

Definitions of terms relating to crystalline polymers (IUPAC Recommendations 2011)*

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Abstract: Recommendations are given concerning the terminology relating to the structure and the morphology of crystalline polymers and the processes of polymer crystallization. They are applicable to cases where polymer crystals are a significant fraction of a system and primarily with crystal structures that are comprised of polymer chains with limited, static, or dynamic disorder. After some general definitions, terms pertaining to structural arrangements at subnanometric scales and to polymer crystal structures are defined. Terms relating to molecular conformation within polymer crystals, morphological aspects, and polymer crystallization are given in subsequent sections.

Keywords: IUPAC Polymer Division; crystalline polymers; crystalline polymer conformation; morphology; polymer crystal structure; polymer crystallization.

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1. INTRODUCTION

The recommendations embodied in this document concern the terminology relating to the structure of crystalline polymers and the processes of polymer crystallization. Crystalline polymers are normally only partly crystalline, and polymer crystals (or crystallites) coexist, therefore, with amorphous regions. Reference to actual polymer crystals of microscopic dimensions is essential to define the characteristic properties of crystalline polymers. Such crystals correspond only very approximately to the infinite, three-dimensionally periodic arrangements of atoms defining the ideal crystalline state.

The document applies mainly to cases where polymer crystals occupy a significant fraction of the volume of a system. The recommendations deal primarily with crystal structures that are comprised of linear, parallel-packed polymer chains, but they are also applicable to crystalline structures where non-parallel chains coexist in the unit cell, such as in the γ -form of isotactic polypropylene. In general, terminology pertaining to macromolecular mesophases [1] will be omitted but crystalline polymers with limited static or dynamic disorder are considered.

After some general definitions (Section 2), the subject is divided into sections dealing, successively, with: local structural arrangements at the scale of a few bond lengths and with polymer crystal structures (Section 3), molecular conformation within polymer crystals (Section 4), morphological aspects (Section 5), and, finally, the essential terminology of polymer crystallization (Section 6). Within each section or subsection, terms are listed alphabetically and an alphabetical index of terms is provided in an appendix.

This document is a revision and expansion of IUPAC recommendations of the same title published in 1989 [2] and relies on the basic definitions of terms in polymer science [3], chemistry [4], physical chemistry [5], and crystallography [6–10]. It is one of a series published by the IUPAC Commission on Macromolecular Nomenclature and subsequently by the IUPAC Subcommittee on Polymer Terminology dealing with definitions of terms in polymer science.

2. GENERAL DEFINITIONS

2.1 amorphous polymer

Polymer in the *amorphous state*.

Note 1: The term may indicate a polymer that, because of its constitution, is unable to crystallize, i.e., a polymer that is not a *crystallizable polymer*. It may also refer to a *crystallizable polymer*, or polymer component that is non-crystalline under the specific circumstances considered.

Note 2: Analytical techniques are generally unable to distinguish between a *polycrystalline polymer* with crystal dimensions below about 2 nm and an amorphous polymer. The 2 nm value is about 2 to 3 times the typical lattice dimensions for many polymers, such as polyethylene and polypropylene.

2.2 amorphous state

State of matter characterized by the absence of long-range molecular order.

Note 1: Some degree of local order of 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 large enough scales, as in liquids.

Note 3: Below the *glass-transition temperature*, a stretched amorphous polymer may remain anisotropic, even after removing the applied stress. Frozen-in residual stress will, however, be present in such a polymer.

2.3 conformation

Spatial arrangement of atoms affording distinction between stereoisomers that can be interconverted by rotations about formally single bonds [4].

2.4 crystalline polymer semicrystalline polymer partially crystalline polymer

Polymer, a significant fraction of which is in the *crystalline state*.

Note 1: Polymers hardly ever crystallize completely, and in virtually any crystalline polymer some amorphous material coexists with the crystalline phase or phases (see also *degree of crystallinity*).

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 “crystalline polymer” is wrongly used for *crystallizable polymer*.

Note 4: The *two-phase model* is frequently used to describe crystalline polymers.

Note 5: Modification of the definition in [2–4].

2.5 crystalline state

State of matter ideally characterized by three-dimensional, long-range order on an atomic scale.

Note: One- or two-dimensional order leads to a mesophase structure [1].

2.6 crystallizable polymer

Polymer that is able to partially crystallize.

2.7 degree of crystallinity, w_c (mass fraction), ϕ_c (volume fraction)

Mass fraction or volume fraction of crystalline phase in a sample of polymer.

Note 1: The mass-fraction and the volume-fraction degrees of crystallinity are related by the equation

$$w_c = \phi_c \frac{\rho_c}{\rho}$$

where ρ and ρ_c are the mass concentrations (mass densities) [5] of the entire sample and of the crystalline phase, respectively.

- Note 2:* In the *two-phase model*, both phases are assumed to have properties identical with those of the pure phases; interphases are ignored.
- Note 3:* The degree of crystallinity can be determined by several experimental techniques. Among the most commonly used are: (i) diffraction, (ii) calorimetry, (iii) mass density measurements, (iv) infrared spectroscopy (IR), (v) solid-state NMR spectroscopy, and (vi) vapor permeability. Highly imperfect *polymer crystals* may not be easily distinguished from *amorphous polymer*. Also, the results given by various techniques may be affected to different extents by temperature, crystal imperfections, and interfacial effects. Hence, the results of measurements of degree of crystallinity using different methods are frequently not in numerical agreement with each other.
- Note 4:* If more than one *crystal polymorph* is present, the evaluation of degree of crystallinity still follows the *two-phase model*. Quantities referring to the crystalline phase become the weighted averages for the different crystalline phases.
- Note 5:* Three-phase models have been proposed, consisting of the crystalline phase, the amorphous phase, and a phase described variously as rigid amorphous, anisotropic amorphous, intermediate, or mesomorphic. Explicit consideration of the interphase, progressively dissipating crystalline order is an alternative approach to make the two-phase model more realistic.
- Note 6:* Various techniques have been used to characterize the “third” phase, including NMR (rigid amorphous), X-ray diffraction (intermediate or anisotropic amorphous), differential scanning calorimetry analyzing the heat of fusion and the change of specific heat at T_g (rigid amorphous), infrared spectroscopy combined with permeability measurements (mesomorphic phase), and Raman spectroscopy (interphase).
- Note 7:* Modification of the definition in [2–4].

2.8 glassy polymer

See *polymer glass*.

2.9 local conformation microconformation

Conformation of a polymer chain at the scale of its constitutional units.

Note: Modification of the definition in [2–4].

2.10 macroconformation

See *molecular conformation*.

2.11 microconformation

See *local conformation*.

2.12 molecular conformation macroconformation

Conformation of a macromolecule as a whole.

Note 1: The molecular conformation of a molecule in a *crystalline polymer* may extend over one or several crystals.

Note 2: The term “configuration” should not be used for *conformation*.

Note 3: Modification of the definition in [2–4].

2.13 partially crystalline polymer

See *crystalline polymer*.

2.14 polymer crystal

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

Note 1: Polymer crystals are usually much smaller and frequently do not display the perfection that is usual for low-molar-mass substances. Sizes range from 2 to 3 nm to a few μm , with more typical values, in one or more dimensions, around 10 nm. See also *polymer crystallite*.

Note 2: Polymer crystals can be twinned (*twinned polymer crystals*) or untwinned (*polymer single crystals*).

Note 3: Modification of the definition in [2–4].

2.15 polymer glass glassy polymer

Amorphous polymer at temperatures below its *glass-transition temperature*.

2.16 semicrystalline polymer

See *crystalline polymer*.

2.17 two-phase model

Model based on the assumption that the polymer sample consists only of domains of a crystalline phase and of an amorphous phase.

Note: See also *degree of crystallinity*.

2.18 unit cell

Structural unit from which a crystal may be formed by translational displacements along the three lattice directions.

Note 1: In crystallography, the lattice vectors defining the three-dimensional crystal periodicity are introduced first, from which the definition of the unit cell follows [6–8].

Note 2: The adopted unit cell is not necessarily the smallest possible. To better describe the crystallographic symmetry, non-primitive cells, i.e., larger cells with higher symmetry, should be used whenever possible.

Note 3: Unlike in the case of low-molar-mass substances, the unit cell of a *polymer crystal* comprises, along the *chain axis*, only segments of the polymer molecules, corresponding to the *translational chain repeating unit*, and does not comprise whole molecules.

Note 4: Modification of the definition in [2–4].

3. LOCAL CONFORMATION AND CRYSTAL STRUCTURE [10–13]

3.1 Chain structure and conformation

3.1.1 axial advancement per constitutional repeating unit, h , SI unit: m unit height

Projected length of a *constitutional repeating unit (CRU)* on the *chain axis*.

Note 1: The axial advancement per CRU is characteristic of the *conformation* of a polymer chain. A large axial advancement per CRU is said to define a more extended conformation and a small axial advancement per CRU is said to define a more contracted conformation.

