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Plastics — Differential scanning calorimetry (DSC) —

Part 7:
Determination of crystallization kinetics

Plastiques — Analyse calorimétrique différentielle (DSC) —

Partie 7: Détermination de la cinétique de cristallisation

Reference number
ISO 11357-7:2002(E)

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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.

International Standards are drafted in accordance with the rules given in the ISO/IEC Directives, Part 3.

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.

Attention is drawn to the possibility that some of the elements of this part of ISO 11357 may be the subject of patent rights. ISO shall not be held responsible for identifying any or all such patent rights.

International Standard ISO 11357-7 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 characteristic reaction-curve temperatures and times, enthalpy of reaction and degree of conversion*
- *Part 6: Determination of oxidation induction time*
- *Part 7: Determination of crystallization kinetics*
- *Part 8: Determination of amount of absorbed water*

Annex A of this part of ISO 11357 is for information only.

Plastics — Differential scanning calorimetry (DSC) —

Part 7:
Determination of crystallization kinetics

1 Scope

This part of ISO 11357 specifies two methods, isothermal and non-isothermal, for studying the crystallization kinetics of partially crystalline polymers using differential scanning calorimetry (DSC).

It is only applicable to melted polymers.

NOTE These methods are not suitable if the molecular structure of the polymer is modified during the test.

2 Normative references

The following normative documents contain provisions which, through reference in this text, constitute provisions of this part of ISO 11357. For dated references, subsequent amendments to, or revisions of, any of these publications do not apply. However, parties to agreements based on this part of ISO 11357 are encouraged to investigate the possibility of applying the most recent editions of the normative documents indicated below. For undated references, the latest edition of the normative document referred to applies. Members of ISO and IEC maintain registers of currently valid International Standards.

ISO 472, *Plastics — Vocabulary*

ISO 11357-1:1997, *Plastics — Differential scanning calorimetry (DSC) — Part 1: General principles*

ISO 11357-3, *Plastics — Differential scanning calorimetry (DSC) — Part 3: Determination of temperature and enthalpy of melting and crystallization*

3 Terms and definitions

For the purposes of this part of ISO 11357, the terms and definitions given in ISO 472, ISO 11357-1 and ISO 11357-3 and the following apply.

3.1
crystallization kinetics

description of the rate of crystallization of a material taking into account the effects of variables such as time, temperature, pressure, stress and molecular structure

NOTE These factors and also any additives, fillers or contaminants can modify the crystallinity of the polymer at the end of crystallization.

3.2
relative crystallinity

α

the ratio between the crystallinity at a particular point in time or a particular temperature and the crystallinity at the end of crystallization

NOTE 1 The relative crystallinity is given by the ratio of the partial enthalpy of crystallization, at each time or each temperature, and the total enthalpy of crystallization ΔH_c:

$$\alpha_{t\ \text{or}\ T} = \Delta H_{t\ \text{or}\ T} / \Delta H_\mathrm{c}$$

where

α_t and ΔH_t	are the relative crystallinity and the enthalpy of crystallization at a given time in the isothermal mode;
α_T and ΔH_T	are the relative crystallinity and the enthalpy of crystallization at a given temperature in the non-isothermal mode.

NOTE 2 In DSC, the relative crystallinity can be determined as the ratio between the partial area of the crystallization peak, at each time or each temperature, and the total area of the peak.

4 Principle

See ISO 11357-1:1997, clause 4.

5 Apparatus and materials

5.1 Differential scanning calorimeter

Use a differential scanning calorimeter meeting the following requirements:

a) capable of generating constant heating and cooling rates, preferably at least 40 °C/min;

b) capable of maintaining the test temperature constant to within ± 0,1 °C for at least 60 min;

c) to h) see ISO 11357-1:1997, subclause 5.1, items c) to h).

5.2 Crucibles

See ISO 11357-1:1997, subclause 5.2.

It may be necessary to verify that the metal of these crucibles does not modify the crystallization kinetics of the polymer.

5.3 Balance

See ISO 11357-1:1997, subclause 5.3.

5.4 Calibration materials

See ISO 11357-1:1997, annex A.

5.5 Purge gas

The gas used shall be a dry inert gas of analytical grade in order to avoid oxidation and hydrolytic degradation.

6 Test specimens

See ISO 11357-1:1997, clause 6.

7 Test conditions and specimen conditioning

See ISO 11357-1:1997, clause 7.

8 Calibration

See ISO 11357-1:1997, clause 8.

