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Plastics — Differential scanning calorimetry (DSC) —

Part 7: Determination of crystallization kinetics

iTeh STANDARD PREVIEW
*Plastiques — Analyse calorimétrique différentielle (DSC) —
Partie 7: Détermination de la cinétique de cristallisation*
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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.

The procedures used to develop this document and those intended for its further maintenance are described in the ISO/IEC Directives, Part 1. In particular, the different approval criteria needed for the different types of ISO documents should be noted. This document was drafted in accordance with the editorial rules of the ISO/IEC Directives, Part 2 (see www.iso.org/directives).

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For an explanation of the voluntary nature of ISO/TC 61, *Plastics*, Subcommittee SC 5, *Physical-chemical properties* standards, the meaning of ISO specific terms and expressions related to conformity assessment, as well as information about ISO's adherence to the World Trade Organization (WTO) principles in the Technical Barriers to Trade (TBT), see www.iso.org/iso/foreword.html.

This document was prepared by Technical Committee ISO/TC 61, *Plastics*, Subcommittee SC 5, *Physical-chemical properties*, in collaboration with the European Committee for Standardization (CEN) Technical Committee CEN/TC 249, *Plastics*, in accordance with the Agreement on technical cooperation between ISO and CEN (Vienna Agreement).

This third edition cancels and replaces the second edition (ISO 11357-7:2015), which has been technically revised.

The main changes compared to the previous edition are as follows:

- an indication of suitable substances for checking the symmetry of the temperature scale has been added;
- the procedure of determination of the start temperature of isothermal crystallisation has been corrected;
- an approach for the dependence of the rate constant of the Nakamura equation on temperature has been added.

A list of all parts in the ISO 11357 series can be found on the ISO website.

Any feedback or questions on this document should be directed to the user's national standards body. A complete listing of these bodies can be found at www.iso.org/members.html.

Plastics — Differential scanning calorimetry (DSC) —

Part 7: Determination of crystallization kinetics

1 Scope

This document specifies two methods (isothermal and non-isothermal) for studying the crystallisation kinetics of partially crystalline polymers using differential scanning calorimetry (DSC).

It is only applicable to molten polymers.

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

2 Normative references

The following documents are referred to in the text in such a way that some or all of their content constitutes requirements of this document. For dated references, only the edition cited applies. For undated references, the latest edition of the referenced document (including any amendments) applies.

ISO 472, *Plastics — Vocabulary*

ISO 11357-1, *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 document, the terms and definitions given in ISO 472, ISO 11357-1, ISO 11357-3, and the following apply.

ISO and IEC maintain terminological databases for use in standardization at the following addresses:

- ISO Online browsing platform: available at <https://www.iso.org/obp>
- IEC Electropedia: available at <https://www.electropedia.org/>

3.1 crystallisation kinetics

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

Note 1 to entry: These factors and also any additives, fillers, or contaminants can modify the crystallinity of the polymer at the end of crystallisation.

3.2 relative crystallinity

α

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

Note 1 to entry: The relative crystallinity can be expressed either as a ratio or as a percentage if multiplied by 100.

Note 2 to entry: In DSC, the relative crystallinity can be determined as the ratio between the partial area of the crystallisation peak, at each time or each temperature, and the total area of the peak.

4 Principle

The principle is as specified in ISO 11357-1.

5 Apparatus and materials

5.1 Differential scanning calorimeter, according to ISO 11357-1.

5.2 Crucibles, according to ISO 11357-1.

It can be necessary to verify that the material used for the crucibles does not modify the crystallisation kinetics of the polymer.

5.3 Balance, according to ISO 11357-1.

5.4 Heating mode calibration materials, according to ISO 11357-1.

5.5 Substances for checking the symmetry of the temperature scale

Suitable substances shall be selected showing low and defined undercooling^{[1],[2]}.

5.6 Purge gas, according to ISO 11357-1.

6 Test specimens

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Test specimens shall be as specified in ISO 11357-1.

7 Test conditions and specimen conditioning

Test conditions and specimen conditioning shall be as specified in ISO 11357-1.

