A Cooperative Molecular Weight Distribution Test

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Synopsis

The development of gel permeation chromatography (GPC) has provided a convenient
tool for the rapid determination of molecular weight distribution. The question has
arisen as to the suitability of the method for specification purposes. The present work,
suggested by the Naval Air Systems Command, represents an attempt to assess the
precision of the method through a series of tests carried out by a number of laboratories
using identical procedures on the same samples. Ten laboratories agreed to take part.
Naval Ordnance Station, Indian Head, worked out standard conditions for operation of
the chromatograph, for calibration of the columns, and for analysis of the GPC curves.
Two samples of polystyrene were used by the various organizations for calibration of
their instruments. Number-average molecular weight, heterogeneity index, and cumul-
ative molecular weight distribution curves were determined on four samples of carboxyl-
terminated polybutadiene (CTPB) and two samples of hydroxyl-terminated polybuta-
diene (HTPB), all unidentified except by letter code. All laboratories used identical
directions for setting up CTPB and HTPB calibration curves which were based on
curves determined from vapor-pressure osmometer molecular weights and GPC count
numbers of fractionated material. Variation among the different laboratories was 0.15
in heterogeneity index, and a maximum of 1200 in molecular weight provided one aber-
rant set of values was eliminated. The six samples had heterogeneity indices from
1.15 to 1.54, while molecular weight varied from approximately 3000 to 6000.
The average coefficient of variation of the molecular weight values was 6.2 ± 0.7%,
which is quite acceptable. Variation in heterogeneity index was too great for specifica-
tion purposes when considered among the different laboratories, but may be sufficiently
good when measured by any one laboratory.

INTRODUCTION

With the necessity for improved specifications for prepolymers used in
propellant binders has arisen the question of the desirability of controlling
specifications for molecular weight distribution. Gel permeation chro-
matography (GPC) has developed rapidly as a tool for the determination
of molecular weight and molecular weight distribution and is probably the
only available method suitable for this purpose. Looking toward the future,
Naval Weapons Center in FY 1971 funded a program at Naval Ordnance

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TABLE I
Participating Organizations

Identification no.	Organization	Personnel
1	Naval Ordnance Station Indian Head, Maryland	M. S. Chang and D. M. French
2	Firestone Tire and Rubber Co. 1200 Firestone Parkway Akron, Ohio	H. E. Adams
3	Defense Research Establishment Valcartier, Courcelette Quebec, Canada	E. Ahad and M. Tremblay
4	United Technology Center Div. of United Aircraft Corp. Sunnyvale, California	H. J. Hyer
5	Phillips Petroleum Co. Bartlesville, Oklahoma	R. P. Zelinski
6	Department of Supply Weapons Research Establishment Salisbury, So. Australia	J. E. Stutchbury
7	Thiokol Chemical Corporation Wasatch Division Brigham City, Utah	D. R. Davis and R. D. Law
8	Explosives Research & Development Establishment Waltham Abbey Essex, England	R. J. J. Simkins

Station, Indian Head, to determine the precision of the GPC method. A cooperative test was envisioned as part of this program.

Invitations to join the cooperative test were sent to seventeen organizations prominent in the propellant industry or suppliers to the industry. Of these, ten agreed to take part. The test has been completed with results turned in from eight groups. These are listed in Table I. Another such test involving GPC polystyrene standards has been carried out by ASTM Committee D-20.70.04, D. D. Bly, Chairman. Data between laboratories "varied by greater than 100%" in this series.[1]

EXPERIMENTAL

Materials

Samples chosen for analysis were four of carboxyl-terminated polybutadiene (CTPB) and two of hydroxyl-terminated polybutadiene (HTPB), as shown in Table II. Some of these materials were quite old, particularly samples B, C, and D, and their present state may not have been representative of their condition at time of manufacture. However, a change in these materials has no bearing on the present test as long as it has occurred before sampling. Experience has shown that properly stored CTPB and HTPB

TABLE II
Identification of Samples

Sample	Type	Trade name	Lot no.	Source
A	CTPB	Butarez CTL-I	1509	Phillips
B	CTPB	Butarez CTL-II	22D7	Phillips
C	CTPB	Telagen CT	1675/1850	General Tire
D	CTPB	HC-434	111M	Thiokol
E	HTPB	Butarez HTS	5593	Phillips
F	HTPB	R45M	805181	Arco

TABLE III
Polystyrene Standards

Pressure Chemical Co.		Heterogeneity Index		NAVORDSTA			
Designation	Mol. wt. M_n[a]	Press. chem.	This paper	Counts at peak	Counts at M_w	Counts at M_n	Mol. M_n from GPC
Styrene	104		1.014	36.8	36.8	36.8	103[d]
Toluene	92			37.1	37.1	37.1	
15a	975	1.10	1.31	27.8	28.2[d]	28.5	944[d]
12a	2050	1.10	1.24	27.0	27.0	27.4	2027
11a	3700[b]	1.10	1.16	25.5	25.4	26.0	3659
8b	9600	1.06	1.12	23.0	23.0	23.3	9966
8a	10300	1.06	1.12	23.0	22.9	23.4	10425
2a	19000[c]	1.05	1.10	21.5	21.6	21.8	18000

[a] Values recorded are the writers' judgment of Pressure Chemical Co. data.

