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Plastics — Differential scanning calorimetry (DSC) —

Part 1: General principles

Plastiques — Analyse calorimétrique différentielle (DSC) —

Partie 1: Principes généraux

Reference number
ISO 11357-1:1997(E)

Foreword

ISO (the International Organization for Standardization) is a worldwide federation of national standards bodies (ISO member bodies). The work of preparing International Standards is normally carried out through ISO technical committees. Each member body interested in a subject for which a technical committee has been established has the right to be represented on that committee. International organizations, governmental and non-governmental, in liaison with ISO, also take part in the work. ISO collaborates closely with the International Electrotechnical Commission (IEC) on all matters of electrotechnical standardization.

Draft International Standards adopted by the technical committees are circulated to the member bodies for voting. Publication as an International Standard requires approval by at least 75 % of the member bodies casting a vote.

International Standard ISO 11357 was prepared by Technical Committee ISO/TC 61, *Plastics*, Subcommittee SC 5, *Physical-chemical properties*.

ISO 11357 consists of the following parts, under the general title *Plastics — Differential scanning calorimetry (DSC)*:

— *Part 1: General principles*

— *Part 2: Determination of glass transition temperature*

— *Part 3: Determination of temperature and enthalpy of melting and crystallization*

— *Part 4: Determination of specific heat capacity*

— *Part 5: Determination of polymerization temperatures and/or times and polymerization kinetics*

— *Part 6: Determination of oxidation induction time*

— *Part 7: Determination of crystallization kinetics*

Annexes A, B and C of this part of ISO 11357 are for information only.

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Plastics — Differential scanning calorimetry (DSC) —

Part 1:
General principles

WARNING — The use of this International 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 health and safety practices and to determine the applicability of regulatory limitations prior to use.

1 Scope

This International Standard specifies a method for the thermal analysis of polymers such as thermoplastics and thermosetting plastics, including moulding materials and composite materials, using differential scanning calorimetry (DSC).

Various determinations can be made on polymers by using differential scanning calorimetry. These determinations are dealt with in parts 2 to 7 of this standard (see the foreword).

2 Normative reference

The following standard contains provisions which, through reference in this text, constitute provisions of this part of ISO 11357. At the time of publication, the edition indicated was valid. All standards are subject to revision, and parties to agreements based on this part of ISO 11357 are encouraged to investigate the possibility of applying the most recent edition of the standard indicated below. Members of IEC and ISO maintain registers of currently valid International Standards.

ISO 291:—[1], *Plastics — Standard atmospheres for conditioning and testing.*

3 Definitions

For the purposes of this International Standard, the following definitions apply:

3.1 differential scanning calorimetry (DSC): A technique in which the difference between the heat flux (power) into a test specimen and that into a reference specimen is measured as a function of temperature and/or time while the test specimen and the reference specimen are subjected to a controlled temperature programme.

It is common practice to record, for each measurement, a curve in which temperature or time is plotted on the x-axis and heat flux difference is plotted on the y-axis.

1) To be published. (Revision of ISO 291:1977)

3.2 reference specimen: A known specimen which is usually thermally inactive over the temperature and time range of interest.

NOTE — Generally an empty pan identical to the one containing the test specimen is used as the reference specimen.

3.3 standard reference material: A material for which one or more of the thermal properties are sufficiently homogeneous and well established to be used for the calibration of DSC apparatus, for the assessment of a measurement method or for assigning values to materials.

3.4 heat flux; thermal power: The amount of heat transferred per unit time (dQ/dt).

NOTE — The total quantity of heat transferred Q corresponds to the time integral of the heat flux

$$Q = \int \frac{dQ}{dt}\, dt$$

where Q is expressed in joules or in joules per unit mass ($J \cdot kg^{-1}$ or $J \cdot g^{-1}$).

3.5 change in enthalpy, ΔH: The quantity of heat absorbed (ΔH positive) or released (ΔH negative) by a test specimen undergoing a chemical or physical change, and/or a temperature change, at constant pressure. ΔH is expressed in joules or in joules per unit mass ($J \cdot kg^{-1}$ or $J \cdot g^{-1}$):

$$\Delta H = \int_{T_1}^{T_2} \frac{dH}{dT}\, dT$$

3.6 specific heat capacity at constant pressure, c_p: The quantity of heat necessary to raise the temperature of unit mass of material by 1 °C at constant pressure, with all other intensive parameters constant:

$$c_p = \frac{1}{m} \times \left(\frac{\partial Q}{\partial T}\right)_p$$

where

∂Q is the quantity of heat, expressed in joules, necessary to raise the temperature of material of mass m by ∂T degrees Celsius at constant pressure;

c_p is expressed in joules per kilogram degree Celsius [J/(kg·°C)] or joules per gram degree Celsius [J/(g·°C)].

