there is an upturn in the distribution curve. As shown by the dashed curve in Figure 4, the weight distribution curve for this fraction is spread over more than a twofold larger range of elution volume than fractions from run 3. The corresponding viscosity results represented by the dashed curve in Figure 6 cover the range of all three fractions from run 3. These results indicate that the narrow distributions determined in samples from efficient fractionations are not the consequence of limited resolution on refractionation.

Guillet and his co-workers also observed that the fractions from branched polyethylenes were narrowly distributed on refractionation.² They cited this as evidence that the fractions contained a narrow distribution of molecular weights. However, in the present case the absolute molecular weight data offer incontrovertible evidence that the fractions are extremely heterogeneous in molecular weight. The combined molecular weight and refractionation results therefore indicate that some factor in addition to molecular weight is controlling the elution behavior.

Analysis of the Fractions by Gel Permeation Chromatography

GPC analyses were carried out on several fractions from two runs on the linear sample and on fractions from PE-76 taken from run 3, for which the corresponding refractionation results on the elution column were discussed in the previous section. The GPC curves for the whole PE-76 sample and one each of a linear fraction, no. 1-15, and a branched fraction, no. 3-16, are compared in Figure 7. These curves have been normalized to represent equal areas under the curve. Compared with the spread of the original PE-76 sample, the branched fraction appears to be quite narrow, especially when it is recalled that the abscissa of the GPC plot is equivalent to a logarithmic scale of molecular weight. Even more important than this comparison is the observation that the branched polyethylene fraction appears to be as narrow as the linear fraction, in marked contrast to the far greater polydispersity of the branched fraction.

The various molecular weight values calculated from the GPC curves for the fractions, in all cases with the use of the calibration for linear

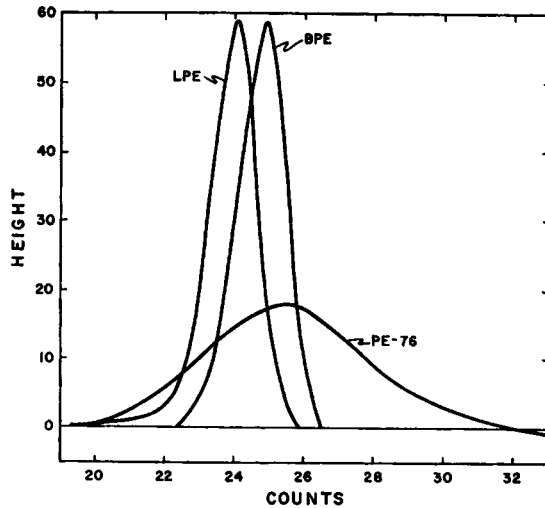


Fig. 7. GPC distribution curves for PE-76, a branched polyethylene fraction (BPE), and a linear polyethylene fraction (LPE), all normalized to equal areas.

polyethylene and a Q factor of 11, to convert calibrated angstrom length to molecular weight, are summarized in Table IV. Considering first the results for the linear fractions, it will be noted that the GPC analyses also

TABLE IV
GPC Fractionation Results

Sample ^a no.	$M_w (\times 10^{-5})$	$M_n (\times 10^{-5})$	M_w/M_n
Linear fractions:			
1-15, ABS	0.970	0.520	1.86
GPC	0.774	0.596	1.30
2-19, GPC	0.925	0.676	1.36
2-70, GPC	1.43	1.09	1.31
2-22, GPC	1.80	1.01	1.78
Branched samples:			
PE-76, ABS	3.65	0.247	14.8
GPC	0.624	0.166	3.75
3-13, ABS	1.15	0.50	2.30
GPC	0.28	0.20	1.40 (1.14) ^b
3-14, ABS	1.55	0.58	2.67
GPC	0.25	0.21	1.19
3-15, ABS	2.37	0.70	3.40
GPC	0.37	0.31	1.19
3-16, ABS	3.40	0.82	4.20
GPC	0.45	0.41	1.10
3-20, ABS	9.0	2.00	4.50
GPC	1.41	0.73	1.93 (1.35) ^b

^a ABS, absolute molecular weight values estimated from distribution curves; GPC, values calculated from GPC with a calibration for linear polyethylene.

