



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 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, -2, -3. The ISO procedures provide additional information not supplied by this test method.

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 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.

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

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 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.

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) or other appropriate means to appropriate size, in thickness or diameter and length that will best fit the specimen containers as in **7.1.5** and will approximately meet the desired weight in the subsequent procedure.

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

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

TABLE 1 Effect of Rate of Temperature Rise on Transition Temperatures

Material	Rate of Temperature Rise (°C / Min.)	T _g Second Heat (°C)	T _c (°C)	T _m First Heat (°C)	T _m Second Heat (°C)
PEEK	5	Too Weak	298.1	342.2	341.7
PEEK	10	Too Weak	293.4	339.4	340.2
PEEK	20	150.6	287.2	339.0	338.7
PEEK	40	156.0	277.7	341.4	338.2
Syndiotactic PP	5	Non Observed	75.0	131.1	130.7
Syndiotactic PP	10	Non Observed	70.0	129.4	129.8
Syndiotactic PP	20	Non Observed	64.9	127.9	129.1
Syndiotactic PP	40	Non Observed	58.8	130.1	130.4

8.4 Use any shape or form listed in 8.1 – 8.3 except when conducting referee tests that shall be performed on films as specified in 8.3.

9. Calibration

9.1 The purge gas shall be used during calibration.

9.2 Calibrate the DSC temperature signal using Practice E967 and the same heating rate to be used in this test method preferably 10°C/min or 20°C/min (see Note 5). (See Section 10 for details.)

9.3 Calibrate the DSC heat flow signal using Practice E968 and the same heating rate as in 9.2 (see Note 5).

9.4 Some instruments allow for the temperature and heat flow calibration to be performed simultaneously. In such cases, use the same heating rate for this method and follow the manufacturer's instruction. Report the heating rate. (See 12.1.3.)

NOTE 5—Use of other heating rates is permitted. However, test results are affected by the heating rate. See Table 1. It is the responsibility of the user of other rates to demonstrate equivalency to this test method.

10. Procedure

10.1 *For First-Order Transition (melting and crystallization):*

10.1.1 The purge gas shall be used during testing. The flow rate of the gas shall be the same as used in the calibration (9.1).

10.1.2 Use a specimen mass appropriate for the material to be tested. In most cases a 5-mg specimen mass is satisfactory. Avoid overloading. Weigh the specimen to an accuracy of $\pm 10 \mu\text{g}$.

10.1.2.1 Intimate thermal contact between the pan and specimen is essential for reproducible results. Crimp a metal cover against the pan with the sample sandwiched in between to ensure good heat transfer. Take care to ensure flat pan bottoms.

10.1.3 Perform and record a preliminary thermal cycle by heating the sample at the same rate used for testing from at least 50°C below to 30°C above the melting temperature to erase previous thermal history.

10.1.4 When the effect of annealing is studied, selection of temperature and time are critical. Minimize the time of exposure to high temperature to avoid sublimation or decomposition. In some cases it is possible that the preliminary thermal cycle will 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.

10.1.5 Hold the temperature for 5 min (10.1.3).

NOTE 6—In cases that high-temperature annealing cause polymer degradation, the use of shorter annealing times is permitted but shall be reported.

10.1.6 Cool to at least 50°C below the peak crystallization temperature using the same rate that was used for heating and record the cooling curve.

10.1.7 Hold the temperature for 5 min.

10.1.8 Repeat heating at the same rate used in 10.1.3 (10°C/min or 20°C/min) and record the heating curve. Use this curve to calculate the enthalpies of transition.

10.1.9 Measure the temperatures for the desired points on the curves: T_{eim} , T_{pm} , T_{efm} , T_{eic} , T_{pc} , and T_{efc} (see Fig. 1). Report two T_{pm} 's or T_{pc} 's if observed.

