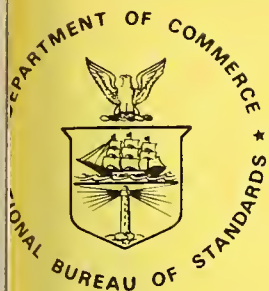


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NBS SPECIAL PUBLICATION **260-61**

U.S. DEPARTMENT OF COMMERCE / National Bureau of Standards

Standard Reference Materials:

THE CHARACTERIZATION OF LINEAR POLYETHYLENE SRM's 1482, 1483, AND 1484

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Standard Reference Materials:

**THE CHARACTERIZATION
OF LINEAR POLYETHYLENE
SRM's 1482, 1483, AND 1484**

Edited by:

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Herman L. Wagner

Center for Materials Science
National Measurement Laboratory
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Washington, D.C. 20234

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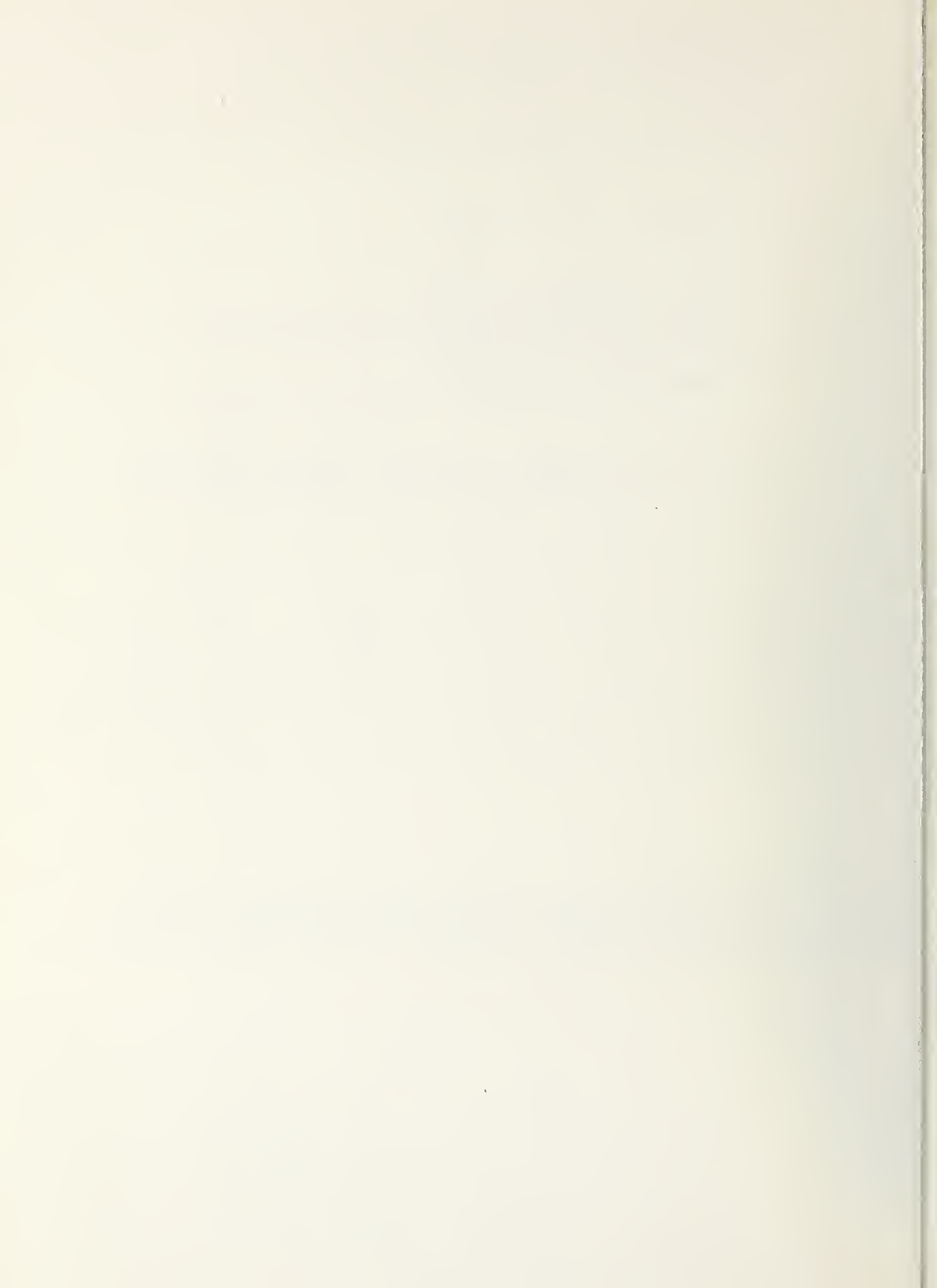
The Characterization of Linear Polyethylene SRM's 1482,
1483, and 1484

Peter H. Verdier
and
Herman L. Wagner, Editors

Center for Materials Science
National Measurement Laboratory
National Bureau of Standards
Washington, D.C. 20234

The National Bureau of Standards has issued a new series of three linear polyethylene Standard Reference Materials, SRM 1482, 1483, and 1484. These polyethylenes have molecular weights of the order of 10,000, 30,000, and 100,000 g/mol, respectively, and ratios M_w/M_n of weight-to number-average molecular weight of the order 1.2. Their number-average molecular weights (by membrane osmometry), weight-average molecular weights (by light scattering), and limiting viscosity numbers in two solvents (by capillary viscometry) are certified; the procedures employed are described in these collected papers previously published in the Journal of Research of the National Bureau of Standards.

Key Words: Capillary viscometry; fraction; light scattering; limiting viscosity number; membrane osmometry; narrow molecular weight distribution; number-average molecular weight; polyethylene; Standard Reference Material; weight-average molecular weight.



The Characterization of Linear Polyethylene SRM's 1482, 1483, and 1484. I. Introduction

Peter H. Verdier and Herman L. Wagner

Institute for Materials Research, National Bureau of Standards, Washington, D.C. 20234

(October 19, 1977)

The National Bureau of Standards has issued a series of three linear polyethylene Standard Reference Materials, SRM 1482, 1483, and 1484. These polyethylenes have molecular weights of the order of 10,000, 30,000, and 100,000 g/mol, respectively, and ratios M_w/M_n of weight- to number-average molecular weight of the order of 1.2. Their number-average molecular weights (by membrane osmometry), weight-average molecular weights (by light scattering), and limiting viscosity numbers in two solvents (by capillary viscometry) are certified; the procedures employed are described in subsequent papers in this series. In the present paper, we describe the preparation of the materials and some of their general properties.

Key words: Fraction; limiting viscosity number; narrow molecular weight distribution; number-average molecular weight; polyethylene; Standard Reference Material; weight-average molecular weight.

1. Purpose

The National Bureau of Standards has issued a series of three linear polyethylene Standard Reference Materials, SRM 1482, SRM 1483, and SRM 1484.* These polyethylenes have molecular weights of the order of 10,000, 30,000 and 100,000 g/mol, respectively, and ratios M_w/M_n of weight- to number-average molecular weight of the order of 1.2. Their number-average molecular weights (by membrane osmometry), weight-average molecular weights (by light scattering), and limiting viscosity numbers in two solvents (by capillary viscometry) are certified; the certificates are reproduced at the end of this paper. They are intended for the calibration and checking of instruments used in polymer technology and science for the determination of properties related to molecular weight and distribution in molecular weight, such as light scattering photometers and gel permeation chromatographs. They should also prove useful as characterized samples for measurements of other physical properties of linear polyethylene.

Succeeding papers of this series describe the experimental methods and data analysis techniques employed to obtain the certificate values of number-average molecular weight [1a],¹ weight-average molecular weight [1b], and limiting viscosity number [1c] of SRM's 1482, 1483, and 1484. In the present paper, we describe the preparation and treatment of these materials, and the results of various semiquantitative measurements employed to estimate such uncertified properties as distribution in molecular weight, impurity content, etc.

2. Description of Materials

Standard Reference Materials 1482, 1483, and 1484 were prepared from fractions produced by Waters Associates,

Inc., Milford, Mass.,² by large-scale gel permeation fractionation of a linear polyethylene from the same stock as Standard Reference Material 1475 (Linear Polyethylene Whole Polymer),* and with physical properties essentially identical with those of SRM 1475. As reported elsewhere [2, 3], SRM 1475 has a degree of branching undetectable by infrared spectroscopy and limiting viscosity number, and an ash content of 0.002 percent. We believe that the fractions will have the same characteristics. In other respects, however, the three fractions have different histories and are discussed separately in the following sections. Gel permeation chromatography of all three Standard Reference Materials shows a single symmetrical peak, without noticeable shoulders and of a width consistent with a ratio M_w/M_n of weight- to number-average molecular weight, estimated as described elsewhere [2], of the order of 1.2.

2.1. SRM 1483

According to the producer, the material for SRM 1483 was made by blending and reprecipitation (from xylene by cooling) of about 600 nine-gram "cuts" obtained by gel permeation fractionation, in Styragel columns, of the parent material in xylene with antioxidant at 135 °C. After the final reprecipitation, the material was washed with acetone and air-dried. Upon delivery to the National Bureau of Standards, the entire stock (about 5.5 kg) was blended in a two-cone porcelain-lined mixer, packed in 46 quart jars and stored under dry nitrogen at reduced pressure.

As a check on homogeneity, two samples were taken from each of five jars chosen at random. Viscosity numbers at five concentrations in 1,2,4-trichlorobenzene were determined as described elsewhere [1c] for each sample. The results showed no statistically significant variation within jars or between jars.

* Available through the Office of Standard Reference Materials, National Bureau of Standards, Washington, D. C. 20234.

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

² Certain commercial equipment, instruments, or materials are identified in this paper in order to 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.

Trace-metal analyses (by emission spectroscopy on $1/2$ g samples) showed iron and magnesium not exceeding 1 ppm. Total volatiles detected by mass spectrometry upon heating the material to 300 °C did not exceed 0.1 percent. Carbon-hydrogen analyses agreed with the values expected for $(\text{CH}_2)_n$ to within 0.1 percent.

2.2 SRM 1482

The gel permeation fractionations which produced the material for SRM 1483 as described above also yielded "cuts" at higher and lower molecular weights. Five batches of the lower molecular weight materials were found to be suitable for a Standard Reference Material with a molecular weight of the order of 10,000. The batches ranged in weight from 100 to 400 g each. Their M_w/M_n ratios, estimated by gel permeation chromatography, were in the range 1.1 to 1.2. The batches were individually reprecipitated as described below, then blended to make the final product.

Reprecipitation was carried out in 1,2,4-trichlorobenzene containing 500 ppm of an antioxidant, 2,6-di-*tert*-butyl-4-methylphenol. For each batch, sufficient solvent to make a solution of concentration 0.5–1 percent (by weight) was first heated to 130 °C under nitrogen, and the polyethylene added to the hot solvent while stirring. The material dissolved in 5–10 min. The solution was allowed to cool, over a period of several hours, to 45–65 °C with gentle stirring. During the cooling the polyethylene precipitated, forming a floating slurry, and the bulk of the liquid phase was pumped out.

The individual slurries were blended by mixing and vigorous stirring for $1/2$ –1 hr. The blended slurry was strained through a 40 mesh screen, filtered on filter paper, and washed three times with acetone. It was then air-dried at room temperature until the acetone content was about 10 percent by weight, dried in a vacuum oven for 13 hrs at 50 °C, and bottled under dry nitrogen at reduced pressure.

Residual 1,2,4-trichlorobenzene content was estimated spectrophotometrically. Four samples of SRM 1482 were dissolved in cyclohexane (at 140 °C under pressure) to give solutions with concentrations from 30 to 160 g/L. The polyethylene was then reprecipitated by cooling to room temperature and removed by filtration. The concentration of 1,2,4-trichlorobenzene in the filtrate was estimated by comparing its optical density at a wavelength of 286 nm with that of solutions of known amounts of 1,2,4-trichlorobenzene in cyclohexane. The 1,2,4-trichlorobenzene content estimated by this method was 0.053, 0.058, 0.059, and 0.065 percent for the four samples. Based on these values, we estimate an upper limit of 0.1 percent residual 1,2,4-trichlorobenzene in SRM 1482.

Total volatile content was estimated by measuring the weight lost by three 0.5 g samples and a blank after heating to 50 °C for one h at a pressure of about 10 Pa. During this period, the blank decreased in weight by 0.1 mg, and the samples decreased by 0.2, 0.3, and 0.4 mg. No further weight loss was observed in either blank or samples after $2\frac{1}{2}$ additional hours of drying under the same conditions. Based on these values, we estimate total volatiles in this material to be 0.1 percent or less.

2.3 SRM 1484

Six batches of the polyethylene "cuts" described in the preceding section were chosen as starting materials for SRM 1484. The batches consisted of 100 to 300 g each. Their gel permeation chromatograms showed major peaks at molecular weights in the vicinity of 100,000, with ratios M_w/M_n in the range 1.1–1.2, and minor peaks, amounting to a few percent of the total material, in the molecular-weight range 600–3600. In order to remove the low molecular-weight components, the individual batches were fractionally reprecipitated as described below.

Fractional reprecipitations were carried out in 1,2,4-trichlorobenzene containing 500 ppm 2,6-di-*tert*-butyl-4-methylphenol. The solvent was preheated and the solutions prepared as described above for SRM 1482, except that the higher molecular-weight material required $1/2$ to 1 h to dissolve. The hot solution was then cooled under nitrogen at a rate of 5–6 °C/h to 80 °C with gentle stirring. During the cooling, most of the higher molecular-weight components precipitated, forming a slurry. The stirring and the nitrogen cover were then discontinued, and the system was left unstirred at 80 °C until the precipitate had all floated to the surface of the liquid. The underlying liquid, containing the low molecular-weight contaminant, was pumped out. Fresh 1,2,4-trichlorobenzene preheated to 82–85 °C was added, and the precipitate was washed by stirring under nitrogen for several minutes, then left unstirred for a minimum of 3 h at 80 °C. The liquid underlying the precipitate was again pumped out and the remaining slurry cooled to room temperature. Gel permeation chromatograms of the resulting precipitates showed no sign of the low molecular-weight contaminant.

The individual slurries were blended by mixing and vigorous stirring for two hours. The blended slurry was filtered on filter paper and washed three times with ethanol and once with acetone. It was then air-dried at room temperature for a week, further dried in a vacuum oven at 50 °C for 8 h, and bottled under dry nitrogen at reduced pressure.

Residual 1,2,4-trichlorobenzene content of SRM 1484 was estimated spectrophotometrically by the method described in section 2.2 for SRM 1482. Measurements on two solutions, of initial SRM 1484 concentrations about 100 g/L, yielded estimates of 1,2,4-trichlorobenzene content of 0.057 and 0.063 percent. From these values, we estimate an upper limit of 0.1 percent residual 1,2,4-trichlorobenzene in SRM 1484.

Total volatile content was estimated by measuring the weight lost by four 0.5 g samples and two blanks after heating to 60 °C for 2 h at a pressure of 10–100 Pa. During this period, the blanks decreased in weight by 0.03 and 0.07 mg, and the samples decreased by 0.11, 0.11, 0.13, and 0.14 mg. No further weight loss was observed in either blank or samples after $2\frac{1}{2}$ additional hours of drying under the same conditions. These values appear to imply a volatile content of about 0.02 percent, which is inconsistent with the observed residual 1,2,4-trichlorobenzene content. We conclude that the drying procedure employed was incapable of removing all the residual 1,2,4-trichlorobenzene. As a result of the fractional reprecipitation of SRM 1484, we believe that 1,2,4-trichlorobenzene is the only likely volatile contami-

nant, and that our estimated upper limit of 0.1 percent residual 1,2,4-trichlorobenzene is also a safe upper limit for total volatiles in SRM 1484.

Note: The word liter is abbreviated lowercase "l" in these Certificates. The approved abbreviation for liter is capital "L".

3. References

- [1] The Characterization of Linear Polyethylene SRM's 1482, 1483, and 1484:
 - (a) Wagner, H. L., and Verdier, P. H., II. Number-Average Molecular Weights by Membrane Osmometry, J. Res. Nat Bur. Stand, (U.S.) **83**, No. 2 (Mar.-Apr. 1978).

