



Designation: D3418 – 21

Standard Test Method for Transition Temperatures and Enthalpies of Fusion and Crystallization of Polymers by Differential Scanning Calorimetry¹

This standard is issued under the fixed designation D3418; 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 standard has been approved for use by agencies of the U.S. Department of Defense.

1. Scope*

1.1 This test method covers determination of transition temperatures and enthalpies of fusion and crystallization of polymers by differential scanning calorimetry.

NOTE 1—True heats of fusion are to be determined in conjunction with structure investigation, and frequently, specialized crystallization techniques are needed.

1.2 This test method is applicable to polymers in granular form or to any fabricated shape from which it is possible to cut appropriate specimens.

1.3 The normal operating temperature range is from the cryogenic region to 600°C. Certain equipment allows the temperature range to be extended.

1.4 The values stated in SI units are the standard.

NOTE 2—This test method does not apply to all types of polymers as written (see 6.8).

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

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

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

E473 Terminology Relating to Thermal Analysis and Rheology

E691 Practice for Conducting an Interlaboratory Study to Determine the Precision of a Test Method

E967 Test Method for Temperature Calibration of Differential Scanning Calorimeters and Differential Thermal Analyzers

E968 Practice for Heat Flow Calibration of Differential Scanning Calorimeters

E1142 Terminology Relating to Thermophysical Properties

E1953 Practice for Description of Thermal Analysis and Rheology Apparatus

2.2 ISO Standards:³

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

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

ISO 11357-3 Plastics—Differential Scanning Calorimetry (DSC)—Part 3: Determination of Temperature and Enthalpy of Melting and Crystallization

3. Terminology

3.1 Specialized terms used in this test method are defined in Terminologies **E473** and **E1142**.

4. Summary of Test Method

4.1 This test method consists of heating or cooling the test material at a controlled rate under a specified purge gas at a controlled flow rate and continuously monitoring with a suitable sensing device the difference in heat input between a

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

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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.

³ Available from American National Standards Institute (ANSI), 25 W. 43rd St., 4th Floor, New York, NY 10036, <http://www.ansi.org>.

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

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. Areas under the crystallization exotherm or fusion endotherm of the test materials are compared against the respective areas obtained by the treatment of a well-characterized standard.

5. Significance and Use

5.1 Thermal analysis provides a rapid method for measuring transitions due to morphological or chemical changes in a polymer as it is heated/cooled at a controlled rate through a specified temperature range. Change in specific heat capacity, heat flow and temperature values are determined for these transitions. Differential scanning calorimetry is 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 have been measured with the aid of this technique; such reactions include oxidation, curing of thermosetting resins, and thermal decomposition.

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

6. Interferences

6.1 Differences in heating or cooling rate as well as the final heating and cooling temperature have an effect on the measured results, especially on the enthalpy of fusion or crystallization. Therefore, departure from conditions specified for a given polymer is not permitted.

6.2 The presence of impurities is known to affect the transition temperature, particularly if an impurity tends to form solid solutions, or to be miscible in the melt phase.

6.3 Uncertain radiation losses at temperatures higher than 400°C have been known to affect the accuracy of results at times.

6.4 Since particle size has an effect upon detected transition temperatures, the specimens to be compared shall be approximately the same particle size **(1-5)**.⁴

6.5 In cases that specimens react with air during the temperature cycle, provision shall be made for running the test under an inert gas blanket to avoid any incorrect measurement. Since some materials degrade near the melting region, care must be used to distinguish between degradation and transition.

6.6 Since milligram quantities of a specimen are used, it is essential to ensure that specimens are homogeneous and representative.

6.7 It is possible that toxic or corrosive effluents are released when heating the material, and be harmful to the personnel or to the apparatus.

6.8 Not all polymers lend themselves to the exact terms of this test method. For some polymers such as polyarylamides,

crystallization is only possible from solution. For other polymers such as crystallizable polystyrene, annealing is only possible above their glass transition temperatures. When this test method is used for polymers of this type, carefully annealed samples must be tested without conditioning.

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 $\pm 0.01^\circ\text{C}$.

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 purge gas at a purge flow rate of 10 to 50 ± 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 sub-ambient 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 0.5 to 20°C/min constant to $\pm 0.1^\circ\text{C}/\text{min}$ or at an isothermal temperature constant to $\pm 0.1^\circ\text{C}$.

7.1.3 *Recording Device*, 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 *Software*, for integrating areas under endothermic valleys or exothermic peaks, or both.

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

7.1.6 Cooling capability to hasten cool down from elevated temperatures, to provide constant cooling rates of 0.5 - 20 °C/min to obtain repeatable crystallization temperatures, to achieve sub-ambient operation, or to sustain an isothermal sub-ambient temperature, or combination thereof.

7.2 *Balance*, capable of weighing to ± 0.0001 grams for transition temperatures and to ± 0.00001 grams for determining enthalpies.

8. Sample

8.1 *Powdered or Granular Specimens*—Avoid grinding if the preliminary thermal cycle as outlined in **10.1.3** 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.

⁴ The boldface numbers in parentheses refer to the list of references at the end of this test method.