Note 2: The value of h is obtained from the equation

$$h = \frac{c}{M_{\text{R}}}$$

where c is the chain identity period and M_{R} is the number of CRUs in c . In cases where the *equivalence postulate* does not apply, h is an average value.

3.1.2 chain axis

Straight line connecting the centers of mass of successive *translational chain repeating units* of a *stem* (see Fig. 1).

Note 1: The chain axis corresponds to the average local direction of extension of a polymer chain.

Note 2: Modification of the definition in [2–4].

3.1.3 chain identity period, c , b , SI unit: m chain repeating distance fiber identity period physical repeating distance

Shortest distance along the *chain axis* for intramolecular translational repetition.

Note 1: The chain identity period equals the projected length of a *translational chain repeating unit* on the chain axis.

Note 2: The chain identity period may differ for different *crystal polymorphs* of a given *crystalline polymer*.

Note 3: In the case of *parallel-chain crystals*, the chain axis is usually taken parallel to the lattice vector c or, rarely, to the lattice vector b . The chain identity period is measured along the chain axis. It is, therefore, usually denoted by c or b . Examples are given in Figs. 1 and 2.

Note 4: The chain identity period may be measured by diffraction methods using crystalline polymer fibers, single crystal mats, and single crystals.

Note 5: Modification of the definition in [2–4].

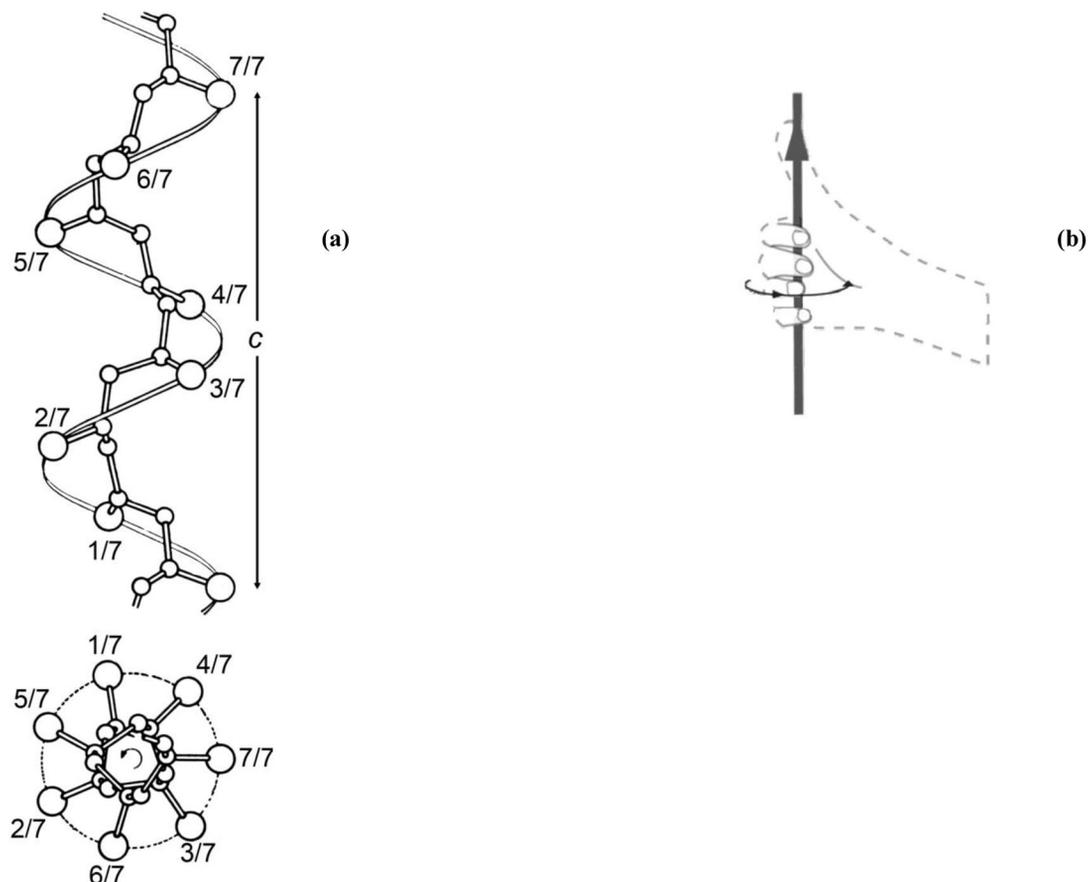


Fig. 1 (a) Helical structure of an isotactic poly- α -olefin, adapted from ref. [11d]. The 7_2 helical conformation shown comprises 7 helix residues, each corresponding to a constitutional repeating unit (CRU) in 2 turns ($M = 7$, $N = 2$, see 3.1.13). The translational chain repeating unit is here composed of 7 CRUs. c denotes the chain identity period. The helical structure shown is the ideal crystalline chain conformation adopted, for example, by isotactic poly(4-methylpent-1-ene) in the so-called form I. Relative displacements along the c axis are given for each CRU in both projection views. The structure shown is a right-handed helix as it complies with the right-hand rule visualized in (b). In right-handed helices the ideal continuous helical trace on the side facing the observer, i.e., for example, the line connecting units 2 and 3 in the side projection in (a), ascends from left to right.

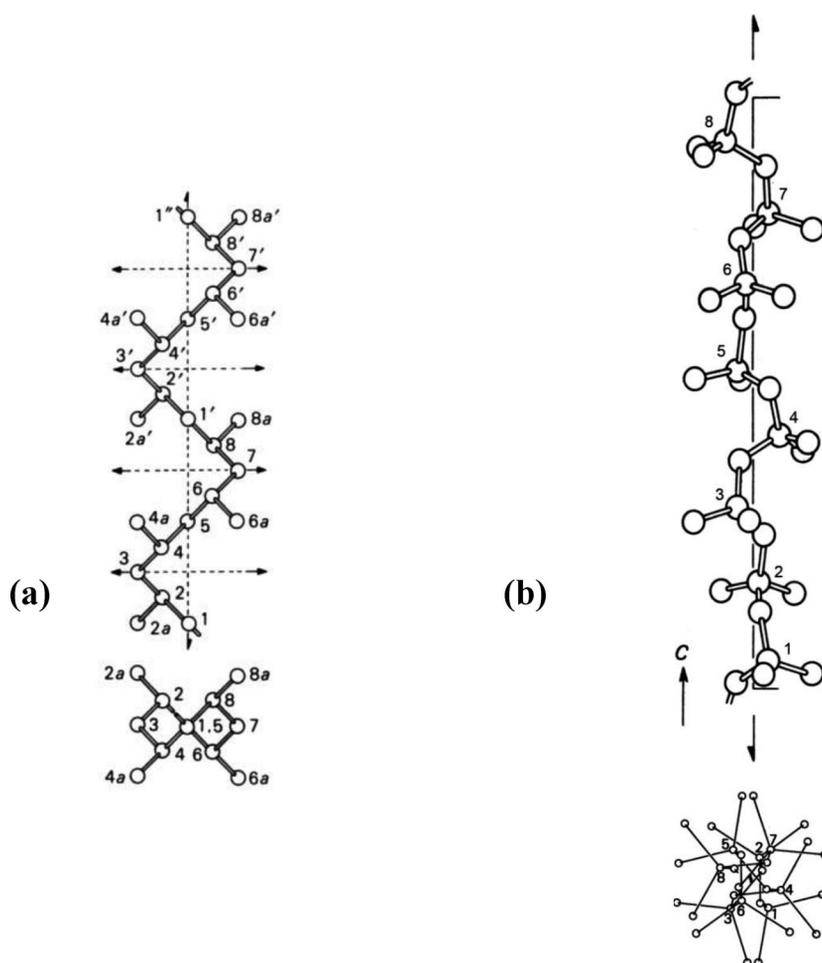


Fig. 2 (a) The 2_1 ideal crystalline conformation of syndiotactic polypropylene [12,13]: the symmetry relationships involving CRUs, each of which also coincides with the conformational repeating unit in this helical structure, is evidenced; a translational chain repeating unit (e.g., from atom 1 to 1') comprises two helical residues (from atom 1 to 5 and from 5 to 1') and four CRUs. (b) The crystallographic 2_1 helix of poly(2-methylpropene) [10], approximating an 8_3 helix: in this case, all the CRUs are not symmetry related; the translational chain repeating unit (from CRU 1 to 8) comprises two helical residues (from CRU 1 to 4, and from CRU 5 to 8, respectively) each of which corresponds to a single conformational repeating unit and four CRUs. Both of the shown helices are right-handed.

3.1.4 chain repeating distance

See chain identity period.

3.1.5 conformational repeating unit

Smallest structural unit of a polymer chain with a given conformation that is repeated along the chain through symmetry operations, including translation [2–4].

Note 1: If no intramolecular symmetry element applies to the chain, except for the translation repetition along the *chain axis*, the conformational repeating unit corresponds to the *translational chain repeating unit*.

