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Branching and Molecular Weight Distribution of Polyethylene SRM 1476

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Synopsis

A method of determining the distribution of branching in a polymer is developed employing limiting viscosity numbers (intrinsic viscosity), gel permeation chromatography (GPC), and absolute molecular weight determinations of fractions of the whole polymer. A molecular weight calibration of the GPC column set is first determined employing these fractions. From the limiting viscosity number measurements of these fractions and their molecular weight distribution determined from the GPC chromatogram, the viscosity–molecular weight relationship is determined by a nonlinear least-squares fitting procedure. For the same molecular weight, the limiting viscosity number of the branched polymer is less than the limiting viscosity number of the linear polymer. From the ratio of the two, the number of branches per unit molecular weight of the branched polymer is calculated. This method was applied to SRM 1476, the standard reference branched polyethylene issued by the National Bureau of Standards. The branching density for the constituents of SRM 1476 rise from zero at molecular weights less than 10,000 to about 6 to 8×10^{-5} at molecular weights of 50,000 and above. The branching of SRM 1476 was also determined by the method of Drott and Mendelson, giving a result in fair agreement with the above method.

INTRODUCTION

Although it has long been recognized that not only molecular weight distribution but also long-chain branching significantly affects polymer properties, particularly rheological behavior, the quantitive assessment of branching has remained a difficult task. Gel permeation chromatography (GPC) has become a commonly employed method of determining molecular weight distribution, but its use is generally limited to linear polymers. This is due to the dependence of the method on hydrodynamic volume, which varies, for polymers of the same molecular weight, with the degree of branching. However, by combining GPC with other techniques, it is possible to obtain information not only about molecular weight distribution but branching as well. In the method proposed by Drott and Mendelson,[1] it is assumed that the branching frequency is the same for all species of varying molecular weight in the sample and that "universal calibration" of the GPC column is valid for branched polymers. In this investigation, a method of determining the molecular weight distribution and the dependence of branching on molecular weight of the species in the polymer without these assumptions is given. The method was applied to SRM 1476,[2] a standard reference material of the National Bureau of Standards. This polymer was fractionated; and, from an examination of many of these fractions

by a combination of GPC, dilute solution viscosity, light scattering, and osmometry, we obtained information about its branching distribution.

EXPERIMENTAL

SRM 1476 was fractionated by the column elution procedure previously described.[3] The Celite column was heated to 127°C, and polymer dissolved in xylene was permitted to flow onto the column, which was then allowed to cool to 50°C overnight. All of the polyethylene, except for a small amount (called fraction 1 AS), precipitated on the column. The xylene at 50°C was then displaced by a poor solvent, 2-butoxyethanol, and the column containing the bulk of the polyethylene was reheated to 127°C. The fractionation proceeded by extraction with mixtures by xylene and 2-butoxyethanol which were successively richer in the better solvent, xylene. Recovery was 97–98%. To obtain sufficient material for this study, ten batches of 20 g each were fractionated separately and corresponding fractions from each fractionation were grouped together into 12 main fractions. These were then refractionated into 122 subfractions.

Most of the fractions and subfractions were characterized by GPC and, in addition, by one or more of the following techniques: dilute solution viscosity to measure limiting viscosity number; light scattering, to measure weight-average molecular weight; and osmometry, to measure number-average molecular weight.

Light-scattering measurements were made in 1-chloronaphthalene at 135°C using a Sofica light scattering photometer previously calibrated with benzene. Unpolarized light at 546 nm was employed with solutions which had been clarified with a Millipore filter of 0.22 μm nominal pore size. Weight-average molecular weights were determined from extrapolation of the scattering data at five concentrations and 11 angles by the Zimm method. The other details of the measurement are similar to those reported[4,5] for the work on SRM 1475.

Light-scattering measurements made on the whole polymer, filtered in the same way through a 0.22-μm Millipore filter, did not yield a satisfactory Zimm plot, showing a severe downturn in the reciprocal scattering function at low viewing angle. Moore and Peck[6] have attributed this to the presence of very high molecular weight polyethylene species. However, when the whole polymer, dissolved in xylene, was first eluted through the Celite column employed in the fractionation and then filtered through the 0.22-μm Millipore, this downturn was much reduced. An estimate of the weight-average molecular weight of the material was made, but the uncertainty is at least 15%. Zimm plots for the fractions were satisfactory.