8 Calibration

8.1 Calibration in heating mode

The calibration shall be done in accordance with ISO 11357-1.

8.2 Symmetry of temperature scale

The symmetry of the temperature scale in the heating and cooling modes shall be checked using materials specified in [5.5](#).

9 Procedure

9.1 General

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

The relative crystallinity is given by the ratio of the partial enthalpy of crystallisation, at each time or each temperature, and the total enthalpy of crystallisation ΔH_c , as given in [Formula \(1\)](#):

$$\alpha_{t \text{ or } T} = \Delta H_{t \text{ or } T} / \Delta H_c \quad (1)$$

where

$\alpha_{t \text{ or } T}$ is the relative crystallinity at a given time, t , in the isothermal mode or at a given temperature, T , in the non-isothermal mode;

$\Delta H_{t \text{ or } T}$ is the enthalpy of crystallisation at a given time, t , in the isothermal mode or at a given temperature, T , in the non-isothermal mode;

ΔH_c is the total enthalpy measured at the end of crystallisation.

9.2 Loading the test specimen into the crucible

The loading of the test specimen shall be done as specified in ISO 11357-1.

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

9.3 Insertion of the crucibles into the instrument

The crucibles shall be inserted into the instrument as specified in ISO 11357-1.

9.4 Melting of the polymer

Prior to isothermal or non-isothermal crystallisation, all crystalline elements in the sample that can modify the crystallisation kinetics shall be molten completely.

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

NOTE 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 crystallisation

At the end of the melting stage, cool the specimen as quickly as possible to the selected temperature at which isothermal crystallisation shall be measured.

A schematic representation of an isothermal crystallisation run is shown in [Figure 2](#).

The time, t_0 , at which the selected temperature is reached, is the start of the isothermal step.

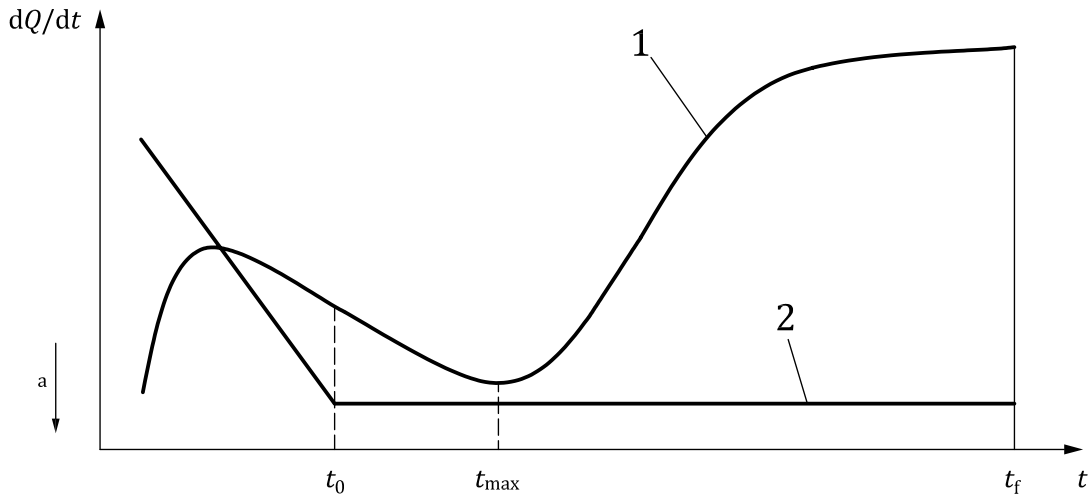
The isothermal crystallisation starts at the initial crystallisation time, t_i , which is obtained by the first deviation of the DSC curve from the extrapolated baseline obtained by interpolation between peak start and end.

The time t_f at which the isothermal step ends (i.e. the time to obtain a complete crystallisation curve) depends on the crystallisation rate. If not clear from the DSC curve, it shall be set to five times the time taken to reach the maximum crystallisation 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 crystallisation starts during cooling (see [Figure 1](#)).

NOTE Limiting instrument factors can be, for example, too high thermal lag or insufficient cooling capabilities.

