

## Elution Column Fractionation of Branched Polyethylene

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### Synopsis

In a systematic study of the elution column fractionation of a well characterized branched polyethylene sample it was found that one of the most important factors contributing to the efficiency was the composition selected for the *p*-xylene-butyl cellosolve eluting mixture. With a mixture representing the critical solvent composition at 126°C., as determined by cloud point measurements, and deposition to an amorphous phase on a fine sand support, viscosity-distribution curves were obtained which were highly reproducible and completely free of any reversal. No further improvement was gained by using an elution temperature other than 126°C. or by the substitution of tetralin or mesitylene for *p*-xylene. Precipitation down a temperature gradient to produce a physical separation of species provided enhanced fractionation but is of doubtful practical interest. Fractionation was readily scaled up from 2 g. to 4 or 6 g., merely by increasing the mixing vessel size from 500 cc. to 1000 cc. There was no loss of efficiency, and fractions with  $\bar{M}_w = 8 \times 10^6$ , more than twentyfold higher than the sample value, were obtained despite eluted polymer concentrations exceeding 0.2%. There is evidence that many of the expected differences in the fractionation behavior of linear and branched polyethylene are erased when a solvent mixture is used which has been adjusted to the appropriate critical composition.

### INTRODUCTION

The fractionation of linear polyethylene samples by column elution methods is now routinely carried out on small samples for analytical purposes<sup>1-3</sup> or on the moderate scale required to supply fractions for molecular characterization.<sup>4,5</sup> In contrast, the fractionation of high-pressure polyethylene by column elution has met with only a limited degree of success. In one of the most extensive studies of the column fractionation of high pressure polyethylene, Guillet and his co-workers<sup>6</sup> achieved a substantial improvement in separation over that afforded by an earlier procedure. However, the resulting distribution curves were still abnormal in appearance, showing only partial resolution of the last 40% of two of the three samples investigated. Further, the whole sample weight-

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average molecular weights calculated from the fractionation data were only  $\frac{1}{10}$  to  $\frac{1}{4}$  the values determined on the original samples by light scattering. In work by Berger and Langhammer,<sup>7</sup> viscosity-distribution curves of more normal appearance were obtained for high-pressure polyethylenes, but these authors as well as others<sup>2</sup> have commented on the unusual difficulties in fractionating high-pressure polyethylene. In none of these studies were fractions of sufficient size obtained to permit the characterization of fraction polydispersity by absolute molecular weight methods. Guillet et al. and Slonaker et al. have inferred from the centrifugation patterns and refractionation data on fractions from both small-scale and large-scale runs that the fractions are quite sharp.<sup>6,8</sup> This conclusion, however, is not in agreement with the large  $\bar{M}_w/\bar{M}_n$  ratios determined by Schuurmans<sup>9</sup> on fractions obtained by standard two-stage fractional precipitation.

The difficulties experienced in the fractionation of high-pressure polyethylene are commonly attributed to the influence of long-chain branching on the solubility behavior. However, at present there is insufficient experimental evidence on the effect of long-chain branching to serve as a critical test of this conclusion. It is possible that the presence of short-chain branching as well as the enormous polydispersity of the samples,  $\bar{M}_w/\bar{M}_n = 20-50$ ,<sup>10</sup> also affect the solubility behavior and, in addition, contribute to the difficulty of selecting conditions which lead to the most efficient column fractionation. Further, the conditions required for the best fractionation of high-pressure polyethylene might very well differ from those established for linear polyethylene.

The foregoing considerations have motivated the present systematic examination of the effect of column operating variables on the fractionation of a well characterized high-pressure polyethylene sample. It was expected that a marked improvement in resolution could be achieved, possibly approaching the limits imposed by factors affecting the solubility behavior rather than the column performance. The detailed molecular characterization of fractions obtained under these optimal conditions might then reveal the extent to which long-chain branching or other identifiable properties of the sample affect the molecular weight separation. The current paper is concerned with experimental details of the fractionation studies which, in fact, lead to the improved fractionation of samples as large as 6 g. This is a sufficient quantity to allow a detailed analysis of the properties of the fractions, which will be the subject of a later paper.

## EXPERIMENTAL

### Samples

The study was carried out on two well characterized polyethylene samples<sup>10</sup> kindly provided by Dr. F. W. Billmeyer, then of the E. I. du Pont de Nemours Company. The linear polyethylene sample PE-85 was prepared by a low-pressure synthesis with a transition metal halide

TABLE I  
Properties of Polyethylene Samples

	PE-85	PE-76
Density, g./cc. <sup>a</sup>	0.955	0.922
CH <sub>2</sub> /100 C.	0.1	2.2
$\bar{M}_w \times 10^{-5}$ <sup>b</sup>	1.44	3.00
$\bar{M}_n \times 10^{-5}$ <sup>c</sup>	0.115	0.113
$[\eta]$ , dl./g. <sup>d</sup>	1.16	0.76
Melt index <sup>e</sup>	2.92	1.95

<sup>a</sup> Annealed 1 hr., 100°C.

<sup>b</sup> Light scattering, after optical clarification by high temperature ultracentrifugation.

<sup>c</sup> Cryoscopy; value determined by osmometry on PE-76,  $\bar{M}_n = 0.27 \times 10^5$ .

<sup>d</sup> Intrinsic viscosities measured in  $\alpha$ -chloronaphthalene at 125°C.