When analysing polymers, care must be taken to ensure that the measured specific heat capacity does not include any heat change due to a chemical reaction or a physical transition.

3.7 baseline: The part of the recorded curve outside, but adjacent to, the reaction or transition zone. In this part of the recorded curve, the heat flux difference is approximately constant.

3.8 virtual baseline: An imaginary line drawn through a reaction and/or transition zone assuming that the heat of reaction and/or transition is zero. It is commonly drawn by interpolating or extrapolating the recorded baseline. It is normally indicated on the DSC curve for convenience (see figure 1).

3.9 peak: The part of the DSC curve which departs from the baseline, reaches a maximum, and subsequently returns to the baseline.

NOTE — The start of the peak corresponds to the start of the reaction or transition.

3.9.1 endothermic peak: A peak in which the energy supplied to the test specimen is greater than the energy corresponding to the virtual baseline.

3.9.2 exothermic peak: A peak in which the energy supplied to the test specimen is less than the energy corresponding to the virtual baseline.

NOTE — In accordance with the accepted conventions of thermodynamics, the enthalpy change is negative when the reaction or transition is exothermic and positive when the reaction or transition is endothermic. The direction corresponding to exothermic or endothermic is normally indicated on the DSC curve.

3.9.3 peak height: The distance between the virtual baseline and the point of maximum height of a peak. The height is expressed in milliwatts. The height is not proportional to the mass of the test specimen.

3.10 characteristic temperatures: The following are the characteristic temperature on a DSC curve:

- onset temperature T_i
- extrapolated onset temperature T_{ei}
- peak temperature T_p
- extrapolated end temperature T_{ef}
- end temperature T_f

