Pure Appl. Chem., Vol. 85, No. 5, pp. 1017–1046, 2013. http://dx.doi.org/10.1351/PAC-REC-12-03-02 © 2013 IUPAC, Publication date (Web): 27 March 2013

Glossary of terms relating to thermal and thermomechanical properties of polymers (IUPAC Recommendations 2013)*

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Abstract: The document gives definitions of terms met in the conventional thermal and thermomechanical characterisation of polymeric materials.

Keywords: definition of terms; IUPAC Polymer Division; polymeric materials; thermal properties; thermomechanical properties.

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1. INTRODUCTION

This document gives definitions of terms related to the thermal and thermomechanical properties of polymers prior to thermal decomposition. The terms are arranged in alphabetical order and cover definitions of relevant terms from physical chemistry, polymer science, and experimental techniques. The document considers to some extent earlier reports related to the terminology of thermal analysis, for example, those published by the International Confederation for Thermal Analysis and Calorimetry

^{*}Sponsoring body: IUPAC Polymer Division: see more details on p. 1045.

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(ICTAC) [1–4], IUPAC Recommendations covered by the *Compendium of Chemical Terminology* [5], the so-called "Gold Book", and the 2nd edition of the *Compendium of Polymer Nomenclature and Terminology* [6], the so-called "Purple Book". These publications were followed as far as possible. Other publications consulted include ISO and ASTM Standards [7–12]. In addition, the recently (2011) published document "Definition of terms relating to crystalline polymers" [13], a revision of a superseded IUPAC recommendation published under the same title in 1989, has necessitated modifications of some older definitions. Thermal analysis is an extensive subject in its own right, and the reader is referred to specialised textbooks for further information, for example, refs. [14–22].

The terms defined in this document and acceptable synonyms are printed in boldface. Terms that are printed in italics are defined elsewhere in this document.

2. GLOSSARY OF TERMS

alpha loss peak

See alpha relaxation peak.

alpha relaxation α-relaxation

Highest-temperature or lowest-frequency relaxation in the loss curve of a polymer.

- *Note 1*: The α -relaxation is commonly related to cooperative conformational changes in macromolecules. These changes typically involve 10–20 main-chain atoms. For a polymer in a *glassy state*, the α -relaxation is characteristic of the *glass transition*.
- *Note 2*: For some *partially crystalline polymers*, for example, polyethylene or polyoxymethylene, the α -relaxation originates from motions within the crystalline regions (the so-called "crystalline relaxation"). In such cases, the β -relaxation usually corresponds to the glass transition.

alpha relaxation peak α-relaxation peak alpha loss peak α-loss peak

Highest-temperature peak or lowest-frequency peak in the loss curve of a polymer.

Note: Secondary relaxation peaks occurring successively at lower temperatures or higher frequencies are termed the beta (β -), gamma (γ -), relaxation or loss peaks.

amorphous polymer

Polymer in the amorphous state [13].

amorphous state

State of matter characterised by the absence of long-range molecular order [13].

- Note 1: Some degree of local order about 1 nm in length may exist in the amorphous state.
- *Note 2*: In the absence of stress, the structure and properties of the amorphous state are generally isotropic at a large-enough scale, as in liquids.

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annealing (in polymer science)

Thermal treatment of a solid polymer material at a fixed or changing temperature, leading to desired changes in its physical structure and properties, without involving complete *melting* or dissolution [13].

- *Note 1*: Annealing of a crystalline polymer is usually carried out by keeping the polymer at temperatures close to but below its melting point.
- *Note 2*: Results comparable to annealing may, in some instances, be attained by exposure of a crystalline polymer to a poor solvent, or to its vapours.
- *Note 3*: In a crystalline polymer, the process of annealing leads to reorganisation, including possibly increased order in existing polymer crystallites, increase of the degree of crystallinity and in the fold period, and can cause changes to more stable crystal polymorphs.
- *Note 4*: In an amorphous polymer, annealing at temperatures lower than the *glass-transition* temperature (T_g) leads to so-called physical aging processes or sub- T_g annealing, which are associated with enthalpy, entropy, and volume changes.

α-loss peak

See alpha relaxation peak.

α -relaxation

See alpha relaxation.

α-relaxation peak

See alpha relaxation peak.

beta loss peak

See beta relaxation peak.

beta relaxation β-relaxation

Second-highest-temperature or second-lowest-frequency relaxation in the loss curve of a polymer.

- Note 1: For an *amorphous polymer*, the β -relaxation is generally related to localised motions involving only a few atoms of a polymer chain or is due to side-group motion.
- *Note 2:* In some *partially crystalline polymers*, the β -relaxation corresponds to the *glass-transition temperature* (see *Note 2* of definition *alpha relaxation*).

beta relaxation peak β-relaxation peak beta loss peak β-loss peak

Second-highest-temperature or second-lowest-frequency peak in the loss curve of a polymer.

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β-loss peak

See beta relaxation peak.

β-relaxation

See beta relaxation.

β-relaxation peak

See beta relaxation peak.

characteristic temperatures

Temperatures obtained from a *differential scanning calorimeter (DSC)* experiment or a *differential thermal analysis (DTA)* experiment that characterise the physical processes occurring.

Note 1: The physical processes frequently studied in polymer science are *crystallisation*, *melting*, and the *glass transition*. See Figs. 1–3, which illustrate the corresponding characteristic temperatures [7]. The ordinate used in the figures is specific heat capacity $c_p/J\cdot K^{-1}\cdot g^{-1}$. When using DSC, the quantity measured is the specific heat flow rate/W·g⁻¹, and when using DTA, the quantity measured is the temperature difference between sample and reference. Both quantities can be converted to c_p by calibration.



Fig. 1 Characteristic temperatures found from a *DSC* or *DTA* cooling experiment involving *crystallisation*. In a heating experiment, the subscripts for "initial" and "final" are interchanged. *Cold crystallisation* can sometimes be observed in a heating experiment.

 $T_{i,cr}$ = initial (onset) crystallisation temperature (at which crystallisation starts).

 $T_{\rm ei,cr}$ = extrapolated initial (onset) crystallisation temperature.

