NBS SPECIAL PUBLICATION **260-42**

Standard Reference Materials:

The Characterization of Linear Polyethylene SRM 1475

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Standard Reference Materials:

The Characterization of
Linear Polyethylene SRM 1475

Herman L. Wagner and Peter H. Verdier, Editors

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THE CHARACTERIZATION OF LINEAR POLYETHYLENE SRM 1475:

The Characterization of Linear

Polyethylene SRM 1475

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The National Bureau of Standards has issued a linear
polyethylene standard reference material, SRM 1475.
This material is certified for weight average mo-
lecular weight (M_w), number average molecular weight
(M_n), Z average molecular weight (M_z), molecular
weight distribution, limiting viscosity numbers in
several solvents, melt flow rate, and density. The
experimental details of the determination and certi-
fication of these properties are given in these col-
lected papers previously published in the Journal of
Research of the National Bureau of Standards.

The Characterization of Linear Polyethylene SRM 1475.
I. Introduction.

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The National Bureau of Standards has issued a linear polyethylene standard reference material, SRM 1475. In this report a general description of the sample is given, and the characterization work described in the subsequent reports is outlined. Some pellet-to-pellet variability was found and estimated.

Key words: Fractionation; linear polyethylene; molecular weight; molecular weight distribution; National Bureau of Standards; pellet variability; standard reference material.

1. Purpose

The National Bureau of Standards has issued a linear polyethylene standard reference material, SRM 1475,** to fill the need for a well-characterized sample of this polymer. The sample may be used for the calibration of instruments for measuring molecular weight and molecular weight distribution, such as light scattering photometers and gel permeation chromatographs. It should also be useful in other areas of polymer research such as dilute solution studies, polymer rheology, and polymer crystal physics.

2. Properties Measured

The characterization results which are described in the succeeding papers in this series [1][1] include a determination of:
(1) Weight average molecular weight by light scattering,
(2) molecular weight distribution by gel permeation chromatography and, from this distribution, weight average, number average, and Z average molecular weights,
(3) limiting viscosity number in 1-chloronaphthalene, 1,2,4-trichlorobenzene, and decalin,
(4) melt flow rate by a melt index type apparatus,
(5) density by ASTM procedures.
No attempt was made to determine number average molecular weight of this whole polymer by osmometry since diffusion of even small amounts of low molecular weight species through the membrane makes such a determination meaningless. However, by calibration of the gel permeation chromatograph with fractions that were well characterized by light scattering and osmometry, it was possible to determine number average molecular weight as well as weight average and molecular weight distribution. With these data, SRM 1475 may be used conveniently for the precise calibration of other gel permeation chromatographs.

In the papers which follow, the various techniques are described. More detail is given in those cases where there has been some deviation from the usual procedure. The certificate for SRM 1475 is reproduced at the end of this paper.

3. Sample Description

The sample of linear polyethylene chosen for SRM 1475, an ALATHON 7050, was kindly donated by the E. I. duPont Company, Wilmington, Delaware.* The material is in the form of pellets, each weighing about 20 mg. An antioxidant, tetrakis[methylene-3-(3',5'-di-t-butyl-4'-hydroxyphenyl)propionate]methane, known commonly as Irganox 1010 (Geigy Chemical Company), was added to the polymer at a concentration of 111 ppm by the manufacturer. The linearity of the polymer is demonstrated, as shown in part II [1], by infrared analysis. Ash content, determined by ashing a 10-gram portion of the sample at 750 °C, was found to be 0.002 percent.

The determination of volatile components, or at least those components soluble in xylene, was made as follows. Three grams of polyethylene and 7 grams of xylene were sealed in one container and 7 grams of xylene was sealed in another as a control. These containers were heated at 140 °C until the contents dissolved. They were cooled to precipitate the polyethylene, opened, and samples of liquid from each were analyzed by gas chromatography.

It is estimated that any xylene-soluble volatiles that amounted to as much as $1/2$ percent of the polyethylene could be readily detected by this method. No evidence of such volatile material was found.

4. Sampling

The sample was received in forty 50-lb bags. To determine the conditions necessary for uniform sampling, polymer variability from pellet-to-pellet and bag-to-bag was determined. The bags were numbered at random from 1 to 40 and samples were taken from the top and bottom of each of bags 1 to 20. Several grams of each of these were mixed and samples drawn from this "pool" to make up blended samples for light scattering, limiting viscosity number, and gel permeation chromatography. These blends were made up of several hundred pellets dissolved in xylene at 140 °C and precipitated in ethanol at room temperature.

Pellet-to-pellet variability was determined by solution viscosity measurements [1d] in 1-chloronaphthalene at concentrations of from 0.06 to 0.12 g/dl at 130 °C on individual pellets and on samples of the blends. The viscosity number, $(\eta - \eta_0)/(\eta_0 c)$, in dl/g, where η is the viscosity of the solution, η_0 is the viscosity of the solvent, and c is the concentration in g/dl, is plotted against concentration in figure 1. The viscosity numbers obtained for the blended samples were fitted by least squares to a linear function of concentration, yielding the straight line shown in the figure. The standard deviation in viscosity number obtained from the least-squares analysis for the blended samples was 0.0034 dl/g (0.38%). The root-mean-square deviation from the straight line of the viscosity numbers obtained for solutions made up from individual pellets was found to be 0.028 dl/g (3.1%). Thus the standard deviation of a single measurement is 0.38 percent and the standard deviation due to pellet-to-pellet variation is

$$[(3.1)^2 - (0.38)^2]^{1/2} = 3.1\%.$$

Since the coefficient of variation is 3 percent, it is recommended that all determinations be performed on samples containing at least 50 pellets or one gram of polymer (or material from a blend of one gram). This will reduce the expectation of the standard error due to pellet variability to less than 0.5 percent.

Details of the method of measurement of melt flow rate and the results obtained are discussed elsewhere [1c]. These measurements were employed to investigate variations in material taken from different regions of the entire material. Forty-two samples for
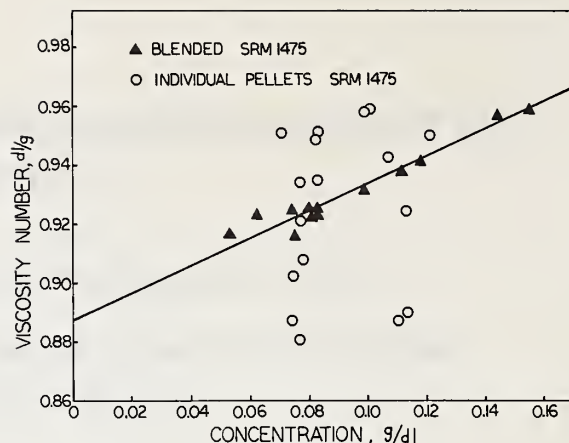
FIGURE 1. *The viscosity number of a blended sample and of individual pellets of SRM 1475 plotted against concentration.*

melt flow rate determination were taken from 13 different regions in seven of the bags. The standard deviation for samples within a region was found to be 2.1 percent, based on 29 degrees of freedom. The standard deviation between regions was found to be 1.7 percent, based on 12 degrees of freedom. We conclude that variations from region to region are too small to be detected by this method.

5. References

[1] The Characterization of Linear Polyethylene 1475:
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  (b) Brown, J. E., Paper III, Density Determination, Ibid, **76A** (Phys. and Chem.), No. 2, 143–144 (Mar.–Apr. 1972).
  (c) Maurey, J. R., Paper IV, Melt Flow Rate, Ibid, **76A** (Phys. and Chem.), No. 2, 145–146 (Mar.–Apr. 1972).
  (d) Christensen, R. G., Paper V, Solution Viscosity Measurements, Ibid, **76A** (Phys. and Chem.), No. 2, 147–149 (Mar-Apr. 1972).
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  (g) Frolen, L. J., Ross, G. S., Wims, A. M., and Verdier, P. H., Paper VIII, Light Scattering Studies on Polyethylenes in 1-Chloronaphthalene, Ibid, **76A** (Phys. and Chem.), No. 2, 156–160 (Mar.–Apr. 1972).
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(Paper 76A2–706)

National Bureau of Standards
Certificate

Standard Reference Material 1475

Linear Polyethylene

(Whole Polymer)

C. A. J. Hoeve, H. L. Wagner, J. E. Brown,
R. G. Christensen, L. J. Frolen, J. R. Maurey, G. S. Ross, and P. H. Verdier

This Standard Reference Material is intended for the calibration of instruments used in polymer science and technology for the determination of molecular weight and molecular weight distribution.

Quantity	Average Values	Estimated Standard Deviation of Average
Molecular Weight		
Weight-average molecular weight[a]	52,000	2,000
Number-average molecular weight	18,310	360
Weight-average molecular weight	53,070	620
Z-average molecular weight	138,000	3,700
Ratio of molecular weights $M_z : M_w : M_n$	7.54:2.90:1	
Molecular weight distribution	See Table 1	
Limiting Viscosity Number (dl/g)		
In 1-chloronaphthalene at 130 °C	0.890	0.0032
In 1,2,4-trichlorobenzene at 130 °C	1.010	.0086
In decahydronaphthalene[c] at 130 °C	1.180	.0032
Melt-Flow Rate (g/10 min)[d]	2.07	.0062
Density (g/cm³)[e]	0.97844	.00004

The bracket labeled [b] spans: Number-average molecular weight, Weight-average molecular weight, Z-average molecular weight, Ratio of molecular weights $M_z : M_w : M_n$, and Molecular weight distribution.

[a] By light scattering in 1-chloronaphthalene at 135 °C.

[b] By gel-permeation chromatography.

[c] "Technical" grade, which assayed at approximately equal proportions of cis- and trans- decahydronaphthalenes.

[d] By a procedure similar to Procedure A, ASTM Method D1238-65T, Test Condition D, 190 °C, load 325 g.

[e] By ASTM Method D1505-67; sample prepared by Procedure A, ASTM Method D1928-68.

Measurements leading to the certification of this material were performed in the Molecular Properties and Characterization Section of the Polymer Division.

Washington, D.C. 20234
November 6, 1969
(Revised December 2, 1971)

J. Paul Cali, Chief
Office of Standard Reference Materials

(over)

The methyl group content as determined by ASTM Method D2238-68 is 0.15 methyl groups per 100 carbon atoms. This shows the polyethylene to be essentially linear. A pellet to pellet coefficient of variation of 3 percent in the limiting viscosity number was found. All determinations should consequently be performed on samples containing at least 50 pellets or one gram of polymer (or material from a blend of one gram). This will reduce the expectation of the standard error due to pellet variability to less than 0.5 percent.

Table 1. Cumulative Molecular Weight Distribution by Gel-Permeation Chromatography

log M	Wt. %	log M	Wt. %	log M	Wt. %
2.800	0.0	4.014	15.2	5.065	90.7
2.865	0.005	4.070	18.1	5.113	92.2
2.929	0.020	4.126	21.5	5.161	93.7
2.992	0.052	4.182	25.2	5.209	94.8
3.056	0.105	4.237	29.3	5.256	95.8
3.119	0.185	4.292	33.7	5.303	96.6
3.181	0.343	4.346	38.5	5.349	97.3
3.243	0.475	4.400	43.4	5.395	97.9
3.305	0.706	4.454	48.5	5.440	98.4
3.366	0.999	4.507	53.5	5.485	98.7
3.427	1.38	4.560	58.3	5.530	99.1
3.488	1.88	4.612	62.9	5.574	99.3
3.548	2.51	4.664	67.3	5.618	99.5
3.607	3.30	4.715	71.4	5.662	99.7
3.667	4.28	4.766	75.1	5.705	99.8
3.725	5.46	4.817	78.5	5.789	99.9
3.784	6.87	4.868	81.6	5.87	100.0
3.842	8.56	4.918	84.4		
3.900	10.50	4.967	86.7		
3.957	12.7	5.016	88.9		

The sample of linear polyethylene was obtained from E. I. du Pont de Nemours and Company of Wilmington, Delaware.

This sample of linear polyethylene has an ash content of 0.002 percent. No volatiles were detected by a gas-chromatographic procedure capable of detecting 0.5 percent volatiles. The manufacturer added 111 ppm of the antioxidant, Irganox 1010 (Geigy), which is tetrakis [methylene-3-(3',5'-di-t-butyl-4'-hydroxyphenyl)propionate] methane.

The differential refractive index in 1-chloronaphthalene, required for the calculation of molecular weight by light scattering, was found to be −0.193 ml/g at 135 °C and 546 nm.

The maximum rate of shear in the Ubbelohde viscometer was about 1500 sec^{-1}. All measurements were carried out at specific viscosities (0.1 or less) which were sufficiently low for negligible dependence on rate of shear.

A series of reports describing investigations required for this certificate will be published in the Journal of Research of the National Bureau of Standards, Volume 76 A, No. 2, 1972.

The Characterization of Linear Polyethylene SRM 1475. II. Determination of Total Methyl Content by Infrared Spectrophotometry.

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An ASTM method was used to determine the methyl content of linear polyethylene SRM 1475 by measuring the absorbance at 1378 cm^{-1} (7.25 nm) of methyl groups on compensated infrared spectra. The methyl content of this polymer was found to be 0.15 methyls per 100 carbon atoms. Considering the methyls to be polymer end groups, the number average molecular weight computed approximates that determined by gel permeation chromatography within the experimental error. These values indicate that the polymer is essentially free of branching.

Key words: Infrared; linear polyethylene; methyl; methylene; number average molecular weight; spectra; spectrophotometry.

1. Introduction

The total methyl group content in polyethylene may be used to estimate the amount of branching in the polymer. If, for example, it is assumed that all chain-ends are methyl groups, then the methyl-group content of the polymer may be combined with its number-average molecular weight, M_n, to yield an estimate of the average number of chain ends per molecule.

In the characterization of SRM 1475, the total methyl content was determined to obtain an estimate of the polymer's linearity. Infrared spectrophotometry was used to determine the methyl content from the absorbance at about 1378 cm^{-1} due to methyl groups. This band is overlapped by bands at 1368 and 1352 cm^{-1}, and therefore cannot be used directly to estimate methyl group content. However, it has been shown [1–5][1] that both the latter two bands and another band at 1304 cm^{-1} arise from methylene-groups in the amorphous or disordered regions only, while the 1378 cm^{-1} band arises from methyl groups in both amorphous and crystalline regions. If we assume [5] that the spectrum of solid polyethylene is a superposition of contributions from amorphous and crystalline regions, then the spectrum arising from methyl groups alone may be obtained as a difference spectrum between two films of the same polymer, but different degrees of crystallinity and appropriately different thicknesses.

In this paper, we report the results for total methyl content in SRM 1475 by the method described in American Society for Testing and Materials (ASTM) Designation: D 2238–68, "Standard Method of Test for Absorbance of Polyethylene Due to Methyl Groups at 1378 cm^{-1}."[2] By this method, the absorbance is measured at the methyl frequency (1378 cm^{-1}) on films which are largely crystalline while compensating for the amorphous methylene absorbance with thinner, less crystalline films. Graphically, the absorbance resulting only from methyl groups is interpolated to the point of zero methylene absorbance at 1304 cm^{-1}. Each of the absorbances at 1378 and 1304 cm^{-1} is corrected for the effect produced by the difference in thickness and density of the crystalline and amorphous films. The resulting absorbance at 1378 cm^{-1} is then used to calculate the number of methyl groups per 100 carbon atoms. The conversion of absorbance to methyls per 100 carbon atoms is computed from the absorbance at 1378 cm^{-1} due to methyl groups in n-hexadecane (cetane).