<sup>e</sup> ASTM D-1238-57T.

catalyst. The high-pressure sample PE-76 was a Fawcett-type polyethylene. Sample designations are those used in the reference cited. Table I summarizes the relevant properties of the two samples based on the published data as well as the additional information supplied with the samples.

### Column Packing

Graded Ottawa sands in two sizes were used, a coarse grain  $-40+200$  mesh and a fine grain  $-200+270$  mesh sand (American Graded Sand Co., Patterson, New Jersey). The sand was washed with water to remove fines and successively with saturated sodium tripolyphosphate, hydrochloric acid, and hydrogen peroxide to remove in turn clay, inorganic oxides, sulfides, and carbonates and to oxidize organic impurities. The sand was then dried at 150°C. for 12 hr. It was necessary to change the sand packing only once during the course of almost fifty runs.

### Solvents

The solvents were the highest graded commercially available and were used as received.

### Viscometry

Viscosity measurements were made at 105°C. on 0.1% *p*-xylene solutions of the fractions. Specially constructed Ubbelohde viscometers with large diameter capillary (ca. 0.5 mm.) were used to reduce the effect of any particle contamination. A flow time in excess of 120 sec. for solvent in the small volume instrument was obtained by the requisite increase in the length of the capillary which was wound in a spiral to minimize the increase in hydrostatic head. Solution filtration was accomplished in an oven at 105°C. by using Gelman Metriceal Alpha 6 (0.45  $\mu$ ) membrane filters. The system devised for the filtration of small solution volumes for viscometry employed a modified Millipore stainless steel microsyringe holder and is shown in Figure 1.

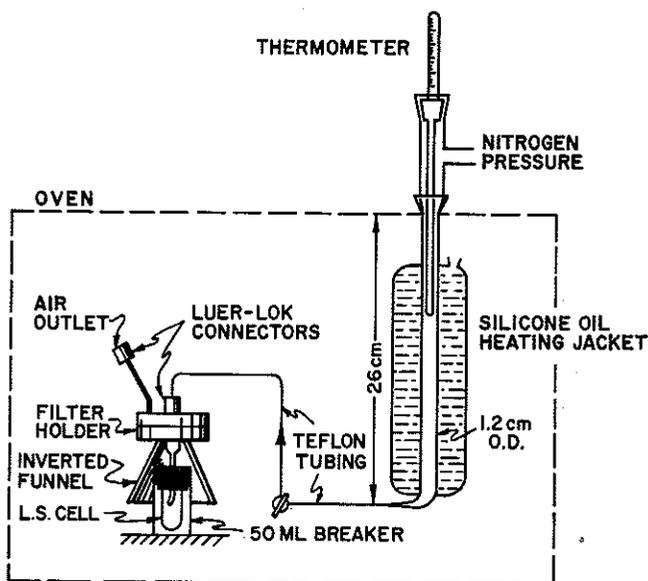


Fig. 1. Filtration system for clarification of solutions.

### Column Design

The column fractionation system shown in Figure 2 is based on that of Francis, Cooke, and Elliott<sup>1</sup> but incorporates a number of modifications, including those first introduced by Shyluk.<sup>11</sup> The sand packing is supported by a coarse porous glass frit, and the column is maintained at constant elution temperature by the reflux of a liquid in the jacket. To expedite heating of the column to the elution temperature it was wrapped uniformly with asbestos-covered Chromel A. In certain experiments a linear temperature gradient was required, and for this purpose the column was also wound with  $\frac{1}{2}$ -in. heating tape with the turns spaced more closely at the top than at the bottom. Finally, the column was blanketed with glass wool insulation.

A closed mixing vessel was used to produce a continuously enriched eluting solvent with a logarithmic increase in solvent concentration.<sup>12,13</sup> The eluting mixture was pumped upward through the column by using a Milton Roy Minipump which delivers an adjustable constant volume flow rate. Upward solvent flow was used to minimize air entrainment and channeling in the column and to counteract possible gravity flow of the swollen polymer gel. To minimize back mixing of the eluted polymer the space above the sand column up to the delivery arm was packed with glass wool. It was necessary to heat the 2 mm. I.D. capillary delivery tube leading to the fraction collector to a temperature  $5^{\circ}\text{C}$ . above the column temperature to prevent plugging. Connections between components of the system, including the return from the reflux condenser, were made with  $\frac{3}{8}$ -in. Teflon tubing and Swagelock connectors.

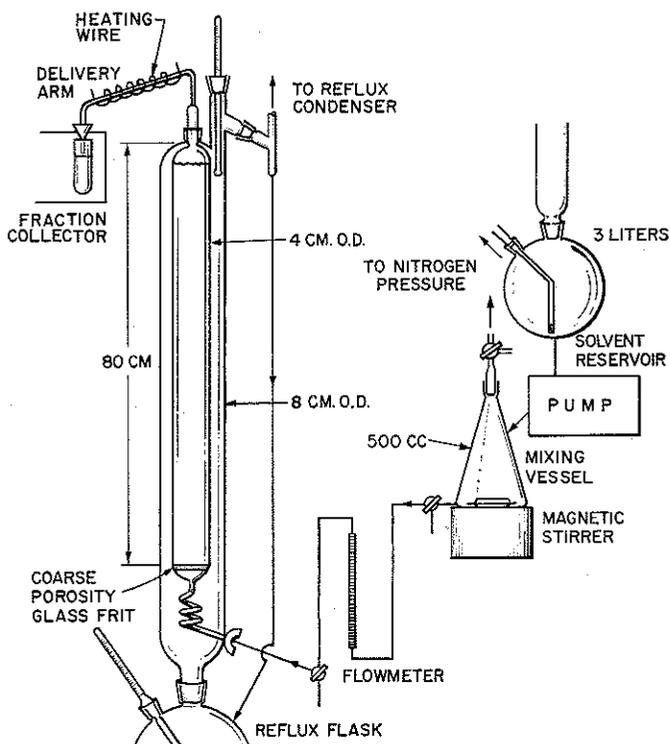


Fig. 2. Design of elution column.