 $T_{p,cr}$ = peak crystallisation temperature (at which the maximum rate of crystallisation occurs).

 $T_{\rm ef,cr}^{\rm p,cc}$ = extrapolated final (end) crystallisation temperature.

 $T_{\rm f,cr}$ = final (end) crystallisation temperature (at which crystallisation stops).

 $\Delta_{cr}h$ = specific enthalpy of crystallisation, unit: J·g⁻¹.

 c_p = specific heat capacity, unit: J·K⁻¹·g⁻¹.

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Fig. 2 Characteristic temperatures found from a DSC or DTA heating experiment involving melting (fusion).

 $T_{i,m}$ = initial (onset) *melting temperature* (at which melting starts).

 $T_{ei,m}^{,m}$ = extrapolated initial (onset) melting temperature. $T_{p,m}$ = peak melting temperature (at which the maximum rate of melting occurs). $T_{ef,m}$ = extrapolated final (end) melting temperature. $T_{ef,m}$ = final (end) melting temperature.

 $T_{\rm f,m}$ = final (end) melting temperature (at which melting stops).

 $\Delta_{cr}h$ = specific enthalpy of fusion, unit: J·g⁻¹.

 c_n = specific heat capacity, unit: J·K⁻¹·g⁻¹.



Fig. 3 Characteristic temperatures found from a DSC or DTA experiment involving a glass transition. The experiment is often carried out by cooling the *polymer melt* rather than heating the *polymer glass* because of the small variation of the transition temperature with the cooling rate in contrast to the more complex situation in a heating experiment; see enthalpy relaxation.

 $T_{i,g}$ = initial (onset) temperature of the glass transition. $T_{\rm ei,g}^{\rm N}$ = extrapolated initial (onset) temperature of the glass transition. $T_g =$ mid-point temperature, equated to the *glass-transition temperature*. $T_{ef,g} =$ extrapolated final (end) temperature of the glass transition. $T_{\rm f,g}$ = final (end) temperature of the glass transition. $c_p^{,\circ}$ = specific heat capacity, unit: J·K⁻¹·g⁻¹.

 Δc_n = change in specific heat capacity, unit: J·K⁻¹·g⁻¹.

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- *Note 2:* The glass transition is usually near the point of inflection of the function $c_n(T)$.
- *Note 3*: In a symmetrical curve, the point of inflection is at ½ of the height of the step of the curve (the mid-point temperature).
- *Note 4*: Alternative methods for evaluating the *glass-transition temperature*, T_g , from DSC or DTA curves exist, for example, evaluation of the temperature of equal specific enthalpy of the glass and the melt.

clearing point

See *clearing temperature*.

clearing temperature, T_{cl} clearing point

Temperature at which the transition between the mesophase with the highest temperature range and the isotropic phase occurs [6].

Note: The clearing temperature of a mesophase is a special case of the more general *isotropisation temperature*.

cold crystallisation

Polymer crystallisation brought about from a *glass*, from a liquid-crystalline state, or a state displaying a low degree of crystallinity at temperatures a little above the *glass-transition temperature* [13].

Note: Cold crystallisation is frequently observed if crystallisation was not completed before sample *vitrification*.

conformational enthalpy

Enthalpy change associated with conformational changes.

Note: In polymers, conformational changes can be associated with *conformational melting*.

conformational entropy

Entropy change associated with conformational changes.

Note: In polymers, conformational changes can be associated with *conformational melting*.

conformational melting

Step-like increase in the conformational entropy of macromolecules, or parts of macromolecules.

- *Note 1*: This melting can be caused by a temperature change or by interaction with a solvent.
- *Note 2*: A helix–coil transition is an example of conformational melting.
- *Note 3*: Conformational melting normally occurs along with crystalline melting in a *partially crystalline polymer*.

conformational transition

Transition between two conformational states.

- Note 1: Conformational melting is a type of conformational transition.
- *Note 2*: Conformational transitions are relevant in biopolymers, for example, nucleic acids and proteins or complex systems like lipid membranes, where a number of neighbouring local minima in the profile of the Gibbs energy are possible. A conformational transition can result in important biological action.

constant oscillation-amplitude method

Forced-resonance method to determine the viscoelastic properties of a material.

Note: Indirect measurement of the energy that has to be added to a material sample to compensate the damping of the oscillation by determination of the change of the resonance frequency of a material sample.

continuous phase transition

See second-order phase transition.

crystalline polymer partially crystalline polymer semicrystalline polymer

Polymer, a significant fraction of which is in the crystalline state [13].

- *Note 1*: Polymers hardly ever crystallise completely, and in virtually any crystalline polymer some amorphous material coexists with the crystalline phase or phases.
- *Note 2*: Crystal dimensions may be as small as about 2 nm in one or more crystallographic direction(s) and usually below 50 nm in at least one direction.
- *Note 3*: Often the term "crystalline polymer" is wrongly used for the term "*crystallisable polymers*".
- Note 4: The two-phase model is frequently used to describe crystalline polymers [13].

crystalline state

State of matter ideally characterised by three-dimensional, long-range order on an atomic scale [13].

Note: One- or two-dimensional order leads to a mesophase structure.

crystallisable polymer

Polymer that is able to partially crystallise.

crystallisation

Formation of a crystalline solid from a solution, melt, vapour, or a different solid phase.

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- *Note 1*: Crystallisation is achieved, for example, by lowering the temperature of a melt or by evaporating the solvent.
- Note 2: Modification of the definition in ref. [5].

damping curve loss curve

Decrease in the deformation amplitude of a material specimen plotted vs. time when the specimen is subjected to a *free oscillation* [6].

Note: See *torsion pendulum* and *logarithmic decrement*.

devitrification (in polymer science)

Formation of a polymer melt from a polymer glass.

Note: Devitrification is usually brought about by heating or exposure to a solvent as liquid or vapour.

dielectric thermal analysis, DETA

Determination of the temperature dependence, at constant frequency, of the complex dielectric constant of a sample, or of the real part or the imaginary part of the complex dielectric constant; or, the determination of the frequency dependence, at constant temperature, of the complex dielectric constant of a sample, or of the real part or the imaginary part of the complex dielectric constant.