Osmotic pressure determination of number-average molecular weight were made in a Hewlett–Packard membrane osmometer in 1-chloronaphthalene at 130°C using a 450 D Arro Laboratory gel cellophane membrane. Data from five concentrations were extrapolated to zero concentration. The details of technique and data analysis are essentially similar to what has been described previously.[7]

GPC data were obtained on a Waters Model 200 apparatus. Styragel columns were employed with nominal exclusion limits ranging from 100 to 10^7 Å. Two column sets were used; column set A was used to give good resolution for high molecular weight polymers, and column set B was used to give good resolution

for lower molecular weight polymers. The calibration of the columns will be discussed below.

The limiting viscosity number $[\eta]$ was measured in 1,2,4-trichlorobenzene at 130°C. The method has also been described elsewhere.[8]

A listing of the subfractions with associated data is given in Table I.

DATA ANALYSIS

Subfractions

Since the elution volume in GPC depends on the hydrodynamic volume of the polymer, which is a function not only of molecular weight but also of degree of branching, calibration with linear fractions in the usual way does not suffice for the study of branched materials. Instead, each of the two column sets used for the subfraction analysis was calibrated with those subfractions of SRM 1476 for which molecular weight averages were determined by light scattering or osmometry. The molecular weight M was assumed to be related to the retention volume v by

$$\log M = A + Bv + Cv^2 \tag{1}$$

where A, B, and C are determined by a least-squares fitting procedure to give the best agreement among the values of M_w, the weight-average molecular weight as determined by light scattering, and M_n, the number-average molecular weight determined by osmometry. The weight- and number-average molecular weights are given in terms of the chromatograms by

$$M_w = \int_0^\infty H(v)\, M(v)\, dv \tag{2}$$

and

$$M_n = 1 \Big/ \int_0^\infty H(v)\, M^{-1}(v)\, \mathrm{dv} \tag{3}$$

where H is the height of the chromatogram normalized to unit area. This method of calibration has been described previously.[9]

For column set A, the following subfractions were used: 7AS6, 10AS12, 12AS3, 12AS8, and 12AS9. This yielded the following calibration of column A:

$$\log M = 19.1603 - 0.7454v + 0.00808v^2 \tag{4}$$

with a mean-square residual of 11%. For the column set B, subfractions 3AS2, 4AS3, 5AS5, 6AS6, 7AS13, 8AS9, 9AS2, 9AS10, and 11AS2 were used to give the following calibration for column B:

$$\log M = 13.484 - 0.1666v - 0.00213v^2 \tag{5}$$

with a mean-square residual of 17%. The calibration depends, of course, on the degree of branching as well as the molecular weight, so that the coefficients in eqs. (4) and (5) depend not only on the column but the degree and distribution of branching of SRM 1476.

The column elution procedure used to prepare the fraction is known to fractionate linear polymers according to molecular weight. On the other hand, in

TABLE I
Branched Subfractions of SRM 1476

Subfraction	M_w	M_n	$[\eta]$, ml/g	Subfraction	M_w	M_n	$[\eta]$, ml/g	Subfraction	M_w	M_n	$[\eta]$, ml/g
3AS2	7,000	4800	23.8	7AS8			60.0	11AS2	186,000	81,800	134
3AS3			30.4	7AS9			59.5	11AS3			158
				7AS10			67.5				
4AS2			26.1	7AS11			78.8	12AS3	75,400		94.6
4AS3	9,830	9,560	30.3	7AS12			71.6	12AS5	376,000	115,800	169
4AS4			35.6	7AS13		44,400	101.8	12AS6	923,000		205
				7AS14			105.7	12AS8	912,000		286
5AS4			34.4	7AS15			104.3	12AS9	772,000	146,000	254.1
5AS5	15,600	14,000	40.0								
5AS6			45.2	8AS8			70.8				
				8AS9			81.6				
6AS4			38.7								
6AS5			41.0	9AS1			138				
6AS6	17,500		45.0	9AS2	120,000		101				
6AS7			48.7	9AS10	116,000	71,600	114				
6AS8			54.6								
				10AS11			123				
7AS5			50.6	10AS12		117,000	150				
7AS6	24,000	24,100	54.6	10AS13			172				
7AS7			57.9	10AS14			175				

