



Designation: D 3418 – 82 (Reapproved 1988)^{e1}

AMERICAN SOCIETY FOR TESTING AND MATERIALS
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Standard Test Method for Transition Temperatures of Polymers By Thermal Analysis¹

This standard is issued under the fixed designation D 3418; 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.

This test method has been approved for use by agencies of the Department of Defense and for listing in the DoD Index of Specifications and Standards.

^{e1}NOTE—Sections 3, 4, and 5 were renumbered, and the safety hazards caveat added editorially in March 1988.

1. Scope

1.1 This test method covers determination of transition temperatures of polymers (Note 1) by differential thermal analysis or differential scanning calorimetry.

NOTE 1—First-order transition temperatures or melting points of semicrystalline polymers may also be determined or approximated by the procedures found in Test Method D 2117 and Test Methods D 789.

1.2 This test method is applicable to polymers in granular form (below 60 mesh preferred, avoiding grinding if possible) or to any fabricated shape from which appropriate samples can be cut.

1.3 The normal operating temperature range is from the cryogenic region to 600°C. With special equipment, the temperature range can be extended.

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

1.5 *This standard may involve hazardous materials, operations, and equipment. This standard does not purport to address all of the safety problems 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.*

2. Referenced Documents

2.1 ASTM Standards:

D 789 Test Methods for Determination of Relative Viscosity, Melting Point, and Moisture Content of Polyamide (PA)²

D 2117 Test Method for Melting Point of Semicrystalline Polymers by the Hot Stage Microscopy Method³

E 473 Definitions of Terms Relating to Thermal Analysis⁴

3. Definitions

3.1 *differential scanning calorimetry (DSC)*—a technique in which the difference in energy inputs into a substance and a reference material is measured as a function of temperature, while the substance and reference material are sub-

jected to a controlled-temperature program. The record is the differential scanning calorimetric or DSC curve. Two modes, power-compensation differential scanning calorimetry (power-compensation DSC) and heat-flux differential scanning calorimetry (heat-flux DSC), can be distinguished, depending on the method of measurement used.

3.2 *differential thermal analysis (DTA)*—a technique in which the temperature difference between a substance and a reference material is measured as a function of temperature while the substance and reference material are subjected to a controlled temperature program. The term *quantitative differential thermal analysis (quantitative DTA)* covers those uses of DTA where the equipment is designed to produce quantitative results.

3.3 For other definitions of terms relating to thermal analysis, see Definitions E 473.

4. Summary of Test Method

4.1 The test method consists of heating or cooling the test material at a controlled rate in a controlled atmosphere and continuously monitoring with a suitable sensing device the difference in temperature or the difference in heat input between a reference material and a test material due to energy changes in the material. A transition is marked by absorption or release of energy by the specimen resulting in a corresponding endothermic or exothermic peak or baseline shift in the heating or cooling curve.

5. Significance and Use

5.1 Thermal analysis provides a rapid method for determining the temperature profile of a material. Transition temperatures can be determined in polymers that possess them. Commercial polymers or, in many cases, the components of a mixture may be identified by this test method. The results of chemical reactions that affect the transition can be studied with the aid of this technique; such reactions include oxidation, the curing of thermosetting resins, and thermal decomposition.

5.2 This test is useful for both specification acceptance and research.

6. Interferences

6.1 An increase or decrease in heating rate from those specified may alter the results. The presence of impurities will affect the transition, particularly if an impurity tends to form solid solutions, or to be miscible in the melt phase.

¹ This test method is under the jurisdiction of ASTM Committee D-20 on Plastics and is the direct responsibility of Subcommittee D20.30 on Thermal Properties (Section D20.30.07).

Current edition approved Jan. 29, 1982. Published March 1982. Originally published as D 3418 – 75. Last previous edition D 3418 – 75.

² Annual Book of ASTM Standards, Vol 08.01.

³ Annual Book of ASTM Standards, Vol 08.02.

⁴ Annual Book of ASTM Standards, Vol 14.02.

Since particle size has an effect upon detected transition temperatures, the samples to be compared should be approximately the same particle size (1 through 5).⁵

6.2 In some cases the sample may react with air during the temperature cycle, causing an incorrect transition to be measured. Where it has been shown that this effect is present, provision shall be made for running the test under vacuum or an inert gas blanket. Since some materials degrade near the melting region, care must be used to distinguish between degradation and transition.