- (b) Han, C. C., Verdier, P. H., and Wagner, H. L., III. Weight-Average Molecular Weights by Light Scattering, J. Res. Nat. Bur. Stand. (U.S.) **83**, No. 2 (Mar.-Apr. 1978).
 - (c) Wagner, H. L., and Verdier, P. H., IV. Limiting Viscosity Numbers by Capillary Viscometry, J. Res. Nat. Bur. Stand. (U.S.) **83**, No. 2 (Mar.-Apr. 1978).
 - [2] Hoeve, C. A. J., et al., The Characterization of Linear Polyethylene SRM 1475 (a series of ten papers), J. Res. Nat. Bur. Stand. (U.S.) **76A**, No. 2, 137-170 (Mar.-Apr. 1972); also available as Wagner, H. L., and Verdier, P. H. Eds., The Characterization of Linear Polyethylene SRM 1475, Nat. Bur. Stand. (U.S.). Spec. Publ 260-42, 39 pages (Sept. 1972).
 - [3] Wagner, H. L. and Hoeve, C. A. J., The Mark-Houwink Equation and Chain Dimensions of Linear Polyethylene in Theta Solvents, J. Polym. Sci., Symposium No. **54**, 327-339 (1976).

National Bureau of Standards
Certificate
Standard Reference Material 1482
Linear Polyethylene
(Narrow Molecular Weight Distribution)

P. H. Verdier and H. L. Wagner

This Standard Reference Material is intended for the calibration and checking of instruments used in polymer technology and science for the determination of molecular weight and molecular weight distribution, and for use as a characterized sample for measurements of other physical properties of linear polyethylene.

Property	Value	Sample standard deviation of value, percent	Number of degrees of freedom	Expected limit of systematic error, percent
Number-average molecular weight, M_n , g/mol ^a	11,400	0.7	18	2 ^b
Weight-average molecular weight, M_w , g/mol ^c	13,600	1.0	6	11 ^{b,d}
Limiting viscosity number, ml/g:				
at 130 °C in 1,2,4-trichlorobenzene	40.2	0.33	28	1
at 130 °C in 1-chloronaphthalene	36.4	0.31	24	1

a. Determined by membrane osmometry in 1-chloronaphthalene at 126 °C.

b. The expected limits of systematic error for the number- and weight-average molecular weights are based on analyses of the osmometry and light-scattering determinations, respectively, without taking account of the necessity of M_w exceeding M_n .

c. Determined by light scattering in 1-chloronaphthalene at 135 °C based on a value of $17.8 \times 10^{-6} \text{ cm}^{-1}$ for the Rayleigh ratio for the vertically polarized scattering of vertically polarized light, of wavelength 546 nm in vacuum, from benzene at 23 °C. This value was derived from published values of the unpolarized Rayleigh ratio and the depolarization ratio for unpolarized light [D. J. Coumou, J. Colloid Sci. 15, 408 (1960)]. The differential refractive index of this polyethylene in 1-chloronaphthalene at 135 °C, also required for the calculation of molecular weight, was found to be -0.195 ml/g at wavelength 546 nm in vacuum, based on the value of 0.1429 ml/g for the differential refractive index of sucrose in aqueous solution at 25 °C [Norberg and Sundelöf, Makromol. Chem. 77, 77 (1964)].

d. The expected limit of systematic error from all sources *except* the vertically polarized Rayleigh ratio for benzene is 4 percent.

Measurements leading to the certification of this Standard Reference Material were performed by J. E. Brown, R. G. Christensen, C. C. Han, J. R. Maurey, P. H. Verdier and H. L. Wagner in the Polymers Division, Institute for Materials Research.

Washington, D.C. 20234
October 18, 1976

J. Paul Cali, Chief
Office of Standard Reference Materials

This sample of linear polyethylene was prepared by recrystallization from 1,2,4-trichlorobenzene and subsequent blending of fractions produced by Waters Associates, Inc. of Milford, Mass., by large-scale gel permeation chromatography, from a linear polyethylene substantially identical with Standard Reference Material 1475 (Linear Polyethylene, Whole Polymer). Both total volatiles, estimated gravimetrically, and residual 1,2,4-trichlorobenzene content, estimated spectrophotometrically, do not exceed 0.1 percent.

The maximum rate of shear in the Ubbelohde capillary viscometers employed for the determination of limiting viscosity numbers was 3000 sec^{-1} for 1,2,4-trichlorobenzene and 2000 sec^{-1} for 1-chloronaphthalene. The maximum specific viscosities were 0.4 in both solvents.

A report describing the investigations required for this and related polyethylene Standard Reference Materials will be published as an NBS Special Publication.

National Bureau of Standards

Certificate

Standard Reference Material 1483

Linear Polyethylene

(Narrow Molecular Weight Distribution)

H. L. Wagner and P. H. Verdier

This Standard Reference Material is intended for the calibration and checking of instruments used in polymer technology and science for the determination of molecular weight and molecular weight distribution, and for use as a characterized sample for measurements of other physical properties of linear polyethylene.

Property	Value	Sample standard deviation of value, percent	Number of degrees of freedom	Expected limit of systematic error, percent
Number-average molecular weight, M_n , g/mol ^a	28,900	1.5	22	2 ^b
Weight-average molecular weight, M_w , g/mol ^c	32,100	2.3	4	11 ^{b,d}
Limiting viscosity number, ml/g:				
at 130 °C in 1,2,4-trichlorobenzene	79.4	0.39	24	1
at 130 °C in 1-chloronaphthalene	70.6	0.39	17	1

a. Determined by membrane osmometry in 1-chloronaphthalene at 129 °C.

b. The expected limits of systematic error for the number- and weight-average molecular weights are based on analyses of the osmometry and light-scattering determinations, respectively, without taking account of the necessity of M_w exceeding M_n .

c. Determined by light scattering in 1-chloronaphthalene at 135 °C based on a value of $17.8 \times 10^{-6} \text{ cm}^{-1}$ for the Rayleigh ratio for the vertically polarized scattering of vertically polarized light, of wavelength 546 nm in vacuum, from benzene at 23 °C. This value was derived from published values of the unpolarized Rayleigh ratio and the depolarization ratio for unpolarized light [D. J. Coumou, J. Colloid Sci. 15, 408 (1960)]. The differential refractive index of this polyethylene in 1-chloronaphthalene at 135 °C, also required for the calculation of molecular weight, was found to be -0.193 ml/g at wavelength 546 nm in vacuum, based on the value of 0.1429 ml/g for the differential refractive index of sucrose in aqueous solution at 25 °C [Norberg and Sundelöf, Makromol. Chem. 77, 77 (1964)].

d. The expected limit of systematic error from all sources *except* the vertically polarized Rayleigh ratio for benzene is 4 percent.

Measurements leading to the certification of this Standard Reference Material were performed by J. E. Brown, R. G. Christensen, J. R. Maurey and H. L. Wagner in the Polymers Division, Institute for Materials Research.

Washington, D.C. 20234
March 9, 1976

J. Paul Cali, Chief
Office of Standard Reference Materials

This sample of linear polyethylene was prepared by Waters Associates, Inc. of Milford, Mass., by large-scale gel permeation chromatography, from a linear polyethylene substantially identical with Standard Reference Material 1475 (Linear Polyethylene, Whole Polymer). Volatiles detected by mass spectrometric analysis upon heating the material to 300 °C did not exceed 0.1 percent. Viscosity numbers of samples chosen at random from different parts of the material showed no statistically significant sample-to-sample variation.

The maximum rate of shear in the Ubbelohde capillary viscometer employed for the determination of limiting viscosity numbers was 3000 sec⁻¹ for 1,2,4-trichlorobenzene and 2000 sec⁻¹ for 1-chloronaphthalene. The maximum specific viscosities were 0.4 in both solvents.

A report describing the investigations required for this and related polyethylene Standard Reference Materials will be published as an NBS Special Publication.

National Bureau of Standards

Certificate

Standard Reference Material 1484

Linear Polyethylene

(Narrow Molecular Weight Distribution)

P. H. Verdier and H. L. Wagner

This Standard Reference Material is intended for the calibration and checking of instruments used in polymer technology and science for the determination of molecular weight and molecular weight distribution, and for use as a characterized sample for measurements of other physical properties of linear polyethylene.

Property	Value	Sample standard deviation of value, percent	Number of degrees of freedom	Expected limit of systematic error, percent
Number-average molecular weight, M_n , g/mol ^a	100,500	3.7	34	4 ^b
Weight-average molecular weight, M_w , g/mol ^c	119,600	1.8	5	11 ^{b,d}
Limiting viscosity number, ml/g:				
at 130 °C in 1,2,4-trichlorobenzene	197.9	0.30	22	1
at 130°C in 1-chloronaphthalene	169.4	0.35	22	1

- a. Determined by membrane osmometry in 1-chloronaphthalene at 130 °C.
- b. The expected limits of systematic error for the number- and weight-average molecular weights are based on analyses of the osmometry and light-scattering determinations, respectively, without taking account of the necessity of M_w exceeding M_n .
- c. Determined by light scattering in 1-chloronaphthalene at 135 °C based on a value of $17.8 \times 10^{-6} \text{ cm}^{-1}$ for the Rayleigh ratio for the vertically polarized scattering of vertically polarized light, of wavelength 546 nm in vacuum, from benzene at 23 °C. This value was derived from published values of the unpolarized Rayleigh ratio and the depolarization ratio for unpolarized light [D. J. Coumou, J. Colloid Sci. 15, 408 (1960)]. The differential refractive index of this polyethylene in 1-chloronaphthalene at 135 °C, also required for the calculation of molecular weight, was found to be -0.191 ml/g at wavelength 546 nm in vacuum, based on the value of 0.1429 ml/g for the differential refractive index of sucrose in aqueous solution at 25 °C [Norberg and Sundelöf, Makromol. Chem. 77, 77 (1964)].
- d. The expected limit of systematic error from all sources *except* the vertically polarized Rayleigh ratio for benzene is 4 percent.

Measurements leading to the certification of this Standard Reference Material were performed by J. E. Brown, R. G. Christensen, C. C. Han, J. R. Maurey, P. H. Verdier and H. L. Wagner in the Polymers Division, Institute for Materials Research.

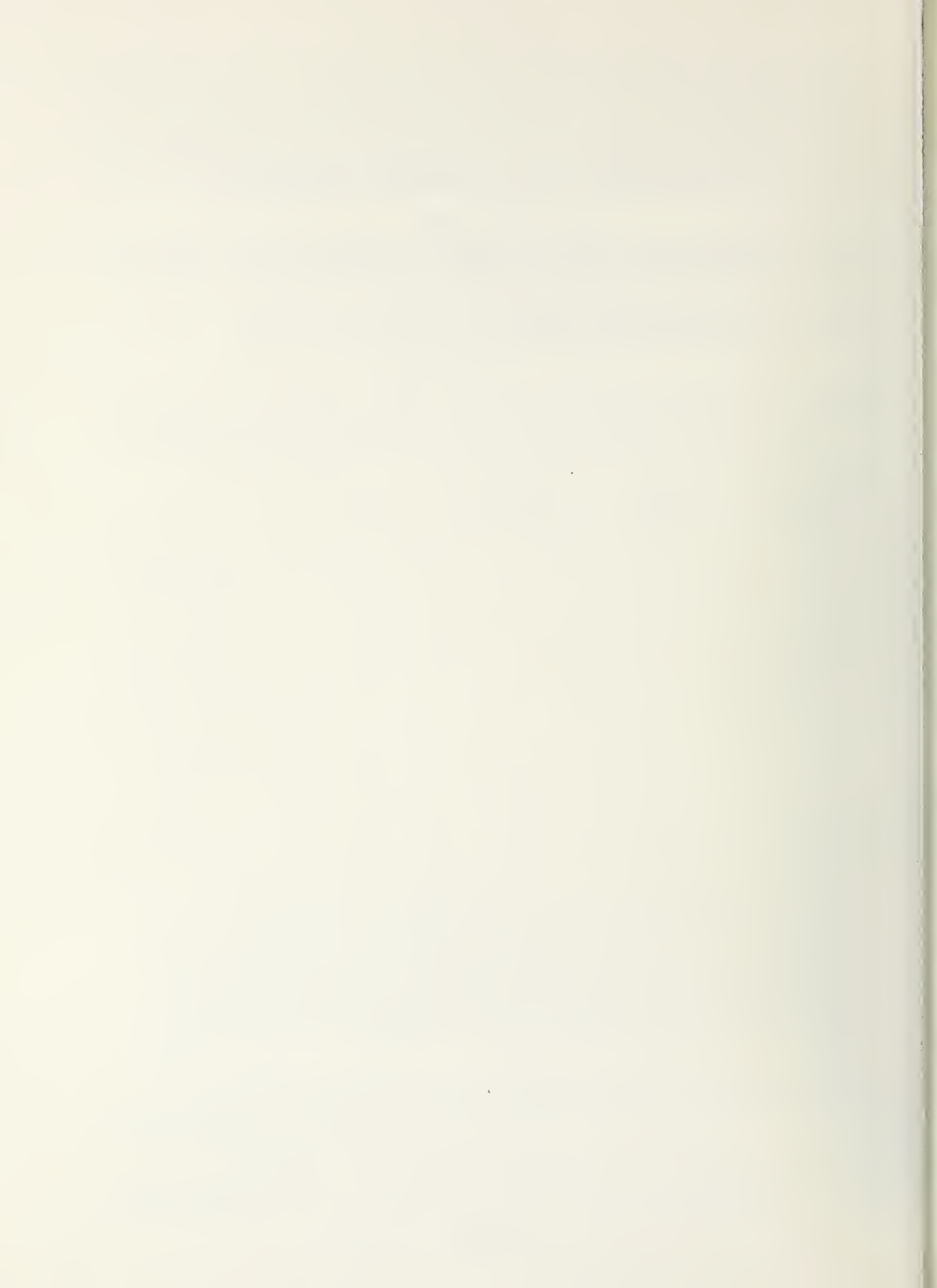
Washington, D.C. 20234
October 18, 1976

J. Paul Cali, Chief
Office of Standard Reference Materials

This sample of linear polyethylene was prepared by fractional recrystallization from 1,2,4-trichlorobenzene and subsequent blending of fractions produced by Waters Associates, Inc. of Milford, Mass., by large-scale gel permeation chromatography, from a linear polyethylene substantially identical with Standard Reference Material 1475 (Linear Polyethylene, Whole Polymer). The fractions as received contained several percent by weight of polyethylene components with molecular weights in the range 1,000-4,000. The amount of this material remaining after the fractional recrystallization is less than 0.5 percent. Both total volatiles, estimated gravimetrically, and residual 1,2,4-trichlorobenzene content, estimated spectrophotometrically, do not exceed 0.1 percent.

The maximum rate of shear in the Ubbelohde capillary viscometers employed for the determination of limiting viscosity numbers was $3,000 \text{ sec}^{-1}$ for 1,2,4-trichlorobenzene and $2,000 \text{ sec}^{-1}$ for 1-chloronaphthalene. The maximum specific viscosities were 0.4 in both solvents.

A report describing the investigations required for this and related polyethylene Standard Reference Materials will be published as an NBS Special Publication.



The Characterization of Linear Polyethylene SRM's 1482, 1483, and 1484. II. Number-Average Molecular Weights by Membrane Osmometry

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(October 19, 1977)

Linear polyethylene Standard Reference Materials SRM 1482, 1483, and 1484 are certified for number-average molecular weight M_n . In this paper the experimental procedures employed for the determination of M_n for these materials by membrane osmometry are described, and the techniques used to analyze the data and to estimate limits of systematic error are discussed.

Key words: Fraction; limiting viscosity number; membrane osmometry; narrow molecular weight distribution; number-average molecular weight; polyethylene; Standard Reference Material; weight-average molecular weight.

1. Introduction

Standard Reference Materials 1482, 1483, and 1484 are linear polyethylenes with relatively narrow distributions in molecular weight, issued by the National Bureau of Standards. Their general characteristics are described in the first paper of this series [1].¹ In the present paper, we describe the determination of their certificate values of number-average molecular weight by membrane osmometry. This well-established [2, 3] technique consists of measuring the equilibrium hydrostatic pressure difference between a solution and pure solvent separated by a membrane permeable to solvent alone, as a function of solution concentration.

2. Experimental

Osmotic pressure measurements were made with a Model 502 Hewlett-Packard Mechrolab Membrane Osmometer.² This instrument, which has been described elsewhere [3], adjusts the hydrostatic pressure on the solvent side of the semipermeable membrane to achieve zero net liquid transfer across the membrane. The pressure is adjusted by varying the solvent level, which is measured with a resolution of 0.01 cm, corresponding to a pressure difference of about 1 Pa for water or typical organic solvents. Gel cellophane membranes, type 450D, obtained from ArRo Laboratories, Inc., were employed. Before use, they were conditioned to 1-chloronaphthalene, the solvent in which measurements were made, by a successive solvent-exchange procedure given in detail previously [4].