Note 2: The conformational repeating unit may differ for different *crystal polymorphs* of a given *crystalline polymer*.

3.1.6 constitutional repeating unit (CRU)

Smallest constitutional unit, the repetition of which constitutes a regular macromolecule, a regular oligomer molecule, or a regular block of a copolymer [3,4].

Note: The CRU is the same for all of the different polymorphs of a given *crystalline polymer*.

3.1.7 directional chain

Polymer chain that may be oriented in two distinguishable, opposite directions along the *chain axis*.

Note 1: The two possible chain orientations can be mutually interconverted through a rotation around a twofold axis orthogonal to the chain axis.

Note 2: Examples of directional chains are poly(amino acids), Nylon 6, polyesters from hydroxyacids, and isotactic poly- α -olefins.

Note 3: Examples of chains that are not directional are polyethylene, syndiotactic poly- α -olefins, and Nylon 6,6.

Note 4: See also *parallel-chain crystal*.

3.1.8 directional stem

Stem of a *directional chain*.

3.1.9 equivalence postulate

Postulate requiring all *constitutional repeating units (CRUs)* of a polymer chain to be related by symmetry [11].

Note 1: The equivalence postulate applies to the *ideal crystalline chain conformation*. It may apply approximately to the *conformation* in the actual crystalline state, or, in rare cases, it may not apply.

Note 2: In cases where the CRU allows for the presence of internal symmetry elements (e.g., polyethylene, (*E*)-1,4-polybutadiene, i.e., poly[(*E*)-but-1-ene-1,4-diyl], (*Z*)-1,4-polybutadiene, i.e., poly[(*Z*)-but-1-ene-1,4-diyl], and poly(pent-1-ene-1,5-diyl), etc.), the postulate may apply to a subunit of the CRU.

Note 3: Modification of the definition in [2–4].

3.1.10 fiber identity period

See *chain identity period*.

3.1.11 fiber repeat unit

See *translational chain repeating unit*.

3.1.12 helicity (of a polymer chain)

helix chirality

helix sense

The chirality of a polymer *helix*, i.e., the property of a helix of being either a *right-handed helix* or a *left-handed helix*.

Note 1: The sequence of bonds along the polymer main chain defines unequivocally the winding and thus the chirality of a continuous polymer chain helix.

Note 2: In polymer literature, a left-handed helix is denoted by the symbol *L* while a right-handed helix is denoted by the symbol *R*. In compliance with prevailing stereochemical terminology conventions [4], the two descriptors *M* (minus) and *P* (plus) are recommended respectively rather than *L* and *R*.

Note 3: Modification of the definition in [4].

3.1.13 helix, M_N

Molecular conformation displaying screw symmetry and generated by regularly repeating *conformations* of the backbone bonds of a macromolecule.

Note 1: An example is shown in Fig. 1.

Note 2: The helix symbol M_N denotes the integer numbers of *helix residues* (*M*) and helical coil windings (helical turns), (*N*), approximated by the sequence of bonds along the polymer main chain (*N*), in a *chain identity period*. *M* and *N* are positive integers, prime to each other, with $M \geq N \geq 1$. *M* may adopt any value, at variance to the case of crystallographic screw axes for which only the values 2, 3, 4, and 6 are acceptable (see also *Note 3* in 3.1.25).

Note 3: The case $M = N = 1$ applies to molecules that present only translational symmetry along the chain and are hence non-helical.

Note 4: A helix with *M* helix residues in *N* turns can be denoted as an “ M_N helix”.

Note 5: For polymers with chiral centers it is necessary to specify, along with the symbol, if the helix is left-handed or right-handed. An example is poly[(*R*)-3-hydroxybutanoate] which adopts a left-handed 2_1 helical conformation. Numerous other cases involve polyaminoacids and polypeptides.

Note 6: In the case of polymers that do not present chiral centers, enantiomeric helix stems of equal energy coexist and can interconvert at high enough temperature or in solution. Unless explicitly indicated, in such cases *right-handed helices* should be represented and referenced with the M_N symbol.

Note 7: The crystallographic screw axis used to describe a helical conformation relates to the discrete helix resulting from the helical arrangement of atoms. The helix turns, as implied by a screw axis, do not necessarily correspond to windings of the continuous polymer helix: thus, the value of *N* used to describe a polymer helix and the value of *N* appearing in the screw axis symbol, may not correspond. For example, the helix repre-

sented in Fig. 1 is unequivocally a right-handed 7_2 helix. Although the atomic coordinates of its mirror image can be represented using a 7_5 right-handed screw axis operator, it is preferable to describe it as a left-handed 7_2 helix as the *helix pitch* of the continuous helix remains the same (i.e., $c/2$).

Note 8: See also *helicity*, *left-handed helix*, *right-handed helix*.

Note 9: Modification of the definition in [2–4].

3.1.14 helix chirality

See *helicity*.

3.1.15 helix pitch, p , SI unit: m

Distance between successive helical windings projected on the *chain axis*.

Note: The value of p is obtained from the equation

$$p = \frac{c}{N}$$

where c is the *chain identity period* and N is the number of helical windings in c .

3.1.16 helix residue

Smallest set of successive *constitutional repeating units (CRUs)* from which the M_N helix can be generated.

Note 1: A helix residue (see Figs. 1 and 2) may consist of one or more CRUs. As an example, in the 2_1 *ideal crystalline conformation* of syndiotactic polypropylene (Fig. 2a), it consists of two monomer units correlated by a twofold symmetry axis orthogonal to the *chain axis*. In the case of the crystallographic 2_1 helix of polyisobutylene, i.e., poly(2-methylpropene) (Fig. 2b), the helix residue is formed by 4 CRUs, which also constitute the CRU while 8 CRUs are present in the *translational chain repeating unit*.

Note 2: Modification of the definition in [2–4].

3.1.17 helix sense

See *helicity*.

3.1.18 ideal crystalline chain conformation

Minimum energy *conformation* of an isolated polymer chain constructed according to the *equivalence postulate* and approximating the conformation found in a crystalline phase.

Note 1: If the symmetry elements present in the crystal do not correspond with those that characterize the ideal crystalline chain conformation, the chain conformation may be distorted in the crystal.

Note 2: Symmetry elements characterizing the ideal crystalline chain conformation may be non-crystallographic (see 3.1.25), i.e., they may not apply to the packing in certain *crystal polymorphs* (see 3.2.6). For example, the ideal crystalline chain conformation of iso-

tactic polypropylene is a 3_1 helix but, while the β -phase crystal structure allows for the helical 3_1 symmetry operator, the α - or the γ -phases of this polymer do not [12–14].

3.1.19 left-handed helix, L , M

Helix in which the continuous helical line, approximating the sequence of bonds along the polymer main chain, winds clockwise moving towards the observer, i.e., seen from the positive axis direction (see Figs. 1 and 2).

Note 1: Developed from helix sense in [2–4].

Note 2: In compliance with prevailing stereochemical terminology conventions the descriptor M (minus) is recommended rather than L , presently widely used in polymer literature.

Note 3: See also *helix*, *helicity*, and *right-handed helix*.

3.1.20 line repetition group

See *rod group*.

3.1.21 multiple helix

Helical arrangement comprising two or more intertwined helical chains sharing the same axis.

Note: The intertwined helical chains are usually identical and displaced along the *chain axis* direction by c/n , where c is the *chain identity period* of the single helix and n the number of helices in the multiple helix.

3.1.22 physical repeating distance

See *chain identity period*.

3.1.23 physical repeating unit

See *translational chain repeating unit*.

3.1.24 right-handed helix, R , P

Helix in which the continuous helical line, approximating the sequence of bonds along the polymer main chain, winds anticlockwise moving towards the observer, i.e., seen from the positive axis direction (see Figs. 1 and 2).

Note 1: Developed from helix sense in [2–4].

Note 2: In compliance with prevailing stereochemical terminology conventions, the descriptor P (plus) is recommended rather than R , presently widely used in polymer literature.

Note 3: See also *helix*, *helicity*, and *left-handed helix*.

3.1.25 rod group line repetition group

Symmetry group of a three-dimensional array of atoms, regularly repeating along one direction.

- Note 1:* The symmetry of isolated polymer chains, with translational periodicity along the *chain axis* direction, may be described by either the rod group [9], or the equivalent line-repetition-group [2,12] approach. Whereas the line-repetition-group description has been developed in the polymer science community, rod groups [9] originate in the crystallographic community and are more systematic. Table 1 shows the symmetry group symbols of some linear polymers according to both the rod-group and the line-repetition-group description.
- Note 2:* Details concerning the symbols used are explained in crystallographic literature [6–9] for rod groups and in references [2,12] for line repetition groups.
- Note 3:* For reasons related to space filling, in the case of crystallographic rod groups [9], only two-, three-, four-, and sixfold screw axes are taken into consideration. Such limitations do not exist in the case of isolated chains for which any helical symmetry may, in principle, be acceptable. In other words, rod groups in [9] are a subset of those applicable to *ideal crystalline chain conformations*.
- Note 4:* The examples given in Table 1 pertain to linear polymers and apply to *ideal crystalline chain conformations*, whereas the crystallographic symmetry of the chain in the crystal is often lower, i.e., some symmetry elements applicable to the ideal crystalline chain conformation do not apply to the crystalline packing.
- Note 5:* Modified from the entry line repetition groups in [2–4] on the basis of the *International Tables of Crystallography*, Vol. E, ref. [9].

