



Standard Practice for Dilute Solution Viscosity of Polymers¹

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1. Scope

1.1 This practice covers the determination of the dilute solution viscosity of polymers. There are several ASTM standards (Test Methods D 789, D 1243, D 1601, and D 4603, and Practice D 3591) 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 D 789.

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 appropriate safety and health 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.

2. Referenced Documents

2.1 ASTM Standards:

- D 445 Test Method for Kinematic Viscosity of Transparent and Opaque Liquids (and the Calculation of Dynamic Viscosity)²
- D 446 Specifications and Operating Instructions for Glass Capillary Kinematic Viscometers²
- D 789 Test Methods for Determination of Relative Viscosity, Melting Point, and Moisture Content of Polyamide (PA)³

2.2 ISO Standard:

3. Terminology

3.1 *Definitions*—Terms and definitions in Terminology D 883 and abbreviations in Terminology D 1600 are applicable to this practice. The following definitions⁹ are applicable to this practice.

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

3.1.1.1 *Discussion*—Also known as the logarithmic viscosity number, η_{ln} . See also 3.1.3.

3.1.2 *intrinsic viscosity*, $[\eta]$, n —the limiting value of the reduced viscosity or the inherent viscosity at infinite dilution

³ Annual Book of ASTM Standards, Vol 08.01.

⁴ Annual Book of ASTM Standards, Vol 08.02.

⁵ Annual Book of ASTM Standards, Vol 08.03.

⁶ Annual Book of ASTM Standards, Vol 14.03.

⁷ Available from American National Standards Institute, 11 W. 42nd St., 13th Floor, New York, NY 10036.

⁸ Available from National Institute of Standards and Technology, U.S. Department of Commerce, Washington, DC 20234.

⁹ International Union of Pure and Applied Chemistry, *Compendium of Macromolecular Nomenclature*, Blackwell Scientific Publications, Oxford, England, 1991.

¹ This practice is under the jurisdiction of ASTM Committee D-20 on Plastics and is the direct responsibility of Subcommittee D20.70 on Analytical Methods.

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² Annual Book of ASTM Standards, Vol 05.01.

of the polymer: $[\eta] = \lim_{c \rightarrow 0} (\eta_i/c) = \lim_{c \rightarrow 0} \eta_{inh}$.

3.1.2.1 *Discussion*—Also known as the limiting viscosity number and in the literature as the Staudinger index. See also 3.1.3.

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

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

3.1.3.2 *Discussion*—This quantity and those defined in 3.1.1 and 3.1.2 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.

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

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

3.1.5 *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, $\eta_i = (\eta - \eta_s)/\eta_s$.

3.1.5.1 *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*,¹⁰ 100-mL or other size found convenient.

6.2 *Transfer Pipets*,¹⁰ 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 $\pm 0.01^\circ\text{C}$ at the desired temperature (usually between 25 and 150°C). Less stringent temperature control ($\pm 0.02^\circ\text{C}$) is satisfactory upon demonstration that the precision of results is not affected.

6.4 *Viscometer*, glass capillary type, as described in Specifications D 446. 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

¹⁰ Glassware should conform to the standards of accuracy in National Institute of Standards and Technology Circular No. C602.

making the next dilution. The viscosity of the pure solvent must be measured separately.

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 D 445.

6.6 *Thermometer*, suitable for the specified test temperature and conforming to the specifications of Specification E 1, Kinematic Viscosity Thermometers ASTM 110C (for use at 135°C) and 118C (for use at 30°C).

6.7 *Fritted Glass Filter Funnel*,¹¹ coarse grade, or equivalent.

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,¹² (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. 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 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.¹³

NOTE 4—**Caution:** 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 5—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 6—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 (Note 8), select them so that the relative viscosity (viscosity ratio) falls in the range from 1.2 to 2.0.

NOTE 7—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 cm³ of solvent to each specimen flask, purge with nitrogen if necessary, and shake on a laboratory shaker. Elevated temperature may enhance the solution rate as suggested in Appendix X1, Practice D 5226, 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.

NOTE 8—**Caution:** 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-cm³ mark by adding solvent maintained at the bath temperature, using a transfer pipet. Mix the contents of the flask(s) thoroughly.

NOTE 9—**Caution:** 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 10—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.

¹¹ The Corning Glass No. 36060, or equivalent, has been found satisfactory for this purpose. The Corning Glass No. 36060 filter is available from Corning Glass Works, Corning, NY 14831.

¹² Available from Dow Corning Corp., Midland, MI; Union Carbide Corp., Linde Silicones Division, New York, NY; and General Electric Company, Silicone Products Dept., Waterford, NY.

¹³ The Wiley mill, available from Scientific Supply houses, has been found satisfactory for this purpose.

NOTE 11—The use of automatic viscometers¹⁴ 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 12—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).¹⁵

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

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

where:

$\ln(\eta/\eta_s)$ = 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), $[\eta]$, is the intercept of the line at zero concentration. The units of the intrinsic viscosity (limiting viscosity number) are cm^3/g .