[b] Described as "Mol. Wt. 4000," but values given range from 2900 to 5200, with average at 3700.

[c] M_w of 19700 with M_w/M_n of 1.05 or 1.10 and value of M_n of 19800.

[d] Calibration curve is not linear in this region. However, for calculations a linear curve was used parallel to the true linear portion of the calibration curve. Counts at M_w will not agree with counts at peak height in such a case.

are stable for periods at least as long as one year, and the results of these tests indicate a change from time of manufacture only for sample D.

During December 1970, the samples were taken from single containers of thoroughly mixed material, poured into 1-ounce glass vials, sealed, and stored at 5°C. Distribution was by air parcel post, and the vials were stored in refrigerators by the recipients.

Single containers of polystyrene 8a and 12a from Pressure Chemical Company were chosen as standards, subdivided, and distributed among the groups. For this purpose, molecular weights were defined as 9600 and 2000, respectively. Some properties of Pressure Chemical Company polystyrenes are shown in Table III.

Calibration and Standard Directions

Calibration of CTPB and HTPB was accomplished using fractions of samples D, E, and F (Table II). Primary and secondary hydroxyl HTPB

represented by samples F and E, respectively, were found to lie on the same calibration curve. Sample A, which contained 30% nonfunctional polybutadiene (NFPB) as plasticizer, was found to have a molecular weight in the proper range by use of the CTPB calibration curve and was designated CTPB for purposes of the test.

Molecular weights for calibration of CTPB and HTPB fractions were determined by vapor pressure osmometry in chloroform solution. Values were determined at least twice at NAVORDSTA (Naval Ordnance Station), and for CTPB also by an outside contractor. The CTPB calibration curve shown in Figure 5, when compared with that of polystyrene, was in fair agreement with that of Mastrolia and co-workers,[2] but above a molecular weight of 5000 not with the data of Screaton and Seeman.[3] There is evidence that the CTPB calibration curve is valid only for material of about 20% to 30% vinyl content. Certainly one would expect this to be true.

A GPC calibration curve is plotted as log molecular weight against elution volume, often the elution volume at the peak of the distribution curve, which is identical with elution volume at the weight-average molecular weight (M_w). Plots of this nature for polystyrene standards were linear only to 4000 molecular weight. Below this point the curve bent down. The CTPB curve exhibited a dip in the region of 4000. Plots were desired not against peak elution volume but against elution volume at the number-average molecular weight (M_n).

To accomplish this result, the GPC distribution curves were statistically analyzed employing a calibration curve formed from the defined molecular weights and the peak elution volume. From this plot the elution volume corresponding to the M_n found by the analysis was read off. A new calibration curve was then drawn using the elution volume at M_n and the defined molecular weights. The distribution curves were again analyzed using the new calibration curve to determine another M_n. Again, elution volumes were read off corresponding to this M_n and a final calibration curve drawn. Further repetition of this process was never necessary. We approached the final position of the calibration curve by successive approximations.

Calibration curves employing elution volume at M_n were linear for polystyrene down to 2000 molecular weight, but bent down below the value. In the case of CTPB the dip was eliminated. The CTPB curve was extrapolated linearly through trimer acid to decanoic acid. Table IV shows NAVORDSTA calibration constants for various polymer series using the equation

$$\log M_n = \log b - mC$$

to express the data, where C is elution volume at M_n in 5-ml counts, and b and m are constants. (Log b)/m is the calculated count number (elution volume) when the molecular weight is 1.0.

Standard conditions for carrying out the cooperative tests where then written up (see Appendix). Several commercial brochures were of some

TABLE IV
Calibration Constants (NAVORDSTA)

Polymer series	Slope m	Intercept $\log b$	$\dfrac{\log b}{m}$	Unperturbed chain dimensions,[a] cm $\times 10 \times 10^{11}$	Known region of approx. linearity, mol. wt.
PS	.168	7.92	47.1	670	2000–20,000
CTPB	.158	7.41	46.9	813	200–20,000
HTPB	.151	7.15	47.4	885	1500–10,000
PPG	.138	6.87	49.8		600–5,000
NFPB	.130	6.55	50.4	>900	1500–7,000

[a] From references 4, 5, and 6.

help.[7,8] Particular Styragel columns had to be specified. Choice of the columns was governed by several years experience with prepolymers of molecular weights in the range 1 to 20,000. Resolution was believed to be greater with the columns chosen than had been the case before. However, it was remarked by three of the participants that resolution was poor at the high molecular weight end of the curves.

