

6: Definitions of Terms Relating to Crystalline Polymers

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PREAMBLE

The recommendations embodied in this document are concerned with the terminology relating to the structure of crystalline polymers and the process of macromolecular crystallization. The document is limited to systems exhibiting crystallinity in the classical sense of three-dimensionally periodic regularity. The recommendations deal primarily with crystal structures that are comprised of essentially rectilinear, parallel-packed polymer chains, and secondarily, with those composed of so-called globular macromolecules. Since the latter are biological in nature, they are not covered in detail here. In general, macromolecular systems with mesophases are also omitted, but crystalline polymers with *conformational disorder* are included.

After a listing of some general definitions relating to crystalline polymers (Section 1), the subject is divided into sections dealing, successively, with local structural arrangements at the scale of a few bond lengths (Section 2), morphological aspects (Section 3), molecular conformation within polymer crystals (Section 4) and, finally, kinetic aspects of crystallization (Section 5). An alphabetical index of terms is provided for the convenience of the reader.

This document relies on the basic definitions of terms in polymer science [1]. It was the second in a series published by the Commission on Macromolecular Nomenclature dealing with definitions of physical and physicochemical terms in the polymer field (for the first in the series, see Reference [2]).

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1 GENERAL DEFINITIONS

1.1 crystallinity

Presence of three-dimensional order on the level of atomic dimensions.

Note: Crystallinity may be detected by diffraction techniques, heat of fusion measurements, etc. Some amount of disorder within the crystalline region is not incompatible with this concept.

1.2 crystalline polymer

Polymer showing *crystallinity*.

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

Note 2: The range of order may be as small as about 2 nm in one (or more) crystallographic direction(s) and is usually below 50 nm in at least one direction.

1.3 degree of crystallinity

Fractional amount of *crystallinity* in a polymer sample.

Note 1: The assumption is made that the sample can be subdivided into a crystalline phase and an amorphous phase (the so-called two-phase model).

Note 2: Both phases are assumed to have properties identical with those of their ideal states, with no influence of interfaces.

Note 3: The degree of crystallinity may be expressed either as the mass fraction, w_c , or as the volume fraction, ϕ_c , the two quantities being related by

$$w_c = \phi_c \rho_c / \rho$$

where ρ and ρ_c are the densities of the entire sample and of the crystalline fraction, respectively.

Note 4: The degree of crystallinity can be determined by several experimental techniques; among the most commonly used are: (i) X-ray diffraction, (ii) calorimetry, (iii) density measurements, and (iv) infrared spectroscopy (IR). Imperfections in *crystals* are not easily distinguished from the amorphous phase. Also, the various techniques may be affected to different extents by imperfections and interfacial effects. Hence, some disagreement among the results of quantitative measurements of *crystallinity* by different methods is frequently encountered.

Note 5: The following expressions for $w_{c,\alpha}$, are recommended, where the subscript α specifies the particular experimental method used.

(i) *By X-ray diffraction*: the degree of crystallinity, $w_{c,x}$, is given by

$$w_{c,x} = I_c / (I_c + K_x I_a)$$

where I_c and I_a are the integrated intensities scattered over a suitable angular interval by the crystalline and the amorphous phases, respectively, and K_x is a calibration constant. If the sample is anisotropic, a suitable average of the diffracted intensity in reciprocal space must be obtained.

(ii) *By calorimetry*: the degree of crystallinity, $w_{c,h}$ is given by

$$w_{c,h} = \Delta_{\text{fus}} h / \Delta_{\text{fus},c} h$$

where $\Delta_{\text{fus}} h$ is the specific enthalpy of fusion of the sample and $\Delta_{\text{fus},c} h$ is the specific enthalpy of fusion of the completely *crystalline polymer* over the same temperature range.

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The value of $\Delta_{\text{fus,c}} h$ may be obtained by extrapolating $\Delta_{\text{fus}} h$ to the density of the completely *crystalline polymer*, which in turn may be obtained from x-ray diffraction data. The specific enthalpies of fusion are temperature-dependent.