### Column Operation

Since the runs were made under a large number of different operating conditions only the common aspects of the operational procedure are described here while specific details are elaborated in the appropriate later sections. In most runs a polyethylene sample of about 2 g. was dissolved in 300 ml. of solvent. The solution was introduced under  $N_2$  pressure to the solvent-filled column from a heated container which fitted into the ground glass top of the column with the delivery arm removed. Upon termination of the reflux in the heating jacket, the column cooled at a rate of about  $20^\circ C./hr.$  over the temperature range in which the polymer precipitates. After the solvent was removed, by pumping through 1200–1600 ml. of nitrogen-purged butyl cellosolve at room temperature, the column was reheated to the elution temperature (butyl acetate at  $126^\circ C.$ ). Elution was carried out starting with pure butyl cellosolve in the mixing vessel in all runs. At  $126^\circ C.$  this “nonsolvent” dissolves about 1% of PE-76.

In a number of experiments comparisons were made of the effect of changes in the nature of the solvent component in the eluting mixture contained in the reservoir. To establish equivalent conditions for these comparisons, as well as in runs made at different elution temperatures, the

concentration of the solvent component was adjusted to that which would just dissolve all of the polymer at the column operating temperature. The proper composition was determined by the visual observation of the cloud point of a 1% polyethylene solution in solvent-nonsolvent mixtures of varying concentration. For normal column operation at 126°C. the critical solvent composition for PE-76 was 47.5% *p*-xylene and 52.5% butyl cellosolve, and for PE-85 it was 52% *p*-xylene.

In all but a few runs the flow rate was 3.5 ml./min. With the 500 ml. mixing vessel, the polymer was completely eluted over a delivered volume of about 3 liters, and about 25–30 fractions of 105 ml. were collected. After precipitation with methanol the polymer was collected on pretared Schleicher and Schull #576 filter paper and dried to constant weight at 75°C. under vacuum. All solvents contained *N*-phenyl 2-naphthylamine as an antioxidant and were purged with nitrogen before use.

### Evaluation of the Fractionation Results

The integral distribution curves were constructed from the fractionation results by the common procedure of plotting the viscosity of a given fraction at the cumulative weight per cent (CW%) corresponding to the weight of all prior fractions plus one-half the weight of the particular fraction. In a set of exploratory runs improvements in the fractionation efficiency were judged in terms of any increase in the reduced specific viscosities in the more efficient runs and in terms of the reduction or elimination of any reversal in less efficient runs. For linear polyethylene this provides unambiguous evidence for improved molecular weight resolution. Although the viscosity of a high-pressure polyethylene fraction depends on the degree of branching as well as molecular weight, it was assumed that viscosity measurements would still provide a valid and sufficiently sensitive preliminary test of molecular weight separation.

## RESULTS AND DISCUSSION

### Disposition of Polyethylene in the Column

The importance of selective deposition in obtaining a preordering of species according to molecular weight on slow cooling of the polyethylene sample in the column is now generally recognized.<sup>2,11</sup> It is widely believed that polyethylene coats the sand particles in layers with the lowest molecular weight species concentrated in the outermost layers, thereby minimizing the effect of diffusional resistance in the extraction process. Despite the importance attached to selective deposition there are no reported observations of the actual state of the polymer in the column. At an early stage of the present work experiments were performed to learn the effect of different conditions on the disposition of the polyethylene following precipitation in the column as well as after reheating to the elution temperature.

The precipitation was carried out from polyethylene solutions at 0.7 and 1.7% concentration onto sand contained in Erlenmeyer flasks placed in an oven. The rate of temperature decrease of the oven was regulated to conform to the column cooling rate. To simulate conditions occurring just prior to elution the substrate-polymer mixture was carefully transferred to a coarse fritted funnel, washed free of solvent at room temperature with butyl cellosolve, then returned to the flask in butyl cellosolve and heated at 126°C. for a specified period of time before cooling to room temperature. The state of the polymer was observed with a Wild M20 polarizing microscope at 62.5 $\times$  and 250 $\times$ . Results of these observations are summarized without presenting any photographs.

When polyethylene, both linear and branched, is slowly precipitated from *p*-xylene at a temperature decrease of about 20°C./min. or less, it was observed that the sample deposits almost completely on the surface of sand if the sand has been thoroughly cleaned by the procedure cited. When viewed between crossed polaroids at room temperature the polyethylene crystallites are evident as minute birefringent regions concentrated on the surface of some sand grains and almost completely absent from others. The proportion of polymer deposited on the surface depends on a number of variables. If the sand is used as received most of the sample appears as larger irregularly shaped particles between the sand grains. Rapid cooling results in very little crystallization on the surface even of clean sand. When deposition is carried out to an amorphous phase from a solvent mixture in which precipitation occurs well above the melting temperature all the sample is deposited between the sand grains in rather large droplets in addition to a small amount of sheaflike particles.