The effect of exclusion of large molecules from a low pore-size gel is an abrupt rise of the GPC distribution curve and a hump at the high molecular weight end. Elution will begin at a higher solvent volume than when high-resolution gel is employed, and the excluding gel will lead to lower calculated molecular weights and lower values of dispersity for the sample.

RESULTS

Values determined by the various laboratories for M_n are shown in Table V. Average deviations from the mean value ranged from 117 to 305 molecular weight units and coefficients of variation of 5.2% to 7.1% were found. The precision of the values is certainly better than that obtained by vapor pressure osmometry.

Figure 1 shows the deviation of molecular weight from the mean values for all the samples grouped according to laboratory. Variation between laboratories is seen to be systematic. That is, each laboratory tends to report values either higher or lower than the average. In any one laboratory, precision is much better than when all the values are considered.

Table VI gives heterogeneity indices M_w/M_n reported by the participants. Average deviation from the mean varied from 0.020 to 0.051 index units, which leads mathematically to coefficients of variation of 1.9% to 5.0%. These results appear satisfactory until we remember that the baseline for dispersity values is 1, not zero. When considered in terms of the heterogeneity index minus 1, coefficients of variation range from 14% to 24%, too great a variation to be acceptable for specification purposes. In terms of a particular case, different laboratories might report dispersity values of 1.20 to 1.30 for a sample of a commonly used pre-

TABLE V
Number-Average Molecular Weight

| Participant | M_n | | | | | |
| | Sample | | | | | |
	A	B	C	D	E	F
1	6700	6253	6409	5278	5044	3078
2	6131	5892	5910	4973	4674	3002
3	5779	6564	6350	5508	5055	3366
4	5840	5430	5200	4450	4180	2640
5	6330	6070	5980	5090	4740	2980
6	6314	6053	6055	5084	4852	2995
7	5923	5896	5396	4886	4362	2985
8	6434	6050	5963	5096	4964	2902
Mean	6181	6015	5908	5046	4734	2993
Aver. deviation from mean	257	220	305	207	246	117
Standard deviation	321	324	421	307	321	200
Coeff. of variation	5.2%	5.3%	7.1%	6.1%	6.8%	6.7%
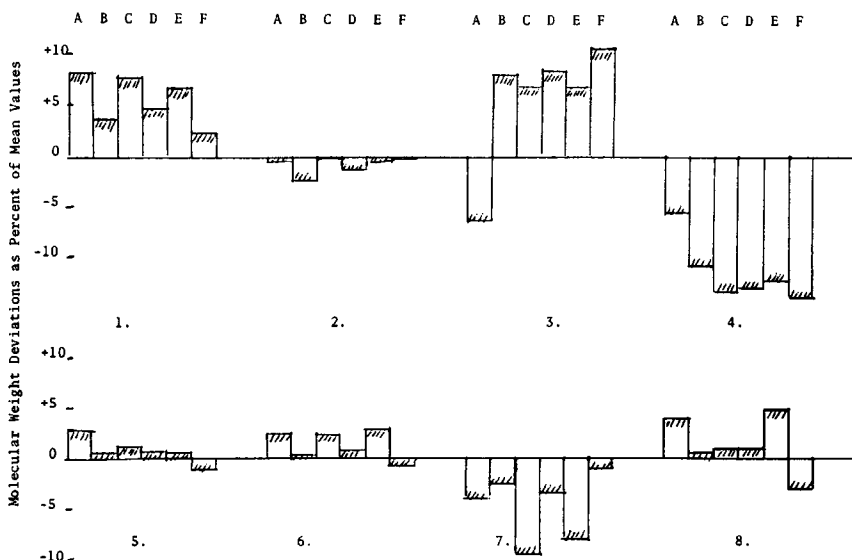
Fig. 1. Consistency of molecular weights from various laboratories.

polymer, while experience shows that the total lot-to-lot variation of the value is about 0.15 dispersity units for this prepolymer.

Figure 2 shows the heterogeneity indices grouped according to laboratory of origin in terms of deviation from the mean as per cent of the mean. There appear again to be systematic differences between results from the various laboratories. Results from single laboratories are more precise

than those averaged from all the participants and may be precise enough for specification purposes.