Solution temperatures at the membrane surface, which were in the range 125–130 °C, could not be measured directly without risk of damage to the membrane. Temperatures were therefore monitored during osmotic pressure

measurements by a copper-constantan thermocouple spring-loaded against the stainless steel membrane clamps. In separate experiments, the temperature difference between this thermocouple and the membrane surface was determined by inserting a second thermocouple at the membrane surface.

Osmotic pressure differences were measured for solutions whose concentrations ranged from 0.7 to 3 g/L for SRM 1482, 1 to 10 g/L for SRM 1483, and 0.5 to 1.4 g/L for SRM 1484. All solutions were made up directly by weight, without employing successive dilution techniques. Concentrations were calculated using values of solvent density and partial specific volume determined pycnometrically in this laboratory. The 1-chloronaphthalene was obtained from commercial material by distillation at reduced pressure after removal of residual naphthalene by sublimation, also at reduced pressure. Solutions were made up without adding antioxidant, since preliminary experiments suggested that its use led to erratic results, possibly due to the formation of gaseous decomposition products in the osmometer. No evidence of degradation was found in the course of this work. Reference readings, with solvent on both sides of the membrane, were taken before and after each solution reading, to take account of slow drifts due to changes in ambient pressure, etc.

3. Results

Number-average molecular weight M_n may be obtained from the variation of osmotic pressure π with solution concentration by means of the familiar virial expansion, expressed in one of the two equivalent forms:

$$\begin{aligned}\pi &= RT(M_n^{-1}c + A_2c^2 + A_3c^3 + \cdots) \\ &= (RT/M_n)(c + \Gamma_2c^2 + \Gamma_3c^3 + \cdots),\end{aligned}\tag{1}$$

where c is solution concentration (weight per unit volume), R and T are the gas constant and the absolute temperature, respectively, and the A 's and Γ 's are the usual virial coefficients. In practice, the quantity actually measured is

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

² Certain commercial equipment, instruments, or materials are identified in this paper in order to 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 difference h in liquid level between solvent and solution, related to the osmotic pressure by $\pi = \rho gh$, where ρ is solvent density and g is the acceleration due to gravity. Thus, M_n may be determined from the coefficient of the first power of concentration in a fit of osmotic pressure (or h) to a polynomial in solution concentration with no constant term. Since the concentrations chosen and the number of terms in eq (1) employed differ for the three Standard Reference Materials, we discuss them separately in the remainder of this section.

3.1 SRM 1483

Five subsets of measurements were made on SRM 1483. Each subset consisted of measurements on five solutions, with concentrations of approximately 1, 2, 3.5, 5.5, and 10 g/L, at a temperature of 128.6 °C. The measured values of h , which ranged from 1 to 15 cm, were fitted by unweighted least squares to a polynomial in the first, second, and third powers of solution concentration, and eq (1) was used to calculate M_n , A_2 , and A_3 from the coefficients so obtained. The standard deviation in h obtained from the least-squares analysis was 0.055 cm, only slightly larger than the repeatability of the measurements. The values of M_n and A_2 obtained are shown in table 1, together with their standard deviations inferred from the least-squares fit. The value of A_2 is consistent with literature values for linear polyethylenes in 1-chloronaphthalene [4–7], and is in reasonable agreement with the value of A_2 obtained for SRM 1483 by light scattering cited in paper III of this series [8]. The value found for A_3 is 0.011 mol cm⁶/g³, with a standard deviation of 0.012 mol cm⁶/g³. Thus, over the range of concentrations employed and to the precision of our measurements, we were unable to obtain a value for the third virial coefficient statistically significantly different from zero. This is hardly surprising, since at the highest concentrations employed, the contribution to the right-hand side of eq (1) from the second and higher virial coefficients is only about 40 percent of the term linear in c , and the contribution to the height difference h from the third virial term is less than 0.4 cm. Curiously, however, the ratio $\Gamma_3/\Gamma_2^2 = A_3/(M_n A_2^2)$ has the value 0.3, remarkably close to the often-employed estimate of $1/4$ for this ratio [2, 9].

3.2 SRM 1482

Five subsets of measurements were made on SRM 1482. Each subset consisted of measurements on four solutions, with concentrations of approximately 0.7, 1, 2, and 3 g/L, at a temperature of 126.3 °C, and observed height differences h ranging from 2 to 9 cm. Preliminary analyses indicated a molecular weight of about 10⁴ g/mol and a second virial coefficient roughly the same as that found for SRM 1483.

Using these values and the approximate relation $\Gamma_3/\Gamma_2^2 = 1/4$ previously cited, we can readily show that at the highest concentration measured, the contribution of the third virial term amounts to a height difference of only 0.002 cm, well below the measuring capability of our equipment. Accordingly, for the analysis of the data the terms in A_3 and Γ_3 on the right-hand sides of eq (1) were ignored, and the measured values of h were fitted by unweighted least squares to a polynomial in the first and second powers of concentration. The standard deviation in h obtained from the fitting was 0.046 cm, an acceptable value. The resulting values of M_n and A_2 are given in table 1, together with their standard deviations inferred from the least-squares fit.

3.3 SRM 1484

The experimental design for measurements on SRM 1484 was substantially different from that used for SRM's 1482 and 1483. If we take a nominal value of 10⁵ g/mol for M_n and take the value of A_2 found for SRM 1483 as a rough estimate of A_2 for SRM 1484, then the approximate relation $A_3/(M_n A_2^2) = 1/4$ gives us an estimate of 3×10^{-3} mol cm⁶/g³ for A_3 . Using these estimates, we find that at a concentration of 10 g/L, the maximum employed for SRM 1483, the expected contributions to the measured height difference from the three terms on the right-hand side of eq (1) are 2.9 cm, 3.2 cm, and 0.9 cm, in that order. Thus, the second term is actually larger than the first, and it seems more than likely that the fourth and higher terms will contribute significantly. Since the primary purpose of this work is the determination of M_n , we restrict ourselves to measurements at and below a concentration c_{\max} of 1.4 g/L rather than include additional terms in eq (1). At c_{\max} , the expected contributions to the measured height difference will be about 0.4 cm, 0.07 cm, and 0.003 cm. The third term is well below the 0.01 cm resolution of the osmometer, and since the size of the terms is decreasing rapidly as we go to successively higher-order terms in concentration, we can be reasonably certain that the higher-order terms may be safely neglected.

Given the maximum concentration c_{\max} to be used and the functional form to be fitted (eq (1) with the last term omitted), the expected precision with which M_n may be estimated by a series of measurements of height difference h at various concentrations not exceeding c_{\max} is a function of the concentrations chosen. It can be shown [10] that for the present case, maximum precision in an estimate of M_n is achieved by taking about one-sixth the measurements at c_{\max} and the other five-sixths at a concentration roughly one-third c_{\max} . At this lower concentration, the predicted height difference is only about 0.14 cm, much lower than is usually measured, and considerable replication is needed to obtain

TABLE 1. Molecular parameters obtained by membrane osmometry on solutions of linear polyethylene Standard Reference Materials 1482, 1483, and 1484, in 1-chloronaphthalene

Standard deviations are obtained from least-squares analyses of the data as described in the text.

Sample	Measurement temperature, °C.	Number-average molecular weight, M_n , g/mol	Standard deviation in M_n , g/mol	Second virial coefficient, A_2 , mol cm ³ /g ²	Standard deviation in A_2 , mol cm ³ /g ²	Number of degrees of freedom
SRM 1482	126.3	1.1397×10^4	0.0080×10^4	1.34×10^{-3}	0.22×10^{-3}	18
SRM 1483	128.6	2.895×10^4	$.045 \times 10^4$	1.12×10^{-3}	$.17 \times 10^{-3}$	22
SRM 1484	129.7	1.005×10^5	$.037 \times 10^5$	1.49×10^{-3}	$.32 \times 10^{-3}$	34

satisfactory precision in the final estimate of M_n . Accordingly, 30 measurements were made at a concentration of about 0.5 g/L, and 6 measurements at a concentration of about 1.4 g/L.

The measured values of h were fitted to a polynomial in the first and second powers of concentration. The standard deviation in h obtained from the fitting was 0.018 cm. The values of M_n and A_2 obtained are given in table 1, together with their standard deviations inferred from the least-squares fit.

4. Systematic Errors

We now list the likeliest sources of systematic error in the estimates of number-average molecular weight described in the preceding section, and attempt to set upper limits on their magnitudes. Individual sources of error are discussed in the following subsections; the resulting error-limit estimates are summarized in table 2, expressed as percent errors applied to M_n .

TABLE 2. Percent errors in M_n introduced by measured quantities and approximations

Source of error	Error in M_n , percent		
	SRM 1482	SRM 1483	SRM 1484
1. Measurement temperature	0.3	0.1	0.1
2. Solvent density in hydrostatic column	0.27	0.27	0.27
3. Solvent density at membrane temperature	0.3	0.25	0.25
4. Solute weights	0.60	0.85	0.19
5. Solvent height scale	0.56	0.99	3.04
6. Change in volume of solvent system with solvent height	-0.06	-0.06	-0.06
7. Bubble compression	-0.34	-0.34	-0.34
8. Permeation of solute through membrane	+0.5	+0.2	—
9. Change in solution density with concentration	-0.06	-0.16	-0.56
10. Cutoff of virial expansion	+0.03	+0.10	+0.25
11. Sum of positive errors	+0.53	+0.3	+0.25
12. Sum of negative errors	-0.46	-0.56	-0.96
13. Maximum magnitude of error from the signed errors combined	0.53	0.56	0.96
4. Root-sum-square of the above maximum magnitude of error and the unsigned errors	1.10	1.47	3.22
5. Expected limit of systematic errors from all sources, including sources not identified and treated here	2%	2%	4%

In practice, M_n is calculated from the relation:

$$M_n = RT/(\rho_h g P), \quad (2)$$

where

R is the gas constant;

T is the absolute temperature of the solution;

ρ_h is the solvent density in the liquid column whose height differences h measure the osmotic pressure;

g is the acceleration due to gravity; and

P is the coefficient of concentration c in a fit of the height differences h to a polynomial in c of the form:

$$h = Pc + Qc^2 + Rc^3 + \dots \quad (3)$$

Of the quantities other than P on the right-hand side of eq (2), only T and ρ_h can be in error by amounts sufficient to affect the final value of M_n noticeably. Errors from these sources are discussed in sections 4.1 and 4.2. Since P is the limit, as c approaches zero, of the ratio h/c , systematic errors in c and in h will give rise to errors in P and therefore in M_n . Systematic errors from these sources are discussed in sections 4.3 and 4.4. Errors may also be introduced by the retention of too few terms on the right-hand side of eq (3) for the concentration range employed; errors from this source are discussed in section 4.5. Finally, the error limits from all the foregoing sources are combined and summarized in section 4.6.

4.1. Errors in Measurement Temperature

As described in section 2, measurement temperatures were monitored by a thermocouple in contact with the clamps which support the membrane. The thermocouple itself is calibrated to 0.1 °C; for SRM's 1483 and 1484 the principal error in measurement temperatures is due to the uncertainty in the temperature difference of about 1 °C between the monitoring thermocouple and the surface of the membrane. We believe that this uncertainty does not exceed 0.5 °C. The resulting relative error in M_n , at a measurement temperature of about 400 K, is seen from eq (2) to be 0.5/400, or 0.1 percent for SRM's 1483 and 1484. The temperature control system was not working properly when measurements were made on SRM 1482, and the temperature varied over several degrees. We believe that the uncertainty in the effective average temperature for all the data is no greater than 1 °C, which would result in a relative error in M_n of 1/400, or 0.3 percent.

4.2. Errors in Solvent Density

Errors in solvent density affect the value of M_n in two ways. First, the density ρ_h of solvent in the hydrostatic head which balances the osmotic pressure difference between solvent and solution enters directly into the calculation of M_n as shown by eq (2). Second, since solutions were made up by weight, rather than by volume, the value of ρ_0 of the solvent density at the measurement temperature affects the calculated values of solution concentrations and thus affects the calculated value of P in eqs (2) and (3). The effect of errors in ρ_0 and M_n is discussed in the following section. We believe that our measured values of ρ_h are accurate to 0.2 percent at a given temperature. However, the temperature of the liquid column is uncontrolled, and is essentially room temperature. During this work, the fluctuations in room temperature were such as to make the effective average temperature uncertain by about 1 °C. Measurements of the variation of the density of 1-chloronaphthalene with temperature in the vicinity of room temperature give a value of about 0.07 percent per °C. Thus, the uncertainty in the temperature of the liquid column adds another 0.07 percent to the uncertainty in ρ_h . The total expected error in ρ_h is therefore 0.27 percent, which by eq (2) leads to a possible error of 0.27 percent in M_n , for all three SRM's.

4.3. Errors in Solution Concentration

As stated in section 2, solutions were made up by weight, and concentrations c were calculated from the relation:

$$c = w\rho_0/[1 - w(1 - \rho_0\bar{v})], \quad (4)$$

where w and \bar{v} are the weight fraction and partial specific volume, respectively, of solute in the solution. Thus, errors in c can arise from errors in w , ρ_0 , and \bar{v} . However, the value of P , and therefore of M_n , is unaffected by errors in \bar{v} . To see this, we observe that P is the limit, as c approaches zero, of the ratio h/c . However, c may also be written as the product of w and the solution density ρ . As c approaches zero, ρ of course approaches ρ_0 , and P can be re-expressed as ρ_0^{-1} times the zero-concentration limit of h/w , and is therefore independent of \bar{v} and inversely proportional to ρ_0 . The relative error in M_n is therefore independent of the error in \bar{v} and equal in magnitude to the relative error in ρ_0 . We believe that the accuracy of our measurement of ρ_0 is 0.2 percent at a given temperature. However, as with ρ_h , the uncertainties in measurement temperature discussed in section 4.1 increase this figure by 0.1 percent for SRM 1482 and by 0.05 percent for SRM's 1483 and 1484. Therefore, our final estimates for errors in M_n arising from errors in ρ_0 are: 0.3 percent for SRM 1482, 0.25 percent for SRM's 1483 and 1484.

Solute and solution weights were measured on semimicro balances accurate to 0.1 mg. The balance used to measure solute weights for SRM 1484 was checked at the values of solute weight actually employed and was found to be accurate to 0.1 percent at those values. In order to estimate the effect of these weighing uncertainties on the values of M_n , a series of comparison calculations was carried out. For each SRM, a reference subset of typical data points was chosen, one at each concentration measured, and a "reference" value of M_n was calculated from this set of points. The value of each solute weight in turn was then increased by its assumed limit of error, and the value of M_n recalculated. The resulting percent changes in the reference values of M_n are shown in table 3, together with the sum of the absolute values of the

individual changes, their algebraic sum, and the square root of the sum of their squares (root-sum-square). The sum of the absolute values represents the error in the case where every weighing is in error by the maximum amount possible and in the direction which maximizes the resulting error in M_n . We reject this estimate as overly pessimistic. The algebraic sum would be the appropriate measure if all the weighings were in error by the same amount, and the root-sum-square would be appropriate if the individual errors were of random sign. Since both these possibilities seem physically plausible, we select as our error estimate the larger of the absolute value of the algebraic sum and the root-sum-square. This turns out to be the algebraic sum for SRM's 1482 and 1483, and the root-sum-square for SRM 1484; the corresponding values are shown in line 4 of table 2.

4.4. Errors in Solvent Heights

Errors in the scale used to measure the solvent heights h will of course cause errors in P and therefore in M_n . The scale was therefore spot-checked with a cathetometer over its entire range. The largest discrepancy found was 0.012 cm. This value was therefore used to obtain error estimates for SRM's 1482 and 1483. However, for SRM 1484, with much smaller measured height differences than the other two, a more precise error limit was needed. The scale was therefore rechecked every 0.01 cm over the region in which height differences were measured for SRM 1484. Over this very limited region of the scale, the largest discrepancy found was 0.0031 cm, and this value was used to obtain error estimates for SRM 1484. The errors in M_n resulting from the assumed errors in h were obtained by the same kind of comparison calculation described in section 4.3 for errors in solute weight; the results are shown in table 3. Again, we reject the sum of the absolute values of the individual changes as being too pessimistic and choose the larger of the absolute value of the algebraic sum of the individual changes and their root-sum-square. As with the errors due to solute weights, this turns out to be the absolute value of the algebraic sum for SRM's 1482 and 1483, and the root-sum-square for SRM 1484; the corresponding values are given in line 5 of table 2.

