

# Crystals and Crystallinity in Polymeric Materials

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## ABSTRACT

A new view of the concepts of crystallinity and crystals in synthetic macromolecules is discussed. In polymeric materials, crystallinity may be present with the concomitant occurrence of large amounts of structural disorder and in the absence of true three-dimensional long-range order. The structures of semicrystalline polymeric materials are discussed in terms of idealized limit models of crystals, where long-range order may be achieved for structural features that are not necessarily coincident with single atoms and are not necessarily point-centered. Typical examples of non-point-centered structural features are the straight lines corresponding to the chain axes of polymer molecules. This view explains the unusual ability of polymers to crystallize even in the presence of a high degree of structural disorder.

## Introduction

A *crystal* is a portion of solid matter in which some kind of long-range *positional* order exists on the level of atomic dimensions in three-dimensional space. This order induces anisotropic properties in that portion of the matter.<sup>1</sup> The popular definition of crystal as a *periodic* array of identical motifs corresponds to a reasonable and generally valid working hypothesis, implying complete long-range positional order of (most) atoms.<sup>2</sup>

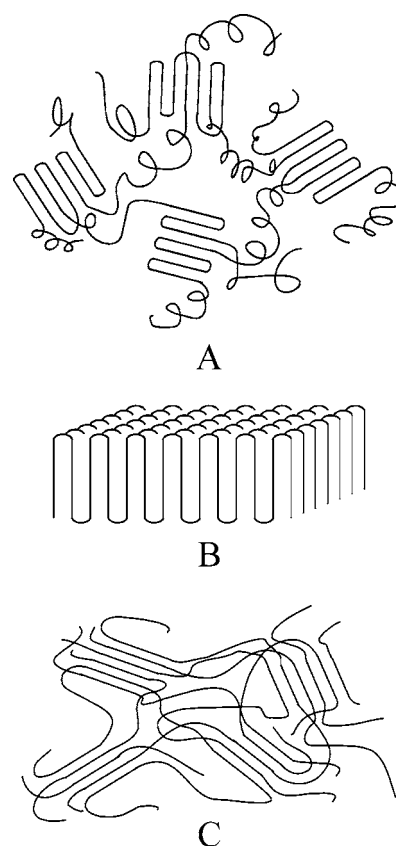
In a slightly enlarged recent definition, a crystal is “any solid having an essentially discrete diffraction diagram”.<sup>3</sup> This definition implies the presence of some kind of long-range three-dimensional periodicity, but not necessarily a *complete* three-dimensional order of atoms.

“Periodicity” is intended as the quality of a motif of recurring at equal intervals in the space. In the ideal *limit* case, the repetition is endless, whereas in real cases it

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**FIGURE 1.** Models of the microstructure of semicrystalline polymers: (A) each chain may run through several crystalline and amorphous regions; (B) model of a tightly folded lamella crystal; (C) fringed micelle model.<sup>4</sup>

extends up to the scale considered as appropriate for the description of material properties.<sup>1</sup> In the ideal limit case, the corresponding model crystal is designated as an “ideal crystal”.

In the following, the term *crystalline* is taken to indicate a material that “has some kind of long-range positional order in three-dimensional space”. *Crystallinity* is the fraction of crystalline matter in the material.

The concepts of crystal and crystallinity in polymeric materials are complex and very far from the ideality because the three-dimensional long-range order is never present and the structural disorder inside crystals is a rule rather than an exception. First of all, at variance with other crystalline materials, such as metals, polymeric materials are never completely crystalline. They are *semicrystalline* and are generally composed of crystals (lamellae) embedded into an amorphous phase, producing a highly interconnected network (Figure 1).<sup>4</sup> The peculiar semicrystalline character of polymers determines their outstanding physical properties.

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The requirement of three-dimensional long-range order may appear to be violated in polymer crystals, unless it is considered as a limit, mainly for the following reasons:

(a) The macromolecules of a polymer are not uniform; that is, they have different molecular masses; a distribution of molecular masses must always be considered.<sup>5</sup>

(b) Constitutional, configurational, and conformational disorders along the polymer chains are always present.<sup>6</sup>

(c) The dimensions of the crystals are very small, mostly in the nanometer range (they are often indicated as crystallites).<sup>4</sup>

Moreover, defects in the mode of packing of macromolecules may be present. Disorder in the packing may occur while some structural features, for instance, some atoms or the axes of helical macromolecules, maintain *periodic positions*. The degree of disorder in the packing or in the single macromolecules is sometimes so high that it is difficult to define this state as *crystalline*, even though we can still observe crystalline entities with a regular shape by microscopy (optical or electronic). This state can be more properly indicated as intermediate between amorphous phase and ordered crystals.<sup>7–9</sup> These *crystalline* forms that present large amounts of disorder, lacking periodicities in one or two dimensions (for example, along or normal to the chain axes) are very common in solid *semicrystalline* polymers and are generally designated *mesophases*.<sup>7–9</sup>

The issue of long-range versus short-range order in polymer crystals has been treated in several papers.<sup>6–12</sup> In this Account, we will describe a modern view of crystallinity and crystalline order in polymers as compatible with the presence of a high degree of disorder and the absence, in many cases, of long-range three-dimensional order. This view is in part the result of our intense research in polymer crystallography.