- *Note 1:* The dielectric constant should strictly be referred to as the relative dielectric permittivity.
- *Note 2*: DETA can be used to characterise relaxation processes in a polymer material, and it complements *DMA*.

differential scanning calorimeter, DSC

Apparatus for conducting a *differential scanning calorimetry* (DSC) experiment.

Note: It is common to use the same abbreviation (DSC) for both differential scanning calorimetry and the apparatus.

differential scanning calorimetry, DSC

Technique that monitors the difference in heat flow-rate, or the difference in electrical energy fed into a sample and into a sample of a reference material as a function of temperature or time.

- *Note 1:* It is common to use the same abbreviation (DSC) for both the technique and a *differential scanning calorimeter*.
- *Note 2*: The two types of DSC, heat-flow DSC and power compensating DSC, produce more or less identical results.
- Note 3: Measurements are usually carried out at a constant heating or cooling rate.
- *Note 4*: A plot of heat flow-rate difference or electrical energy input versus time or temperature is called a DSC curve.

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- *Note 5*: DSC is used to determine and characterise thermally induced changes, such as *crystallisation*, *melting*, and the *glass transition*. See Figs. 1–3.
- *Note 6*: The corresponding enthalpy change and the heat capacity of the sample as functions of temperature can be calculated. See Figs. 1–3.

differential thermal analyser, DTA

Apparatus for conducting a differential thermal analysis experiment.

Note: It is common to use the same abbreviation (DTA) for both differential thermal analysis and the apparatus.

differential thermal analysis, DTA

Technique that monitors the temperature difference between the sample temperature, T_s , and the temperature of a reference material, T_r , at constant heating rate or cooling rate as a function of time or temperature.

- *Note 1:* It is common to use the same abbreviation (DTA) for both the technique and a *differential thermal analyser*.
- Note 2: Measurements are usually carried out at a constant heating or cooling rate.
- Note 3: A plot of the temperature difference vs. time or temperature is called a DTA curve.
- *Note 4*: DTA is used to determine and characterise thermally induced changes in materials such as *crystallisation*, *melting*, and the *glass transition*. See Figs. 1–3.
- *Note 5*: The corresponding enthalpy change and the heat capacity of the sample as functions of temperature can be calculated. See Figs. 1–3.

dilatometer

Apparatus for conducting a dilatometry experiment.

dilatometry

The measurement of changes with time in the volume, length, width, or thickness of a material sample caused by temperature changes under negligible load or by chemical reaction.

- *Note 1*: One-dimensional changes are often measured using mechanical displacement detection. Volume changes are often determined using an inert confining liquid, for example, mercury.
- *Note 2*: Measurement of an applied hydrostatic pressure allows the determination of pressure–volume–temperature (p,V,T) diagrams.
- *Note 3*: A polymerisation reaction is an example of a chemical reaction that can be studied using a *dilatometer*.
- *Note 4*: See *thermodilatometry*.

discontinuous phase transition

See first-order phase transition.

dynamic-load thermomechanical analysis, DLTMA

Thermomechanical analysis carried out using a sinusoidal stress.

dynamic mechanical analyser, DMA

Apparatus for conducting a dynamic mechanical analysis experiment.

Note: It is common to use the same abbreviation (DMA) for both dynamic mechanical analysis and the apparatus.

dynamic mechanical analysis, DMA

Technique that monitors the complex modulus of a material sample (usually as *storage modulus* and *loss modulus*) as a function of time, temperature, or frequency when the sample is subjected to a *forced* or *free sinusoidal oscillation* of stress or strain.

- *Note 1*: It is common to use the same abbreviation (DMA) for both the technique and a *dynamic mechanical analyser*.
- Note 2: Torsional braid analysis is a special type of dynamic mechanical analysis.

dynamic viscometer

Apparatus that uses a forced, non-resonance method to determine the viscoelastic properties of a material sample.

Note: A sinusoidal displacement is applied to one end of a strip-like sample, and the response of the material is measured at the opposite end, allowing the angle between the stress and the strain, the phase angle, δ [6], to be obtained directly.

enthalpy relaxation

Enthalpy change observed near the *glass transition* when a sample is heated at a rate different from that at which it was cooled down, or observed after *annealing* in the *glassy state* below the *glass-transition temperature*.

- *Note 1*: Enthalpy relaxation is caused by the transformation of a glassy material to a more stable glass.
- Note 2: Enthalpy relaxation can be described by the Kohlrausch-Williams-Watts equation.
- *Note 3*: Moduli, stress–strain behaviour, and molecular motions are affected by enthalpy relaxation.
- Note 4: Enthalpy relaxation reflects physical aging.

equilibrium melting temperature, T_m^0 , SI unit: K

Temperature at which perfect *polymer crystals* of infinite thickness melt under equilibrium conditions [13].

- *Note 1*: The equilibrium melting temperature can be determined, for example, from a *Hoffman–Weeks plot.*
- *Note 2*: The transition occurring at the equilibrium melting temperature is a *first-order phase transition*.
- Note 3: See melting temperature.

first-order phase transition discontinuous phase transition

Transition in which the molar Gibbs energy or molar Helmholtz energy of the two phases (or the chemical potentials of all components in the two phases) are equal at the transition point, but their first derivatives with respect to temperature and pressure (e.g., molar enthalpy and molar volume) are discontinuous at the transition point.

- Note 1: Modified from the definition in ref. [5].
- *Note 2*: At a first-order transition, two phases coexist and can be transformed into one another by a change in a field variable such as pressure, temperature, magnetic field, or electric field.
- Note 3: Crystallisation and melting, see Figs. 1 and 2, are first-order phase transitions.

forced oscillation

See forced sinusoidal oscillation.

forced sinusoidal oscillation forced oscillation sinusoidal oscillation

Deformation of a material by the application of a small sinusoidal strain (γ) such that

 $\gamma = \gamma_0 \cos \omega t$

where γ_0 and ω are positive constants [6].

