

## Fractionation of Linear Polyethylene with Gel Permeation Chromatography. IV

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### Synopsis

Reproducibility was examined on the GPC fractionation of linear polyethylenes. The experiences over the period of two and a half years were used. Calibration was done with the same batches of narrow distribution polystyrene standards. A control sample of broad-distribution polyethylene was run at each calibration. The reproducibility over ten calibrations with this control was in terms of standard deviation of ca.  $\pm 10\%$  for the number-average and ca.  $\pm 15\%$  for the weight-average chain length. The fractionation data of 36 commercial resins were corrected by using the control sample as an additional standard. The correction was very effective in decreasing the scattering of the data in the intrinsic viscosity-molecular weight plot, especially when the viscosity average was used for the molecular weight expression.

### INTRODUCTION

In the previous papers of this series,<sup>1-3</sup> two key questions, i.e., calibration and resolution, of gel permeation chromatography (GPC) were discussed. Also, examples of fractionation curves were presented to show that GPC could reveal interesting details of molecular weight distribution (MWD). The emphasis of these works was the examination of GPC as an operational tool for the characterization of linear polyethylenes.

The present work is a review of our experience over the past two and a half years. The nature of the operation has been the characterization of selected samples rather than the quality control for the production. The calibration and reproducibility of the data are the primary interests of this review. Thirty-six samples from different manufacturing processes have been treated.

### RESULTS

#### Reproducibility Examined by Use of a Control Sample

The calibration for our operation was done with the same batches of the narrow MWD polystyrene. It was performed whenever about a dozen samples were run consecutively within two to three days. Among these samples, a control sample<sup>2,3</sup> was always included. The control sample had a melt index<sup>4</sup> of 0.4 and a broad MWD; the ratio of weight-

TABLE I  
 Reproducibility of GPC with Control Sample—Cumulative Fractions

Calib. no.	Date	Sample concn., g/100 ml	Weight fractions at polystyrene equivalent molecular length $A_i$									
			117 Å	480 Å	1,220 Å	4,000 Å	9,800 Å	20,200 Å	48,000 Å			
1	6-67	0.25	—	0.19	0.36	0.635	0.81	0.885	0.950			
2	10-67	0.25	0.03	0.15	0.325	0.63	0.795	0.885	0.947			
3	5-68	0.5	0.045	0.185	0.38	0.635	0.81	0.897	0.953			
4	7-68	0.5	0.043	0.165	0.355	0.61	0.80	0.885	0.943			
5	1-69	0.5	0.040	0.17	0.345	0.595	0.795	0.875	0.943			
6	5-69	0.5	0.036	0.16	0.31	0.58	0.755	0.855	0.928			
7	8-69	0.5	0.053	0.19	0.38	0.65	0.82	0.897	0.955			
8	6-69	0.5	0.034	0.185	0.38	0.625	0.82	0.903	0.973			
9	11-69	0.5	0.042	0.17	0.38	0.67	0.80	0.895	0.965			
10	12-69	0.5	0.045	0.175	0.37	0.67	0.83	0.905	0.960			

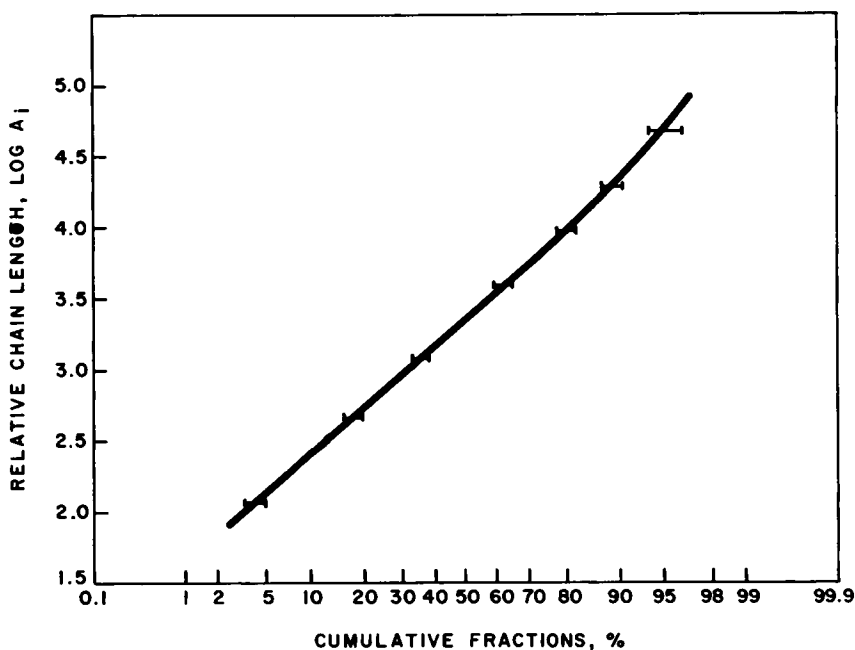


Fig. 1. Reproducibility of 10 GPC runs with 10 different calibrations.