^b Values in parentheses calculated by excluding lowest and highest ends, totalling about 4.5% of the fraction.

show that these are rather polydisperse, in general accord with the conclusion from the absolute molecular weight data. However, with the exception of fraction 2-22 the GPC M_w/M_n values are smaller than the corresponding values recorded in Table III. For fraction 1-15 in Table IV it is apparent that the discrepancy in M_w/M_n is due to a difference of 15–20% between the GPC and absolute molecular weights. Since these differences occur in opposite directions, the net effect is a reduction in the GPC M_w/M_n ratio. There is some variation in comparative absolute and GPC M_w/M_n values due, in part, to the fact that the GPC results for the different fractions were taken from runs on three different sets of columns.

Considering now the GPC results for the branched samples, the values tabulated for the whole PE-76 sample illustrate the marked sharpening of the distribution resulting from the effect of long-chain branching on the GPC behavior. However, it is the GPC-derived M_w/M_n values for the several PE-76 fractions that are of special importance. Three of these fractions have GPC M_w/M_n ratios that are less than 1.2 despite corresponding values derived from absolute molecular weight data that vary from 2.3 to 4.2. The larger GPC dispersities of fractions 3-13 and 3-20 are due to tailing rather than any marked broadening of the central peak. If the species at the low and high ends, totalling about 4.5% of these fractions, are excluded, the GPC M_w/M_n ratio for fraction 3-13 decreases from 1.35 to 1.14, a value consistent with the several fractions that follow, whereas for fraction 3-20 the value decreases from 1.95 to 1.35. In the first case it appears likely that the tailing is due to something that occurred during the GPC analysis, but in the second case it is also possible that the tailing is characteristic of this high molecular weight fraction. In any case the results indicate that all of the branched fractions are very narrow, including over 95% of the two fractions 3-13 and 3-20.

The contrast between the small GPC and large absolute molecular weight measurements of polydispersity in these branched fractions might be considered merely another example of the sharpening of the GPC distribution by long-chain branching, similar to the effect observed with the whole PE-76 sample. However, the interpretation of the curves in terms of molecular weight tends to obscure the true significance of these results. Studies of the GPC fractionation behavior of branched polystyrenes of controlled structure as well as the GPC behavior of randomly branched polyethylenes have shown that the effective parameter controlling the elution behavior of linear and branched polymers alike is the hydrodynamic volume of the solvated polymer molecule.^{13,14} On this basis it can be deduced from the GPC curves of the branched fractions that the distribution of molecular sizes is extremely narrow despite the broad distribution of molecular weights in these fractions. This conclusion implies that fractionation on the elution column was governed in large part by molecular size.

It might be argued that the influence of molecular size comes into play as a secondary effect that owes its importance to the role of diffusion in

controlling the extraction of species during the elution process, the branched species being favored by higher diffusion constants. However, the refractionation experiments on the elution column revealed that the original fractions were narrowly distributed in terms of solubility. Accordingly, any kinetic effects under the conditions of elution used here must have been minimal. It appears necessary to conclude that molecular size plays a major role in determining the equilibrium solubility behavior in these branched polyethylene fractions.