the case of branched polymers, the separation into fractions probably occurs on the basis of branching as well as molecular weight of the species so that the fractions and subfractions probably differ in branching as well as in molecular weight. However, a single calibration curve of molecular weight versus elation volume was obtained for each set of columns despite the fact that the elution volume depends on both the branching and molecular weight of the polymer. We conclude, therefore, that the branching of the fractions are dependent mainly on their molecular weight, so that their chromatograms are determined mainly by their molecular weight. Some of the differences between the molecular weight averages of the subfractions calculated from the calibrating eqs. (4) or (5) and their measured values may be due to variations in branching of the subfractions.

We now wish to find a relationship between limiting viscosity number $[\eta]_b$ and molecular weight for the species which constitute SRM 1476. We assume that this relationship may be represented by the empirical relationship

$$\log [\eta]_b = P + Q \log M + R(\log M)^2 \tag{6}$$

The limiting viscosity number of a fraction may be computed from its chromatogram by integrating over the species in the fraction:

$$[\eta]_c = \int_0^\infty H(v)\, [\eta]_b\, dv \tag{7}$$

where $[\eta]_b$ is the limiting viscosity number of the species with retention volume v. By eqs. (6) and (7),

$$[\eta]_c = \int_0^\infty H(v) \exp [P + Q \log M + R (\log M)^2]\, dv \tag{8}$$

The limiting viscosity number $[\eta]_c$ of a fraction may be computed from eqs. (1) and (8) for assumed values of P, Q, and R. A series of values of v are chosen, and the molecular weight M corresponding to each value of v is calculated. Then the integrand of eq. (8) in computed for each value of v, and the integral is numerically evaluated to give the calculated limiting viscosity number $[\eta]_c$ of the fraction. This value may be compared to the measured value $[\eta]_m$ of the subfraction.

In order to determine the relationship of limiting viscosity number to molecular weight, the constants P, Q, and R in eq. (6) must be determined. This was done by the procedure shown in Figure 1. The limiting viscosity numbers $[\eta]_m$ of 40 fractions were measured and GPC chromatogram of the fractions were obtained. Then, the limiting viscosity numbers of each of the fractions were computed from their chromatograms by eqs. (1) and (8). These calculated values were compared with the measured values of limiting viscosity numbers. The values of P, Q, and R were then changed and new values of $[\eta]_c$ computed from the chromatograms. This iteration is continued until the values of P, Q, and R that yield the best possible agreement between the calculated and measured limiting viscosity numbers are obtained and the relationship given by eq. (6) is determined.

The viscosity-average molecular weight of these 40 fractions ranged from 9000 to 400,000, and the limiting viscosity numbers ranged from 23.9 to 205 ml/g. The viscosity–molecular weight relation obtained in this way is given by

$$\log [\eta]_b = -1.4587 + 0.8658 \log M - 0.0326(\log M)^2 \tag{9}$$

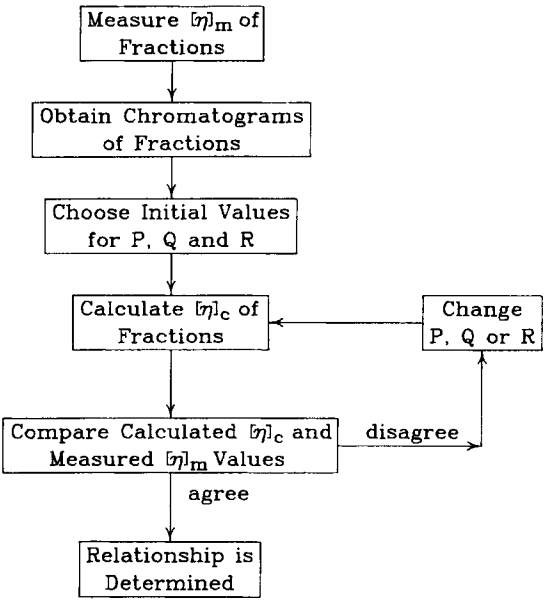

Fig. 1. Flow chart of procedure used to determine the relationship between limiting viscosity number and molecular weight of branched polyethylene.