## Crystallinity and X-ray Diffraction in Polymers

The capability of polymers to crystallize (crystallizability) implies, in general, an “identity period” along the chain axes of macromolecules. In the corresponding “ideal crystals”, the polymer molecules have an infinite chain length and a perfect regularity in the chemical constitution, in the configuration, and in the conformational sequences of the monomeric units along the chain.<sup>6</sup>

The requirement of a regular conformation is satisfied in most cases by a succession of structural units that occupy geometrically (not necessarily crystallographically) equivalent positions with respect to a chain axis (equivalence postulate).<sup>6,13</sup>

Lack of order in polymer crystals may arise whenever a given unit along the polymer chain, having constitution, configuration, or conformation different with respect to an idealized model, is included in a crystalline lattice without impairing the packing of close neighboring chains.<sup>6–9,14</sup> Furthermore, even in the case of regular constitution, configuration, and conformation, disorder may be present in the crystals due to physical defects in

the mode of packing, whereby long range positional order only for some structural features is maintained.<sup>6,8</sup>

The complex nature of macromolecules in polymeric materials, which always include constitutional and configurational defects along the chain, polydispersity of the molecular masses, and the easy inclusion of defects inside the crystallites, generally prevents obtaining single crystals of a suitable size for the collection of X-ray diffraction data with the techniques normally used for single crystals of low molecular weight compounds.<sup>15</sup> The dimensions of polymeric single crystals are instead suitable for electron diffraction. The structural analysis is further complicated by the fact that crystalline polymers are always characterized by a complex morphology, consisting of amorphous, crystalline, and intermediate regions (Figure 1). Furthermore, polymers very often present a complex polymorphism in the solid state, which in some cases may prevent the preparation of a sample containing a single-crystalline form.

The structural study is generally performed by X-ray diffraction of uniaxially oriented fibers or, when fibers cannot be obtained, of powder samples containing randomly oriented crystals.<sup>15</sup> In all cases, the X-ray diffraction patterns of semicrystalline polymers present a few number of Bragg reflections and a large amount of diffuse scattering. The diffuse scattering originates from the amorphous contribution and the presence of structural disorder.<sup>16</sup> The Bragg peaks are broad because of the small average dimensions of crystallites and overlap at high values of the  $2\theta$  diffraction angle; furthermore, the Bragg diffraction rapidly vanishes with increasing diffraction angle.<sup>15</sup> On the other hand, the electron diffraction intensity of single crystals may be seriously affected by multiple scattering effects and is generally limited by the fact that only a small region of the reciprocal space is usually accessible.<sup>17</sup>

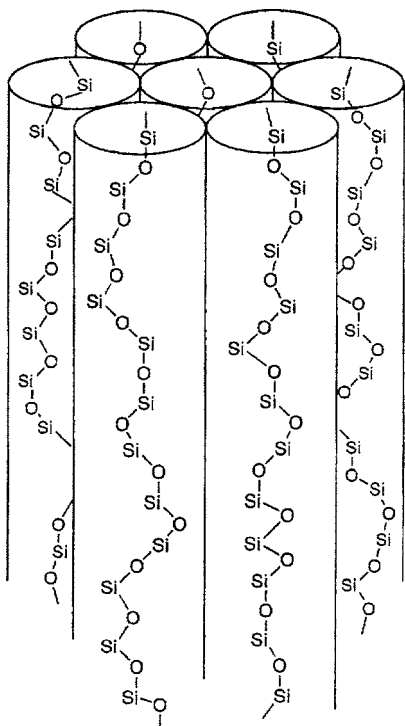
The paucity and overlapping of diffraction data, even when electron diffraction patterns of single crystals are available, is generally compensated by use of trial-and-error methods for solving the crystal structures of polymers, which involves construction of a priori models of the conformation and the packing of the polymer chains in the unit cell.<sup>15</sup>

## Classification of Disordered Crystals in Polymeric Materials

Depending on the features present in the X-ray fiber diffraction patterns, it is useful to distinguish the following main classes of disordered crystals:<sup>7,8</sup>

(i) The long-range three-dimensional periodicity is maintained only for some characterizing points of the structure. In these cases, there is only a partial three-dimensional order and the X-ray diffraction patterns present sharp reflections and diffuse halos.

(ii) The long-range positional three-dimensional order is maintained only for some structural features that are not point-centered, for example, the chain axes. Structures characterized by conformationally disordered chains with



**FIGURE 2.** Columnar pseudo-hexagonal packing of poly(di-*n*-alkylsiloxane) molecules. Reproduced from ref 18 with permission. Copyright 1997 Elsevier.

a long-range order in the position of the chain axes belong to this class (Figure 2). The X-ray fiber diffraction patterns of this kind of disordered structures are characterized by sharp reflections on the equator and diffuse halos on the layer lines.

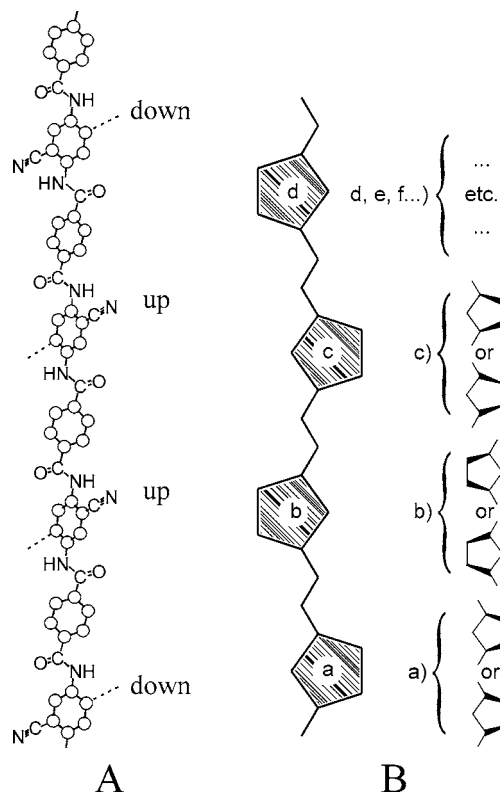
(iii) The long-range positional order of some features is maintained only in two or in one dimension, for example, along the chain axis. Examples may be provided by structures characterized by conformationally ordered parallel chains with disorder in the lateral packing of the chains. The X-ray fiber diffraction patterns of these kinds of disordered structures are characterized by the presence of well-defined layer lines and diffuse scattering.