On reheating the sample in butyl cellosolve at 126°C. the polymer in all cases detaches from the sand surface. After  $\frac{1}{2}$  hr. the polymer has the appearance of swollen filaments or film fragments still mostly attached to the sand. Heating for 1 hr. is sufficient for complete removal of the polymer and for coalescence to spherical droplets of varying size. With increasing incubation time the smallest droplets disappear, and a slow increase in the average droplet size occurs. Probably this coalescence would be accelerated under the flowing solvent conditions in the actual run. Attempts to improve the polymer-surface compatibility by treatment of the clean sand with chlorosilane or trichlorosilane only resulted in an increase in the amount of polymer deposited between the sand particles and did not offer any improved retention on reheating.

From this set of experiments it is evident that the state of the polymer under elution conditions is very different from that which is proposed in explanations of the improved fractionation gained by selective deposition. The present observations emphasize the importance of choosing conditions which limit droplet size, coalescence, and flow in the column. For example, it was noted that polymer droplets of substantially smaller size are produced when fine grain sand is used, -270+325, compared to -40+200 mesh, and this, as expected, enhanced the fractionation.

### Fractionation of Linear Polyethylene

A series of exploratory runs were conducted on the linear polyethylene sample to gain the necessary experience with the fractionation and analyses prior to a detailed study of the fractionation of the high pressure sample. Several of the variations in conditions are of interest since they differ from those that have been reported previously. A comparison of the effect of changes in the asymptotic composition, that is the composition of the solvent in the reservoir, is shown in Figure 3 for runs on 2-g. samples. At 48% *p*-xylene about 7% of the polymer sample was not eluted from the column, providing general confirmation of the limiting solvent composition of 52% *p*-xylene previously determined by cloud-point measurements at 126°C. The three filled circles below the horizontal cut-off line in Figure 3 represent data taken on fractions from this run. When the *p*-xylene concentration is increased to 52%, the fractionation is free of any reversals and final fractions in this run (open circles in Fig. 3) reach exceptionally high reduced specific viscosities ( $\eta_{sp}/c$ ). The maximum  $\eta_{sp}/c$  of 11.7 would correspond to a molecular weight<sup>3,5</sup> of about  $1.5 \times 10^6$ , some tenfold higher than the weight-average molecular weight of the sample. Further increasing the *p*-xylene concentration to 56.5% results in the distribution represented by the dashed curve. This curve is shifted toward higher  $\eta_{sp}/c$  values at a given CW% but suffers a reversal and lower final  $\eta_{sp}/c$  values. These adverse effects are probably due to the more rapid volume rate of change in solvent composition, especially over the critical region in which the highest molecular weight portion of the sample is eluted.

It was found that eluent flow rates of 5.0 and 7.0 ml./min. as well as

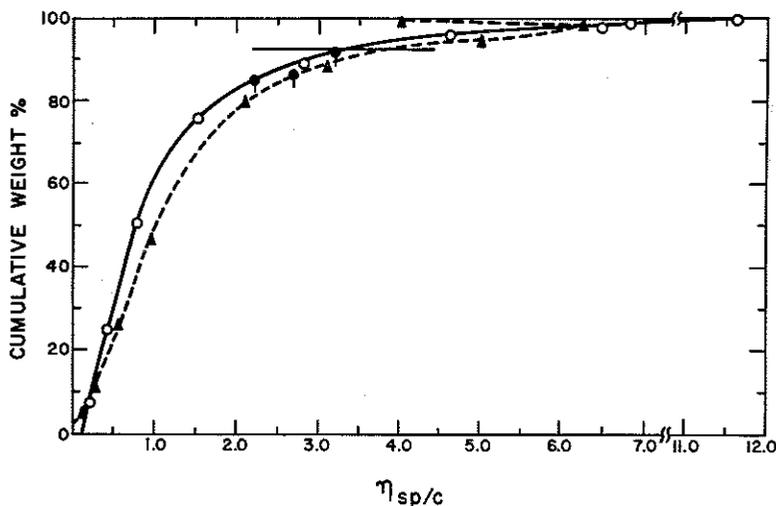


Fig. 3. Effect of asymptotic solvent composition on the fractionation of PE-85: (●) 2-g. sample, 48% *p*-xylene; (O) 2-g. sample, 52% *p*-xylene; (▲) 3-g. sample, 56.5% *p*-xylene; all with 500 cc. mixing vessel, 3.5 ml./min. flow rate.

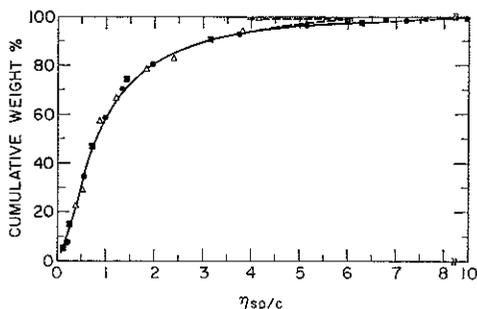


Fig. 4. Effect of flow rate and sample size on fractionation of PE-85: (●) 2-g. sample, 4.3 ml./min.; (■) 2-g. sample, 7.0 ml./min.; (Δ) 5-g. sample, 3.5 ml./min.; all with 500 cc. mixing vessel, 52% *p*-xylene asymptotic solvent composition.

the standard 3.5 ml./min. could be used on 2-g. samples without impairing resolution, as the comparison in Figure 4 shows. No further improvement in the runs on 2-g. samples was achieved by reducing the cooling rate during sample deposition from 20°C./hr. to 6–8°C./hr. or by precipitation of the sample to an amorphous phase from a tetralin–butyl cellosolve solution adjusted to the composition of incipient precipitation at 145°C.