and is shown by the solid curve in Figure 2. The viscosity-average molecular weight M_v of a subfraction is defined as the solution of the equation

$$\log [\eta]_c = P + Q \log M_v + R (\log M_v)^2 \tag{10}$$

The points in Figure 2 represent the observed values of limiting viscosity number plotted against the viscosity-average molecular weight obtained from the solution of eq. (9) with final values of P, Q, and R. The relative error of $[\eta]$ (residual standard deviation) is 9%. Also shown is the Mark–Houwink relation for linear polyethylene,[10] plotted as a dashed line and given by

$$[\eta]_l = 0.0392 M^{0.725} \tag{11}$$

The linear and branched curves are coincident for $M < 10{,}000$, so that species of molecular weight up to 10,000 have little or no detectable long-chain branching.

The extent of branching may be expressed by the ratio G of the limiting viscosity number of a branched polymer species to that of the linear species of the *same molecular weight:*

$$G = [\eta]_b/[\eta]_1 \tag{12}$$

G is plotted as a function of molecular weight for SRM 1476 in Figure 3. The relationship of G to the ratio g of the mean squares of the radii of gyration, $\langle s \rangle^2$, of branched to linear polymer of the same molecular weight has not been settled, but we have employed the relationship proposed by Zimm and Kilb[11]:

$$G = g^{1/2} = \{\langle s \rangle_b{}^2/\langle s \rangle_1{}^2\}^{1/2} \tag{13}$$

Zimm and Stockmayer[12] have derived the following relationship between g and

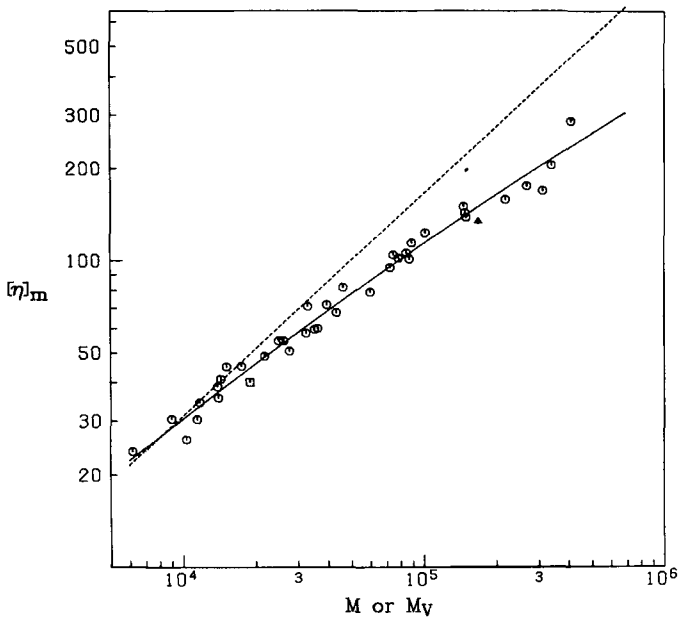

Fig. 2. Relationship of limiting viscosity number to molecular weight of branched polyethylene SRM 1476. Subfractions 5AS5 and 11AS2 are shown by a square and triangle, respectively; other subfractions are shown by circles, and the calculated relationship is shown by the curve. The limiting viscosity number of linear polyethylene is shown by the dotted line.

the number of branch points n_w for a randomly branched polydisperse polymer having trifunctional branch points:

$$g = \frac{6}{n_w}\frac{1}{2}\left(\frac{2+n_w}{n_w}\right)^{1/2}\ln\left[\frac{(2+n_w)^{1/2}+n_w{}^{1/2}}{(2+n_w)^{1/2}-n_w{}^{1/2}}-1\right] \tag{14}$$

From eqs. (10) to (14), n_w was calculated as a function of molecular weight. Then, the number of branch points per unit molecular weight

$$\lambda = n_w/M \tag{15}$$

was calculated and is shown in Figure 4. The curve shows that $\lambda = 0$ for molecular weights less than 10^4, as expected from the results of Figure 2, and that λ then rises quickly to $(5\text{–}8) \times 10^{-5}$, but does not change appreciably after that. Because of the sensitivity of λ to errors in the experimental data, we cannot assert that the maximum is real.

