



Standard Test Method for Enthalpies of Fusion and Crystallization of Polymers by Differential Scanning Calorimetry (DSC)¹

This standard is issued under the fixed designation D 3417; 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

1.1 This test method covers the determination of heat of fusion and heat of crystallization of polymers by differential scanning calorimetry.

1.2 This test method is applicable to polymers in granular form (below 60 mesh preferred, avoid 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.

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

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

NOTE 2—This test method may be used in conjunction with Test Method D 3418 or E 794 to simultaneously determine the temperatures of melting and crystallization.

NOTE 3—This test method may not be applicable to all types of polymers as written (see 6.6).

NOTE 4—Uncertain radiation losses at temperatures higher than 400°C may affect the accuracy of results.

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 5—The test method is similar but not equivalent to ISO 11357-1 and 11357-3. The ISO standard provides additional information not supplied by this test method.

2. Referenced Documents

2.1 ASTM Standards:

D 3418 Test Method for Transition Temperatures of Polymers by Thermal Analysis²

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).

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² *Annual Book of ASTM Standards*, Vol 08.02.

E 473 Terminology Relating to Thermal Analysis³

E 793 Test Method for Heats of Fusion and Crystallization by Differential Scanning Calorimetry³

E 794 Test Method for Melting and Crystallization Temperatures by Thermal Analysis³

E 968 Practice for Heat Flow Calibration of Differential Scanning Calorimeters³

E 1142 Terminology Relating to Thermophysical Properties³

2.2 ISO Standards:⁴

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

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 E 473 and E 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 comparing the areas under the crystallization exotherm or fusion endotherm of the test material against the respective areas obtained by the similar treatment of a well-characterized standard.

5. Significance and Use

5.1 Differential scanning calorimetry provides a rapid method for determining enthalpy changes accompanied by the first-order transitions of materials. The heat of fusion, the heat of crystallization, and also the effect of annealing can be determined in polymers that possess them. Differential scanning calorimetry may be used to assist in identifying specific polymers, polymer alloys, and certain polymer additives that exhibit thermal transitions.

³ *Annual Book of ASTM Standards*, Vol 14.02.

⁴ Available from American National Standards Institute, 11 W. 42nd St., 13th Floor, New York, NY 10036.

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

6. Interferences

6.1 An appreciable increase in particle size above that specified can alter the heat of fusion or crystallization.

6.2 Changes in heating and cooling rate as well as in final heating or cooling temperatures have a considerable effect on the measured heats of fusion or crystallization. Therefore, departure from conditions specified for a given polymer is not permitted.

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

6.4 Too large a specimen size above that specified can cause error in the heat measurement.

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

6.6 Not all polymers lend themselves to the exact terms of this test method. Some polymers such as polyarylamides can be crystallized only from solution. Other polymers such as crystallizable polystyrene can only be annealed above their glass transition temperature. 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*, composed of:

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 ± 10 mK (0.01°C).

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

7.1.1.4 *Means of Sustaining a Test Chamber Environment*, of inert purge gas at a purge flow rate of 10 to 50 mL/min ± 5 %.

NOTE 6—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 0.5 to 20°C/min constant to ± 0.1 °C/min or at an isothermal temperature constant to ± 0.5 °C for at least 60 min.

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

7.1.5 *Containers* (pans, crucibles, vials, 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 to 20°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 ± 10 μ g.

8. Sampling

8.1 *Powdered or Granular Specimens*—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, punch, or cork borer (Size No. 2 or 3) to appropriate dimensions, in thickness or diameter and length, that will best fit the specimen capsule and will approximate the desired mass in the subsequent procedure.

8.3 *Film or Sheet Specimens*—For films thicker than 0.04 mm (0.015 in.), see 8.2. For thinner films, cut disks to fit in the specimen capsules.

8.4 Any shape or form listed in 8.1, 8.2, and 8.3 may be used except for referee tests that shall be performed on films as specified in 8.3.

9. Calibration

9.1 Calibrate the DSC heat flow signal using Practice E 968 and the same heating rate (that is, 10°C/min) to be used in this test method (see Note 8).

10. Procedure

10.1 Weigh a specimen of 5 to 10 mg to an accuracy of 10 μ g.

NOTE 7—Other specimen sizes may be used but shall be reported.