2. Experimental Procedure

Films were prepared from SRM 1475 pellets taken from each container and blended as described in the first paper of this series [6]. In accordance with the ASTM procedure, several films ranging in thickness from 0.01 to 0.04 cm were molded in a hydraulic press heated to 168 °C. The molten polyethylene in the mold assembly was then quenched in an ice-water mixture. Films prepared in this manner are designated reference films. Four films about 0.05 cm thick were also molded from the SRM pellets by the above procedure except that these films were annealed so as to produce an increase in density of at least 0.02 g/cm^3 greater than the density of the quenched reference films. The annealed films will later be referred to as

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[1] Figures in brackets indicate the literature references at the end of this paper.

samples I through IV. Difference spectra of each sample (high crystalline content) were obtained with three or four of the thinner reference films (low crystalline content). The spectra were recorded in the region from about 1430 to 1250 cm^{-1} using the prism optics of a double-beam, infrared spectrophotometer, (Perkin-Elmer Model 221).[3] From these spectra, which range from partial to over-compensation of the absorption due to amorphous methylene groups, the absorbance at the methyl frequency, A_{1378}, and that at the methylene frequency, A_{1304}, were determined as directed by the ASTM method.

3. Results and Discussion

Effective absorptivities, α, at 1378 and 1304 cm^{-1} were calculated from the difference spectrum of each sample-reference pair by the relation $\alpha = A/(d_s t_s - d_r t_r)$, where A is absorbance and d_s, t_s, d_r and t_r are sample density, sample thickness, reference density, and reference thickness, respectively. The resulting pairs, $(\alpha_{1304}, \alpha_{1378})$, were plotted as shown in figure 1, together with the straight line determined by a linear least squares fit. The value of α_{1378}, on the least squares line, corresponding to $\alpha_{1304} = 0$ is the absorptivity in cm^2/g at 1378 cm^{-1} at which the methylene absorptivity at 1304 cm^{-1} is completely compensated. This quantity is designated K' in table 1. The number of methyl groups per 100 carbon atoms is also shown in table 1. The methyl concentration is computed from the product of K' and a calibration factor derived from measurements on cetane, as described in the ASTM procedure.

High density (linear) polyethylene chains may be presumed to be terminated with methyl groups as demonstrated by Willbourn [4] in a study of chain branching in polyethylene. If we assume two methyl groups per chain, then our estimate of 0.15 methyl groups per 100 carbon atoms leads to an estimate of 18,700 for the number-average molecular weight, M_n. This value closely approximates the M_n (18,310) from the gel permeation chromatography measurement as shown in Paper X of this series [7]. This correlation and the density [8] suggests that the polymer, SRM 1475, is essentially free of branching.
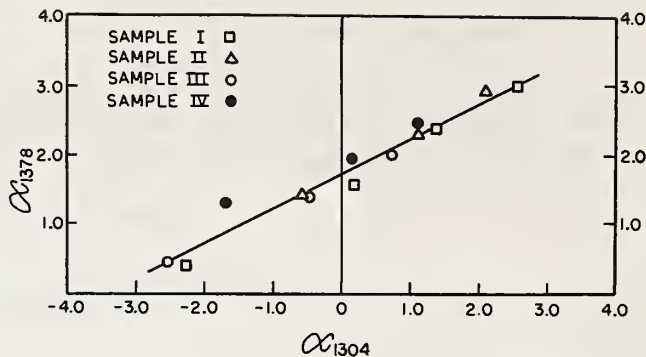
FIGURE 1. *Ordinate: Absorptivity, α_{1378}, cm^2/g; Abscissa: Absorptivity, α_{1304}, cm^2/g.*

The line shown in this graph represents a least squares fit of the absorptivity at 1378 cm^{-1} resulting from methyl groups against the absorptivity at 1304 cm^{-1} arising from amorphous methylene groups. The slope is equal to 0.51 ± 0.03 with the intercept at 1.74 ± 0.05 where the symbol $\pm$ stands for the standard deviation in these quantities inferred from the linear least-squares fit. The intercept represents the methyl absorption at perfect compensation for the methylene groups.

TABLE 1. *Results of methyl group determination from compensated spectra*

Absorptivity K', cm^2/g	Sample standard deviation of K'	CH$_3$ groups per 100 C atoms
1.74	0.053	0.15

K' in cm^2/g is the reduced absorptivity of methyl groups, at complete compensations for the absorption due to methylene groups determined for SRM 1475.

4. References

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[7] Ross, G. S. and Frolen, L. J., J. Res. Nat. Bur. Stand. (U.S.), 76A (Phys. and Chem.), No. 2, 163–170 (Mar.–Apr. 1972). Paper X of this series.
[8] Brown, J. E., J. Res. Nat. Bur. Stand. (U.S.), 76A (Phys. and Chem.), No. 2, 143–144 (Mar.–Apr. 1972). Paper III of this series.

(Paper 76A–707)

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[3] Certain commercial equipment, instruments, or materials are identified in this paper in order to adequately specify the experimental procedure. In no case does such identification imply recommendation or endorsement by the National Bureau of Standards, nor does it imply that the material or equipment identified is necessarily the best available for the purpose.

The Characterization of Linear Polyethylene SRM 1475. III. Density Determination

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The density of SRM 1475 at 23 °C was determined by ASTM method D 1505–67 on samples prepared by Procedure A of ASTM method D 1928–68, with the result 0.9784 g/cm³.

Key words: Crystallization; degree of crystallinity; density; linear polyethylene; polymer; recrystallization.

1. Introduction

The density of polyethylene crystallized from its melt is sensitive to a number of factors which influence the degree of crystallinity. Among these factors are: the polymer's previous thermal history and crystallization temperature which affect the perfection and rate of crystal growth [1–4],[1] the average molecular weight and its distribution [3], and the amount of branching [5–6].

In this paper we report the results of the density measurements on linear polyethylene SRM 1475. The density measurements and the sample preparation were performed using standard methods of the American Society for Testing and Materials (ASTM). It was necessary to specify closely the preparation of the samples used in this determination since the density of polyethylene depends to such an important extent on the polymer's previous history. From our experience, it should be possible to duplicate these results closely provided that the same methods are followed.

2. Experimental Procedure

Three composite samples, weighing about 100 g each, were made up separately as described in the first paper of this series [7] by blending equal amounts of the SRM 1475 pellets taken from the tops and bottoms of each of the original containers. These three composite samples will subsequently be referred to as blend I, II, and III.

Test samples (plaques) were prepared from blend I by Procedure A of ASTM Designation: D 1928–68, "Standard Method for Preparation of Compression-Molded Polyethylene Test Samples."[2] In accordance with this procedure, the pellets of blend I were made into a crepe on a roll mill. The polyethylene was milled for about four minutes at a temperature sufficiently high to cause the polymer to flux but not to drip. Pieces were cut from the cooled crepe and compression molded into 3 mm thick plaques at 178 °C using picture-frame-like chases.[3] The mold assembly containing the molten polyethylene was removed from the press and quenched to room temperature in a water bath. The mold assemblies containing the quenched plaques were then placed in a heated oven and maintained at 170 °C, well above the crystal melting point, for 1 h or more in order to destroy the polymer's previous thermal history. The temperature of the oven was then lowered to 50 °C at a rate of 5 °C/hr. After the plaques had come to room temperature, several specimens (2–3 mm on a side) were cut from each plaque for the density measurements.

As a check on the sensitivity of the ASTM procedure to variations in the preparative technique, plaques of blends II and III were prepared somewhat differently. Plaques of blend II were prepared as described above except that the milling time (about 2 minutes) was just long enough at about 125 °C to cause the pellets to fuse into a sheet. The plaques of blend III were not molded from a milled crepe. These plaques were compression-molded from the pellets. Except for the milling process, the test samples (plaques) of blend III were quenched, recrystallized, and cooled to room temperature by the same techniques described for blends I and II.

The density of the three blends was determined by the procedure given in ASTM Designation: D1505–67, "Standard Method of Test for Density of Plastics by the Density-Gradient Technique."[2] The density of each specimen taken from the recrystallized plaques was determined by graphical interpolation of its equilibrium height in the density-gradient liquid

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[1] Figures in brackets indicate the literature references at the end of this paper.
[2] Available from the American Society for Testing and Materials, 1916 Race Street, Philadelphia, Pennsylvania 19103.

[3] Although paragraph 5.6 of the ASTM procedure calls for a preheating period of 5 min, we have employed a time of 15 s.

maintained at 23 ± 0.1 °C. Isopropanol and water were used as the density-gradient liquids. The column was calibrated by a series of glass beads whose density was known to within ± 0.0001 g/cm³. The sensitivity of the column was found to be about 0.0002 g/cm³ per mm column height, and the position of beads and specimens could be read to about 1 mm.

3. Results and Discussion

The molding and recrystallization of the plaques and the density measurements were performed on several different days according to ASTM procedures for sample preparation and density measurement. No significant day-to-day variation was found in the results. It was concluded that the preparation and recrystallization of the samples were consistent from one experiment to the next to within the precision of the density determination. The average density of twelve specimens taken from five samples (plaques) of blend I was found to be 0.97844 g/cm³ with a sample standard deviation of a single determination of 0.00014 g/cm³. The sample standard deviation of the mean of the twelve determinations is therefore 0.00004 g/cm³. These values of the mean density and the sample standard deviation of the mean are reported on the certificate for SRM 1475. The range of the measurements was from 0.9784 to 0.9786 g/cm³.

The average of ten density measurements on blend II was found to be 0.97817 g/cm³ with a standard deviation of a single determination of 0.00010 g/cm³. The density measurements for blend III gave a result of 0.97493 g/cm³ with a standard deviation of a single measurement of 0.00045 g/cm³, based on 21 measurements. These results are summarized in table 1. From the sample standard deviations and the systematic uncertainties associated with the calibrating beads,

we conclude that the overall accuracy of our measurements is well within the 0.05 percent limit cited in the ASTM procedure.

Although the 0.03 percent difference between the densities of blends I and II is statistically significant, for practical purposes this difference is unimportant in view of the 0.05 percent estimate of accuracy given in the ASTM procedure. On the other hand, the density of blend III (unmilled samples) is materially lower than that of blends I and II, and its standard deviation of a single measurement is much larger than those of blends I and II. These differences cannot be ascribed to differences in the crystallinity of the samples, for the parts of the procedure which might be expected to affect crystallinity (molding, quenching, recrystallization) were identical for all three blends. Nor can the differences be attributed to the lack of mixing of the individual pellets during the preparation of blend III, since pellet-to-pellet variation would be expected to yield a larger sample standard deviation for blend III than for blends I and II, but the same mean density. The most likely explanation of both the lower mean density of blend III and its larger sample standard deviation seems to be the presence of small voids resulting from the lack of milling and fluxing. This explanation is reinforced by the fact that specimens taken from plaques of blend III, even though carefully selected, appeared to contain small regions of entrapped air.

We conclude that the preparatory milling and fluxing stipulated in the ASTM procedure is essential if the stated precision of the procedure is to be realized.

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(Paper 76A2–708)

TABLE 1. *Density at 23 °C of Linear Polyethylene SRM 1475*

	Blend I	Blend II	Blend III
Average density, g/cm³............	*0.97844	0.97817	0.97493
Standard deviation of a single measurement......................	0.00014	0.00010	0.00045
Number of measurements........	12	10	21

* Certificate value.

The samples of blend I were prepared from pellets of polyethylene which had been fluxed and milled twice as long (about 4 minutes) as blend II. The samples of blend III were molded from the polyethylene pellets.

The Characterization of Linear Polyethylene SRM 1475. IV. Melt Flow Rate.

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The melt flow rate of SRM 1475 was determined to be 2.07 g/10 min at 190 °C under a load of 325 g by a method similar to procedure A of ASTM method D 1238–65T. This value is the average of determinations on 42 samples with a standard deviation of a single measurement of 0.040 g/10 min, and a range of 1.991 g/10 min to 2.132 g/10 min.

Key words: Extrusion plastometer; load; melt flow rate; orifice; orifice die; preliminary extrudate; test extrudate.

1. Introduction

Melt flow rate is widely used in polymer technology as a product specification since this value, which includes a statement of the load and temperature under which it is obtained, gives an indication of the processing properties of the polymer. The value of melt flow rate is expressed as the mass of polymer melt pushed from the heated cylinder of the extrusion plastometer through its precision bore orifice by its piston in a period of time, the standard units of the value being grams per ten minutes (g/10 min).

In this paper, we report the determination of melt flow rate for linear polyethylene SRM 1475. Use of the same measurements to investigate the uniformity of the material is described elsewhere [1].[1]

2. Experimental Procedure

2.1. Instrument and Method

The melt flow rate determinations were made with a commercial extrusion plastometer,[2],[3] by a method similar to Procedure A described in "Tentative Method of Measuring Flow Rates of Thermoplastics by Extrusion Plastometer," ASTM Designation: D 1238–65T.[4]

The dimensions of the plastometer cylinder, piston assembly and orifice, and the combined masses of the piston and passenger weight were found to comply with the instrument specifications described by the ASTM method.

In compliance with the ASTM method, the temperature indicator of the extrusion plastometer was calibrated with respect to a standardized iron-constantan thermocouple mounted in an undisturbed column of polymer melt in the plastometer cylinder. The thermocouple junction was fixed at the axis of the cylinder, 12.7 mm above the top surface of the orifice die in the bottom of the cylinder. An equilibrium temperature reading of 189.9 °C was observed on the mercury column thermometer in the cylinder while the thermocouple indicated the equilibrium temperature of the polyethylene melt to be 190.0 °C at the prescribed calibration point. Thus, prior to each series of flow rate determinations, the cylinder of the extrusion plastometer was brought to thermal equilibrium with a constant reading of 189.9 °C on the mercury column thermometer.

Further study of the temperature at other distances up to 48 mm above the orifice, under conditions required by the calibration procedure, indicated that the temperature was uniform above the 12.7 mm height in the undisturbed melt column. However, the temperature of the melt 1 mm above the orifice was 0.7 deg lower than the temperature of the melt 12.7 mm above the orifice. This thermal gradient at the bottom of the undisturbed melt column is probably at least partially erased in an actual flow rate determination by the downward flow of the piston-driven melt through the orifice.

A separate study of the effect of temperature indicated that the flow rate of SRM 1475 was not significantly altered by a temperature change of 1 deg from the specified test temperature, 190 °C.

The orifice die was found to have a bore diameter of 2.096 mm, well within the ASTM specification tolerance limits. Bore diameter tolerance gauges were used to test the bore of the orifice die frequently between series of flow rate determinations. According to this test, no detectable change occurred in

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[1] Figures in brackets indicate the literature references at the end of this paper.

[2] Certain commercial equipment, instruments, or materials are identified in this paper in order to adequately specify the experimental procedure. In no case does such identification imply recommendation or endorsement by the National Bureau of Standards, nor does it imply that the material or equipment identified is necessarily the best available for the purpose.

[3] Model 3, Tinius Olsen Testing Machine Company, Willow Grove, Pennsylvania 19090.

[4] Available from the American Society for Testing and Materials, 1916 Race Street, Philadelphia, Pennsylvania 19103.

the bore diameter during the entire course of the flow rate study.

2.2. Procedure

Because of the relatively high fluidity of the melt of the linear polyethylene, the light load of conditions D of the ASTM method was chosen for the flow rate determination. Conditions D of the ASTM method specify the temperature of the melt to be 190 °C, and the load (combined apparent masses of piston assembly and passenger weight) to be 325 grams.