Temperature calibration shall be carried out in the heating mode only. The temperature correction terms in the isothermal or cooling mode are determined by linear extrapolation of values measured at different heating rates.

The linearity of the temperature scale in the heating and cooling modes shall be checked using materials which do not supercool. The use of the liquid-liquid transition of liquid crystals or the use of 4,4'-azoxyanisole is recommended.

9 Procedure

9.1 General

The study of the crystallization kinetics of polymers can be done in an isothermal or a non-isothermal mode.

9.2 Loading the test specimen into the pan

See ISO 11357-1:1997, subclause 9.2.

To avoid self-heating, the mass of the specimen shall be chosen based on the heat evolved by the crystallization of the material. If the object of the measurements is to compare various grades of a polymer, maintain the mass within ± 0,5 mg.

9.3 Insertion of the pans into the instrument

See ISO 11357-1:1997, subclause 9.3.

9.4 Melting of the polymer

In the two methods, isothermal and non-isothermal, the first step in the thermal cycle is the melting of the polymer.

The object of this step is to destroy all the crystalline elements of the sample that could modify the crystallization kinetics.

This is usually achieved by heating at a rate of 10 °C/min or 20 °C/min to a temperature about 30 °C above the extrapolated end melting temperature and holding it there for 3 min to 5 min.

Preliminary trials can be done to optimize these conditions and to prevent this step from changing the molecular structure of the polymer.

9.5 Isothermal crystallization

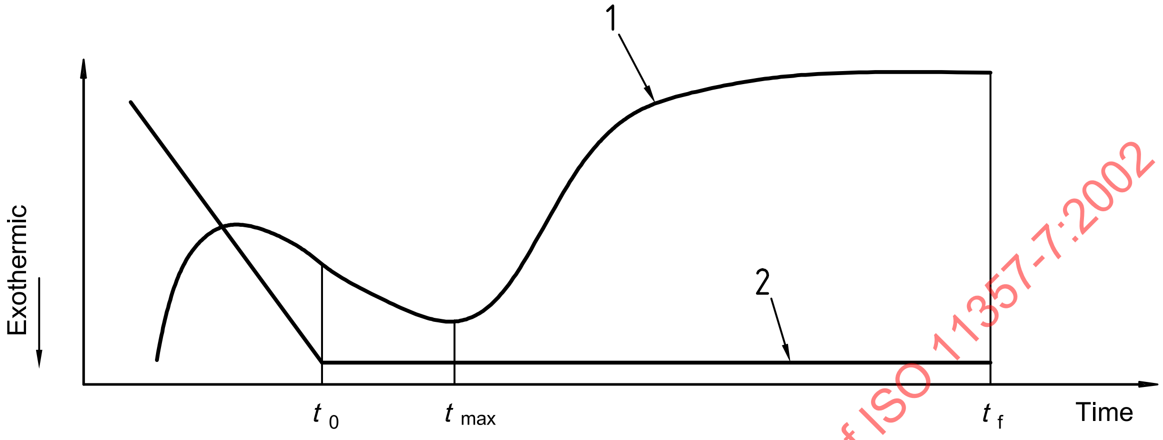
At the end of the melting stage, cool the specimen as quickly as possible to the selected temperature.

The time t_0 at which crystallization starts is the start of the isothermal step.

The time t_f at which the isothermal step ends, i.e. the time to obtain a complete crystallization curve, depends on the crystallization rate. It is usually at least five times the time taken to reach the maximum crystallization rate t_max.

Carry out at least three runs at different temperatures.

The isothermal temperatures are limited by the specifications of the instrument, and data shall be rejected when the crystallization starts during cooling (see Figure 1).