For crystals of class i, even in the presence of a high amount of structural disorder, a unit cell may be still defined.<sup>6,8</sup> This, for instance, occurs in the two extreme cases of Figure 3, where complete constitutional disorder in the up or down orientation of the  $-\text{CN}$  groups in Figure 3A<sup>19</sup> and complete configurational disorder of the cyclopentane moieties in Figure 3B<sup>20</sup> are present.

Crystalline forms presenting a large amount of disorder of the kind ii or iii may be called mesomorphic modifications.<sup>7-9</sup> The presence of a high amount of disorder in these solid mesophases frequently prevents the definition of a unit cell, and only average periodicities along some lattice directions may be defined.<sup>9</sup>

### Crystal Structures of Class i

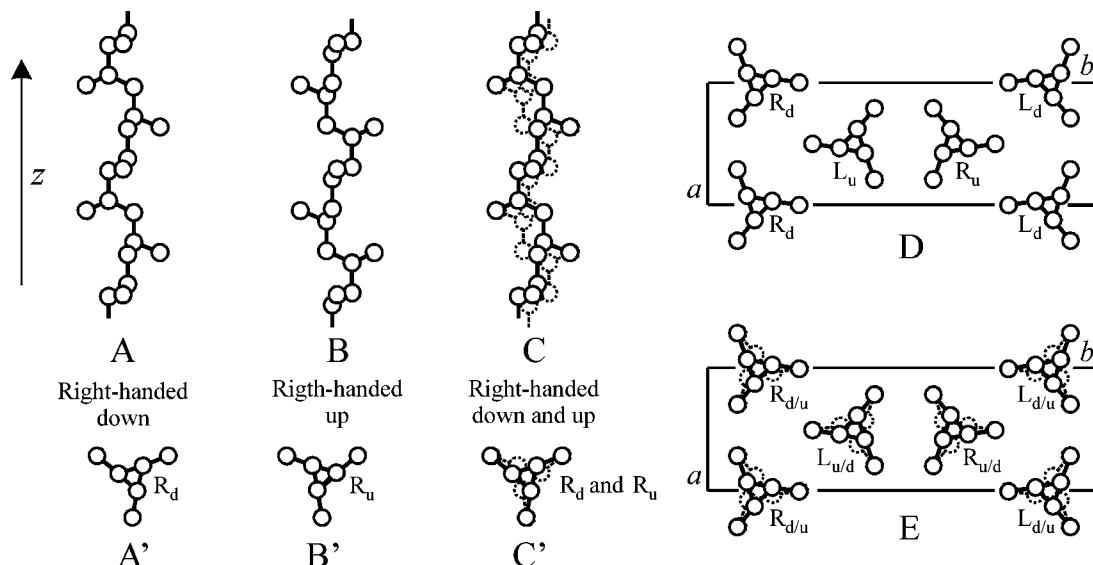
The crystal structures of polymeric materials belonging to class i may be conveniently described adopting the concepts of *limit ordered* and *limit disordered* model structures.<sup>7,8</sup>



**FIGURE 3.** Chemical structures of poly(2-cyano-1,4-phenylene terephthalamide)<sup>19</sup> with complete constitutional disorder (up or down  $-\text{CN}$  groups, A) and poly(vinylene-1,3-cyclopentylene)<sup>20</sup> with complete configurational disorder (*S,R* or *R,S* cyclopentane rings, B).

A limit ordered model is an idealized description of the structure in a given space group, resulting in a fixed position of all atoms in the crystal with a perfect three-dimensional order. A limit disordered model is an idealized description in a space group with statistical occupancy of some or all of the equivalent positions.<sup>7,8</sup> Structural disorder may arise indeed, while the same unit cell is maintained, for instance, whenever polymer chains or even layers of chains may assume different and equivalent positions in the unit cell without changing the steric interactions with the neighboring chains. In these cases, the substitution of chains or layers of chains does not produce large disturbance of the packing, so that the crystallinity and the same lattice geometry are preserved. An ideal fully disordered structure characterized by disorder corresponding to the statistical substitution of chains or layer of chains can be described by a limit disordered model, which actually may describe the relative position of atoms in the long range. This concept may be useful to interpret the presence of diffuse scattering in a diffraction pattern. A limit ordered model may be, instead, appropriate for the description of the relative position of atoms in the short range and the occurrence of sharp lines in diffraction experiments.

The real crystalline forms are, generally, intermediate between limit ordered and limit disordered models, the amount of disorder being dependent on the condition of crystallization and thermal and mechanical treatments of the samples.