In accordance with the ASTM procedure, each sample was first preheated in the plastometer for 6 minutes, and the preliminary extrudate cut from the bottom of the orifice. Test segments were then cut from the extrudate at 1 minute intervals for 11 minutes, and were examined for bubbles as they emerged from the plastometer. The ASTM procedure calls for the use of bubble-free samples obtained during the first 3 minutes. We found, however, that it was virtually impossible to obtain bubble-free samples of SRM 1475 within 3 minutes. Attempts were therefore made, as suggested in the ASTM procedure, to eliminate the bubbles by manually forcing out some of the melt during the preheat period. These attempts were unsuccessful and this modification was therefore not employed. Among the first five segments collected, however, at least two were completely free of bubbles, and generally one or two additional segments contained only bubbles so few and small that their individual flow rate values were not distinguishable from the values for the completely bubble-free segments. The extrudate from the fourth through the eleventh 1 min intervals contained no bubbles. In order to obtain measurements on bubble-free materials while staying as close as possible to the conditions specified by the ASTM procedure, we therefore determined flow rate for the certificate from the bubble-free segments obtained during the first 5 min. In order to investigate the effect of exceeding the prescribed time of 3 min, we also determined the flow rate from all the bubble-free segments obtained during the entire 11 min interval. The results obtained are described in the following section.

It was found unnecessary to apply the severe orifice-cleaning techniques, described in the ASTM method, between flow rate determinations of this particular polyethylene. It was found satisfactory to ram out the residual polyethylene with a soft copper wire of diameter nearly as large as that of the orifice bore, while the die was still hot. No effect on the flow rate values could by detected when this technique was applied between determinations.

3. Results and Discussion

Flow-rate measurements were obtained on a total of 42 samples, taken from thirteen different regions of the total supply of SRM 1475. As described elsewhere [1], no variation could be found from region to region. The results for the 42 samples were therefore pooled. The mean flow rate, based on segments obtained during the first 5 min as described in the preceding section, was found to be 2.07 g/10 min, with a sample standard deviation of 0.040 g/10 min, a range of 1.991 to 2.132 g/10 min, and a sample standard deviation of the mean of 0.0062 g/10 min. The mean value and the sample standard deviation of the mean are the values reported on the certificate for SRM 1475.

Measurements on segments collected during the entire 11 min period, well beyond the 3 min limit specified in the ASTM procedure, yielded a mean flow rate of 2.06 g/10 min, with a sample standard deviation of 0.038 g/10 min and a range of 1.987 to 2.142 g/10 min. The close agreement between the two calculations in mean value, standard deviation, and range suggests that either a longer preheat period or a longer measurement period could be used for this material without affecting the observed flow rate.

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(Paper 76A2–709)

The Characterization of Linear Polyethylene SRM 1475.
V. Solution Viscosity Measurements

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(December 15, 1971)

The limiting viscosity numbers of linear polyethylene SRM 1475 were determined at 130 °C in 1,2,4-trichlorobenzene, 1-chloronaphthalene, and decalin. Technique, including use of a novel solution transfer method, is described.

Key words: 1-chloronaphthalene; decalin; linear polythylene; limiting viscosity number; solution viscosity; 1,2,4-trichlorobenzene; viscometer.

1. Viscosity Measurements

Limiting viscosity number is a readily measured physical property which can be related empirically to molecular weight. A number of empirical relationships between limiting viscosity number and molecular weight of polyethylenes have been published [1–6].[1]

The limiting viscosity number $[\eta]$ is defined as the limit as the concentration c approaches zero of the viscosity number, $(\eta_s - \eta_0)/(\eta_0 c)$, where η_s and η_0 are the viscosities of the solution and solvent, respectively, in the limit of zero shear rate. Thus, $[\eta]$ may be determined by measuring the viscosity number over a range of finite concentrations and extrapolating to zero concentration, provided the solution and solvent viscosities are independent of shear rate.

The limiting viscosity number of SRM 1475, described in Part I of this series [7], has been determined in several solvents so that data can be compared with that already published, and also so that the sample can serve as a basis for interlaboratory comparison of technique.

Viscosity measurements were made in a Ubbelohde viscometer fitted with a removable sintered glass filter in the neck through which the viscometer is filled. Such a viscometer is described in ASTM D 1601–61.[2] Solutions were made up by weight in 25 cm³ flasks. The solvents used and their densities at 130 °C were: 1-chloronaphthalene, 1.098 g/cm³; 1,2,4-trichlorobenzene, 1.323 cm³; and decalin, 0.801 g/cm³. The polymer was weighed on an electric microbalance. Dissolution of the polymer was accomplished by heating at 140 °C with occasional vigorous agitation by magnetic stirrer. Usually an hour of heating and stirring sufficed.

The 1-chloronaphthalene was carefully purified and appeared to be about 99.5 percent pure by gas chromatographic analysis. The 1,2,4-trichlorobenzene was technical grade and appeared to be about 98.5 percent pure by gas chromatographic analysis. The decalin used was technical grade which had been subjected to a simple vacuum distillation to remove gross impurities. An assay showed approximately equal proportions of *cis-* and *trans-*decahydronaphthalenes.

All solvents used contained 0.1 percent 2,6-*di-tert-*butyl-4-methylphenol (Ionol) as an antioxidant, and the automatic viscometer used kept the solutions under nitrogen during measurement. It is believed that degradation of the polymer was negligible under these conditions, since little change in the flow times occured even when the solutions were left in the viscometer as long as overnight. Also, dilutions were not made, but rather a separate solution was used for each concentration. Under conditions such as long heating to dissolve high molecular weight fractions, significant degradation can occur. This is usually evinced by much larger scattering of points in the plot for the extrapolation to limiting viscosity number, since the extent of degradation is likely to vary from sample to sample.

The solutions were transferred into the viscometer by a wash-bottle-like siphon (see fig. 1) which was found to be more convenient than a heated pipette. Due to the low thermal mass of the fine glass tubing, it was found unnecessary to preheat the siphon. The viscometer was rinsed twice with about 4 cm³ of the solution,then about 10 cm³ was siphoned in for the flow time measurement. An automatic viscometer timer (Hewlett-Packard Model 5901B Autoviscometer[3]) was used to operate the viscometer and measure the flow times, while the viscometer was thermostatted in a Hewlett-Packard 5901A Constant Temperature Bath.[3]

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[1] Figures in brackets indicate the literature references at the end of this paper.
[2] Available from the American Society for Testing and Materials, 1916 Race Street, Philadelphia, Pennsylvania 19103.

[3] Certain commercial equipment, instruments, or materials are identified in this paper in order to adequately specify the experimental procedure. In no case does such identification imply recommendation or endorsement by the National Bureau of Standards, nor does it imply that the material or equipment identified is necessarily the best available for the purpose.

FIGURE 1. *Solution transfer siphon.*

TABLE 1.

Solvent	Limiting viscosity number, dl/g	Slope of viscosity number versus concentration, (dl/g)²
1-chloronaphthalene...............	[a] 0.890 ± 0.0032	0.48
1,2,4-trichlorobenzene.............	1.010 ± .0086	.55
decahydronaphthalene[b]..........	1.180 ± .0032	.72

[a] Uncertainties quoted are estimated standard deviations obtained from linear least squares fits of viscosity number versus concentration.
[b] Technical grade, which assayed at approximately equal proportions of *cis-* and *trans-* decahydronaphthalenes.
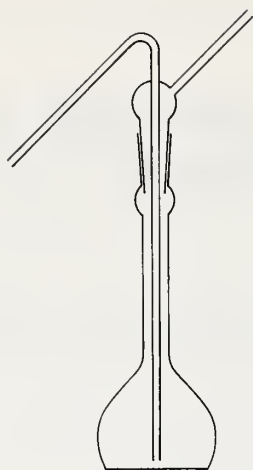
Advantages of an automatic viscometer timer are that the same amount of liquid is automatically drawn up to each time and that the flow time is measured to 0.001 seconds. The former contributes to the uniformity of the measurement, the latter makes possible the use of very dilute solutions, which greatly facilitates reliable extrapolations to zero concentration. A third advantage is that the cleanliness of the viscometer can be judged by the reproducibility of the flow times. Ordinarily, flow times will fall in a range of 0.03 seconds or less. In the presence of lint or dust the flow time will drift or will be randomly erratic with a range of up to 0.2 seconds.

Kinetic energy corrections were made in all cases [8]. These amounted to about 1.2 percent for 1,2,4-trichlorobenzene solutions, and about 0.3 percent for the decalin and 1-chloronaphthalene solutions. The rate of shear in the Ubbelohde viscometer used was about 1000–1500 seconds^{-1}. Measurements on a higher molecular-weight linear polyethylene fraction ($M_n = 355,300$, $M_w = 688,000$) at shear rates from 20 to 1500 s^{-1} reveal no dependence of measured viscosity number on shear rate. We therefore assume that the measured viscosity numbers of SRM 1475 exhibit no shear-rate dependence in this region.

Since the flow time (corrected to allow for kinetic energy of the effluent from the capillary) in a Ubbelohde viscometer is proportional to solution viscosity, the viscosity number can be written $(t_s - t_0)/(t_0 c)$, where c is concentration and t_s and t_0 are flow times for solution and solvent respectively. The standard deviation in the viscosity number of aliquots of the same solution was found to be slightly less than 0.3 percent. The viscosity numbers were fitted by least squares to linear functions of concentration; the limiting viscosity numbers were obtained as the resulting constant terms. The results are given in table 1. The viscosity numbers are plotted against concentration in figure 2, which also shows the straight lines obtained from the least-squares analysis.

Considerable care must be exercised in making viscosity measurements when decalin is used as the sol-

FIGURE 2. *Limiting viscosity numbers of SRM 1475.*

vent. Errors can easily arise due to the widely differing properties of the *cis-* and *trans-*isomers of decahydronaphthalene. The *cis-*isomer has a boiling point about 10 °C higher, a density about 3 percent greater, and a viscosity about 20 percent higher than the *trans-*isomer. If the solutions are made up by weight, density must be measured for each batch of solvent. Since the isomers differ in volatility, condensation in the upper part of the viscometer can change the isomeric composition in the solution. The resulting error in flow time can cause errors of 5 percent or more in the viscosity number. These errors were minimized in he present work by repeatedly equilibrating the viscometer with fresh portions of solvent. After reproducible solvent flow times were obtained, the flow times of the solutions were measured. We believe that by the use of these techniques, the errors due to the variable composition of decalin have been reduced to less than 1 percent.

2. References

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(Paper 76A2–710)

The Characterization of Linear Polyethylene SRM 1475. VI. Preparation of Calibrating Fractions

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Fractions for use in calibrating a gel permeation chromatograph were prepared by a Desreux column extraction method. The construction and operation of the fractionating system are described.

Key words: Column extraction fractionation; fractionation; linear polyethylene.

1. Introduction

In the process of determining the molecular weight distribution of SRM 1475 [1][1] it was necessary to calibrate a gel permeation chromatograph [2] with linear polyethylene. Fractions of linear polyethylene were used for this purpose. The fractions were subsequently used to establish relations between limiting viscosity number (intrinsic viscosity) and molecular weight [3]. The requisite fractions were prepared by a column extraction [4] technique, using a solvent system which has been described in considerable detail by Chiang [5] and others.

2. Experimental Procedure

The fractionation apparatus was constructed as depicted in figure 1. The column temperature is maintained by surrounding it with a narrow, deep oil bath, $20 \times 20 \times 90$ cm. The stirrer and heater are placed inside a long tube to promote efficient thermal exchange between the top and bottom of the tank.

The solvent inlet to the column is a small concentric tube reaching to the bottom of the packed column. The efflux collects above the column packing and is periodically drawn off through a slightly larger tube concentric with the inlet tube. The liquid is forced out by nitrogen pressure. The 8 cm diameter column is packed
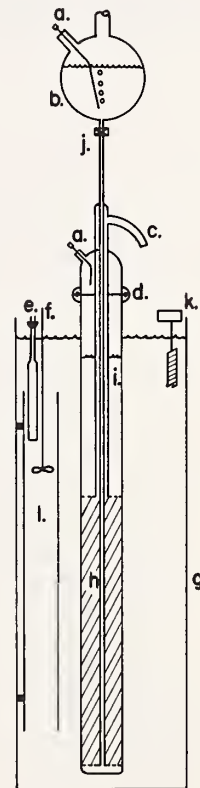

FIGURE 1. *Section of fractionation apparatus.*

(a) nitrogen inlets; (b) preheating flask; (c) efflux siphon; (d) o-ring flange; (e) heater; (f) stirrer; (g) tank; (h) packed column; (i) effluent liquid; (j) inlet tube; (k) thermoregulator; (l) circulating tube.

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[1] Figures in brackets indicate the literature references at the end of this paper.

with Johns-Manville Celite No. 545[2] to a depth of about 55 cm. The free liquid volume of the packed column is about 2000 cm³.

In operation, the column was heated to 127 °C, the polymer in xylene was allowed to flow in, and the column was allowed to cool slowly overnight. All of the polyethylene except a small amount of low molecular weight was thereby precipitated in the column. The cooling rate at 90 °C was about 0.2 °C/min. The cooled (50 °C) xylene was displaced by a poor solvent, 2-butoxyethanol, while the precipitated polyethylene was retained in the column. The column was reheated to 127 °C, causing the polyethylene to melt and swell with the poor solvent. The column was then extracted with mixtures of xylene and 2-butoxyethanol which were successively better solvents. The solutions of extracted polyethylene were siphoned into flasks containing cold ethanol. The polyethylene was filtered out, washed with ethanol, air dried, and then dried in vacuum at 50 °C.

All solvents contained 0.1 percent Ionol (2,6-di-tert.-butyl-4-methylphenol) as an antioxidant. They were preheated under nitrogen to over 130 °C before being admitted to the column. This served to degas the solvent, preventing the formation of bubbles in the column. Typical input concentration was 1 percent

polymer in xylene. Extracting mixtures were 15–55 percent xylene. Recovery was ordinarily 97–98 percent, but no great effort was made to obtain absolutely quantitative recovery of material.

Samples PE 7 to PE 180 were prepared by fractionating SRM 1475. Yield was three to six grams of each sample. Samples PE 200 to PE 600 were prepared from Phillips Marlex 6002. These fractions contained two to four grams each.

Light-scattering [6], osmometry [7], and gel permeation chromatography [2] studies were carried out with these samples. The final results are tabulated in paper X of this series [2].

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(Paper 76A2–711)

The Characterization of Linear Polyethylene SRM 1475. VII. Differential Refractive Index of Polyethylene Solutions

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The value of *dn/dc* for polyethylene in 1-chloronaphthalene at 135 °C, required for the determination of molecular weight by light scattering, was found to vary with molecular weight. Similar changes were found in 1,2,4-trichlorobenzene, the gel permeation chromatograph solvent. The absolute value of *dn/dc* decreases by about 2 percent as the polymer molecular weight increases from 12,000 to 110,000.

Key words: 1-chloronaphthalene; *dn/dc*; differential refractive index; refractometer; refractive index; 1,2,4-trichlorobenzene.