It is also possible to determine from the data in Table IV whether the effect of long-chain branching is to increase or decrease the solubility of the polymer. If the effect were to decrease the solubility, then any fraction would consist of lower molecular weight branched species mixed with high molecular weight linear species. In fact, the major discrepancy between the GPC and absolute molecular weights for the branched fractions in Table IV is the very large differences in M_w values compared to those in M_n values. For example, in fraction 3-15 there is more than a sixfold difference in the absolute and the GPC M_w values but only a twofold difference in the M_n values. This indicates that the hydrodynamic volume of the low molecular weight species is closer to that of polyethylene of the same molecular weight, while the hydrodynamic volume of the high molecular weight species in this fraction, including molecular weights well above 2.4×10^5 , is about equal to that of linear polyethylene of almost tenfold lower molecular weight. These comparisons provide direct evidence that the fractions consist of highly branched, high molecular weight species mixed with lower molecular weight, less branched species. Apparently, long-chain branching increases polymer solubility.

Effect of Branching on Solubility

It is possible to make some additional observations on the solubility behavior of the branched and linear polyethylene samples from the elution curves. A comparison of the molecular weight-eluant composition curves for PE-76 and PE-85 is shown in Figure 8. Two runs for each sample have been included, because the eluant composition is not only a function of molecular weight but also depends somewhat on the chosen fractionation conditions. Despite some differences between the individual curves for each sample it is evident that for any given solvent composition the molecular weight of the branched polymer eluted is much higher than that of the linear polymers. This difference is smaller, less than a factor of 2, at the lower molecular weights but increases with molecular weight, such that at 45% *p*-xylene the molecular weights of the branched and linear polymers eluted differ by a factor of 10. The pronounced difference in solubility is also evident in the fact that about 7% of the linear sample is not eluted in an asymptotic composition of 48% *p*-xylene, while a larger PE-76 sample is completely eluted at 47.5% *p*-xylene. This behavior is in agreement with the difference in cloud-point solvent compositions previously determined for PE-76 and PE-85.¹

The foregoing conclusions are consistent with the interpretation of the GPC results, which also suggest that branching produces an increase in the polymer solubility. The additional published information concerning the effect of long-chain branching on solubility is very limited. It might be noted that Stockmayer and Fixman¹⁶ concluded from a theoretical analysis that the critical temperature for a branched polymer of infinite molecular weight would be the same as that of a linear polymer. However, no prediction could be made about the possible effect of branching on the phase equilibrium of finite molecular weight species. The observation made by Thurmond and Zimm¹⁶ that different fractions of a branched polystyrene all had a zero second virial coefficient in a butanone-2-propanol mixture of fixed composition, regardless of degree of branching or molecular weight,

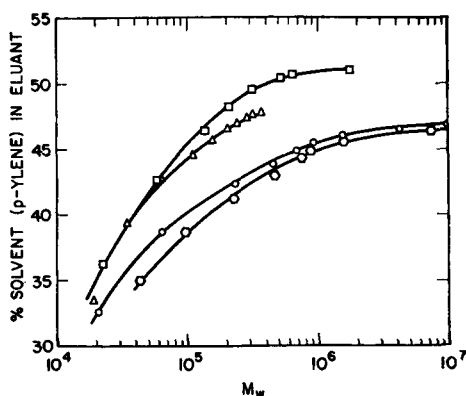


Fig. 8. Molecular weight versus elution solvent (*p*-xylene) concentration for (upper curves) PE-85 runs and (lower curves) PE-76 runs.

bears out the theory. There were no determinations of the effect of branching on solubility.

Perhaps the only other experimental evidence in this problem are the results of Wigja et al.,¹⁷ who found that it was possible to fractionate polyvinyl acetate, mainly on the basis of the degree of branching, by the choice of a particular two-component solvent system. Using a different solvent mixture fractionation was achieved primarily on the basis of molecular weight. This raises the interesting possibility that the influence of branching on solubility in some cases might be varied by the choice of the solvent.

Molecular Weight Distributions

The polydispersity of the fractions affects the reliability of any molecular weight distribution constructed from the fractionation data besides the accuracy of the whole sample average molecular weight values obtained by summation over the derived molecular weight distributions. Since a simple and instructive treatment of the latter problem exists, this will be dealt with first.