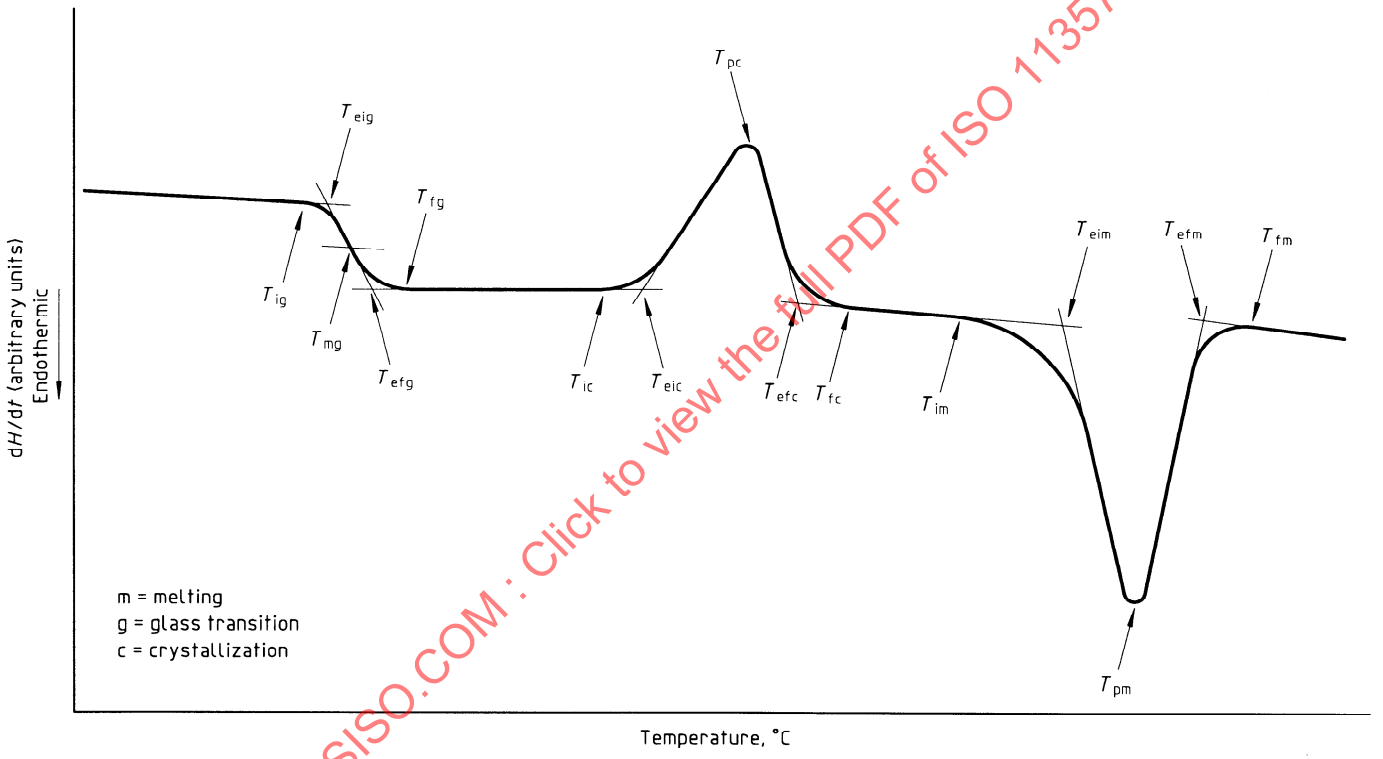

Figure 1 — Typical DSC curve

4 Principle

The difference between the heat flux into a test specimen and that into a reference specimen is measured as a function of temperature and/or time, while the test specimen and the reference specimen are subjected to a controlled temperature programme under a specified atmosphere.

NOTE — Two types of DSC, power-compensation DSC and heat-flux DSC, may be carried out. They are distinguished by the design of instrumentation used for measurement, as follows:

a) Power-compensation DSC: The difference between the heat flux into the test specimen and that into the reference specimen is measured as a function of temperature or time while varying the temperature of the specimens in accordance with a controlled programme, keeping the temperature of both specimens equal.

b) Heat-flux DSC: The difference in heat flux derived from the temperature difference between a test specimen and a reference specimen is measured as a function of temperature or time while varying the temperature of the specimens in accordance with a controlled programme. In this type of measurement, the difference in temperature between the test specimen and reference specimen is proportional to the difference in heat flux.

5 Apparatus and materials

5.1 Differential scanning calorimeter, the main features of which are as follows:

a) the capability to generate constant heating and cooling rates between 0,5 °C/min and 20 °C/min;

b) the capability to maintain the test temperature constant to within ± 0,5 °C for at least 60 min;

c) the capability to carry out step heating or any other heating mode;

d) a gas-flow rate in the range 10 ml/min to 50 ml/min, controllable to ± 10 %;

e) temperature signals with 0,1 °C resolution and noise below 0,5 °C;

f) facilities for calibration and use with a minimum test specimen mass of 1 mg (or with smaller quantities if required by specific applications);

g) a recording device which is capable of automatically recording the DSC curve, and of integrating the area between the curve and the virtual baseline with an error of less than 2 %;

h) a specimen holder assembly which has one or more holders for pans.

5.2 Pans, for test specimens and reference specimens, all made of the same material and of equal mass. The pans shall be physically and chemically inert under the measurement conditions to both the test specimen and the atmosphere.

The pans should preferably be made of a material with a high thermal conductivity. They shall be able to be fitted with lids and sealed so that they can withstand the overpressure which can arise during measurement.

5.3 Balance, capable of measuring the specimen mass with an accuracy of ± 0,01 mg.

5.4 Standard reference materials (see annex A).

5.5 Gas supply, analytical grade.

6 Test specimen

The test specimen may be in the liquid or solid state. If in the solid state, it may be in the form of a powder, pellets or granules, or may be cut from sample pieces. The test specimen shall be representative of the sample being examined and shall be prepared and handled with care. If the specimen is taken from sample pieces by cutting, care shall be taken to prevent heating, polymer reorientation or any other effect that may alter the properties. Operations such as grinding that could cause heating or reorientation and could therefore change the thermal history of the sample shall be avoided. When aggregates or powders are involved, two or more specimens shall be taken. The method of sampling and test specimen preparation shall be stated in the test report.

NOTE — Incorrect specimen preparation can affect the properties of the polymers examined. For further information, see annex B.

7 Test conditions and specimen conditioning

7.1 Test conditions

Prior to any testing, switch the equipment on for at least one hour to allow the electronics to temperature-equilibrate. Maintain and operate the instrument in an atmosphere as specified in ISO 291.

NOTE — It is advisable to protect the instrument from air draughts, exposure to direct sunlight and/or sharp changes in temperature, pressure or electric supply during measurements.