TABLE 3. Percent errors in number-average molecular weight M_n introduced by assumed errors in solute weight and in solvent heights

	SRM 1482	SRM 1483	SRM 1484
Number of solutions in reference subset	4	5	2
Percent changes in M_n from assumed errors in solute weight	0.23, -0.16, 0.29, 0.24	0.34, 0.44, 0.37, -0.34, 0.04	0.17, -0.08
Algebraic sum of above	0.60	0.85	0.09
Sum of absolute values of above	0.92	1.53	0.25
Root-sum-square of above	0.47	0.75	0.19
Percent changes in M_n from assumed errors in solvent height	-0.23, 0.15, -0.29, -0.19	-0.40, -0.48, -0.38, 0.29, -0.02	-3.01, 0.46
Sum of absolute values of above	0.86	1.57	3.47
Algebraic sum of above	-0.56	-0.99	-2.55
Root-sum-square of above	0.44	0.79	3.04

Errors in solvent height can also arise from changes in the volume of the solvent reservoir system with height. The quantity actually measured is not strictly the liquid level of solvent, but rather the position of a reservoir of solvent connected to the osmometer by flexible tubing. If the volume of the tubing changes slightly with changes in the height of the reservoir, the liquid level within the reservoir will change, and the true height difference between solvent and solution will be the difference in scale reading plus the change in solvent level within the reservoir at the two heights. This error was estimated by comparing the difference in solvent meniscus level at two positions near the top and bottom of the total range of 40 cm, measured directly with a cathetometer, with the difference in osmometer scale readings at the two positions. The difference in the scale readings was found to be 0.022 cm larger than the difference measured with the cathetometer. This amounts to a scaling error in h of 0.022/40 or 0.06 percent, and a corresponding error in M_n of -0.06 percent, shown in line 6 of table 2.

Changes in the length of the control bubble whose motion is used to sense liquid flow give rise to a third source of error in solvent height. When the solvent level changes in response to changes in solution concentration, the hydrostatic pressure on the control bubble changes and the bubble expands or contracts. Treating the bubble as a perfect gas, which is adequate for our present purpose, we can easily show that the relative error in h is given by $b\rho_h g/P_0$, where b is the length of the bubble and P_0 is atmospheric pressure. Assuming a maximum bubble length of 3 cm (a very safe upper limit), we find an error in h from this source of 0.34 percent. The control bubble is located directly underneath the membrane. Its expansion when the concentration of solution in the osmometer is increased therefore gives rise to an apparent increase in h , or a decrease in the apparent value of M_n . The resulting error in M_n of -0.34 percent is shown in line 7 of table 2.

Measured values of h will be too low if the membrane is not completely impermeable to solute. Although experience suggests that permeation should be negligible for the membranes and solutes employed in this work, limits of error from this source were estimated for SRM's 1482 and 1483 as described below.

Membrane permeation effects were estimated for SRM 1482 by comparing the values of h obtained for a solution of SRM 1482 using the 450D membranes normally employed in his work with the values obtained for the same solution with an appreciably thicker membrane (ArRo 600D). The measured value of h was about 13 cm, and the value obtained with the thicker membrane was larger than that obtained with the normal membrane by 0.03 ± 0.04 cm. Taking the worst case, we have a maximum difference of 0.07 cm, which implies a maximum relative error in M_n of $0.07/13$, or +0.5 percent.

Errors from membrane permeation were estimated for SRM 1483 by looking for a slow decrease in h with time resulting from such leakage. No such drifts were observed for a solution which gave a value of h of about 13 cm. We estimate that we could have observed a drift of 0.01 cm, and that such a drift might imply a total decrease of 0.02 cm, allowing for instrumental response time. We therefore estimate the limit of error from membrane permeation for SRM 1483 as $0.02/13$, or +0.2 percent.

Finally, the difference in density between solvent and solution gives rise to an error in h . In practice, h is measured as the change in reading when solution in the sample side of the osmometer is replaced by solvent. The sample tube is filled to the same height in both cases. If the densities of solvent and solution are different, as is usually the case, replacing solution by solvent will give rise to a purely hydrostatic pressure change, and the observed value of h will be the sum of this change and the change arising from the osmotic pressure difference across the membrane. The change in hydrostatic pressure is just $ag(\rho - \rho_0)$, where a is the height above the membrane surface to which the sample tube is filled and ρ is the solution density. The resulting change in the measured h is then $a(\rho_0 - \rho)/\rho_h$. The difference $\rho_0 - \rho$ is given by $c(\rho_0\bar{v} - 1)$, so the error in h is just $ac(\rho_0\bar{v} - 1)/\rho_h$. Using eqs (2) and (3), we find that the resulting relative error in M_n is given by:

$$M_n ag(1 - \rho_0\bar{v})/(RT).$$

For our osmometer and operating conditions, this error is -0.06 percent, -0.16 percent, and -0.55 percent for SRM's 1482, 1483, and 1484, respectively, as shown in line 9 of table 2.

4.5. Errors due to Cutoff of Virial Expansion

As discussed in section 3, only the first two terms on the right-hand side of eq (1) were employed for the analysis of the data for SRM's 1482 and 1484. Although contributions from the third and higher virial coefficients are smaller than the resolution of the osmometer, their neglect nevertheless constitutes a source of systematic error. In order to estimate the magnitude of the error involved, we estimate the third term on the right-hand side of eq (1) by making the assumption $\Gamma_3 = \Gamma_2^2/4$. As discussed in section 3, the data obtained for SRM 1483 are at least not inconsistent with this assumption. This allows us to estimate the contribution to h of the third term on the right-hand side of eq (3). Its neglect in the analysis may be treated as an error in the measured h at each concentration measured; the resulting error in M_n may then be obtained by making use of the estimates of the effect of errors in h on M_n obtained by comparison calculations as described in section 4.4. In this case, since the "errors" in h are of the same sign for all the measured solutions, we take the algebraic sum of the individual changes in M_n given in table 3, each scaled by the ratio of the third virial term in h to the error in h assumed in table 3. The resulting errors of +0.03 percent and +0.25 percent for SRM's 1482, and 1484, respectively, are shown in line 10 of table 2.

For SRM 1483, contributions from the third virial coefficient are already included in the analysis. In this case, we wish to set bounds on the possible contributions from the fourth and higher virial coefficients. In the absence of any means of estimating the fourth virial coefficient theoretically, we resort to the expedient of examining the relative sizes of the three terms in the right-hand side of eq (1) at the highest concentration measured. They turn out to be in the ratio 1:0.324:0.026. Thus, the third virial term is only about 8 percent of the second, and the second is about 32 percent of the first. It seems adequately cautious to assume that as a

maximum, the fourth term will be to the third as the second is to the first. Then we have as a maximum estimate:

$$\Gamma_4 = \Gamma_2\Gamma_3.$$

Treating the contribution to h from a hypothetical fourth virial coefficient of this magnitude as an error in h , in a manner analogous to that described above for the third virial terms for SRM's 1482 and 1484, we obtain an estimated error in M_n for SRM 1483 of +0.10 percent, as shown in line 10 to table 2.

4.6. Summary

Estimates of the contributions of individual sources to the overall systematic error in M_n are summarized in table 2. Errors which may be in either direction are shown unsigned; errors which can only be in one direction are shown with the appropriate signs. We believe that for errors which can be either positive or negative, the sum of the absolute values of the individual contributions gives an overly pessimistic estimate of total error. In addition, the total error from all the signed sources together cannot exceed the greater of the sum of all the positive errors, shown in line 11 of table 2, and the negative of the sum of all the negative errors, shown in line 12. This quantity, the maximum possible error arising from the signed error sources, is shown in line 13. In order to combine its effects with those of the unsigned error estimates, we form the root-sum-square, shown in line 14. Finally, to take account of any sources of error not explicitly considered here, we round each of the estimates so obtained upward to

the next whole percent. The resulting estimates of limits of systematic error, shown on line 15 of table 2, are those given on the certificates for SRM's 1482, 1483, and 1484.

5. References

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The Characterization of Linear Polyethylene SRM's 1482, 1483, and 1484

III. Weight-Average Molecular Weights by Light Scattering

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Linear polyethylene Standard Reference Materials SRM 1482, 1483, and 1484 are certified for weight-average molecular weight M_w . In this paper the experimental procedures employed for the determination of M_w for these materials by light scattering are described, and the techniques used to analyze the data and to estimate limits of systematic error are discussed.

Key words: Fraction; light scattering; limiting viscosity number; narrow molecular weight distribution; number-average molecular weight; polyethylene; Standard Reference Material; weight-average molecular weight.

1. Introduction

Standard Reference Materials SRM 1482, 1483, and 1484 are linear polyethylenes with relatively narrow distributions in molecular weight, issued by the National Bureau of Standards. Their general characteristics are described in the first paper of this series [1].¹ In the present paper, we describe the determination of their certificate values of weight-average molecular weight M_w from measurements of the scattering of light by solutions of the SRM's in 1-chloronaphthalene at 135°C.

The use of light scattering to determine the molecular weight and size of macromolecules in dilute solution is well established [2]. The usual practice is to measure the scattering from the macromolecules in solution relative to that from a material of known scattering power. The measurements reported in this paper, and consequently the certificate values of M_w , are referred to values published by Coumou [3] for the scattering of light of wavelength 546 nm from benzene at 23°C.

The value of the differential refractive index dn/dc is needed to obtain weight-average molecular weights from light scattering data. The differential refractometer employed for this purpose was calibrated with aqueous solutions of sucrose at 25°C, using values for the differential refractive index for this system published by Norberg and Sundelöf [4].

2. Experimental

2.1. Light Scattering

a. Apparatus

A "SOFICA 42,000 Photo Gonio Diffusometer" light scattering photometer was used for scattering measurements.²

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

² Certain commercial equipment, instruments, or materials are identified in this paper in order to 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.

Light of nominal wavelength 546 nm was used, polarized with the electric vector of the incident beam normal to the plane containing the incident and scattered wave vectors (vertical polarization). A green filter and a vertical polarizer were placed in the paths of both the incident and the scattered beam. Measurements were made at 135°C with the scattering cells immersed in a vat of silicone oil which had been filtered through a glass frit before use.

A glass rod supplied by the photometer manufacturer was used as a working standard. Its scattering relative to that of benzene was measured at room temperature at a scattering angle of 90°, at the wavelength and polarization used for measurements on polyethylene solutions. During the course of the measurements, the optical alignment of the photometer was checked periodically by comparing the scattering signals from solvent at scattering angles of 45 and 135°. The signals were found to differ by less than 1 percent in all cases. The effects of alignment errors of this size on the values obtained for the mean-square radius and the weight-average molecular weight are discussed in sections 3.2 and 4.9, respectively.

The benzene used for calibrating the photometer was prepared from Certified A.C.S. grade benzene. The starting material was first extracted eight times with concentrated H_2SO_4 , four times with a 5 percent aqueous solution of NaOH, and four times with distilled water. It was then dried by mixing with anhydrous $CaCl_2$, and fractionally distilled in glass over sodium metal. Finally, it was passed through a column of silica gel and adsorption alumina to adsorb any remaining fluorescent impurities.

b. Preparation of Solutions

Commercial grade 1-chloronaphthalene was distilled at reduced pressure after removal of residual naphthalene by sublimation, also at reduced pressure. Immediately before use, dissolved air was swept out of the solvent by bubbling oxygen-free nitrogen gas (The Matheson Co., "prepurified grade") through it at room temperature for at least 1 h. Polyethylene solutions were made up by weight, and their

concentrations were calculated using values of solvent density and partial specific volume at 135 °C determined pycnometrically in this laboratory. The polyethylene samples were dissolved at 135 °C with gentle stirring. They were then filtered, as described in section 2.1.3, directly into the light-scattering cells and the scattering recorded. In preliminary experiments, the filters employed showed discoloration and signs of disintegration after 2 h exposure to 1-chloronaphthalene at 140 °C. Evidence of degradation (discoloration, increased and erratic small-angle scattering) was also found when filtered solutions were kept at 135 °C for more than 2 h, but no such evidence was found in less than 2 h. The final measurements were therefore scheduled so that the total exposure time of the filters to hot 1-chloronaphthalene was less than 1/2 h in all cases, and so that no more than 2 h elapsed between the beginning of heating and completion of the measurements of each solution.

c. Measurement Procedure

Before each use, xylene vapor was allowed to condense on the inside surfaces of the inverted light scattering cells, to remove dust. Polyethylene solutions or solvent were filtered directly into the cells through a hypodermic syringe heated to 135 °C and fitted with a "Swinney Adapter" filter holder (Millipore Corp., Bedford, Mass.). For measurements on SRM's 1483 and 1484 and their associated solvent readings, solutions and solvents were filtered through 0.22 μm MF Millipore filters (No. GSWPO 2500) made of mixed esters of cellulose. No external pressure was applied during the filtration.

The scattering from SRM 1482 was much smaller than that from the other two polyethylenes, and noise from dirt and dust was a more serious problem. For measurements on this material, the final de-dusting of the scattering cells by condensed xylene vapor was preceded by boiling in xylene, soaking in hot chromic acid, and successive rinsing in tap water, distilled water, and ethanol. Two stacked 0.22 μm Millipore filters were used to filter SRM 1482 solutions and solvent into the scattering cells. External pressure of about 0.5 psi* was applied during filtration and adjusted to give a flow rate of about 1/2 mL/min., in order to make the total exposure time of the filter to hot 1-chloronaphthalene less than 1/2 h.

For all three SRM's, the filter was first rinsed with the preheated material to be measured (solvent or solution), to remove detergent added during the filter manufacturing process and surface dust. Three rinses of about 2 ml each were then filtered into the scattering cell and discarded. Finally, 8 to 10 ml were filtered into the cell for measurement, and the cell was placed in the photometer and allowed to reach thermal equilibrium.

Measurements of scattered intensity were made at scattering angles from 45 to 135° in 15° steps. The scattering signal at 90° from the glass rod used as a working standard was measured after each solution or solvent measurement. For measurements on SRM 1483, solvent measurements were made in three of the five scattering cells used. The three sets of solvent measurements were averaged, and the average readings used for the analysis of the measurements on all the solutions. For measurements on SRM's 1482 and 1484, solvent measurements were taken in every cell used for

solution measurements, and the solvent scattering intensities obtained for each cell were used for the analysis of measurements on solutions taken with that cell. In addition, each cell was always placed in the photometer with the same angular orientation to minimize the effects of imperfections in the cells.

Seven sets of measurements were made on SRM 1482, five sets on SRM 1483, and six sets on SRM 1484. Each set consisted of measurements on solutions with nominal concentration of: 3, 4, 5, 6.5, 8, 10, and 12 g/L for SRM 1482; 2, 3, 4.5, 6, and 10 g/L for SRM 1483; 0.6, 0.8, 1, 1.3, 1.8, 2.3, and 3 g/L for SRM 1484. For SRM 1483, each set contained one solution at each of the nominal concentrations; some sets for SRM's 1482 and 1484 omitted at most one of the nominal concentrations. Thus, the sets of measurements on SRM 1483 are equivalent, and those for SRM's 1482 and 1484 are nearly so.

2.2. Differential Refractive Index

The differential refractometer employed for measurements on SRM's 1482, 1483, and 1484 has been described elsewhere [5]. For the present work, it was modified slightly by the addition of a condensing lens between the mercury lamp source and the slit. The instrument was calibrated with 7 solutions of sucrose, with concentrations from 6.3 to 26 g/L, at 25 °C. The sucrose solutions were made up by weight, and their concentrations were calculated using the density tables of Schneider et al.[6]. Otherwise, the equipment and measurement techniques employed in this work were identical with those described in [5].

