



Standard Test Method for Determination of Weight-Average Molecular Weight of Polymers By Light Scattering¹

This standard is issued under the fixed designation D4001; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval. A superscript epsilon (ϵ) indicates an editorial change since the last revision or reapproval.

1. Scope*

1.1 This test method describes the test procedures for determining the weight-average molecular weight M_w of polymers by light scattering. It is applicable to all nonionic homopolymers (linear or branched) that dissolve completely without reaction or degradation to form stable solutions. Copolymers and polyelectrolytes are not within its scope. The procedure also allows the determination of the second virial coefficient, A_2 , which is a measure of polymer-solvent interactions, and the root-mean-square radius of gyration $(s^2)^{1/2}$, which is a measure of the dimensions of the polymer chain.

1.2 The molecular-weight range for light scattering is, to some extent, determined by the size of the dissolved polymer molecules and the refractive indices of solvent and polymer. A range frequently stated is 10,000 to 10,000,000, is often extended in either direction with suitable systems and by the use of special techniques.

1.2.1 The lower limit to molecular weight results from low levels of excess solution scattering over that of the solvent. The greater the specific refractive increment dn/dc (difference in refractive indices of solution and solvent per unit concentration), the greater the level of solution scattering and the lower the molecular weight that shall be determined with a given precision.

1.2.2 The upper limit to molecular weight results from the angular dependence of the solution scattering, which is determined by the molecular size. For sufficiently large molecules, measurements must be made at small scattering angles, which are ultimately outside the range of the photometer used.

1.3 The values stated in SI units are to be regarded as standard.

1.4 *This standard does not purport to address all of the safety concerns, if any, associated with its use. It is the responsibility of the user of this standard to establish appro-*

priate safety and health practices and determine the applicability of regulatory limitations prior to use.

NOTE 1—There is no known ISO equivalent to this standard.

2. Referenced Documents

2.1 *ASTM Standards*:²

IEEE/ASTM SI-10 American National Standard for Use of the International System of Units (SI): The Modern Metric System

3. Terminology

3.1 *Definitions*—Units, symbols, and abbreviations are in accordance with **IEEE/ASTM SI-10**.

4. Significance and Use

4.1 The weight-average molecular weight is a fundamental structure parameter of polymers, which is related to many physical properties of the bulk material, such as its rheological behavior. In addition, knowledge of the weight-average molecular weight, together with knowledge of the number-average molecular weight from osmometry, provides a useful measure of the breadth of the molecular-weight distribution.

4.2 Other important uses of information on the weight-average molecular weight are correlation with dilute-solution or melt-viscosity measurements and calibration of molecular-weight standards for use in liquid-exclusion (gel-permeation) chromatography.

4.3 To the extent that the light-scattering photometer is appropriately calibrated, light scattering is an absolute method and is therefore be applied to nonionic homopolymers that have not previously been synthesized or studied.

5. Apparatus

5.1 *Volumetric Flasks*, 100-mL, or other convenient size.

5.2 *Transfer Pipets*.

¹ This test method is under the jurisdiction of ASTM Committee D20 on Plastics and is the direct responsibility of Subcommittee D20.70 on Analytical Methods.70.05).

Current edition approved Nov. 1, 2013. Published November 2013. Originally approved in 1981. Last previous edition approved in 2006 as D4001-93 (2006). DOI: 10.1520/D4001-13.

² For referenced ASTM standards, visit the ASTM website, www.astm.org, or contact ASTM Customer Service at service@astm.org. For *Annual Book of ASTM Standards* volume information, refer to the standard's Document Summary page on the ASTM website.

*A Summary of Changes section appears at the end of this standard

5.3 *Photometer*, whose major components, described in [Appendix X1](#), are a light source, a projection optical system, a sample-cell area, a receiver optical system, a detector system, and a recording system. Typical photometers are described and summarized (1)³ in the literature.

5.4 *Differential Refractometer*, with sensitivity of approximately 3×10^{-6} refractive-index units, capable of measuring the specific refractive increment dn/dc at the wavelength and temperature of the scattering measurements (2).

NOTE 2—Specific refractive increments are tabulated (2,3) for many polymer-solvent systems.

5.5 *Refractometer*, Abbé type or equivalent, capable of measuring the refractive indices of solvents and solutions at the wavelength and temperature of the scattering measurements.

5.6 *Spectrophotometer*, capable of measuring the absorbance of solutions at the wavelength of the scattering measurements.

5.7 *Laminar-Flow Clean-Air Station*, to provide a dust-free area for preparing and cleaning solutions and filling the scattering cell.

5.8 *Filters and Filter Holders*, for cleaning solvents and solutions. Membrane filters with pore sizes from 0.10 to 0.45 μm , used in glass or plastic filter holders, are recommended.