By using the optimal conditions established for the fractionation of the 2-g. samples, it was possible to fractionate a 4-g. sample as well as a 5-g. sample with almost comparable resolution. A comparison of the results obtained in the fractionation of the 5-g. sample are shown in Figure 4. Although some molecular weight reversal occurs in this case, the data fall on the distribution curve defined by the more efficient 2-g. fractionations to a cumulative weight of over 90%.

Thus by using the critical asymptotic solvent composition it appears possible to fractionate moderate quantities of a linear polyethylene sample with little difficulty, and, as shown in Figure 4, to obtain a distribution curve which is highly reproducible under a variety of fractionation conditions. The maximum concentration of eluted polymer has been identified as one of the most important factors controlling the success of the fractionation.<sup>14–16</sup> It is, therefore, of interest to note that although the maximum eluted fraction concentration in this work was about 0.17% in the 2-g. runs and as high as 0.34% and 0.45% in the 4-g. and 5-g. sample runs, respectively, the resolution compares favorably with that reported by Kokle and Billmeyer<sup>3</sup> for column fractionations carried out at an eluted concentration of only 0.017% (see especially sample 84, which resembles closely in molecular weight and heterogeneity the sample used in the present work). This suggests that there is little to be gained by reducing the eluted fraction concentration to the extremely low values that are sometimes recommended.

#### Fractionation of High-Pressure Polyethylene

In the earliest set of runs on PE-76 the effect of the asymptotic solvent composition was studied at four *p*-xylene concentrations chosen to bracket

the 47.5% limiting *p*-xylene concentration determined by cloud-point measurements at 126°C. All runs were made on 2-g. samples precipitated to a crystalline phase from pure *p*-xylene at 20°C./hr. in a column filled with the coarse grain sand, and elution was carried out with a 500 cc. mixing vessel. The results of the several runs appear in Figure 5 (note that ordinate starts at 50 CW%). Although there is no reversal in the fractionation data obtained even at the highest *p*-xylene concentration, 52%, the resolution is evidently more limited than the results obtained at the two successively lower concentrations, 50.5% and 48.5% *p*-xylene. Apparently the best resolution is achieved at 48.5% *p*-xylene, which is 1% above the critical solvent concentration. Fractionation with 46.2% *p*-xylene, which is just below the critical concentration leads to some reversion in the viscosity of the final fractions. One run was also tried with a cooling rate of 6–8°C./hr. instead of 20°C./hr. but the fractionation results were no different from those of the prior run at 48.5% *p*-xylene.

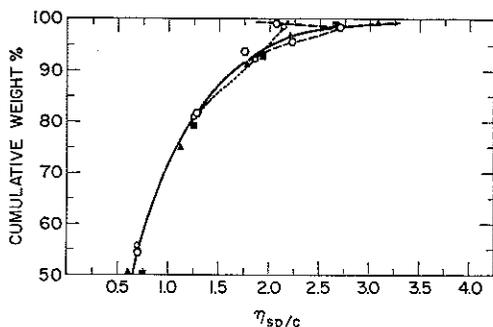


Fig. 5. Effect of asymptotic solvent composition on the fractionation of PE-76: (○) 52% *p*-xylene; (■) 50.5% *p*-xylene; (▲) 48.5% *p*-xylene; (○) 46.2% *p*-xylene; all with 2-g. sample, 500 cc. mixing vessel, 3.5 ml./min. flow rate.

This set of runs again emphasizes the effectiveness of using an asymptotic solvent composition very close to the critical value as observed in the work on the linear polyethylene sample, PE-85. Rather surprisingly, the maximum concentration of eluted polymer is about 0.17% in the run on PE-76 made at the preferred solvent composition. This is the same as the maximum concentration delivered under the optimal conditions for the fractionation of a 2-g. sample of linear polyethylene and, perhaps, suggests a similarity in the solubility behavior of both the linear and branched samples in the appropriately adjusted solvent.

The melting temperature of linear as well as the branched polyethylene lies well above the theta temperature in *p*-xylene. Therefore, precipitation on cooling of the solution occurs by crystallization. The enhanced fractionation of linear polyethylene under these conditions suggests that a partial sorting out of different molecular weight species occurs, either as a direct consequence of the molecular weight dependence of the melting temperature at low molecular weights<sup>17</sup> or indirectly through the possible

influence of molecular weight on the kinetics of crystallization.<sup>18,19</sup> There is no reason to expect that the fractionation of high-pressure polyethylene would benefit from the same mechanism. Since short chain branching affects the melting temperature and long-chain branching affects the solubility, it is possible that any separation achieved as a result of selective crystallization during deposition would interfere with the solubility based fractionation on elution.