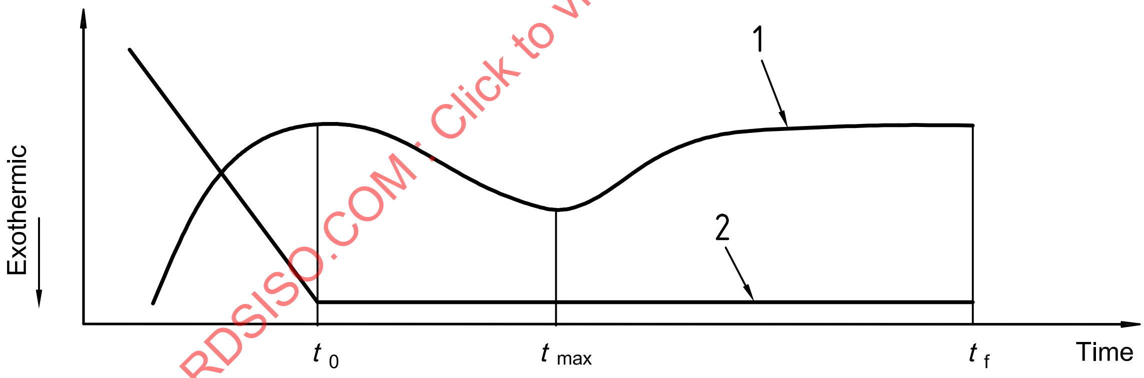


Key

1 DSC signal

2 Temperature plot

Figure 1 — Bad isothermal run



Key

1 DSC signal

2 Temperature plot

Figure 2 — Good isothermal run

9.6 Non-isothermal crystallization

At the end of the melting stage, cool the specimen at the selected constant cooling rate to at least 10 °C to 20 °C below the final crystallization temperature.

Carry out at least three runs at different cooling rates.

NOTE It is recommended that the cooling rates used are close to the highest rate at which the instrument is able to maintain the rate linear over the whole cooling-temperature range.

10 Expression of results

10.1 General

See also ISO 11357-3, clause 10.

10.2 Isothermal crystallization

For each run at a specific isothermal temperature, determine the variation in α as a function of time (α_t) and record the following values (see Figures 3 and 4):

— the time to reach the maximum crystallization rate (measured to the top of the crystallization peak)	t_{max}
— the relative crystallinity at t_{max}	$\alpha_{t_{\text{max}}}$
— the time to reach a relative crystallinity of 0,5	$t_{0,5}$
— the enthalpy of crystallization	ΔH_{c}
— the initial and the final crystallization times	t_{ic} and t_{fc}
— the time to the end of the isothermal	t_{f}

NOTE The initial crystallization time is the point at which the exothermic peak begins to deviate from the baseline and the final crystallization time is the point at which the exothermic peak returns to the baseline (see ISO 11357-3).