7.2 Conditioning of test specimens

Condition test specimens before measurements as specified in the relevant material standard or by a method agreed between the interested parties.

NOTES

1 Unless other conditions are specified, it is recommended that test specimens are conditioned in accordance with ISO 291.

2 Results obtained by DSC can be greatly affected by conditioning.

8 Calibration

8.1 General

Calibrate the energy and temperature measurement devices of the calorimeter at least in accordance with the instrument manufacturer's recommendations.

NOTES

1 The calibration function $K(T)$ (see 8.3) cannot be expressed as a simple proportionality factor since it varies with temperature. It is essential therefore to carry out calibration with at least two standard reference materials for each parameter, i.e. temperature and energy. Most recommended standard reference materials, as given in annex A, can be used for both temperature and energy calibrations.

2 Calibration is affected by:

— the type of calorimeter used;

— the gas used and its flow rate;

— the type of specimen pan used, its dimensions and its position in the specimen holder;

— the mass of the test specimen;

— the heating and cooling rates;

— the type of cooling system used.

It is therefore advisable to define the conditions of the actual determination as precisely as possible and carry out the calibration using the same conditions. Computer systems associated with DSC instruments may automatically correct some of the parameters.

3 It is advisable to carry out calibrations regularly. It is considered good practice to check the temperature and energy measurement devices using standard reference materials which have melting points close to the temperature range used for the material being analysed.

8.2 Temperature calibration

Carry out the temperature calibration as follows:

— choose at least two standard reference materials having a transition temperature in or near the temperature range to be examined;

— determine the transition temperatures for the standard reference materials under the same conditions as those to be used for the test specimen, where the transition temperatures of the standard reference materials are defined as the intercept of the extrapolated baseline and the tangent to the leading flank of the transition peak at the point of maximum gradient (i.e. the extrapolated onset temperature);

— determine the temperature calibration function by comparison of the nominal values with the recorded values, unless it can be obtained automatically from an associated computer system by feeding in the nominal and recorded values.

NOTE — Correctly calibrated instruments give consistent results in the heating mode, but not necessarily in the cooling mode (because of supercooling).

Since there are no standard reference materials for the cooling mode, temperature calibration can be carried out in the heating mode only, and shall be performed each time the test conditions are changed. More frequent checks may be carried out as required. Temperature calibration repeatability shall be better than 2 %.

8.3 Energy or thermal-power calibration

Calibration of the DSC instrument with respect to energy (in joules) or thermal power (in watts) allows a determination of the calibration function $K(T)$, or instrument sensitivity, versus temperature. Sensitivity, which is generally expressed in milliwatts per millivolt, relates the electrical signal $E(T)$ indicated by the instrument to the power $P(T)$ passing into the test specimen at temperature T, as follows:

$$P(T) = K(T) \times E(T)$$

or, expressed in the form of integrals,

$$\int_{t_1}^{t_2} P(T)\,\mathrm{d}t = \int_{t_1}^{t_2} K(T) \times E(T)\,\mathrm{d}t$$

Depending on the type of DSC instrument and the temperature range being examined, calibration may be carried out either by direct measurement or by comparison, with the true values, of the readings indicated by the instrument for the enthalpy of fusion or heat capacity of the standard reference materials.

NOTE — It is advisable to refer to the instrument manufacturer's documents when choosing the calibration method.

Carry out the calibration as follows:

— choose two or more standard reference materials which have a suitable heat capacity and a melting point in or near the temperature range to be examined;

— examine the standard materials under the same conditions as those which will be used for the test specimen;

— record the plot of E versus temperature for the heat of transition or heat capacity;

— determine the energy or thermal-power calibration function by comparison of the nominal values with the recorded values, unless it can be obtained automatically by an associated computing system by feeding in the nominal and recorded values.

Energy calibration checks shall be carried out at regular intervals. The repeatability of such checks shall be better than 2 %.

9 Procedure

9.1 Setting up the apparatus

9.1.1 Switch on the instrument at least one hour prior to any testing to allow the electronics to temperature-equilibrate.

9.1.2 Place empty pans of the same nominal mass in the holders of the specimen holder assembly. Adjust the conditions to those which will be used for the actual determination. The DSC curve should be a straight line over the required temperature range.

When a straight line cannot be obtained, record the DSC curve after confirming its repeatability.