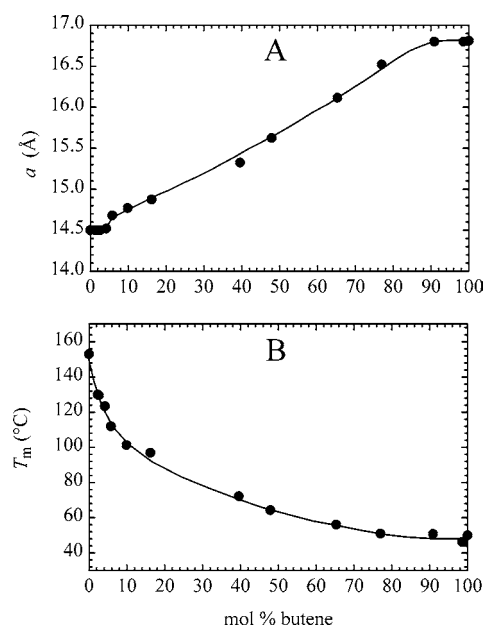
**FIGURE 4.** Three-fold isomorphous helical chains of iPP with pendant  $-\text{CH}_3$  groups down (A, A') and up (B, B') with respect to the  $z$ -axis, in projections parallel (A, B) and perpendicular (A', B') to the chain axis. Up (u) and down (d) chains have the same steric hindrance since the side methyl groups may assume the same positions (Figure 4C, C'). Limit ordered model structure (space group  $P2_1/c$ )<sup>22</sup> (D) and limit disordered model structure (space group  $C2/c$ )<sup>21</sup> (E) of the  $\alpha$  form of iPP are shown. R and L indicate right-handed and left-handed helices, respectively.

As illustrative examples of disordered lattices of kind i, the following classic cases occurring in important classes of high polymers are presented.

**Substitutional Isomorphism of Different Chains.** The model shown in Figure 4 is a typical example of crystal lattice affected by disorder due to isomorphous substitution of different chains.<sup>21,22</sup> The 3-fold helical chains of isotactic polypropylene (iPP) of a given chirality may present the lateral methyl groups down (Figure 4A, A') or up (Figure 4B, B') with respect to the methine carbon atoms to which they are bound.<sup>21</sup> Isomorphous up and down (anti-clined)<sup>6,13</sup> chains have a similar external steric hindrance because the methyl groups may assume the same position (Figure 4C, C'). Therefore, disorder in the positioning of up and down chains may be present because if isomorphous, anti-clined helices of iPP substitute each other in the same site of the lattice, the same steric interactions with neighboring chains are involved.

In the limit-ordered model proposed for the  $\alpha$  form of iPP (Figure 4D), up and down chains follow each other according to a well-defined pattern.<sup>22</sup> The limit disordered model (Figure 4E) corresponds to a statistical substitution of up and down isomorphous helices in each site of the lattice.<sup>21</sup> The real crystalline modifications of the  $\alpha$  form of iPP<sup>21,22</sup> are intermediate between the limit ordered and limit disordered models of Figure 4D,E, the degree of disorder being dependent on the thermal and mechanical history of the sample.

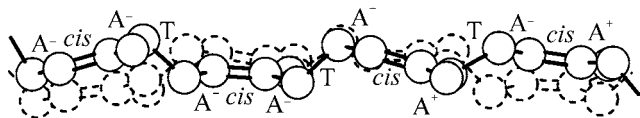
**Substitutional Isomorphism of Different Monomeric Units.** Classic examples of polymer crystals including disorder due to isomorphous substitution of monomeric units in the crystal lattices are isotactic butene-3-methylbutene or styrene-*o*-fluorostyrene copolymers<sup>6</sup> and syndiotactic propene-butene-1 copolymers<sup>8,23</sup> (Figure 5), which are crystalline in the whole range of compositions. In these cases, the presence of monomeric units of different chemical structure, statistically distributed along



**FIGURE 5.** Values of the  $a$ -axis of the unit cell (A) and melting temperature (B) of syndiotactic propene-butene-1 copolymers as a function of the 1-butene content.<sup>23</sup>

the polymer chains, does not prevent the crystallization of the resulting copolymers. When the composition of the copolymer is changed, some of the crystal lattice parameters may undergo continuous and regular variations (Figure 5A), inducing gradual changes of other properties (e.g., solubility, melting temperature, Figure 5B).<sup>6,8,23</sup>

Different comonomeric units are able to cocrystallize in the same lattice if the shape of the backbone chain and therefore the chain conformation is not affected by the constitutional disorder.<sup>6</sup> In vinyl copolymers, the maintenance of the macromolecular chain conformation requires a regular configuration of the monomeric units with different constitutions.



**FIGURE 6.** Models of the chain conformation of *cis*-1,4-polyisoprene in the crystalline state. The models indicated with solid and dashed line correspond to a different succession of conformations of the monomeric units and present similar lateral encumbrance.

**Conformational Isomorphism.** For polymers with a regular constitution and configuration, the conformation adopted by the chains in the crystalline state is generally regular. However, three-dimensional long-range crystalline order may be maintained even when the conformation of the macromolecules is disordered.<sup>14</sup> The term conformational isomorphism refers to the more or less random occurrence in the same lattice site of different but almost isoenergetic conformers of the same portion of a molecule.<sup>14</sup> A classic example of conformational isomorphism in the crystals is provided by *cis*-1,4-polyisoprene (natural rubber), studied by Nyburg<sup>24</sup> and by Natta and Corradini.<sup>25a</sup> The X-ray diffraction data of natural rubber are accounted for by disordered models of the chain conformation,<sup>25b</sup> characterized by a statistical sequence of monomeric units having successive bonds in the conformations  $A^+TA^-$  (*cis*) or  $A^-TA^+$  (*cis*), such as those shown in Figure 6 ( $A^+$ ,  $A^-$ , and T standing for torsion angles close to  $+120^\circ$ ,  $-120^\circ$ , and  $180^\circ$ , respectively).

