

Fractionation of Linear Polyethylene with Gel Permeation Chromatography. Narrow Molecular Weight-Distribution Samples

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Synopsis

Four samples of narrow molecular weight-distribution polyethylene were fractionated with gel permeation chromatography (GPC). The polyethylenes had been prepared by hydrogenating linear polybutadienes (products of Phillips Petroleum Company). The values of molecular weights were furnished by the supplier of the samples. They were measured by absolute methods, i.e., light scattering and osmometry. The polydispersities of these polymers by GPC were found to be narrower than those by the absolute methods, when the polydispersity was expressed in the polystyrene equivalent of chain length. Recalculation on the basis of polyethylene standards did not increase the values of polydispersity. Continuous calibration curves were constructed by using a very broad-distribution polyethylene. The use of these calibration curves gave the polydispersity values in good agreement with those obtained by the absolute methods.

INTRODUCTION

In the previous papers on this subject,¹⁻⁵ application of gel permeation chromatography (GPC) to commercial polyethylenes was reported. The calibration problems and the reproducibility of the results had been extensively examined. The present work concerns GPC fractionation of narrow molecular weight-distribution (MWD) samples. They were prepared by hydrogenating polybutadienes (HPBD) (Phillips Petroleum Company).

EXPERIMENTAL

Samples

Four samples of HPBD were used. The sample designations and the molecular weights are listed in Table I.

The values of \bar{M}_n are in good agreement between two independent measurements. This provides approximate measure in the extent of error involved in values of \bar{M}_w/\bar{M}_n , although \bar{M}_w measurements were not duplicated.

TABLE I
Narrow Molecular Weight-Distribution Polyethylenes (HPBD)

Sample	$\bar{M}_w \times 10^{-4a}$	$\bar{M}_n \times 10^{-4a}$	\bar{M}_w/\bar{M}_n^a	$\bar{M}_n \times 10^{-4b}$	\bar{M}_w/\bar{M}_n^c
16 MH	1.64	1.41	1.16	1.42	1.14
108 MH	10.80	8.20	1.32	8.60	1.26
194 MH	19.40	12.60	1.54	13.00	1.49
420 MH	42.00	15.80	2.66	14.00	3.00

^a Data provided by Phillips Petroleum Company.

^b Data by osmometry.

^c \bar{M}_w by Phillips Petroleum Company and \bar{M}_n of this work.

GPC Operation

The operating conditions were the same as before.² The sample concentration was 0.25%. Solvent was 1,2,4-trichlorobenzene; temperature was 137°C; injection time was 120 sec, and the flow rate was 1 cc per minute. Four columns with polystyrene gels having nominal capacity of 7×10^6 , 3×10^6 , 10^6 , and 10^8 ångströms were used.

The runs were duplicated four months apart. At each time, polystyrene standards were run to establish calibrations. The polystyrene-based calibrations were nos. 5 and 6 of the previous study.⁴ Also, a broad molecular weight-distribution polyethylene was used as a supplemental standard.⁴

RESULTS

The fractionation results are given in Table II in terms of the number- and the weight-average molecular lengths, \bar{A}_n and \bar{A}_w , expressed in equivalency of polystyrene molecules.

Two sets of the GPC results are in good agreement with each other, except for \bar{A}_n of 194 MH. The GPC trace of this sample with calibration 5 had a baseline uncertainty, and a low molecular weight fraction appeared to

TABLE II
Fractionation Data of HPBD Samples Based on Polystyrene Standards

Sample	Poly- styrene calibration no.	$\bar{A}_w \times 10^{-3}$	$\bar{A}_n \times 10^{-3}$	\bar{A}_w/\bar{A}_n	\bar{M}_w/\bar{M}_n^a
	6	1.06	0.958	1.11	
108 MH	5	6.69	6.31	1.06	1.32
	6	7.25	6.33	1.15	
194 MH	5	11.87	11.24	1.06	1.54
	6	11.67	8.80	1.33	
420 MH	5	24.53	14.08	1.74	2.66
	6	26.35	15.06	1.75	