The branching of subfractions 5AS5 and 11AS2 has been studied by Bovey et al.[13] using ^{13}C nuclear magnetic resonance. They measured 1.0 and 8.3 long branches per weight-average molecule for subfractions 5AS5 and 11AS2, respectively. By averaging values of n_w over the molecular weight distributions (as determined from their chromatograms) of these subfractions, we computed values of 0.9 and 12 for subfraction 5AS5 and 11AS2, respectively. Considering the uncertainties in both methods, the agreement is good.

MAIN FRACTIONS

The values of λ were also calculated from the chromatograms of the main fractions in order to provide a check of the previous calculations. These chro-

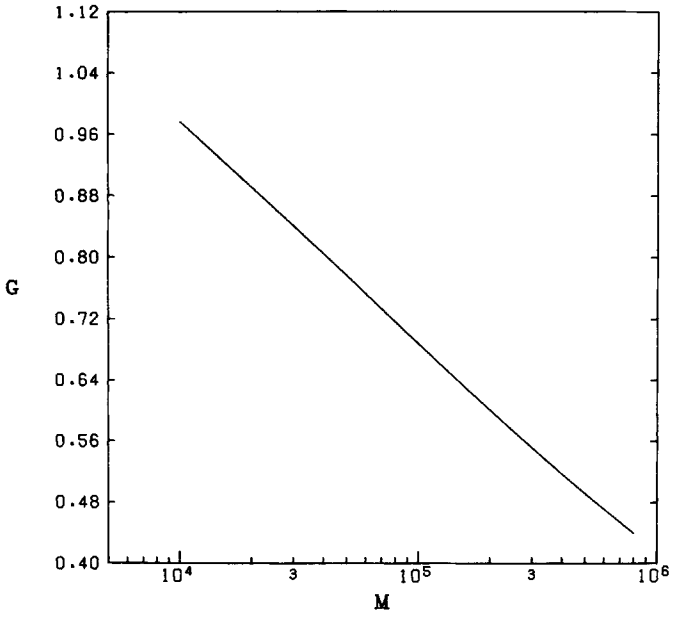

Fig. 3. Ratio, G, of limiting viscosity numbers of branched to linear polymer vs molecular weight.

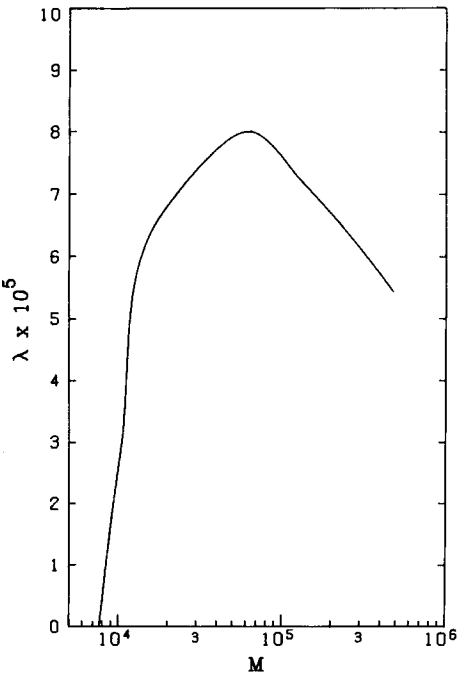

Fig. 4. Number of branch points, λ, per unit molecular weight for branched polyethylene SRM 1476.

TABLE II
Branched Main Fractions of SRM 1476

Fraction	$\lambda \times 10^5$	M_v	$[\eta]_{obs}$
3AS	0	7,200	24.6
4AS	0	9,800	30.6
5AS	0	13,500	38.6
6AS	6.2	19,300	45.5
7AS	7.4	27,800	56
8AS	7.6	40,600	70
9AS	3.6	76,500	112.5
10AS	8.3	1,940,000	152.5
11AS	4.7	1,680,000	164.2

matograms were not obtained on the same column set as the subfractions, but instead were obtained on a set calibrated with linear polyethylenes. Hence, it was necessary to use the Drott–Mendelson method to find values of λ.