Table 1 Ideal crystalline chain symmetries of some *crystalline polymers*.^a

| Rod group [9] | Line repetition group [2,12] | Polymer |
|---------------|------------------------------|--|
| $p1$ | $t1$ | (<i>E</i>)-1,4-Polyisoprene, i.e., poly[(<i>E</i>)-1-methylbut-1-ene-1,4-diyl] |
| $p3_1$ | $s(3/1)$ | Isotactic polypropylene ($M_N = 3_1$, see def. 3.1.13) |
| $p222_1$ | $s(2/1)$ | Syndiotactic polypropylene ($M_N = 2_1$, helical modifications I and II) |
| $pm11$ | tm | Nylon 7,7, i.e., poly[<i>N,N'</i> -(heptane-1,7-diyl)heptanediamide] |
| $pc11$ | tc | Poly(vinylidene fluoride), i.e., poly(1,1-difluoroethene) (modification II) |
| $p\bar{1}$ | ti | (<i>E</i>)-1,4-Poly(2,3-dimethylbutadiene) |
| $p211$ | $t2$ | Syndiotactic polypropylene (modification IV) |
| $pmcm$ | $s(2/1)dm$ | Polyethylene |

^aAlthough symbols are generally different, there is complete correspondence of symmetry elements in the rod group and the line repetition group conventions. In the former case, symmetry elements and their symbols are the standard crystallographic symmetry elements [6,9]. For line repetition groups, symbols are defined in references [2,12].

3.1.26 rotation per helix residue, t , unit: rad unit twist

Angle of rotation about the *chain axis* per *helix residue*.

Note: The value of t is obtained from the equation

$$t = \frac{2\pi N}{M}$$

where N is the number of helix turns in a *chain identity period* c and M is the number of helix residues in c . In cases where the *equivalence postulate* does not apply, t is an average value.

3.1.27 stem

Rodlike portion of a polymer chain, usually comprising a few *translational chain repeating units*, and connected to non-rod-like portions, or chain ends, or both.

Note: Modification of the definition in [2–4].

3.1.28 translational chain repeating unit physical repeating unit fiber repeat unit

Smallest structural unit of a polymer chain that is repeated by translation in the crystal lattice along the *chain axis*.

Note: The translational chain repeating unit may differ for different *crystal polymorphs* of a given *crystalline polymer*.

3.1.29 unit height

See *axial advance per constitutional repeating unit*.

3.1.30 unit twist

See *rotation per helix residue*.

3.2 Packing of chains in polymer crystals

3.2.1 anticlinal stems

Stems in a crystal having opposite side-group orientations with respect to the *chain axis* (see Fig. 3a).

Note 1: Anticlinal stems occur in crystalline poly- α -olefins, and also in regioregular poly(3-alkylthiophenes), polyphosphazenes, and polysiloxanes.

Note 2: See 3.2 in [3, Chap. 2] and the entry “isomorphous structures” in [4].

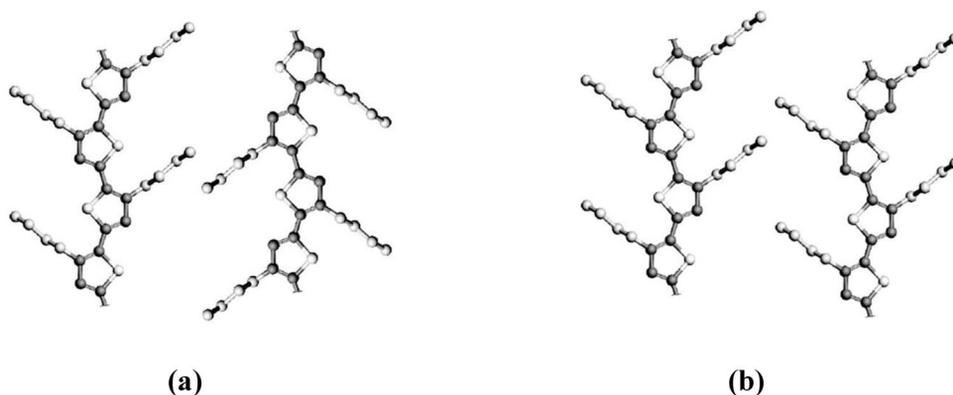


Fig. 3 (a) Pairs of *anticlinal stems* and (b) pairs of *isoclinal stems* of regioregular poly(3-butylthiophene), i.e., poly(3-*n*-butylthiophene-2,5-diyl), see definitions 3.2.1 and 3.2.9. Since regioregular poly(3-*n*-butylthiophene-2,5-diyl) is also a *directional chain*, (a) is an example of *antidiagonal packing* of two chains, while (b) is an example of *isodirectional packing*.

3.2.2 antidiagonal packing antiparallel packing

In a *parallel-chain crystal*, the crystalline packing of *directional stems* with opposite *chain axis* orientations.

Note 1: See also *parallel-chain crystal*.

Note 2: Usually, *stems* of opposite orientations occur in equal numbers in parallel-chain crystals.

3.2.3 antiparallel packing

See *antidiagonal packing*.

3.2.4 crystal modification

See *crystal polymorph*.

3.2.5 crystal polymorph crystal modification crystalline form

One of the different crystalline phases in which a given substance is able to crystallize.

Note 1: Different polymer crystal polymorphs are characterized by different crystal lattices and different packing of *stems*.

Note 2: A given polymer in its different crystal polymorphs may display the same *conformation* and the same *chain identity period*, but possibly involve packing of isochiral only or of enantiomeric helices (e.g., isotactic polypropylene in its α -form, β -form, and γ -form [14]; syndiotactic polypropylene, forms I and II [12,13]). Polymorphs are, in such cases, isoconformational, and polymorphism is determined only by different modes of packing.

Note 3: In other cases, along with the packing, the *local conformations* of chains are different in its different crystal polymorphs. The chain identity period and the symmetry will also differ (e.g., isotactic poly(but-1-ene), crystal forms I, II, and III; syndiotactic polypropylene, crystalline forms I, III, and IV) [10–13].

Note 4: See also the entry “polymorphic transition” in [4].

3.2.6 crystalline form

See *crystal polymorph*.

3.2.7 frustration

Feature of crystalline packing characterized by different crystalline arrangements of chain *stems* at two (or more) sites that would be expected to be equivalent.

Note 1: The term “frustration” signifies that some chains can achieve the minimum energy *conformation* or an optimal packing arrangement, while others cannot.

Note 2: An example of a *crystalline polymer* structure exhibiting frustration is the β -polymorph of isotactic polypropylene [14d].

3.2.8 isochiral stem packing

Crystalline packing of *stems* having the same *helicity*.

Note: The term is applicable to macromolecules that are chiral or adopt a chiral *conformation* in the crystal (e.g., a helical conformation).

3.2.9 isoclinal stems

Stems in a crystal having the same side-group orientation with respect to the *chain axis* (see Fig. 3b).

Note 1: Isoclinal stems occur, for example, in crystalline poly- α -olefins, regioregular poly(3-alkylthiophenes), polyphosphazenes, and polysiloxanes .

Note 2: See 3.2 in [3, Chap. 2] and the entry “isomorphous structures” in [4].

3.2.10 isodirectional packing parallel packing

In a *parallel-chain crystal*, the crystalline packing of *directional stems* with the same *chain axis* orientation.

Note 1: See also *parallel-chain crystal*.

Note 2: The term “isodirectional packing” is less ambiguous than the more common “parallel packing”. The latter is often used in the description of crystalline polymorphs of natural polymers (e.g., cellulose I [15]).

Note 3: Crystal packings in which all chains are isodirectional are very unlikely in the case of synthetic polymers except in as-polymerized systems, provided a directional extended-chain crystallization process immediately follows polymerization.

3.2.11 packing of chain stems

Spatial arrangement of polymer chain *stems* in a *polymer crystal*.

Note 1: Crystals require tridimensional translational periodicity in their packing.

Note 2: The mode of packing is influenced by the kinetics and thermodynamics of the crystallization process. In some cases, pre-existing structural organization and *chain folding* may also play a role.

3.2.12 parallel packing

See *isodirectional packing*.

3.2.13 polymorphic polymer crystal

Polymer crystal formed by domains of different *crystal polymorphs* of the same polymer.

Note: Isotactic polypropylene has been shown to form crystals containing α - and γ -phase domains in which well-defined relationships between the lattices of the two phases [16] in different domains are preserved.