average to number-average molecular weight,  $\bar{M}_w/\bar{M}_n$ , was about 14. Its molecular weights ranged from ca. 500 to above 2 million; the highest molecular weight fraction was suspected to reach 3 to 4 million. This molecular weight range was quite adequate as a control for the present study.

The operating conditions are those defined previously,<sup>2</sup> except for the sample concentration being 0.25 or 0.50 g/100 ml. The effect of the concentration has not been detected within the experimental error. Solvent was 1,2,4-trichlorobenzene; four columns of nominal capacities of  $10^3$ ,  $10^5$ ,  $3 \times 10^6$ , and  $7 \times 10^6$  Å were used.

In Table I, the results of ten repeated runs of the control are shown; each run was performed at a different time with each independent calibration. The cumulative fractions are shown at the counts corresponding to the polystyrene molecular length indicated. The average values and their standard deviations are shown in Figure 1. From this figure, the standard deviations in molecular weights at given cumulative fractions can be estimated. They are approximately  $\pm 15\%$  at 4 cumulative per cent and  $\pm 27\%$  at 95 cumulative per cent. Between these extremes, the standard deviations are approximately  $\pm 5\%$  to  $\pm 13\%$ .

The same results are presented in Table II in terms of the average molecular lengths and their ratios. The standard deviation for  $\bar{A}_n$  is about  $\pm 10\%$ , and for  $\bar{A}_w$  about  $\pm 15\%$ . The deviations increase more and more for the higher average molecular weights. This fact shows

TABLE II  
 Reproducibility of GPC with Control Sample—Average Molecular Length

Calib. no.	Date	Sample concn., g/100 ml	Equivalents to polystyrene molecular length, Å									
			$\bar{A}_n \times 10^{-2}$	$\bar{A}_v \times 10^{-3}$	$\bar{A}_w \times 10^{-3}$	$\bar{A}_z \times 10^{-4}$	$(\bar{A}_{z+1}) \times 10^{-5}$	$\bar{A}_w/\bar{A}_n$	$\bar{A}_z/\bar{A}_w$	$(\bar{A}_z + 1)/\bar{A}_z$		
1	6-67	0.25	7.67	6.38	9.73	5.94	1.06	12.7	6.1	1.79		
2	10-67	0.25	8.06	6.50	9.80	5.79	1.04	12.2	5.9	1.80		
3	5-68	0.5	7.00	5.58	10.06	6.12	1.04	14.4	6.08	1.71		
4	7-68	0.5	6.31	6.55	10.16	6.47	1.16	16.1	6.36	1.80		
5	1-69	0.5	7.46	6.87	10.35	5.67	0.97	13.9	5.48	1.71		
6	5-69	0.5	6.42	7.80	11.75	6.34	1.08	18.3	5.40	1.71		
7	8-69	0.5	6.94	5.59	8.42	4.80	0.842	12.1	5.70	1.75		
8	6-69	0.5	7.08	4.89	7.08	3.47	0.607	10.0	4.90	1.75		
9	11-69	0.5	7.13	5.36	7.81	3.77	0.643	11.0	4.83	1.70		
10	12-69	0.5	5.53	5.37	8.28	5.48	1.03	15.0	6.62	1.87		
Average			6.96	6.09	9.34	5.39	0.95	13.6	5.74	1.76		
Standard deviation, %			±9.9	±13.7	±14.5	±18.3	±40.4	±17.4	±11.0	±3.0		

the difficulty in reproducing the fractionation at the high molecular weight tail. The deviation for the ratio of molecular weights is about 17% for  $\bar{A}_w/\bar{A}_n$ ; it decreases for the ratios of the higher averages. However, because the calibration standard is not available at the high molecular weight region,  $\bar{A}_z$  and  $\bar{A}_{z+1}$  are very arbitrary values.<sup>3</sup> Therefore, no further discussion is given on these higher averages in this paper. The values of  $\bar{A}_n$  and  $\bar{A}_w$  will be calibrated with the aid of methods other than GPC.