1. Introduction

Since the change of refractive index with concentration, *dn/dc* (differential refractive index), enters as a squared term in the light scattering equation, its accuracy is of considerable importance for obtaining reliable values of molecular weight of polymers. The first determination of *dn/dc* of polyethylene in 1-chloronaphthalene (table 1) found in the literature was by Nichols and was reported by Billmeyer [1].[1] It was measured at 90 °C and 125 °C using a divided cell technique, giving values of −0.199 ml/g and −0.191 ml/g respectively. The latter value is the one most often quoted. Kobayashi, Chitale, and Frank [2], using an interferometer technique, obtained a some-

what lower value at 90°, namely −0.183. Nicholas [3] found a very low value (−0.257 at 125 °C) using a Rayleigh differential refractometer at concentrations of 0.15 to 0.7 g/100 ml. This result seems to be completely out of line with the other values reported and may be due to the greater errors incurred working at low concentrations. The use of such low concentrations would appear to be unnecessary inasmuch as *dn/dc* is found to be constant at the concentrations used in this work, which range from 0.5 g/100 ml to 4 g/100 ml.

Most of the other literature values fall in the range of −0.188 to −0.199 [4,5,6]. The recent data are those of Drott and Mendelson [7], Chiang and Rhodes [8] and Benoit et al. [9]. Drott and Mendelson provide considerable detail about their procedure, which appears to

TABLE 1. *Literature values of* dn/dc *for polyethylene in 1-chloronaphthalene*

					dn/dc in ml/g			
Refs.	1	2	3	6	22	7	8	9
Temp. °C								
90	−0.199	−0.183			−0.198			
99.5							−0.1924	
104.5							−.1927	
105				−0.188				
109							−.1934	
114							−.1927	−0.1957
120							−.1917	
125	−.191		−0.257		−.195	−0.195	−.1911	
127								−.1967
128								−.1955
135							−.190	
139								−.1956
140						−.191		−.1961
145								−.1967

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[1] Figures in brackets indicate the literature references at the end of this paper.

be thorough and careful, and obtained a value of −0.191 at 140 °C and −0.195 at 125 °C. Chiang believes his values for a low molecular weight branched sample of −0.195 at 80 °C [10] are consistent with his values for higher molecular weights which range from −0.193 at 100 °C to −0.190 at 135 °C. Benoit et al. measured dn/dc between 141 °C and 150 °C finding values about $2\frac{1}{2}$ percent higher than those of Chiang and Billmeyer. The change in dn/dc with temperature is insignificant in this temperature range.

In view of the uncertainties described above and the importance of accurate values of dn/dc, it appeared necessary to make as accurate a determination as possible for the Standard Reference Materials Program. It soon became evident that dn/dc was to some extent a function of molecular weight. This may account for some of the discrepancies in the literature but these could not be readily resolved because in most cases no characterization is provided for the polyethylene used in the dn/dc measurement. It was also necessary to measure the variation with molecular weight in 1,2,4-trichlorobenzene since this solvent is used in gel permeation chromatography with the assumption that dn/dc is constant.

2. Experimental Procedure

The determination of the change of refractive index with concentration is most conveniently accomplished by a differential refractometer. The instrument employed here was the image displacement type, in which light passes through a cell consisting of two adjacent prismatic compartments, one containing solvent, the other dilute solution. It may be easily shown that in the limit as the difference Δn between the refractive index of solution and of solvent becomes small, the displacement Δd of the imaged light source from its position with pure solvent in both compartments of the cell becomes proportional to Δn, i.e.,

$$\Delta n = k \Delta d$$

where k is the proportionality constant and is determined by calibration with a substance of known refractive index.

2.1. Optical System

The optical system, consisting of the elements shown in figure 1, is mounted on an optical bench 125 cm long. Light from an air cooled mercury lamp passes
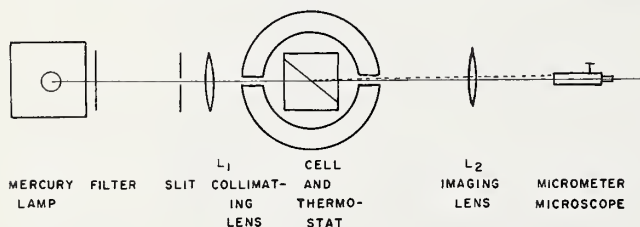
through a combination of filters which transmits green monochromatic light at 5460 Å. This light enters a slit, passes through the collimating lens, L_1, then through the cell, where the deviation due to the refractive index difference takes place. The displaced slit, imaged by the lens, L_2, is observed with a micrometer eyepiece having a 10 mm scale and a drum divided to 0.01 mm. The entire optical system is carefully aligned so that the collimated beam is normal to the face of the cell. The system was stable in that once the optical components were fixed the reading did not change over a period of several days with a given solvent in both compartments of the cell.

2.2. Glass Cell

The sample cell, supplied commercially [11][2] is a sinter fused Pyrex optical cell 15 mm square with plane parallel windows. The partition is set at such an angle that the light beam forms an angle of incidence of approximately 69° with the normal to the surface of the partition. This cell is provided with a fused top with openings which are closed by Teflon stoppers, thus eliminating the problem of evaporation which in the past has caused troublesome temperature gradients at high temperatures.

2.3. Cell Holder

In order to achieve temperature stability over long periods of time and to keep the temperature difference between the two compartments of the cell down to a few hundredths of a degree, considerable care was necessary in the design of the cell holder. As in the apparatus discussed by Benoit et al. [9], the cell is set into a rectangular opening in the center of a cylindrical aluminum block, 4 in in diameter and 5 in high (fig. 2) containing a $\frac{3}{8}$ in hole for passage of the light beam. Aluminum 1100 was used because of its superior heat conductivity. The aluminum block is positioned by three bakelite pins inside a $\frac{1}{3}$ in thick brass shell of 5 in diameter, leaving a half inch air space to minimize heat loss. Both the aluminum block and the brass shell are heated by coils of wire embedded in silicone rubber. Additional heat is supplied by means of four rod heaters inserted into holes in the block and by another coil heater, also embedded in silicone rubber, underneath the brass shell. The temperature of the cell holder is maintained by a thermistor temperature controller. The entire assembly is insulated by a laminate composed of eight layers of balsa wood alternating with aluminum foil. Short term temperature fluctuations of the aluminum block were of the order of 0.001 °C. Drift during a set of measurements was no greater than 0.01 °C.

Brice [12] recommends that the temperature difference between solvent and solution should be no greater than 0.01 °C. Attempts to measure this difference by simply inserting thermocouples into each

MERCURY   FILTER   SLIT L_1 CELL L_2 MICROMETER
LAMP   COLLIMAT-   AND   IMAGING   MICROSCOPE
              ING   THERMO-   LENS
              LENS   STAT

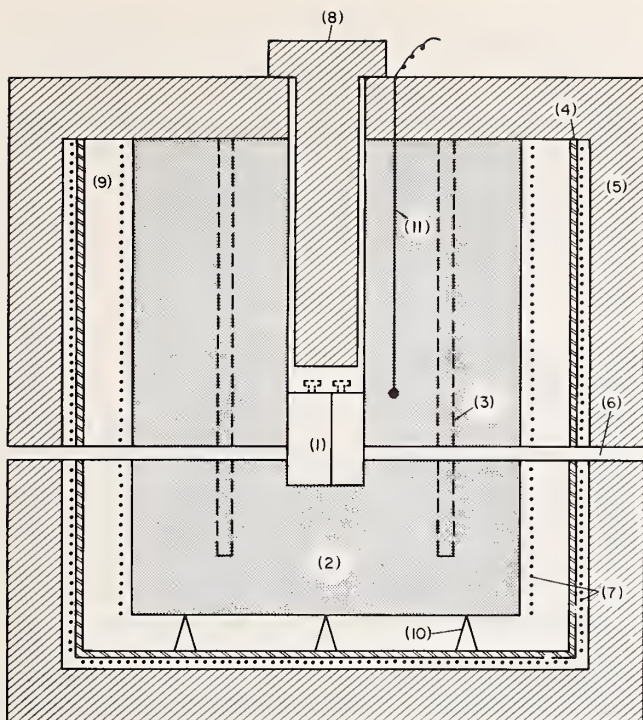FIGURE 1. *Optical system, schematic.*

FIGURE 2. *Heating block for cell.*

(1) Divided cell, (2) aluminum cylinder, (3) cartridge heaters, (4) brass shell, (5) balsa wood-aluminum foil laminate, (6) opening for light path, (7) heaters embedded in silicone rubber, (8) balsa wood cap, (9) air space, (10) bakelite positioning pins, (11) thermistor.

compartment were unsuccessful, probably because of heat loss through the openings for the thermocouple leads and through the leads themselves. In view of the construction described above it is doubtful that a significant difference existed. In any case the effect of such a difference would be cancelled since measurements were made first with solution on one side and solvent on the other and again with solution and solvent reversed.

3. Materials

3.1. Solvents

Reagent grade 1-chloronaphthalene was double distilled, center cuts being taken each time. Observ-

able impurities were less than 0.05 percent by gas liquid chromatography. The 1,2,4-trichlorobenzene, technical grade, was not further purified and 0.05 percent Ionol (2,6-di-*tert.*-butyl-4-methylphenol) was added as an antioxidant in order to use the same material used in the gel permeation apparatus [13]. Gas liquid chromatography revealed only a single major peak containing at least 99 percent of the material.

3.2. Polymers

Measurements of dn/dc were made on several polyethylenes. They are: (1) SRM 1475, the linear polyethylene standard reference material described previously [14]; (2) fractions of SRM 1475 obtained by column extraction of this polyethylene [15]; (3) SRM 1476, the branched polyethylene standard reference material. The available data are provided in the certificate for this material. Additional details will be given in a forthcoming publication; (4) fraction R 1201–7 is a linear polyethylene supplied by the Monsanto Chemical Company; (5) AC–6 is a polyethylene wax obtained from the Allied Chemical Corporation.

The number average molecular weights of these materials were obtained in various ways, as indicated in tables 2 and 3. Some were obtained by direct measurement by osmometry [16]; others were determined by gel permeation chromatography (G.P.C.) [13]. The number average molecular weights of fractions 12x and 7y were estimated from molecular weight measurements made on other fractions prepared by the same process. For three of the samples (AC–6, R 1201–7, and SRM 1476), the values supplied by the manufacturer were used.

4. Procedure

For each concentration two readings of the displacement of the light beam were made. The first was taken with the solvent on one side and solution on the other and another reading was taken with these reversed. One-half the difference between the two readings multiplied by the calibration constant gave the value of the refractive index difference Δn. This is similar to the procedure of Brice and Halwer [12] ex-

TABLE 2. dn/dc *of Polyethylenes in 1-Chloronaphthalene at 135 °C*

Sample	M_n	dn/dc, ml/g	Stand. dev. of dn/dc,[e] ml/g	No. of points [e]
SRM 1475....................................	[a] 18,310	−0.1932	0.00016	5
SRM 1476....................................	[b] 25,200	−.1916	.00028	5
Fraction R 1201–7........................	[b] 12,300	−.1931	.00042	3
Fraction PE 15............................	[c] 13,500	−.1929	.00035	3
Fraction 12x................................	[d] 110,000	−.1883	.00088	2
Fraction PE 120..........................	[c] 112,200	−.1879	.00059	4

[a] Value obtained from Gel Permeation Chromatography [13].
[b] Value provided by manufacturer.
[c] Determined by osmometry [16].
[d] Estimated as described in text.
[e] The estimated standard deviation of the slope, calculated by linear regression of the refractive index difference, Δn, on the concentration c, assuming a zero intercept. The number of points in each regression line is shown in column 5.
For convenience all standard deviations are given to two significant figures, with no implication that such precision is warranted.

TABLE 3.   dn/dc of Polyethylenes in 1,2,4-Trichlorobenzene at 135 °C

Sample	M_n	dn/dc, ml/g	Stand. dev. of dn/dc,[d] ml/g	No. of points [d]
AC–6......................................	[b] 2,000	− 0.1085	0.00028	3
SRM 1475..............................	[a] 18,310	− .1085	.00015	5
Fraction 12 AC........................	[a] 34,800	− .1082	.00019	3
Fraction 7y..............................	[c] 77,000	− .1073	.00038	3
Fraction 12x............................	[c] 110,000	− .1063	.00014	4

[a] Value obtained from Gel Permeation Chromatography [13].
[b] Approximate value, supplied by manufacturer.
[c] Estimated as described in text.
[d] The estimated standard deviation of the slope, calculated by linear regression of the refractive index difference, Δn, on the concentration c, assuming a zero intercept. The number of points in each regression line is shown in column 5.
For convenience all standard deviations are given to two significant figures, with no implication that such precision is warranted.

cept that since it is not possible, as in their apparatus, to rotate our cell housing because of its large bulk, the cell is kept fixed and the contents reversed. Readings with solvent on both sides were made occasionally to make certain that the beam's position through the center of the cell had not shifted.

Solutions were made up by weight, and concentrations were calculated from measurements of solvent densities and partial specific volumes. The densities at 135 °C of 1-chloronaphthalene and 1,2,4-trichlorobenzene were found to be 1.095 g/ml and 1.315 g/ml respectively. The partial specific volumes were approximated from measurements of the change in density on dissolving the polymer to specified concentrations. The values obtained were 1.29 ml/g in 1-chloronaphthalene at a concentration of 0.03 g/ml and 1.30 ml/g in 1,2,4-trichlorobenzene at a concentration of 0.01 g/ml. It was assumed that at the low concentrations employed here the partial specific volume is constant, so that the volume increase on dissolving polymer is equal to the weight of the polymer multiplied by this approximate partial specific volume. The polymer was dissolved in the solvent at 140 °C and about 1.5 ml was transferred by a heated hypodermic syringe to the cell. The compartment was not cleaned and dried when its content was changed but was thoroughly rinsed beforehand with solvent and solution of the new concentration. A period of at least 15 min was allowed after transfer for temperature equilibration before readings were taken. The standard error (15 readings) was about 2×10^{-6} in Δn or about 0.2 percent. The least square slopes computed from these data show a standard deviation of the slope of from 0.1 to 0.5 percent, as shown in tables 2 and 3. The standard deviation of the slope for the standard reference sample is about 0.1 percent.

No refractive index data at 135 °C are available for calibration of differential refractometers. We therefore calibrated our instrument with aqueous solutions of NBS sucrose at 25 °C and assumed the calibration did not change with temperature. The most likely cause for a change in calibration would be a change in the angle of the glass partition of the cell. Measurements in a cell similar to ours by Benoit et al. [9] of sodium chloride solutions up to 70 °C did not reveal any changes with temperature.

The partial specific volume of sucrose in water was taken as 0.618 ml/g at 25 °C [19]. The value of 0.1429 ml/g for dn/dc at 5460 Å at 25 °C, obtained by Norberg and Sundeloff [18], was employed in the calibration of the apparatus. This value agrees very well with the results of other authors [19–21]. Bodmann [21] has shown that dn/dc is constant up to concentrations of at least 0.025 g/ml. We found that the displacement Δd of the light beam is linear with concentration for concentrations as high as 0.04 g/ml and displacements up to 5 mm, the limit of our instrument scale. The calibration constant k for our instrument was found to be 1.1417×10^{-3} refractive index units per mm deflection, with a standard deviation of 0.1 percent.

