ASTM INTERNATIONAL

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Standard Practice for
Dilute Solution Viscosity of Polymers[1]

This standard is issued under the fixed designation D2857; 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~~ Scope*

1.1 This practice covers the determination of the dilute solution viscosity of polymers. There are several ASTM standards (Test Methods D789, D1243, D1601, and D4603, and Practice D3591) that describe dilute solution viscosity procedures for specific polymers, such as nylon, poly(vinyl chloride), polyethylene, and poly(ethylene terephthalate). This practice is written to augment these standards when problems arise with which the specific procedure is not concerned, or when no standard is available for the polymer under investigation.

1.2 This practice is applicable to all polymers that dissolve completely without chemical reaction or degradation to form solutions that are stable with time at a temperature between ambient and 150°C. Results are usually expressed as relative viscosity (viscosity ratio), inherent viscosity (logarithmic viscosity number), or intrinsic viscosity (limiting viscosity number) (see 3.1).

1.3 For polyamides, relative viscosity values by this procedure are not equivalent to those determined by Test Methods D789.

1.4 The values stated in SI units are to be regarded as standard. No other units of measurement are included in this standard.

1.5 *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 appropriate ~~safety~~ safety, health, and ~~health~~environmental practices and determine the applicability of regulatory limitations prior to use.*

NOTE 1—This standard and ISO 1628, "Plastics—Determination of Viscosity Number and Limiting Viscosity Number," are technically equivalent.

1.6 *This international standard was developed in accordance with internationally recognized principles on standardization established in the Decision on Principles for the Development of International Standards, Guides and Recommendations issued by the World Trade Organization Technical Barriers to Trade (TBT) Committee.*

2. Referenced Documents

2.1 *ASTM Standards:*[2]
D445 Test Method for Kinematic Viscosity of Transparent and Opaque Liquids (and Calculation of Dynamic Viscosity)
D446 Specifications and Operating Instructions for Glass Capillary Kinematic Viscometers
D789 Test Method for Determination of Relative Viscosity of Concentrated Polyamide (PA) Solutions
D883 Terminology Relating to Plastics
D1243 Test Method for Dilute Solution Viscosity of Vinyl Chloride Polymers
D1600 Terminology for Abbreviated Terms Relating to Plastics

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

D1601 Test Method for Dilute Solution Viscosity of Ethylene Polymers

D3591 Test Method for Determining Logarithmic Viscosity Number of Poly(Vinyl Chloride) (PVC) in Formulated Compounds

D4603 Test Method for Determining Inherent Viscosity of Poly(Ethylene Terephthalate) (PET) by Glass Capillary Viscometer

D5226 Practice for Dissolving Polymer Materials

~~E1~~E2251 Specification for ~~ASTM Liquid-in-Glass Thermometers~~Liquid-in-Glass ASTM Thermometers with Low-Hazard Precision Liquids

2.2 *ISO Standard:*

1628/1 Guidelines for the Standardization of Methods for the Determination of Viscosity Number and Limiting Viscosity Number of Polymers in Dilute Solution[3]

2.3 *National Institute of Standards and Technology Document:*

Circular No. C602 Testing of Glass Volumetric Apparatus[4]

3. Terminology

3.1 *Definitions:*

3.1.1 ~~Terms and definitions in~~ For definitions of terms pertaining to plastics used in this test method, refer to Terminology D883 ~~and~~. For abbreviations ~~in~~ used in this test method, refer to Terminology D1600 ~~are applicable to this practice. The following definitions~~, unless otherwise indicated. ~~are applicable to this practice.~~

3.1.2 *inherent viscosity, η_{inh} , n*—the ratio of the natural logarithm of the relative viscosity to the mass concentration of the polymer, *c:* $\eta_{inh} = (\ln \eta_r)/c$.

3.1.2.1 *Discussion—*
Also known as the logarithmic viscosity number, η_{ln}. See also 3.1.4.

3.1.3 *intrinsic viscosity, [η], n*—the limiting value of the reduced viscosity or the inherent viscosity at infinite dilution of the polymer:

$$[\eta] = \lim_{c \to 0} (\eta_i /c) = \lim_{c \to 0} \eta_{inh}.$$

3.1.3.1 *Discussion—*
Also known as the limiting viscosity number and in the literature as the Staudinger index. See also 3.1.4.

3.1.4 *reduced viscosity, n*—the ratio of the relative viscosity increment to the mass concentration of the polymer, *c*, that is, η_i/c.

