



Designation: D 3418 – 99

# Standard Test Method for Transition Temperatures of Polymers By Differential Scanning Calorimetry<sup>1</sup>

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 ( $\epsilon$ ) indicates an editorial change since the last revision or reapproval.

*This standard has been approved for use by agencies of the Department of Defense.*

## 1. Scope\*

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

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

NOTE 2—This test method may be used in conjunction with Test Methods D 3417D 3417 or E 793E 793 to simultaneously determine the enthalpies of melting and crystallization.

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 specimens 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 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 3—This standard is similar but not equivalent to ISO 11357-1 and ISO 11357-2. The ISO procedures provide additional information not supplied by this test method.

## 2. Referenced Documents

### 2.1 ASTM Standards:

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

D 3417 Test Method for Enthalpies of Fusion and Crystallization of Polymers by Differential Scanning Calorimetry

E 473 Terminology Relating to Thermal Analysis<sup>3</sup>

E 563 Practice for Preparation and Use of Freezing Point Reference Baths<sup>4</sup>

E 793 Test Method for Heats of Fusion and Crystallization by Differential Scanning Calorimetry<sup>3</sup>

E 794 Test Method for Melting and Crystallization Temperature by Thermal Analysis<sup>3</sup>

E 967 Practice for Temperature Calibration of Differential Scanning Calorimeters and Differential Thermal Analyzers<sup>3</sup>

E 1142 Terminology Relating to Thermophysical Properties<sup>3</sup>

E 1356 Test Method for Glass Transition Temperatures by Differential Scanning Calorimetry or Differential Thermal Analysis<sup>3</sup>

E 1953 Practice for Description of Thermal Analysis Apparatus<sup>3</sup>

### 2.2 ISO Standards:<sup>5</sup>

11357-1 Plastics—Differential Scanning Calorimetry (DSC)—Part 1: General Principles

11357-2 Plastics—Differential Scanning Calorimetry (DSC)—Part 2: Determination of Glass Transition Temperature

## 3. Terminology

3.1 Specialized terms used in this test method are defined in Terminologies E 473E 473 and E 1142E 1142.

## 4. Summary of Test Method

4.1 This test method consists of heating or cooling the test material at a controlled rate in a specified purge gas at a controlled flow rate 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

<sup>1</sup> 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).

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<sup>2</sup> Annual Book of ASTM Standards, Vol 08.01.

<sup>3</sup> Annual Book of ASTM Standards, Vol 14.02.

<sup>4</sup> Annual Book of ASTM Standards, Vol 14.03.

<sup>5</sup> Available from American National Standards Institute, 11 W. 42nd St., 13th Floor, New York, NY 10036.

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

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 measuring transitions due to morphological or chemical changes, or both, in a polymer as it is heated/cooled through a specified temperature range. Change in specific heat capacity, heat flow (in conjunction with Test Method D 3417D 3417), and temperature values can be determined for these polymer transitions. Differential scanning calorimetry can be used to assist in identifying specific polymers, polymer alloys, and certain polymer additives, which exhibit thermal transitions. Chemical reactions that cause or affect certain transitions can be measured with the aid of this technique; such reactions include oxidation, the curing of thermosetting resins, and thermal decomposition.

5.2 This test method is useful for both specification acceptance, process control, and research.

## 6. Interferences

6.1 An increase or decrease in heating rate from those specified can alter the results. The presence of impurities will affect the calculated transition temperature, particularly if an impurity tends to form solid solutions, or to be miscible in the melt phase. Since particle size has an effect upon detected transition temperatures, the specimens to be compared should be approximately the same particle size (1-5).<sup>6</sup>

6.2 In some cases the specimens may react with air during the temperature cycle, causing an incorrect transition temperature 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 a specimen are used, it is essential to ensure that specimens are homogeneous and representative.

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

## 7. Apparatus

7.1 *Differential Scanning Calorimeter (DSC)*—The essential instrumentation required to provide the minimum differential scanning calorimetric capability for this test method includes:

7.1.1 *DSC Test Chamber*—This chamber is composed of the following:

7.1.1.1 *Furnace(s)*, to provide uniform controlled heating (cooling) of a specimen and reference to a constant temperature or at a constant rate within the applicable cryogenic to 600°C temperature range of this test method.

7.1.1.2 *Temperature Sensor*, to provide an indication of the specimen temperature to  $\pm 10$  mK (0.01°C).

7.1.1.3 *Differential Sensor*, to detect heat flow difference between the specimen and reference equivalent to 1 mW.

7.1.1.4 *Means of Sustaining a Test Chamber Environment* of inert purge gas at a purge flow rate of 10 to 50  $\pm$  5 mL/min.

NOTE 4—Typically, 99+ % pure nitrogen, argon or helium are employed when oxidation in air is a concern. Unless effects of moisture are to be studied, use of dry purge gas is recommended and is essential for operation at subambient temperatures.

7.1.2 *Temperature Controller*, capable of executing a specific temperature program by operating the furnace(s) between selected temperature limits at a rate of temperature change of 10 to 20°C/min constant to  $\pm 0.1$ °C/min or at an isothermal temperature constant to  $\pm 0.1$ °C.

7.1.3 *Recording Device*, either digital or analog, capable of recording and displaying any fraction of the heat flow signal (DSC curve) including the signal noise as a function of temperature.

7.1.4 *Containers* (pans, crucibles, vials, and so forth) that are inert to the specimen and reference materials and which are of suitable structural shape and integrity to contain the specimen and reference in accordance with the specific requirements of this test method.

7.1.5 *Cooling capability* to hasten cool down from elevated temperatures, to provide constant cooling rates of up to 10°C/min, to achieve subambient operation, or to sustain an isothermal subambient temperature, or combination thereof.

7.2 *Balance*, with a capacity of 100 mg or greater to weigh specimens or containers, or both, to  $\pm 10$   $\mu$ g.

## 8. Sample

8.1 *Powdered or Granular Specimens*—Avoid grinding if the 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 specimen.

8.2 *Molded or Pelleted Specimens*—Cut the specimens 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 specimen capsule and will approximate the desired weight in the subsequent procedure.

8.3 *Film or Sheet Specimens*—For films thicker than 40  $\mu$ m, see 8.2. For thinner films, cut slivers to fit in the specimen capsules or punch disks, if the circular specimen capsules are used.

## 9. Calibration

9.1 Calibrate the DSC temperature signal using Practice E 967E 967 and the same heating rates (that is, 10 or 20°C/min, or both) to be used in this test method (see Note 5).

## 10. Procedure

10.1 *For First-Order Transition:*

<sup>6</sup> The boldface numbers in parentheses refer to the list of references at the end of this test method.