(iii) *By density measurements*: the degree of crystallinity, $w_{\text{c,d}}$, is given by

$$w_{\text{c,d}} = \frac{\rho_c(\rho - \rho_a)}{\rho(\rho_c - \rho_a)}$$

where ρ , ρ_c and ρ_a are the densities of the sample, of the completely *crystalline polymer* and of the completely amorphous polymer, respectively.

(iv) *By infrared spectroscopy*: the degree of crystallinity, $w_{\text{c,i}}$, is given by

$$w_{\text{c,i}} = \frac{1}{a_c \rho l} \log_{10}(I_0/I)$$

where I_0 and I are, respectively, the incident and the transmitted intensities at the frequency of the absorption band due to the crystalline portion, a_c is the mass decadic absorption coefficient of the crystalline material and l is the thickness of the sample.

1.4 (polymer) crystal

Crystalline domain usually limited by well-defined boundaries.

Note 1: Polymer crystals frequently do not display the perfection that is usual for low-molar-mass substances.

Note 2: Twinned polymer crystals are, sometimes, erroneously referred to as ‘crystals’.

Note 3: Polymer crystals that can be manipulated individually are often called (polymer) single crystals. A single crystal may contain different *fold domains*.

1.5 (polymer) crystallite

Small crystalline domain.

Note 1: A crystallite may have irregular boundaries and parts of its constituent macromolecules may extend beyond its boundaries.

Note 2: This definition is not identical with that used in classical crystallography.

1.6 unit cell

Smallest, regularly repeating material portion contained in a parallelepiped from which a *crystal* is formed by parallel displacements in three dimensions [3].

Note 1: Unlike in the case of low-molar-mass substances, the unit cell of *polymer crystals* usually comprises only parts of the polymer molecules and the regularity of the periodic repetition may be imperfect.

Note 2: In the case of *parallel-chain crystals*, the chain axis is usually denoted by c or, sometimes, b .

Note 3: This definition applies to the so-called primitive unit cell. In practice, the effective unit cell may consist of more than one primitive unit cell.

1.7 molecular conformation

Conformation of the macromolecule as a whole.

Note 1: In the polymer literature, molecular conformation is sometimes referred to as macroconformation.

Note 2: In molecular conformations involving parallel *stems*, the latter may be confined to the same *crystal* or may also extend over several *crystals*.

1.8 local conformation

Conformation of a macromolecule at the scale of the constitutional units.

Note: In the polymer literature, local conformation is sometimes referred to as microconformation.

2 TERMINOLOGY RELATING TO LOCAL CONFORMATION AND STRUCTURAL ASPECTS [4]

2.1 chain axis

Straight line parallel to the direction of chain extension, connecting the centres of mass of successive blocks of chain units, each of which is contained within an *identity period* (see Fig. 1).

2.2 (chain) identity period

(chain) repeating distance

Shortest distance along the *chain axis* for translational repetition of the chain structure.

Note 1: The chain identity period is usually denoted by *c*.

Note 2: An example is given in Fig. 1.

2.3 (chain) conformational repeating unit

Smallest structural unit of a polymer chain with a given conformation that is repeated along that chain through symmetry operations [5].

2.4 geometrical equivalence

Symmetry correspondence among units belonging to the same chain.

Note: The symmetry elements always bear a special relationship to the *chain axis* (see also the note, Definition 2.9).

2.5 equivalence postulate

Working hypothesis that the chain monomeric units are geometrically equivalent [6].

2.6 helix

Molecular conformation of a spiral nature, generated by regularly repeating rotations around the backbone bonds of a macromolecule.

Note: An example is shown in Fig. 1.

2.7 helix residue

Smallest set of one or more successive configurational base units that generates the whole chain through helical symmetry.

2.8 class of helix

Number of skeletal chain atoms contained within the *helix residue*.

2.9 line repetition groups

Possible symmetries of arrays extending in one direction with a fixed *repeating distance* [3, 5, 7].