- *Note 1:* γ may be in simple shear or uniaxial deformation.
- *Note 2:* γ_0 is the strain amplitude.
- *Note 3:* ω is the angular velocity of the circular motion equivalent to a sinusoidal frequency v with $\omega = 2\pi v$. The unit of ω is rad-s⁻¹.
- *Note 4*: For linear viscoelastic behaviour, a sinusoidal stress (σ) results from the sinusoidal strain with $\sigma = \sigma_0 \cos(\omega t + \delta) = \sigma_0 \cos \delta \cos \omega t \sigma_0 \sin \delta \sin \omega t$.
- Note 5: See free oscillation.

fragile glass

Glass characterised by a large value of the *fragility index* (*m*).

Note 1: See strong glass.

- *Note 2*: A very fragile glass has $m \approx 250$.
- *Note 3*: A fragile glass has a markedly non-Arrhenius-type temperature dependence of the viscosity and *relaxation time*.
- *Note 4*: The *Vogel–Fulcher–Tammann equation* can be used to describe the relaxation-time behaviour of a fragile glass.

fragility index, m

Quantity characterising the fragility or the strength of a glass at a given temperature

$$m = \left(\frac{d \log_{10} \tau}{d \left(\frac{T_g}{T}\right)}\right)_{T = T_g}$$

 τ = relaxation time [s]; T_g = glass-transition temperature [K]; T = temperature [K].

- Note 1: The value of the fragility index depends on the thermal history of the glass.
- *Note 2:* The values of *m* range from $m \approx 16$ for a very *strong glass* to $m \approx 250$ for a very *fragile glass.*

free oscillation free sinusoidal oscillation

Oscillatory deformation of a material specimen with the motion generated without the continuous application of an external force [6].

- *Note 1*: For any real sample of material, the resulting oscillatory deformation is one of decaying amplitudes.
- Note 2: See forced sinusoidal oscillation.

free sinusoidal oscillation

See free oscillation.

fusion

See melting.

gamma loss peak

See gamma relaxation peak.

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gamma relaxation γ-relaxation

Third-highest-temperature or third-lowest-frequency relaxation in the loss curve of a polymer.

gamma relaxation peak γ-relaxation peak gamma loss peak γ-loss peak

Third-highest-temperature or third-lowest-frequency peak in the loss curve of a polymer.

Note: The γ -peak is typically related to localised motions involving side groups or a few atoms of a polymer chain.

γ-loss peak

See gamma relaxation peak.

γ-relaxation

See gamma relaxation.

γ-relaxation peak

See gamma relaxation peak.

glass

Amorphous matter in the glassy state, i.e., below its glass-transition temperature [13].

- *Note 1*: A glass is usually described as a solid, as most physical properties vary in a manner similar to those in the *crystalline state*. However, considering the ongoing debate about the nature of the *glass transition*, and the ability of some *glasses* to flow, some authors prefer to consider glasses in the context of the liquid state.
- *Note 2*: The creep compliance [6] of a *glass* is less than 10^{-9} N⁻¹·m², and the dynamic viscosity [6] larger than 10^4 Pa·s.

glass transition (in polymer science)

Process in which a *polymer melt* changes on cooling to a *polymer glass* or a polymer glass changes on heating to a polymer melt [13].

Note 1: Phenomena occurring at the glass transition of polymers are still subject to ongoing scientific investigation and debate. The glass transition presents features of a *second-order transition* since thermal studies often indicate that the molar Gibbs energies, molar enthalpies, and the molar volumes of the two phases, i.e., the *melt* and the *glass*, are equal, while the heat capacity and the expansivity are discontinuous. However, the glass transition is generally not regarded as a thermodynamic transition in view of the inherent difficulty in reaching equilibrium in a polymer glass or in a polymer melt at temperatures close to the *glass-transition temperature*.

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- *Note 3*: In a *partially crystalline polymer* the glass transition occurs only in the amorphous parts of the material.
- Note 4: The definition is different from that in ref. [5].
- *Note 5*: The commonly used term "glass-rubber transition" for glass transition is not recommended.

glass-transition temperature (in polymer science), T_{g} , SI unit: K

Temperature at which the glass transition occurs [13].

- *Note 1*: Crystallisation rates of *crystallisable polymers* become infinitely slow below T_{o} .
- *Note 2*: The value of T_g measured depends on the cooling or heating rate used, on the analytical technique used in its determination, and in many instances, on previous thermal treatment.
- *Note 3*: T_g can be determined by a number of different techniques ranging from *DSC*, *DTA*, *DETA*, *DMA*, to spectroscopic methods which allow the determination of *relaxation times* or temperatures. It can also be determined as the temperature at which the rates of change of various physical properties, such as specific volume, entropy, enthalpy, refractive index, and viscosity, undergo a large increase or decrease. See Fig. 4.



Fig. 4 *Glass-transition temperature* determined from the intercept of the linear extrapolated temperature functions of, for example, the volume V, the enthalpy H, and the entropy S in a glassy state (left) and in the melt (right), respectively.

- *Note 4*: It is often only possible to determine experimentally a temperature range over which the glass transition occurs, rather than a single transition temperature.
- *Note 5*: The definition is different from that given in ref. [5].
- *Note 6*: The commonly used term "glass-rubber transition temperature" for glass-transition temperature is not recommended.
- Note 7: See also characteristic temperatures.

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glassy polymer

See polymer glass.

glassy state

State of amorphous matter below its glass-transition temperature [13].

Hoffman-Weeks plot

Plot of melting temperature, $T_{\rm m}$, vs. crystallisation temperature, $T_{\rm cr}$.

- Note 1: A Hoffman–Weeks plot is used to determine the equilibrium melting temperature, $T_{\rm m}^0$.
- *Note 2*: $T_{\rm m}^0$ is determined as the intersection of the straight line that describes $T_{\rm cr} = T_{\rm m}$ with the extrapolated curve that is drawn through the experimental data points $(T_{\rm cr}, T_{\rm m})$.

isotropisation temperature

Temperature at which a transition from any anisotropic state to an isotropic liquid occurs.

Note: In mesomorphic systems, the isotropisation temperature is usually called *clearing temperature*.

Kauzmann temperature, T_0

Temperature at which the extrapolation of the entropy of a super-cooled liquid is equal to the entropy of its crystalline state.