Figure 3 shows the extremes of cumulative molecular weight distribution curves found by all the participants for sample A. The variation is

TABLE VI
Heterogeneity Indices

| | M_w/M_n | | | | | |
| | Sample | | | | | |
Participant	A	B	C	D	E	F
1	1.26	1.31	1.26	1.42	1.18	1.63
2	1.26	1.25	1.20	1.37	1.15	1.54
3	1.37	1.21	1.18	1.23	1.11	1.40
4	1.18	1.22	1.19	1.37	1.18	1.58
5	1.22	1.25	1.22	1.37	1.16	1.53
6	1.24	1.25	1.24	1.41	1.15	1.55
7	1.29	1.32	1.34	1.47	1.16	1.49
8	1.22	1.31	1.23	1.39	1.15	1.61
Mean	1.255	1.266	1.233	1.379	1.154	1.541
Av. deviation from mean	.040	.032	.036	.044	.020	.051
Standard deviation	.057	.043	.055	.069	.022	.072
Coeff. of var.[a]	4.6%	3.4%	4.5%	5.0%	1.9%	4.7%
Coeff. of var.[b]	22%	16%	24%	18%	14%	14%

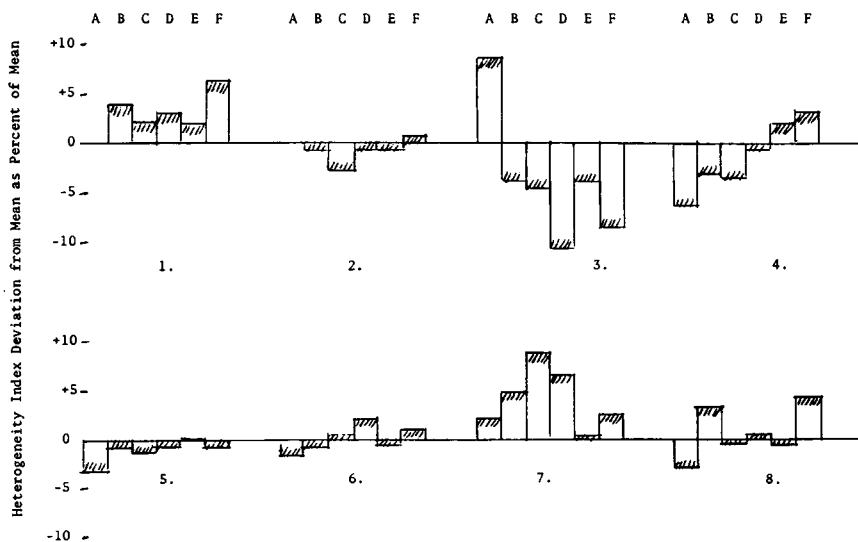[a] Based on mean value.
[b] Based on mean value minus 1.

Fig. 2. Consistency of dispersity results from various laboratories.
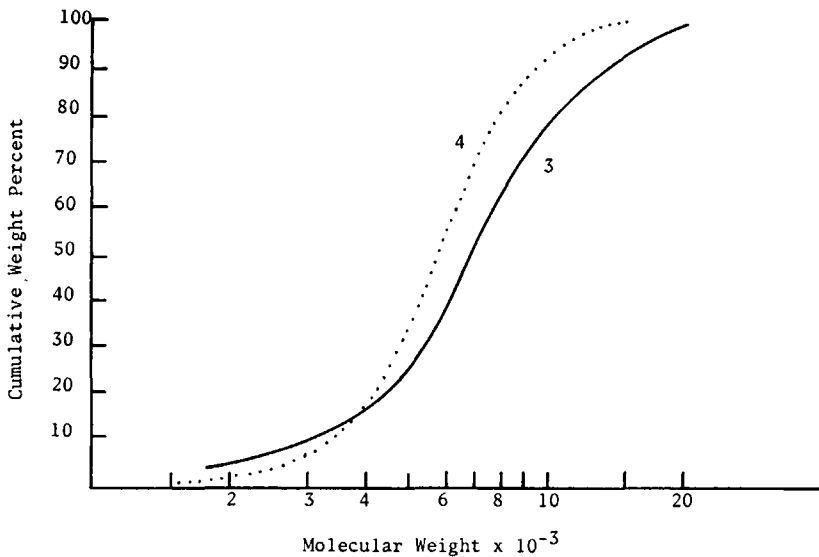
Fig. 3. Extremes of cumulative distribution curves, sample A.

certainly greater than the variation to be expected in any one laboratory but is consistent with the reported dispersity values.

DISCUSSION

The present work has disclosed differences in molecular weight and heterogeneity index values reported by various laboratories which are greater than the error found by single laboratories. The cause of these differences is of interest. It is noteworthy that participants 1 and 3 report molecular weights above the average, while groups 4 and 7 report values below the average. In regard to dispersity, groups 1 and 7 report values above the average, with group 3 below the average. Sample A must be excluded for group 3.