### Calibration with the Control Sample

In the preceding section, it was shown that the calibration based on the polystyrene standards is not adequate to reproduce the MWD data of the control. In this section, a method is explored to use the control sample as a supplementary standard. A rather simple and expedient method is presented stepwise, and a more basic approach will be discussed later.

#### MWD of the Control Sample

The fractionation data of the control by calibration no. 3 was selected as a reference. The selection was made because the same conversion factor of 17.5 could be applied to both  $\bar{A}_w$  and  $\bar{A}_n$  in calculating  $\bar{M}_w$  and  $\bar{M}_n$ , as shown in Table III. The value of  $\bar{M}_w$  was calculated from the

TABLE III  
MWD Data of Control by Calibration No. 3 and Conversion  
to Absolute Molecular Weights

$\bar{A}_n$	Conversion factor	$\bar{M}_n$	
		GPC	Infrared spectroscopy
700	17.5	12,250	12,300
$\bar{A}_w$	Conversion factor	$\bar{M}_w$	
		GPC	Melt rheology
10,060	17.5	176,000	177,000

Newtonian viscosity,  $\eta_0$ , at 190°C of  $6.9 \times 10^5$  poises. The following equation<sup>5</sup> was used for the conversion:

$$\log \eta_0 = -12 + 3.4 \log \bar{M}_w. \quad (1)$$

The value of  $\bar{M}_n$  was based on endgroup analysis, the terminal unsaturation by infrared spectroscopy.

#### Correction of Fractionation Data

Now that  $\bar{A}_w$  and  $\bar{A}_n$  by calibration no. 3 can be converted to  $\bar{M}_w$  and  $\bar{M}_n$  by the factor 17.5,  $\bar{A}_w$  and  $\bar{A}_n$  by another calibration can also be converted to  $\bar{M}_w$  and  $\bar{M}_n$ :

$$17.5(\mathfrak{F}_w)_I(\bar{A}_w)_I = 17.5(\bar{A}_w)_3 = \bar{M}_w$$

$$17.5(\mathfrak{F}_n)_I(\bar{A}_n)_I = 17.5(\bar{A}_n)_3 = \bar{M}_n$$

where  $\mathfrak{F}_w$  and  $\mathfrak{F}_n$  are correction factors for the respective averages, and the subscript I refers to a specific calibration. The values of  $(\mathfrak{F}_w)_I$  were evaluated from the data in Table II. Then, assuming that these factors were applicable to  $\bar{A}_w$  of other samples, the corrected  $\bar{A}_w$  was obtained for 36 samples. For these samples either one of the ten calibrations given in Table II had originally been used. All ten calibrations were used, but no sample was repeatedly run with different calibrations. The samples included both injection and extrusion grades of resins, covering a melt index<sup>4</sup> range of ca. 0.1 to 20. Some of the samples had either ethyl or butyl branches in amounts less than three branches per 1000 carbon atoms. Also, some samples were suspected of having long branches in an amount less than one branch per ten molecules. If long

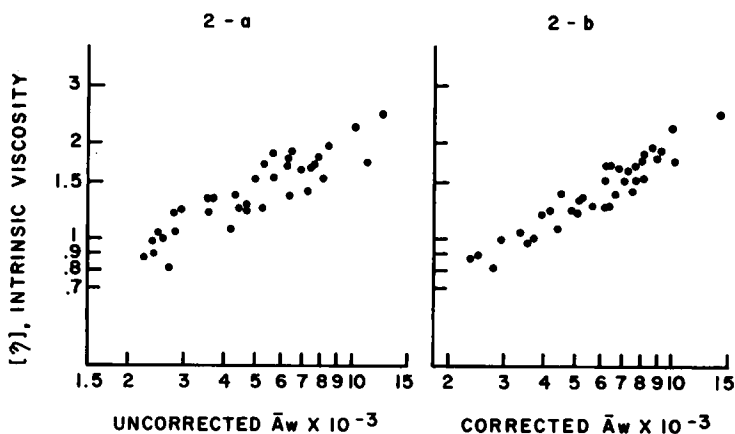


Fig. 2. Relationship between intrinsic viscosity in tetrahydronaphthalene at 130°C and weight-average chain length of GPC.