3.2.14 racemic packing

Packing in a polymer crystal in which stems of opposite *helicity* coexist in equal numbers.

Note: Applicable to macromolecules that are chiral or adopt chiral conformations in the crystal. One example of the former case is the crystal structure in which poly(L-lactide) and poly(D-lactide) *stems* coexist in equal numbers, i.e., the so-called poly(lactide) stereo-complex [17]. The second case is much more frequent: it applies to most isotactic vinyl polymer *crystal polymorphs* where the polymer chains are not intrinsically chiral but adopt helical, and thus chiral conformations. *Left-handed helices* and *right-handed helices* are, however, isoenergetic and equiprobable and coexist in equal numbers, often giving rise to centrosymmetric crystals. Examples are the α - and γ -*crystal polymorphs* of isotactic polypropylene [11d,12–14] the rhombohedral *crystal polymorph* $R\bar{3}c$ of isotactic polystyrene [10,11d,12,13].

3.2.15 symmetry breaking in (polymer) crystals

Vanishing, in a specific *crystal polymorph*, of selected symmetry elements present in other crystal polymorphs, or in selected minimum energy *conformations* of isolated molecules of a given substance.

Note 1: The symmetry elements that vanish are frequently intramolecular. Symmetry breaking in polymers [13] in such cases leads to deviations from the *ideal crystalline chain conformation* and from the *equivalence postulate*.

Note 2: Crystal polymorphs affected by symmetry breaking are usually stable at low temperature under conditions that optimize packing energy.

3.3 Disorder in polymer crystals

3.3.1 configurational disorder

Structural disorder resulting from the co-crystallization of different configurational repeating units [2,3].

Note: The term is applicable to some atactic polymers (e.g., poly(vinyl fluoride)).

3.3.2 conformational disorder

Structural disorder within crystals resulting from the coexistence of identical configurational repeating units with different *conformations*.

Note 1: Conformational disorder may affect main chains, side chains, or both.

Note 2: Modification of the definition in [2–4].

3.3.3 lattice distortion

Structural disorder resulting from the misalignment or distortion of *unit cells* within crystals.

3.3.4 orientational disorder

Structural disorder at given crystallographic positions, resulting from the statistical coexistence within crystals of *directional stems* with opposite orientations.

Note 1: A typical example is provided by the statistical coexistence of chains with opposite orientations at each crystallographic position in the crystal structures of poly- α -olefins, for example, in the α -form of polypropylene [11d,12–14a].

Note 2: Adapted from the definition of “chain-orientational disorder” in [2–4].

3.3.5 paracrystal

Crystal model characterized by *lattice distortions* and hence by limited order along given lattice directions [18].

3.3.5.1 correlated paracrystalline disorder

See *paracrystalline disorder of the second kind*.

3.3.5.2 paracrystalline disorder of the first kind uncorrelated paracrystalline disorder

Structural disorder in a *paracrystal*, resulting from uncorrelated displacements of the atoms around their average positions.

Note: Displacements are generally due to thermal vibrations.

3.3.5.3 paracrystalline disorder of the second kind correlated paracrystalline disorder

Structural disorder in a *paracrystal*, resulting from permanent atomic displacements from the ordered crystallographic positions.

3.3.5.4 paracrystalline distortion factor, g_{ik}

Ratio of the statistical fluctuation Δa_{ik} of a lattice vector a_i along the direction a_k

$$g_{ik} = \frac{\Delta a_{ik}}{a_k}$$

Note 1: Values of g range from 0 (distortion-free crystal) to 0.03 (typical bulk polymer), to 0.12 (SiO_2 glass) to 1 (Boltzmann gas).

Note 2: g can be determined from measurements of the integral breadth of successive orders of Bragg reflections [18b].

3.3.5.5 uncorrelated paracrystalline disorder

See *paracrystalline disorder of the first kind*.

3.3.6 structural disorder

Any deviation from the ideal three-dimensional regularity of the polymer crystal structure.

Note 1: Structural disorder may be either static or dynamic. An example involving the former is *orientational disorder*, while examples of dynamic disorder are the inter-conversion between different side-chain conformations in the crystalline structures of higher poly- α -olefins, poly(3-alkylthiophenes), or poly(dialkylphosphazenes).

Note 2: Solid-state NMR spectroscopy may distinguish between static and dynamic structural disorder.

Note 3: Diffraction techniques may reveal structural disorder, usually with no distinction between static and dynamic.

3.4 Polymer co-crystals

3.4.1 crystalline polymer-inclusion complex

Crystal comprising a polymer guest within a low-molar-mass host.

Note 1: A number of different crystalline polymer-inclusion complexes may be obtained, for example, by the crystallization of polyethylene, 1,4-polybutadiene, and other polymers within urea [10], perhydrotriphenylene [10,19], or cyclotriphosphazene [20] crystals.

Note 2: The *stems* in polymer inclusion complexes are generally isolated. They are often not conformationally ordered.

Note 3: See also the entry “inclusion compound” in [4].

3.4.2 crystalline-polymer molecular complex

Crystalline molecular complex between different polymers.

Note: Very few examples of polymer complexes are known. The best characterized is the complex of isotactic and syndiotactic poly(methyl methacrylate) [21].

3.4.3 isomorphous polymer co-crystal

Crystal consisting of two or more structurally different polymers, resulting in *macromolecular isomorphism*.

Note 1: See also *macromolecular isomorphism*.

Note 2: Examples are polytetrafluoroethene and poly(vinylidene fluoride), poly(3-hydroxybutanoate), and poly(3-hydroxypentanoate) [22].

3.4.4 macromolecular isomorphism

Shape-similarity of different *constitutional repeating units (CRUs)* [22] allowing statistical cocrystallization within the same crystal structure.

Note 1: The different CRUs may either belong to the same copolymer chain (*copolymer isomorphism*) or originate from different homopolymer chains (*homopolymer isomorphism*).

Note 2: Isomorphism means that the crystal structure is essentially the same throughout the complete range of compositions, except for minor lattice constant variations; in the cases of isodimorphism or isopolymorphism, two or more crystal structures, respectively, are required to cover the complete range of compositions.

Note 3: Different from the definition in [2–4].

3.4.4.1 copolymer isomorphism

Macromolecular isomorphism involving copolymers.

Note: Examples are isotactic copolymers of propene and but-1-ene, copolymers of propene and ethene, and various polyesters [22].

3.4.4.2 homopolymer isomorphism

Macromolecular isomorphism involving two homopolymers with different *constitutional repeating units*.

Note: See also *isomorphous polymer co-crystals*.

3.4.5 nanoporous polymer crystal

Polymer crystal presenting empty volume elements that can host low-molar-mass guest species.

Note: A nanoporous polymer crystal is often obtained (e.g., in the case of syndiotactic polystyrene) by removing the low-molar-mass guest species from a *polymer clathrate* [23].

3.4.6 polymer-based crystalline molecular complex

See *polymer co-crystal*.

3.4.7 polymer clathrate

Polymer co-crystal in which low-molar-mass guest species are hosted in molecular-sized cages or cavities containing more than one guest molecule.

Note 1: Polymer clathrates are formed by many polymers with low-molar-mass compounds, particularly water. Examples are frequent among biological polymers (e.g., amylose) but also some synthetic polymers give polymer clathrates (e.g., poly(ethylene oxide) with various inorganic and organic species).

Note 2: Guest molecules are often packed isolated from each other or in columns.

3.4.8 polymer co-crystal polymer-based crystalline molecular complex polymer mixed crystal

Crystal structure in which at least two substances coexist, one of which is a polymer.

Note 1: Types of polymer co-crystals are: (1) *polymer clathrate*, (2) *isomorphous polymer co-crystal*, (3) *crystalline polymer-inclusion complex*. Examples are provided under each separate entry.

Note 2: See also *polymer co-crystallization*.

3.4.9 polymer mixed crystal

See *polymer co-crystal*.

4. MOLECULAR CONFORMATION WITHIN POLYMER CRYSTALS [24–26]

4.1 adjacent re-entry model

Model of *folded-chain crystal* in which *chain folds* regularly connect adjacent *stems* along the *fold plane*.

Note 1: The adjacent re-entry model includes both the *regular adjacent re-entry* and the *irregular adjacent re-entry model*.

Note 2: Modification of the definition in [2–4].

4.1.1 irregular adjacent re-entry model

Adjacent re-entry model in which the *fold period* can vary.

4.1.2 regular adjacent re-entry model

Idealized *adjacent re-entry model* in which the *fold periods* are assumed to have all the same length.

Note: This model is probably only approached for isothermal growth at small *supercooling* from dilute solution.

4.2 chain-extended crystal

Folded-chain crystal in which each macromolecule makes one, or, at most, a few *folds*.

4.3 chain folding

Conformational feature in which a loop connects two adjacent *stems* belonging to the same *polymer crystal*.