^a Data by Phillips Petroleum Company.

be overlooked. The values of \bar{A}_w/\bar{A}_n were generally smaller than those of \bar{M}_w/\bar{M}_n and the differences increased with molecular weight. This is contrary to many observations, where GPC values of \bar{A}_w/\bar{A}_n are larger than true \bar{M}_w/\bar{M}_n due to the peak broadening by axial diffusion of polymer molecules. The data with polystyrene standards indicate the peak broadening (Table III).

TABLE III
Fractionation Data of Polystyrene Standards

Sample	$\bar{M}_w \times 10^{-3a}$	$\bar{M}_n \times 10^{-3a}$	\bar{M}_w/\bar{M}_n^a	\bar{A}_w^b	\bar{A}_n^b	\bar{A}_w/\bar{A}_n^b
117	5.0	4.6	1.09	125	110	1.13
480	19.85	19.65	1.01	489	416	1.17
1220	51.0	49.0	1.04	1,163	955	1.22
4160	173	164	1.05	3,750	3,053	1.23
9800	411	392	1.07	9,500	8,120	1.17
20200	867	773	1.12	20,300	17,700	1.15
48000	2,145	1,780	1.20	43,300	33,600	1.29

^a Data provided by Waters Associates, Inc., 61 Fountain Street, Framingham, Massachusetts.

^b GPC results.

A question is whether resolution is poorer for polyethylene than for polystyrene. Or, it may be that polyethylene standards should have been used instead of polystyrene standards.

The data given in Table IV were calculated from the same GPC traces except that polyethylene samples (HPBD) themselves were used as the calibration standards. The calibration curve (Fig. 1) was constructed as a plot of log of molecular weight against count number, both corresponding to the elution peaks. The molecular weight at the peak, M_p , was not known and was estimated according to the following formula:

$$\frac{M_p - \bar{M}_n}{\bar{M}_w - \bar{M}_n} = \frac{A_p - \bar{A}_n}{\bar{A}_w - \bar{A}_n} \quad (1)$$

The values of A_p and M_p are also listed in Table IV.

The HPBD-based calibration did not significantly change the values of \bar{M}_w/\bar{M}_n from \bar{A}_w/\bar{A}_n in Table II. This might be because the four points were inadequate for the purpose of calibration (Fig. 1), or the formula of eq. (1) was not precise.

Shown in Figure 2 are calibration curves obtained by the use of a broad molecular weight polyethylene. The method of determining these curves were described before.⁵ This method of calibration has a distinct advantage in that the curve is continuous, revealing the details of the relationship between molecular weight and GPC count. Such detail in Figure 2 cannot be obtained by the use of a limited number of narrow fractions which provide only a number of discrete points. Using the same GPC traces but

TABLE IV
 Fractionation Data of HPBD Samples Based on HPBD Samples Themselves

Sample	HPBD calibra- tion no ^a	$A_p \times$ 10^{-3}	$M_p \times$ 10^{-4}	$\bar{M}_w \times$ 10^{-4}	$\bar{M}_n \times$ 10^{-4}	\bar{M}_w/\bar{M}_n	\bar{M}_w/\bar{M}_n^b
16 MH	5	1.0	1.62	1.58	1.49	1.06	1.16
	6	1.0	1.51	1.47	1.45	1.01	
108 MH	5	6.6	10.2	—	—	—	1.32
	6	8.0	12.9	12.2	11.0	1.10	
194 MH	5	11.5	15.4	15.7	13.9	1.13	1.54
	6	12.0	20.2	19.6	15.9	1.23	
420 MH	5	29	53.1	40.5	21.2	1.91	2.66
	6	31	52.8	43.5	25.4	1.71	

^a Numbers in this table and those in Table II correspond to the same GPC traces.