Kohlrausch-Williams-Watts equation, KWW equation

Equation describing the *enthalpy relaxation*, ΔH , which is observed during the *annealing* of polymers in the *glassy state* at a temperature, T_a , lower than T_g

$$\Delta H(t_{\rm a}) = \Delta c_p \left(T_{\rm g} - T_{\rm a}\right) \exp\left[-\left(\frac{t_{\rm a}}{\tau}\right)^{\beta}\right]$$

 ΔH = difference of the enthalpy in the initial, glassy state, and the enthalpy of the glassy state after annealing; t_a = time of annealing; Δc_p = difference in heat capacity at the *glass-transition temperature*, T_g , and the starting temperature of the annealing process, T_a ; τ = *relaxation time* at T_a ; β = exponential factor.

- *Note 1*: The exponential factor β has a value between 0 and 1, and characterises the asymmetry of the distribution of relaxation times.
- *Note 2*: Moduli, stress–strain behaviour, and molecular motions are affected by enthalpy relaxation, which reflects physical aging.

linear thermodilatometry

Technique in which one dimension of a substance under negligible load is measured as a function of temperature while the substance is subjected to a controlled temperature program.

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Note: See *thermodilatometry*.

logarithmic decrement, Λ

Natural logarithm of the ratio of the displacement of a *damping curve* separated by one period of the displacement [6].

Note: If equals the n^{th} displacement of the damping curve and equals the $(n + 1)^{\text{th}}$ displacement (n = 1, 2, 3, ...), then $\Lambda = \ln(A_n/A_{n+1})$.

loss curve

Plot of *loss tangent* (tan δ) vs. the temperature or the frequency of the *forced sinusoidal oscillation* [6].

loss factor

See loss tangent.

loss modulus, in general M'', SI unit: Pa in simple shear deformation G'', SI unit: Pa in uniaxial deformation E'', SI unit: Pa

Ratio of the amplitude of the stress 90° out of phase with the strain ($\sigma_0 \sin \delta$) to the amplitude of the strain (γ_0) in the forced sinusoidal oscillation of a material [6].

$$M'' = \frac{\sigma_0 \sin \delta}{\gamma_0}$$

- Note 1: Definition taken from ref. [6], with "forced sinusoidal oscillation" replacing "forced oscillation".
- *Note 2*: For the definitions of the symbols used, see *forced sinusoidal oscillation*. In a linear viscoelastic material, the strain $\gamma = \gamma_0 \cos \omega t$ produces a stress $\sigma = \sigma_0 \cos(\omega t + \delta) = \sigma_0 \cos \delta \cos \omega t \sigma_0 \sin \delta \sin \omega t$.
- Note 3: The loss modulus characterises the viscous response of a material.

loss tangent, tan δ loss factor

Tangent of the phase angle (δ) between stress and strain during a *forced sinusoidal oscillation*.

- *Note 1*: Definition taken from ref. [6], with "forced sinusoidal oscillation" replacing "forced oscillation".
- *Note 2:* tan δ is also equal to the ratio of *loss modulus* to *storage modulus*.

master curve

Viscoelastic spectrum of a polymer or polymer material constructed using the *time-temperature superposition (TTS) principle*, so that the spectrum covers a wide range of lengths of time or frequencies of measurement.

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- *Note 1*: A master curve is usually constructed by superimposing a sequence of isothermal measurements of a viscoelastic property vs. time.
- Note 2: See time-temperature superposition principle and Williams-Landel-Ferry equation.

mechanical melting

Mechanically induced transition of matter in the crystalline or glassy state to its melt.

melt

Matter in the amorphous state above its glass-transition temperature [13].

Note 1: A melt has the physical properties of a liquid.

Note 2: See polymer melt.

melt flow index, MFI, unit: g·(min)⁻¹ **melt flow rate,** MFR **melt volume flow melt mass flow rate**

Mass of a polymer in grams that flows through a calibrated orifice at constant temperature under a specified load over a 10-min period.

- *Note 1*: There is no suitable SI unit for MFI.
- Note 2: Specified loads are mandated for specific polymers.
- *Note 3*: The values of MFI as a function of load can give information on the molar mass distribution.
- Note 4: Standard procedures for determining MFI are given in refs. [8,9].

melt flow rate, MFR

See melt flow index.

melt mass flow rate

See melt flow index.

melt volume flow

See melt flow index.

melting (in polymer science) **fusion**

Conversion of crystalline matter into a liquid by the application of heat or pressure, or both.

melting point

See *melting temperature*.

melting temperature, $T_{\rm m}$, SI unit: K melting point

Temperature at which the last trace of crystallinity disappears upon heating.

- *Note 1*: This temperature usually refers to the highest temperature of the melting range, i.e., when the last and therefore the most perfectly ordered crystals or the largest crystals melt.
- *Note 2*: An experimentally determined melting temperature is not necessarily identical with the equilibrium melting temperature. See *equilibrium melting temperature* and *Hoffman–Weeks plot*.
- *Note 3*: Experimentally determined values of the melting temperature may depend on the method and the experimental conditions, for example, sample mass, heating rate, etc.
- *Note 4*: If $T_{\rm m}$ is determined using *DSC* or *DTA*, then the *characteristic temperature* used should be stated, see Fig. 2 and ref. [6].
- Note 5: See also characteristic temperatures.

modulated heat flow, MHF

Heat flow in a modulated-temperature DSC experiment.

modulated-temperature DSC, MTDSC

DSC experiment in which a small sinusoidal modulation overlays the change in temperature with time.

Note 1: The resulting *DSC* data can be separated, by Fourier analysis, into components in-phase with the modulation (*reversing heat flow*) and out-of-phase with the modulation (*non-reversing heat flow*).

 $\underbrace{\left(\frac{\partial H}{\partial t}\right)_{p}}_{\text{total heat flow}} = \frac{dQ}{dt} = \underbrace{C_{p}\frac{dT}{dt}}_{\text{reversing heat flow}} + \underbrace{f(T,t)}_{\text{non-reversing heat flow}}$

The total heat flow is the average value calculated from the measured signals during the

modulated heat flow (MHF). C_p is the heat capacity of the sample, $\frac{dT}{dt}$ is the heating rate.