Note: Modification of the definition in [2–4].

4.4 extended-chain crystal

Polymer crystal in which the chains are in a fully extended conformation, i.e., each chain forms a single *stem*.

4.5 fold

Looped section of a polymer chain connecting two *stems* in a *folded-chain crystal*.

Note: Modification of the definition in [2–4].

4.6 fold length

See *fold period*.

4.7 fold period, L_f , SI unit: m fold length

Thickness of a lamellar *parallel-chain crystal* in the direction of its *stems*.

Note 1: The fold period corresponds to the *long period* in the case of solution crystallized stacked lamellar crystals with the *chain axis* perpendicular to the lamellar surface.

Note 2: In melt-crystallized polymers, consisting of *lamellar crystals* with the chain axis perpendicular to the lamellar surface, the fold period is shorter than the long period because the amorphous layer includes not only the *folds* but other non-crystallized components.

Note 3: For lamellar crystals with chains whose axes are not normal to the lamellar surface, the fold period is longer than the long period.

Note 4: The fold period is controlled by the crystallization temperature.

4.8 folded-chain crystal

Polymer crystal consisting predominantly of macromolecules that traverse the crystal repeatedly by folding as they emerge at its external surfaces.

Note: The re-entry of the macromolecule into the crystal is generally assumed to be at adjacent or near-adjacent *stems* in the lattice (see *adjacent re-entry model*). In some cases, the *switchboard model* may, however, apply.

4.9 fringed-micelle model

Model of a *crystalline polymer* in which the various crystallized segments of individual macromolecules belong predominantly to different crystals.

Note: Modification of the definition in [2–4].

4.10 globular-chain crystal

Polymer crystal comprised of macromolecules having globular *molecular conformations*.

Note 1: Globular proteins usually form globular-chain crystals.

Note 2: Modification of the definition in [2–4].

4.11 non-parallel-chain crystal

Polymer crystal in which the *stems* are aligned along two or more different crystallographic directions.

Note: So far, the only example of non-parallel-chain polymer crystal is the γ -polymorph of isotactic polypropylene, where double-layers of parallel chains alternate with identical double-layers rotated by approximately 80° [14b].

4.12 parallel-chain crystal

Polymer crystal resulting from a *parallel packing* of *stems*, irrespective of possible opposite stem orientation.

Note 1: In the literature, the term is often used inappropriately referring to parallel-chain crystals with *isodirectional packing* of stems, as opposed to parallel-chain crystals with *antidirectional packing*. This distinction is, of course, only relevant for polymers with *directional chains*.

Note 2: According to the present definition, parallel-chain crystals of directional chains may, in principle, show three main types of packing: (1) *isodirectional packing*, with all chains in a given crystal sharing the same orientation; (2) *antidirectional packing*, with chains alternating in direction along at least one lattice plane (as required by *chain folding* and the *adjacent re-entry model*); and (3) packing of the chains with various degrees of *orientational disorder*.

Note 3: Modification of the definition in [2–4].

4.13 solidification model

Model of *crystalline polymer* formed by lamellar crystallization from the *melt*, in which some stems of a macromolecule belong to one crystal, whilst other stems of the same macromolecule are in different crystals.

4.14 switchboard model

Model of a *folded-chain crystal* in which chain *folds* connect *stems* within the same crystal and essentially at random distances from each other.

Note 1: In crystals where this model applies, adjacent stems are often not from immediately consecutive portions of the macromolecule.

Note 2: Modification of the definition in [2–4].

4.15 tie molecule (in polymer science)

Molecule comprising segments that connect different crystals.

5. MORPHOLOGICAL ASPECTS [24–27]

5.1 amorphous domain

Phase domain consisting of matter in the *amorphous state*.

Note: The linear dimensions of *amorphous domains* in *crystalline polymers* range from 1 nm upwards.

5.2 axialite

Multilayer aggregate consisting of *lamellar crystals* growing out from a common edge, or from a common (screw dislocation) axis [24–26].

Note 1: In many instances, axialites are *spherulites* at early development stages.

Note 2: If grown on a substrate and if the axis is normal to the substrate, a *hedrite* can develop.

Note 3: If an axialite is grown in solution, or if the axis of the axialite is parallel to the substrate, the lamellae tend to splay as they grow.

Note 4: Modification of the definition in [2–4].

5.3 bundle crystal

Crystal in which the chains predominantly extend from the crystal surface, resulting in a *fringed-micelle model* morphology.

5.4 dendrite

Crystalline morphology having a “tree-like” appearance [2–4,24–26].

Note 1: Dendrites are generally crystallographically *single crystals* or twins sharing a common orientation.

Note 2: Modified from the definition in [2–4].

5.5 fold domain

Portion of a *polymer crystal* wherein the *fold planes* have the same orientation [2–4].

Note 1: The term generally applies to solution-crystallized polymer *lamellar crystals*.

Note 2: *Lamellar crystal sectors* are frequently fold domains.

5.6 fold plane

Crystallographic plane containing a large number of *stems* connected by *chain folding*.

Note 1: The term generally applies to solution-crystallized polymer *lamellar crystals* but, in some cases, also to melt-crystallized crystals.

Note 2: Fold planes are normally assumed to be parallel to the lateral crystal face in the corresponding *fold domain*, while angles between fold planes and the *fold-surface* are usually close to 90° but in some instances can be as low as 45°.

Note 3: Modification of the definition in [2–4].

5.7 fold surface

Each of the two basal surfaces of a *folded-chain crystal*, in which the *folds* approximately lie.

Note: Modification of the definition in [2–4].

5.8 hedrite

Polyhedral aggregate of *lamellar crystals* resulting in a morphology that resembles that of a *polymer single crystal*, at least from one viewing direction.

Note: A hedrite is a type of *axialite*.

5.9 lamellar crystal

Crystal of large extension in two dimensions and of relatively small and uniform thickness [24–27].

Note 1: A lamellar crystal usually has a thickness between 5 and 50 nm, while lateral dimensions can reach a few μm . It may be found individually or in aggregates. The parallel-chain *stems* intersect the lamellar plane at an angle between 45° and 90° .

Note 2: The lamellae often have a pyramidal shape, or present corrugations, owing to differences in their *fold domains*; as a result, different *fold planes* and *fold surfaces* can result from the lamellar morphology.

Note 3: Modification of the definition in [2–4].

5.10 lamellar crystal sector

Portion of a *lamellar crystal*, often bounded by a well-defined crystal face.

Note 1: The term generally applies to solution-crystallized lamellar crystals. Sectors are described using the indexing of the crystal face bounding it.

Note 2: The *fold plane* prevailing in a sector is normally assumed to correspond to the crystal face bounding the sector.

Note 3: For some crystal morphologies, the *fold surfaces* of a sector make an angular discontinuity with the fold surfaces of contiguous sectors.

Note 4: Lamellar crystal sectors in *folded-chain crystals* correspond to *fold domains*.

5.11 lath crystal ribbon crystal

Lamellar crystal extending predominantly along one lateral dimension.

Note: Modification of the definition in [3,4].

5.12 long period, L , SI unit: m long spacing

Average periodicity (repeating distance) of the layers of *lamellar crystals* in a stacked assembly.

Note: The long period is usually measured by SAXS (small-angle X-ray scattering), SANS (small-angle neutron scattering), atomic force microscopy (AFM), or transmission electron microscopy (TEM), and is the sum of the average thickness of the lamellar crystals and the average thickness of the amorphous inter-lamellar region.

5.13 long spacing

See *long period*.

5.14 multilayer aggregate

Stack of *lamellar crystals* generated by a spiral growth at one or more screw dislocations or possibly by a single *primary nucleus*.

Note 1: Found in some solution crystallized polymers, like polyethylene [24–27] and poly[3,3-bis(chloromethyl)oxacyclobutane] [28].

Note 2: The *fold period* in the primary nucleus is plausibly greater than in the remainder of the crystals in the aggregate.

5.15 phase domain

Region of a material that is uniform in chemical composition and physical state [3,4].

5.16 polycrystalline polymer

Crystalline polymer in which a large number of *polymer crystallites* coexist.

Note: Polymer crystallites and *amorphous domains* in a specimen may be organized randomly or with some degree of order. Examples of ordered or partially ordered polycrystalline polymers are *polymer fibers*, *spherulites*, and *multilayer aggregates*.

5.17 polymer crystallite

Small polymer crystal.

Note 1: Typical lateral dimensions are a few nanometers.

Note 2: A polymer crystallite may have irregular boundaries, and its constituent macromolecules may extend beyond the boundaries of the crystallite.

Note 3: Polymer crystallites generally crystallize from the *melt*, from the *glassy state*, or from concentrated solutions giving rise to a *polycrystalline polymer*.

Note 4: Modification of the definition in [2–4].

5.18 polymer fiber

Uniaxially oriented polymer filament with macroscopic cylindrical symmetry, in which the average direction of the polymer chain axis coincides with the cylindrical symmetry axis.