3.1.4.1 *Discussion—*
Also known as the viscosity number. The unit must be specified; cm^3 /g is recommended.

3.1.4.2 *Discussion—*
This quantity and those defined in 3.1.2 and 3.1.3 are neither viscosities nor pure numbers. The terms are to be looked upon as traditional names. Any replacement by consistent terminology would produce unnecessary confusion in the polymer literature.

3.1.5 *relative viscosity, η_r , n*—the ratio of the viscosity of the solution, η, to the viscosity of the solvent, η_s, that is, $\eta_r = \eta / \eta_s$.

3.1.5.1 *Discussion—*
Also known as the viscosity ratio.

3.1.6 *relative viscosity increment, η_i , n*—the ratio of the difference between the viscosities of solution and solvent to the viscosity of the solvent, that is, $\eta_i = (\eta - \eta_s)/\eta_s$.

3.1.6.1 *Discussion—*
The use of the term specific viscosity for this quantity is discouraged, since the relative viscosity increment does not have the attributes of a specific quantity.

4. Summary of Practice

4.1 General procedures are given for the determination of the dilute solution viscosity of polymers, including descriptions of apparatus, reagents and materials, and sample preparation, as well as measurement procedures and calculations.

4.2 If detailed test methods are available for the polymers of interest, such as those mentioned in 1.1, this practice provides information of a general nature to augment the detailed treatments in the relevant test methods.

5. Significance and Use

5.1 The determination of dilute solution viscosity provides one item of information towards the molecular characterization of polymers. When viscosity data are used in conjunction with other molecular parameters, the properties of polymers depending on their molecular structure may be predicted.

5.2 Viscosity is dependent on molecular weight distribution, so with certain restrictions, satisfactory correlations can be obtained between dilute-solution viscosity and molecular parameters such as molecular weight or chain length. The most limiting restrictions that must be observed are as follows:

5.2.1 It must be known that the polymers used to establish the correlations and those to which they are applied do not consist of or contain branched species. Basically a measure of molecular size and not molecular weight, the dilute solution viscosity can be correlated appropriately with molecular weight or chain length only if there is a unique relationship between the mass and the size of the dissolved polymer molecules. This is the case for linear, but not for most branched, polymers.

5.2.2 For reasons similar to those outlined in 5.2.1, it must be required that the polymers to which the correlations are applied have the same chemical composition as those used in establishing the relationships.

5.3 For polymers meeting the restrictions of 5.2, empirical relationships can be developed between the dilute solution viscosity of a polymer and its hydrodynamic volume or average chain dimension (radius of gyration or end-to-end distance). Such relationships depend upon any variables influencing this molecular size of the dissolved polymer. The most important of these variables are solvent type and temperature. Thus, the solution viscosity of a given polymer specimen depends on the choice of these variables, and they must always be specified with the viscosity for complete identification.

5.4 The solution viscosity of a polymer of sufficiently high molecular weight may depend on rate of shear in the viscometer, and the viscosity of a polyelectrolyte (polymer containing ionizable chemical groupings) will depend on the composition and ionic strength of the solvent. Special precautions beyond the scope of this practice are required when measuring such polymers.

5.5 Finally, the viscosity of polymer solutions may be affected drastically by the presence of recognized or unrecognized additives in the sample, including but not limited to colorants, fillers, or low-molecular-weight species.

6. Apparatus

6.1 *Volumetric Flasks,*[5] 100-mL or other size found convenient.

6.2 *Transfer Pipets,*[5] sizes between 1 and 25 mL, as required. Transfer pipets for use with polymer solutions should have about 2 mm cut from their lower tips to permit more rapid transfer of the solution to the viscometer.

6.3 *Constant-Temperature Bath,* capable of maintaining ±0.01°C at the desired temperature (usually between 25 and 150°C). Less stringent temperature control (±0.02°C) is satisfactory upon demonstration that the precision of results is not affected.

6.4 *Viscometer,* glass capillary type, as described in Specifications D446. Efflux time for the solvent and temperature used shall be greater than 200 s (except that efflux time for semimicro viscometers shall be greater than 80 s), to eliminate the need for kinetic energy corrections.

6.4.1 Two types of viscometers are commonly used: One is a constant-volume device of simple construction, recommended for use where solution viscosity is to be measured at a single concentration, as for determination of the reduced viscosity (viscosity number) or inherent viscosity (logarithmic viscosity number). It may also serve for the determination of the intrinsic viscosity (limiting viscosity number) through measurement of several solutions having different concentrations.