branches were present, the  $\bar{A}_w$  was the hydrodynamically equivalent value to that of the linear molecule. Also, the samples consisted of the products of five different processes. In Figure 2, the intrinsic viscosity is plotted against  $\bar{A}_w$  for these 36 samples. The uncorrected  $\bar{A}_w$  is used for Figure 2a and the corrected one, for Figure 2b. The intrinsic viscosity was measured at 130°C in tetrahydronaphthalene. Neither branching nor different manufacturing process could systematically account for the spread of the data. At a constant intrinsic viscosity, the largest spread in the log  $\bar{A}_w$  axis is  $\pm 30\%$  of  $\bar{A}_w$  for Figure 2a and  $\pm 25\%$  for Figure 2b. It appears that the present method of correcting  $\bar{A}_w$  is effective in improving the precision of the data. However, even after the correction, there is  $\leq \pm 25\%$  of spread in  $\bar{A}_w$ ; the cause must be examined further.

## Effect of Polydispersity in Mark-Houwink's Equation

### *Relationship Between Intrinsic Viscosity and Weight-Average Molecular Weight*

The data of Figure 2b were replotted in Figure 3 with appropriate markings each corresponding to the narrow, medium, and broad distribution samples. The three categories in polydispersity were somewhat arbitrarily defined as follows:

*Polydispersity Expressed as  $\bar{A}_w/\bar{A}_n$*

*Narrow:* 2.95 – <5.5

*Medium:* 5.5 – 8.5

*Broad:* >8.5 – 27.9

Within a given group of polydispersity, the data points of Figure 3 are randomly distributed. Therefore, further breakdown in polydispersity is meaningless. Also, in Figure 3 two relationships are shown by the lines; the upper line is for fractional samples,<sup>6</sup>

$$[\eta] = 3.9 \times 10^{-4} \bar{M}_w^{0.74} \text{dl/g}, \quad (2)$$

in decahydronaphthalene at 135°C. The lower line is for unfractionated samples,<sup>6</sup>

$$[\eta] = 2.55 \times 10^{-4} \bar{M}_w^{0.74} \text{dl/g}, \quad (3)$$

in the same solvent at the same temperature.

The intrinsic viscosity in decahydronaphthalene at 135°C was converted to that in tetrahydronaphthalene at 130°C by the factor 1.16 given by Tung.<sup>6,7</sup> The  $\bar{M}_w$  and the coefficients of eqs. (2) and (3) were converted by the previously mentioned factor, 17.5, to derive the corresponding equations for  $\bar{A}_w$ .

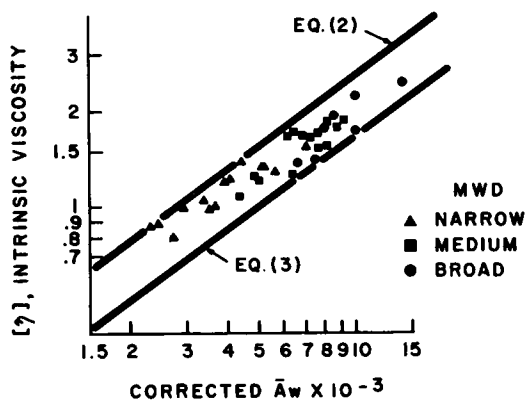


Fig. 3. Effect of polydispersity on relationship between intrinsic viscosity and weight-average chain length.

The trend in Figure 3 is that the points belonging to the broad-distribution samples lie in the higher molecular weight region and that the points for the narrow-distribution samples are in the lower molecular weight region. The points for the medium polydispersity samples are seen between. Unfortunately, as they are, no clear trend may be seen on the effect of polydispersity.

However, if we are guided by the relationships of eqs. (2) and (3), it appears that the points for the narrow distributions are closer to the upper line, those for the broad distributions are closer to the lower line, and those for the medium distributions lie between. If we assume the exponent of Mark-Houwink's equation to be 0.74 and independent of the polydispersity,

$$[\eta] = K\bar{A}_w^{0.74}, \quad (4)$$

the coefficient  $K$  may be related to  $\bar{A}_w/\bar{A}_n$ . Unfortunately, the data presented here are not sufficient to derive such a relationship. The reasons are that (1) the molecular weight range is not wide enough, and (2) there is too much scattering of data within a given polydispersity. Visual inspection of Figure 3 gives the spread of the data within a given polydispersity as  $\leq \pm 18\%$ .