Note 1: A crystalline polymer fiber generally consists of *lamellar crystals* or fringed micelle-type crystals (see *fringed micelle model*) with an interconnecting amorphous phase, or, rarely, of *extended-chain crystals*.

Note 2: The cylindrical symmetry shown by crystalline polymer fibers is not at the molecular scale but results from the random orientation of crystallites around the axis of the fiber.

5.19 polymer fibril

Small diameter *polymer fiber* consisting of a small number of polymer chains.

5.20 polymer single crystal

Individually distinct *polymer crystal* whose lattice, at crystallization, is characterized by a single orientation.

Note 1: Polymer single crystals obtained from dilute solutions are comparatively large, i.e., they have lateral dimensions typically of a few micrometers, which can reach tens of micrometers in some instances. They are normally delimited by well-defined boundary surfaces and may, in rare instances, be manipulated individually.

Note 2: The thickness of individual polymer single crystals (inclusive of the *fold surfaces* thickness) is now measured by AFM (atomic force microscopy) along with transmission electron microscopy, while average values are derived using SAXS (small-angle X-ray scattering) and SANS (small-angle neutron scattering).

Note 3: See also *polymer crystal* and *twinned polymer crystal*.

5.21 ribbon crystal

See *lath crystal*.

5.22 row structure

Polycrystalline polymer morphology resulting from *nucleation* of polymer *lamellar crystals* by multiple fibrillar structures or by macroscopic linear objects such as fibers.

Note 1: *Shish-kebab structures* are the simplest form of row structures.

Note 2: Row structures result frequently by *heteroepitaxy*.

5.23 shish-kebab structure

Polycrystalline polymer morphology consisting of a linear fibril-like core (*shish*) of predominantly extended polymer chains overgrown epitaxially by *lamellar crystals* (*kebabs*), the *stems* of which are parallel to the fibril axis.

Note 1: Shish-kebab structures result usually by *homoepitaxy* and can be considered the simplest form of *row structures*.

Note 2: Modification of the definition in [2–4].

5.24 spherulite (in polymer science)

Approximately spherical polycrystalline object emanating from a common center and consisting of a continuously diverging skeleton produced by frequent splaying and branching of *lamellar crystals* [26].

Note 1: Spherulite dimensions can range from micrometers to centimeters, depending essentially upon the presence of impurities giving rise to *heterogeneous nucleation*, upon the regularity of the polymer, upon crystallization procedures, and upon thermal treatments.

Note 2: The center of a spherulite is often similar to that of an *axialite*, but splaying is generally predominant, leading to spherical symmetry after sufficient growth.

Note 3: If the *primary nucleus* consists of a foreign particle, *nucleation* may occur at various sites of the particle, with different initial lamellar orientations. Splaying will occur but the similarity to an axialite at the center of the spherulite will be missing.

Note 4: The initial outgrowing, splaying *dominant lamellae* define the spherulite boundary, with the interstices filled by *subsidiary lamellae*.

- Note 5:* Growth continues, usually until impingement between spherulites occurs, with some interpenetration of dominant lamellae at the boundaries.
- Note 6:* The more frequent the branching of the dominant lamellae and the greater the angle of divergence (splay), the smaller the radius at which the near-spherical envelope will be achieved in unimpeded growth.
- Note 7:* Reduced branching and smaller splay may extend the early, non-spherically symmetric, often axialitic, objects to greater radii and leave more space to be filled in by subsidiary lamellae and by *amorphous polymer*.
- Note 8:* If crystallization takes place in a film whose thickness is much smaller than the spherulite radius, the spherulite becomes, in essence, a two-dimensional circular section of a sphere at its equator.
- Note 9:* Amorphous polymer will be segregated between subsidiary lamellae within the spherulite, and between different spherulites.
- Note 10:* Modification of the definition in [3,4], see also *axialite*.

5.24.1 dominant lamellae (in a spherulite)

Lamellar crystals radiating from the center of the *spherulite* which, by splaying, constitute the initial skeleton of the spherulite.

- Note 1:* Crystallization of dominant lamellae is largely associated with *primary crystallization*.
- Note 2:* In the *isothermal crystallization* of *crystalline polymers* there is normally a single population of dominant lamellae, characterized by a single thickness.
- Note 3:* The thickness and perfection of dominant lamellae is greater than for *subsidiary lamellae*, especially in *non-isothermal crystallization*.

5.24.2 infilling lamellae (in a spherulite)

See *subsidiary lamellae*.

5.24.3 subsidiary lamellae (in a spherulite) infilling lamellae (in a spherulite)

Lamellar crystals nucleated either epitaxially or incoherently on *dominant lamellae*.

- Note 1:* Subsidiary lamellae can appear as pockets of lamellae in different locations within a *spherulite*, with no well-defined relation to dominant lamellae.
- Note 2:* Crystallization of subsidiary lamellae is generally associated with *secondary crystallization*, but may start before dominant lamellae meet at spherulite boundaries.
- Note 3:* The thickness and perfection of subsidiary lamellae is reduced as compared to dominant lamellae, especially in *non-isothermal crystallization*.
- Note 4:* In typical *crystalline polymers* there may be populations of subsidiary lamellae characterized by bimodal thickness distributions.

5.25 transcrystalline layer

Polycrystalline layer nucleated and shaped by a pre-existing planar surface within or in contact with a *polymer melt*.

- Note 1:* Examples are crystallization around macroscopic fibers in a polymer-fiber composite or at the surface of injection-molded articles (see also *row structure*).
- Note 2:* In growth from unoriented melts, as in compression-molding, the transcrystalline layer consists of closely spaced, highly asymmetric *spherulites*, nucleated on the surface and elongated in the direction normal to the surface of the molded articles.
- Note 3:* In growth from oriented melts, as in injection-molding, two transcrystalline layers may result. The first is the skin layer and is formed by individual lamellae, while the second consists of spherulites. Both grow preferentially in the direction perpendicular to the flow direction and the external surface of the molded articles.

5.26 twinned polymer crystal

Polymer crystal in which two or more single crystalline domains of the same *crystal polymorph*, with different lattice orientations, coexist.

- Note 1:* Some of the lattice directions, very often the chain axis directions, remain parallel in the different domains of twinned crystals.
- Note 2:* The lattice orientations in the different domains of twinned crystals are generally symmetry-related.
- Note 3:* See also *polymer crystal* and *polymer single crystal*.

6. POLYMER CRYSTALLIZATION [24–27,29–32]

6.1 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.

- Note 1:* Annealing of a *crystalline polymer* is usually carried out by keeping the polymer at temperatures close to but somewhat 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 vapors.
- Note 3:* In a crystalline polymer, the process of annealing leads to *reorganization*, including possibly increase of order in existing *polymer crystallites*, increase of *degree of crystallinity*, increase in *fold period*, and changes to more stable *crystal polymorphs*.

6.2 Avrami equation

Equation describing crystallization kinetics, of the form

$$\Phi_c = 1 - \exp(-Kt^n)$$

where Φ_c is the crystalline volume fraction developed at constant temperature after a time t has elapsed. K and n are parameters. K is temperature-dependent.

Note 1: According to the original theory [33], n is an integer (or a half-integer) from 1 to 4. Considering different heterogeneous or multistage nucleation modes, additional non-integer values may be considered [30] and, analyzing data, n is often treated as an adjustable parameter.

Note 2: Modification of the definition in [2–4].

6.3 cellulation

Division of the growth front of individual or groups of *dominant lamellae* into divergent “cells”, with the impurities and the less crystallizable molecules segregated between the cells and at the *spherulite* boundaries.

6.4 cold crystallization

Polymer crystallization 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*.

6.5 confined-spaces crystallization

Polymer crystallization occurring inside elongated cavities, spheres, galleries, or layers formed by a host material different from the polymer.

Note 1: Morphology and polymorphism may be significantly affected by confined crystallization.

Note 2: At least one dimension of the cavities must be of the order of a few nanometers, i.e., close to typical dimensions of a *polymer crystallite* and, in particular, to lamellar thickness.

Note 3: *Stems* may be isolated in the cavities of the frequently nonpolymeric host material, as in the cases of zeolites and the fully *trans*-form of perhydrotriphenylene in the crystalline state. In such cases, the polymer stems are usually highly disordered [19].

Note 4: Stems may aggregate in small, disordered *bundle crystals* or in relatively large *lamellar crystals*, typically within layered inorganic materials.

Note 5: Spherical structures may result from the crystallization of one of the two components in a heterogeneous polymer blend (e.g., in a polyethylene-polycarbonate blend) [34] while lamellar, hexagonally packed cylindrical and inverse cylindrical morphologies are frequent in block copolymers [35a] with a crystallizable block (e.g., in poly(ethylene oxide)-*block*-polystyrene) [35b]).

6.6 degree of supercooling, ΔT , SI unit: K degree of undercooling

Temperature difference between the *equilibrium melting temperature* and the temperature of a *supercooled melt*.