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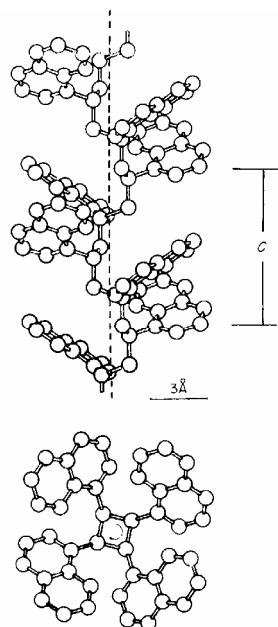


Fig. 1. Side view (above) and end view (below) of the macromolecule of isotactic poly[1-(1-naphthyl)ethane-1,2-diyl] in the crystalline state. The helix symbol is $s(2^*4/1)$. The *chain axis* is shown by the dashed line, and *c* is the *chain identity period*. Hydrogen atoms are omitted. [From P. Corradini and P. Ganis. *Nuovo Cimento*, Suppl. **15**, 96 (1960)].

Note: Linear polymer chains in the crystalline state must belong to one of the line repetition groups (see Table 1 for some examples). Permitted symmetry elements are: the identity operation (symbol 1); the translation along the *chain axis* (symbol *t*); the mirror plane orthogonal to the *chain axis* (symbol *m*) and that containing the *chain axis* (symbol *d*); the glide plane containing the *chain axis* (symbol *c*); the inversion centre, placed on the *chain axis* (symbol *i*); the two-fold axis orthogonal to the *chain axis* (symbol 2); the helical, or screw, symmetry where the axis of the *helix* coincides with the *chain axis*. In the latter case, the symbol is $s(A^*M/N)$, where *s* stands for the screw axis, *A* is the class of the *helix*, $*$ and / are separators, and *M* is the integral number of residues contained in *N* turns, corresponding to the *identity period* (*M* and *N* must be prime to each other) [8, 9] (see Fig. 1). The class index *A* may be dropped if deemed unnecessary, so that the *helix* may also be simply denoted as $s(M/N)$ [5, 7].

2.10 structural disorder

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

Note: Examples of structural disorder in *crystalline polymers* are given in Table 2.

2.10.1 lattice distortion

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

Table 1. Chain symmetry of some crystalline polymers

Line repetition group [a]	Polymer (source-based name, structure-based name)
t1	<i>trans</i> -1,4-polyisoprene, poly[(E)-1-methylbut-2-ene-1,4-diyl]
s(A [*] M/N)	isotactic polypropene, poly(1-methylethane-1,2-diyl) ($M/N=3/1$, A=2)
s(A [*] M/N)2	syndiotactic polypropene, poly(1-methylethane-1,2-diyl) ($M/N=2/1$, A=4, helical modification)
tm	poly(<i>N,N'</i> -heptane-1,7-diylheptanediamide), poly(iminoheptanedioyliminoheptane-1,7-diyl)
tc	poly(1,1-difluoroethene), poly(1,1-difluoroethane-1,2-diyl) (modification 2)
ti	diisotactic poly[ethene- <i>alt</i> -(E)-but-2-ene], diisotactic poly(1,2-dimethylbutane-1,4-diyl)
s(5 [*] 2/1)m	poly(cyclopentene), poly(cyclopentane-1,2-diyl)
s(14 [*] 2/1)d	poly(hexamethylene adipamide), poly(iminohexanedioyliminohexane-1,6-diyl)
tcm	syndiotactic 1,2-polybuta-1,3-diene, poly(1-vinylethane-1,2-diyl)
s(1 [*] 2/1)dm	polyethylene, poly(methylene), PE

[a] See the note, Definition 2.9 for explanation of symbols.