3. Results

3.1. Differential Refractive Index

The experimental determination of the differential refractive index dn/dc described in detail in [5] consists essentially of the measurement of the displacement d of an optical slit image resulting from the substitution of a solution of concentration c for solvent in one side of a measuring cell. For dilute solutions, d is proportional to c ; the ratio $k = d/c$ is proportional to dn/dc . In practice, k is determined by measuring displacement for several concentrations and fitting the observed displacements to $d = kc$. Calibration is accomplished by determining the value k_0 for a material of known differential refractive index $(dn/dc)_0$; then for substance i we have:

$$(dn/dc)_i = (dn/dc)_0 k_i / k_0. \quad (1)$$

Displacements were measured as a function of concentration for SRM's 1482, 1483, and 1484 at 135 °C in 1-chloronaphthalene, and for aqueous solutions of sucrose at 25 °C. Table 1 shows the resulting values k_i (in arbitrary units), together with the estimates $s_i(d)$ and $s_i(k_i)$ of standard deviation in d and k , respectively, and the number of degrees of freedom F_i , equal in each case to one less than the number of concentrations measured. The values of $s_i(d)$ for the four materials are consistent with the physically plausible assumption that they are all estimates of the same quantity, i.e., the inherent imprecision of the measurement of d is independent of the sample. We therefore form a pooled

* 1 psi equals approximately 7×10^3 Pa.

TABLE 1. Results of differential refractive index measurements at wavelength in vacuum 546 nm.

in the headings, k_i is the result of fitting the observed displacements d (in arbitrary units) obtained with solutions of substance i of concentrations c to the form $d = kc$ by least squares; $s_i(d)$ and $s(k_i)$ are the standard deviations in d and k_i , respectively, obtained from the least-squares analysis; F_i is the number of degrees of freedom associated with $s_i(d)$ and $s(k_i)$; $s'(k_i)$ is the standard deviation in k obtained by using a pooled value for $s(d)$ as described in the text; dn/dc and $s(dn/dc)/|dn/dc|$ are the differential refractive index and its relative standard deviation, respectively, calculated as described in the text.

Substance	Range of concentration g/L	k_i	$s_i(d)$	$s(k_i)$	F_i	$s'(k_i)$	$s'(k_i)/ k_i $, percent	dn/dc , mL/g	$\frac{s(dn/dc)}{ dn/dc }$, percent
Sucrose ^a	6.3 to 26	167.46	0.00386	0.08	6	0.15	0.09	0.1429 ^b	—
SRM 1482 ^c	6.3 to 15	-228.4	0.00878	0.38	7	0.32	0.14	-0.1949	0.17
SRM 1483 ^c	5.6 to 13	-225.6	0.00477	0.22	5	0.34	0.15	-0.1925	0.17
SRM 1484 ^c	5.6 to 13	-224.4	0.00987	0.43	6	0.32	0.14	-0.1920	0.17
Pooled	—	—	0.00744	—	24	—	—	—	—

^a Aqueous solutions at 25 °C.

^b Value from [4], used for calibration.

^c At 135 °C in 1-chloronaphthalene.

estimate of the variance $v(d) = s^2(d)$ as the average of the individual estimates of variance, weighted by the number of degrees of freedom associated with each estimate:

$$s(d) = [v(d)]^{1/2} = [F^{-1} \sum_i F_i v_i(d)]^{1/2} = [F^{-1} \sum_i F_i s_i^2(d)]^{1/2}, \quad (2)$$

where $F = \sum_i F_i$ and the index i is summed over the four samples. We then use this pooled value to form improved estimates $s'(k_i) = s(k_i)s(d)/s_i(d)$. Values of $s'(k_i)$ and the associated relative standard deviations $s'(k_i)/|k_i|$ are shown in table 1. We then obtain the relative standard deviation in the ratios k_i/k_0 , where the subscript zero denotes the measurements on sucrose solutions, as:

$$s(k_i/k_0)/|k_i/k_0| = \{[s'(k_i)/k_i]^2 + [s'(k_0)/k_0]^2\}^{1/2}. \quad (3)$$

Finally, we observe that by eq (1), the relative standard deviation $s(dn/dc)/|dn/dc|$ in dn/dc is just $s(k_i/k_0)/|k_i/k_0|$. Values of dn/dc calculated from the k 's and the literature value for dn/dc of sucrose by eq (1) are shown in table 1 for SRM's 1482, 1483, and 1484, together with the associated values of $s(dn/dc)/|dn/dc|$.

3.2. Light Scattering

In principle [2], light scattering data from polymer solutions of concentrations c at scattering angles θ may be analyzed by fitting cg/I_c to a power series in c and $\sin^2(\theta/2)$, where g is unity for vertical polarization (and $\cos^2\theta$ for horizontal polarization), $I_c = \sin\theta[I(\theta, c) - I(\theta, 0)]/I_G$, I_G is the scattering signal from the glass working standard at $\theta = 90^\circ$, and $I(\theta, c)$ is the scattering signal from a solution of concentration c at scattering angle θ :

$$cg/I_c = \sum_{ij} C_{ij} c^i \sin^{2j}(\theta/2). \quad (4)$$

In order to use eq (4) for the estimation of molecular parameters, we must first decide how many terms on the right-hand side must be included to provide an adequate fit to the experimental data. The dependence of cg/I_c upon c and upon $\sin^2(\theta/2)$ reflects solute-solute interactions and

solute size, respectively. Since both effects increase with increasing molecular weight, we expect the highest molecular-weight material to provide the most sensitive test of adequacy of fit. Accordingly, preliminary scattering data for SRM 1484, with the highest molecular weight of the three SRM's, were first plotted as c/I_c versus $\sin^2(\theta/2)$ at constant concentration and versus c at constant scattering angle, to see whether a linear expansion (i.e., retaining only C_{00} , C_{01} , and C_{10}) would provide an adequate fit. The plots revealed that the linear approximation was clearly inadequate in this case; in particular, the constant-angle plots versus c showed distinct curvature. The effect of including second-order terms in eq (4) (C_{02} , C_{11} , and C_{20}) was therefore investigated by a series of least-squares analyses of the data. Inclusion of C_{20} was found to reduce the residual standard deviation in c/I_c by 55 percent, while inclusion of C_{11} resulted in a reduction of only 4 to 10 percent and inclusion of C_{02} increased the residual standard deviations slightly. The number and range of concentrations were not sufficient for inclusion of higher terms in c (C_{30} , etc.) to be sensible. The final analyses on all three SRM's were therefore carried out including C_{20} but not the other second-order terms:

$$c/I_c = C_{00} + C_{01}\sin^2(\theta/2) + C_{10}c + C_{20}c^2. \quad (5)$$

The coefficients in eq (5) are related to the weight-average molecular weight M_w , molecular mean-square radius R_G^2 , and second and third virial coefficients A_2 and A_3 by [2, 7]:

$$M_w = (K'C_{00})^{-1}, \quad (6)$$

$$R_G^2 = 3[\lambda_0/(4\pi n)]^2 C_{01}/C_{00} \quad (7)$$

$$A_2 = 1/2 K' C_{10}, \quad (8)$$

$$A_3 = 1/3 K' C_{20}, \quad (9)$$

$$K' = 4\pi^2 n_B^2 (dn/dc)^2 / (\lambda_0^4 N_A V_v^B S), \quad (10)$$

where:

λ_0 is the wavelength in vacuum of the scattered light, set at 546 nm in this work,

n and n_B are the indices of refraction of the solvent and benzene, taken as 1.586 [8] and 1.503 [3], respectively,

dn/dc is the differential refractive index of the solution, measured as described in 3.1,

N_A is Avogadro's number, taken as $6.022 \times 10^{23} \text{ mol}^{-1}$,

V_v^B is the Rayleigh ratio for the vertically polarized scattering of vertically polarized light from benzene, used for calibration and obtained as described in the following paragraph, and

S is the measured ratio I_G/I_B of the scattering signal obtained from the glass working standard to that obtained from benzene.

The "vertical-vertical" Rayleigh ratio V_v is related to the Rayleigh ratio U_u for the unpolarized scattering of unpolarized light and the depolarization ratio ρ_u for unpolarized light by:

$$V_v = U_u(2 - \rho_u)/(1 + \rho_u). \quad (11)$$

Using the published [3] values for benzene

$$U_u = 15.8 \times 10^{-6} \text{ cm}^{-1}$$

and $\rho_u = 0.41$, we obtain

$$V_v^B = 17.8 \times 10^{-6} \text{ cm}^{-1}.$$

The uncertainty in M_w introduced by the use of this derived Rayleigh ratio is discussed in section 4.4.

As described in section 2.1c, from five to seven sets of measurements were made on each SRM. Each set consisted of scattering measurements on from five to seven solutions, together with solvent measurements, at seven scattering angles. The sets for each SRM are equivalent or nearly so. The data in each set were fitted by least squares to eq (5), and the resulting values of C_{00} , C_{01} , C_{10} , and C_{20} were used to calculate M_w , R_G^2 , A_2 , and A_3 using eq (6)–(10). The estimates obtained from each set were then averaged. The resulting mean values and sample standard deviations of the mean are given in table 2, together with values of the molecular radius of gyration $(R_G^2)^{1/2}$, the ratio $A_3/(M_w A_2^2)$, and the number of degrees of freedom (equal in each case to one less than the number of sets).

The values of M_w in table 2 may be compared with the number-average molecular weights M_n determined by membrane osmometry and reported in paper II of this series [9]. It will be seen that M_w is slightly greater than M_n for all three SRM's, yielding estimates of the ratio M_w/M_n in the range 1.1 to 1.2, consistent with estimates obtained by gel permeation chromatography [1]. The values obtained for the second virial coefficient are in crude but satisfactory agreement with those obtained by membrane osmometry [9] and with literature values for linear polyethylenes in 1-chloronaphthalene [7, 10–12]. In addition, the ratios $A_3/(M_w A_2^2)$ are consistent with the often-cited estimate [13] of $1/4$. On the other hand, the values obtained for R_G^2 are clearly absurd, since they indicate that SRM 1482 in solution is more than half again as large as SRM 1483, which has a molecular weight $2^{1/2}$ times as large as SRM 1482. The obviously large errors in R_G^2 are almost certainly due to a combination of instrumental misalignment and incomplete removal of dust from the solute. For SRM's 1482 and 1483, the intensity at $\theta = 45^\circ$ is only 2–3 percent greater than that at $\theta = 135^\circ$. Consequently an error from either source of 1 percent in the scattering at 45° relative to that at 135° would result in errors of 35–100 percent in R_G^2 . Clearly, these values for R_G^2 must be treated as no more than very rough estimates.

4. Systematic Errors

We now list the likeliest sources of systematic error in the estimates of weight-average molecular weight described in the preceding section, and attempt to set upper limits on their magnitudes. Individual sources of error are discussed in the following subsections; the resulting error-limit estimates are summarized in table 3, expressed as percent errors applied to M_w .

According to eq (6), M_w is the reciprocal of the product $K'C_{00}$, where K' is given by eq (10). The effects of errors in the quantities that enter into K' are discussed in sections 4.1–4.5. The coefficient C_{00} may be written as the zero-angle, zero-concentration limit of the quantity

$$cg \csc \theta / [S_G(\theta, c) - S_G(\theta, 0)],$$

where $S_G(\theta, c)$ is the ratio of the signal obtained at scattering angle θ from a solution of concentration c to that obtained from the glass working standard at the same instrumental gain. Because of the non-ideality of the polarizers placed in the path of the incident and scattered light, the geometric factor g is not strictly unity; the resulting error is discussed in section 4.6. It is clear that systematic errors in $S_G(\theta, c)$ and c will affect the value of C_{00} and therefore of M_w ; errors from these sources are discussed in sections 4.7 and 4.8. The assumptions implicit in the use of eq (5), (6) and (10) introduce several possible sources of error; these are discussed in sections 4.9–4.14. Finally, the error limits from all the foregoing sources are combined and summarized in section 4.15.

4.1. Index of Refraction of Benzene

The index of refraction of benzene at 546 nm and 23 °C is given in [3] as 1.503. We believe that this value should be good as stated, i.e., to 1 part in 1500. Since n_B appears in K' as the square, the resulting relative error in M_w is 2/1500 or 0.1 percent.

4.2. Differential Refractive Index

Errors in our values for the differential refractive index of the SRM's arise both from possible errors in the literature value for the differential refractive index of sucrose solutions, used for calibration, and from the imprecision of our measurements. We believe that the value of dn/dc for sucrose in [4] is accurate to 1 percent. The relative standard deviation of our own measurements, shown in table 1, is 0.17 percent for each of the SRM's. We choose the 95 percent confidence limit corresponding to this value as a reasonable error limit. The Student t factor [14] for 24 degrees of freedom and 95 percent confidence limits is 2.064; the 95 percent confidence limit is therefore 2.064×0.17 percent, or 0.35 percent. Finally, since dn/dc appears in K' as the square, the resulting errors in M_w from the literature sucrose value and our own measurements are 2 percent and 0.7 percent respectively.

TABLE 2. Molecular parameters obtained by light scattering on solutions of linear polyethylene Standard Reference Materials 1482, 1483, and 1484 in 1-chloronaphthalene at 135 °C. Numbers in parentheses are sample standard deviations of the mean.

Sample	Weight-average molecular weight, ^a M_w , g/mol	Molecular mean-square radius, ^b R_G^2 , cm ²	Molecular radius of gyration, ^b $(R_G^2)^{1/2}$, Å	Second virial coefficient, ^c A_2 , mol cm ³ /g ²	Third virial coefficient, ^c A_3 , mol cm ⁶ /g ³	$\frac{A_3}{M_w A_2^2}$	Number of degrees of freedom
SRM 1482	13.63×10^3 (0.13×10^3)	1.79×10^{-12} (0.16×10^{-12})	133.7 (6.0)	1.59×10^{-3} (0.08×10^{-3})	1.28×10^{-2} (0.37×10^{-2})	0.35 (0.19)	6
SRM 1483	32.1×10^3 (1.6×10^3)	6.75×10^{-13} (0.53×10^{-13})	82.2 (3.2)	1.09×10^{-3} (0.10×10^{-3})	1.34×10^{-2} (0.60×10^{-2})	0.63 (0.37)	4
SRM 1484	119.6×10^3 (2.2×10^3)	4.75×10^{-12} (0.10×10^{-12})	217.9 (2.4)	1.03×10^{-3} (0.10×10^{-3})	2.8×10^{-2} (1.7×10^{-2})	0.40 (0.20)	5

^a Systematic errors in weight-average molecular weight are discussed in section 4 of the text and summarized in table 3.

^b As discussed in section 3.2 of the text, there is reason to believe that these values are subject to large systematic errors.

^c We have not attempted to estimate systematic errors in these quantities.

TABLE 3. Percent errors in M_w introduced by assumed errors in measured quantities and approximations

Source of Error	Error in M_w , percent		
	SRM 1482	SRM 1483	SRM 1484
1. Index of refraction of benzene	0.1	0.1	0.1
2. Literature value of differential refractive index of sucrose	2.0	2.0	2.0
3. Measured value of differential refractive index of SRM's relative to that of sucrose	0.7	0.7	0.7
4. Wavelength of radiation	0.5	0.5	0.5
5. Rayleigh ratio V_v for benzene, derived from literature values of U_u and ρ_u	10.	10.	10.
6. Measured ratios I_G/I_B	0.4	0.4	0.4
7. Polarizer errors	0.0	0.0	0.0
8. Measured ratios $S_G(\theta, c)$	0.3	0.3	0.3
9. Solvent density	0.2	0.2	0.2
0. Solute weights	0.3	0.4	1.2
1. Reflection correction	0.0	0.0	0.0
2. Instrumental misalignment	0.7	0.7	0.7
3. Refraction correction	0.4	0.4	0.4
4. Anisotropy of polyethylene	0.1	0.1	0.0
5. Temperature dependence of scattering of glass working standard	0.4	0.4	0.4
6. Cutoff of virial expansion	0.7	1.4	0.9
7. Sum of all the above except (5)	6.8	7.6	7.8
8. Root-sum-square of all the above except (5)	2.5	2.8	2.8
9. Expected limit of systematic errors from all sources except (5), including sources not identified and treated here	4.0	4.0	4.0
0. Root-sum-square of (5) and (19)	11.	11.	11.