6.7 degree of undercooling

See *degree of supercooling*.

6.8 epitaxial crystallization

Growth of crystals on other crystals involving a precisely defined mutual orientation of their lattices.

Note 1: The process involves *heterogeneous nucleation* of the growing crystals by the substrate crystal faces.

Note 2: The term *epitaxy* is used to define the relationship existing between the substrate crystals and those grown on top of them.

6.8.1 epitaxy

Ordered spatial relationship existing between the substrate crystals and those grown by *epitaxial crystallization* on top of the substrate crystals.

Note 1: If the crystals are of the same substance, but possibly of different *crystal polymorphs*, the term *homoepitaxy* is used, while *heteroepitaxy* involves crystals of two different substances.

Note 2: The term *epitaxy* is sometimes used for *epitaxial crystallization*. This use is not recommended.

Note 3: Examples involving polymers are given under the terms *homoepitaxy* and *heteroepitaxy*.

6.8.2 heteroepitaxy

Epitaxy between crystals of different substances.

Note 1: Heteroepitaxy may occur between crystals of different polymers. However, the heteroepitaxy of low-molecular-weight systems (e.g., alkanes) on *polymer crystals* (e.g., polyethylene), and of polymer crystals on crystals of low-molecular-weight substances can also occur. Heteroepitaxy has also been observed for polymer crystals on ionic substances and minerals like clay and mica [24,25].

Note 2: For some polymers, heteroepitaxy may be used to favor by *nucleation* the development of a crystalline phase that is not obtained normally.

Note 3: Polymer crystals with unusual orientations with respect to the substrate may be obtained by *epitaxial crystallization* involving heteroepitaxy.

Note 4: Heteroepitaxy is often used to enhance nucleation and reduce *spherulites'* size in commercial processes.

6.8.3 homoepitaxy

Epitaxy between crystals of the same substance.

Note 1: Homoepitaxy may occur between crystals of the same *crystal polymorph* but different morphology as in the crystallization of *chain-folded crystals* on fibril-like *extended-chain crystals* in *shish-kebabs*. Similarly, in *non-isothermal crystallization*, *lamellar crystals* of lower thickness are often nucleated on thicker crystals, preserving a unique orientation of the crystal lattice.

Note 2: A less frequent homoepitaxy may occur, as for the α -polymorph of isotactic polypropylene, between crystals of the same crystal polymorph and morphology but with a different, well-defined orientation of the crystal lattice [36].

Note 3: Homoepitaxy may allow the development of crystals of the same polymer but in two distinct crystal polymorphs with well-defined mutual orientations, as in the case of γ -isotactic polypropylene grown on α -isotactic polypropylene [37].

Note 4: A new crystal layer, initiated by *secondary nucleation*, or the formation of a *twinned polymer crystal*, can be seen as a form of homoepitaxy.

6.9 equilibrium melting temperature, T_m° , SI unit: K

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

Note 1: Crystallization or *recrystallization* of a given polymer can occur only at temperatures significantly below T_m° .

Note 2: The amount and type of structural defects in a polymer, such as comonomer units, and regularity errors, affect the actual melting temperature. In cases where the structural defects are included in the crystals, the equilibrium melting temperature is also affected.

6.10 glass

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

Note: 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.

6.11 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.

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

Note 2: In the case of polymers, conformational changes of segments, consisting typically of 10–20 main chain atoms, become infinitely slow below the glass-transition temperature.

Note 3: In *crystallizable polymers*, heating a polymer glass above the glass transition, very frequently leads to some crystallization, allowed by the onset of greater segmental mobility.

Note 4: The definition is different from that in [4].

6.12 glass-transition temperature (in polymer science), T_g , SI unit: K

Temperature at which the *glass transition* occurs.

- Note 1:* Crystallization rates of *crystallizable polymers* below T_g become infinitely slow.
- 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:* The glass-transition temperature can be determined by a number of different techniques, ranging from thermal analysis to dielectric relaxation, dynamic mechanical analysis, density, viscosity measurements, and spectroscopies which allow the determination of relaxation times.
- Note 4:* It may often be more useful to refer to a temperature range over which the *glass transition* occurs, rather than to a single transition temperature.
- Note 5:* The definition is different from that in [4].

6.13 glassy state

State of amorphous matter below its *glass-transition temperature*.

6.14 isothermal crystallization

Crystallization taking place at constant temperature.

6.15 melt

Matter in the *amorphous state* above its *glass-transition temperature*.

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

Note 2: See also *polymer melt*.

6.16 non-isothermal crystallization

Crystallization taking place under varying temperature conditions.

6.17 nucleation (in polymer crystallization) primary nucleation (in polymer crystallization)

Formation of the smallest crystalline entity (*primary nucleus*), the further growth of which is thermodynamically favored.

Note 1: *Homogeneous nucleation* or *heterogeneous nucleation* may occur.

Note 2: Modification of the definition in [2,3]. Different from the definition in [4].

6.17.1 heterogeneous nucleation

Nucleation taking place on a pre-existing surface.

6.17.2 homogeneous nucleation

Nucleation taking place in a homogeneous phase.

6.17.3 primary nucleation (in polymer crystallization)

See *nucleation*.

6.17.4 primary nucleus

The smallest crystalline entity, the further growth of which is thermodynamically favored.

Note: See also *nucleation*.

6.17.5 secondary nucleation

Nucleation of a new molecular layer on a growing crystal face.

Note: Secondary nucleation refers to the further growth of an already-existing crystal.

**6.17.6 self-nucleation
self-seeding**

Heterogeneous nucleation by crystals of the same polymer.

6.17.7 self-seeding

See *self-nucleation*.

6.18 polymer co-crystallization

Crystallization, within the same crystal, of a polymer and at least one other component.

Note: The following possibilities need to be considered: (1) a polymer and a low-molar-mass species forming a *polymer clathrate*; (2) a molecular complex of different polymers (see *polymer co-crystal*); and (3) different polymers displaying some degree of isomorphism (*isomorphous polymer co-crystal*).

6.19 polymer melt

Polymer in the *amorphous state* above its *glass-transition temperature*.

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

Note 2: The term applies both to *crystallizable polymers* and to polymers that are unable to crystallize. 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 crystallization does not occur (see *Note 3*), the term *supercooled melt* can be used to define more accurately the thermodynamic state of the system.

Note 3: When a crystallizable polymer undergoes crystallization (see also *degree of crystallinity* and *crystalline polymer*), the remaining amorphous component cannot be considered a polymer melt. Flow is inhibited by *polymer crystallites*, which physically crosslink the amorphous component or constrain it at the surface of *polymer crystals*.

6.20 primary crystallization

First stage of crystallization forming *spherulites*, considered to be completed when most of the spherulite surfaces impinge on each other.

Note 1: In *isothermal crystallization*, primary crystallization is often described by the *Avrami equation*, with modifications of the equation being used for *non-isothermal crystallization*.

Note 2: Primary crystallization ends when the crystallization of *dominant lamellae* is in essence completed, whereas *subsidiary lamellae* crystallize usually during both primary and *secondary crystallization*.

Note 3: Modification of the definition in [2–4].

6.21 recrystallization (in polymer science)

Reorganization of crystals proceeding through partial or complete melting, or dissolution in a solvent, either isothermally or during heating.

Note 1: Recrystallization 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 changes to a more stable morphology.

Note 2: Modification of the definition in [2,3]. Different from the definition in [4].

6.22 reorganization (in polymer crystallization)

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 (i.e., the *fold period*) increases.

Note 1: *Secondary crystallization* may be involved in the reorganization process.

Note 2: Reorganization may result from *annealing* or by exposure to a poor solvent, or to its vapor.

Note 3: Modification of the definition in [2–4].

6.23 secondary crystallization

Crystallization occurring after *primary crystallization*.

Note 1: Secondary crystallization usually proceeds at a lower rate than primary crystallization.

Note 2: Modification of the definition in [2–4].

6.24 segregation (in polymer crystallization)

Rejection of segments of macromolecules, or of a fraction of macromolecules, or of impurities, or of combinations thereof, from growing crystals [2,3].

Note 1: The rejected macromolecules are usually those of insufficient molar mass, differing constitution (e.g., branching), or configuration (e.g., tacticity) from those undergoing crystallization.

Note 2: In spherulitic growth from the *melt*, segregation can lead to *cellulation*.

Note 3: Different from the definition in [4].

6.25 supercooled melt undercooled melt

Metastable *melt* of a *crystallizable polymer* at temperatures below its *equilibrium melting temperature* T_m° .

Note 1: The term is not applicable to the amorphous component of a *crystalline polymer*, i.e., after crystallization has occurred.

Note 2: See also *polymer melt*.

6.26 supercooling undercooling

The process of cooling a *melt* to a temperature below its *equilibrium melting point*, without crystallization occurring.

6.27 undercooled melt

See *supercooled melt*.

6.28 undercooling

See *supercooling*.

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