6.4.2 The second type viscometer, commonly called a dilution viscometer, is a time-saving device for the determination of intrinsic viscosity (limiting viscosity number) since it does not require constant liquid volume for operation. Several concentrations of a polymer solution can be tested by adding a known quantity of the solvent at the test temperature directly to the viscometer, mixing, measuring the viscosity, and then making the next dilution. The viscosity of the pure solvent must be measured separately.

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[5] Glassware should conform to the standards of accuracy in National Institute of Standards and Technology Circular No. C602.

6.4.3 An alternative procedure is to start with the minimum volume of the pure solvent, then add aliquots of a concentrated stock solution to the viscometer to obtain values of the relative viscosity (viscosity ratio) at successively higher concentrations. The choice of procedures is dictated by the range of volumes with which the viscometer will operate and the range of concentrations desired for test.

6.5 *Timer,* graduated in divisions of 0.1 s or less, as described in Test Method D445.

6.6 *Thermometer,* suitable for the specified test temperature and conforming to the specifications of Specification ~~E1~~E2251~~, Kinematic Viscosity Thermometers ASTM 110C (for use at 135°C) and 118C (for use at 30°C).~~.

6.7 *Fritted Glass Filter ~~Funnel,~~Funnel—~~coarse grade, or equivalent.~~*Funnel, Hirsh-type; borosilicate glass; with coarse fritted disc, pore size: 40-60 μm.

7. Reagents and Materials

7.1 *Solvents,* as required, or as recommended in Appendix X1.

7.2 *Heat Transfer Liquid,* for constant temperature bath.

NOTE 2—The following materials have been used as heat-transfer liquids: (*1*) silicone oil, (*2*) mineral oil, (*3*) peanut oil, (*4*) water, and (*5*) water-miscible liquid, such as glycerin or ethylene glycol. The material selected must not discolor or smoke on prolonged exposure at the test ~~temperature; in some cases discoloring may be inhibited by the use of an antioxidant.~~ temperature. The use of water or a water-miscible liquid facilitates cleaning glassware used in the test.

7.3 *Nitrogen,* for purging.

8. Sample Preparation

8.1 Do not predry or condition the sample unless the material is known to be hygroscopic.

8.2 If it is known that the sample dissolves only slowly in the selected solvent, pretreating the sample to reduce its particle size ~~may be~~ is advisable.

NOTE 3—Some samples can be pulverized conveniently in a rotary cutting mill with a 20-mesh screen at the outlet of its pulverizing chamber. (**Warning**—Take care to avoid overheating the sample during pulverization, which might lead to thermal degradation. Low-melting polymers, or hard, tough samples, often can be satisfactorily pulverized only at very low temperature as provided by dry ice or liquid nitrogen.)

9. Procedure

9.1 Weigh an appropriate sample into a tared 100-mL volumetric flask (or weigh and transfer quantitatively to the flask). If the sample is known to oxidize easily in the subsequent dissolution step, the flask may be purged with nitrogen.

NOTE 4—Solution concentrations for some common polymers are recommended in Appendix X1. Since other sizes of volumetric flasks may be used, depending on the viscometer size and the amount of sample available, adjust sample weights and the solvent and solution volumes accordingly.

NOTE 5—For greater reliability of results, select the sample size on the basis of experiment to give a relative viscosity (viscosity ratio) near 1.5. If several concentrations of a solution of a single sample are to be used (see Warning in 9.2), select them so that the relative viscosity (viscosity ratio) falls in the range from 1.2 to 2.0.

NOTE 6—Preparation of a single solution may often suffice, either for determining the relative viscosity (viscosity ratio) or inherent viscosity (logarithmic viscosity number), or as a stock solution for use in a dilution viscometer to determine the intrinsic viscosity (limiting viscosity number). If more than one solution concentration is desired, weigh a series of specimens (often four) into separate flasks, selecting specimen weights to give the desired solution concentration.

9.2 Add approximately 50 cm^3 of solvent to each specimen flask, purge with nitrogen if necessary, and shake on a laboratory shaker. Elevated temperature ~~may enhance~~ enhances the solution rate as suggested in Appendix X1, Practice D5226, or specific test methods, but this approach should be used with caution. Some polymers and solvents have limited high-temperature stability.