4.3. Wavelength of Light

The light-scattering photometer employed for this work uses a mercury lamp in conjunction with a green filter in the incident beam which selectively transmits the so-called "mercury green line," and a similar filter in the scattered beam to remove any possible fluorescence from the solution. However, at the relatively high operating pressure of the mercury lamp, the green-line radiation is appreciably broadened. The light-scattering experiment senses the inverse fourth power average of the wavelength, as may be seen from eqs (5)–(10). Broadening of the radiation therefore produces an apparent shift in the effective wavelength. In addition, at sufficiently high pressures the center of the "green line" spectrum may shift. In order to estimate the size of the errors introduced into M_w by these effects, we measured the combined optical transmission curve of the two green filters placed in the incident and scattered light paths. Using this transmission curve and a plot of the spectral distribution of lamp output supplied by the lamp manufacturer, we calculated the inverse-fourth power average wavelength of the scattered light reaching the detector, obtaining a result of 549.6 nm, 3.5 nm larger than the nominal value of 546.1 nm for the mercury green line. If the actual value of the inverse-fourth power average wavelength could be determined with sufficient accuracy, it could be used instead of the nominal value. However, the data on the spectral distribution of the lamp output are given to a resolution of only 5 nm, and in addition are merely representative data for the type of lamp employed, rather than measured values for the lamps actually used. Direct measurement of the spectral distribution of the lamps used in this work was impractical, partly because of the relatively short lifetime of individual lamps, which resulted in several different lamps being used in the course of the measurements. We have therefore used the nominal value of the wavelength in our calculations, and have treated the deviation of 3.5 nm as a systematic error. In order to ascertain the effect of an error in wavelength of this size upon M_w , we first note from eqs (6) and (10) that the strongly wavelength-dependent quantities which appear in the calculation of M_w are λ_0 itself and the index of refraction and Rayleigh ratio for benzene. From eq (10) and (11), the wavelength dependence of the calculated M_w is that of the

expression $(\lambda_0^4 U_u / n_B^2) (2 - \rho_u) / (1 + \rho_u)$. Using the values reported by Coumou [3] for U_u , n_B , and ρ_u at wavelengths of 436 nm and 546 nm, we find that with increasing wavelength, U_u decreases more strongly than λ_0^{-4} , while n_B and ρ_u remain essentially constant. As a result, the combined expression increases by only 13 percent as the wavelength decreases from 546 nm to 436 nm. Assuming a roughly linear dependence of the expression on wavelength, we find that a change of 3.5 nm corresponds to an error of 0.42 percent in M_w . Allowing for some nonlinearity and for the neglect of the wavelength dependence of dn/dc , we believe that 0.5 percent is a safe upper limit for systematic errors in M_w arising from uncertainty in the wavelength of the light used.

4.4 Rayleigh Ratio of Benzene

As described in section 3.2, the value of the "vertical-vertical" Rayleigh ratio for benzene was calculated from published [3] values of U_u and ρ_u , using eq (11). However, the quantities directly measured were not U_u and ρ_u , but rather U_u and U_v , the unpolarized scattering from vertically polarized light. Now V_v is simply expressed in terms of U_u and U_v as:

$$V_v = \frac{3}{2} U_v - U_u, \quad (12)$$

and the standard deviation in V_v resulting from known standard deviations in (independent) measurements of U_v and U_u may be estimated as the square root of the sum of the squares of the standard deviations in U_u and the quantity $\frac{3}{2} U_v$. The standard deviations in U_u and U_v are given by Coumou as 3 percent and "better than 2 percent," respectively. In order to convert the relative standard deviation in U_v to an absolute standard deviation, we use eq (12) to back-calculate $\frac{3}{2} U_v$ from the published value of U_u and the value of V_v calculated from eq (11), obtaining finally an implied standard deviation in V_v of $0.82 \times 10^{-6} \text{ cm}^{-1}$, or 4.6 percent. From this estimate of standard deviation and the account of experimental techniques given in [3], we believe that 10 percent is a reasonable upper limit for systematic error in the value of V_v for benzene, and therefore for errors in our values of M_w from this source.

4.5. The Ratio I_G/I_B

Seven replicate measurements were made of the ratio I_G/I_B of the scattering signal obtained with the glass working standard to that obtained with benzene, at a scattering angle of 90° . The resulting standard deviation of the mean value of the ratio was 0.11 percent. Using the Student t factor for 6 degrees of freedom, we obtain 95 percent confidence limits of 0.3 percent. The value of the ratio for the glass rod employed was about 2.5, close enough to unity that both signals could be measured without changing gain settings. Thus the only further source of error in the ratio is in the non-linearity of the detection system. If we allow 0.3 percent for error from this source, then we obtain our combined estimate for errors in I_G/I_B and M_w from both sources as the square root of the sum of the squares of the individual error estimates, or 0.4 percent.

The geometric factor g in eq (4) is unity only if the vertically oriented polarizers in the incident and scattered beams transmit no horizontally polarized light at all. In the general case, we must consider both components of polarization in both the incident and scattered beams. Let ζ_i be the ratio of the transmission coefficients for horizontally and vertically polarized light for the polarizer in the incident beam, and let ζ_s be the corresponding ratio for the polarizer in the scattered beam. Then the observed scattering signal will be proportional to $V_v + \zeta_s H_v + \zeta_i V_h + \zeta_i \zeta_s H_h$, where V and H denote the vertically and horizontally polarized components, respectively, of the scattered radiation, and the subscripts v and h denote the vertically and horizontally polarized components, respectively, of the incident radiation. The ratio $H_v/V_v = V_h/V_v$ is the depolarization ratio ρ_v for vertically polarized light, related to ρ_u by $\rho_v = \rho_u / (2 - \rho_u)$. By considering the geometry of the scattering system, we find [15] that the H_h component of the scattering observed at an angle θ is the sum of two components, one independent of depolarization and proportional to $\cos^2 \theta$, the other arising from depolarized scattering and proportional to $\rho_v \sin^2 \theta$. The observed scattering signal is then proportional to

$$1 + (\zeta_i + \zeta_s) \rho_v + \zeta_i \zeta_s (\cos^2 \theta + \rho_v \sin^2 \theta).$$

The measured values of ζ_i and ζ_s for the polarizers in our instrument are 0.9×10^{-3} and 1.0×10^{-3} , respectively, therefore the term in $\zeta_i \zeta_s$ is negligible. The estimated optical anisotropies of polyethylenes discussed in section 4.12 imply values of ρ_v less than 0.8×10^{-3} , so the term $(\zeta_i + \zeta_s) \rho_v$ can also be neglected for the polyethylene measurements. Finally, for the calibrating measurements on benzene we have $\rho_u = 0.41$, which gives $\rho_v = 0.26$. The error in the benzene measurements is therefore $(0.9 + 1.0) \times 0.26 \times 10^{-3}$, which is zero to the nearest 0.1 percent, and is entered on line 7 of table 3.

4.7. The Ratios $S_G(\theta, c)$

The measured values $S_G(\theta, c)$ of the scattering from polyethylene solutions and solvent relative to the scattering from the glass working standard are subject to errors arising from non-linearity of the detection system. However, scattering from solvent and from the most dilute solutions, to which the value of M_w is most sensitive, were measured at the same gain settings as the glass working standard. Therefore, we believe that the estimated error of 0.3 percent used in section 4.5 is also adequate as an estimate of systematic error in $S_G(\theta, c)$.

4.8. Solution Concentration

As stated in section 2.1b, solutions were made up by weight. Concentrations c were calculated from the relation

$$c = w\rho = w\rho_0 / [1 - w(1 - \rho_0 \bar{v})], \quad (13)$$

where w , ρ , ρ_0 , and \bar{v} are weight fraction, solution density, solvent density, and partial specific volume, respectively. Thus, errors in c can arise from errors in w , ρ_0 , and \bar{v} . However, the value of M_w is unaffected by errors in \bar{v} . This can be seen by observing that the coefficient C_{00} in eq (5) from which M_w is calculated by eq (6), is the zero-angle zero-concentration limit of the product of c and a quantita

which is a function f of the scattering angle and measured scattering signals. As c approaches zero, ρ approaches the limiting value ρ_0 , so that using the left-hand equality of eq (13), we can rewrite C_{00} as ρ_0 times the zero-angle, zero-concentration limit of the product wf . Thus errors in \bar{v} will not affect the final value of M_w ; errors in ρ_0 will produce relative errors of the same size in M_w . We believe that our value for solvent density is accurate to 0.2 percent, as shown on line 9 of table 3.

Solute and solvent weights were measured on semimicro balances accurate to 0.1 mg. The resulting errors in solvent weights are of the order of a few parts per million, and can be neglected. In order to estimate the effect of errors in solute weights on the values of M_w obtained, a series of comparison calculations was carried out. For each SRM, one of the sets of measurements described in section 2.1c was chosen, and the value of M_w obtained from this set was taken as a "reference" value. The value for each solute weight in

turn was then increased by 0.1 mg and the value of M_w recalculated. The resulting percent changes in the reference values of M_w are shown in table 4, together with the sum of the absolute values of the individual changes, their algebraic sum, and the square root of the sum of their squares (root-sum-square). The sum of the absolute values represents the error if every weighing is in error by the maximum amount possible and in the direction which maximizes the resulting error in M_w . We reject this estimate as overly pessimistic. The absolute value of the algebraic sum would be the appropriate measure if all the weighings were in error by the same amount, and the root-sum-square would be appropriate if the individual errors were of random sign. Since both these possibilities seem physically plausible, we select as our error estimate the larger of the absolute value of the algebraic sum and the root-sum-square. As shown in table 4, this turns out to be the root-sum-square in all three cases. The corresponding values are shown on line 10 of table 3.

TABLE 4. Percent errors in weight-average molecular weight M_w introduced by assumed errors of 0.1 mg in solute weights

	SRM 1482	SRM 1483	SRM 1484
Number of solutions in reference subset	7	5	7
Percent changes in M_w from assumed changes in solute weight	-0.30, -0.09, 0.00, 0.06, 0.04, 0.02 -0.04	0.38, 0.10, -0.06, -0.08, 0.03	-1.06, -0.49, -0.11, 0.19, -0.22, 0.21, -0.08
Sum of absolute values of above	0.55	0.65	2.36
Algebraic sum of above	-0.31	0.37	-1.12
Root-sum-square of above	0.32	0.41	1.23

4.9. Reflection Correction

As a result of the reflection of light from the surface of the scattering cell, the signal observed at a scattering angle θ will include a component due to light scattered through an angle $\pi + \theta$. Several expressions have been given [2b, 7, 6] for the magnitude of this effect, which depends upon the system geometry and upon the indices of refraction of the scattering solution, the scattering cell, and the surrounding medium. When the effect is large, for example when the surrounding medium is air, explicit correction must be made to the observed scattering signals. For the work reported here, the surrounding medium was a silicone oil with an index of refraction of about 1.5, so that all three media have about the same index of refraction. In this case, the correction will be very small, and it will suffice to set an upper limit on the error introduced by its neglect.

The fraction f_r of light reflected at a perpendicular interface between regions with index of refraction n_1 and n_2 is given by Fresnel's formula as $f_r = [(n_1 - n_2)/(n_1 + n_2)]^2$. In the present case, all the indices of refraction involved are about 1.5; the maximum difference between them is about 0.1, giving a value of f_r about 0.001. The fraction of radiation scattered through $\pi + \theta$ appearing in the output at scattering angle θ is approximately [7] $2f_r$, or about 0.002. Suppose we wish to estimate an intercept a in the equation $y = a - bx$, where y is inversely proportional to the intensity of the scattering signal and $x = \sin^2(\theta/2)$, but the intensities observed (denoted by primes) are linear combinations of the "true" intensities at θ and $\pi + \theta$:

$$I_1' = (1 - \delta)I_1 + \delta I_2; \quad (14)$$

$$I_2' = \delta I_1 + (1 - \delta)I_2,$$

where the subscripts 1 and 2 denote scattering angles θ and $\pi + \theta$, respectively. We wish to find the error in the intercept a , determined from measurements at two points (x_1, y_1) and (x_2, y_2) , where $y_i = 1/I_i$, due to the use of I_1' and I_2' instead of I_1 and I_2 . Clearly the size of the error depends upon the relative sizes of I_1 and I_2 ; if I_1 is equal to I_2 no amount of mixing will produce an error in the intercept. Here we are interested in the case where I_2 is only slightly smaller than I_1 , and we write:

$$I_1' = I_2'(1 + \epsilon). \quad (15)$$

Solving for the apparent intercept in terms of (x_1, y_1') and (x_2, y_2') and using eqs (14) and (15) as appropriate, we find after some manipulation that to second order in δ and ϵ , the relative error in the intercept is given by

$$\delta\epsilon(x_2 + x_1)/(x_2 - x_1).$$

Taking the maximum and minimum scattering angles used for x_2 and x_1 , we have $(x_2 + x_1)/(x_2 - x_1) = \sqrt{2}$. For SRM 1484, with the strongest angle-dependence of the three SRM's, the observed scattering signal at 135° was about 6 percent larger than that at 45° . Then we have $\epsilon = 0.06$, and the relative error in M_w from neglect of the reflection correction is $0.002 \times 0.06 \times \sqrt{2}$, or about 0.02 percent for SRM 1484 and even less for the other two SRM's. To the nearest 0.1 percent, this is zero, and is so entered on line 11 of table 3.

4.10. Instrumental Misalignment

As described in section 2.1a, the optical alignment of the photometer was checked by observing that the scattering signals obtained from solvent at angles of 45 and 135° differed by less than 1 percent. From consideration of the instrument geometry and the alignment procedure, it appears that the likeliest misalignment is a constant offset in the scattering angle. For the vertically polarized scattering of vertically polarized light from solvent, the signal observed at scattering angle θ should be proportional to $\csc \theta$. It can easily be shown that in this case, a difference in scattering signal at 45 and 135° of 1 percent could be produced by an offset in the scattering angle of only 0.3°, which is consistent with our estimate of the accuracy of the alignment. Using the notation of section 4.9, we find that the relative error in the intercept a , and therefore in M_w , arising from equal and opposite relative errors $\delta/2$ in y_1 and y_2 is given by

$$(x_1 + x_2 + 2x_1x_2b/a)(\delta/2)/(x_2 - x_1).$$

For x_1 and x_2 corresponding to scattering angles of 45 and 135° respectively, this reduces to the simpler form

$$\delta(1 + \frac{1}{4}b/a)\sqrt{2}.$$

Thus the error increases with b/a , which is proportional to the mean-square radius. However, even for SMR 1484, the term $\frac{1}{4}b/a$ is only about 0.05, and the error given by the above expression for $\delta = 0.01$ is 0.7 percent for all three SRM's.

4.11. Refraction Correction

The observed scattering signal is proportional to both the scattering volume "seen" by the detector and the angular aperture of the detector optics. In general, both these quantities are functions of the index of refraction of the scattering liquid and of the system geometry. Equation (10) is written for the special case where the size and uniformity of the incident light beam are such that the incident intensity is constant over the region "seen" by the detector. For the instrument employed in this work, this condition is only approximately satisfied and eq (10) is not strictly valid. In principle, the factor n_B^2 in eq (10) should be replaced by a function of n_B , the index of refraction n_S of the solutions being measured, the system geometry, and integrals of intensity over various parts of the beam profile. However, for our present purpose it is neither practical nor necessary to obtain the exact expression. It is shown elsewhere [17] that in the special case where the incident beam dimension is much smaller than the region "seen" by the detector, the shape of the beam profile is irrelevant and the correct expression is obtained by replacing n_B^2 in eq (10) by $n_S n_B (n_B + z)/(n_S + z)$, where z is a function of system geometry equal to about 1/9 for our instrument. The correction factor to be applied to eq (10) in this case would then be just $(n_S/n_B)(n_B + z)/(n_S + z)$. This represents the limiting case; in our instrument the beam and the detector aperture are roughly the same size. The correction will then be smaller, and we can use the small-beam expression as an upper limit on the error in eq (10) from refraction effects. Taking $n_B = 1.503$ and $n_S = 1.586$, we find a correction factor of 1.004, or a limiting error of 0.4 percent.

4.12. Anisotropy of Polyethylene

Equations (6) and (10) are derived on the assumption that the light scattered by the solute is not depolarized. When the solute is optically anisotropic, M_w in eq (6) should be replaced by $M_w(1 + \xi)$, where the correction term ξ is given [18] by:

$$\xi = (1/45)(1/M)(\langle \gamma^2 \rangle / M)[4\pi n_S N_A / (dn/dc)]^2, \quad (16)$$

where $\langle \gamma^2 \rangle$ is the mean-square optical anisotropy of the solute molecules. For polyethylene, $\langle \gamma^2 \rangle$ is given approximately [19] as $267 \times 10^{-50} \text{ cm}^6$ per CH_2 group. The ratio $\langle \gamma^2 \rangle / M$ is just 1/14 of this, or $1.91 \times 10^{-49} \text{ cm}^6/\text{g}$. Using this value, and values already cited for the other quantities in eq (16), we find values for ξ of 0.001, 0.0005, and 0.0001 for SRM's 1482, 1483, and 1484, respectively. The corresponding error estimates are shown on line 14 of table 3, rounded to the nearest 0.1 percent.

