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Plastics — Differential scanning calorimetry (DSC) —

Part 7: Determination of crystallization kinetics

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Foreword

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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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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 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 crystallization 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 crystallization 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 terminology 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
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 1 to entry: 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
ratio between the crystallinity at a particular point in time or a particular temperature and the crystallinity at the end of crystallization

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 crystallization 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 crystallization 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

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 crystallization 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 crystallization, at each time or each temperature, and the total enthalpy of crystallization 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 crystallization 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 crystallization.

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 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 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 crystallization, all crystalline elements in the sample that can modify the crystallization 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 crystallization

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

A schematic representation of an isothermal crystallization run is shown in Figure 2.

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

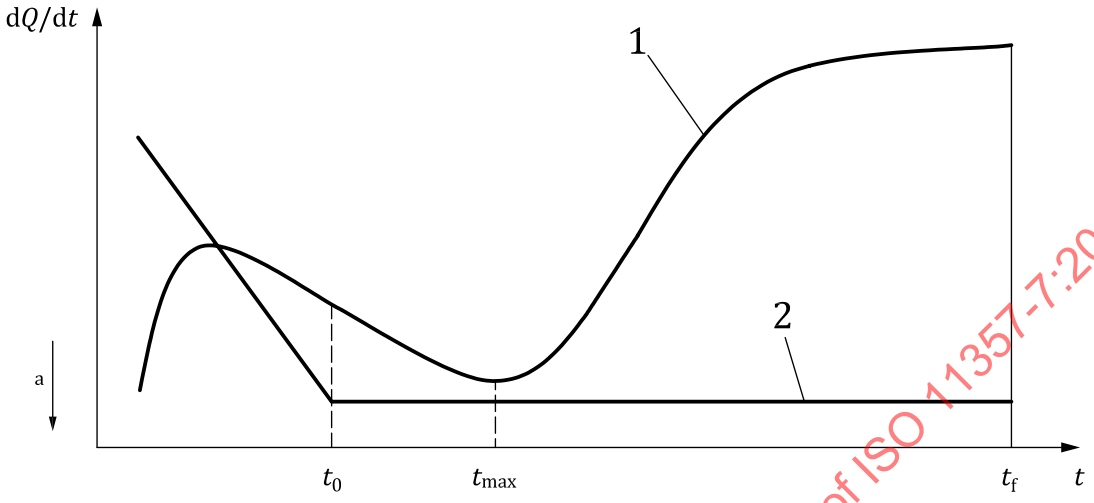
The isothermal crystallization starts at the initial crystallization time, t_i, which is obtained by the first deviation of the DSC curve from the extrapolated baseline obtained by interpolation between peak start and end.

The time t_f at which the isothermal step ends (i.e. the time to obtain a complete crystallization curve) depends on the crystallization rate. If not clear from the DSC curve, it shall be set to 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).

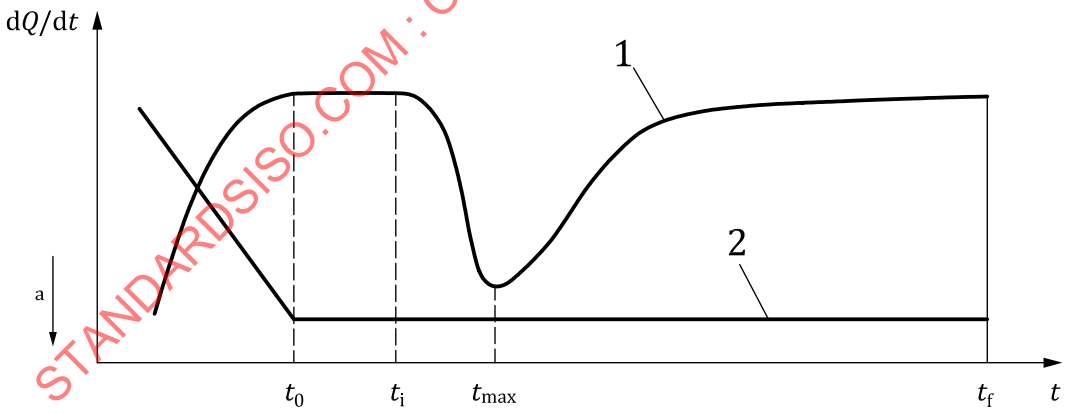
NOTE Limiting instrument factors can be, for example, too high thermal lag or insufficient cooling capabilities.