^b Data by Phillips Petroleum Company.

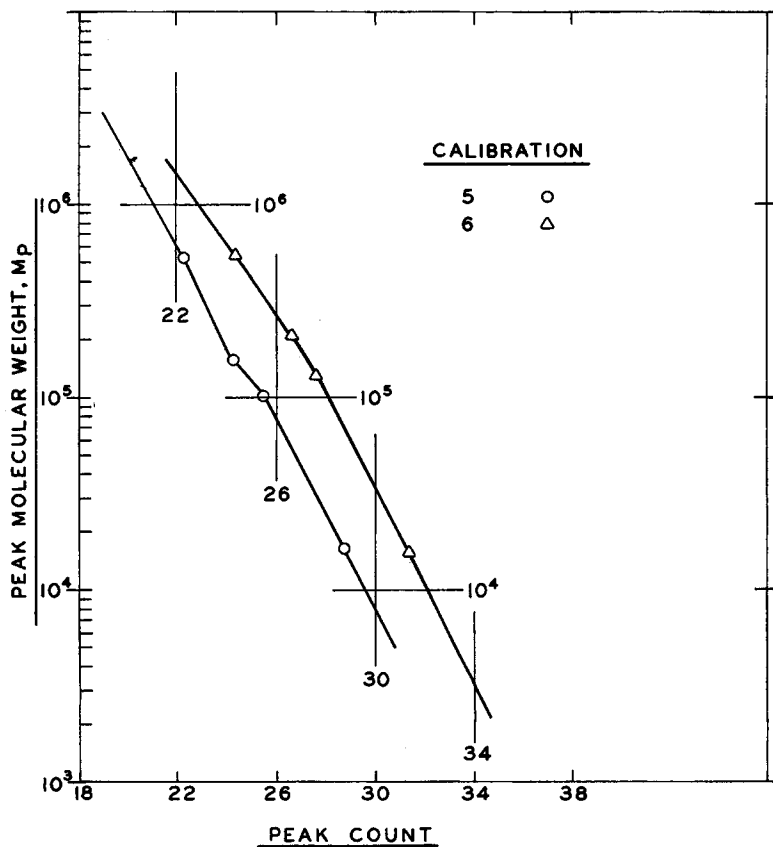


Fig. 1. Calibration curves with polyethylene standards (HPBD polymers).