5.8.1 For water and aqueous solutions, and for organic solvents that do not attack the material, the use of polycarbonate (Nucleopore) filters is recommended. These filters have the advantages of high flow rate without the use of gas pressure, minimal retention of solute on the filter, and efficient cleaning action. For other solvents, the use of cellulosic filters (Millipore or equivalent) is recommended.

NOTE 3—Sintered-glass filters is sometimes used, but these are relatively expensive and difficult to clean between uses. Centrifugation is sometimes used, but this step requires special care and techniques, or special scattering cell design, to be satisfactory.

6. Reagents and Materials

6.1 *Solvents*, as required. Since dn/dc is a function of composition, solvents shall be of high purity. Significant errors in molecular weight, which depends on the square of dn/dc , will be incurred if literature values of dn/dc are employed and the actual value of this quantity is different because of impurities in the solvent.

6.2 *12-Tungstosilicic Acid*, as standard for calibration of photometer.

7. Sample

7.1 The sample must be homogeneous, and must be thoroughly free of all foreign impurities. If at all possible, samples to be used for light-scattering measurements must be specially treated from synthesis on to minimize exposure to or contamination with particulate impurities. Gels that consist of very high-molecular-weight particles, are sometimes formed during synthesis and will interfere with the analysis. All such particu-

late matter must be removed, sometimes with considerable difficulty. It should be understood that when this is done, the remaining sample is no longer truly representative of the entire polymer. The extent of the difference from the original sample will depend on the removal techniques employed.

NOTE 4—Reduction of sample particle size in a clean Spex or Wiley mill speeds solution and, with slow-dissolving materials, is essential if the measurements are to be made in a reasonable time. Overheating with consequent sample degradation must be avoided during the milling process. Hard, tough samples or those with low melting points are handled by mixing with clean dry ice, milling the mixture, and then allowing the dry ice to sublime. Clean dry ice may be obtained by opening a tank of carbon dioxide to the atmosphere. Commercial dry ice has often been shown to be contaminated.

8. Preparation of Dust-Free Cell and Contents

8.1 Clean all glassware, including the scattering cell, with a suitable detergent to remove grease and other contaminants. Use of an ultrasonic cleaning bath is recommended. Rinse glassware at least four times with distilled water to remove all traces of detergent, and dry in a clean, dust-free drying oven.

NOTE 5—A laminar-flow clean-air station is recommended for providing a dust-free area for solution preparation and filtration. If a clean-air station is not used, a closed area in a location free of drafts and of sufficient size to hold the filter unit, scattering cell, and other glassware shall be used.

8.2 Filter solvent directly into the scattering cell. First rinse the cell several times with 5 to 10 mL of filtered solvent each, to remove dust particles. Upper surfaces of the interior of the cell shall be well washed down. Close the cell with a cap similarly rinsed with filtered solvent. After rinsing, fill the cell with the minimum amount of solvent required to bring the liquid level above the point where the light beam in the photometer passes through the cell.

NOTE 6—Use of a small filter holder fitting between a hypodermic syringe and needle is convenient where only small quantities of liquids are filtered. A cell cap, with a hole just large enough to insert the needle, is used.

8.3 Place the scattering cell in the photometer, or in an equivalent strong light beam, and examine it in the dark, viewing at small scattering angles. Bright specks of dust must not be visible; if they are, the cell was not rinsed completely or the filtration procedure is inadequate.

8.4 Subsequent use of the clean cell for adding increments of filtered solution or for replacing solvent with solution requires no further rinsing, except to ensure that residual solvent remaining, after the cell is emptied, is removed and replaced with solution.

9. Procedure

9.1 Calibrate the light-scattering photometer. This calibration is required to convert measurements of scattered light intensity from arbitrary to absolute values, an essential step in the calculation of molecular weight. The calibration procedure, which is lengthy and requires great care to obtain accurate results, is given in [Appendix X2](#). The calibration constant of most photometers remains stable for long periods of time, however, so making the calibration procedure infrequent.

³ The boldface numbers in parentheses refer to the list of references at the end of this test method.

9.2 Prepare a stock solution of polymer, noting the precautions of Sections 7 and 8, at a concentration estimated as follows: For a polymer of $M_w = 100,000$ in a solvent such that $dn/dc \approx 0.2$ mL/g (for example, polystyrene in 2-butanone), the stock solution shall be in the range from 10 to 20 g/L. Since scattered intensity is proportional to M_w and to the square of dn/dc , estimates of the stock-solution concentration required for other samples and systems is made. Prepare no more stock solution than is required by the following procedure.