Table 2. Examples of structural disorder occurring in crystalline polymers

Type of structural disorder	Examples Polymer (source-based name , structure-based name)
(i) lattice distortion	as in usual crystallization (i.e., mechanical strain, lattice dislocation, impurities etc.)
(ii) chain orientation disorder	isotactic polypropene, poly(1-methylethane-1,2-diyl) [12], isotactic polystyrene, poly(1-phenylethane-1,2-diyl) [13], poly(1,1-difluoroethene), poly(1,1-difluoroethane-1,2-diyl)-form II [14]
(iii) configurational disorder	atactic polymers capable of crystallization: poly(vinyl alcohol), poly(1-hydroxyethane-1,2-diyl) [15], poly(vinyl fluoride), poly(1-fluoroethane-1,2-diyl) [16] (see Fig. 2)
(iv) conformational disorder	high-temperature polymorph of <i>trans</i> -1,4-polybuta-1,3-diene, poly[(E)-but-1-ene-1,4-diyl] [17] (Fig. 3); <i>cis</i> -1,4-polyisoprene, poly[(Z)-2-methylbut-2-ene-1,4-diyl] [17] (Fig. 4)
(v) copolymer isomorphism	poly(acetaldehyde- <i>co</i> -propionaldehyde) poly[oxy(methylmethylene)/oxy(ethylmethylene)] [19] isotactic poly(but-1-ene- <i>co</i> -3-methylbut-1-ene) isotactic poly(1-ethylethane-1,2-diyl/1-isopropylethane-1,2-diyl) [20] isotactic poly(styrene- <i>co</i> -4-fluorostyrene) isotactic poly[1-phenylethane-1,2-diyl/1-(4-fluoro-

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homopolymer isomorphism

phenyl)ethane-1,2-diy] [21]
mixtures of isotactic poly(4-methylpent-1-ene) and
isotactic poly(4-methylhex-1-ene)
mixtures of isotactic poly(1-isobutylethane-1,2-diy)
and isotactic poly[1-(2-methylbutyl)ethane-1,2-diy]
[22]

2.10.2 chain-orientational disorder

Structural disorder resulting from the statistical coexistence within the *crystals* of identical chains with opposite orientations.

Note: A typical example is provided by the up-down statistical coexistence of anticlined chains in the same *crystal* structure.

2.10.3 configurational disorder

Structural disorder resulting from the statistical co-crystallization of different configurational repeating units (see Fig. 2).

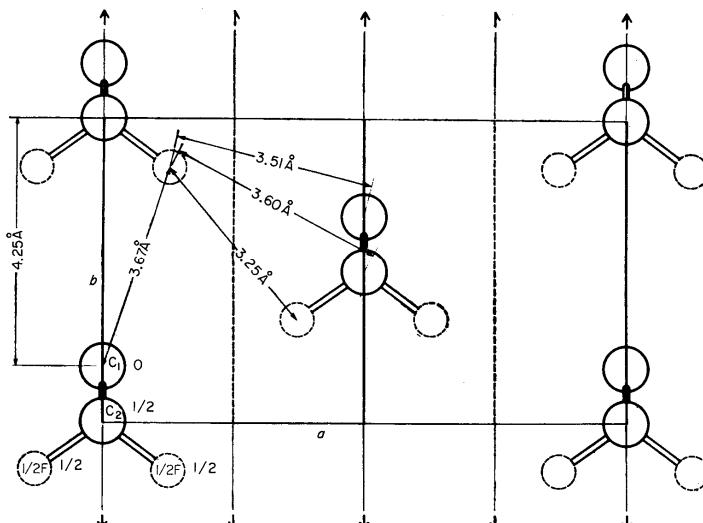


Fig. 2. End projection of atactic poly(vinyl fluoride) [poly(1-fluoroethane-1,2-diy)] chains in the crystalline state. Broken circles show fluorine atoms with 50% probability [16].

2.10.4 conformational disorder

Structural disorder resulting from the statistical co-existence within the *crystals* of identical configurational units with different conformations (see Figs. 3 and 4).

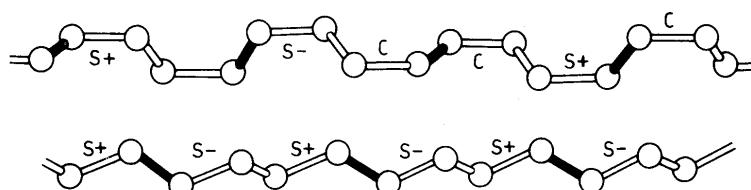


Fig. 3. Chain conformation of the disordered (above) and ordered (below) polymorphs of *trans*-1,4-polybutadiene (poly[(E)-but-1-ene-1,4-diy]) in the crystalline state. The heavy black lines designate the double bonds and the symbols S+, S- and C the conformation [17].