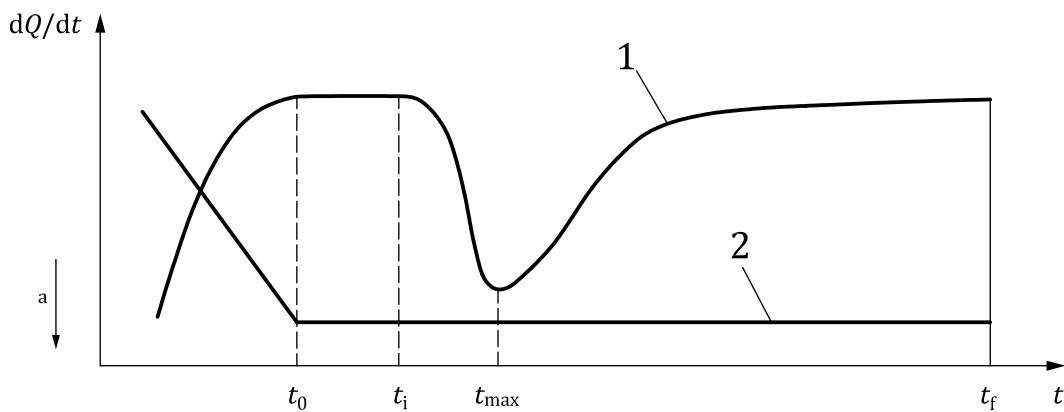


- Key**
- 1 DSC signal
 - 2 temperature plot
 - dQ/dt heat flow rate
 - t time
 - a Exothermic direction.

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Figure 1 — Bad isothermal run — Crystallisation started before isothermal temperature reached



- Key**
- 1 DSC signal
 - 2 temperature plot
 - dQ/dt heat flow rate
 - t time
 - a Exothermic direction.

Figure 2 — Good isothermal run — Crystallisation started after isothermal temperature is reached

9.6 Non-isothermal crystallisation

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

Carry out at least three runs at different cooling rates.

The cooling rates used shall not exceed 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.

NOTE The values calculated in [10.2.1](#) and [10.2.2](#) can be used to compare different polymers.

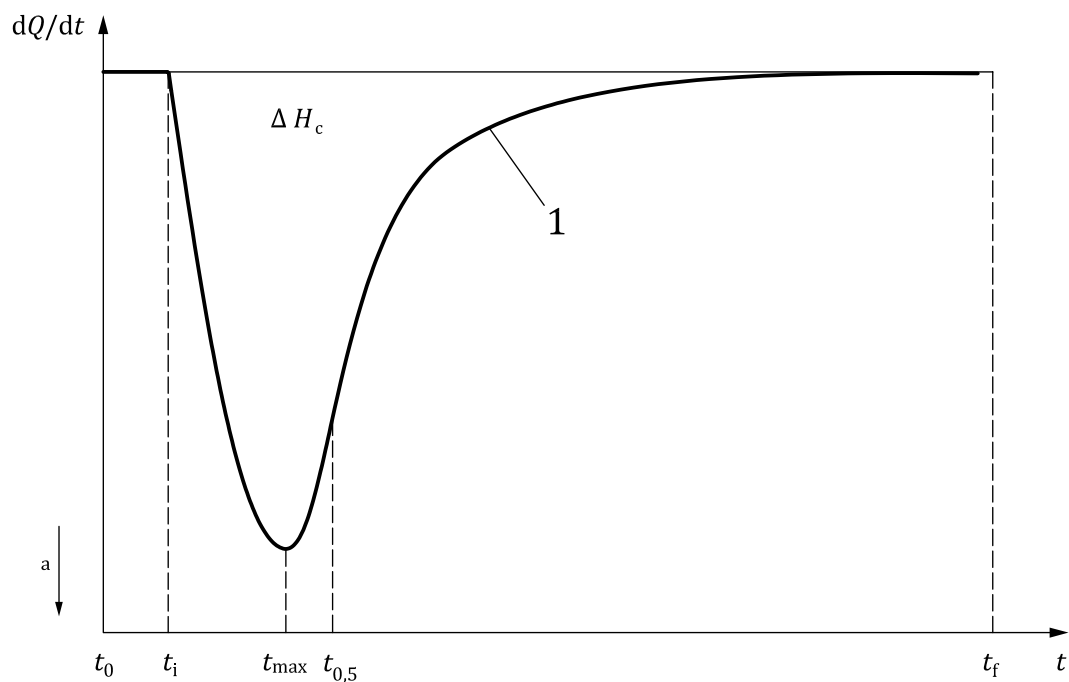
The study of the crystallisation kinetics of polymers is still evolving and there are many models to describe the kinetics. The literature shall be used for the actual determination of the kinetics (see [Annex A](#)).