If solution preparation requires an elevated temperature, subject a flask of pure solvent to the same conditions as the polymer solution. (**Warning**—Complete solution of all of the specimen is essential. When solution appears complete, examine the flask with care to be sure that no undissolved material, gel particles, or foreign matter is present.)

9.3 Place the volumetric flasks containing the solution(s) and the pure solvent in the constant-temperature bath maintained at the test temperature. After temperature equilibrium has been achieved (10 to 30 min) complete the dilution to the 100-cm^3 mark by adding solvent maintained at the bath temperature, using a transfer pipet. Mix the contents of the flask(s) thoroughly. (**Warning**—Be sure that the solution is uniformly mixed. If the test temperature is above ambient, avoid cooling the flask excessively while mixing.)

9.4 Where necessary to prevent oxidation, purge the viscometer with a slow stream of nitrogen. With the viscometer permanently positioned in the constant-temperature bath at the required temperature, transfer a suitable amount of solution into the viscometer using a suitably modified transfer pipet (see 6.2). Pressure filtration through a fritted glass filter into the viscometer is often desirable, but care must be taken not to lose solvent during the process.

NOTE 7—If the solution is to be handled at elevated temperatures, the transfer pipet may be fitted with a suitable heating mantle to retard precipitation of polymer from the solution during the transfer.

9.5 After temperature equilibration has been achieved (a minimum of 10 min), bring the liquid level in the viscometer above the upper graduation mark by means of gentle air (or, preferably, nitrogen) pressure or suction applied to the arm opposite the capillary. Allow the solution to drain down through the capillary. To measure the efflux time, start the timer exactly as the meniscus passes the upper graduation mark, and stop it exactly as the meniscus passes the lower mark.

NOTE 8—The use of automatic viscometers can reduce the tedium and increase the precision of this step.

9.6 Determine the efflux time (see 9.5) at least three times each for the solution and for the pure solvent. Three consecutive readings should agree to within 0.1 s or 0.1 % of their mean, whichever is greater. Larger variations may result from foreign control in the viscometer or from inadequate temperature control, and require repetition of the experiment after their cause is located and corrected.

10. Calculation

10.1 *Relative Viscosity (Viscosity Ratio)*—Calculate the relative viscosity (viscosity ratio) from the average efflux time for the solvent, t_s, and the average efflux time for the solution, t, as follows:

$$\text{Relative Viscosity} = t/t_s$$

NOTE 9—Strictly, the relative viscosity (viscosity ratio) is defined as η/η_s where η and η_s are the viscosities of the solution and solvent, respectively, and are related to the corresponding efflux times by:

$$\eta = Ct\rho - E\rho/t^2$$
$$\eta_s = Ct_s\rho_s - E\rho_s/t_s^2$$

where:
C and E = constants for the particular viscometer used.
The equation in 10.1 follows if the second term in these relations, a kinetic-energy correction, is negligible and the respective solvent and solution densities, ρ_s and ρ, are substantially equal. This kinetic energy correction is negligible for the recommended viscometers and efflux times (see section 6.4).[6]

10.2 *Inherent Viscosity (Logarithmic Viscosity Number)*—Calculate the inherent viscosity (logarithmic viscosity number) ratio for each solution concentration as follows:

$$\text{Inherent Viscosity} = \ln(\eta/\eta_s)/c$$

[6] Cannon, M. R., Manning, R. E., and Bell, J. D., "Viscosity Measurement: The Kinetic Energy Correction and a New Viscometer," *Analytical Chemistry*, Vol 32, 1960, pp. 355–358.

where:

ln(η/η_s) = natural logarithm of the relative viscosity (viscosity ratio), and
c = solution concentration in g/cm^3 of solution.

The units of inherent viscosity (logarithmic viscosity number) are, therefore, cm^3/g.

10.3 *Intrinsic Viscosity (Limiting Viscosity Number)*—Plot the inherent viscosity (logarithmic viscosity number) versus concentration, for several solution concentrations, on rectilinear graph paper as shown in Fig. 1. Draw the best straight line through the points and extrapolate it to zero concentration. The intrinsic viscosity (limiting viscosity number), [η], is the intercept of the line at zero concentration. The units of the intrinsic viscosity (limiting viscosity number) are cm^3/g.