The calibration was carried out with four linear polyethylene fractions and a sample of $C_{94}H_{190}$. Weight- and number-average molecular weights had been determined for the fractions by light scattering and osmometry, giving a 9-point calibration curve computed by the method referred to previously. The values of λ for each of the main fractions from 3AS to 11AS and viscosity-average molecular weights found by this method are shown in Table II. Fraction 1AS, which, as indicated above, was xylene soluble at 50°C, and fraction 2AS, which was made up of inhomogeneous particles, were not analyzed. The results for sample 12AS are questionable because the chromatogram went beyond the column calibration and are not included.

These values of λ are in general agreement with the values found for the subfractions (Fig. 4), considering the sensitivity of λ to errors in the limiting viscosity number and in chromatography.

WHOLE POLYMER

GPC measurements were also made on the whole polymer filtered in two different ways. In Figure 5, the solid chromatogram was obtained with ordinary filtration through a 0.45-μm pore size Millipore filter, and the dashed chromatogram was obtained with the polymer put through the Celite column in xylene solution, and then filtered through the same size filter before injection. This was the same Celite column used for fractionation. The Celite apparently removes some of the higher molecular weight species which are not removed by filtration.

The column set employed was calibrated with only linear fractions. In order not to assume, as in the Drott–Mendelson method, a constant λ, we employed a method which utilizes "universal calibration" in conjunction with the relationship between molecular weight and viscosity, eq. (10), found for subfractions of this polymer. The calibration of the column with linear fractions is represented by

$$\log M = A_l + B_l v + C_l v^2 \tag{16}$$

The universal calibration assumption holds that the hydrodynamic volume

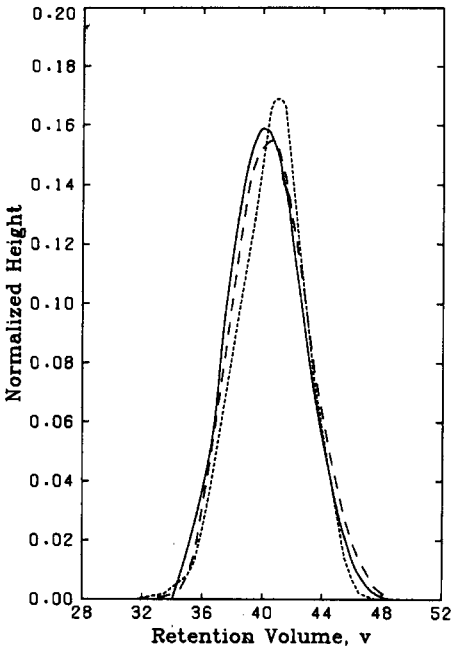

Fig. 5. GPC chromatograms of whole polymer SRM 1476 after filtration through a 0.45-μm Millipore filter (solid curve) and after filtration through a Celite column and a 0.45-μm Millipore filter (dashed curve). The dotted curve was obtained by summing the chromatograms of the main fractions 3AS to 12AS. All chromatograms are normalized to unit area.

$$U_v = M[\eta] \tag{17}$$

at a particular elution volume v is the same for branched and linear polymer. Combining eqs. (16) and (17) with the Mark–Houwink equation, eq. (11), we find for the linear polymer

$$\log U_v = \log [\eta]\,[M] = \log k + (a + 1)A_l + (a + 1)B_l v + (a + 1)C_l v^2 \tag{18}$$

From eqs. (9) and (15), we obtain for the branched polymer

$$\log U_v = P + (Q + 1) \log M + R(\log M)^2 \tag{19}$$

Molecular-weight averages of the branched polymer were computed from its chromatogram by use of eqs. (18) and (19). For every retention volume v included in the chromatogram, the value of log U_v was computed by eq. (18). Then, the corresponding value of the molecular weight was found by solving eq. (19). Thus, the molecular weight corresponding to each retention volume in the chromatogram was determined; so that by integrating the molecular weight over the chromatogram, the molecular weight averages were obtained. Also, the molecular weight distribution of the whole polymer was calculated from the chromatogram obtained with filtration only through a 0.45-μm Millipore filter, and it is shown in Figure 6. The limiting viscosity number for the whole polymer is also similarly obtained from the chromatogram and eqs. (6), (18), and (19). The results are shown in Table III in the first three columns. The weight-average molecular weight obtained by light scattering is higher than that obtained by GPC and is at least partially due to the very large uncertainties in the results