10.1.10 In case of dispute determine T_m and T_c at a heating rate of 10°C/min.

where:

T_{eim} = melting extrapolated onset temperature, °C,
 T_{efm} = melting extrapolated end temperature, °C,
 T_{pm} = melting peak temperature, °C,
 T_{eic} = crystallization extrapolated onset temperature, °C,
 T_{pc} = crystallization peak temperature, °C, and
 T_{efc} = crystallization extrapolated end temperature, °C.

NOTE 7—The actual temperature displayed on the temperature axis depends upon the instrument type (for example, specimen temperature, program temperature, or specimen-program temperature average). Follow any recommended procedures or guidelines of the instrument manufacturer to obtain specimen temperature at the point of interest.

10.2 *For Glass Transition:*

10.2.1 The purge gas shall be used during testing. The flow rate of the gas shall be the same as used in the calibration (9.1).

10.2.2 Use a specimen mass appropriate for the material to be tested. In most cases, a 10-mg specimen mass is satisfactory. Weigh the specimen to an accuracy of $\pm 10 \mu\text{g}$.

10.2.3 Perform and record a preliminary thermal cycle by heating the sample at a rate of 20°C/min from at least 50°C below to 30°C above the melting temperature to erase previous thermal history.

10.2.4 Hold the temperature for 5 min. (See Note 6.)

10.2.5 Quench cool to at least 50°C below the transition temperature of interest.

10.2.6 Hold the temperature for 5 min.

10.2.7 Repeat heating at a rate of 20°C/min, and record the heating curve until all desired transitions have been completed. (See Note 5.)