9.2 Loading the test specimen into the pan

9.2.1 Select pans of the appropriate volume, ensuring that they are clean.

9.2.2 Use two identical pans, one for the test specimen and one (empty or not) as a reference specimen.

9.2.3 Weigh the sample pan, together with its lid, to the nearest 0,01 mg.

9.2.4 Load the test specimen into the sample pan.

9.2.5 If required, seal the pans with lids.

9.2.6 Reweigh the sample pan.

9.3 Insertion of the pans in the instrument

Use tweezers or any other suitable tool to place the pans in the specimen holders, ensuring that there is good contact between the test specimen and the pan and between the pan and holder. Close the cover of the specimen holder assembly.

9.4 Temperature-scanning measurement

9.4.1 Programme the instrument to carry out the required thermal cycle. Two types of programme can be used: continuous or stepwise.

9.4.2 Start the determination. The control operations required during the determination depend on the type of determination and on the degree of computer assistance associated with the instrument. Refer to the instrument manufacturer's documents.

9.4.3 Bring the specimen holder assembly back to room temperature and take out the pan containing the test specimen. Examine the pan to determine whether there is any deformation or overflow. If the cell becomes contaminated from specimen overflow, clean the cell in accordance with the manufacturer's instructions.

9.4.4 Weigh the pan with the test specimen. If any mass loss is observed, this could have created an extra enthalpy change.

9.4.5 If a chemical change is suspected, open the pan and inspect the test specimen. Pans which have been damaged shall not be used for further measurements.

9.4.6 Process the data in accordance with the instrument manufacturer's instructions.

DSC measurements on polymers are greatly affected by the thermal history and morphology of the sample and test specimen. It is recommended that the determination is carried out twice, the second analysis being run after cooling at a defined cooling rate to ensure consistent results. See annex B for further information.

9.5 Isothermal measurement

NOTE — Depending on the type of instrument used, two different isothermal procedures are available, with the test specimen being introduced at room temperature or at a specified measurement temperature.

9.5.1 Test specimen introduced at room temperature

9.5.1.1 Place the pans in the specimen holders and programme the instrument to reach the "pre-stage" temperature at a fast scanning rate.

9.5.1.2 When a stable baseline has been obtained, bring the temperature to the specified measurement temperature as quickly as possible.

9.5.1.3 Maintaining the temperature at this value, record the DSC curve as a function of time.

9.5.1.4 Allow the instrument to continue to run, with the test conditions constant after the endo/exothermic reaction or transition has finished until a stable baseline has been obtained again.

NOTE — Five minutes has been found suitable.

9.5.1.5 Cool the instrument at the end of the determination and remove the pans.

9.5.1.6 Weigh the pan containing the test specimen.

9.5.1.7 Process the data in accordance with the instrument manufacturer's instructions.

NOTE — In some cases, it is possible to raise the instrument temperature directly to the specified measurement temperature. In such cases, the baseline is obtained at room temperature. This alternative may only be used if the material undergoes no reactions or transitions between room temperature and the measurement temperature.

9.5.2 Test specimen introduced at any measurement temperature

9.5.2.1 Programme the instrument to reach the specified measurement temperature.

9.5.2.2 Allow the instrument temperature to reach steady-state conditions.

9.5.2.3 Place the pans in the specimen holders at this temperature and record the DSC curve as a function of time.

9.5.2.4 Allow the instrument to continue to run, with the test conditions constant, after the endo/exothermic reaction or transition has finished until a stable baseline has been obtained again.

NOTE — Five minutes has been found suitable.

9.5.2.5 Cool the instrument at the end of the determination and remove the pans.

9.5.2.6 Weigh the pan containing the test specimen.

9.5.2.7 Process the data in accordance with the instrument manufacturer's instructions.

9.5.2.8 If the test specimen overflows during the determination, clean the specimen holder assembly. Follow the instrument manufacturer's instructions for cleaning and confirm that the calibration carried out is still valid using at least one temperature and energy reference material.

10 Test report

The test report shall include the following information, as applicable:

a) a reference to this International Standard;
b) all information necessary for complete identification of the material analysed;
c) the type of DSC instrument used;
d) the type of pan used;
e) the standard reference materials, their characteristics and the mass used in each case;
f) the gas and gas-flow rate used in the specimen holder assembly;
g) details of sampling, preparation of the test specimen and the specimen-conditioning procedures used;
h) the mass of the test specimen;
i) the thermal history of the sample and test specimen before the test;
j) the temperature programme parameters, including the initial temperature, heating rate, final temperature and cooling rate;
k) the change in the mass of the test specimen (if any);
l) the test results;
m) the date of the test.