It is common practice, even with branched polyethylene, to calculate fraction molecular weights from viscosity data by using an appropriate viscosity-molecular weight relation calibrated by light scattering or one of the colligative methods. The resulting data provide a means of calculating whole-sample M_n and M_w values from the appropriately weighted summation over the differential distribution or by fitting the data to model distribution functions.

The effect of fraction polydispersity on the whole sample M_n and M_w values calculated by the above-mentioned procedure has been treated by Bohdanecky et al.¹⁸ It was assumed that the fractions could be described by a Schulz type of distribution and that all had the same polydispersity characterized by the distribution parameter h . Under these conditions the ratio of the number-average molecular weight (M_n^*) of the sample, calculated by summation over the *weight-average* molecular weights of the fractions, to that (M_n) obtained by summation over the *number-average* molecular weights of the fractions is equal to the ratio M_w/M_n for the fractions:

$$M_n^*/M_n = M_w/M_w^* = (h + 1)/h = M_w/M_n$$

As indicated, the same relation also holds for the ratio of the calculated sample weight-average molecular weights M_w/M_w^* , where M_w and M_w^* are calculated by summation over the weight- and the number-average molecular weights of the fractions, respectively.

This analysis has been applied to the fractionation data from PE-76. To avoid the tedious process of graphical differentiation, needed to extract the weight fraction distribution curve, whole sample molecular weight values were calculated directly from the weight- and number-average molecular weight data by the method suggested by Mussa.¹⁹ This involves summation of the area under the properly defined integral distribution curves by using the ordinate value of cumulative weight as the independent variable. In calculating M_n the distribution curves were extrapolated linearly from molecular weight 20,000 to an intercept of 5000. The exclusion of molecular weights below 5000 from the summation is consistent with the permeability of osmometer membranes to low molecular weight species.

The two sets of values obtained by this procedure are compared in Table V. The values of M_n and M_w obtained by graphical integration are close to those calculated by direct summation over the number- and weight-average molecular weight distribution curves listed in Table I. It is

TABLE V
Comparison of PE-76 Molecular Weights and Polydispersities Calculated from Fractionation Results

M_n	M_n^*	M_n^*/M_n
23,500	38,000	1.6
M_w	M_w^*	M_w/M_w^*
513,000	112,000	4.6

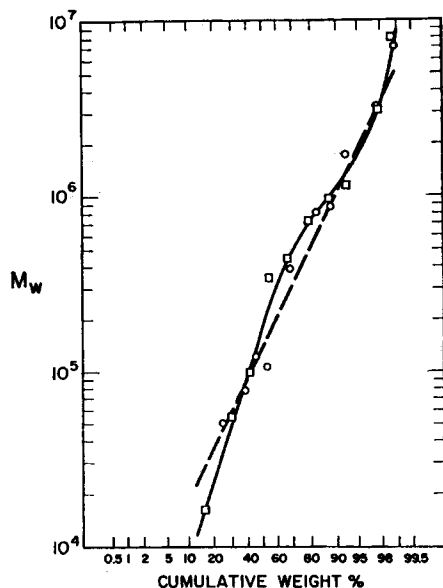


Fig. 9. Wesslau plot of M_w results for PE-76: (—) taken from integral distribution, Figure 2: (---) best straight-line fit to data points.

apparent that the M_w/M_w^* value is fully consistent with the polydispersity determined by absolute molecular weight methods on the fractions from the higher molecular weight portion of PE-76. Similarly, the value of M_n^*/M_n , which might appear low, in fact is consistent with the M_w/M_n values of the low molecular weight fractions, which make the dominant contribution to M_n . These comparisons illustrate the effect of fraction polydispersity in PE-76 fractions on the calculated average molecular weights and lend confidence to the similar analysis of other branched polyethylene fractionation data.