These disordered models have energy not far from minima of the internal energy of isolated chains and produce an average identity period close to the experimental value of the chain axis of 8.23 Å. The disordered models of Figure 6 not only account for the low-temperature diffraction patterns of stretched fibers of natural rubber<sup>26</sup> but are also able to provide a semiquantitative explanation of the low melting enthalpy.<sup>25b</sup> The case of natural rubber provides an example of the possibility to keep a chain straight, even with a statistical succession

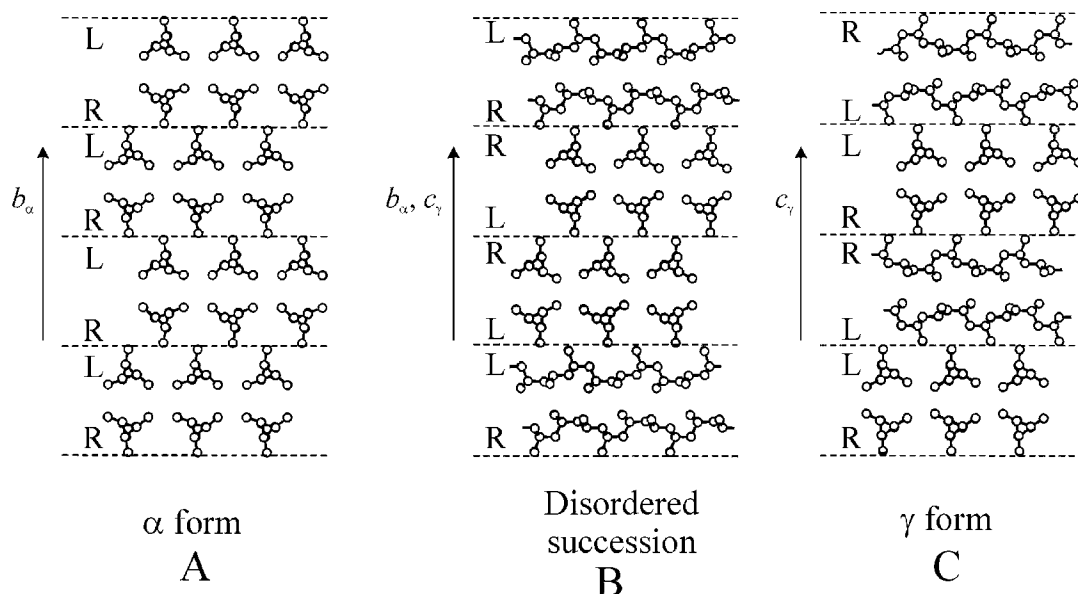
of structural units having widely different internal rotation angles, so that a certain short-range order is preserved allowing crystallization.<sup>6</sup>

#### Stacking Fault Disorder and Kink-Band Disorder.

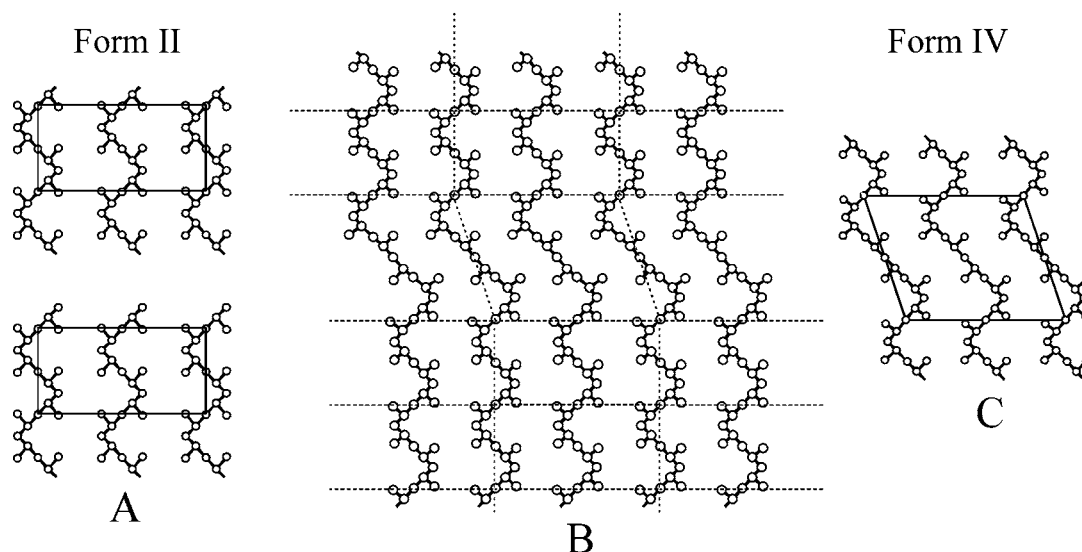
Stacking fault disorder in polymers arises from defects in the stacking of ordered layers of macromolecules along one lattice direction. It originates whenever first neighboring chains are tightly interlocked with bulges and grooves along one lattice direction, forming rows of parallel chains (layers), and more loosely packed along the direction normal to the layers.<sup>8</sup> Along the latter direction different modes of packing of first neighboring chains are feasible at a low cost of free energy. This kind of disorder produces the broadening of reflections in the X-ray diffraction patterns and streaks in the electron diffraction patterns of single crystals.<sup>8</sup>

Disorder in the stacking of ordered layers of chains along one crystallographic direction is present in the  $\beta$  form of syndiotactic polystyrene, in forms I and II of syndiotactic polypropylene, in the  $\alpha$  and  $\gamma$  forms of isotactic polypropylene, and in many other cases.<sup>8</sup> As an example, the case of the  $\gamma$  form of iPP is presented (Figure 7).<sup>27</sup>