5. Results and Discussion

The values of dn/dc for various polyethylenes in 1-chloronaphthalene are listed in table 2. The value for the linear sample, SRM 1475 at 135 °C is − 0.193 ml/g and for the branched sample, SRM 1476, is − 0.192. The numbers fall into two groups: values of − 0.192 to − 0.193 for low number average molecular weights (11,000–25,000) and a decidedly higher value, − 0.188 for the higher molecular weights. In order to obtain a better idea of the molecular weight dependence and to determine whether gel permeation chromatography intensities need to be corrected for molecular weight, dn/dc was measured in 1,2,4-trichlorobenzene over a range of molecular weights. These are enumerated in table 3 and a plot of these values against $1/M_n$ is shown in figure 3. The change in dn/dc in going from an M_n of 12,000 to 110,000 is about the same in both solvents, a decrease of about 2 percent in absolute value. Several
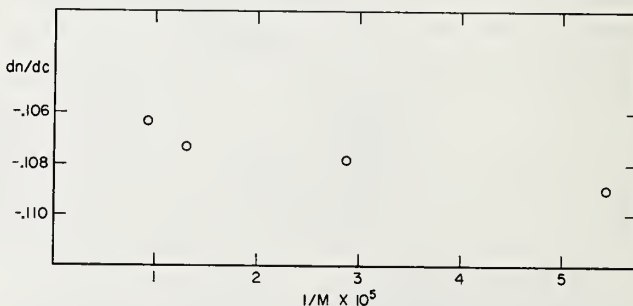

FIGURE 3.   Differential refractive index in 1,2,4-trichlorobenzene.

factors contribute to the belief that this is a real change. It is outside the limits of error of the determination, for which the standard deviation is of the order of 0.5 percent. Different fractions of the same molecular weight, such as 12x and PE 120 in one case, and R 1201–7 and PE 15 for another, the latter two coming from different starting polymers, have the same values of dn/dc. The infrared spectra of the whole polymer SRM 1475 and a high molecular weight fraction, showing a smaller dn/dc, are similar, indicating the absence of some chemical group which might account for the difference in dn/dc.

Unfortunately it was not possible to measure dn/dc for fractions of M_n greater than 110,000 because of the difficulties of handling the extremely high viscosities of these fractions at the concentrations needed to give meaningful results. For most determinations concentrations ran between 0.5 to 4 g/100 ml but were limited to no greater than 2 g/100 ml for the high molecular weight samples.

6. Conclusion

Because dn/dc changes with molecular weight, it is necessary to use the correct value of dn/dc in light scattering work, as is done in Paper VIII of this series [23]. Although 1-chloronaphthalene measurements were not made for the intermediate molecular weight range, the measurements in trichlorobenzene are extensive enough to show that dn/dc changes continually so that interpolation should provide sufficiently precise values for the former solvent. No data are available, however, at number averages greater than 110,000, and since it can not be assumed that the absolute value of dn/dc decreases without limit, the value at high molecular weights is taken, for the present, as constant at -0.188 ml/g in 1-chloronaphthalene.

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(Paper 76A2–712)

The Characterization of Linear Polyethylene SRM 1475

VIII. Light-Scattering Studies on Polyethylenes in 1-Chloronaphthalene

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Light-scattering measurements have been made on a series of linear polyethylene fractions and a linear polyethylene standard reference material (SRM 1475). All measurements were made in 1-chloronaphthalene at 135 °C, and over an angular range from 45 ° to 135 °. The data were analyzed to obtain the weight average molecular weights, second virial coefficients and root-mean square end-to-end distances.

Key words: End-to-end distance; light scattering; linear polyethylene; polyethylene fractions; M_w; second virial coefficient; solution properties.

1. Introduction

Several investigators [1, 2][1] have used the technique of light scattering to obtain weight-average molecular weights, second virial coefficients and radii of gyration for polyethylene in dilute solutions. In this paper, we report the results of light scattering studies on a series of linear polyethylene fractions with molecular weight ranging from about 1.9×10^4 to about 6.9×10^5. The weight-average molecular weights reported here were employed in the calibration of a gel permeation chromatograph used [3] to obtain the molecular weight distribution of Standard Reference Material 1475, Linear Polyethylene. We also report the direct determination of weight-average molecular weight for SRM 1475 by light scattering.

2. Experimental Procedure

2.1 Apparatus

The light scattering photometer described by McIntyre and Doderer [4] was used for most of the studies reported here. However, a few measurements were made on a modified Brice-Phoenix Photometer (Phoenix Precision Instrument Company, Philadelphia, Pa.).[2] Consistent results were obtained from the two instruments, and data from both instruments are included in the analysis of results.

All measurements on polyethylene solutions were made at 135 °C, using a heated cell holder [5] designed and constructed in this laboratory. A schematic drawing of the cell holder is shown in figure 1. It consists of two concentric cylinders wrapped with heating wire, insulated with alternating layers of balsa wood and aluminum foil bonded together with silicone rubber adhesive. A slot, not shown in the figure, extends slightly more than halfway around the oven at the height of the sample cell to provide paths for the in-
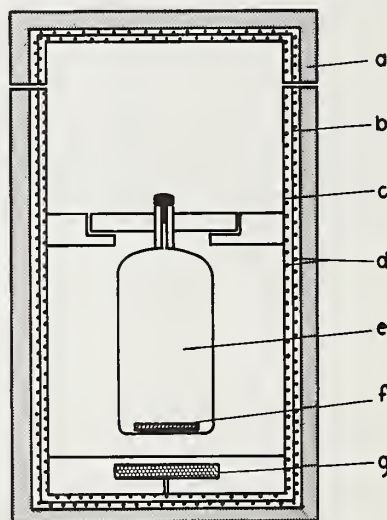

FIGURE 1. *Schematic drawing of high temperature oven for light scattering cells.*

a. Insulation, b. outer cylinder, c. inner cylinder, d. heating wire, e. light scattering cell, f. stirring bar, g. rotatable magnet.

cident, transmitted and scattered light. A small rotatable magnet under the sample cell permits stirring when desired. The scattering cells used with the oven are clear Pyrex cylindrical cells fitted with capillary necks and Teflon stoppers to minimize contamination by dust.

Measurements on polyethylene were made with the outer cylinder heated to 130 °C and the temperature of the inner cylinder controlled to maintain the sample at 135 °C. No attempt was made to monitor the temperature of the solutions in the light scattering cell while measurements were being taken. However, in preliminary tests, the temperature at various points in the stirred solvent was monitored with thermocouples. The liquid attained a steady temperature of 135° in 15 minutes and thereafter showed temperature variations of less than ± 0.05 °C during a period of one hour.

A solution of polystyrene in toluene was used as a working standard to calibrate the instrument. Measurements of absolute scattering on the working standard were made at room temperature (about 25 °C) in a semi-octagonal sample cell with a clear (unblackened) back surface. The temperature control employed for the higher-temperature measurements on polyethylene was felt to be unnecessary for the room-temperature reference measurements. The oven and cell holder described above were therefore not used for the reference measurements.

2.2. Preparation of Samples

The preparation of the linear polyethylene fractions is described in paper VI of this series [6]. The solvent employed was Fisher Reagent Grade 1-chloronaphthalene which was passed through activated 28–200 mesh silica gel before use. Gas chromatographic analysis of the solvent showed less than 0.1 percent observable impurity. Before being filled with solution, the light scattering cells were cleaned with hot chromic acid, rinsed with distilled water, dried in a dust-free atmosphere, and rinsed from three to five times with filtered 1-chloronaphthalene.

Each sample was prepared by adding approximately 10 cm³ of solvent to a weighed amount of polyethylene, stirring at 130–135 °C until the polyethylene dissolved (usually 1 to 1½ h) and weighing the resulting solution. The sample was then filtered as described below into a weighed scattering cell. After light scattering measurements had been taken, second and third concentrations were prepared for measurement by adding approximately 5 cm³ increments of filtered solvent, weighing the scattering cell before and after each addition. Weight per unit volume concentrations were calculated from the weights of solvent and solute, solvent density, and partial specific volume [7] of polyethylene in 1-chloronaphthalene. For some representative samples, the final concentration was checked by evaporating 10 cm³ of the solution and weighing the residue. In all cases, the concentration so obtained agreed with that calculated from the known dilutions to within 1 percent.

The samples were filtered with a heated 40 cm³

hypodermic syringe fitted with a "Swinney Adapter" filter holder (Millipore Corp., Bedford, Mass. 01730). A ball joint sealed to the top of the syringe allowed the rate of filtration to be controlled with nitrogen gas under pressure. The nitrogen pressure was adjusted to give a flow rate of approximately 1 drop per second. Faster flow rates resulted in less clean samples as determined by their erratic scattering at low angles. Two Metricel type, Alpha–6 filter discs with a nominal pore size of 0.4 μm (Gelman Instrument Co., Ann Arbor, Mich. 48106) were used for each filtration. These discs had been found to be resistant to 1-chloronaphthalene and could be used at temperatures up to 150 °C without apparent damage. They were rinsed with the material to be filtered before use, and were changed after each filtration.

During filtration, the syringe was heated by placing it in a glass tube wrapped with heating wire and maintained at 135–140 °C. The needle of the syringe was inserted into the capillary neck of the light-scattering cell, and the filtration was carried out in a stagnant air box to minimize contamination by dust.

2.3. Scattering Measurements

Scattered intensities were measured at eleven scattering angles ranging from 45° to 135°. Measurements on SRM 1475 were made at 25 concentrations, in the range from 1.7×10^{-3} to 20.8×10^{-3} g/cm³. Measurements on each of the seven fractions listed in table 1 were made at six concentrations. The concentrations chosen varied with the molecular weights of the fractions, from a range of 1.8×10^{-2} to 5.7×10^{-2} g/cm³ for PE 15 to a range of 0.7×10^{-3} to 2.6×10^{-3} g/cm³ for PE 600. Measurements were also made on pure solvent. The incident illumination in all cases was the mercury green line of wavelength 5461 Å, plane-polarized with its electric vector perpendicular to the scattering plane.

As mentioned previously, a solution of polystyrene in toluene was used as a working standard. The absolute scattering of the working standard at 90° was first determined. As each polyethylene solution was measured, the scattered intensity from the working standard at 90° was also recorded. Thus, the quantity actually obtained was the ratio of the scattering from the solution (or solvent) at each angle to that of the working standard at 90°.

3. Treatment of the Data

The use of light scattering to determine molecular weight and size parameters of macromolecules in dilute solution is well established [8]. At sufficiently low concentrations and small scattering angles, the ratio of solution concentration to scattered light intensity may be expanded in a Taylor series in concentration and in the sine of half the scattering angle. For plane-polarized monochromatic light scattered through an angle θ, the result for a solution of monodisperse

material may be expressed in the form [9]:

$$\frac{Kc}{R_\theta} = \frac{1}{M} + \frac{h^2 R_G^2}{3M} + 2A_2c + \ldots, \quad (1)$$

with:

$$K = (4\pi^2 n^2/\lambda_0^4 N_A)(dn/dc)^2(1-\cos^2\psi\sin^2\theta), \quad (2)$$

$$R_\theta = r^2[I(\theta,c) - I(\theta,0)]/(vI_0), \quad (3)$$

and

$$h = (4\pi/\lambda)\sin(\theta/2) = (4\pi n/\lambda_0)\sin(\theta/2), \quad (4)$$

where

c is solution concentration (weight per unit volume),
M is the molecular weight of the solute,
R_G is the radius of gyration of the solute,
A_2 is the second virial coefficient of the solution,
λ_0 is the wavelength *in vacuo* of the radiation,
n is the index of refraction of the solvent at wavelength λ_0,
$\lambda = \lambda_0/n$ is the wavelength of the radiation in the solvent,
N_A is Avogadro's number,
dn/dc, the so-called differential refractive index, is the derivative (at constant temperature and pressure and in the limit of zero concentration) of solution refractive index with respect to concentration,
θ is the angle between the incident and scattered wave vectors,
ψ is the angle between the electric vector of the incident radiation and the plane containing the incident and scattered wave vectors,
I_0 is the intensity of the incident radiation,
$I(\theta,c)$ is the scattered intensity at angle θ for a solution of concentration c,
r is the distance from the scattering center to the point at which the scattered intensity is observed, and
$v = v(n,\theta)$ is the volume of solution from which the scattered radiation is observed.

For the special cases $\psi = \pi/2$ and $\psi = 0$ (so-called vertical and horizontal polarization), the last factor in eq (2) becomes unity and $\cos^2\theta$, respectively. (The usually-quoted result for unpolarized incident radiation is obtained by averaging over all possible values of ψ, in which case the factor becomes $(1+\cos^2\theta)/2$.)

For a solution of polydisperse material, it can be shown [10, 11] that eq (1) still holds at sufficiently small scattering angle and low concentration, provided M is replaced by M_w, the weight-average molecular weight, R_G^2 is replaced by its z-average, $\langle R_G^2 \rangle_z$ [12], and A_2 is replaced by an "effective" value without simple interpretation [11].

In order to use eqs (1)-(4) to relate observed scattering to molecular parameters, it is necessary to know the functional dependence of the scattering volume, v, upon n and θ. For the geometry of our instrument, the scattering volume is inversely proportional to the square of the index of refraction of the material in the scattering cell [13,14]. A simple geometrical

argument suggests that for scattering angles not too close to 0° or 180°, the scattering volume should vary as the cosecant of the scattering angle. (The validity of the approximation was established for the present work, in the course of checking the alignment of the instrument, by measurements on fluorescein solutions.) Thus we can write

$$v(n,\theta) = v_0 n^{-2}\csc\theta. \quad (5)$$

Finally, the observed intensities must be corrected for the effects of reflections at the entrances and exits of the scattering cells, as discussed by Kratohvil [15]. When light impinges perpendicularly upon an interface between two regions with indices of refraction n_1 and n_2, the fraction f reflected is given by Fresnel's formula: $f = [(n_1 - n_2)/(n_1 + n_2)]^2$. In the light-scattering experiment, such interfaces occur at both the inside and the outside surfaces of the walls of the scattering cells. If we make the usual assumption that the difference between the index of refraction of the solution inside the scattering cell and the index of the glass in the cell walls is so small as to cause negligible reflection, we are left with only the interfaces between the cell walls and the air outside the cell to consider. By counting up the various possible paths resulting from multiple reflections of the incident and scattered beams, we can readily show that for a circularly cylindrical scattering cell, the observed intensity $I'(\theta,c)$ is related to the "true" intensity $I(\theta,c)$ (i. e., that which would be observed in the absence of reflections) by

$$I(\theta,c) = (1-f)^{-2}[(1+f^2)I'(\theta,c) - 2fI'(\pi-\theta,c)], \quad (6)$$

where $f = [(n_g - 1)/(n_g + 1)]^2$, and n_g is the index of refraction of the cell wall glass. Equation (6) is in agreement, to first order in f, with the approximate result obtained by Kratohvil [15] for this case.

For the semioctagonal cell used to determine absolute scattering by the working standard, only the intensity of the beam scattered through an angle $\theta = \pi/2$ and the intensity I_0 of the incident (unscattered) beam need be considered. For right-angle scattering, the light paths for this cell are identical with those for a circularly cylindrical cell, and the special case $I = I'$ obtained from eq (6) for $\theta = \pi/2$ also applies to this cell. For the incident beam, observed after passage through the semioctagonal cell, it can easily be shown that

$$I_0 = I_0'(1+f)/(1-f). \quad (7)$$

For the present work, the quantity $R_{\pi/2,s} = r^2 I_s/(vI_0)$, where we denote by I_s the intensity of right-angle scattering from the working standard, was first determined as described by McIntyre [13]. The intensity ratio I_s/I_0 was measured with the use of a set of calibrated filters, and was corrected for reflections as described above. For the semioctagonal cell employed, the quantities r and v_0 were obtainable from the

instrument geometry, and the scattering volume v was obtained from eq (5).