These considerations suggested that further improvement in the fractionation might be gained by precipitation of PE-76 to an amorphous phase. As a test of this postulate precipitation was carried out from a 1.5% solution of the polymer in a tetralin-butyl cellosolve mixture (38:62, v/v). Precipitation to an amorphous phase from this solvent mixture begins somewhat below 145°C. and continues down to about 105°C. Although the same procedure failed to improve the fractionation of linear polyethylene, the results for PE-76 showed a marked increase in the viscosity of the final fraction,  $\eta_{sp}/c = 0.32$  as compared to  $\eta_{sp}/c = 0.24$  obtained with a sample precipitated to a crystalline phase. However, when fine grain sand was used as a column packing, there was a general improvement in resolution and there was no longer evidence for consistent superiority of fractionations based on deposition to an amorphous phase, at least with 2-g. samples. Nonetheless, precipitation to an amorphous phase was employed in examining the further variations of the small scale fractionation discussed next and later in scaling up the fractionation.

The column temperature of 126°C. has been established as the preferred elution temperature for linear polyethylene,<sup>1</sup> but no prior inquiry had been made as to whether this is best choice for high pressure polyethylene. Therefore, runs were carried out at three additional temperatures, 110, 119, and 130°C. in each case, the adjusted critical solvent composition determined by cloud-point measurements at the respective temperatures being used. The run at the lowest temperature resulted in a noticeable shift of the distribution curve to lower  $\eta_{sp}/c$  values for cumulative weights above 70% but the runs at 119 and 130°C. differed only marginally from the fractionation at 126°C. These results do not provide any justification for a change in the elution temperature.

Specific effects in the column fractionation of polymers with different solvents under otherwise identical conditions have been reported.<sup>16,20,21</sup> It has also been noted in the fractionation of branched poly(vinyl acetate) that the separation with one solvent mixture proceeded mainly on the basis of molecular weight while with another solvent mixture separation occurred mainly on the basis of long-chain branching.<sup>22</sup> Accordingly, a limited inquiry was made into the effect of substituting other solvents for *p*-xylene in the eluent mixture. Tetralin and mesitylene were chosen because their solubility parameters are close to *p*-xylene. Runs were made at the predetermined critical concentration, 41% tetralin and 47% mesitylene, as well as at concentrations higher in each case by 1.5%. Some of the results are summarized in Figure 6. Although no reversal occurred

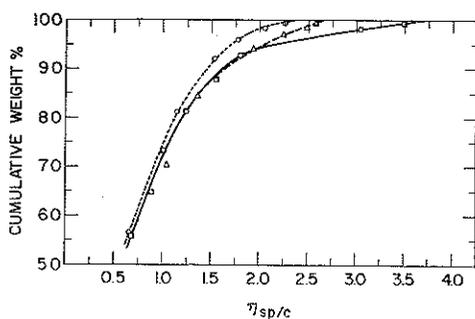


Fig. 6. Effect of different solvents on the fractionation of PE-76: (O) 42.5% tetralin; (□) 47.5% *p*-xylene; (Δ) 47.0% mesitylene; all with 2-g. sample, 500 cc. mixing vessel, 3.5 ml./min. flow rate.

in any of the several runs, it is evident that the resolution obtained with the substitution of either of these solvents for *p*-xylene is more limited.

In summary, it appears that the effective fractionation of 2-g. samples of the branched polyethylene, as judged by fraction viscosities, can be carried out by the use of an asymptotic solvent mixture adjusted to the critical composition. There is some evidence for the advantage of selective precipitation of the sample to an amorphous phase but otherwise the required conditions of fractionation are the same as those used for linear polyethylene.

### Scaling Up the Fractionation of High-Pressure Polyethylene

Fractionations were carried out under several different conditions, as summarized in Table II, on samples of 4–6 g., the minimum quantity required to supply fractions of adequate size for characterization by absolute molecular weight methods. Attempts were first made to fractionate 4-g. quantities of polymer under the same conditions successfully used with

TABLE II  
Fractionation Conditions for Larger-Scale PE-76 Runs<sup>a</sup>

Run	Sample, size, g.	Fraction volume, cc.	Mixing vessel, cc.	Max. concn., g./100 ml.	$\eta_{sp}/c_{max}$ , dl./g.	Reversal
1	4	105	500	0.27	0.25	Yes, minor
2	4	105	500	0.35	0.36	Yes, minor
3	4	175	1000	0.15	0.45	No
4	6	175	1000	0.22	0.43	No
5	6	60	1000	0.23	0.46	Yes, minor
6	4	175	500	0.29	0.33	No
7	6	175	500	0.27	0.19	} Incomplete resolution
8	10	170	1000	0.35	0.17	

<sup>a</sup> Asymptotic solvent composition, 47.5% *p*-xylene except run 1, 47.5% mesitylene. Flow rate 3.5 ml./min. except run 2, 2.0 ml./min. Precipitation to an amorphous phase runs 1–5; precipitation down temperature gradient, runs 6–8.

2-g. samples. With mesitylene as the solvent component in the eluent the results of the 4-g. run were identical with the earlier 2-g. run despite an increase in the maximum concentration of eluted polymer from 0.17% to 0.27%. When *p*-xylene was used as the solvent component and the flow rate reduced from 3.5 ml./min. to 2 ml./min. (run 2 in Table I and Fig. 7), resolution improved significantly over that obtained with mesitylene. Although in this case the maximum eluted polymer concentration increased to 0.35%, the highest fraction had a value of  $\eta_{sp}/c = 0.36$ , a substantial increase over the value obtained in mesitylene. In fact, the resolution and the distribution curve in this run are comparable to the most efficient 2-g. runs. However, there is evidence of some minor molecular weight reversal.