Note 2: Use of the terms "oscillating DSC (ODSC)" and "modulated DSC (MDSC)" is discouraged.

multiplexing

Technique used in *dynamic mechanical analysis* in which a specimen is subjected to the superposition of a number of *forced sinusoidal oscillations* of different frequencies.

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Pure Appl. Chem., Vol. 85, No. 5, pp. 1017–1046, 2013

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Note: In one experiment, this technique delivers the frequency dependence of the mechanical properties at all the frequencies covered by the forced sinusoidal oscillations.

non-reversing heat flow

In *modulated-temperature DSC*, the component of the total heat flow that is out-of-phase with the temperature modulation.

- *Note 1*: The out-of-phase component of the total heat flow relates to kinetic processes like crystallisation, melting, evaporation, or condensation.
- Note 2: The term "non-reversing" must not be confused with "irreversible".

partially crystalline polymer

See crystalline polymer.

polymer crystal

Polymer domain exhibiting three-dimensional crystalline order at the atomic scale [13].

Note: Polymer crystals are usually much smaller and frequently do not display the perfection that is usual for crystals of low-molar-mass substances. Sizes range from 2 to 3 nm to a few μ m, with more typical values around 10 nm in one or more dimensions.

polymer glass glassy polymer

Amorphous polymer at temperatures below its glass-transition temperature [13].

primary crystallisation

First stage of *crystallisation* forming spherulites. It is considered to be completed when most of the spherulite surfaces impinge on each other [13].

Note: In isothermal crystallisation, primary crystallisation is often described by the Avrami equation or the Kolmogorov–Johnson–Mehl–Avrami equation, with modifications of the equation being used for non-isothermal crystallisation.

polymer melt

Polymer in the amorphous state above its glass-transition temperature [13].

- *Note 1*: A polymer melt has the physical properties of a viscoelastic liquid.
- *Note 2*: The term applies both to *crystallisable polymers* and to polymers that are unable to crystallise. In the latter case, no specifications are needed. In the former case, in the range between the glass-transition temperature and the *equilibrium melting temperature*, the polymer melt is metastable, and, as long as crystallisation does not occur (see *Note 3*), the term *supercooled polymer melt* can be used to define more accurately the thermodynamic state of the system.

Note 3: When a crystallisable polymer undergoes crystallisation, the remaining amorphous component cannot be considered a polymer melt. Flow is inhibited by polymer crystallites, which physically cross-link the amorphous component or constrain it at the surface of *polymer crystals*.

quench cooling

See quenching.

quenching quench cooling

Process of rapidly decreasing the temperature of a substance.

- *Note 1*: Quenching can sometimes prevent or reduce *crystallisation* by cooling a substance into an amorphous state.
- Note 2: A quenched sample is usually not in a thermodynamic equilibrium state.

recrystallisation (in polymer science)

Reorganisation of crystals proceeding through partial or complete *melting*, or dissolution in a solvent, either isothermally or during heating [13].

Note: Recrystallisation is likely to result in an increase in the degree of crystallinity, or crystal perfection, or both and can result in changes to a more stable crystal structure or larger crystals, or changes to a more stable morphology.

relaxation

Process that takes a system back towards equilibrium after a disturbance from equilibrium.

Note 1: Modified from the definition in ref. [5].

Note 2: See also stress relaxation.

relaxation map

Plot of the logarithm of the relaxation time vs. the reciprocal temperature.

relaxation spectrum spectrum of relaxation times

Range of *relaxation times* describing stress relaxation in a polymer.

Note: Modified from the definition in ref. [6].

relaxation time, τ , SI unit: s

Time characterising the response of a viscoelastic liquid or solid to the instantaneous application of a constant strain [6].

Note 1: After the relaxation time has elapsed a property has decreased to 1/*e* of its initial value.

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Note 2: See stress relaxation.

reorganisation (in polymer crystallisation)

Process by which (i) amorphous or partially ordered regions of a polymer become incorporated into crystals, (ii) a change to a more stable crystal structure takes place, (iii) defects within crystals decrease, or (iv) the average thickness of lamellae (the fold period) increases [13].

- Note 1: Secondary crystallisation may be involved in the reorganisation process.
- *Note 2*: Reorganisation may result from *annealing*, or by exposure to a poor solvent or its vapour.

reversing heat flow

In *modulated-temperature DSC* the heat-capacity component of the total heat flow that is in-phase with the temperature modulation.

- *Note 1*: The reversing-heat-flow component contains the changes in the heat capacity, C_p , of the specimen, in particular during the glass transition.
- Note 2: The term "reversing" must not be confused with "reversible".

secondary crystallisation

Crystallisation occurring after primary crystallisation [13].

Note: Secondary crystallisation usually proceeds at a lower rate than primary crystallisation.

secondary loss peak

See secondary relaxation peak.

second-order phase transition continuous phase transition

Transition in which the first derivatives of the molar Gibbs energy or molar Helmholtz energy (or the chemical potentials of all the components) with respect to temperature and pressure are continuous but their second derivatives with respect to temperature and pressure (e.g., heat capacity, thermal expansion, compressibility) are discontinuous at the transition point.

- *Note 1*: The *glass transition* is not strictly a second-order transition since it is not a transition between two thermodynamic equilibrium states but a kinetically controlled process where cooperative motions of chain segments become infinitely slow below the *glass-transition temperature*. See *glass transition*.
- *Note 2*: An order–disorder transition or the transition at the Curie-point are examples of second-order transitions.

secondary relaxation

Second-, third-, fourth-, ... highest-temperature or second-, third-, fourth-, ... lowest-frequency *relax- ation* in the *loss curve* of a polymer.

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Note: See *beta relaxation* and *gamma relaxation*.

secondary relaxation peak secondary loss peak

Any peak in a *loss curve* either at a lower temperature than the temperature of the *alpha relaxation peak* or at a higher frequency than the frequency of the alpha relaxation peak.

Note 1: See *alpha*, *beta*, and *gamma relaxation* peaks.