A number of explanations may be advanced to explain the variations in results between laboratories. These would include improper placement of the calibration curves, improper reading of distribution curves or calculation of results, differences in resolution of columns, and changes in solvent flow rate. The placement of the CTPB and HTPB calibration curves was examined as carried out by groups 1, 2, and 7 with results as shown in Table VII. These three groups placed these curves correctly in the same way, and yet their results were quite different.

Figure 4 shows the polystyrene calibration curves found by five groups. The column resolution found by groups 2 and 6 was less than that found by groups 1 and 7, with an intermediate value from group 4. In this connection, group 1 found that replacement of one set of columns with another of the same type did not appreciably change the resolution of the columns or the results of the tests. Nevertheless, it is true that the column resolu-

TABLE VII
Molecular Weights Employed at Equal Elution Volumes

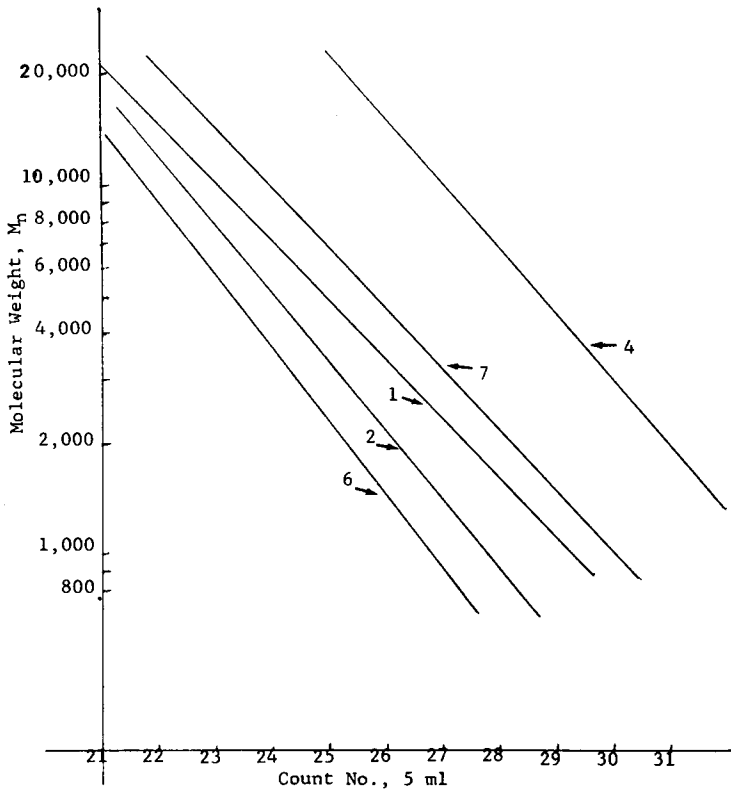|	Mol. wt.		
	Lab. 1 Polystyrene	Lab. 2 Polystyrene	Lab. 7 Polystyrene
HTPB			
1,000	1950	2000	2000
10,000	26,000	26,000	26,000
CTPB			
1,000	1650	1700	1670
10,000	19,000	19,000	19,000

Fig. 4. Polystyrene elution volumes from five groups.

tion found by the various participants was not the same. Volume eluted between 1000 and 10,000 molecular weight varied from 25 to 31 ml for the five laboratories represented in Figure 4. Of these groups, the two laboratories with the highest resolution columns consistently reported high dispersity values. No such correlation, however, is apparent with regard to the molecular weight values.

APPENDIX

Standard Conditions for Operation of Waters Gel Permeation Chromatograph for Hydrocarbon Prepolymer Samples

Solvent: Tetrahydrofuran (Baker Analyzed Reagent, or Eastman Kodak Co.)
Flow Rate: 0.97–1.00 ml/min
Pump Pressure: 110 psi or greater
Sample Column Pressure: $\simeq$95 psi, consistent with flow rate
Reference Column Pressure: Constant, about 30 psi
Temperature: Room, 25°C; degasser, 52°C; inlet, 25°C; oven (columns), 25°C; siphon, 25°C; refractometer base, plate, 36°C, refractometer heat, exchanger, 30°C
Sample: 2 ml of a 0.2% to 0.6% by weight solution
Injection Time: 120 sec
Sample Columns in Order (4 ft, ³/₈ in. O.D., Styragel): 12,000–5000, Å > 700 plates/ft, Cat. #39713; 2, 700–2000 Å, > 700 plates/ft, Cat. #39712; 1, 100–350, Å > 700 plates/ ft, Cat. #39710
Sensitivity: IX
Chart Speed: 0.1 in./min
  The tests being completed, the following changes are suggested in the standard conditions:
Flow Rate: 0.98–1.02 ml/min, but which, when set, shall not vary more than ±0.5%. Variations, due to temperature changes, for instance, shall be corrected before each injection by changing the pump stroke using a stop watch to time the syphon
Pressures: Consistent with flow rate
Temperature: Room, 25° ± 2°C
Injection Time: 120 sec beginning immediately after a chart spike mark, which shall be taken as the zero count point
Chart Speed: Omit