*Relationship Between Intrinsic Viscosity and  
Viscosity-Average Molecular Weight*

The effect of the polydispersity on Mark-Houwink's equation observed in the previous section may be eliminated if the viscosity-average molecular weight is used instead of the weight-average molecular weight. The viscosity average is defined in terms of the relative chain length,  $\bar{A}_v$ , as

$$\bar{A}_v = \left[ \int A_i^\alpha \left( \frac{dW_i}{dA_i} \right) dA_i \right]^{1/\alpha} \quad (5)$$

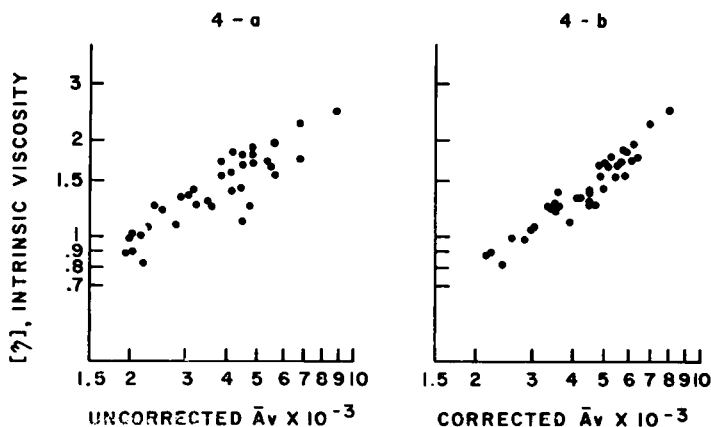


Fig. 4. Relationship between intrinsic viscosity and viscosity-average chain length.



where  $\alpha$  is the exponent of Mark-Houwink's equation for monodispersed polymers, and  $W_i$  is the weight fraction of polymer having a polystyrene equivalent of molecular length  $A_i$ . In Figure 4, the plots of  $[\eta]$  versus  $\bar{A}_v$  are shown, where Figure 4a has the uncorrected  $\bar{A}_v$  and Figure 4b, the corrected  $\bar{A}_v$ . The correction for  $\bar{A}_v$  is made in the same manner as that for  $\bar{A}_w$ ; that is,  $\bar{A}_v$  of the control in calibration no. 3 was used as a reference. The method of the correction is seen to be quite effective in decreasing the amount of the scatter in the plot. The spread of the plot of Figure 4b is not related to other molecular variables such as small amounts of branching. Therefore, it may be interpreted as a measure of the reproducibility of GPC. The largest spread is about  $\pm 16\%$ .

The exponent,  $\alpha$ , of eq. (5) for this work was 0.67. Although the exact value of  $\alpha$  is not yet known, perhaps larger value, e.g., 0.74, should have been used, eqs. (2) and (3).

### Reproducibility Within One Calibration

A correction method for improving the reproducibility was demonstrated in the preceding sections. After the correction, there still seems to be an error of  $< \pm 16\%$  for  $\bar{A}_v$ . Therefore, the reproducibility within one calibration and within several days of operation was investigated. Table IV shows the results. Calibration no. 3 and the control sample were used.

The reproducibilities of  $\bar{A}_n$  and  $\bar{A}_w$  were shown to fall within ca.  $\pm 10\%$  of their values; that for  $\bar{A}_v$  was within  $\pm 15\%$ . The reproducibilities expressed as the standard deviation were comparable to the values reported by the National Bureau of Standards<sup>8</sup> for a resin having a melt index of 2. The data of run no. 6 (Table IV) were those previously selected as reference. The values of  $\bar{A}_n$  and  $\bar{A}_w$  of this run are very similar to the average values shown in the table.