Key

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

Figure 1 — Bad isothermal run — Crystallization 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 — Crystallization started after isothermal temperature is reached

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 K to 20 K below the final crystallization 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 crystallization 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 crystallization kinetics

10.2.1 Isothermal crystallization

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 crystallization time, t_i;

— time to reach the maximum crystallization rate, t_{max}

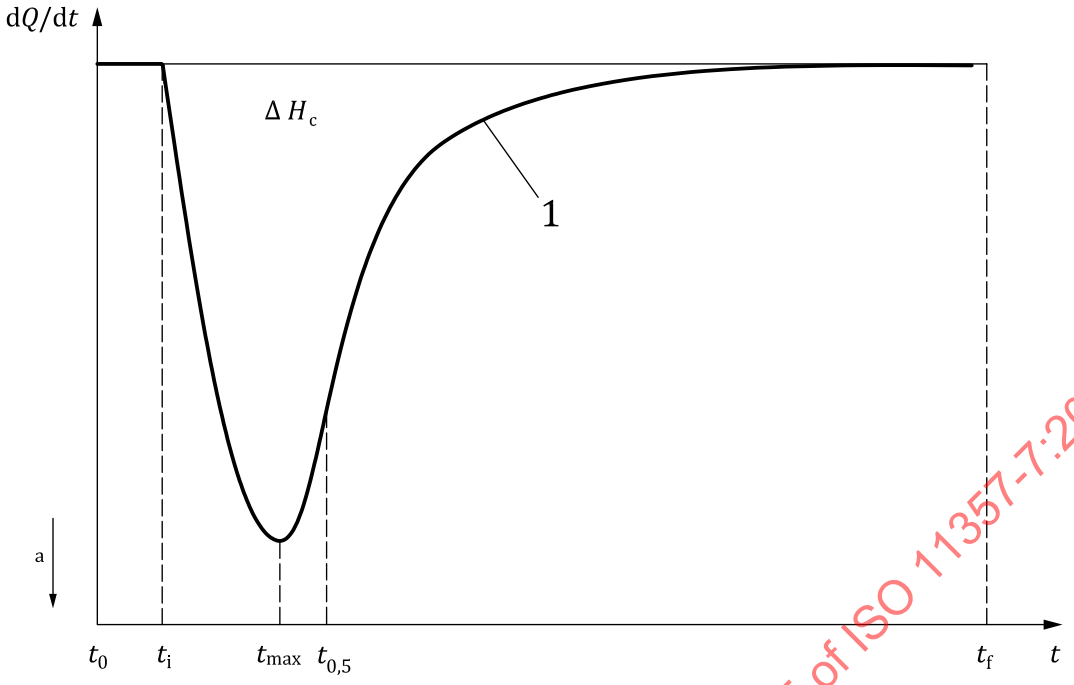
(measured to the top of the crystallization peak);

— relative crystallinity at t_{max}, $a_{t\,max}$;

— time to reach a relative crystallinity of 0,5, $t_{0,5}$;

— enthalpy of crystallization, ΔH_c;

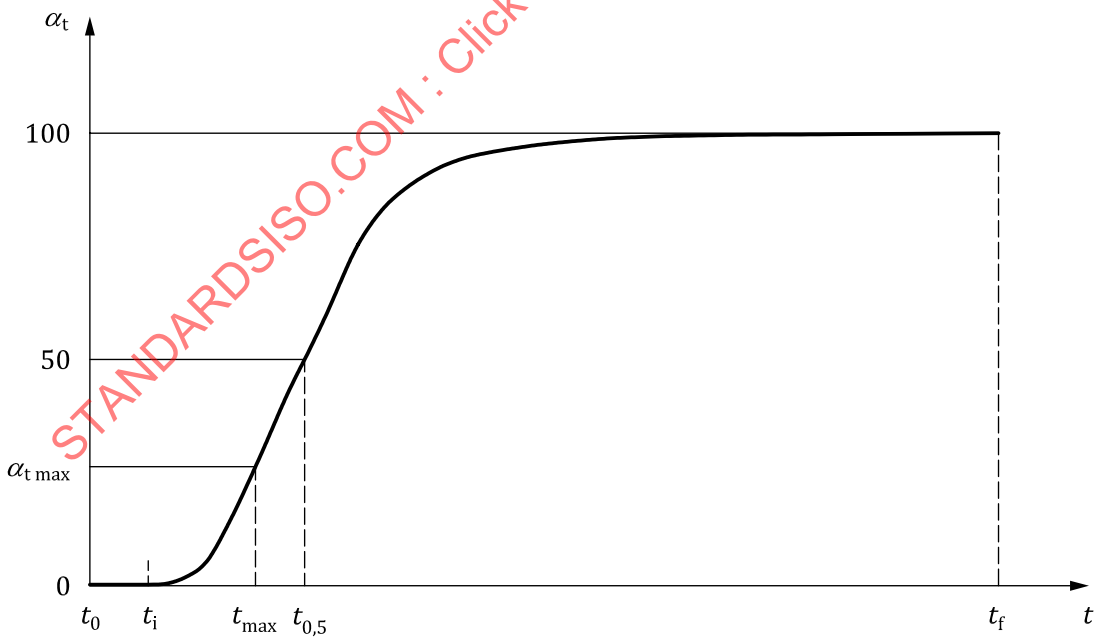
— time to the end of crystallization, t_f.