NOTE 13—The reduced viscosity (viscosity number $(\eta - \eta_s)/\eta_s c$) may be calculated and plotted versus concentration on the same graph

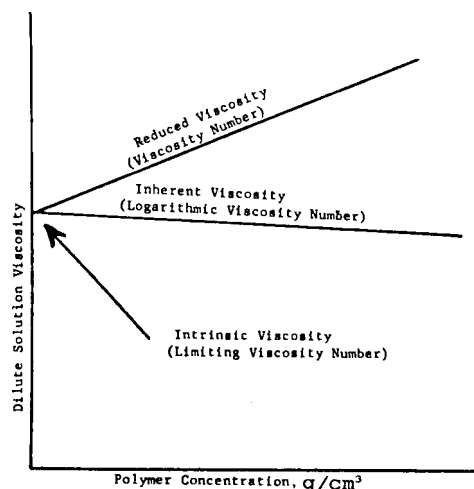


FIG. 1 Example of Plot to Determine Intrinsic Viscosity (Limiting Viscosity Number)

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 6 is observed, the extrapolation lines should be accurately straight.

NOTE 14—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.¹⁶

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.

11.1.4 The solvent employed and the test temperature.

NOTE 15—ISO 1628/1 recommends a test temperature of $25 \pm 0.05^\circ\text{C}$ and use of kinetic energy corrections for some viscometers, so exercise caution when comparing data obtained by both test methods.

12. Precision and Bias¹⁷

12.1 *Precision*—Based on test methods for vinyl chloride polymers in Test Method D 1243, and poly(ethylene terephthalate) in Test Method D 4603, within-laboratory repeatability of

¹⁴ Suitable automatic viscometer equipment is available from Cannon Instruments, State College, PA, and Schott America, Yonkers, NY.

¹⁵ 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.

¹⁶ Billmeyer, F. W., Jr., "Methods for Estimating Intrinsic Viscosity," *Journal of Polymer Science*, Vol 4, 1949, pp. 83-86.

¹⁷ Supporting data are available from ASTM Headquarters. Request RR:D20-1189.

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 D 789)

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

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 $0.0040 \pm 0.0002 \text{ g/cm}^3$, or by convenient dilution from $0.010 \pm 0.00002 \text{ g/cm}^3$.

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 .

X1.2.4 If pigments or other fillers are present, the resin may be dissolved in methylene chloride and the solution filtered. The methylene chloride may be evaporated from the resulting clear solution to leave the resin in the form of a thin film which may be sampled for viscosity measurements after drying several hours at 125°C .

X1.3 Poly(Methyl Methacrylate)

X1.3.1 The recommended solution concentration is $0.0020 \pm 0.00002 \text{ g/cm}^3$; but the recommendation of Note 5 should be understood to supersede this.

X1.3.2 The recommended dissolving conditions are 30°C for 24 h in 1,2-dichloroethane (ethylene dichloride).

X1.3.3 The recommended test temperature is 30°C .

X1.3.4 Pretreatment of the sample should not include cutting or grinding in such a way as to cause shear degradation of the polymer.

X1.4 Poly(Vinyl Chloride)

X1.4.1 *Using Cyclohexanone as Solvent:*

X1.4.1.1 *Solvent:* Cyclohexanone, laboratory or distilled technical grade, boiling point 155 to 156°C (760 mm HG).

X1.4.1.2 Samples should be dried to a moisture content $<1 \%$.

X1.4.1.3 The recommended dissolving conditions are $85 \pm 10^\circ\text{C}$ for 4 to 12 h.

X1.4.1.4 The recommended test temperature is 30°C .

X1.4.1.5 The recommended solution concentration is $0.0020 \pm 0.00002 \text{ g/mL}$.

NOTE X1.1—The limiting viscosity number may be estimated from data obtained at a single concentration by use of the following equation:¹⁸

$$(\eta) = 1/4[(\eta - \eta_o)/\eta_o c] + 3/4[\ln(\eta/\eta_o)/c]$$

X1.4.1.6 *Precision:*

X1.4.1.6.1 *Repeatability*—Duplicate results by the same analyst should not be considered suspect unless they differ by more than 1 %.

X1.4.1.6.2 *Reproducibility*—The average result of two determinations reported by one laboratory should not be considered suspect unless it differs from that of another laboratory by more than 2 %.

X1.4.2 *Using Tetrahydrofuran as Solvent:*

X1.4.2.1 The recommended solvent is tetrahydrofuran.

X1.4.2.2 Samples should be dried to a moisture content below 0.1 %.

X1.4.2.3 The recommended dissolving temperature is 60°C maximum. Dissolution should be complete in about 10 min.

X1.4.2.4 The recommended test temperature is 30°C .

X1.4.2.5 The recommended solution concentration is $0.0020 \pm 0.00002 \text{ g/mL}$.

X1.4.2.6 *Precision:*

X1.4.2.6.1 *Reproducibility*—Repeated sampling of the same resin lot in the same laboratory has produced the following results:

Number of Tests	Mean	Standard Deviation	Inherent viscosity
26	0.952	0.004	

¹⁸ Schulken, R. M., and Sparks, M. L., *Journal of Polymer Science*, JPSCA, Vol 26, 1957, p. 227.

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