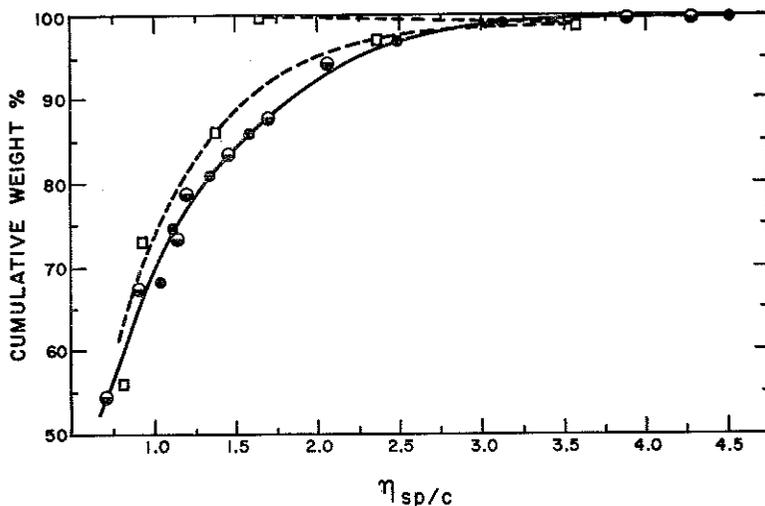


Fig. 7. Scaling up the fractionation of PE-76: (□) 4-g. sample, 500 cc. mixing vessel; (●) 4-g. sample, 1000 cc. mixing vessel; (⊖) 6-g. sample, 1000 cc. mixing vessel.

Increasing the mixing vessel from 500 to 1000 cc. doubles the volume of eluent for each incremental change in solvent concentration. Since this should effect a proportional reduction in the concentration of eluted polymer, further improvement in resolution is expected.<sup>15</sup> The results obtained with the use of a one liter mixing vessel and with conditions otherwise identical to those of run 2 are shown in Figure 7. The maximum concentration of eluted polymer has decreased to 0.15% (Table II), comparable to the concentration in 2-g. runs with a 500 cc. mixing vessel. The entire distribution curve (above 50 CW%) has been shifted to higher  $\eta_{sp}/c$  values, there is no reversal, and  $\eta_{sp}/c$  has increased to a maximum value of 4.5, exceeding the results of the best 2-g. runs. Under precisely the same conditions it was also possible to fractionate a 6-g. sample (run 4) with equivalent resolution. As Figure 7 shows, the distribution curve faithfully reproduces that obtained on the 4-g. run. No alteration in the

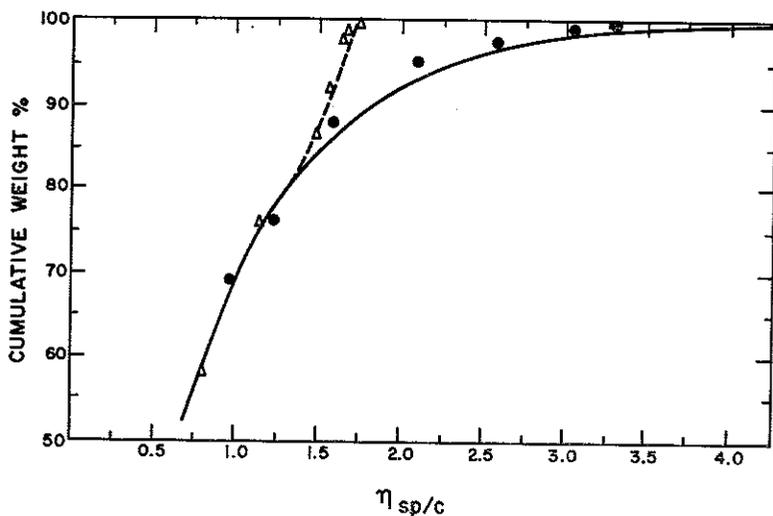


Fig. 8. Fractionation of PE-76 following deposition down a temperature gradient: (●) 4-g. sample, 500 cc. mixing vessel; (Δ) 10-g. sample, 1000-cc. mixing vessel; (—) run 3, Table II.

distribution curve resulted when the 6-g. run was repeated with a threefold reduction in the volume collected for each fraction (run 5).

It appeared that further improvement in efficiency might be realized by altering the method of sample deposition, since, as reported earlier, the polymer when precipitated to an amorphous phase is distributed almost entirely as free droplets between the sand grains and progressive droplet coalescence occurs after reheating and during the course of elution. As a modification of the conventional method of sample deposition several runs were made in which the polymer was precipitated down a temperature gradient similar to the approach first used by Krigbaum and Kurz.<sup>23</sup> A 1.5% solution of the polymer in a tetralin-butyl cellosolve mixture of near critical composition at 145°C. was introduced to the column at a flow rate of about 3.5 ml./min. Since the top of the column was held at 145°C. and the bottom at 105°C. the highest molecular weight species are precipitated near the top of the column with progressively lower molecular weight species precipitated further down the column in the cooler zones. The physical separation thereby imposed on the different molecular weight species should assist in preserving the fractionation occurring during deposition and should limit any remixing of species during the elution process.