Calibration of Columns

  1. Using the standard conditions above, obtain GPC distribution curves on Pressure Chemical Company polystyrene standards 8a and 12a with molecular weights defined as 9600 and 2000 and "chain lengths" defined as 232 and 48 Å, respectively.
  2. On three-cycle semilog graph paper, plot log molecular weight (9600 and 2000) against count number at peak height obtained from the above distribution curves and draw a line through the two points, as illustrated in Figure 5.
  3. Using the plot, calculate the number-average molecular weight (M_n) from the GPC curves of the two polystyrene samples employing the method described below in the section entitled "Analysis of GPC Curves."
  4. From the plot of molecular weight against count number, find the count numbers corresponding to M_n as determined immediately above. These will be provisional count numbers at molecular weights 9600 and 2000. Draw a straight line including these two points on the semilog plot. This line will be the provisional polystyrene calibration curve.
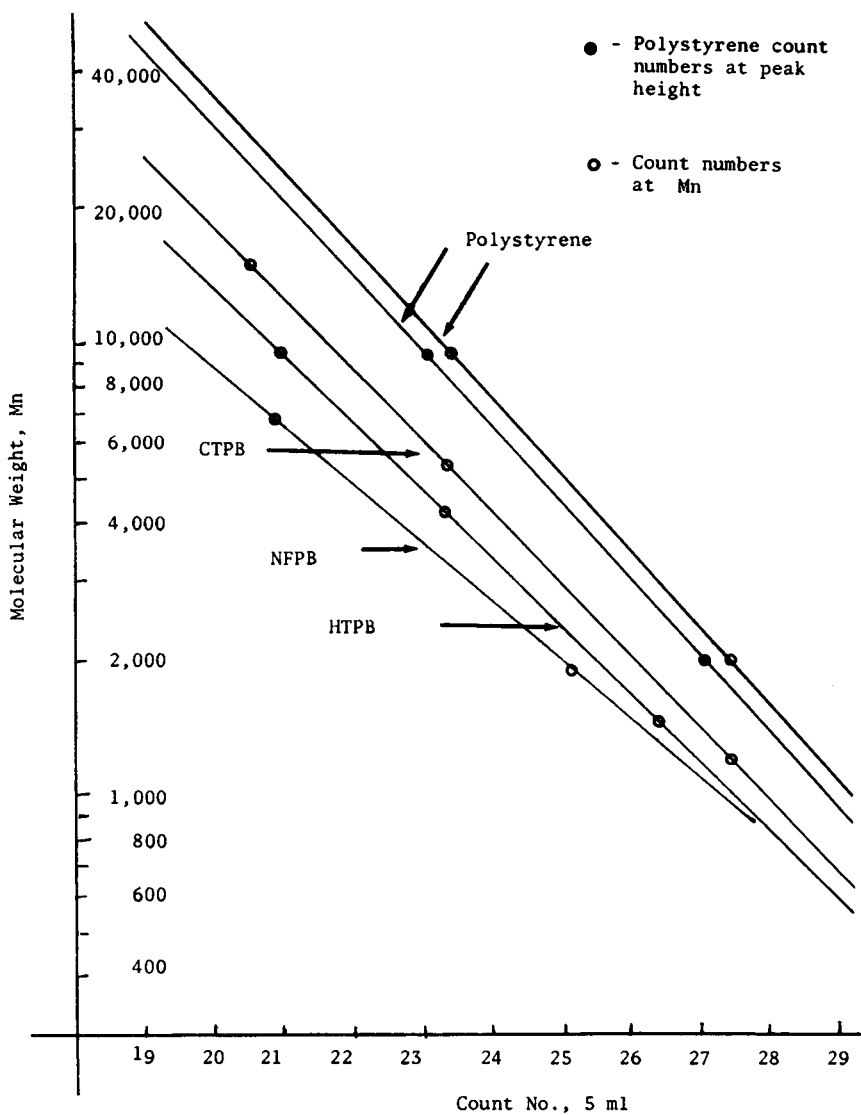
Fig. 5. Molecular weight–elution volume calibration curves.