10.2.8 The glass transition is more pronounced at faster heating rates. A heating rate of 20°C/min is the preferred

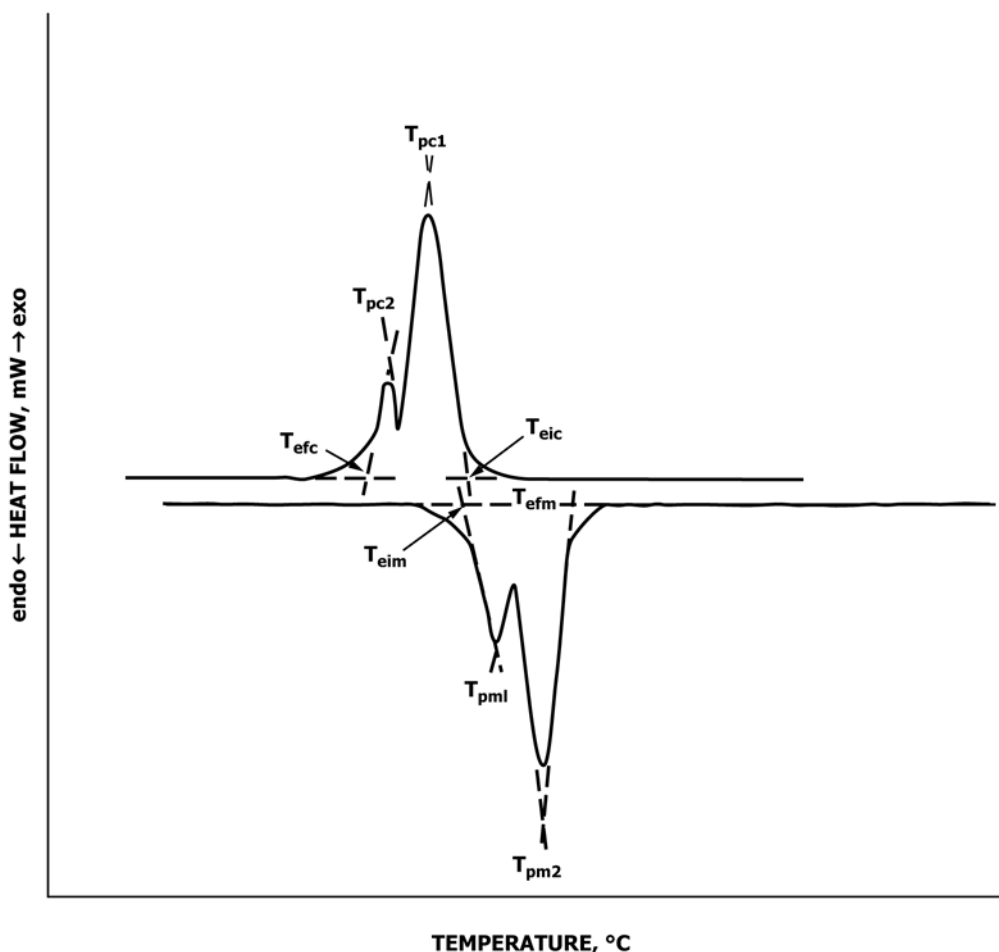


FIG. 1 First-Order Transition of Nylon

heating rate for T_g measurements. The instrument shall be calibrated at the same heating rate used for testing. If both first- and second-order transitions (T_m and T_g , respectively) are to be determined in the same run, use the same heating rate as used in 10.1.8 for both transitions and determine results from the second heating step (10.1.8). Report the heating rate. (See 12.1.3.)

NOTE 8— T_g obtained using Procedure 10.1 will be different from T_g measured using procedures 10.2.3 – 10.2.7. Therefore, the heating rate must be reported as described in 12.1.3.

10.2.9 In case of dispute determine T_g at a heating rate of 20°C/min.

10.2.10 Measure temperatures T_{eig} , T_{mg} , and T_{efg} (see Fig. 2):

where:

T_{eig} = extrapolated onset temperature, °C,
 T_{mg} = midpoint temperature, °C, and
 T_{efg} = extrapolated end temperature, °C.

A new baseline will likely be established after the transition, rather than a peak (see Note 9). For most applications, the T_{mg} temperature is more meaningful. In those cases, designate T_{mg} as the glass transition temperature (T_g) in place of the extrapolated onset for the glass transition curve.

NOTE 9—Stress relaxation peaks, caused by annealing, that appear in

some polymers above the glass transition are normally eliminated by the preliminary thermal cycle and a new baseline will be established after the transition.

11. Calculation for Heat of Fusion and Crystallization

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 (Fig. 3 and Fig. 4).

11.2 The method described in 11.1 is not applicable for certain materials. In such cases, other graphical means must be developed for enclosing the peak areas as agreed upon between the manufacturer and the purchaser (4-8).

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:

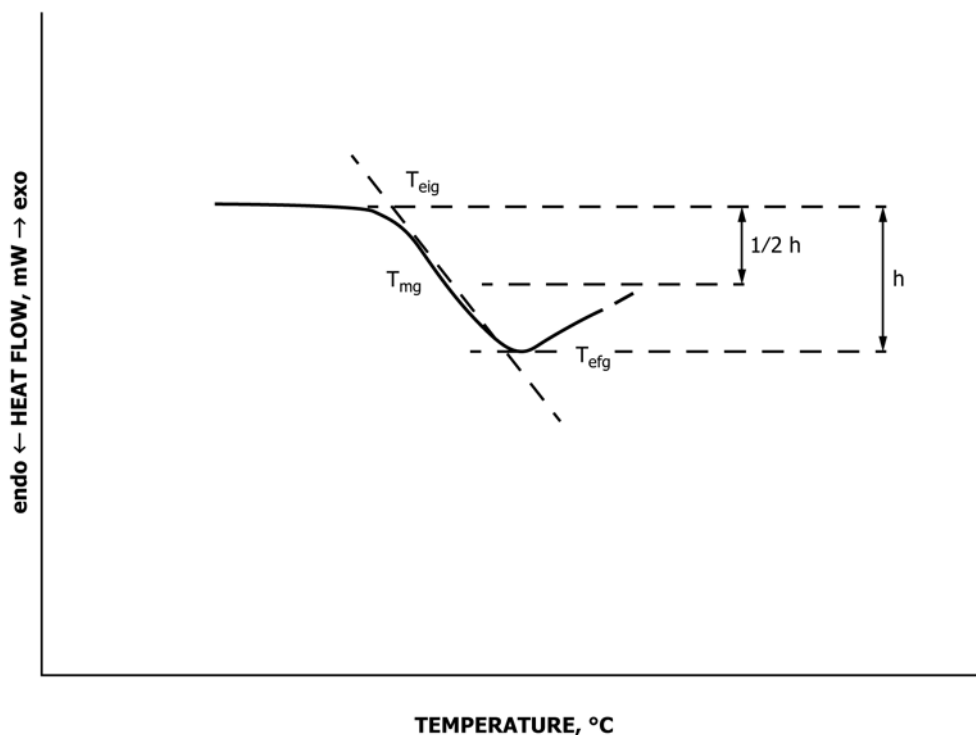


FIG. 2 Assignment of Glass Transition of Poly(Methyl Methacrylate) (PMMA)

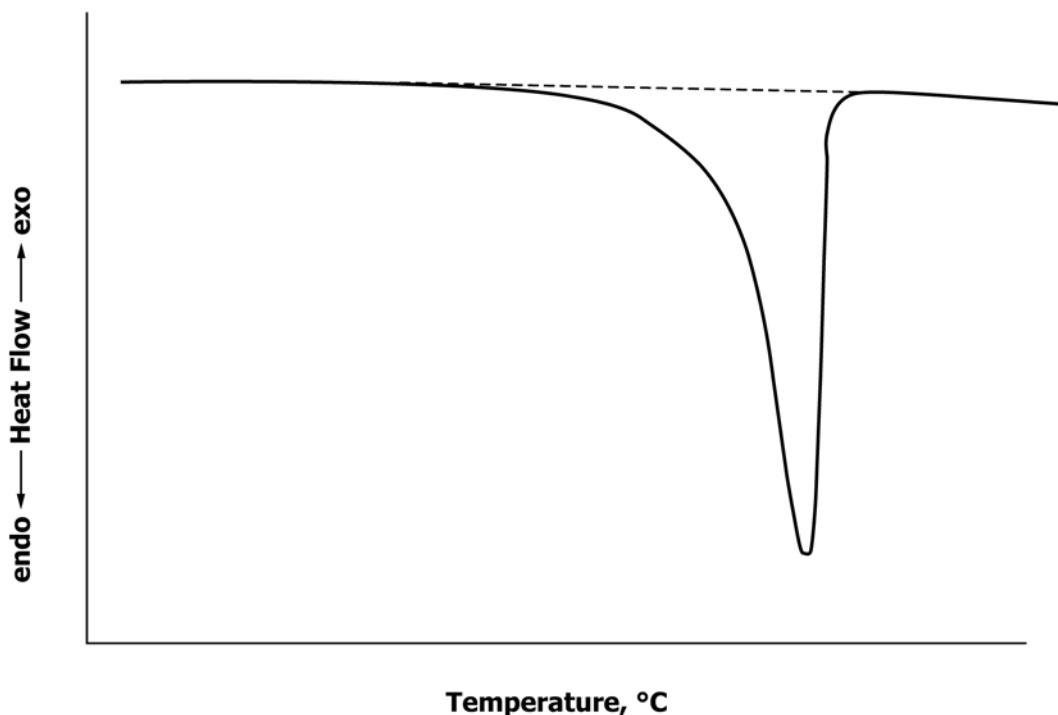


FIG. 3 Typical Heating Curve for Polyethylene

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

12.1.2 Description of instrument used for the test,

12.1.3 Statement of the mass, dimensions, geometry, and materials of the specimen container, and the heating rate.

12.1.4 Description of temperature calibration procedure,

12.1.5 Identification of the sample atmosphere by purge gas flow rate, purity, and composition, including humidity, if applicable,