Append the DSC curve to the test report.

Annex A
(informative)

Standard reference materials

Table A.1 — Transition or melting temperatures and enthalpies of fusion for various reference materials

Reference material	Transition or melting point (equilibrium temp.) °C	Enthalpy of fusion $J \cdot g^{-1}$	NIST reference number
Cyclohexane (transition)	– 83 [1]		NIST GM757
Mercury (melting)	– 38,9	11,47	NIST SRM2225
1,2-Dichloroethane (melting)	– 32 [1]		NIST GM757
Cyclohexane (melting)	7 [1]		NIST GM757
Phenyl ether (melting)	30 [1]		NIST GM757
o-Terphenyl (melting)	58 [1]		NIST GM757
Biphenyl (melting)	69,2	120,2	NIST SRM2222
Potassium nitrate (transition)	127,7		NIST GM758
Indium (melting)	157	28,42	NIST GM758
Potassium perchlorate (transition)	299,5		NIST GM758, GM759
Tin (melting)	231,9	60,22	NIST SRM2220, GM758
Lead (melting)	327,5	23,16	
Zinc (melting)	419,6	107,38	NIST SRM2221a
Silver sulfate (transition)	430		NIST GM758, GM759
Quartz (transition)	573		NIST GM759, GM760
Potassium sulfate (transition)	583		NIST GM759, GM760
Potassium chromate (transition)	665		NIST GM759, GM760
Barium carbonate (transition)	810		NIST GM760
Strontium carbonate (transition)	925		NIST GM760

1) Peak temperature.

NOTE — NIST is the US National Institute of Standards and Technology.

Table A.2 — Reference material for glass transition temperature

Reference material	Extrapolated onset temperature °C	Mid-point temperature °C	NIST reference number
Polystyrene	104,5	107,5	NIST GM754

Table A.3 — Reference material for measurement of specific heat capacity

Reference material	NIST reference number
Sapphire	NIST SRM720

Annex B
(informative)

General recommendations

This test method is suitable for comparative measurements on polymeric materials. However, the results obtained using the method are often influenced by systematic errors such as incorrect calibration, baseline correction or specimen preparation. It is strongly recommended that polymeric standard reference materials (similar to those materials being routinely analysed) be established for analysis with the materials being tested. This will allow comparison of data obtained from different instruments, test dates, specimen preparation procedures, etc.

It is not recommended that measurements are continued beyond the decomposition temperature of the sample polymer. This decomposition could lead to contamination of the specimen holder assembly from materials in uncovered pans or an explosion from those in sealed pans. Very high temperatures or large temperature-scanning ranges could also cause alteration in the linearity of the calibration settings, resulting in erroneous results.

The interpretation of a multipeak DSC curve is fairly straightforward when these peaks are separable [see subclause 3.7 of ISO 11357-3:—[1)], *Plastics — Differential scanning calorimetry (DSC) — Part 3: Determination of temperature and enthalpy of melting, crystallization and other transitions*]. More often, DSC curves will have peaks that are not separable. These types of curve are a result of several reactions and/or transitions occurring simultaneously. In these cases, the only thermal properties that can be determined are overall enthalpy, onset temperature and extrapolated onset temperature of the first reaction or transition, extrapolated end temperature and end temperature of the last reaction or transition, and several peak temperatures. It is not always possible to identify all of these individual reactions and/or transitions by DSC alone. In some cases, it may be helpful to adjust the heating and/or cooling rates to further separate these phenomena. However, care should be exercised as the cooling rate can have a significant effect in the characteristic temperature(s) observed in the heating scan that follows cooling.

It is typical for polymers in which such phenomena occur that the DSC curve has several peaks during the first heating scan while it has only one peak during the second heating scan. This second heating scan is normally the one that follows a fairly rapid, uniform cooling cycle. The information obtained in the first heating scan may be indicative of the prior thermal processing that the polymer has been subjected to (such as manufacturing and specimen preparation). Therefore, it is advisable when analysing polymers to carry out three DSC runs: first heating, then cooling and finally second heating. Using this procedure in conjunction with a record of the initial mass of the polymer in the pan and the mass of the polymer in the pan before and after the second heating can aid identification of the various peaks observed. To obtain information on the thermal properties of the sample material without the influence of thermal-processing history, the second-scan results should be used.

1) To be published.