Note 2: The use of the term "secondary relaxation transition peak" is discouraged.

secondary relaxation temperature, $T_{\beta}, T_{\gamma}, \cdots$

Temperature characterising a secondary relaxation peak identified as the temperature at which the *loss modulus* (or *loss tangent*), measured by *DMA* or *DETA*, exhibits a maximum at the measurement frequency, due to the occurrence of localised motions involving only short segments of the polymer chains, or side groups of the polymer chains.

semicrystalline polymer

See crystalline polymer.

shift factor, a_T

Multiplier used to change the interval of time or the range frequencies of measurement of a viscoelastic property at a given temperature, T_1 , so that the values of the property superimpose on the values measured at a reference temperature, T_0 .

Note 1: The shift factor is temperature dependent but independent of the time or frequency.

Note 2: See Williams–Landel–Ferry (WLF) equation.

sinusoidal oscillation

See forced sinusoidal oscillation.

softening point

See Vicat softening temperature.

softening temperature softening point

See Vicat softening temperature.

spectrum of relaxation times

See relaxation spectrum.

in simple shear deformation G', SI unit: Pa in uniaxial deformation E', SI unit: Pa

Ratio of the amplitude of the stress in phase with the strain ($\sigma_0 \cos \delta$) to the amplitude of the strain (γ_0) in the forced sinusoidal oscillation of a material [6].

$$M' = \frac{\sigma_0 \cos \delta}{\gamma_0}$$

- *Note 1*: Definition taken from ref. [6], with "forced sinusoidal oscillation" replacing "forced oscillation".
- *Note 2*: For the definitions of the symbols used, see *forced sinusoidal oscillation*. In a linear viscoelastic material, the strain $\gamma = \gamma_0 \cos \omega t$ produces a stress.

 $\sigma = \sigma_0 \cos(\omega t + \delta) = \sigma_0 \cos \delta \cos \omega t - \sigma_0 \sin \delta \sin \omega t$

Note 3: The storage modulus characterises the elastic response of a material.

stress relaxation

Change in stress with time after the instantaneous application of a constant strain.

strong glass

Glass characterised by a small value of the fragility index (m).

- Note 1: See fragile glass.
- *Note 2*: A very strong glass has $m \approx 16$.
- *Note 3*: A strong glass has an approximately Arrhenius-type temperature dependence of the viscosity and *relaxation time*.

supercooled polymer melt

Metastable *melt* of a crystallisable polymer at temperatures below its *equilibrium melting temperature*.

Note: Definition as in ref. [13] for the term "supercooled melt".

Tammann's 2/3rd rule

Empirical rule that states that in a partially crystalline polymer the *glass-transition temperature* can be reasonably approximated by a value equal to two-thirds of the *melting temperature*, T_m/K .

thermal analysis

Measurement of a physical property of a substance or its reaction products (or both) as a function of temperature, while the substance is heated or cooled in a controlled manner.

Note: Definition consistent with ref. [4] and with definition recommended by the International Confederation for Thermal Analysis and Calorimetry.

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thermal history (in polymer science)

Thermal treatment a polymer material has experienced before its characterisation or measurement of its properties.

Note: Thermal history affects many physical properties. Its influence can be modified or removed by *annealing*.

thermal lag

Delay of the response of a system to a change in temperature.

thermally stimulated current, TSC

Electrical current observed during heating caused by the thermally initiated *relaxation* of the frozen-in electrical polarisation of a sample.

Note: See also *thermally stimulated depolarisation*.

thermally stimulated depolarisation

Relaxation of frozen-in electrical polarisation caused by a temperature increase.

Note: The effect is measured through the *thermally stimulated current*.

thermobalance

See thermogravimetric analyser.

thermochromism

Thermally induced reversible colour change of a substance.

Note: Thermochromism is displayed by polymers (i) containing functional groups that change colour upon temperature change (e.g., a spiropyran polymer), (ii) with temperature-dependent electronic absorption spectra, or by (iii) liquid-crystalline polymers at mesophase transitions.

thermodilatometry

dilatometry (in thermal analysis)

Technique in which a dimension (or dimensions) of a substance under negligible load is (are) measured as a function (or functions) of temperature while the substance is subjected to a controlled temperature program.

- *Note 1*: Apparatuses are available to measure one-dimensional changes using mechanical displacement detection. Volume changes can be determined in an inert confining fluid (e.g., Hg).
- *Note 2*: Measurement under variation of the applied hydrostatic pressure allows the determination of pressure–volume–temperature (p,V,T) diagrams.
- *Note 3: Linear thermodilatometry* and *volume thermodilatometry* are distinguished on the basis of the number of dimensions measured.

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Note 4: Definition and notes are modifications of those in ref. [4].

thermogravimetric analyser, TGA thermobalance

Apparatus for conducting thermogravimetric analysis.

Note: It is common to use the same abbreviation (TGA) for both *thermogravimetric analysis* and the apparatus.

thermogravimetric analysis, TGA thermogravimetry, TG

Technique that monitors the mass of the sample as a function of time or temperature while the temperature of the sample, in a specified atmosphere, is heated or cooled in a controlled manner.

- *Note 1:* It is common to use the same abbreviation (TGA) for both the technique and a *thermo-gravimetric analyser*.
- *Note 2*: Very often, TG is used in combination with *DTA*, Fourier transform-infrared spectroscopy (FT-IR), gas chromatography (GC), or mass spectroscopy (MS) in so-called hyphenated techniques.

thermogravimetry, TG

See thermogravimetric analysis.

thermoluminescence, TL

Luminescence arising from a reaction between species trapped in a rigid matrix and released as a result of an increase in temperature [4].

thermoluminescence analysis, TLA

Technique that monitors the light that is emitted from a sample against time or temperature while the temperature of the sample, in a specified atmosphere, is heated in a controlled manner.

thermomechanical analyser, TMA

Apparatus for conducting thermomechanical analysis.

Note: It is common to use the same abbreviation (TMA) for both *thermomechanical analysis* and the apparatus.

thermomechanical analysis, TMA

Technique that monitors the deformation of a sample under stress as a function of time or temperature while the temperature of the sample, in a specified atmosphere, is heated or cooled in a controlled manner.