A comparison of the M_w values calculated from fractionation data with the results of light scattering on three branched polyethylene samples has been reported by Guillet and his co-workers.² The M_w^* values were calculated from fraction molecular weights determined from an $[\eta]-M_n$ relation. The ratio M_w/M_w^* was 2.5, 5.5, and 10.5 for the three samples and indicates an average fraction polydispersity in the higher molecular weight portions of the sample that is of like magnitude. Their results, however, are further complicated by two factors: first, the fractionation in all cases was somewhat inefficient in the high molecular weight region and, second, there is no assurance that the viscosity-number-average molecular weight relation used was applicable to the several samples, especially in the higher molecular weight region, which contributes strongly to the weight-average molecular weight, owing to possible differences in the extent of long-chain branching and the heterogeneity of fractions from different samples.

The distribution curves for a number of branched commercial polyethylenes have been reported by Berger and Langhammer.²⁰ Because of the variability of the results they found it necessary to determine the distribution curve by averaging over four or more repeated fractionations. In analyzing the fractionation data they followed the procedure used by Guillet and also arrived at M_w/M_n ratios that appear to be substantially lower than the commonly accepted range of values.⁴ No absolute molecular weight values for the whole samples were reported for comparison with the fractionation results.

In the interests of providing a comparison with other published results the fractionation data of PE-76 have also been fitted to several model distribution functions. In Figure 9 the M_w data are plotted on log probability paper as a test of the applicability of the Wesslau distribution.²¹

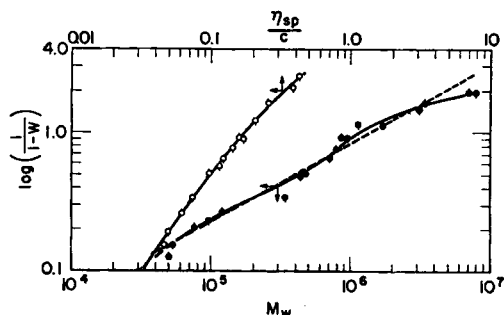


Fig. 10. Tung plot of results for PE-76: (O) viscosity data from two runs; (●) M_w data with full curve taken from integral distribution, Figure 2, and dashed curve best straight-line fit to data points.

Since the data do not conform to a straight line on these coordinates, the Wesslau distribution is not acceptable.¹¹ Nevertheless, the dashed straight line through the data leads to a value for M_w of 5×10^5 and for M_n of 0.352×10^5 . Both values are consistent with the results, obtained by graphical integration over the M_w distribution curve, that appear in Table V.

A test of the applicability of the log normal distribution proposed by Tung²² is shown by the log-log plot Figure 10. The viscosity data can be fitted by a line with continuous curvature or by two straight lines of somewhat different slopes, as shown, resembling certain of the data analyzed by Tung. The curvature in the plot of the M_w data is even more complex. However, the straight line through the data points leads to a value for M_w of 3.8×10^5 and for M_n of 0.4×10^5 , which again are not inconsistent with the values in Table V.

In Figure 11 is presented the comparison between the M_w and the two calculated Beasley distribution curves.²³ Curve 1 was calculated for $M_w = 3.0 \times 10^5$ and $M_n = 0.333 \times 10^5$, the cryoscopic molecular weight for PE-76, and curve 2 employed the same M_w but substituted $M_n = 0.266$

$\times 10^5$, corresponding to the osmotic-pressure molecular weight. As noted by others,²⁴ there are very large differences between the experimentally defined distribution and the theoretical distributions. The experimental curve is shifted to far higher molecular weights over most of the distribution, but the theoretical curves have a more pronounced high molecular weight tail. Owing to certain unrealistic assumptions in the theoretical treatment and to the non-uniformity of reactor conditions, differences between the experimental and the Beasley distributions are expected. However, the polydispersity of the fractions introduces a serious problem in reconstructing any distribution curve.