TABLE IV  
Reproducibility Within One Calibration

Run no.	Day	Sample concn., g/100 ml	$\bar{A}_n \times 10^{-2}$	$\bar{A}_v \times 10^{-3}$	$\bar{A}_w \times 10^{-3}$	$\bar{A}_w/\bar{A}_n$
1	1st	0.25	6.31	5.59	9.89	15.7
2	1st	0.50	6.34	6.10	11.10	17.5
3	2nd	0.25	7.41	6.75	10.73	14.5
4	2nd	0.25	7.37	6.03	9.41	12.8
5	2nd	0.50	6.98	5.14	8.92	12.8
6	2nd	0.50	7.00	5.58	10.06	14.4
7	5th	0.50	7.10	6.16	9.81	13.8
Average			6.93	5.91	9.99	14.5
Range of error $\pm\%$			$< \pm 9.0$	$< \pm 14.2$	$< \pm 11.1$	$< \pm 20.6$
Standard deviation, %			$\pm 6.0$	$\pm 8.3$	$\pm 4.1$	$\pm 10.7$
NBS data on standard deviation <sup>8</sup>			6.6	—	3.7	—

## DISCUSSION

### Reproducibility

Reproducibility of GPC was examined by using the same sample of polyethylene as a control. Calibration was done with the same batches of polystyrene standards. The standard deviation of  $\bar{A}_n$  and  $\bar{A}_w$  for ten runs with corresponding ten calibrations were ca.  $\pm 10\%$  and  $\pm 15\%$ , respectively (Table II). This result was obtained over a period of two and half years. Within five days and with one calibration, the standard deviations for seven runs were  $\pm 6.0\%$  for  $\bar{A}_n$  and  $\pm 4.1\%$  for  $\bar{A}_w$  (Table IV). Even within one day, similar deviations were found in four repeated runs. A major cause of the deviations must lie in the GPC operation rather than in the uniformity of the control resin, because the melt rheology data were very reproducible.

The GPC results at one calibration must be made comparable to those at another calibration. The correction factors for the average molecular weights were derived by using the control as a supplementary standard. One specific run at one calibration was selected as a reference. The application of the correction factors to the results of the other 36 resins appears to improve reproducibility. However, the results with these 36 resins were all single determinations. With some of these resins, the runs should have been repeated at different calibrations and then corrected against the control.

By using the correction method, the scatter of the data in the Mark-Houwink plot was significantly decreased. With the larger number of point extended over the lower and the higher molecular weight ranges than shown here, the exponent of the equation may be determined precisely. This can be done by proper selection of the value for the exponent to give a minimum scattering of the points in the  $[\eta]$ -versus- $\bar{M}_v$  plot. Also, the degree of polydispersity may be incorporated into the  $[\eta]$ - $\bar{M}_w$  relationship.

The scatter of the data in the above relationship may arise from an error in reproducibility within a given calibration. If so, the magnitude of deviation may be compared to the data in Table IV. The range of the error in  $\bar{A}_v$  estimated from Figure 3b is  $< \pm 16\%$ , which is similar to  $< \pm 14\%$  shown in Table IV. On the other hand, the range of the error in  $\bar{A}_w$  estimated from Figure 4 is  $< \pm 18\%$ , which is about twice that shown in Table IV,  $< \pm 11\%$ . These comparisons are not intended to be exact, however. The former results from a single determination with many samples, whereas the latter stems from repeated runs with the same sample.

### Suggested Operating Procedure

Narrow-distribution polystyrene standards are commonly used for calibration. Narrow-distribution polyethylenes are also used. The use of such standards has some drawbacks in that the high molecular weight

standards are very difficult to obtain. This limits the range of the calibration and introduces uncertainty in the values of  $\bar{M}_w$  and the higher average molecular weights.<sup>3</sup> Instead, it is suggested here to use a broad-distribution polyethylene as a standard. Molecular weight distribution of such a standard should encompass the entire range of practical interest. MWD of the standard should be predetermined with the aid of independent methods other than GPC. A cumulative expression of MWD is to be prepared. Whenever necessary, the GPC can be calibrated by running this standard and plotting the cumulative fractions against the counts. Comparison of this plot with the cumulative MWD plot enables one to prepare the curve of molecular weights versus counts. This calibration curve is continuous and superior to the one consisting of the limited number of points corresponding to narrow MWD standards. Even with the improved calibration method, the errors of a single GPC run may be as much as  $\pm 18\%$  in  $\bar{M}_w$ . Repeated runs and averaging the values are necessary to reduce the errors further.

The computer program used in converting the GPC trace to MWD information is the one by Pickett, Cantow, and Johnson.<sup>9</sup> The author is grateful to Chevron Research Company for making this program available to us. He is indebted to R. D. Hoffman and R. T. Guliana for the intrinsic viscosity determinations and the compilation of the data. Table I and Figure 1 were contributed by R. D. Hoffman (present address: Applied Research Laboratories, U.S. Steel Corporation, 125 Jamison Lane, Monroeville, Pennsylvania 15146).

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