10.2 Purge the cell with an inert purge gas (that is, nitrogen, argon, or helium) at 10 to 50 ± 5 mL/min.

10.3 Perform and record a preliminary thermal cycle by heating the specimen at a rate of 10°C/min under inert purge gas atmosphere from 50°C below to 30°C above the melting point, or to temperatures high enough to remove previous thermal history. The selection of temperature and time are critical when the effect of annealing is studied. Minimize the time of exposure to high temperatures.

NOTE 8—Other heating rates may be used but shall be reported. It is the responsibility of the user of other rates to demonstrate equivalency to this standard.

10.4 Hold temperature for 10 min (10.3).

NOTE 9—For some polymers, this high-temperature annealing may result in degradation of the specimen. In such cases, shorter annealing times may be used but shall be reported.

10.5 Cool to at least 50°C below the peak crystallization temperature at a rate of 10°C/min, and record the cooling curve. Use this curve for the calculation of the heat of crystallization (ΔH_c).

10.6 Repeat 10.3 when the calorimeter is thermally stable and in control at a heating rate of 10°C/min and record the heating curve. Use this curve for the calculation of the heat of fusion (ΔH_f).

11. Calculation

11.1 Construct a baseline by connecting the two points at which the melting endotherm or freezing exotherm deviate from the relatively straight baseline, caused by a signal that is proportional to the difference in heat flow between the reference and specimen capsules (Figs. 1 and 2).

11.2 For certain materials the method described in 11.1 may not be applicable, and other graphical means must be developed for enclosing the peak areas as agreed upon between the manufacturer and the purchaser (1-5).⁵

11.3 Integrate the area under the fusion heat flow endotherm or crystallization exotherm as a function of time to yield enthalpy or heat (mJ) of the transition.

11.4 Calculate the mass normalized enthalpy or heat of transition by dividing the enthalpy obtained in 11.3 by the mass of the test specimen. Report this mass normalized enthalpy of transition (J/g).

12. Report

12.1 Report the following information:

12.1.1 Complete identification and description of the material tested, including source and manufacturer's code,

12.1.2 Description of the instrument used,

12.1.3 Statement of the material of the specimen holder and style and average rate of linear temperature change,

12.1.4 Description of calibration procedure,

12.1.5 Identification of the specimen atmosphere by pressure, flow rate, purity, and composition, and

12.1.6 Heat of fusion or crystallization, or both, (J/g).

13. Precision and Bias

13.1 The precision of this test method for measuring the enthalpies of melting and crystallization is essentially equal to the precision stated in Test Method E 794.

13.2 An interlaboratory study was conducted in 1998 in which the enthalpy of melting and crystallization for a polypropylene and a metallic sample was tested by nine laboratories.

13.3 Precision:

13.3.1 Within laboratory variability may be described using the repeatability value (r), obtained by multiplying the relative standard deviation by 2.8. The repeatability value estimates the 95 % confidence limit.

13.3.2 Repeatability values of $r = 10$ and 3.4 % were obtained for enthalpy of melting and crystallization, respectively.

13.3.3 Between laboratory variability may be described using the reproducibility value (R) obtained by multiplying the relative standard deviation by 2.8. The reproducibility value estimates the 95 % confidence limit.

13.3.4 Reproducibility values of $R = 22$ and 7.3 % were obtained for the enthalpy of melting and crystallization, respectively.

13.4 Bias:

13.4.1 An estimation of bias is obtained by comparing the enthalpy of melt obtained for a metallic tin sample to literature