For measurements made on the working standard at 90° in the circularly cylindrical scattering cells, we can use the definition of $R_{\pi/2,s}$ and eq (5) to write

$$v_0 I_0/r^2 = I_s n_s^2/R_{\pi/2,s}, \qquad (8)$$

where n_s is the index of refraction of the working standard. With the use of eqs (2)–(6), the left-hand side of eq (1) can be rewritten in the form

$$\frac{Kc}{R_\theta} = \frac{4\pi^2 n_s^2 c (1 - \cos^2 \psi \sin^2 \theta) \csc \theta (dn/dc)^2}{\lambda_0^4 N_A R_{\pi/2,s}}$$

$$\times \left(\frac{I_s}{I(\theta, c) - I(\theta, 0)} \right). \qquad (9)$$

Thus, measurement of the scattering of the solution relative to that of the working standard (the last factor on the right-hand side of eq (9)), together with the value of dn/dc for the solution, yields Kc/R_θ. Equation (1) may then be used to determine M_w, $\langle R_G^2 \rangle_z$, and A_2 from the dependence of Kc/R_θ upon c and θ.

In order to extract molecular parameters from experimental values of Kc/R_θ, we employ the well-known Zimm method [16]. If we plot Kc/R_θ as a function of $\sin^2(\theta/2) + kc$, where k is a constant chosen for convenience, we obtain an array of points through which lines of constant concentration and lines of constant angle can be drawn, as exemplified in figure 2. Extrapolation of each of the constant-concentration lines to zero angle gives a set of points which constitute a plot of Kc/R_0 versus kc. According to eq (1), such a plot intersects the Kc/R_θ-axis at $1/M_w$, with a limiting slope of $2A_2/k$. In the same way, extrapolation of each of the constant-angle lines to zero concentration yields a plot of $\lim_{c \to 0} [Kc/R_\theta]$ versus $\sin^2(\theta/2)$. Combining eqs (1) and (4), we find:

$$\lim_{c \to 0}[Kc/R_\theta] = M_w^{-1}[1 + (16/3)\pi^2\lambda^{-2}\langle R_G^2 \rangle_z \sin^2(\theta/2)].$$

The intercept is therefore again $1/M_w$, and the limiting slope is a measure of $\langle R_G^2 \rangle_z$. In the special case of a linear random-coil chain one can estimate the mean-square distance, $\langle L^2 \rangle$, between the ends of the chain by using the relation [17] $\langle L^2 \rangle = 6 \langle R_G^2 \rangle$, although this
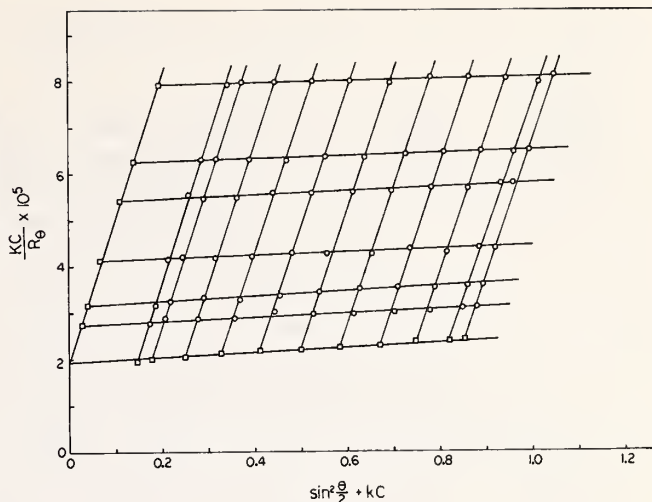

FIGURE 2. *Typical Zimm plot (Kc/R_θ versus $\sin^2(\theta/2) + kc$) obtained for linear polyethylene in 1-chloronaphthalene at 135 °C.*

The concentration c is expressed in g/cm³; the arbitrary constant k was chosen to have a value of 10 cm³/g. The other symbols are explained in the text. The circles are experimental values; the squares are extrapolations to zero angle at constant concentration and to zero concentration at constant angle.

relation has been established only for chains with Gaussian random-flight statistics.

4. Results

The results obtained for the linear polyethylene fractions and for SRM 1475 are summarized in table 1, together with the values of dn/dc used in calculating Kc/R_θ. For SRM 1475 and the fractions with M_w less than 200,000, measured values [7] of dn/dc were used. For fractions with M_w greater than 200,000, measured values of dn/dc were not available, but measurements on the lower-molecular-weight fractions appeared to suggest that by this point, dn/dc had reached a constant value of -0.188 ml/g independent of molecular weight. This value of dn/dc was therefore used in calculating Kc/R_θ for the fractions of M_w above 200,000.

Values of Kc/R_θ for each fraction and for SRM 1475 were analyzed by the Zimm technique, as described in the preceding section. In all cases, plots of Kc/R_θ versus $\sin^2(\theta/2) + kc$ were found to be linear throughout the entire angular range. A typical plot, obtained for SRM 1475, is shown in figure 2. For clarity, the plot

TABLE 1. *Weight-average molecular weights* M_w, *second virial coefficients* A_2, *and rms end-to-end lengths* $\langle L^2 \rangle^{1/2}$, *for linear polyethylenes in 1-chloronaphthalene at 135 °C.*

The uncertainties shown are estimates of the standard deviations obtained from linear least squares analyses of the corrected experimental scattering intensities, as described in the text.

Sample	dn/dc, ml/g	$M_w \times 10^{-3}$, g/mol	$A_2 \times 10^3$, mol · cm³/g²	$\langle L^2 \rangle^{1/2} \times 10^{-3}$, Å
PE 15	−0.193	19.1 ± 2.4	1.9	0.4
PE 40	−.191	49.4 ± 2.0	1.6	.6
PE 60	−.190	82.2 ± 7.1	1.6	.6
PE 120	−.188	170 ± 16	1.4	.7
PE 180	−.188	210 ± 30	1.2	.9
PE 350	−.188	520 ± 42	1.3	1.4
PE 600	−.188	688 ± 67	1.2	2.1
SRM 1475	−.193	52.0 ± 2.0	....	....

shows the data for only six of the 25 concentrations actually employed. The lack of downward curvature in the plots suggests that the samples were adequately cleaned [18].

The linear extrapolations necessary to obtain M_w, $\langle R_G^2 \rangle_z$, and A_2 were carried out by unweighted linear least-squares analyses. The results are given in table 1, together with estimates of the standard deviation in M_w inferred from the least-squares analyses. The values of the rms end-to-end length, $\langle L^2 \rangle^{1/2}$, given in table 1 were obtained from the values found for $\langle R_G^2 \rangle_z$ by use of the approximate relation $\langle L^2 \rangle = 6 \langle R_G^2 \rangle$, as described in the preceding section. It is clear from the lack of smoothness in the variation of A_2 and $\langle L^2 \rangle^{1/2}$ with molecular weight that they are to be regarded as no more than crude estimates. Estimates of the standard deviations in $\langle R_G^2 \rangle_z$ and A_2 from the least-squares analyses were unrealistically low (typically, about 5 per cent for A_2 and 50–100 Å for $\langle L^2 \rangle^{1/2}$), and are therefore not shown in the table. Values of $\langle R_G^2 \rangle_z$ and A_2 were not calculated for SRM 1475.

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[10] Kerker, op. cit., Ch. 8.
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$$\langle R_G^2 \rangle_z = \sum_i n_i M_i^2 R_{Gi}^2 \Big/ \sum_i n_i M_i^2 ,$$

where n_i is the number of molecules of the i-th component, of molecular weight M_i and radius of gyration R_{Gi}.
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The Characterization of Linear Polyethylene SRM 1475. IX. Number Average Molecular Weight of Fractions by Membrane Osmometry

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The number average molecular weights of a series of fractions of linear polyethylene have been determined using a high speed membrane osmometer. The M_n values of the fractions, which were prepared by an elution technique, were used in GPC calibration and subsequent characterization of linear polyethylene SRM 1475. The molecular weights, measurement techniques, and the precision of the measurements are presented.

Key words: Concentration dependence; linear polyethylene; membrane; number average molecular weight; osmometer; osmotic pressure; virial coefficient.

1. Introduction

In the course of the characterization of the linear polyethylene Standard Reference Material 1475 described in this series of papers [1],[1] the molecular weight distribution was determined [2] by gel permeation chromatography. The gel permeation chromatograph was calibrated with linear polyethylene fractions obtained [3] by a column elution technique. These fractions were characterized for use in the calibration procedure by determining their number- and weight-average molecular weights. Determination of the weight-average molecular weights from light-scattering studies is described elsewhere [4]. In the present paper, we report the determination of the number-average molecular weights, M_n, ranging from about 8,000 to about 350,000, from osmotic pressure measurements.

2. Experimental Procedure

2.1. Apparatus

Osmotic pressure measurements were made with a Hewlett-Packard Mechrolab Membrane Osmometer, Model 502[2]. This instrument, which has been described elsewhere [5], consists essentially of a photocell for detecting liquid flow across a semipermeable membrane, monitored by the motion of a bubble in a capillary tube, and a servomechanism for balancing the osmotic pressure by varying the liquid level on the solvent side of the membrane. It is characterized by rapid response time (of the order of a few minutes with a suitable membrane), negligible solvent transfer across the membrane [6], and small sample volume (about 0.3 ml).

2.2. Membranes

The semipermeable membranes employed were gel cellophane membranes, type 450D, obtained from Arro Laboratories, Inc. When received, they were swollen in an isopropanol-water solution. The following procedure was used to condition them to 1-chloronaphthalene, the solvent used in this work: 24 hours in 50 percent ethanol solution; rinsing with ethanol; 48 hours in ethanol; 24 hours in a 1:1 mixture of ethanol and acetone; 24 hours in a 1:1 mixture of acetone and toluene; rinsing with toluene; 24 hours in toluene; rinsing with 1-chloronaphthalene; heating (with an infrared lamp) in 1-chloronaphthalene under reduced pressure for a minimum of 1 hour, to drive off dissolved gases.

2.3. Procedure

Polyethylene solutions were made up by weight in distilled Fisher reagent grade 1-chloronaphthalene, in concentrations ranging from 0.5 to 12 g/l. Osmotic pressure measurements were made by first placing pure solvent in both sides of the osmometer and recording the level on the solvent side, then flushing out and filling the sample side with one of the solutions and recording the new solvent level. Several measurements were made for each solution. The reference solvent height was checked between solutions by flushing and refilling the sample side with pure solvent. The osmotic pressure for each solution is then given directly as the hydrostatic pressure

difference between solvent and solution. All measurements were made at a temperature of 130 °C.

3. Results and Discussion

In order to obtain values of M_n from the variation of osmotic pressure with solution concentration, we start with the familiar virial expansion, expressed in one of the two equivalent forms:

$$\pi/c = RT\left[\frac{1}{M_n} + A_2 c + A_3 c^2 \ldots\right],$$

$$= (\pi/c)_0 [1 + \Gamma_2 c + \Gamma_3 c^2 + \ldots], \qquad (1)$$

where π is the osmotic pressure of a solution of concentration c (weight per unit volume), relative to that of pure solvent, R and T are the gas constant and absolute temperature, respectively, the A's and Γ's are the virial coefficients, and the subscript zero denotes the limit of zero concentration.

According to eq (1), M_n is obtained directly from the zero-concentration intercept of a plot of π/c versus c. Such plots are shown in figure 1 for three typical fractions, PE 7, PE 120, and PE 350. Although the plot for PE 7, the lowest molecular-weight fraction, is essentially linear, the plots for the higher molecular-weight fractions show distinct curvature, and extrapolation to zero concentration presents a problem. In principle, the extrapolation may be performed by fitting π/c to a polynomial in c, thus determining some of the virial coefficients higher than the second. In the present case, however, the precision of the data and the concentration range spanned do not appear to warrant the determination of more than two parameters. We therefore resort to the approximate relationship $\Gamma_3 = \frac{1}{4}\Gamma_2^2$, which is frequently found to give

satisfactory results for polymer solutions in good solvents at sufficiently low concentrations [5, 7]. With the aid of this relation, and neglecting terms beyond the third virial coefficient, eq (1) may be rewritten in the form:

$$(\pi/c)^{1/2} = (\pi/c)_0^{1/2}(1 + \tfrac{1}{2}\Gamma_2 c). \qquad (2)$$

To the extent that the approximations implied in obtaining eq (2) are justified, a plot of $(\pi/c)^{1/2}$ versus c should yield a straight line with a zero-concentration intercept of $(RT/M_n)^{1/2}$ and a slope of $(RT/M_n)^{1/2}\Gamma_2/2$. Figure 2 shows the data of figure 1 replotted as $(\pi/c)^{1/2}$ versus c. The plot is clearly much more nearly linear than that of figure 1. We have therefore used a linear least-squares analysis to fit $(\pi/c)^{1/2}$ to a linear function of concentration, according to eq (2). The dashed lines in figure 1 are plots of eq (2), using the parameters obtained from the least-squares analysis. It is clear that for the higher molecular-weight fractions, use of a simple linear plot would introduce significant errors into the limiting zero-concentration value of π/c, and therefore of M_n.

The results of the least-squares analyses are shown in table 1. The standard deviations for the values of M_n range from about 0.1 percent for PE 7 to 2–4 percent for the higher molecular-weight fractions. For the lower molecular-weight fractions, accuracy is limited by the diffusion of solute through the membrane, as discussed by Staverman et al. [8, 9] and by Tung [10]. From observation of the drift in hydrostatic pressure over periods of an hour or more, we conclude that errors arising from this source are much smaller than the reproducibility of the measurements, even for the lowest molecular-weight fractions reported here. The accuracy of the M_n values for the high molecular-weight fractions is limited primarily by uncertainties arising from the use of the approximate eq (2) to fit the data. In the absence of information on the behavior of the higher virial coefficients, it is very difficult to estimate the uncertainty introduced by the use of eq (2). It is our feeling, however, that for all the fractions, the errors in M_n from all sources are unlikely to exceed 10 percent.
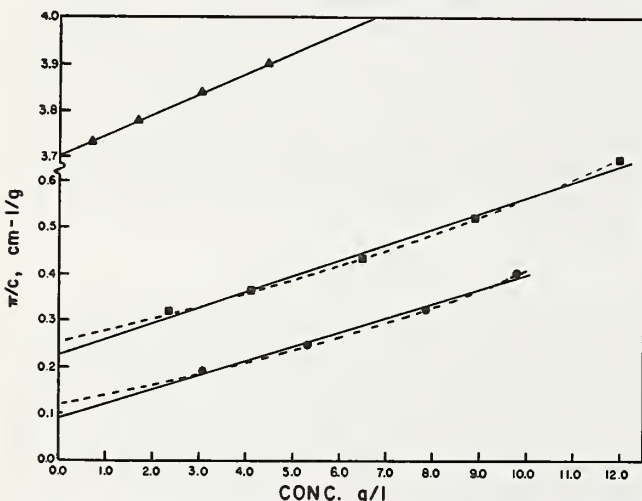
FIGURE 1. *Plots of π/c versus c, where π is osmotic pressure and c is concentration, for solutions of three fractions of linear polyethylene, PE 7 ($\triangle$), PE 120 ($\square$), and PE 350 ($\bigcirc$), in 1-chloronaphthalene.*
The solid lines are the results of linear least-squares fits of π/c versus c; the dashed lines are the results of linear least-squares fits of $(\pi/c)^{1/2}$ versus c.
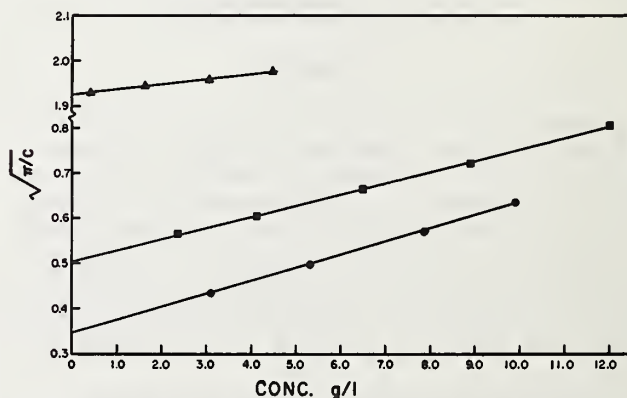
FIGURE 2. *The data of figure 1, replotted as $(\pi/c)^{1/2}$ versus c.*
The solid lines are the results of linear least-squares fits of the data in this form, and are equivalent to the dashed lines in figure 1.