4.13. Temperature Dependence of Scattering of Glass

Since the glass rod used as a working standard was compared with benzene at 23 °C and with the polyethylene solutions at 135 °C, any temperature dependence in the scattering from the glass rod will give rise to errors in our values of M_w . It appears [20] that for the type of glass used for the working standard, the temperature-dependent scattering should amount to no more than 1 percent of the total scattering, and the temperature dependence of this part should be no stronger than the first power of the absolute temperature. The resulting maximum error, for comparisons between 23 and 135 °C, is 0.4 percent.

4.14. Cutoff of Virial Expansion

As described in section 3.2, virial coefficients beyond the third were not included in the analysis of the light-scattering data. At the solution concentrations employed in this work, their contribution should be negligible. Nevertheless, their neglect constitutes a source of systematic error, upon which we now attempt to set a limit. We first examine the relative sizes of the terms C_{00} , $C_{10}c$, and $C_{20}c^2$ in eq (5) at the maximum concentrations at which measurements were taken for each of the three SRM's. The relative sizes turn out to be 1.00 : 0.52 : 0.08 for SRM 1482, 1.00 : 0.70 : 0.15 for SRM 1483, and 1.00 : 0.74 : 0.09 for SRM 1484. The series all appear to be converging at a satisfactory rate. In addition, in each case the ratio of the third term to the second is appreciably smaller than the ratio of the second term to the first. Lacking any means of estimating the size of the fourth virial coefficient directly, it seems sufficiently cautious to suppose that the ratio of the fourth term to the third will be no larger than the ratio of the second term to the first, i.e., $C_{30} \leq C_{10}C_{20}/C_{00}$. In terms of the virial coefficients, this amounts to the assumption $A_4 \leq \frac{3}{2} M_w A_2 A_3$ using the relation $A_4 = \frac{1}{4} K' C_{30}$, the analogue of eqs. (8) and (9) for the fourth virial coefficient. The effect of a value of C_{30} of this maximum size upon the value of M_w was found by a technique similar to the method described in 4.8 for estimating the effects of errors in solute weights. For each

SRM, a typical set of measurements was chosen as a reference set, and the corresponding value of M_w taken as the reference value. An "error" term $C_{30}c^3$, with C_{30} determined as described above, was then subtracted from each value of c/I_c in the set, and the value of M_w recalculated. The resulting changes of 0.7 percent, 1.4 percent, and 0.9 percent for SRM 1482, 1483, and 1484, respectively, are shown on line 16 of table 3.

4.15. Summary

Estimates of the contributions of individual sources to the overall systematic error in M_w are summarized in table 3. It will be seen that the uncertainty in the Rayleigh ratio for benzene, shown on line 5 of table 3, completely overwhelms all the other uncertainties. Furthermore, it is based on literature values, which may be subject to future revision. Therefore, we first consider all the listed sources of error *except* the Rayleigh ratio of benzene. The sums and root-sum-squares of these are also shown in table 3. As discussed in 4.8, we believe that the simple sum is an overly pessimistic estimate of error, and that the root-sum-square is more realistic. However, both to temper this judgment and to allow for other sources of error not considered here explicitly, we form our final, "best" estimates by increasing the root-sum-squares values of 2.5 to 3 percent in line 18 to 4 percent, as shown on line 19. Finally, we form the root-sum-square of this value with the uncertainty in the Rayleigh ratio for benzene to obtain final estimates for systematic errors from *all* sources of 11 percent, as shown on line 20 of table 3 and on the certificates for SRM's 1482, 1483, and 1484.

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The Characterization of Linear Polyethylene SRM's 1482, 1483, and 1484. IV. Limiting Viscosity Numbers by Capillary Viscometry

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Linear polyethylene Standard Reference Materials SRM 1482, 1483, and 1484 are certified for limiting viscosity number in 1,2,4-trichlorobenzene and 1-chloronaphthalene at 130 °C. In this paper the experimental procedures employed for the determination of limiting viscosity numbers for these materials by capillary viscometry are described, and the techniques used to analyze the data and to estimate limits of systematic error are discussed.

Key words: Capillary viscometry; fraction; limiting viscosity number; narrow molecular weight distribution; number-average molecular weight; polyethylene; Standard Reference Material; weight-average molecular weight.

1. Introduction

Standard Reference Materials 1482, 1483, and 1484 are linear polyethylenes with relatively narrow distributions in molecular weight, which are issued by the National Bureau of Standards. Their general characteristics are described in the first paper of this series [1].¹ In the present paper, we describe the determination of their certificate values of limiting viscosity number at 130 °C in 1,2,4-trichlorobenzene (TCB) and in 1-chloronaphthalene (1CN). The determination of limiting viscosity number by capillary viscometry is relatively simple. Although the relationship between limiting viscosity number and molecular weight remains analytically intractable, it has been well established empirically for linear polyethylene in the solvents and at the temperature cited above [2].

2. Experimental

Viscosity measurements were made with a Cannon-Ubbelohde filter stick viscometer (Cannon Instrument Co., State College, Pa.,² size 75) immersed in a constant-temperature bath. Flow times in the viscometer were measured with a Hewlett-Packard Autoviscometer, Model 5901B.

Flow times were measured in both solvents for solutions whose concentrations ranged from 2 to 9 g/L for SRM 1482, 1 to 5 g/L for SRM 1483, and 0.3 to 2 g/L for SRM 1484. All solutions were made up directly by weight, without employing successive dilution techniques. Concentrations were calculated using values of solvent density and partial specific volume determined pycnometrically in this laboratory. The 1CN was obtained from commercial material by distillation at reduced pressure after removal of residual naphthalene by sublimation, also at reduced pressure. Several sources of TCB were used, without apparent effect on

the results obtained. From 0.05 to 0.1 percent of the antioxidant 2,6-di-*tert*-butyl-4-methylphenol was added to all solvents. The polyethylenes were dissolved by heating the solvent to 130–140 °C with occasional stirring, and the solutions were then transferred to the viscometer through a sintered glass frit, as described in ASTM D 1601–61.³ A few minutes were allowed for thermal equilibration, then flow times were measured repeatedly until a value stable to 10 ms or so was obtained. The flow times measured in this way ranged from 70 to 100 s in TCB, and from 100 to 150 s in 1CN.

3. Results

The solution viscosity $\eta(c)$ may be expanded as a power series in solution concentration c :

$$\eta(c) = P' + Q'c + R'c^2 + \dots \quad (1)$$

The viscosity number, defined as $[\eta(c) - \eta(0)]/[\eta(0)c]$, is then:

$$[\eta(c) - \eta(0)]/[\eta(0)c] = Q'/P' + (R'/P')c + \dots$$

The limiting viscosity number, for which we shall employ the symbol Λ in this paper,⁴ is just the zero-concentration limit of the viscosity number [3], and is given by the ratio Q'/P' of the coefficients in eq (1). The zero-concentration derivative of viscosity number with respect to concentration is usually expressed as $\Lambda^2 k'$, where k' is called the Huggins coefficient [3] and is given in terms of the coefficients in eq (1) by $P'R'/Q'^2$.

For a properly designed capillary viscometer, the solution viscosity is almost proportional to the product of solution density and measured flow time [4]. The departure from

¹ Figures in brackets indicate 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 Available from the American Society for Testing and Materials, 1916 Race Street, Philadelphia, Pa. 19103.

⁴ The symbols LVN and $[\eta]$ are often used to denote this quantity; here we prefer a symbol which is not an acronym and is free of punctuation marks.

proportionality is due to a combination of kinetic energy effects and hydrodynamic effects at the ends of the capillary. For the viscometer design and Reynolds numbers used in this work, the relationship between viscosity and flow time is given approximately [5] by:

$$\eta/\rho = Ct_m - Et_m^{-2}, \quad (2)$$

where ρ is the density of the liquid, t_m is the measured flow time through the capillary, and C and E are constants of the viscometer, determined experimentally. Since only ratios of viscosities are needed for the determination of limiting viscosity number and Huggins coefficient, it is convenient to introduce a "corrected" flow time t , defined by:

$$t = t_m(1 - Kt_m^{-3}), \quad (3)$$

with $K = E/C$. In terms of t , eq (2) becomes $\eta/\rho = Ct$, and using eq (1), we can write the product ρt as a polynomial in concentration:

$$\rho(c)t(c) = P + Qc + Rc^2 + \dots, \quad (4)$$

where P , Q , and R are equal to the corresponding primed quantities in eq (1) divided by the viscometer constant C , and we have $\Lambda = Q/P$, $k' = PR/Q^2$.

In the remainder of this section, we discuss first the method used to obtain the constant K for the viscometer employed in this work, then the procedures used to obtain limiting viscosity numbers and Huggins coefficients for SRM's 1482, 1483, and 1484 from the "corrected" flow times, and finally the procedures employed to estimate the effect of shear rate upon the results.

3.1. Correction for Kinetic Energy and End Effects

The correction factor K in eq (3) was determined by measuring flow times for two certified viscosity standards (Cannon Instrument Co., State College, Pa.), of known viscosity and density. One (N4) of these was chosen to give a flow time close to that obtained with 1,2,4-trichlorobenzene, the less viscous of the solvents in which limiting viscosity numbers are reported. The other (S3) was chosen to have a very long flow time, giving a "correction" Kt_m^{-3} of about 3×10^{-5} . Six measurements were made with N4 and four with S3. A measurement consisted of charging the viscometer with liquid and measuring flow time repeatedly until a constant flow time was reached. The resulting mean flow times were used in eq (2) to determine K . Letting the subscripts N and S refer to measurements made on N4 and S3, respectively, we write eq (2) for each mean flow time and solve the resulting pair of equations for E/C , obtaining:

$$K = E/C = (rt_N - t_S)/(rt_N^{-2} - t_S^{-2}), \quad (5)$$

where $r = \eta_S \rho_N / (\eta_N \rho_S)$.

The standard deviations of the mean flow times amounted to about 0.01 percent for both liquids. Using Student t factors [6] for 5 and 3 degrees of freedom, we obtain 95 percent confidence limits of 0.02 percent and 0.03 percent for flow time measurements on N4 and S3, respectively. The effects of these uncertainties upon the value of K , and ultimately upon the values of Λ , are discussed in section 4.3.

3.2. Limiting Viscosity Numbers

Limiting viscosity numbers were determined, for each SRM and each solvent, by measuring flow times for solvent and for solutions of several different concentrations. The measured flow times were first converted to "corrected" flow times, using eq (3). The corrected flow times were then multiplied by solution densities calculated from measured values of solvent density and partial specific volume. In preliminary studies, it was found that for concentrations c such that the ratios $\rho(c)t(c)/[\rho(0)t(0)]$ were less than 1.4, plots of $\{\rho(c)t(c)/[\rho(0)t(0)] - 1\}/c$ versus c appeared linear, in accordance with eq (4). The certification measurements were therefore carried out in this concentration range, and the products $\rho(c)t(c)$ were fitted by least squares to second-order polynomials in solution concentration c , as shown in eq (4). The limiting viscosity numbers Λ and Huggins coefficients k' were then obtained as the ratios Q/P and PR/Q^2 of the coefficients in eq (4).

In principle, the flow time for a given viscometer, solvent, and temperature ought to be constant in time. In practice, however, solvent flow times appeared to be materially more reproducible within a single day than over longer periods. Standard deviations of solvent flow times measured within a single day were typically about 16 ms; standard deviations of flow times measured on different days were about twice this value. Measurements on each SRM and in each solvent were therefore grouped into subsets, each consisting of one or two values of solvent flow time and values of flow time for several solutions. All the measurements in each subset were made on the same day. The flow times in each subset were fitted separately by least squares to eq (4). For each SRM and each solvent, several subsets of data were obtained, leading to several estimates of Λ and k' . In some cases, the subsets were far from equivalent, some subsets containing twice as many measurements as others. The structure of the subsets and data analysis techniques employed are discussed separately for each of the three SRM's in the following subsections.

a. SRM 1482

Five subsets of measurements on SRM 1482 were made in each solvent. Each subset consists of from six to twelve flow time measurements, including solvent flow times. The solutions had nominal concentrations of 2, 3, 4.5, 7, and 9 g/L. Some nominal concentrations were omitted from some of the subsets; other subsets contain more than one solution of the same nominal concentration. Consequently, the estimates of Λ and k' obtained from the separate subsets differ appreciably in precision. The final estimates of Λ and k' in each solvent were therefore taken as weighted averages of the estimates from the individual subsets, obtained as described in the following paragraph.

Let the number of flow time measurements (of both solvent and solutions) in the i th subset be N_i . The least squares analysis for the i th subset yields an estimate Λ_i of limiting viscosity number, together with an estimate $v_i(t)$ of the variance in flow time inferred from the mean-square differences between observed and calculated (from eq (4)) flow times, and an estimate $v(\Lambda_i)$ of the variance in Λ_i . Each estimate $v(\Lambda_i)$ is the product of $v_i(t)$ and a factor obtained from the covariance matrix for the i th subset by standard

techniques [6]. The scatter in the values $v(\Lambda_i)$ therefore reflects both the differences between the covariance matrices for the subsets and the scatter in the individual estimates $v_i(t)$. We now make the assumption that all the $v_i(t)$ for a given solvent are estimates of the same quantity $v(t)$. Since three parameters are fitted in each subset analysis, the number F_i of degrees of freedom associated with $v_i(t)$ is just $N_i - 3$. Our best estimate of $v(t)$ is given by the average of the $v_i(t)$ over all the subsets, weighted by the F_i , i.e.,

$$v(t) = F^{-1} \sum_i F_i v_i(t),$$

where $F = \sum_i F_i$ and the summations are taken over all the subsets for a given solvent. We can then obtain improved estimates $v'(\Lambda_i)$ of the variance in Λ_i , which are free of the scatter in the individual estimates $v_i(t)$, as

$$v'(\Lambda_i) = v(\Lambda_i) v(t) / v_i(t).$$

Finally, we obtain our overall estimate of Λ as the average of the Λ_i , weighted inversely by the $v'(\Lambda_i)$, i.e.,

$$\Lambda = \left[\sum_i v'(\Lambda_i)^{-1} \right]^{-1} \sum_i v'(\Lambda_i)^{-1} \Lambda_i, \quad (6)$$

with variance $v(\Lambda)$ given by

$$v(\Lambda) = \left[\sum_i v'(\Lambda_i)^{-1} \right]^{-1}, \quad (7)$$

with F degrees of freedom. Finally, the standard deviation $s(\Lambda)$ in Λ is obtained as $s(\Lambda) = [v(\Lambda)]^{1/2}$. Overall estimates of k' and $s(k')$ are obtained by an exactly analogous procedure. The results are given in table 1.

b. SRM 1483

Five subsets of measurements on SRM 1483 were made in TCB. Each subset contains five solution flow times, for solutions with nominal concentrations of 1, 2, 3, 4, and 5 g/L, and two solvent flow times. Since the subsets are essentially equivalent, we obtain our final values for Λ and k' as the unweighted averages of the estimates from the individual subsets. Three parameters are determined for each subset, so four degrees of freedom are associated with the estimates of the variance in Λ and k' from each subset. Additional estimates of the variance in Λ and k' , also

associated with four degrees of freedom, are obtained from the set of five individual subset estimates of Λ and k' . Our final estimates of the variance in the subset values of Λ and k' are then formed as the unweighted average of the six individual estimates, one from each subset analysis and one from the set of subset values of Λ and k' , and are associated with a total of 24 degrees of freedom. The estimated variances $v(\Lambda_m)$ and $v(k'_m)$ of the final mean values of Λ and k' are then of course just $1/5$ the estimated variances $v(\Lambda)$ and $v(k')$ of the individual values.

The estimated variance $v(t)$ and standard deviation $s(t)$ in flow time are not used directly in the calculation of Λ , k' and their variances. They may be obtained by observing that for equivalent subsets, the ratio $v(t)/v(\Lambda)$ of the variance of a single measurement of flow time to the variance of a single subset determination of Λ is constant. Choosing the quantity $\sum_i v_i(t) / \sum_i v(\Lambda_i)$ to estimate this ratio, we have

$$\begin{aligned} v(t) &= s^2(t) = v(\Lambda) \sum_i v_i(t) / \sum_i v(\Lambda_i) \\ &= 5v(\Lambda_m) \sum_i v_i(t) / \sum_i v(\Lambda_i), \end{aligned} \quad (8)$$

where $v(\Lambda_i)$ and $v_i(t)$ are the estimated variances in Λ and in t , respectively, obtained from the i th subset analysis.