10.2 Methods of determination of crystallisation kinetics

10.2.1 Isothermal crystallisation

For each run at a specific isothermal temperature, determine the variation in α as a function of time (α_t) using [Formula \(1\)](#) and record the following values (see [Figure 3](#) and [Figure 4](#)):

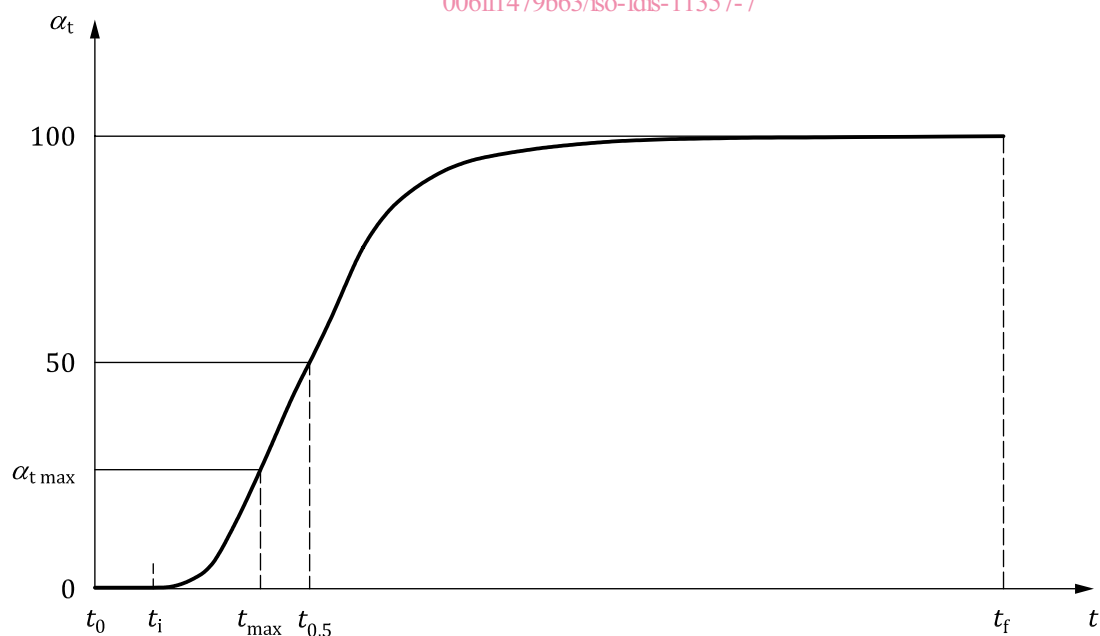
- starting time of the isothermal step ($t = 0$), t_0 ;
- initial crystallisation time, t_i ;
- time to reach the maximum crystallisation rate, t_{\max}
(measured to the top of the crystallisation peak);
- relative crystallinity at t_{\max} , $a_{t_{\max}}$;
- time to reach a relative crystallinity of 0,5, $t_{0,5}$;
- enthalpy of crystallisation, ΔH_c ;
- time to the end of crystallisation, t_f .



Key
 1 DSC signal
 dQ/dt heat flow rate
 t time
 a Exothermic direction.

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Figure 3 — DSC signal during the isothermal step
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Key
 α degree of crystallisation
 t time

Figure 4 — Variation in α_t during the isothermal step