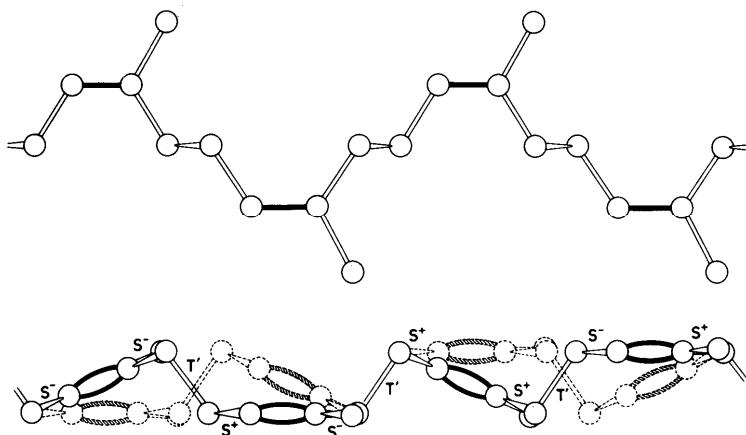


Fig. 4. Different possible conformations of *cis*-1,4-polyisoprene (poly[(*Z*)-2-methylbut-2-ene-1,4-diy]) in the crystalline state, as viewed sideways along two orthogonal axes [17].

2.10.5 macromolecular isomorphism

Statistical co-crystallization of different constitutional repeating units, which may either belong to the same copolymer chains (copolymer isomorphism) or originate from different homopolymer chains (homopolymer isomorphism).

Note: Isomorphism is a general term: in the strict sense, the *crystal* structure is essentially the same throughout the range of compositions; in isodimorphism or isopolymorphism, there are two or more *crystal* structures, respectively, depending on composition.

3 TERMINOLOGY RELATING TO MORPHOLOGICAL ASPECTS [9, 10]

3.1 lamellar crystal

Type of *crystal* with a large extension in two dimensions and a uniform thickness.

Note: A lamellar crystal is usually of a thickness in the 5-50 nm range, and it may be found individually or in aggregates. The parallel-chain *stems* intersect the lamellar plane at an angle between 45° and 90° . The lamellae often have pyramidal shape owing to differences in the *fold domains*; as a result, one can deduce different *fold planes* and *fold surfaces* from the lamellar morphology.

3.2 lath crystal

Lamellar crystal prevailingly extended along one lateral dimension.

3.3 multilayer aggregate

Stack of *lamellar crystals* generated by spiral growth at one or more screw dislocations.

Note: The axial displacement over a full turn of the screw (Burgers vector) is usually equal to one lamellar thickness.

3.4 long spacing

Average separation between stacked *lamellar crystals*.

Note: The long spacing is usually measured by small-angle x-ray or neutron diffraction.

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3.5 axialite

Multilayer aggregate, consisting of *lamellar crystals* splaying out from a common edge.

3.6 dendrite

Crystalline morphology produced by skeletal growth, leading to a ‘tree-like’ appearance.

3.7 fibrous crystal

Type of *crystal* significantly longer in one dimension than in either of the other two.

Note: Fibrous crystals may comprise essentially extended chains parallel to the fibre axis; however, macroscopic polymer fibres containing chain-folded crystals are also known.

3.8 shish-kebab structure

Polycrystalline morphology of double habit consisting of *fibrous crystals* overgrown epitaxially by *lamellar crystals*, the *stems* of which are parallel to the fibre axis.

3.9 spherulite

Polycrystalline, roughly spherical morphology consisting of lath, fibrous or *lamellar crystals* emanating from a common centre.

Note: Space filling is achieved by branching, bending or both, of the constituent fibres or lamellae.