The structure of the  $\gamma$  form of iPP is quite unusual, being the first example of a polymer structure characterized by the packing of nonparallel chain axes (Figure 7C).<sup>28</sup> iPP samples prepared with the traditional Ziegler–Natta catalysts generally crystallize in the stable  $\alpha$  form (Figure 7A), whereas iPP samples prepared with the homogeneous metallocene catalysts crystallize more easily in the  $\gamma$  form (Figure 7C) and in disordered modifications (Figure 7B) intermediate between  $\alpha$  and  $\gamma$  forms.<sup>27</sup> The disorder corresponds to the statistical succession along the  $b_\alpha$  ( $c_\gamma$ ) axis direction of double layers of chains with the chain axes either parallel (like in the  $\alpha$  form) or nearly perpendicular (like in the  $\gamma$  form). Inside the same crystalline domain local arrangements of the double layers of chains,



**FIGURE 7.** Limit ordered models of the  $\alpha^{21}$  (A) and  $\gamma^{28}$  (C) forms of iPP and disordered succession of bilayers of chains<sup>27</sup> (B). The dashed horizontal lines delimit bilayers of chains in the 3/1 helical conformation. R and L indicate right-handed and left-handed helices, respectively.



**FIGURE 8.** Limit ordered models of packing of forms II (A) and IV (C) of sPP and model of a conformationally disordered modification of form II, presenting kink bands (B), intermediate between forms II and IV. A kink band in form II of sPP, with  $(T_2G_2)_n$  helices, is characterized by a defective region with  $(T_2G_2T_6G_2)_n$  conformational sequence, as in form IV.<sup>31</sup>

piled along the  $b_a$  ( $c_y$ ) axis, typical of the  $\alpha$  form (with parallel chains) and typical of the  $\gamma$  form (with chains nearly perpendicular) are present (Figure 7B).<sup>27</sup> The amount of  $\gamma$  form obtained by melt crystallization of metallocene-made iPPs and the degree of disorder depend on the microstructure of chains and, in particular, on the amount, combination, and distribution of defects of stereoregularity and regioregularity.<sup>27</sup> The polymorphic behavior and the order–disorder phenomena in iPP can be described by a *continuum* of disordered modifications intermediate between  $\alpha$  and  $\gamma$  forms.<sup>27</sup>

A particular kind of stacking fault disorder, typical of polymeric materials, is the *kink-band disorder*. It occurs when inside the crystals of macromolecules having a given conformation portions of the chains assume a different conformation. These portions of chains are clustered in planes so that the parallelism of the chains is preserved.<sup>8</sup> The defective conformation involves all the molecules in the crystallite, at the same level, forming kink bands. There are at least three examples of important crystalline polymers presenting kink-band disorder, polyethylene obtained by crystallization under pressure,<sup>29</sup> poly(vinylidene fluoride) in forms I and II,<sup>30</sup> and syndiotactic polypropylene (sPP) in form II<sup>31</sup> (Figure 8).

Kink-band disorder in form II of sPP (Figure 8) occurs in samples having a relatively low degree of stereoregularity, quench-precipitated from solution,<sup>31</sup> or in copolymers of sPP with ethylene.<sup>8</sup> In this case, kink-bands defects originates from the presence of portion of chains in *trans*-planar conformation in chains having a prevailing 2-fold helical conformation (Figure 8). The kink-band disordered modifications appear as intermediate structures between the limit ordered model structures of forms II and form IV of sPP.<sup>31</sup>

### Crystal Structures of Class ii and iii

Polymer crystals belonging to class ii and iii are characterized by the typical feature of crystalline order, that is, the

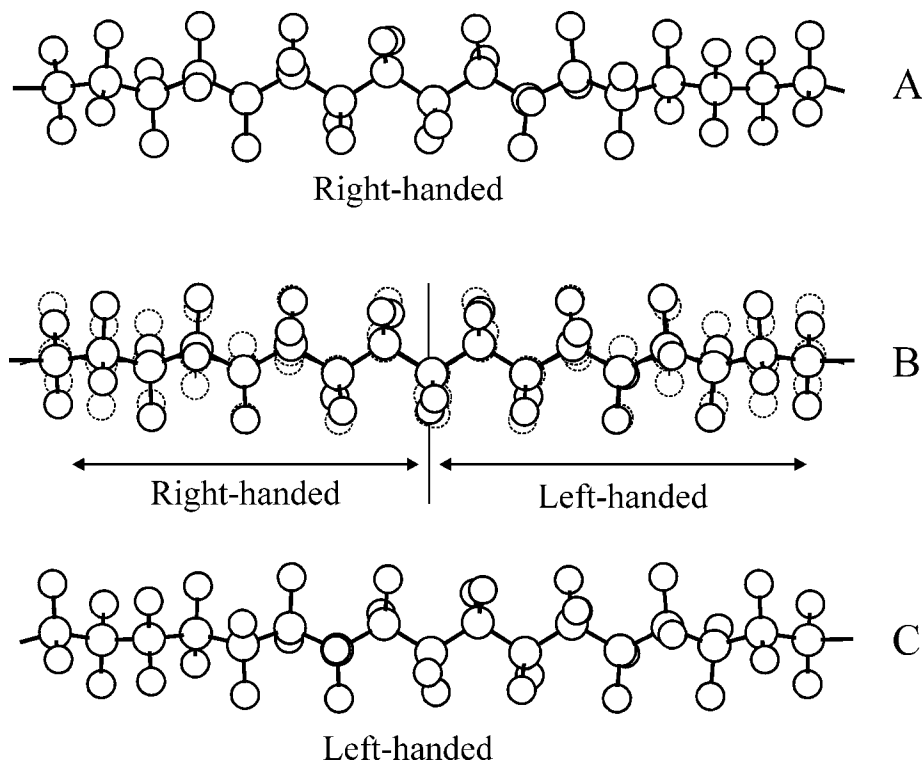
packing of parallel chains, but a large amount of structural disorder, higher than in cases of class i. The presence of disorder induces lack of short-range order in the positions of atoms although long-range order of some structural feature may be still present.<sup>7–9</sup> These structures may be considered as intermediate between perfectly crystalline and completely amorphous phases and can be called “mesomorphic forms” or “solid mesophases”.<sup>7–9</sup>