Note 1: It is common to use the same abbreviation (TMA) for both the technique and a *thermo-mechanical analyser*.

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- Note 2: The stress may be compression, tension, flexure, or torsion.
- *Note 3*: If the stress is sinusoidal, the technique is called *dynamic-load thermomechanical analysis (DLTMA).*
- *Note 4*: When the stress is too low to cause deformation, TMA monitors a dimension of the sample, and in this role the technique is called *thermodilatometry*.

thermomechanical properties

The temperature dependence of deformability or mechanical properties of a polymer sample.

thermomicroscopy

Thermo-optometry carried out observing a sample under a microscope.

thermo-optometry

Any thermoanalytical technique that monitors an optical property of a sample, against time or temperature while the temperature of the sample, in a specified atmosphere, is heated or cooled in a controlled manner.

Note: Two established examples are *thermomicroscopy* and *thermoluminescence*.

time-temperature superposition principle, TTS principle

Principle stating that the value of a viscoelastic property measured at a given temperature, after a given length of time or at a given frequency, is equal to the value of the property at a different temperature after a length of time or at a frequency equal to the given length of time or given frequency multiplied by a *shift factor*, a_T , with the value of the shift factor being independent of length of the time or frequency.

Note: The *Williams–Landel–Ferry (WLF) equation* provides a semi-empirical relation between the shift factor a_T and the temperature, at temperatures near the *glass-transi-tion temperature*, T_g .

torsional braid analysis

Dynamic mechanical analysis in which the material sample to be analysed is coated onto a braid of inert fibres as support.

Note: The fibres should not have thermal transitions in the same temperature or frequency ranges as the material sample being analysed.

torsion pendulum

Device consisting of a disc or other body of large moment of inertia mounted on one end of a torsionally flexible elastic rod or wire, the other end of which is fixed.

Note: When the disc is displaced by a (small) angle around its primary rotational axis it will undergo a simple harmonic oscillation after it is released as long as the torque of the rod or the wire is proportional to the torsion angle.

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torsional pendulum analysis

Dynamic mechanical analysis performed using a torsion pendulum.

- *Note 1:* A strip-shaped polymer sample is mounted on a torsion pendulum and subjected to a small torque. The decay in the amplitude of the *free sinusoidal oscillation* is observed over a range of temperatures.
- Note 2: Storage (shear) modulus G', loss (shear) modulus G'', and the loss-tangent can be calculated from the logarithmic decrement, Λ .

transition temperature (in dynamic mechanical and dielectric thermal analysis)

Temperature at which a maximum in the temperature dependence of a *loss curve* obtained using *dynamic mechanical* or *dielectric thermal analysis* is observed.

- *Note 1:* A transition temperature is also identified as an α -, β -, or γ -transition defining an α -, β -, or γ -relaxation.
- Note 2: The value of a transition temperature can depend on the measuring frequency.

Vicat hardness

See Vicat softening temperature.

Vicat softening point

See Vicat softening temperature.

Vicat softening temperature softening point Vicat softening point Vicat hardness

Temperature at which a thermoplastic polymer reaches a specific degree of softness as measured by a standard test.

- *Note 1*: Usually this temperature is determined using standardised methods, such as indentation tests [10,11], or the ring–ball method [12] that characterise the dimensional stability of a polymer to heating. These standardised methods are often polymer specific.
- *Note 2*: For an amorphous polymer, the softening temperature is close to the *glass-transition temperature*, and for a crystalline polymer the softening temperature is close to but lower than the *melting temperature*.

viscoelastic spectrum

Double logarithmic plot of a viscoelastic property vs. frequency of measurement or interval of time of measurement at constant temperature.

vitrification (in polymer science)

Formation of a polymer glass from a polymer melt.

Note: Vitrification is usually brought about by cooling.

Vogel-Fulcher-Tammann equation, VFT equation

Equation describing the time-dependence of a *relaxation time* that deviates from an Arrhenius-type temperature dependence.

$$\tau = \tau_0 \exp\left(\frac{B}{T - T_0}\right)$$

 τ /s = relaxation time; τ_0 /s = relaxation time at the *Kauzmann temperature*, *B*/K = constant; *T*/K = temperature; T_0 /K = Kauzmann temperature.

Note: See fragile glass.

volume thermodilatometry

Technique in which the volume of a substance under negligible load is measured as a function of temperature while the substance is heated or cooled in a controlled programme.

Note: See *thermodilatometry*.

Williams-Landel-Ferry equation, WLF equation

Equation describing the temperature dependence of the *shift factor*, a_T , for *time-temperature superposition*

$$\log_{10} a_{\rm T} = \frac{-C_1(T_1 - T_0)}{C_2 + (T_1 - T_0)}$$

 C_1 and C_2 are empirical constants, T is the temperature of measurement, and T_0 is the reference temperature.

Note: The WLF equation is usually applied with the reference temperature, T_0 , equal to the *glass-transition temperature*, T_g . The values of the constants C_1 and C_2 depend on the type of polymer and are valid over a limited range of temperature, from T_g to about $T_g + 50$ K [23].

3. LIST OF ABBREVIATIONS

DETA	dielectric thermal analysis
DLMTA	dynamic-load thermomechanical analysis
DMA	dynamic mechanical analyser, dynamic mechanical analysis
DSC	differential scanning calorimeter, differential scanning calorimetry
DTA	differential thermal analyser, differential thermal analysis
FT-IR	Fourier transform-infrared spectroscopy
GC	gas chromatography
KWW	Kohlrausch–Williams–Watts
MFI	melt flow index
MFR	melt flow rate

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MHF	modulated heat flow
MTDSC	modulated-temperature DSC
MS	mass spectroscopy
TG	thermogravimetry
TGA	thermogravimetric analyser, thermogravimetric analysis
TL	thermoluminescence
TLA	thermoluminescence analysis
TMA	thermomechanical analyser, thermomechanical analysis
TTS	time-temperature superposition
VFT	Vogel–Fulcher–Tammann
WLF	Williams-Landel-Ferry

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