9.3 Select one of the following measurement schemes:

9.3.1 Where the volume of liquid required for measurement in the photometer is varied by at least a factor of two, it is recommended that the scattering from the minimum volume of solvent be measured first, followed by measurement of solutions prepared in the cell by the addition of weighed or volumetrically measured aliquots of filtered stock solution. From four to six such solutions shall be measured, the most concentrated consisting of approximately equal volumes of solvent and stock solution if its concentration is selected in accordance with 9.2, and the least concentrated being about one fourth this concentration. A specific example is given in [Appendix X3](#).

9.3.2 If the volume of liquid in the scattering cell cannot be varied as in 9.3.1, it is necessary to prepare and filter into the cell from four to six separate solutions covering the range suggested in 9.3.1.

9.3.3 A further alternative is to measure the most concentrated solution first (for this purpose, the stock solution concentration estimated in 9.3.1 shall be reduced by a factor of two), followed by successive dilutions with solvent. The scattering from the pure solvent must be measured in a separate step. If necessary, start dilution sequences at two or more concentration levels to obtain the range specified in 9.3.1.

9.4 Measure the scattering of the pure solvent, filtered into the cell as described in Section 8, and of each of the series of filtered solutions described in 9.3, following the instructions provided with the photometer or in the literature (4), being sure that the following steps are included. (This procedure is based on the scheme of 9.3.1.)

9.4.1 *Instrument Check*—See that the photometer is prepared for measurement, with the lamp lit, high voltage supplied to the photomultiplier detector, and all components fully warmed up and stabilized.

9.4.2 *Solvent Preparation*—Fill the cleaned scattering cell with filtered solvent as described in Section 8, insert it in the instrument, and align it as required.

9.4.3 *Intensity Level*—Select the wavelength-isolating filter to be used. Turn the detector to the specified angle and set the level of high voltage, or adjust the slit openings, as called for to provide an appropriate solvent reading. In subsequent steps, do not readjust these variables, but change amplifier gain by known factors or insert neutral filters of known transmittance as required to maintain readings on scale.

9.4.4 *Solvent Measurement*—After the cell has remained undisturbed in the photometer for 10 to 15 min to allow residual dust to settle out, read and record the scattered intensity at angles of 30°, 90°, 150°, and at least three pairs

between, symmetrically placed with respect to 90°, as available on the photometer used.

9.4.5 *Reference*—Turn the phototube to the specified reference angle, adjust amplifier gain or insert neutral filters as required, insert the reference standard, and read and record the indicated reference intensity.

9.4.6 *Solution Measurement*—Prepare and filter into the cell the solutions required in 9.3. Mix thoroughly, allow a few minutes for residual dust to settle out, and measure each solution as in 9.4.4.

9.5 Determine solution concentrations. Since filtration through membrane filters has been known to result in retention of some polymer on the filter, it is necessary to determine the solution concentrations after filtration.

9.5.1 If successive concentrations are generated in the cell from a stock solution filtered under constant conditions, only the concentration of the filtered stock solution need be determined; otherwise, the concentration of each solution measured must be determined.

9.5.2 Determine the concentrations of solutions, as required, by one of the following methods. Use standard analytical techniques where applicable.

9.5.2.1 Evaporate a portion of the solution to constant weight. It is necessary to do this at high temperatures, namely, above the glass transition temperature and under vacuum, to remove tightly bound solvent. Because solvent is sometimes very difficult to remove, such a procedure for determining concentration must be verified by other techniques before being adopted.

9.5.2.2 Determine the ultraviolet absorbance of the solution at a suitable wavelength.

9.5.2.3 Determine the difference in refractive index between solution and solvent, using a differential refractometer, for cases where the specific refractive increment is known.

9.5.3 For cases where a series of solutions is produced in the cell, calculate the actual solution concentrations from that of the stock solution by standard volumetric or gravimetric analytical methods.

9.6 If the specific refractive increment dn/dc is not known, determine it using solutions of known concentrations; the same solutions used for light scattering measurements shall be utilized. The specific refractive increment is the slope of the straight line relating solution-solvent refractive-index difference, Δn , to solution concentration, c . Since the relation is linear, determination of Δn for one value of c suffices, but multiple determinations are recommended to reduce the uncertainty of the value of dn/dc . For use and calibration of the differential refractometer, follow the instructions supplied with the instrument.

9.7 If the refractive index of the solvent is not known for the wavelength and temperature of the measurements, determine it using a conventional refractometer. If the refractive indices of the polymer solutions used differ significantly from that of the solvent, determine them also.

9.8 If the polymer absorbs light, or is suspected of absorbing light, at the wavelength of the scattering measurement, an absorption correction ([Appendix X4](#)) must be applied.