TABLE 1. *Values of number-average molecular weight,* M_n, *and second virial coefficient,* A_2, *for solutions of polyethylene in 1-chloronaphthalene at 130 °C, inferred from measurements of osmotic pressure,* π, *versus concentration,* c, *by linear least-squares fit of the data to the form* $(\pi/c)^{1/2} = (RT/M_n)^{1/2} (1 + M_n A_2 c/2)$, *where R and T are the gas constant per mole and the absolute temperature, respectively.*

Number in parentheses following the M_n values are the standard deviations in M_n obtained from the linear least-squares analyses. The last column shows the number of solution concentrations at which each sample was measured.

Sample	M_n	$A_2 \times 10^4$, mol cm³/g²	Number of concentrations
PE 7...........	7,730(10)	15.78	4
PE 15..........	13,500(60)	11.48	5
PE 20..........	20,700(240)	11.16	4
PE 40..........	49,700(1,350)	10.29	5
PE 60..........	61,000(2,400)	9.00	5
PE 120........	112,200(1,900)	8.74	5
PE 180........	142,800(3,400)	8.44	5
PE 200........	200,600(5,800)	8.44	4
PE 350........	241,400(8,300)	7.05	4
PE 600........	355,300(1,400)	6.46	5

Values of the second virial coefficient, A_2, obtained in the least-squares analyses are also shown in table 1. Because of the uncertainties introduced by the use of eq (2) and by the precision of the experimental data, they should be regarded only as rough estimates of A_2 for these systems.

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(Paper 76A2–714)

The Characterization of Linear Polyethylene SRM 1475. X. Gel Permeation Chromatography

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The determination of the integral molecular weight distribution (MWD) of the linear polyethylene sample (SRM 1475) by means of gel permeation chromatography (GPC) is described. Both the experimental and mathematical details of column calibration and sample analysis are included.

Key words: Gel permeation chromatography (GPC); linear polyethylene; molecular weight distribution (MWD); number average; weight average.

1. Introduction

Heretofore the molecular weight characterization of polymer samples issued by the National Bureau of Standards has been primarily limited to the reporting of the number average molecular weight, M_n, and the weight average molecular weight, M_w. This paper describes the determination of the integral molecular weight distribution (MWD) of the linear polyethylene sample (SRM 1475) using the technique of gel permeation chromatography (GPC).

Prior to 1964 the determination of the MWD of a polymer was a tedious, time-consuming task. The first step was to fractionate the polymer using either batch fractionation or elution chromatographic techniques, both of which take advantage of changes in solution properties as a function of molecular weight. Then M_n and M_w measurements were made on each fraction, and, by knowing the weight percent of each fraction and by making certain simplifying assumptions about the molecular weight distribution of each fraction, the MWD was constructed.

In 1964, J. C. Moore first published his work on a process which he called gel permeation chromatography [1].[1] In GPC a dissolved sample of polymer

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[1] Figures in brackets indicate the literature references at the end of this paper.

is carried into and through a packed column by an appropriate solvent stream. The packing is such that the polymer is separated by molecular size, the larger molecules eluting first. By using the appropriate sensing devices, a function of the quantity of each molecular species is graphically displayed on a strip-chart recorder against the volume of solution emerging from the column (elution volume).

Thus, providing the system has been calibrated, one can determine the *MWD* for a given polymer sample in a very short time (usually less than one day). In the past, for each polymer system, the calibration procedure has required the use of well-characterized fractions of the polymer. This paper describes the techniques for the use of such fractions to provide a calibration curve, as well as the methods used to determine the *MWD* of our linear polyethylene whole polymer (SRM 1475). This Standard Reference Material, with its certified *MWD*, may then be used to calibrate other gel permeation chromatographs without requiring the use of fractions.

2. Description of Apparatus

The particular gel permeation chromatographic apparatus used was the Waters Model 200 (analytical scale) GPC.[2,3] This instrument is designed to analyze samples in the milligram range. The range of molecular weights which can be analyzed is dependent upon column selection. The pertinent features of the apparatus include, in order of flow: (1) a solvent reservoir, (2) a solvent degasser and preheaters, and (3) a precision metering pump with an adjustable pumping rate. The solvent flow emerging from the pump is split, one portion going into a set of columns being used for sample injection, and the other portion flowing through a second set of columns (reference set). Multi-port valving is used to inject the dissolved sample into the appropriate set of columns for analysis. The materials emerging from the two sets of columns pass through the two sides of a differential refractometer cell. The refractometer is stated by the manufacturer to be capable of detecting a difference of 10^{-7} in refractive index. The electronic output from the refractometer is recorded on a chart recorder, providing a continuous record of the difference in refractive index between the two streams. From the refractometer the sample-solvent mixture flows directly into a dump-syphon (5 ml capacity). When the syphon empties a spike is displayed on the recorder trace. In GPC language each spike or pip is referred to as a "count," and the sample injection is timed to coincide with a count, labeled the zeroth one. Temperature controls are provided for regulating the temperature throughout the column, detector, and syphon system. The one modification made to the Model 200 GPC was to provide a Teflon cover for the top of the syphon, to minimize solvent evaporation.

In the Model 200 GPC, each column is a 4-foot long, thin (3/8 in diameter) stainless steel tube packed with beads of a rigid, crosslinked polystyrene gel. The gel was prepared, characterized, and packed in the columns by Waters Associates, Inc. Five such columns were connected in series to form the column set used for the analysis. The columns had nominal exclusion limits of 1×10^7, 1×10^6, 1×10^5, 1×10^4, and 1×10^3 angstroms. This particular nomenclature [1] describes the minimal length in angstroms of a polystyrene molecule which will be excluded from permeation into the pores of the particular bead packing. The reference column set was a five column set having similar nominal exclusion limits.

3. Column Broadening Effects

From the cursory information in the introduction one might assume that a sample of monodisperse material injected into the GPC column would emerge from the column without change in concentration, producing a rectangular area as a recorder trace, having a base length equal to the volume of the sample injected. However, as is well known [2], in any chromatographic procedure the elution profile is broadened due to longitudinal diffusion in the column, producing, in the case of a single component, a bell-shaped curve. Therefore, in the case of a polydisperse polymer the height of the chromatogram at any point is due to the cumulative effect of the presence of many neighboring molecular weights. The amount of broadening observed is a function of the molecular weight, becoming larger as the molecular weight increases. The observed width is due to: (1) the actual *MWD*, (2) the spreading which occurs during flow through connecting tubing, (3) the effect due to spreading in the interstitial volume of the column packing, (4) the diffusional spreading within the pores, and (5) the effects of any adsorption within the system. The combined result may be not only spreading or broadening, but also skewing of the chromatogram.

Attempts to obtain analytical and numerical corrections for column broadening have been made by Tung and others [3–5], and the general state-of-the-art of GPC correction of broadening and skewing has been discussed by Hamielec [6, 7]. Fortunately, these effects tend to cancel out when the molecular weight distribution of a relatively broad material is obtained on a GPC column calibrated with much narrower fractions of the same material. Since the work reported here meets this condition, throughout this paper we assume that column broadening effects can be neglected. The validity of this assumption is discussed in section 9.

4. The Molecular Weight Distribution

In this section we describe the method used to calibrate the GPC. As stated in the preceding section, we assume that column broadening effects are not

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significant. In the notation of Frank [8], the calibration curve and the elution chromatogram are respectively:

$$m = m(v) \tag{1}$$

$$Z(m) = N(v). \tag{2}$$

In (1) the molecular weight, m, is a function of the elution volume, v. $Z(m)$ is the number of molecules in the particular sample having molecular weights which are greater than m; conversely $N(v)$ is the number of molecules in the sample which elute at volumes which are less than or equal to v. We define $z(m)dm$ as the number of molecules having molecular weights between m and $m + dm$, such that:

$$-z(m) = dZ(m)/dm = (dN/dv)(dv/dm)$$

$$= (1/m')(dN/dv), \tag{3}$$

where m' is the slope of the calibration curve, $m(v)$ versus v.

For this development we assume that the height, h, of the chromatogram from the base line results solely from the presence of molecules all having the same molecular weight, m, for each corresponding elution volume, v. In particular it is assumed that the detector responds linearly to the mass of the sample. Thus:

$$m\, dN(v)/dv = kh(v) \tag{4}$$

Combining (3) with (4), we obtain:

$$z(m) = -kh/mm' \tag{5}$$

Here k is an unknown instrumental scaling factor. The number-, weight-, and z-average molecular weights M_n, M_w, and M_z are given by:

$$M_n = \frac{\int mz(m)\,dm}{\int z(m)\,dm} = \frac{\int (h/m')\,dm}{\int (h/mm')\,dm}$$

$$= \frac{\int h(v)\,dv}{\int [h(v)/m(v)]\,dv}, \tag{6}$$

$$M_w = \frac{\int m^2 z(m)\,dm}{\int mz(m)\,dm} = \frac{\int (mh/m')\,dm}{\int (h/m')\,dm}$$

$$= \frac{\int m(v)h(v)\,dv}{\int h(v)\,dv}, \tag{7}$$

$$M_z = \frac{\int m^2(v)h(v)\,dv}{\int m(v)h(v)\,dv}. \tag{8}$$

The integral MWD is obtained in the following fashion. We define a function $w(m)$ by

$$w(m) = kh(v) \tag{9}$$

Then the cumulative weight percent, i.e., the weight percent of polymer of molecular weight less than M, is given by

$$100 \int_0^M w(m)\,dm \Big/ \int_0^\infty w(m)\,dm.$$

The integral MWD is usually given as cumulative weight percent versus log molecular weight.

5. The Calibration Curve

In this section we will presuppose that the column selection has been made such that $\log m$ is a nearly linear function of v in the molecular weight range of interest. Further, we will assume that we already have a calibration curve for polystyrene using the same column set.

The development of the calibration curve for any particular polymer usually starts from the preparation and characterization of narrow molecular weight fractions. The molecular weight range covered by the fractions should at least encompass the expected distribution of any samples to be subsequently analyzed. By *classical* characterization methods such as osmometry and light scattering, the average molecular weights M_n and M_w are determined for each fraction. One of two general methods is then used in producing a reliable calibration. In the first method we define M_0 as being that molecular weight species which elutes at the peak of a chromatogram, and we assume that a reasonable value of M_0 can be assigned by knowing both M_n and M_w. In the second method we assume that, for each fraction, we know the general form of the calibration curve, eq (1).

A. Method One

In this development we assume that the peak molecular weight, M_0, can be approximated by:

$$(M_n + M_w)/2 = M_0. \tag{11}$$

This assumption would appear reasonable to a first approximation providing that the polydispersity, M_w/M_n, is sufficiently close to unity, and that the chromatogram is symmetrical and single-peaked. From the individual chromatograms of the fractions we can determine the elution volume v_0 corresponding to M_0.

A preliminary calibration curve is constructed using the pairs of M_0 and v_0 values, and a least-squares fitting routine is employed to determine whether the points can be best described by a first, a second, or a third degree polynomial. Comparison of this preliminary calibration curve with the polystyrene calibration curve obtained with the same column set, should show qualitative similarity, i.e., the inflection points and general curvature at all elution volumes should be similar. Next equations (6) and (7), in conjunction with the preliminary calibration curve, are used to calculate M_n's and M_w's from the GPC chromatograms of the individual fractions, and from the preliminary calibration curve we determine the corresponding elution volumes. We now use the values of M_n and M_w (classically determined) together with the elution volumes (GPC determined) and plot these points on the preliminary calibration curve. This type of plot should reveal that most of the calculated points fall on or near the calibration curve. However, if all the number-average molecular weight points lie on one side of the curve and all of the weight-average molecular weight points lie on the other side, this is usually an indication of extreme broadening and skewness of the chromatograms resulting from poor column selection or poorly chosen operational parameters.

Assuming that this latter possibility did not arise, we now refit the data, using only the classically determined M_n's and M_w's and their calculated elution volumes (GPC), and at this point we consider that the best fit has been obtained.

B. The Second Calibration Method

In this method we assume that for our narrow distribution fractions (M_w/M_n from 1.1 to 1.7) the portion of the calibration curve for each fraction will be adequately represented by the relationship:

$$m(v) = \exp(a - bv). \qquad (12)$$

Of course we do not assume that the parameters a and b are the same for all fractions. Again following the development by Frank [8], we incorporate eq (12) into eqs (6) and (7). By using eq (12) in the denominator of (6) and in the numerator of (7), we obtain two expressions for the parameter a:

$$a_n = \ln M_n + \ln \int_0^\infty e^{bv} h(v)\,dv - \ln \int_0^\infty h(v)\,dv \qquad (13)$$

and

$$a_w = \ln M_w + \ln \int_0^\infty h(v)\,dv - \ln \int_0^\infty e^{-bv} h(v)\,dv. \qquad (14)$$

After equating a_n with a_w, simultaneous solution of eqs (13) and (14) yields unique values for the parameters a and b. If this were done for each fraction, a plot using eq (12) over the particular molecular weight range involved should result in a collection

of straight lines which define the calibration curve exactly.

Both the first and second methods herein described have the disadvantage that M_n and M_w have to be known for each fraction; further, an error in either M_n or M_w seriously affects the calculation. A modification of the second method allows calibrational information to be obtained when only M_n or only M_w is known for a fraction, and, in addition, may provide insight into the question of whether or not error exists in M_n or M_w as determined classically.

Rather than solving eqs (13) and (14) simultaneously to obtain a unique pair of values for the parameters a and b, we can, by treating each equation separately, obtain the functional dependence of a_n and a_w on b over the range of values for which b may be expected to lie. Either equation (13) or equation (14) implies a functional relationship between a and b, i.e., $a = a(b)$. The calibration curve (or rather, our estimate of it based on one determination of M_n or M_w) is then one of the family of curves.

$$\ln m(v) = a(b) - bv, \qquad (15)$$

and must therefore be tangent to the envelope of the family at some point. The envelope is easily obtained, in the usual way, as the simultaneous solution of eq (15) and the result of partial differentiation of eq (15) with respect to b at constant m and v, i.e.,

$$v = da/db. \qquad (16)$$

For each point $(v, m(v))$ on the calibration curve, the abscissa v is given by eq (16) and the ordinate $m(v)$ by eq (15). A calibration curve may then be estimated from measurements of M_n and/or M_w on a series of fractions by plotting the envelope obtained for each measurement and requiring that the calibration curve be tangent or nearly so to each envelope at some point. Since this technique uses each experimental value of M_n and M_w independently, it can be useful in identifying individual molecular weight measurements which may be in error.

6. Experimental Procedures

All samples were dissolved in nitrogen-saturated, 1,2,4-trichlorobenzene (TCB) (filtered technical grade) at 135 °C using magnetic stirring. They were then filtered under nitrogen pressure through regenerated cellulose filters having an average pore size of 0.45 microns. The GPC column oven was operated at approximately 135 °C, and nitrogen-saturated TCB was used. Five hundredths of one percent by weight of 2,6-di-tert.-butyl-4-methylphenol was added to the TCB as an antioxidant.