5. Analyze the GPC curves again as in paragraph 3 above, using the provisional polystyrene calibration curve, and calculate a new M_n. Find the count numbers corresponding to the new values of M_n. These will be the final count numbers at molecular weights 9600 and 2000. Draw a straight line including these two points on the semilog plot. This line will be the polystyrene calibration curve.

6. At count numbers corresponding to molecular weights of 30,000, 10,000, and 2,000 from the polystyrene calibration curve, place points on the semilog figure at 15,000, 5,400, and 1,200 molecular weight. A straight line through these points constitutes the CTPB calibration curve. For example, see Figure 5.

7. At count numbers corresponding to molecular weights of 25,000, 10,000, and 3,000 from the polystyrene calibration curve, place points on the semilog figure at 9600,

4300, and 1450 molecular weight. A straight line through these points constitutes the HTPB calibration curve. See Figure 5.

8. At count numbers corresponding to molecular weights of 25,000 and 5,000 from the polystyrene calibration curve, place points on the semilog figure at 6700 and 1900 molecular weight. A straight line through these points constitutes the nonfunctional polybutadiene calibration curve. See Figure 5 (see note 1 below).

Analysis of GPC Curves

1. Number each 5-ml count on the distribution curve obtained from the GPC. See Figure 6.

2. Draw a baseline across the base of the curve from the beginning of the curve until the end of the curve.

3. With a ruler measure the height in mm from the baseline of the GPC curve at half-count intervals. The height of the curve at the greatest height (peak) should be included as one of the values. Thus, the intervals will not necessarily coincide with the whole count numbers previously numbered.

4. List the heights (H_i) and corresponding half-count values on a table similar to Table VIII. Refer to the calibration curve (Fig. 5), count number versus molecular weight for the particular polymer being measured, and place values of molecular weight corresponding to the half-count values (M_i) in the fifth column of the table (see notes 2 and 3 below).

5. Add the heights in the second column of the table beginning with the height corresponding to the highest count number value, and place the cumulative heights in column 3 of the rable.

TABLE VIII
Calculation of Molecular Weights[a] and Dispersity[b] from GPC Curves

Sample	(1) Count no.	(2) Height H, mm	(3) Cumulative height	(4) Cumulative wt., %	(5) Mol. wt. M	(6) H/M	(7) $H \times M$ $\times 10^{-3}$
CTPB, etc.	19.2	0					
	19.7	25	739	100	20,000	.00125	500
	20.2	49	714	96.6	17,000	.00288	833
	20.7	57	665	90.0	14,000	.00407	798
	21.2	54	608	82.3	12,000	.00450	648
	21.7	55	554	75.0	10,000	.00550	550
	22.2	70	499	67.5	8,100	.00864	567
	22.7	93	429	58.1	6,800	.01368	632
	23.2	106	336	45.5	5,800	.01828	615
	23.7	94	230	31.1	4,800	.01958	451
	24.2	66	136	18.4	4,000	.01650	264
	24.7	35	70	9.5	3,300	.01061	116
	25.2	19	35	4.7	2,800	.00679	53
	25.7	9	16	2.2	2,300	.00391	21
	26.2	5	7	0.9	1,900	.00263	10
	26.7	2	2	0.3	1,600	.00125	3
	27.2	0	0	0.0			
		739				.12007	6061

[a] $M_n = \dfrac{759}{0.12007} = 6154$; $M_w = \dfrac{6061000}{739} = 8202$

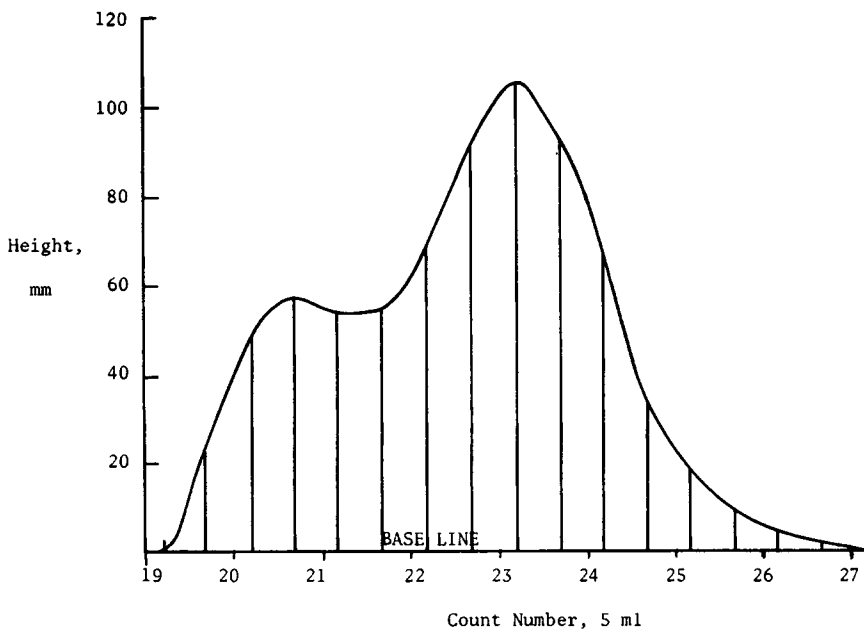[b] $D = M_w/M_n = \dfrac{8202}{6154} = 1.33$

Fig. 6. Gel permeation chromatograph curve.