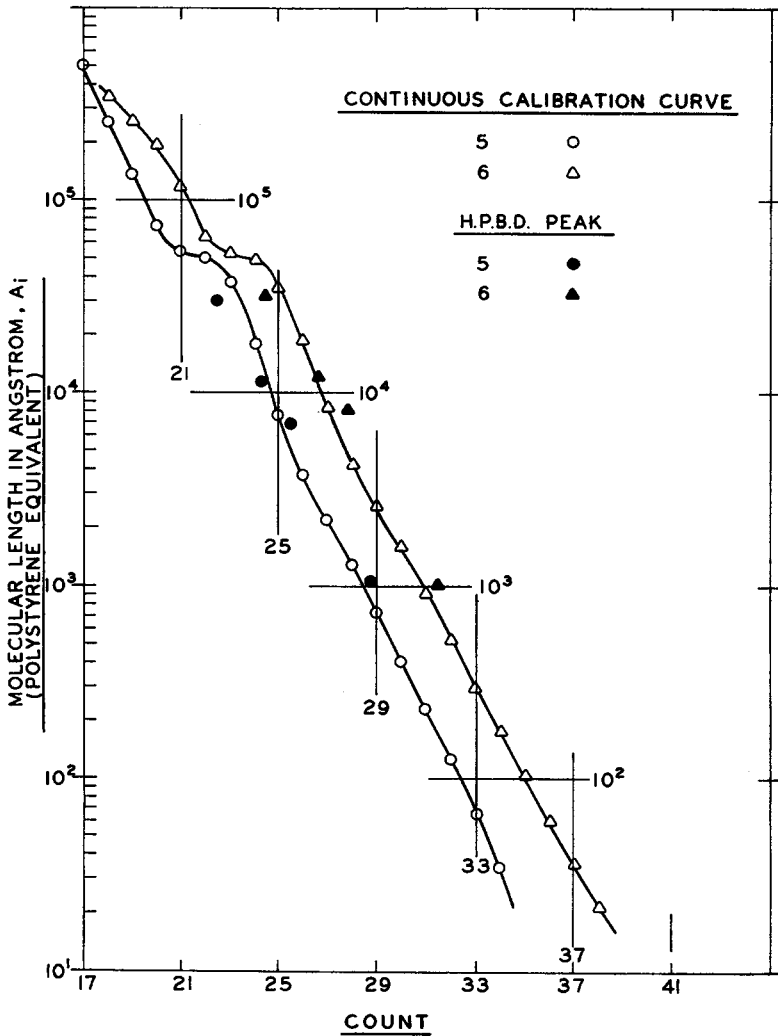


Fig. 2. Calibration curves with a polyethylene standard (Broad molecular weight polymer).

with these calibration curves, the molecular weights of HPBD samples were calculated and are shown in Table V.

According to this calculation, \bar{M}_w/\bar{M}_n values are larger than the previous two in Tables II and IV. Except for the data of 194 MH, the molecular weight ratios are still somewhat smaller than the values provided by Phillips Petroleum Company. However, the differences seen with the first three samples may be within the precision of the GPC method. The discrepancy in the data of the last sample, 420 MH, is larger and requires further investigation.

DISCUSSION

The GPC fractionation of polymer is based on the separation according to the size of molecules in solution. The size concerned depends upon the molecular chain lengths and the interaction of polymer molecules with a given solvent. Accordingly, a universal relationship was discovered by Benoit for the GPC separation, which includes many polymer-solvent systems.⁶ On this basis, then, it is not surprising that polystyrene-based values of polydispersity, \bar{A}_w/\bar{A}_n , of HPBD were smaller than the correct values of \bar{M}_w/\bar{M}_n . Subsequent use of polyethylene calibration gave \bar{M}_w/\bar{M}_n values almost equal to the correct values.

TABLE V
Fractionation Data of HPBD Samples Based on Polyethylene Calibration

Sample	Poly- ethylene calibration no. ^a	$\bar{M}_w \times 10^{-4}$	$\bar{M}_n \times 10^{-4}$	\bar{M}_w/\bar{M}_n	\bar{M}_w/\bar{M}_n^b
16 MH	5	1.40	1.32	1.06	1.16
	6	1.27	1.15	1.10	
108 MH	5	9.05	8.05	1.12	1.32
	6	9.20	7.55	1.22	
194 MH	5	24.5	16.6	1.47	1.54
	6	21.0	12.6	1.67	
420 MH	5	48.0	24.5	1.97	2.66
	6	48.7	23.2	2.10	

^a Numbers in this table and those in Tables II and IV correspond to the same GPC traces.

^b Data by Phillips Petroleum Company.

However, the GPC based \bar{M}_w/\bar{M}_n is still smaller than or equal to the correct \bar{M}_w/\bar{M}_n . Because of the axial diffusion of polymer, the GPC-based values are expected to be larger than the correct values. The presently observed discrepancy may be due to the experimental error. Particularly for the highest molecular weight HPBD, 420 MH, the calibration curves (Fig. 2) may have some uncertainty. The high molecular weight tail of the GPC trace of this sample corresponds to the S-shaped portion of the calibration curves.

With the broad molecular weight-distribution sample of IUPAC round-robin, we observed a similar S-shape at the same molecular weight region.⁵ However, Drott⁷ with this sample did not observe the S-shape; his GPC was run at a lower concentration. The overloading of GPC, and subsequent poorer separation of the high molecular weight fraction, appear to be the cause of the S-shape.

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