We assumed that the calibration curve for polyethylene would be similar to that for polystyrene and hence selected the column combinations used herein because they produced a nearly linear polystyrene calibration curve.

The degree of replication which can be achieved in successive chromatograms resulting from a series of

identical experiments appears to be almost totally dependent upon base-line stability. Of the various factors affecting this stability, we found that the constancy of both fluid flow and temperature was the most important. We were fortunate in that our GPC was in an area in which both the air temperature and air circulation were well controlled, and this, coupled with stable line voltages, gave good temperature stability throughout the system. We found that the constancy of solvent flow could be improved upon by keeping both of the column throttle valves in their open position, regulating solvent flow solely by adjustment of the pumping stroke. Under these conditions a point by point comparison of the heights of the chromatograms resulting from supposedly identical experiments showed maximum deviations of approximately ±1 percent, and a comparison of the areas of the chromatograms showed a maximum deviation of less than ±2 percent. Uncertainties of this magnitude could be explained almost completely by the observed base-line instability.

A change in operating parameters may result in a change of the chromatogram obtained with gel permeation chromatography. Ideally, perhaps, one would like to use samples of very small size and of vanishing concentration together with very small flow rates, but, practically, one compromises by using samples whose size and concentration are such that good detector response is obtained, and a flow rate such that the experiment can be run in a reasonable amount of time. A large number of experiments were run, varying each of the operating parameters in turn. We found that between the extremes of 0.2 and 2.0 ml/minute no discernible change occurred in the chromatograms resulting from replicate experiments. We therefore chose to use 0.5 ml/minute as the flow rate which would be used. With the whole polymer (SRM 1475) a change in the concentration from 0.02 to 0.2 weight percent caused no observable change in the calculated weight versus elution volume distribution. We therefore chose to use a 0.1 weight percent concentration for the whole polymer. The acceptable range of concentration varied for each fraction, but we found that the use of concentrations such that the resulting viscosities were similar to that of the 0.1 weight percent of the whole polymer was a good workable rule. The detector response was such that for a 0.1 weight percent concentration of whole polymer, an injection time of two minutes was required to produce a 1/2 to 2/3 full scale deflection of the recorder pen at the peak elution, and this injection time was used throughout.

For the final calibration, three independently prepared concentrations of each calibrating material were used. For each material, the three concentrations were such as to cause peak heights of nearly full scale, one-half of full scale, or one-quarter of full scale. When any two chromatograms within each triplicate set were compared in respect to height ratio at each elution volume, or in respect to area ratios, these were, within the precision of the experiment, identical to the ratios of the known concentrations. Therefore,

within the limits of our sensitivity, we believe that there was no dn/dc (refractive index change in respect to concentration) dependence with molecular weight. This observation is not in conflict with paper VII of this series [9], wherein, when greater sensitivity and precision was used, there indeed was shown to be a dn/dc dependence with molecular weight.

The integration of the chromatograms was performed numerically using Simpson's one-third rule, using an elution increment of 0.2 count.

7. Determination of the Calibration Curve

We used both polyethylene fractions and linear hydrocarbon samples in the determination of the calibration curve. Zone-refined samples of n-$C_{36}H_{74}$ and n-$C_{94}H_{190}$ were used. The values assigned to the hydrocarbon samples were the calculated molecular weights, and these calculated molecular weights were assigned to the peak elution volumes. Table 1 lists these materials together with the M_n and M_w values associated with each. These were determined by membrane osmometry and light scattering experiments. For details of the fractionation and of the determination of the molecular weights see papers VI, VIII and IX of this series [10–12]. Included also in table 1 are the GPC determined moments using the final calibration curve.

The calibration curve used in this work was determined by the use of method 1. For the preliminary determination of the calibration curve the chromatograms of the hydrocarbon samples and those of the fractions for which both M_n and M_w had been determined were used. As can be seen from table 1, the differences between the classical and GPC values of M_w for PE 350 and PE 60 do not appear consistent with those for the other fractions. The same discrepancies are shown when method 2 is employed (see fig. 2), and as a result we did not use the M_w values for these two fractions in the final determination of the calibration curve. In addition the M_w values for PE 200 and PE 20 were not available and only M_n values were employed. A plot of the final calibration curve is shown in figure 1, together with the points corresponding to M_0, M_n, and M_w for the fractions and the hydrocarbons.

The best least squares fit, using Method 1, was found to be a quadratic of the form ($\log M = a + bv + cv^2$), having the following coefficients and standard deviations:

$$a = 7.4 \quad \pm 1.2$$
$$b = 0.106 \quad \pm 0.07$$
$$c = -0.0051 \pm 0.0009$$

The standard deviation of the molecular weight was ±0.047 log M units. The volume v is in units of count.

Method 2 was also investigated. Figure 2 shows the calibration curve as derived by method 1, together with the envelope plots for each material used in the calibration. Figure 3 shows the same calibration curve, superimposed on which are the individual line segments calculated for the individual calibrating materials. The unusual behavior associated with the two

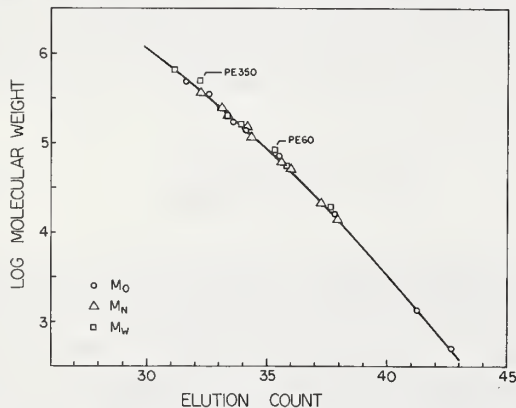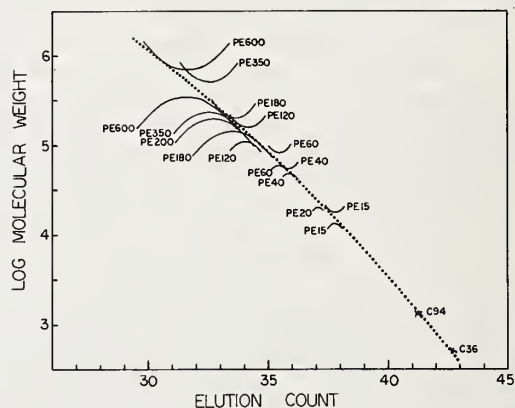| Sample	$M_n \times 10^{-4}$ [a]	$M_w \times 10^{-4}$ [b]	M_w/M_n	GPC analysis [c]		
				$M_n \times 10^{-4}$	$M_w \times 10^{-4}$	M_w/M_n
PE600..................	35.5	68.8	1.9	39	67	1.7
PE350..................	24.1	[d] 52.0	2.2	26	40	1.5
PE200..................	20.1	....	....	21	32	1.5
PE180..................	14.3	21.0	1.5	14.0	21	1.5
PE120..................	11.2	17.0	1.5	12.2	16	1.3
PE60	6.1	[d] 8.22	1.3	6	6.9	1.2
PE40	4.97	4.94	1.0	4.6	5.2	1.1
PE20	2.07	....	....	2.2	2.5	1.1
PE15	1.35	1.91	1.4	1.4	1.6	1.1
C_{94} Calc $M = 0.132 \times 10^4$			(1.00)	0.146	0.154	1.05
C_{36} Calc $M = 0.0506 \times 10^4$			(1.00)	.047	.049	1.04

[a] = results from membrane osmometry.
[b] = results from light scattering.
[c] = results of using the samples to calibrate the GPC, then analyzing the samples using calculated calibration curve.
[d] Not employed in construction of calibration curve. See text.

hydrocarbon samples results from using their calculated molecular weight to describe both M_n and M_w in eqs (13) and (14), and the slopes of these lines probably reflect the column dispersion. While the calibration curve was determined solely by method 1, it is obvious from figures 2 and 3 that method 2 would have produced a nearly identical curve.

It was interesting to note that the polyethylene calibration curve remained unchanged for approximately a year of continuous running. Immediately after starting up there would be an apparent shift of calibration, but the columns would return to their previous state after approximately 48 hours of running time. During this year the solvent and the general operational parameters were not changed.

8. Analysis of SRM 1475

The data in table 2 result from the analysis of twelve samples of SRM 1475, listed as samples 1 through 12. Each of the twelve samples was prepared from 25–75 pellets as described in section 6. The mean values and sample standard deviations of the mean for M_n, M_w,

FIGURE 2. *The calibration curve derived by use of Method One (dotted line) together with the calculated envelopes for each calibration sample.*

FIGURE 1. *The calibration curve derived by use of Method One, showing all calibration points.*
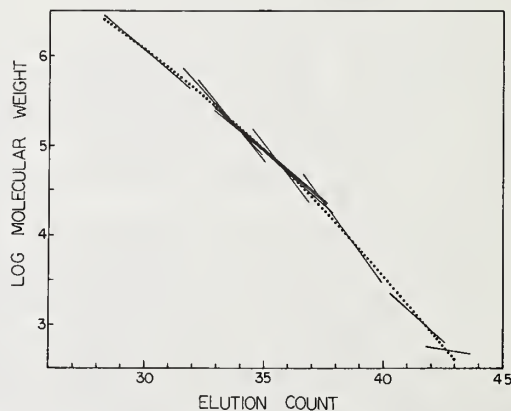
FIGURE 3. *The calibration curve derived by use of Method One (dotted line) together with the calculated line segments for each calibration sample for which both M_n and M_w are known.*

and M_z are those shown on the certificate for SRM 1475.

TABLE 2. *Gel permeation chromatographic analysis of SRM 1475*

Sample number	$M_n \times 10^{-4}$	$M_w \times 10^{-4}$	$M_z \times 10^{-5}$
1	1.833	5.503	1.518
2	1.789	5.309	1.490
3	1.681	5.013	1.291
4	1.726	5.247	1.369
5	1.921	5.451	1.351
6	2.019	5.149	1.200
7	2.068	5.400	1.243
8	1.820	5.065	1.220
9	1.883	5.538	1.534
10	1.789	5.310	1.489
11	1.657	5.032	1.277
12	1.789	5.669	1.583
Mean	1.831	5.307	1.380
Estimated standard deviation	0.125	0.214	0.127
Estimated standard deviation of mean	.036	.062	.037

Samples 1 through 4 were also subjected to a modified treatment, in order to check the effects of the handling procedure. After the solutions had been made up as described in section 6, and aliquots taken for the original chromatograms, the remaining portions of the solutions were allowed to cool to room temperature, precipitating the polymer, reheated and stirred as before to redissolve the material, and fresh aliquots rerun on the GPC column. The results obtained for the original and rerun materials are shown in table 3. If degradation or other modification of the sample occurred in the handling procedure, one might expect to find trends in the results for the original and rerun materials. No such trends are apparent, and the differences between original and rerun values are not inconsistent with the sample-to-sample spreads implied by the sample standard deviations given in table 2. We conclude that the effects of our sample handling procedure are not observable.

TABLE 3. *Effect of rerunning SRM 1475 samples*

Sample Number	$M_n \times 10^{-4}$	$M_w \times 10^{-4}$	$M_z \times 10^{-5}$
1	1.833	5.503	1.518
1, rerun	1.852	5.374	1.363
2	1.789	5.309	1.490
2, rerun	1.741	5.296	1.469
3	1.681	5.013	1.291
3, rerun	1.674	5.196	1.410
4	1.726	5.247	1.369
4, rerun	1.745	5.276	1.395

The integral *MWD* was obtained by summing the chromatograms for samples 1 through 12. In view of the lack of trend in the reruns of samples 1 through 4 described above, the rerun chromatograms were in-

cluded in the final sums. The resulting molecular weight distribution is given in table 4 and on the certificate for SRM 1475. Since this distribution is based on an "average" chromatogram, the values of M_n, M_w, and M_z obtained from it will not necessarily agree precisely with those quoted in table 2, which are obtained by averaging molecular weights from the individual chromatograms. From the *MWD*, we obtain values of 17,900, 52,900, and 139,000 respectively for M_n, M_w, and M_z. These may be compared with the values 18,310, 53,070, and 138,000, respectively, shown in table 2.

TABLE 4. *Cumulative molecular weight distribution of SRM (1475) by gel permeation chromatography*

log M	Wt. percent	log M	Wt. percent	log M	Wt. percent
2.800	0.0	4.014	15.2	5.065	90.7
2.865	.005	4.070	18.1	5.113	92.2
2.929	.020	4.126	21.5	5.161	93.7
2.992	.052	4.182	25.2	5.209	94.8
3.056	.105	4.237	29.3	5.256	95.8
3.119	.185	4.292	33.7	5.303	96.6
3.181	.343	4.346	38.5	5.349	97.3
3.243	.475	4.400	43.4	5.395	97.9
3.305	.706	4.454	48.5	5.440	98.4
3.366	.999	4.507	53.5	5.485	98.7
3.427	1.38	4.560	58.3	5.530	99.1
3.488	1.88	4.612	62.9	5.574	99.3
3.548	2.51	4.664	67.3	5.618	99.5
3.607	3.30	4.715	71.4	5.662	99.7
3.667	4.28	4.776	75.1	5.705	99.8
3.725	5.46	4.817	78.5	5.789	99.9
3.784	6.87	4.868	81.6	5.87	100.0
3.842	8.56	4.918	84.4		
3.900	10.50	4.967	86.7		
3.957	12.7	5.016	88.9		

9. Discussion and Conclusion

For both calibration and analysis, no corrections have been applied to take into account the effects of column broadening in the GPC system. While such effects are obviously present, it would appear that in this particular case, they do not significantly affect the validity of the analysis. Evidence to this effect may be found in the general agreement between values of M_w/M_n obtained from the chromatograms of the individual fractions and the classically determined ratios. Since SRM 1475 is substantially broader than the individual fractions, we conclude that column broadening effects are not likely to introduce serious errors into the molecular weight distribution obtained for SRM 1475.

The internal consistency of the experiment was checked by comparing chromatograms obtained from sixteen fractions of a sample of SRM 1475 with the chromatogram of the whole polymer. The polymer was fractionated into sixteen fractions using a conventional column elution technique [10]. The fractions were analyzed using GPC, and the areas under the result-

ing chromatograms were normalized to the weight of the respective fraction. These normalized curves were summed. When this reconstructed "whole polymer" was analyzed, the number- and weight-average molecular weights were calculated to be 17,400 and 53,300 respectively, whereas the best GPC values for the whole polymer were calculated as 18,300 and 53,100.

The results given herein reflect primarily on the precision of the measurement. A statement as to the absolute accuracy is impossible at this time; however, it is our opinion that the errors reflected in the uncertainty of the GPC analysis are largely those associated with the light scattering and membrane osmometry analyses of the calibrating samples.

Individual credit has not been given to some of the specific experimental and analytical details used herein. In many instances original credit is not known, but a great many of these details are to be found in references [8, 13, and 14].

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16. ABSTRACT (A 200-word or less factual summary of most significant information. If document includes a significant bibliography or literature survey, mention it here.)

The National Bureau of Standards has issued a linear polyethylene standard reference material, SRM 1475. This material is certified for weight average molecular weight (M_w), number average molecular weight (M_n), Z average molecular weight (M_z), molecular weight distribution, limiting viscosity numbers in several solvents, melt flow rate, and density. The experimental details of the determination and certification of these properties are given in these collected papers previously published in the Journal of Research of the National Bureau of Standards.

Key words, continued:
index; standard reference material; viscosity; weight average molecular weight; Z average molecular weight.

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