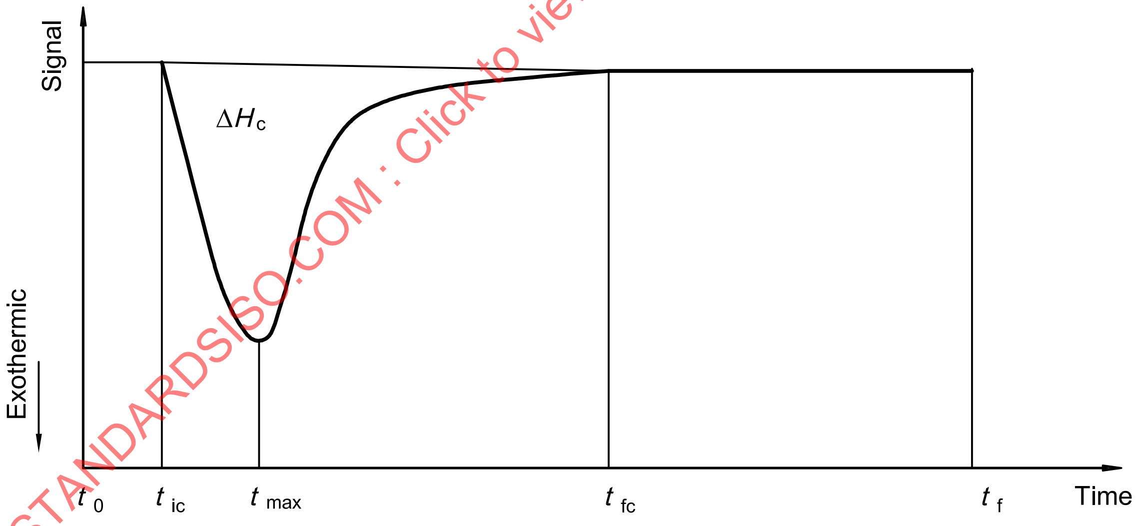


Figure 3 — DSC signal during the isothermal step

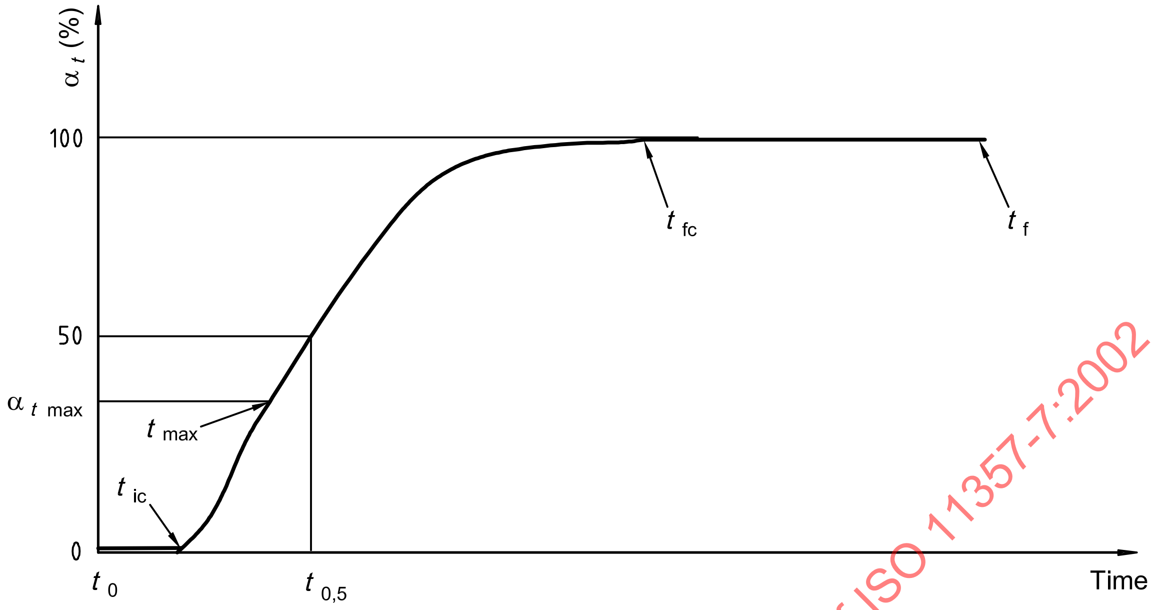


Figure 4 — Variations in α_t during the isothermal step

10.3 Non-isothermal crystallization

For each run, specify the cooling rate, determine the variation in α as a function of the temperature (α_{T}) and record at least during the cooling step the following values (see Figures 5 and 6):

— the peak crystallization temperature	T_{pc}
— the relative crystallinity at T_{pc}	$\alpha_{T_{\text{pc}}}$
— the enthalpy of crystallization	ΔH_{c}
— the initial and the final crystallization temperatures	T_{ic} and T_{fc}

NOTE The initial and the final crystallization temperatures are the points at which the exothermic peak begins to deviate from and returns to the in theory straight baseline (see ISO 11357-3).