Key

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

Figure 3 — DSC signal during the isothermal step



Key

α	degree of crystallization
t	time

Figure 4 — Variation in α_t during the isothermal step

10.2.2 Non-isothermal crystallization

For each run, specify the cooling rate, determine the variation in α as a function of temperature (α_T) using Formula (1) and record at least the following values (see Figure 5 and Figure 6) during the cooling step:

— initial crystallization temperature, T_i;

— peak crystallization temperature, T_{pc};

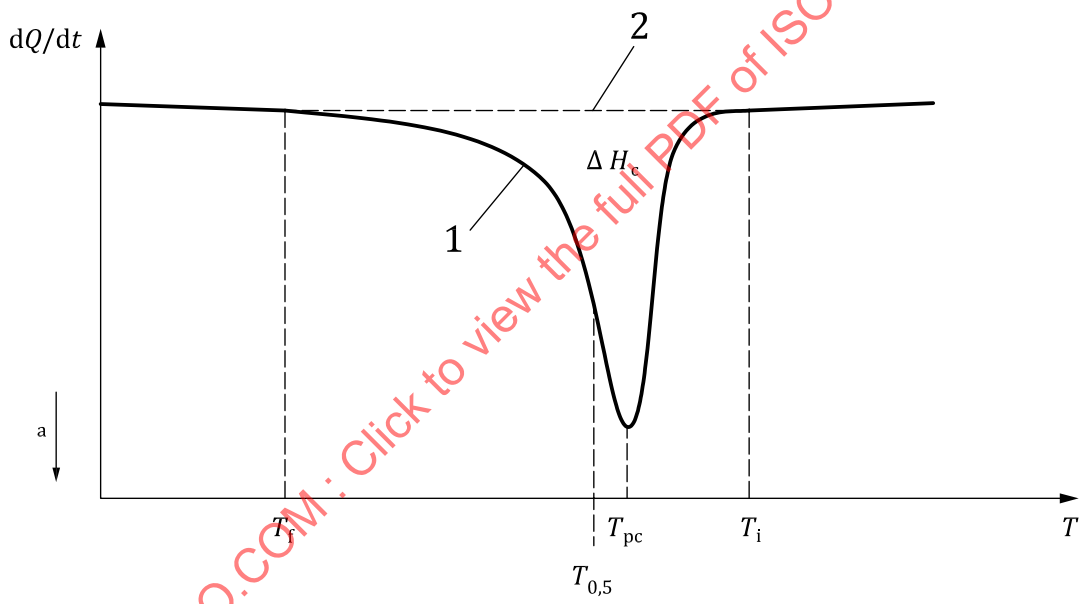
— temperature to reach a relative crystallinity of 0,5, $T_{0,5}$;

— relative crystallinity at T_{pc}, α_{Tpc};

— enthalpy of crystallization, ΔH_c;

— final crystallization temperatures, T_f.

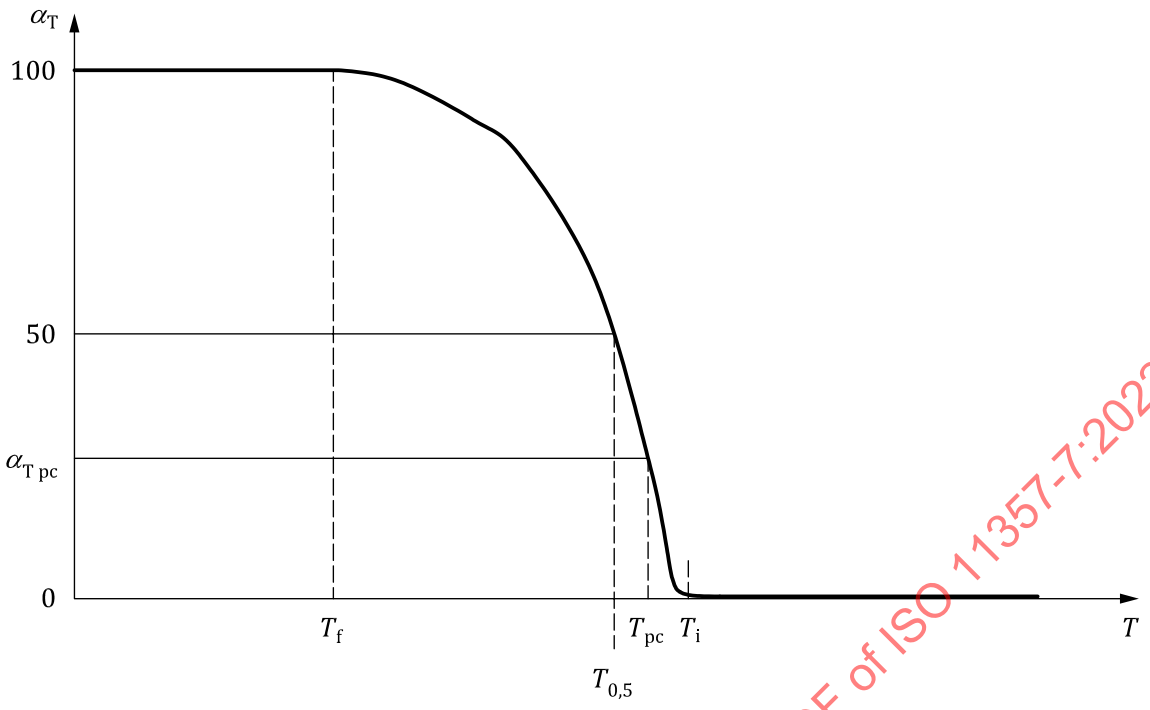
NOTE The initial and the final crystallization temperatures are the points at which the exothermic peak begins to deviate from and returns to the extrapolated straight baseline (see ISO 11357-3).