6.3 Since milligram quantities of sample are used, it is essential to ensure that samples are homogeneous and representative.

6.4 Toxic or corrosive effluents, or both, may be released when heating the material, and could be harmful to the personnel or to the apparatus.

7. Apparatus

7.1 *Differential Thermal Analyzer or Differential Scanning Calorimeter*, capable of heating or cooling at rates up to at least 20 ± 1 °C/min and of automatic recording of difference in temperature (or difference in heat input) between the sample and a reference material, to the required sensitivity and precision. Increasing the heating rate has been found to produce sharper transition curves. For comparison the same heating rate shall be used.

7.2 *Sample Tubes* or pans or other sample holders. Borosilicate glass tubes are used for certain application and aluminum or other metal pans of high thermal conductivity for others.

7.3 *Thermocouple Reference Junction*, consisting of a stirred bath of ice/water slurry or electronic type.

7.4 *Reference Material*—Glass beads, alumina powder, silicon carbide, or any material known to be unaffected by repeated heating - cooling and free from interfering transitions. The thermal diffusivity of the reference should be as close as possible to those of the sample.

NOTE 2—Reference materials for fiber samples may be fibrous.

7.5 *Recording Charts* for temperature-recording apparatus, with suitable graduations for measurement of either temperature differential or energy differential against temperature or time.

7.6 *Nitrogen* or other inert gas supply, for blanketing sample.

7.7 *Hypodermic Punch* (optional), as shown in the figure illustrating the Punch for Cutting Disks in Test Methods D 789 or the figure illustrating the Hypodermic Punch in Test Method D 2117.

8. Calibration

8.1 Using the same heating rate to be used for samples, calibrate the temperature scale of the apparatus with appropriate standard reference materials covering the temperature range of interest. For many commercial polymers, this range may be defined by the following substances:

Standard	Melting Point, °C
NBS 758	125 to 435
NBS 759	295 to 675
NBS 760	570 to 940
Benzoic acid	122.4
Indium	156.4
Tin	231.9
Lead	327.4
Zinc	419.50

8.2 When lead is used as a standard, a fresh sample should be used each time.

9. Sample

9.1 *Powdered or Granular Samples*—Avoid grinding if preliminary thermal cycle as outlined in 10.1.2 is not performed. Grinding or similar techniques for size reduction often introduce thermal effects because of friction or orientation, or both, and thereby change the thermal history of the sample.

9.2 *Molded or Pelleted Samples*—Cut the samples with a microtome, razor blade, hypodermic punch, paper punch, or cork borer (size No. 2 or 3) to appropriate size, in thickness or diameter and length that will best fit the sample holder and will approximate the desired weight in the subsequent procedure.

9.3 *Film or Sheet Samples*—For films thicker than 0.04 mm (0.015 in.), see 9.2. For thinner films, cut slivers to fit in the sample tubes or punch disks, if the circular sample pans are used.

10. Procedure

10.1 For First-Order Transition:

10.1.1 Use a sample weight appropriate for the material to be tested. In most cases 5 mg sample weight is satisfactory. An appropriate sample weight results in 25 to 95 % scale deflection of the recording system when acceptable sensitivity is used. Avoid overloading.

10.1.1.1 When differential thermal analysis is used, intimate thermal contact between the sample and clean thermocouple or other temperature probe is essential for reproducible results. Use sample packing technique appropriate to the apparatus.

10.1.1.2 When differential scanning calorimetry is used, intimate thermal contact between the pan and sample is essential for reproducible results. Crimp a metal cover against the pan with the sample sandwiched in between to assure good heat transfer. Take care to ensure flat pan bottoms.

10.1.2 Perform and record a preliminary thermal cycle by heating the sample at a rate of 10°C/min under nitrogen atmosphere from ambient to 30°C above the melting point or up to a temperature high enough to erase previous thermal history. The selection of temperature and time are critical when effect of annealing is studied. Minimize the time of exposure to high temperature to avoid sublimation or decomposition. In some cases the preliminary thermal cycle may interfere with the transition of interest, causing an incorrect transition or eliminating a transition. Where it has been shown that this effect is present, omit the preliminary thermal cycle.

10.1.3 Hold temperature for 10 min (10.1.2).

⁵ The boldface numbers in parentheses refer to the list of references at the end of this test method.