12.1.6 Results of the transition measurements using the temperature parameters cited in Fig. 1, or any combination of parameters suitable for the purpose in hand. T_{pm} and T_{eic} that

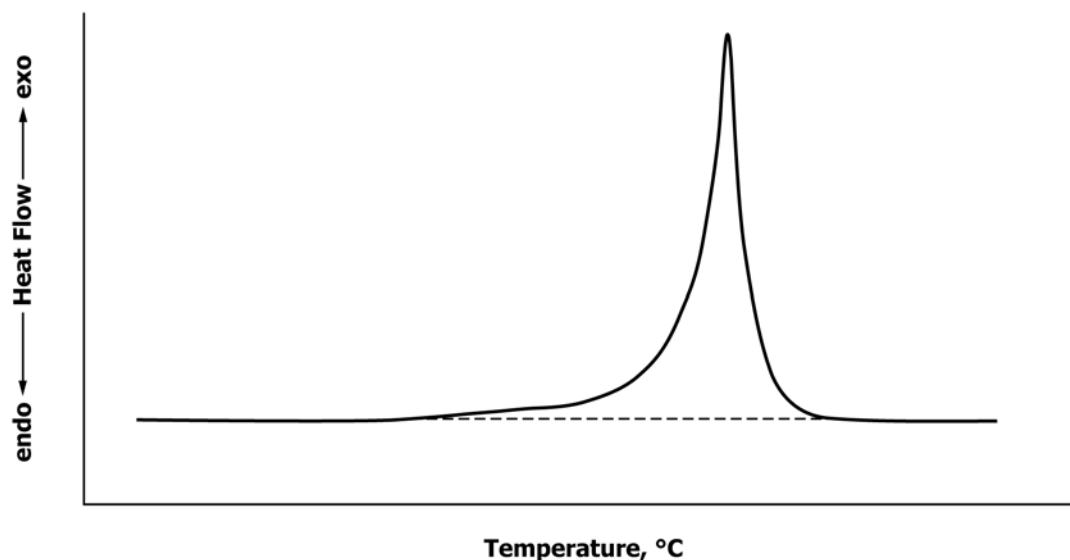


FIG. 4 Typical Freezing Curve for Polyethylene

are commonly used as single characteristic temperatures for the first-order transition of semicrystalline polymers but must be identified by including the subscript.

12.1.7 Heat of fusion or crystallization, or both, and,

12.1.8 Any side reaction (for example, crosslinking, thermal degradation, or oxidation), and the reaction identified if possible.

13. Precision and Bias⁵

13.1 Tables 2-6 are based on a round robin study conducted in 2007 in accordance with Practice E691, involving five materials tested by seven laboratories. Not all materials and tests were performed by every lab, due to the limitation of individual lab. All the samples were prepared at one source, but the individual test specimens were prepared at the laboratories that tested them. Each laboratory obtained two test results for each material.

NOTE 10—A program is being set up to re-evaluate the repeatability and reproducibility of this method at heating rates of 10°C/min and 20°C/min. The effect of the different heating rates on the transition temperatures and enthalpies will also be evaluated.

13.2 Concept of “r” and “R”: If S_r and S_R have been calculated from a large enough body of data, then:

13.2.1 Repeatability: Two results obtained within one laboratory shall be judged not equivalent if they differ by more than the “r” value for that material. “r” is the interval representing the critical difference between two test results for the same material, obtained by the same operator using the same equipment on the same day in the same laboratory.

13.2.2 Reproducibility: Two test results obtained by different laboratories shall be judged not equivalent if they differ by more than the “R” value for that material. “R” is the interval representing the critical difference between two test results for

TABLE 2 Glass Transition Temperature, °C

Materials	Average	S_r^A	S_R^B	r^C	R^D
PET	76.2	0.19	1.12	0.55	3.18
PC	149.3	0.24	0.66	0.69	1.88

^A S_r = the within-laboratory standard deviation of the average.