Within class ii, we include solid mesophases characterized by conformationally disordered chains with long-range order in the position of chain axes.<sup>9–12</sup> The relative orientation of the chains around the chain axes and the relative height of the chains along the chain axes are disordered. However, in most cases, residual correlation in the position of atoms of close neighboring chains may be still present. This is indicated by the presence in the X-ray fiber diffraction patterns of distinct layer lines that show maxima in positions off the meridian.<sup>9</sup>

Among the mesomorphic forms of class ii, we include the high-temperature form I of poly(tetrafluoroethylene) (PTFE),<sup>32</sup> characterized by disorder in the conformation of the chains and long-range order only in the pseudo-hexagonal placement of the chain axes. The conformational disorder in form I of PTFE is due to the presence of helix reversal defects along the chains (Figure 9).<sup>32</sup>

A pseudo-hexagonal packing of conformationally disordered chains also characterizes the high-temperature phase of *trans*-1,4-poly(1,3-butadiene),<sup>9</sup> the crystalline pseudo-hexagonal polymorph of atactic polyacrylonitrile (PAN),<sup>33</sup> the polymorphic form of polyethylene stable at high temperature and pressure,<sup>9</sup> the pseudo-hexagonal mesomorphic form of ethylene–propylene rubbers,<sup>34</sup> and many other mesophases.<sup>9</sup> In the case of PAN, the presence of configurational disorder in the crystalline state necessarily implies the presence of conformational disorder to alleviate intramolecular strains<sup>33</sup> (Figure 10).

In solid mesophases of class ii, the disorder of the chain conformation does not destroy the crystallinity because



**FIGURE 9.** Models of 15/7 PTFE helical chain, right-handed (A) and left-handed (C), corresponding to a sequence of torsion angles  $\dots T^+T^+T^+ \dots$  and  $\dots T^-T^-T^- \dots$ , respectively, with  $T^+ = -T^- = +165.7^\circ$ , and model of PTFE helical chain including a helix reversal (B) of kind corresponding to a sequence of torsion angles  $\dots T^+T^+T^+ (T^+T^+T^-) T^-T^-T^- \dots$ , modeled according to ref 32.

of the similar shape of the various conformational units.<sup>14</sup> The occurrence of cases of conformational isomorphism of the main chain demonstrates that a polymer chain can remain straight, as if it was constrained to run inside the walls of a tight cylinder, while its conformational freedom remains of the same order of magnitude as in the melt.<sup>8,9,14</sup>

Comblike polymers such as poly(di-*n*-alkylsiloxanes) and poly(phosphazenes) also show pseudo-hexagonal mesophases of class ii characterized by a high degree of conformational disorder not only of the polymer backbone but also of the flexible side groups.<sup>10–12</sup> According to a generalized view given by Allegra and Meille,<sup>12</sup> these hexagonal mesophases gain entropy from optimization of the organization of the side groups and the chain backbone; the flexible main chains, indeed, become quite rigid as a consequence of their “self-compacting” elastic nature, due to the presence of lateral groups (Figure 11).<sup>12</sup>

The recently established crystal structure of the alternating ethylene–norbornene copolymers (ENCs) represents another case of crystal structure of class ii, where long-range periodicity is maintained in three dimensions only for the center of mass of the norbornene units but not for the atomic positions.<sup>8,35</sup>

Mesomorphic forms belonging to class iii are characterized by chains in ordered conformations with a high degree of disorder in the packing. In these cases, periodicity occurs only along the chain direction; lateral correlations in the relative position and orientation of the chains exist only in the short range. Within this class, we include mesophases obtained by stretching a solid sample at temperatures lower than the glass transition temperature

(syndiotactic polystyrene, nylon 6, poly(ethylene terephthalate) (PET)) or by quenching the melt at low temperatures, such as the so-called “smectic” iPP<sup>36</sup> and sPP.<sup>8,9</sup>

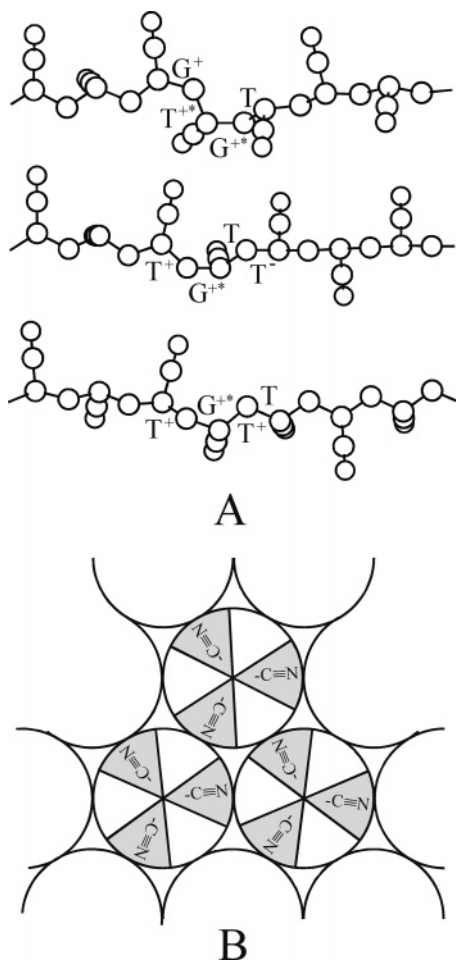
In a limit disordered structural model of the mesomorphic form of PET (Figure 12), the chains are characterized by a high degree of conformational disorder, able to retain the straightness of the chain and an average periodicity of 10.3 Å.<sup>9,37</sup>