Fractionation of a 4-g. sample by this procedure with the use of a 500 cc. mixing vessel (run 6) provided encouraging results when compared with run 2, even though the flow rate was almost twice as high. As shown in Figure 8, the data are free of any reversal, and the points fall close to the distribution curve obtained in the best 4- and 6-g. runs which is represented by the solid curve in the figure. In this run, precipitation down the temperature gradient appears to be almost equivalent in effect to doubling the

mixing vessel size. A further increase of the sample size to 6 g. with a 500 cc. mixing vessel (run 7) resulted in poor fractionation. A run on a 10-g. sample was also attempted with precipitation down a temperature gradient from a 2% solution and an increase in mixing vessel size to 1000 cc. The resolution of the last 20% of the sample, as shown in Figure 8, is rather poor. But it is interesting to note that there is no reversal, and further that the points below 80% CW fall on the distribution curve defined by efficient 4- and 6-g. fractionations.

Perhaps with further attention to details precipitation down a temperature gradient would render acceptable fractionation at a 10 g. level with a 1000 cc. mixing vessel. However, based on the performance with samples as large as 6 g., there is little doubt that a 10-g. sample could be fractionated in the present column by using the normal and more convenient procedure for sample deposition merely by increasing the mixing vessel size to 2000 cc.

A full examination of the quality of the fractionation in efficient 4-g. and 6-g. runs in terms of absolute molecular weights and other analytical methods will be provided in a second paper. However, it is useful to remark at this point that the weight-average and the number-average molecular weight integral distribution curves constructed from these results are also free of any molecular weight reversals, confirming the utility of viscosity data as a reliable test of the fractionation efficiency even for branched polyethylene. Further, the molecular weight results provide evidence of exceptional resolution since fraction weight-average molecular weight values as high as  $8 \times 10^6$  are obtained. Nonetheless, the fractions are found to be appreciably polydisperse. An explanation for this apparently conflicting behavior is developed in the second paper.<sup>24</sup>

## DISCUSSION AND CONCLUSIONS

The present work has shown that it is possible to fractionate a moderately branched high-pressure polyethylene sample in quantities up to 6 g. on a column no larger than that commonly used for samples of less than 2 g. With the proper selection of conditions, which includes the use of an eluent of near critical solvent composition, precipitation to an amorphous phase, and a fine grain sand support, it is possible to obtain fractionation which is free of any reversals in viscosity, even at the 6 g. level. The results are highly reproducible and there is evidence of an exceptionally high degree of molecular weight resolution.

These results imply that the distorted distribution curves obtained by Guillet<sup>6</sup> do not reflect an intrinsic feature of the molecular weight distribution in his samples but are more likely the consequence of somewhat inefficient fractionation. In addition, the claim that a linear solvent gradient or that a temperature gradient are required in the fractionation of high-pressure polyethylene is questionable in view of the success of the current work using a logarithmic solvent gradient and a uniform column temperature.

The results of this study also serve to emphasize the similarity in the conditions required for the efficient fractionation of the linear and branched

polyethylene samples. The most economical conditions, which involve a minimum total eluent volume, are obtained in both cases by the use of an eluent mixture which is close to the critical solvent composition for the particular polymer. In the most efficient fractionations, the maximum concentration of eluted polymer is the same for both the linear and branched polymer, suggesting a similarity in the solubility behavior. Further, the most favorable elution temperature is about 126°C. for both types of sample. This suggests that the adverse effects of much higher or lower elution temperatures are due to some aspect of the polymer-solvent interactions, perhaps the effect on swelling of the polymer, which is not particularly sensitive to the differences in polymer melting temperature, branching, or molecular weight in the adjusted solvents. These several examples give the impression that many of the expected differences in the fractionation behavior of the linear and branched samples have been erased by the simple expedient of adjusting the eluent mixture to the respective critical composition for each polymer sample.

In view of the broad similarity in the conditions required for the efficient fractionation of the branched and linear polyethylene excepting, perhaps, deposition to an amorphous phase, there is no reason why the several variations of the elution method devised for the large scale fractionation of linear polyethylene cannot be used with equal success for branched polyethylene. In particular, Henry's method of precipitating large quantities of linear polyethylene on a stirred suspension of Celite<sup>4</sup> has already been used with a branched polyethylene sample by Salovey and Hellman<sup>25</sup> with apparent success.

The information concerning the state of the polymer in the column during elution provides a basis for understanding certain general problems encountered in column fractionation. If it is common for all polymers to detach from the support during elution, then it is easier to understand the unusual difficulty in fractionating the highest molecular weight portion of the sample. Although the amount of polymer remaining at this stage is small the polymer is highly swollen and the droplets readily undergo flow and coalescence. Further, if the polymer is present in droplet form or otherwise detached from the support, it is not surprising that excessively slow flow rates might lead to poorer resolution, as observed by Guillet<sup>6</sup> as well as in the present work, or that under certain conditions the polymer undergoes bulk flow in the column.<sup>16</sup> It is also clear that a finely divided support offers the twofold advantage of reducing the size of the droplets formed on release of polymer from the support and in restricting droplet coalescence and mobility. On the other hand, the present information on the state of the polymer in the column adds to the difficulty in accounting for the effectiveness of selective deposition. It almost appears that the main result is to produce a finely divided polyethylene sample, resembling the approach favored by Sreaton,<sup>26</sup> although the benefit of slow cooling argues for some useful contribution from prefractionation.

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