^B S_R = the between-laboratories standard deviation of the average.

^C r = repeatability limit = $2.83 \times S_r$

^D R = reproducibility limit = $2.83 \times S_R$

TABLE 3 Melting Peak Temperature, °C

Materials	Average	S_r^A	S_R^B	r^C	R^D
PE	123.0	0.28	0.62	0.79	1.75
PP	160.6	0.29	1.55	0.83	4.38
PET	249.2	0.18	0.58	0.51	1.65
PA-6	220.3	0.30	0.81	0.84	2.29

^A S_r = the within-laboratory standard deviation of the average.

^B S_R = the between-laboratories standard deviation of the average.

^C r = repeatability limit = $2.83 \times S_r$

^D R = reproducibility limit = $2.83 \times S_R$

TABLE 4 Crystallization Peak Temperature, °C

Materials	Average	S_r^A	S_R^B	r^C	R^D
PE	109.8	0.08	1.73	0.21	4.90
PP	111.7	0.80	1.94	2.28	5.50
PET	194.9	0.54	1.52	1.52	4.29
PA-6	183.4	0.62	1.07	1.74	3.02

^A S_r = the within-laboratory standard deviation of the average.

^B S_R = the between-laboratories standard deviation of the average.

^C r = repeatability limit = $2.83 \times S_r$

^D R = reproducibility limit = $2.83 \times S_R$

the same material, obtained by different operators using different equipment in different laboratories.

13.2.3 Any judgment in accordance with 13.2.1 or 13.2.2 would have an approximate 95 % (0.95) probability of being correct. (Warning—The explanation of “r” and “R” are only intended to present a meaningful way of considering the approximate precision of this test method. The data in Tables 2-6 are not intended to be applied to acceptance or rejection of materials, as these data apply only to the materials tested in the

⁵ Supporting data have been filed at ASTM International Headquarters and may be obtained by requesting Research Report RR:D20-1249.

TABLE 5 Heat of Fusion, J/g

Materials	Average	S_r^A	S_R^B	r^C	R^D
PE	86.0	2.79	16.1	7.90	45.6
PP	89.6	1.24	12.9	3.50	36.4
PET	41.1	1.13	5.01	3.20	14.2
PA-6	62.0	1.40	9.00	3.97	25.5

^A S_r = the within-laboratory standard deviation of the average.

^B S_R = the between-laboratories standard deviation of the average.

^C r = repeatability limit = $2.83 \times S_r$.

^D R = reproducibility limit = $2.83 \times S_R$.

TABLE 6 Heat of Crystallization, J/g

Materials	Average	S_r^A	S_R^B	r^C	R^D
PE	64.6	1.70	17.4	4.82	49.3
PP	95.6	1.03	5.21	2.90	14.7
PET	45.9	0.99	1.93	2.81	5.46
PA-6	63.8	1.46	2.93	4.12	8.30

^A S_r = the within-laboratory standard deviation of the average.

^B S_R = the between-laboratories standard deviation of the average.

^C r = repeatability limit = $2.83 \times S_r$.

^D R = reproducibility limit = $2.83 \times S_R$.

round robin and are unlikely to be rigorously representative of other lots, formulations, conditions, materials, or laboratories. When using this test method apply the principles outlined in Practice E691 to generate data specific to other materials and laboratories (or between specific laboratories). The principles of 13.2 through 13.2.3 would then be valid for such data.)

13.3 There are no recognized standards by which to estimate the bias of this method.

14. Keywords

14.1 crystallization; crystallization temperature; differential scanning calorimetry (DSC); enthalpy; first-order transition; glass transition; heat of crystallization; heat of fusion; heat of transition; melting; melting temperature; polymer; transition temperature

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SUMMARY OF CHANGES

Committee D20 has identified the location of selected changes to this standard since the last issue (D3418 - 12^{e1}) that may impact the use of this standard. (May 1, 2015)

(1) Added Table 1 to Note 5.

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