4 TERMINOLOGY RELATING TO MOLECULAR CONFORMATION WITHIN POLYMER CRYSTALS [9, 10]

4.1 tie molecule

Molecule that connects at least two different *crystals*.

4.2 stem

Crystallized, rodlike portion of a polymer chain connected to non-rodlike portions, or chain ends, or both.

4.3 chain fold

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

4.4 fold

Loop connecting two different *stems* in a folded chain.

4.5 fold plane

Crystallographic plane defined by a large number of *stems* that are connected by *chain folds*.

4.6 fold surface

Surface approximately tangential to the *folds*.

4.7 fold domain

Portion of a *polymer crystal* wherein the *fold planes* have the same orientation.

Note: The sectors of *lamellar crystals* frequently represent *fold domains*.

4.8 adjacent re-entry

Model of *crystallinity* in which *chain folds* regularly connect model adjacent *stems*.

4.9 switchboard model

Model of *crystallinity* in which the crystallized segments of a macromolecule belong to the same *crystal*, although the *stems* are connected randomly.

4.10 fringed-micelle model

Model of *crystallinity* in which the crystallized segments of a macromolecule belong predominantly to different *crystals*.

4.11 folded-chain crystal

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

Note: The re-entry of the chain into the *crystal* is assumed to be adjacent or near-adjacent within the lattice.

4.12 parallel-chain crystal

Type of *crystal* resulting from parallel packing of *stems*, irrespective of the *stems'* directional sense.

4.13 extended-chain crystal

Polymer crystal in which the chains are in an essentially fully extended conformation.

4.14 globular-chain crystal

Type of *crystal* comprised of macromolecules having globular conformations.

Note: Globular-chain crystals usually occur with globular proteins.

5 TERMINOLOGY RELATING TO CRYSTALLIZATION KINETICS [10, 11]

5.1 nucleation

Formation of the smallest crystalline entity, the further growth of which is thermodynamically favoured.

Note: Nucleation may be classified as primary or secondary. Primary nucleation can be homogeneous or heterogeneous; if heterogeneous nucleation is initiated by entities having the same composition as the crystallizing polymer, it is called self-nucleation. Secondary nucleation is also known as surface nucleation.

5.2 molecular nucleation

Initial crystallization of a small portion of a macromolecule, after which further crystallization is thermodynamically favoured.

Note: Molecular nucleation may give rise to a new *crystal* or increase the size of a pre-existing one.

5.3 Avrami equation

Equation, describing crystallization kinetics, of the form:

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

where ϕ_c is the crystalline volume fraction developed at time t and constant temperature, and K and n are suitable parameters.

Note 1: K is temperature-dependent.

Note 2: According to the original theory, n should be an integer from 1 to 4, the value of which should depend only on the type of the statistical model; however, it has become customary to regard it as an adjustable parameter that may be non-integral.

Note 3: The Avrami equation addresses the problem that *crystals* growing from different nuclei can overlap. Accordingly, the equation is sometimes called the ‘overlap equation’.

5.4 primary crystallization

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

Note: In isothermal crystallization, primary crystallization is often described by the *Avrami equation*.

5.5 secondary crystallization

Crystallization occurring after *primary crystallization*, usually proceeding at a lower rate.

5.6 reorganization

Molecular process by which (i) amorphous or poorly ordered regions of a polymer specimen become incorporated into *crystals*, or (ii) a change to a more stable *crystal* structure takes place, or (iii) defects within the *crystals* decrease.

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

Note 2: Reorganization may result from annealing.

Note 3: (i) and (iii) may also be called crystal perfection.

5.7 recrystallization

Reorganization proceeding through partial melting.

Note: Recrystallization is likely to result in an increase in the *degree of crystallinity*, or crystal perfection, or both.

5.8 segregation

Rejection of a fraction of macromolecules, or of impurities, or both, from growing *crystals*.

Note: The rejected macromolecules are usually those of insufficient relative molecular mass, or differing in constitution or configuration (e.g., branching, tacticity, etc.).