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

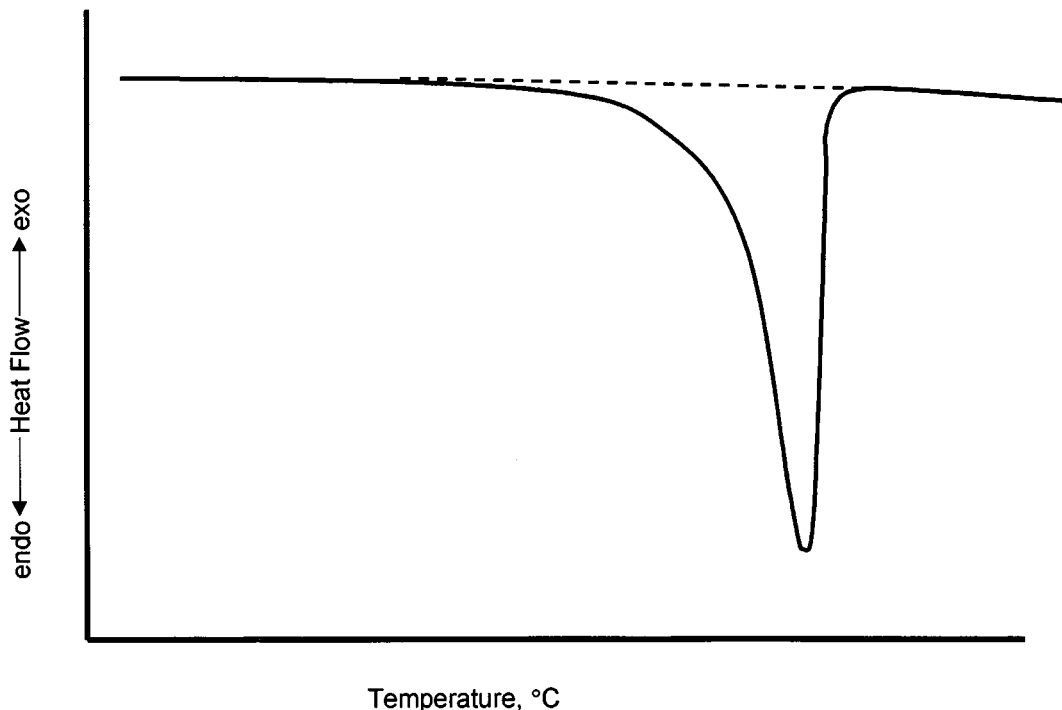


FIG. 1 Typical Heating Curve for Polyethylene

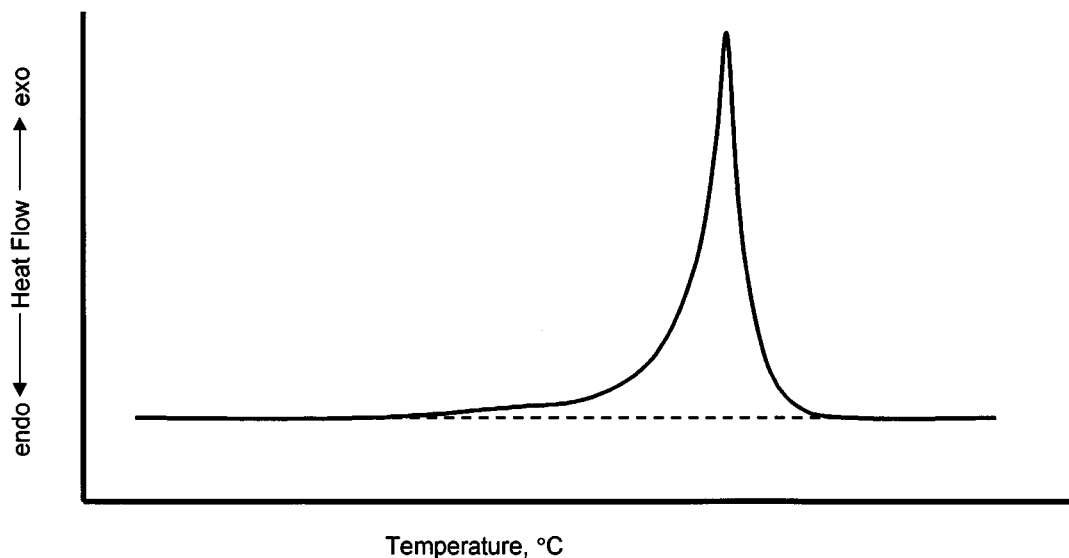


FIG. 2 Typical Freezing Curve for Polyethylene

values for this material. That is, bias = (mean observed enthalpy of melting) – (known value).

13.4.2 The bias was found to be less than 0.1 %. This indicates an absence of significant bias.

14. Keywords

14.1 crystallization; differential scanning calorimetry (DSC); enthalpy; heat of crystallization; heat of fusion; heat of transition; melting; polymer

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