## Concluding Remarks

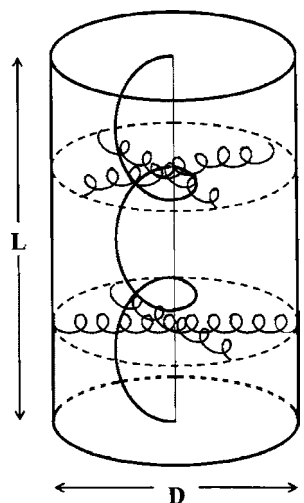
In this Account, the concept of *crystallinity* in polymeric materials compatible with the absence of long-range order is discussed. Crystals of polymers represent the most striking example where the requirement of the presence of three-dimensional long-range order of atoms appears to be violated, unless it is considered as a limit.

Disorder arises by defects in the chemical structure or in the physical arrangement of macromolecules. In many cases, different kinds of disorder are correlated and simultaneously present. Defects can also be affected by a high mobility, but this cannot be seen by the X-ray diffraction analysis using conventional techniques. In general, crystallinity implies the packing of parallel chains. An important exception to this “rule” is the  $\gamma$  form of isotactic polypropylene characterized by a nonparallel arrangement of the chain axes.<sup>28</sup>

In a general unified view of crystallinity, it should be underlined that structures characterized by a three-dimensional long-range positional order, realized through the translation along a number of vectors lower than three

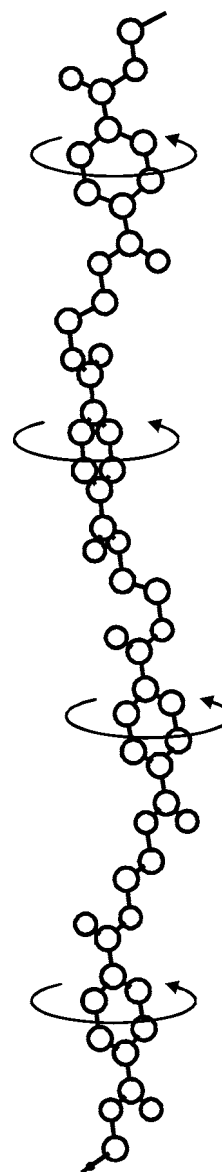


**FIGURE 10.** Models of chain conformation (A) and packing (B) of PAN. In the crystals, configurationally irregular chains are conformationally disordered and in almost extended conformations (A). In the pseudo-hexagonal packing of the chain axes, some short-range order in the orientation of  $-CN$  groups is preserved (B).<sup>9,33</sup>



**FIGURE 11.** Idealized elastic model of a self-compacting chain: the lateral groups act as a system of axially symmetric springs so that the chains, having a cylindrical shape, may be regarded as an elastic continuum. Reproduced from ref 12 with permission. Copyright 2004 American Chemical Society.

(if the structural features are not point-centered, but extended along lines or in planes), must be comprised in



**FIGURE 12.** Model of the disordered chain conformation of PET in the mesomorphic form, characterized by lack of any long-range correlation between the planes of the phenyl rings along the chains.<sup>37</sup>

the definition of “crystal”. This definition may be helpful for a unified description of crystal structures including large amounts of structural disorder. Examples of structures where the long-range positional order in three-dimensional space may be achieved through the operation of two translation vectors, defining the position of the straight lines that correspond to the chain axes, are provided by structures characterized by conformationally disordered chains with a long-range order in the position of the chain axes, of the kind shown in Figures 2 and 10.<sup>9</sup>

Finally, let us point out the fact that the structural organization of polymers in crystals associated with polymorphism and disorder phenomena may strongly influence the properties of a given material. For instance, metallocene-made iPPs with different microstructures show different polymorphic behavior and different mechanical properties.<sup>27</sup> The complex polymorphism and order–disorder phenomena of poly(vinylidene fluoride)



is responsible for its piezoelectric behavior.<sup>30</sup> The low melting enthalpy of natural rubber is linked to the disorder of the chain conformation in the crystals.<sup>25</sup> PTFE at high temperatures is able to form thin films with a perfectly uniform orientation of the chain axes when a bar of solid PTFE is moved under weak pressure against a hot surface. This plastically crystalline nature is linked to the high mobility of the atoms parallel to the chain axes in the mesomorphic modification stable at high temperatures.<sup>38</sup> The formation of the mesomorphic hexagonal phase of polyethylene stable at high pressures plays an important role in the growth of extended chain crystals in the usual orthorhombic form.

Therefore, if on one hand departures from the ideal long-range order may be considered as a disturbance, in practice, these “deviations” from the ideal may turn out to be useful since they may induce additional and desirable properties in the final products.

The comprehension of the factors that determine the different kinds and amount of disorder in the crystals of polymers and, in general, in various materials, through the methods and the language of structural analysis, can allow the setup of processing conditions and the rational choice of the starting substance for the development of new materials with improved and unprecedented performances.

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