6. Normalize the cumulative heights (column 3) by dividing individual cumulative heights by the total cumulative height and multiplying by 100. Place these values in column 4 of the table.

7. In column 6, place values of H_i/M_i proportional to the number of moles (n_i) of polymer. In column 7, place values of $H_i \times M_i$.

8. Sum the values found in columns 2, 6, and 7 of H_i, H_i/M_i, and $H_i \times M_i$.

9. Perform the following calculations:

$$M_n = \frac{\Sigma\, n_i M_i}{\Sigma\, n_i} = \frac{\Sigma \text{ column 2}}{\Sigma \text{ column 6}}$$

$$M_w = \frac{\Sigma\, n_i M_i^2}{\Sigma\, n_i M_i} = \frac{\Sigma \text{ column 7}}{\Sigma \text{ column 2}}$$

$$\frac{M_w}{M_n} = \text{heterogeneity index or polydispersity}$$

10. Plot a cumulative distribution curve by plotting column 4 as a function of column 5, as shown in Figure 7.

11. Report as the result of the test the three values obtained in paragraph 9 and figure obtained in paragraph 10.

Note 1: Calibration of nonfunctional polybutadiene was carried out using three molecular weight fractions (10% vinyl) and four samples of unfractionated material (10% and 20% vinyl). Molecular weights were determined repeatedly by VPO on purified material. The calibration does not agree with that of Runyon[9] on higher molecular weight polybutadienes from Phillips Petroleum Company (7% vinyl).

Note 2: At first glance, the use of equal elution volume intervals (count numbers) appears incorrect since molecular weight is not a linear function of elution volume. However, when the weight of material in the resulting unequal molecular weight intervals is considerd, it can be shown that the procedure used here (and generally elsewhere) is nearly correct.
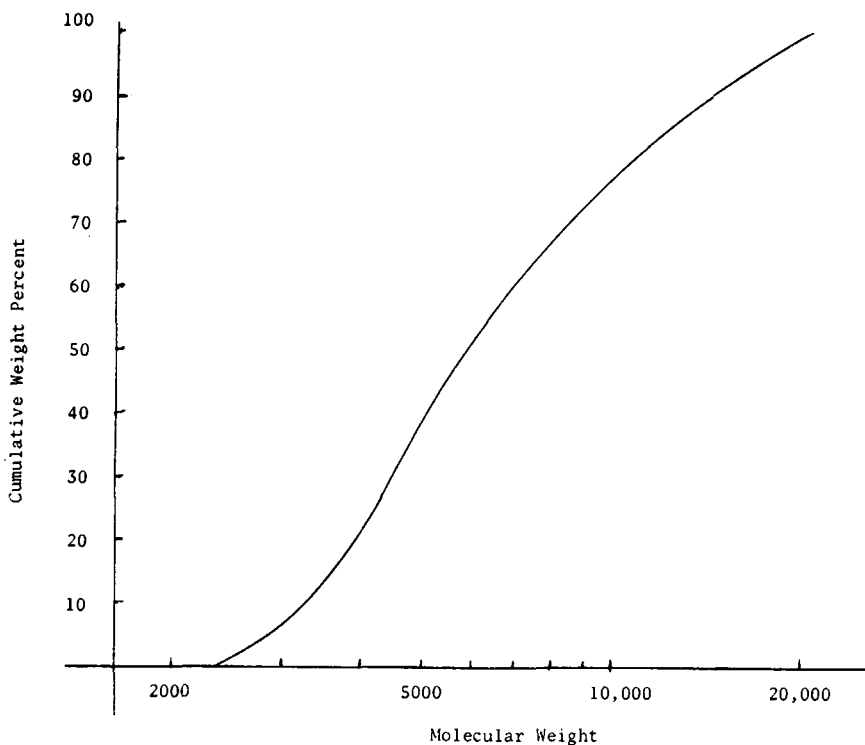
Fig. 7. Cumulative distribution plot.

Note 3: Although the use of "Q factors" relating chain length and molecular weight makes for simpler procedures since only one calibration curve is needed for all polymers, this method is not employed because the Q factor has been found to vary with molecular weight.

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