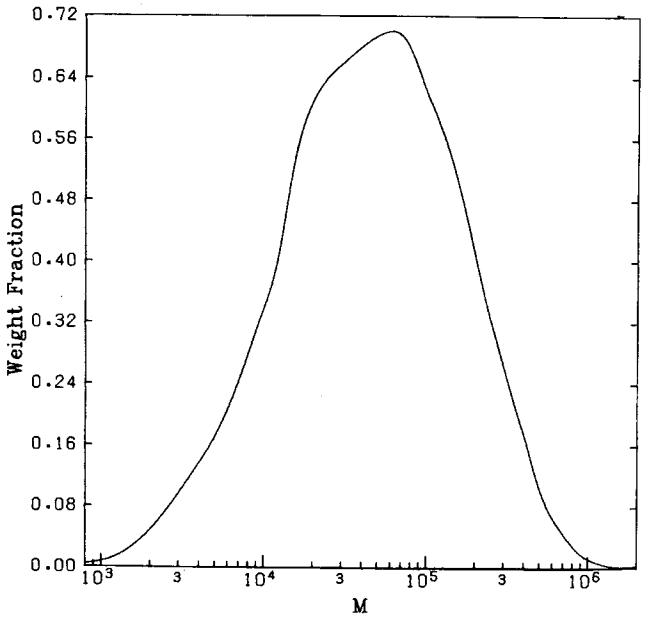

Fig. 6. Molecular weight distribution in log molecular weight of SRM 1476 after filtration through a 0.45-μm Millipore filter.

attributable to the influence of high molecular-weight particles on the light scattering data. The variation in molecular weight with filtration procedure shown in the table is also not surprising for branched polyethylenes, since the number and size of these particles are a function of the filtration procedure.

We compare in Table III the results obtained as described above with those obtained by the Drott–Mendelson method, which assumes constant λ. The difference in the average molecular weights between the two methods is small.

As a check on the consistency of these methods, the chromatograms of the main fractions from 3AS to 12AS were weighted by their fractional composition as determined by the original fractionation data for SRM 1476, yielding the dotted curve shown in Figure 5. The chromatogram of SRM 1476 filtered through Celite is seen to agree best with the summation of the main fractions, very likely because both were filtered by the Celite. The lower molecular weight (high retention volume) tail of the fraction-summed chromatogram contains a smaller amount of material than either of the whole polymer chromatograms, probably because fractions 1AS (2.7% of the total) and 2AS (3.7% of the total) were not included. We have no explanation of why there is disagreement at the high molecular weight end, with the summation chromatogram showing a somewhat narrower distribution. The chromatogram for the sum of main fractions was analyzed as above, employing eq. (10) to give the results shown in Table III.

SUMMARY

We have obtained an estimate of the branching and molecular weight distribution of SRM 1476, the branched polethylene standard reference material issued by the National Bureau of Standards. This was obtained by combining

TABLE III
Analysis of SRM 1476

Filtration method	By eq. (10)			By Drott–Mendelson			By sum of fractions		Light scattering
	M_w	M_n	$[\eta]$, ml/g[a]	M_w	M_n	$\lambda \times 10^5$	M_w	M_n	M_w
0.45-μm Millipore	96,500	22,700	94.0	102,500	23,700	8.8	105,000	25,000	140,000
Celite column + 0.45-μm Millipore	90,700	19,500	89.5	90,900	20,100	6.3			

[a] Certificate value is 90.24 ml/g.

data from a detailed examination of fraction by light scattering, osmometry, viscosity, and GPC techniques. Although the results show reasonable internal consistency, they are subject to the many sources of error which are usual with these techniques, such as 10–15% errors in light scattering and osmometry as well as errors that are caused by the presence of the very high molecular weight species in branched polyethylene. The quantity of these species removed by filtration will vary with technique and is not easily controlled. In many of the fractions, their presence is shown by high molecular weight tails in the chromatograms, so that a small uncertainty in the baseline of a chromatogram can result in a large error in distribution. Nevertheless, these estimates of branching and molecular weight should enhance the usefulness of SRM 1476 and provide a starting point for further investigation of branched polyethylenes.

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