If the correct distribution were approximated, rather arbitrarily, as the curve drawn midway between the M_w and the M_n integral distribution

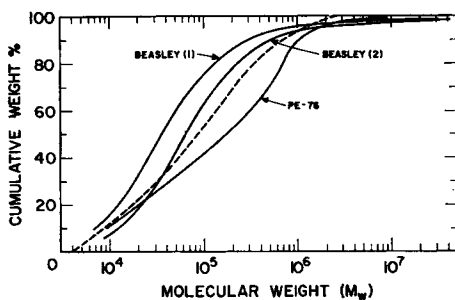


Fig. 11. Comparison of PE-76 M_w distribution with Beasley distribution: (1) calculated for $M_w = 3 \times 10^5$ and $M_n = 1.33 \times 10^4$; (2) calculated for $M_w = 3 \times 10^5$ and $M_n = 2.66 \times 10^4$; (---) drawn midway between M_w and M_n distribution curves of Figure 2.

curves of Figure 2, as represented in Figure 11 by the dashed line, the effect would be to decrease the calculated M_w value, as required for better agreement with the light-scattering value in Table I, and also to yield a somewhat improved fit to the Beasley distribution. This suggests that an analysis that properly takes into account the fraction polydispersity would lead to a significant change in the derived distribution curve, perhaps, with closer agreement to the Beasley distribution. However, the problem is complicated by the redistribution of species that has occurred due to the influence of branching on solubility. This rules out the use of any treatment of the fractionation data that is based on a Flory-Huggins type of partition function, such as Beale's method.²⁵ Perhaps a statistical method²⁶ that uses explicitly the weight- and number-average molecular weights of the fractions, such as the direct binomial method, would prove useful in reconstructing the molecular weight distribution. In addition it should be noted that the redistribution of branched species will affect any conclusions regarding the distribution of long-chain branching derived from results on the fractions as Guillet has done.²⁴ This problem will be considered further in another paper.

CONCLUSIONS

The various types of analysis that have been carried out on the high-pressure polyethylene fractions provide considerable insight into the factors controlling the solubility of branched polyethylene and also an evaluation of the separation that can be achieved by means of a solubility-based fractionation. It is clear that under properly chosen elution column conditions integral distribution curves are obtained that are free from any reversals or other abnormalities, whether based on viscosity results or absolute weight-average, or number-average, molecular weight values. Moreover, the whole-sample molecular weights calculated from the fractionation results are consistent with the directly measured values indicating that it is possible to obtain realistic molecular weight measurements from a very polydisperse high-pressure polyethylene sample and its fractions.

Although the wide range of molecular weights encompassed in the fractions suggests that the separation is comparable to that obtained with linear polyethylene, the combined M_w and M_n data show that the fractions are appreciably polydisperse. The M_w/M_n ratio increases from less than 1.5 in the early fractions to an almost constant value of 5 in the last 40% of the sample. In view of this polydispersity in molecular weight, the narrow distributions obtained when the fractions are submitted to refractionation on the elution column indicate that some factor in addition to molecular weight controls the polymer solubility. The explicit link between polymer solubility and long-chain branching is provided by the extremely narrow distribution of molecular sizes revealed by the GPC analyses which, further, lead to the deduction that long-chain branching increases polymer solubility. In sum, the results of this study indicate that long-chain branching plays a major role in determining the equilibrium polymer solubility. The results also provide a basis for reconciling the disparate observations on the polydispersity of branched polyethylene fractions made by Guillet and Schuurmans, as cited in the introduction to this paper, without resorting to the assumption that there were major differences in the amount of long-chain branching in the samples. However, the marked differences in polydispersity of elution column fractions reported in two recent studies of the GPC analysis of high-pressure polyethylene^{27,28} judging from the data presented, can probably be attributed to different levels of long-chain branching in the samples that were used.

The authors gratefully acknowledge the financial support of the National Science Foundation (Grant in Aid No. GP 2781), which has made this study possible. This paper also reports research undertaken in part at the U.S. Army Natick (Mass.) Laboratories.

The findings in this report are not to be construed as an official position of the Department of the Army.

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Received October 9, 1967

Revised November 29, 1967