Key

1 DSC signal
2 baseline
dQ/dt heat flow rate
T temperature
a Exothermic direction.

Figure 5 — DSC signal during the cooling step



Key

α degree of crystallization

T temperature

Figure 6 — Variation in α_T during the cooling step

11 Precision

The precision of this method is not known because interlaboratory data are not available at the time of publication.

12 Test report

The test report shall be as specified in ISO 11357-1. Additionally, the following values calculated in Clause 10 shall be included as test results:

— times, in minutes, to one decimal place;

— temperatures, in °C, to one decimal place;

— cooling rates, in K/min, to two significant figures;

— relative crystallinities, in %, rounded to the nearest whole number;

— 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, the curves should be attached to the test.

Annex A
(informative)

Formulae for crystallization kinetics of polymers

A.1 Isothermal crystallization

A.1.1 Avrami formula

$$\alpha_t = \alpha_f \cdot \left[1 - exp\left(-k \cdot t^n\right)\right] \tag{A.1}$$

where

α_t is the crystallinity of the polymer at time t;

α_f is the crystallinity of the polymer at the end of crystallization;

k is the rate constant at the isothermal temperature T;

t is the time;

n is the Avrami exponent.

A.1.2 Sestak Berggren formula

$$\mathrm{d}\alpha / \mathrm{d}t = Z \cdot \alpha^m \cdot (1-\alpha)^n \cdot \exp[-E/(RT)] \tag{A.2}$$

where

α is the relative crystallinity;

t is the time;

Z is the pre-exponential factor;

m, n are reaction orders;

E is the activation energy;

R is the gas constant;

T is the absolute temperature.

A.2 Non-isothermal crystallization

A.2.1 Ozawa formula

$$\alpha(T) = 1 - \exp\left[-K_0(T) \cdot \frac{1}{C^m}\right] \tag{A.3}$$

where

$\alpha(T)$ is the relative crystallinity at temperature T;

C is the cooling rate $(-\mathrm{d}T/\mathrm{d}t)$;

$K_0(T)$ is the function describing the cooling process;

m is the Ozawa exponent.

A.2.2 Nakamura formula

$$\alpha(T)=1-\exp\{-[\frac{1}{C}\cdot\int_{T(0)}^{T(t)}(k(T))^{1/n}\cdot\mathrm{d}T]^n\} \quad \text{(A.4)}$$

where

$\alpha(T)$ is the relative crystallinity at temperature T;

C is the cooling rate $(-\mathrm{d}T/\mathrm{d}t)$;

$k(T)$ is the rate constant at temperature T;

n is the Avrami exponent.

For the dependence of the rate constant on temperature, $k(T)$, the Formula (A.5) can be derived based on the Hoffman-Lauritzen growth theory[3],[4]:

$$k(T)=A\cdot\exp\left(\frac{-U}{R\cdot(T-T_\infty)}\right)\cdot\exp\left(\frac{-K_\mathrm{G}}{T\cdot\Delta T\cdot f}\right) \quad \text{(A.5)}$$

where

A is the pre-exponential factor;

U is the activation energy of segmental jumps in polymers, this parameter has an universal value of 6,3 kJ/mol;

T_∞ is the temperature at which the crystallization transport is finished, this temperature is 30 K below the glass transition temperature T_g, i.e. $T_\infty = T_\mathrm{g} - 30\,K$;

K_G is the kinetic parameter for nucleation;

ΔT is the undercooling under the equilibrium melting point T_m, i.e. $\Delta T = T_m - T$;

f is the correction factor $f = 2\cdot T/(T_m + T)$.