NOTE 10—The reduced viscosity (viscosity number ($\eta - \eta_s)\eta_s c$) may be calculated and plotted versus concentration on the same graph with the inherent viscosity (logarithmic viscosity number). The two lines should extrapolate to the same point (the intrinsic viscosity or limiting viscosity number) at $c = 0$; plotting both functions may serve to fix the intrinsic viscosity (limiting viscosity number) with greater accuracy. If the limitation on relative viscosity (viscosity ratio) stated in Note 5 is observed, the extrapolation lines should be accurately straight.

NOTE 11—For some polymer-solvent systems, the slopes of the lines of reduced viscosity (viscosity number) and inherent viscosity (logarithmic viscosity number) versus concentration are closely similar for all samples normally encountered. For such systems, the intrinsic viscosity (limiting viscosity number) can be approximated from data obtained at a single concentration by one of the formulas tabulated by Billmeyer.[7]

11. Report

11.1 Report the following information:

11.1.1 Complete identification of the sample.

11.1.2 Conditioning procedure, if any.

11.1.3 One or more of the following:

11.1.3.1 The relative viscosity (viscosity ratio), given to one significant figure beyond the decimal point, followed by the concentration of the test solution in g/cm^3.

11.1.3.2 The inherent viscosity (logarithmic viscosity number) in cm^3/g, carried to one significant figure beyond the decimal point, followed by the concentration of the test solution in g/cm^3.

11.1.3.3 The intrinsic viscosity (limiting viscosity number) in cm^3/g, carried to the decimal point.
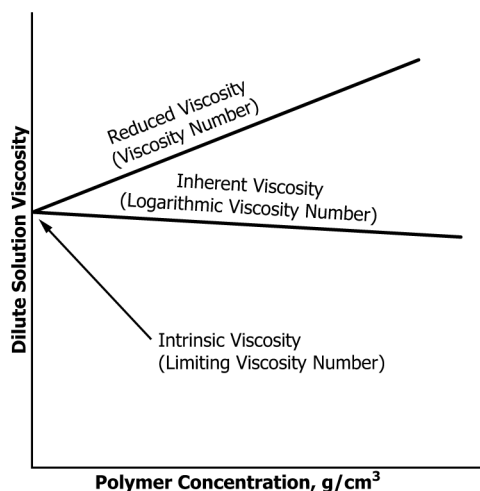

FIG. 1 Example of Plot to Determine Intrinsic Viscosity (Limiting Viscosity Number)

[7] Billmeyer, F. W., Jr., "Methods for Estimating Intrinsic Viscosity," *Journal of Polymer Science*, Vol 4, 1949, pp. 83–86.

11.1.4 The solvent employed and the test temperature.

Note 12—ISO 1628/1 recommends a test temperature of 25 $\pm$ 0.05°C and use of kinetic energy corrections for some viscometers, so exercise caution when comparing data obtained by both test methods.

12. Precision and Bias[8]

12.1 *Precision*—Based on test methods for vinyl chloride polymers in Test Method D1243, and poly(ethylene terephthalate) in Test Method D4603, within-laboratory repeatability of 1.5 to 2.0 % should be expected. Repeatability between laboratories ranged from 2.2 to 3.5 % for these same test methods.

12.2 *Bias*—Since viscosity numbers are available only from these measurements, there can be no estimate of bias.

13. Keywords

13.1 flow and flow rate—thermoplastics; polymers—molecular weight; viscosity—dilute–solution; viscosity—intrinsic; viscosity—plastics

APPENDIX

(Nonmandatory Information)

X1. RECOMMENDED SOLVENTS AND SOLUTION CONCENTRATIONS

X1.1 Polyamide (in accordance with Test Methods D789)

X1.1.1 The recommended solution concentration is 0.0050 $\pm$ 0.00002 g/cm^3.

X1.1.2 The recommended dissolving conditions are: for formic acid (90 $\pm$ 0.2 % in water), 30°C; for *m*-cresol (11 to 12°C melting point), 95 to 100°C (2-h maximum), or 8 h at 50°C.

X1.1.3 The recommended test temperature is 30°C.

X1.2 Polycarbonate

X1.2.1 The recommended solution concentration is 0.0040 $\pm$ 0.0002 g/cm^3, or by convenient dilution from 0.010 $\pm$ 0.00002 g/cm^3.

X1.2.2 The recommended dissolving conditions are: for methylene chloride, 30°C, or for *p*-dioxane (dry), 60°C.

X1.2.3 The recommended test temperature is 30°C.

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[8] Supporting data have been filed at ASTM International Headquarters and may be obtained by requesting Research Report RR:D20-1189.