Four subsets of measurements on SRM 1483 were made in ICN. Three of these were identical in structure with the subsets in TCB. The fourth subset differed from the other three only in the omission of one of the solvent flow time measurements. We shall refer to this subset as the six-point subset, and to the others as the seven-point subsets. We first obtain estimates of Λ , k' , $v(\Lambda)$, $v(k')$, and $v(t)$ from the three equivalent seven-point subsets, in a way analogous to the method employed for the measurements on SRM 1483 in TCB. The variances so obtained are associated with 14 degrees of freedom, four from each subset and two from the subset-to-subset variation. We then combine these estimates with those from the six-point subset, associated with three degrees of freedom, in the way described in section 3.2a, obtaining the final values given in table 1, with a total of 17 degrees of freedom.

c. SRM 1484

Five subsets of measurements on SRM 1484 were made in each solvent. Each subset contains one or two flow times for

TABLE 1. Limiting viscosity numbers and Huggins coefficients for solutions of linear polyethylene Standard Reference Materials 1482, 1483, and 1484 in 1,2,4-trichlorobenzene (TCB) and 1-chloronaphthalene (ICN) at 130 °C, obtained by capillary viscometry. Standard deviations $s(t)$ in viscometer flow times are also shown, as an indication of the overall precision of the measurements.

Solvent	Material	$s(t)$ seconds	Limiting viscosity number, Λ , mL/g	Standard deviation in Λ , mL/g	Huggins coefficient, k'	Standard deviation in k'	Number of degrees of freedom
TCB	SRM 1482	0.052	40.15	0.13	0.399	0.011	28
	SRM 1483	.056	79.40	.31	.419	.013	24
	SRM 1484	.039	197.93	.60	.462	.010	22
ICN	SRM 1482	.064	36.36	.11	.446	.011	24
	SRM 1483	.064	70.56	.28	.461	.016	17
	SRM 1484	.064	169.38	.60	.526	.014	22

solvent, flow times for two solutions with nominal concentrations of 0.6 g/L, and one flow time each for solutions with nominal concentrations of 0.4, 0.8, 1.2, and 1.8 g/L. Since the number of solvent flow times is not the same in every subset, the subsets are not equivalent. They were therefore analyzed by the same technique employed for SRM 1482 and described in section 3.2a. The results are shown in table 1.

3.3 Shear Rate Dependence

At low rates of shear, the viscosity of a solution of flexible macromolecules is independent of shear rate. At higher rates of shear, however, solution viscosity decreases with increasing shear rate. The possibility of dependence of our measured viscosities upon shear rate was investigated by a series of comparison measurements in two capillary viscometers with different shear rates. Since shear-rate dependence increases with increasing molecular weight, measurements were made on solutions of SRM 1484, the highest in molecular weight of the three SRM's.

The maximum shear rate in a capillary viscometer is given [7] in terms of the flow time t and the bulb volume V and capillary radius a of the viscometer by the expression $4V/(\pi a^3 t)$. For the viscometer employed for the measurements described in section 3.2, hereafter referred to as the reference viscometer, this gives a maximum shear rate of about $3 \times 10^3 \text{ s}^{-1}$ for measurements in TCB at 130 °C. The viscometer employed for comparison had a maximum shear rate of about $6 \times 10^3 \text{ s}^{-1}$ for the same solvent and temperature.

Flow times for solvent and for a solution of SRM 1484 with a nominal concentration c of 1 g/L were measured in both viscometers. The kinetic energy and end effect correction factor K , determined as described in section 3.1, was applied to the flow times measured with the reference viscometer. The corresponding correction for the comparison viscometer was found to be negligible from the manufacturer's calibration measurements. The ratios $t(c)/t(0)$ of solution flow time to solvent flow time were 1.219 for the reference viscometer and 1.221 for the comparison viscometer. The difference between them is consistent with our estimated precision of 0.001 in the ratio, and is in the opposite direction from the expected effect of shear-rate dependence, which would lead to a smaller ratio at higher shear rates. Thus we are unable to detect any shear-rate dependence in our results.

4. Systematic Errors

We now list the likeliest sources of systematic error in the estimates of limiting viscosity number described in the preceding section, and attempt to set upper limits on their magnitudes. Individual sources of error are discussed in the following subsections; the resulting error-limit estimates are summarized in table 2, expressed as percent errors applied to Λ .

In this work, Λ is calculated as the ratio Q/P of coefficients in eq (4), which are obtained by fitting the product $\rho(c)t(c)$ to a second-order polynomial in solution concentration c by least squares. Here $\rho(c)$ is solution density and $t(c)$ is related to the measured flow time $t_m(c)$ in the viscometer by eq (3). The correction factor K in eq (3) is obtained as described in section 3.1. The concentration is given by the product $w\rho(c)$, where w is the weight fraction of solute in the

solution, and $\rho(c)$ is given in terms of the solvent density $\rho(0)$ and the partial specific volume \bar{v} by:

$$\rho(c) = \rho(0)/[1 - w(1 - \rho(0)\bar{v})]. \quad (9)$$

Systematic errors in $\rho(0)$, \bar{v} , K , w , and $t_m(c)$ will therefore affect the calculated values of Λ directly. The effects of errors in the first three of these quantities can be exhibited explicitly. For this purpose, we first write, using eq (4):

$$\Lambda = \mathcal{L}\{[\rho(c)t(c) - \rho(0)t(0)]/[\rho(0)t(0)c]\}, \quad (10)$$

where we use the symbol $\mathcal{L}\{ \}$ to mean the zero-concentration limit of the quantity within the curly brackets. We then use eq (3) and (9) to re-express the limit in eq (10) in terms of a limit which involves only the directly measured quantities w and $t_m(c)$. After some rearrangement, and making use of the fact that the limit of a product is the product of the limits of the factors when all the limits involved exist, we find:

$$\Lambda = \rho(0)^{-1} [[1 + 2Kt_m(0)^{-3}] / [1 - Kt_m(0)^{-3}]^{-1} \times \mathcal{L}\{ [t_m(c) - t_m(0)] / [wt_m(0)] \} + 1] - \bar{v}, \quad (11)$$

from which the effects of errors in $\rho(0)$, K , and \bar{v} upon Λ may be obtained directly.

TABLE 2. Percent errors in limiting viscosity numbers introduced by measured quantities

Source of error		Error in limiting viscosity number, percent					
	Solvent	1,2,4-trichloroben- zene			1-chloronaphthalene		
	Material	SRM 1482	SRM 1483	SRM 1484	SRM 1482	SRM 1483	SRM 1484
Solvent density		0.20	0.20	0.20	0.20	0.20	0.20
Partial specific volume		.10	.05	.02	.11	.06	.02
Solute weights		.19	.14	.38	.18	.15	.36
Timer		.19	.19	.20	.13	.14	.15
Flow time correction factor K		.28	.28	.28	.08	.08	.08
Measurement temperature		.10	.10	.10	.10	.10	.10
Root-sum-square of the above		.46	.43	.56	.34	.32	.46
Sum of the individual error estimates		1.06	.96	1.18	.80	.73	.91
Expected limit of systematic errors from all sources, including sources not identified and treated here		1	1	1	1	1	1

In the following subsections, the effects of errors in solution concentration and density, errors in measured flow time, and errors in K are discussed in sections 4.1, 4.2, and 4.3, respectively. Since Λ is in general temperature-dependent, errors in the measurement temperature will give rise to implicit errors in Λ ; these are discussed in section 4.4. Finally, the error limits from all sources are combined and summarized in section 4.5.

4.1 Errors in Solution Concentration and Density

The effects of errors in solution density resulting from errors in solvent density and partial specific volume are shown by eq (11). We believe that for both solvents, our measurements of $\rho(0)$ are accurate to 0.2 percent, and that our values of \bar{v} are accurate to about 3 percent, or 0.04 mL/g. By eq (11), a 0.2 percent relative error in $\rho(0)$ will lead to a 0.2 percent relative error in Λ , and an absolute error of 0.04 mL/g in \bar{v} will lead to an absolute error of the same size in Λ , leading to the relative errors in Λ shown in table 2.

The most direct source of possible systematic errors in solution concentrations is the balances used to weigh solute and solvent. Solute weights for SRM 1482 and solvent weights for all three SRM's were measured on semimicrobalances accurate to 0.1 mg. Solute weights for SRM 1483 and SRM 1484 were measured on an electrobalance accurate to 0.04 mg. The resulting errors in solvent weights are of the order of a few parts per million, and can be neglected. In order to estimate the effect of errors in the solute weights on the values of Λ , a series of comparison calculations was carried out. For each SRM and each solvent, a reference subset of typical data points was chosen, one at each concentration measured, and a "reference" value of Λ was calculated from this set of points. The value for each solute weight in turn was then increased by its assumed limit of error, and the value of Λ recalculated. The resulting percent changes in the reference values of Λ are shown in table 3, together with the sum of the absolute values of the individual changes, their algebraic sum, and the square root of the sum of their squares (root-sum-square). The sum of the absolute values represents the error in the case where every weighing is in error by the maximum amount possible and in the direction which maximizes the resulting error in Λ . We reject this estimate as overly pessimistic. The algebraic sum could be the appropriate measure if all the weighings were in error by the same amount, and the root-sum-square would be appropriate if the individual errors were of random sign. Since both these possibilities seem physically plausible, we select as our error estimate the larger of the absolute value of the algebraic sum and the root-sum-square. This turns out to be the absolute value of the algebraic sum for all three SRM's

in TCB and for SRM 1482 in 1CN, and the root-sum-square for SRM's 1483 and 1484 in 1CN. The corresponding values are shown in table 2.

A second possible source of systematic error in solution concentrations would arise if buoyancy corrections were not applied to solute and solvent weighings. Buoyancy corrections were applied to all measured solute and solvent weighings for SRM 1484, but not for SRM's 1482 and 1483. From the definition of weight fraction and the usual expression for the buoyancy correction, it is easily seen that as the concentration tends to zero, the correction factor $f(c)$ by which the "apparent" weight fraction (i.e., with uncorrected weighings) should be multiplied to give the true weight fraction approaches the limiting value

$$f(0) = (1 - \rho_a/\rho_v)/(1 - \rho_a/\rho_u),$$

where ρ_a , ρ_u , and ρ_v are the densities of air, solute, and solvent, respectively. It is clear from the form of the limit expression in eq (11) that the limit is converted to its "corrected" value by dividing it by $f(0)$. Although this correction amounts to only about 0.03 percent for polyethylene in TCB and 1CN, it affects the last digit in the values of Λ given in table 1, and was therefore applied to the data for SRM's 1482 and 1483.

4.2. Timer Errors

Viscometer flow times are measured to 0.001s. Spot checking suggests that they are accurate to at least 0.01s. The errors in Λ resulting from assumed errors in flow time of 0.01s were obtained by the same kind of comparison calculation described in 4.1 for errors in solute weight; the results are shown in table 4. Again, we reject the sum of the absolute values of the individual changes as being too pessimistic, and choose the larger of the absolute value of the algebraic sum of the individual changes and their root-sum-square. Since the viscosity number is essentially measured by the difference between solvent and solution flow times, it is not surprising that the algebraic sum of the individual changes including solvent is nearly zero. We therefore choose the root-sum-square as our error estimate, as shown in table 2.

TABLE 3. Percent errors in limiting viscosity number Λ introduced by assumed errors in solute weights

Material	SRM 1482	SRM 1483	SRM 1484
Measurements in TCB: Percent changes in Λ from assumed errors in solute weight	-.04, -.07, -.09, -.07, +.08	-.02, -.07 -.08, -.04, +.07	-.01, -.20, -.17, -.14, +.14
Sum of absolute values of above	0.35	0.26	0.66
Algebraic sum of above	-0.19	-0.14	-0.38
Root-sum-square of above	0.16	0.13	0.33
Measurements in 1CN: Percent changes in Λ from assumed errors in solute weight	-.03, -.06, -.10, -.08, +.09	+.004, -.08, -.10, -.03, +.07	+.03, -.17, -.19, -.19, +.17
Sum of absolute values of above	0.36	0.28	0.75
Algebraic sum of above	-0.18	-0.14	-0.35
Root-sum-square of above	0.17	0.15	0.36

TABLE 4. Percent errors in limiting viscosity number Λ introduced by assumed errors in measured flow times

Material	SRM 1482	SRM 1483	SRM 1484
Measurements in TCB: Percent changes in Λ from assumed changes in: Solution flow times	+0.03, +0.05, +0.06, +0.05, -0.05	+0.02, +0.07, +0.07, +0.03, -0.06	+0.01, +0.08, +0.06, +0.05, -0.04
Solvent flow time	-0.16	-0.15	-0.16
Sum of absolute values of above	0.40	0.40	0.40
Algebraic sum of above	-0.02	-0.02	0.00
Root-sum-square of above	0.19	0.19	0.20
Measurements in 1CN: Percent changes in Λ from assumed changes in: Solution flow times	+0.02, +0.03, +0.05, +0.04, -0.04	-0.002, +0.05, +0.065, +0.018, -0.04	-0.01, +0.05, +0.05, +0.05, -0.04
Solvent flow time	-0.10	-0.10	-0.11
Sum of absolute values of above	0.28	0.28	0.31
Algebraic sum of above	0.00	-0.01	-0.01
Root-sum-square of above	0.13	0.14	0.15

4.3. Errors in K

As described in section 3.1, the correction factor K was determined from the flow times t_N and t_S of two calibrating liquids of known viscosity and density. Equation (5) gives K in terms of t_N , t_S , and the ratio r of the viscosities and densities of the calibrating liquids. The ratio r is equivalent to the ratio of flow times measured in special viscometers used for calibration. We believe that r is accurate to 0.1 percent. As stated in section 3.1, 95 percent confidence limits of 0.02 percent and 0.03 percent can be assigned to our measured values of t_N and t_S , respectively. Using the numerical values for these quantities in eq (5), we find that changes of these amounts in r , t_N and t_S produce changes in K of 10 percent, 2 percent, and 3 percent respectively. The root-sum-square of the three error limits is 11 percent in K . The products $Kt_m(0)^{-3}$ which occur in eq (11) are equal to 0.0088 for TCB and 0.0025 for 1CN. From eq (11), errors of 11 percent in these products result in errors in Λ of 0.28 percent and 0.08 percent for measurements in TCB and 1CN, respectively, shown in table 2.

4.4. Errors in Measurement Temperature

It is clear from eq (11) that so long as we have

$$Kt_m(0)^{-3} \ll 1$$

and $\bar{v} \ll \Lambda$, the temperature dependence of Λ will be essentially that of the product of $\rho(0)^{-1}$ and the limit

$$\mathcal{L}\{[t_m(c) - t_m(0)]/[wt_m(0)]\}.$$

The decrease in solvent density with temperature is roughly 0.1 percent per °C for both TCB and 1CN, which would lead to an increase in Λ of about the same size. Estimates of the temperature dependence of the limit quantity are not available. However, Chiang [8] has reported a decrease in Λ of 0.2 percent per °C for linear polyethylenes in six theta solvents, consisting of aromatic hydrocarbons, ethers, and

alcohols, and Flory, Ciferri and Chiang [9] report a decrease of 0.1 percent per °C for linear polyethylenes in three n alkanes. Since the temperature dependence of $\rho(0)$ will always contribute an *increase* in Λ with increasing temperature, typically of about 0.1 percent per °C, it appears that the limit quantity must decrease with temperature at two or three times this rate. Lacking more directly applicable data we choose 1 percent per °C as a safe upper limit for the change in Λ with temperature in the solvents employed in this work. We believe that our measurements of the viscometer bath temperature are accurate to 0.1 °C. The corresponding uncertainty in Λ of 0.1 percent is shown in table 2.

4.5. Summary

Estimates of the contributions of individual sources to the possible systematic errors in Λ are summarized in table 2 together with their sums and root-sum-squares. As previously discussed, we believe that the sum of the absolute values of the individual errors is an unduly pessimistic estimate of the error from all the sources discussed here, and that the root-sum-squares constitute a more reasonable estimate. To take account of sources of error not considered explicitly here, we round each of the root-sum-square estimates, which range from 0.32 percent to 0.56 percent, upward to 1 percent in all cases. Finally, we note that our final error estimates of 1 percent are exceeded by the sum of the absolute values of individual error estimates in only two out of the six cases and that the largest sum of absolute values, for SRM 1484 in TCB, is only 1.18 percent. We therefore believe that our arbitrary limits of 1 percent for systematic errors from all sources are quite likely to be realistic. These estimates are those given on the certificates for SRM's 1482, 1483, and 1484.

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