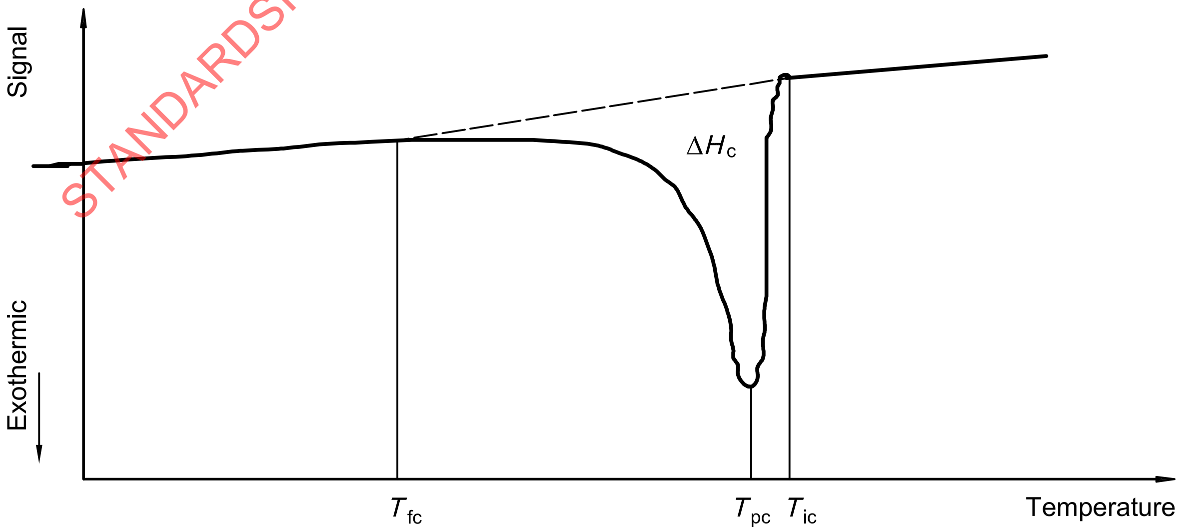


Figure 5 — DSC signal during the cooling step

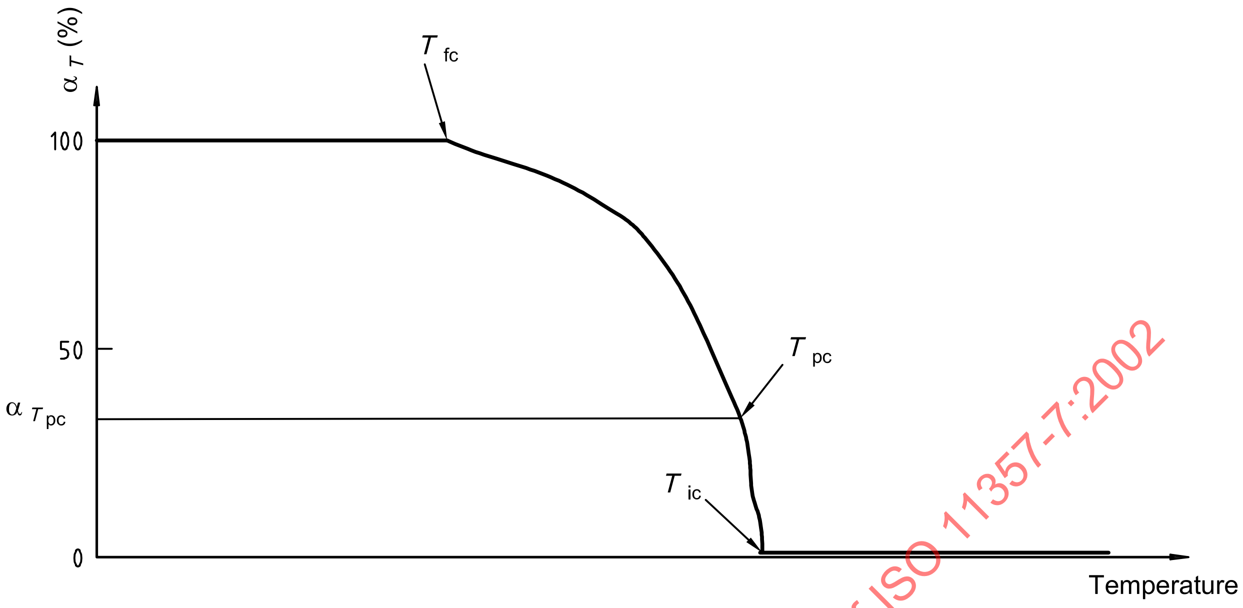


Figure 6 — Variation in α_T during the cooling step

10.4 Crystallization kinetics

The values calculated in 10.2 and 10.3 can be used to compare different polymers.

The study of the crystallization kinetics of polymers is still evolving and there are many models to describe the kinetics. The literature has to be used for the actual determination of the kinetics (see annex A).

11 Precision

The precision of this method is not known because inter-laboratory data are not available.

12 Test report

See ISO 11357-1:1997, clause 10.

Include as test results the values calculated in clause 10 of this part of ISO 11357:

- the times, in minutes, to three significant figures;
- the temperatures, in °C, to two significant figures;
- the cooling rates, in °C/min, to two significant figures;
- the relative crystallinities, in %, rounded to the nearest whole number;
- the enthalpy of crystallization, in kJ/kg or J/g, to two significant figures.

If the kinetics parameters have been determined, specify the model used with the constants and the calculated values. Where the experimental curves can be compared to curves calculated using the model, it is recommended that the curves be attached to the test report.

Annex A
(informative)

Equations for crystallization kinetics of polymers

A.1 Isothermal crystallization

A.1.1 Avrami equation

$$x_t = x_\infty \times \left[1 - \mathrm{exp}\left(kt^n\right)\right]$$

where

x_t is the crystallinity of the polymer at time t;

x_∞ is the crystallinity of the polymer at the end of crystallization;

k is the rate constant at the isothermal temperature T;

n is the Avrami exponent.

A.1.2 Sestak Berggren equation

$$\mathrm{d}\alpha/\mathrm{d}t = Z\alpha^m \left(1 - \alpha\right)^n \mathrm{exp}\left(E/\mathrm{R}T\right)$$

where

n, m are reaction orders;

E is the activation energy;

R is the gas constant;

T is the absolute temperature;

Z is the pre-exponential factor;

α is the relative crystallinity.

A.2 Non-isothermal crystallisation

A.2.1 Ozawa equation

$$\alpha\left(T\right) = 1 - \mathrm{exp}\left[-K_0\left(T\right)\frac{1}{C^m}\right]$$