Chiral Crystallization of Helical Polymers[†]

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ABSTRACT: Crystallization of achiral or racemic helical polymers in chiral crystals is quite frequent and while in some cases it may relate to the thermodynamic stability of the chiral polymorph, in others it must be associated with kinetic factors. Analysis of the available literature data suggests that in the second instance a key role must be played by the nucleation step, i.e. specifically by the formation of precrystalline entities. Furthermore a survey of the chiral crystal structures for helical polymers evidences that they are frequently characterized by a quasi-hexagonal packing. The hexagonality index H, defined as the ratio of the largest to the smallest distance between the axis of the reference helix and its six nearest neighbors, appears to be a reliable indicator of the presence of helices of a single handedness or, respectively, of both in a given crystal structure. A detailed analysis of the general energetic and entropic factors favoring chiral crystallization of helical polymers is carried out. It is shown that a hexagonal or pseudohexagonal arrangement (i.e. the 6-fold coordination) in either the crystalline or precrystalline state, promotes chiral crystallization and is in its own turn favored by clustering of isochiral helices.

Introduction

Polymers very often crystallize in chiral crystals, implying that within the individual crystallite all the chains share the same chirality, even when the molten or dissolved polymer is achiral. A statistical analysis in this field is difficult because of the degree of uncertainty still involved in the crystal structure determination of polymers, and in any case it is beyond the scope of this article. However, even a superficial survey of the literature reveals that crystallization of achiral or racemic polymers in chiral space groups is more frequent and relevant than similar occurrences with low molecular weight compounds. On the other hand hardly any general reasons have been proposed to explain why crystals comprising only helices of the same handedness may be more stable than those containing a racemic mixture. In fact, normally, the opposite is assumed and, at least in some cases that will be discussed below, the higher stability of racemic crystals appears in agreement with experimental evidence. Since the segregation of chains with the same chirality is a process with a low "a priori" probability, the question is particularly puzzling. We therefore decided to investigate possible reasons favoring chiral crystallization, devoting particular attention to the precrystallization step which must be of key importance in determining whether the nascent crystal will be chiral or not. Intuitively, chiral crystallization of achiral polymeric materials may be related to the occurrence of helical conformations and to the difficulty of interconversion between helices of opposite chirality once the crystal is developed.

General principles and guidelines which allow some rationalization of the solid state organization of polymers have been discussed by a number of authors.[1–5] A notable specific feature of polymers as opposed to low molecular weight systems is their tendency to the hexagonal close-packed arrangement of chains,[1,4,5] which is easily understood considering that chain stems can be roughly approximated by cylindrical shapes. The pseudohexagonal arrangement of cylinders represents also a first-approximation model to the local structure of polymers in the amorphous state.[6] It is a distinctive feature of rotationally disordered chains typical of polymeric mesophases which have been recently referred to as "columnar".[7] In these structures parallel chains display two-dimensional order in the plane perpendicular to their axis (at least with respect to the axis positions), whereas correlation between them is absent along the axial direction. Models that are locally very similar and include only a few polymer chains apply to small crystal-like associations of a few chain stems (i.e. "bundles"[8]), acting as subcritical nuclei in homogeneous crystallization processes both from solution[9] and from the melt.[10] We should note that the hexagonal close-packed or, more generally, the pseudohexagonal model is certainly not the only possibility and in certain cases other arrangements[11] (e.g. tetragonal or pseudotetragonal) may occur in mesomorphic polymer systems. However, as a more or less disordered chain stem approaches cylindrical encumbrance the pseudohexagonal arrangement will be by far the most favored one and represents a distinctive feature of the macromolecular solid state organization.

In the present paper we will attempt to show that chiral crystallization of nonchiral helical polymers should be thermodynamically favored in some cases, i.e. when pseudohexagonal crystalline packing is stable. In other instances it may result from the pseudohexagonal arrangement of helices in the precrystallization state (mesophases, nuclei, etc.) which may be "frozen in" for kinetic reasons in polymer crystals. The arguments will in general be limited to the synthetic polymer field because it is nearer to the background of the authors and because the occurrence of intermolecular hydrogen bonds generally present in biological macromolecules may complicate the analysis.

Chiral Crystallization of Helical Polymers: The Crystal Structures

The essential feature of crystallizable polymers is that, apart from notable exceptions, they consist of regular sequences of a chemical repeat. In principle these units can be either chiral, if they contain an asymmetric center, or achiral. On the contrary *helical conformations* adopted by polymer molecules in the crystalline state *are intrinsically chiral*, even if the

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[†] To our friend Mario Farina, whose keen interest in the chirality of polymers inspired the present study, on the first anniversary of his death (June 30, 1995).

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Table 1. Selected Data for Helical Polymers Displaying both Chiral and Achiral Modifications

polymer	phase	ϱ_{calc} (g/cm^3)	helix	Chir[a]	$T_{\mathrm{m(exp)}}$ (°C)	E[b] (kJ/mol)	H[c]	ref
it-polypropylene	α	0.94	3_1	n	175	0.0	1.55	22
	β	0.92	3_1	y	155	0.4	1.00	23
it-poly(1-butene)	I	0.95	3_1	n	136	0.0	1.73	24
	II	0.92	11_3	n	102		1.41	25
	III	0.90	4_1	y	96		1.17	26
poly(pivalolactone)	α	1.23	2_1	n	236	0.0	1.57	27
	γ	1.19	2_1	y	219	0.3	1.21	28
poly(*tert*-butylene sulfide)	o.i.[d]	1.10	3_1	n	210		1.32	29
	o.a.[d]	1.08	3_1	y	162		1.00	29
it-1,4-*cis*-poly(2-methylpentadiene)	α	1.00	2_1	n	175	0.0	1.57	30
	β	0.96	2_1	y	165	1.1	1.28	30

[a] n = achiral structure, y = chiral structure. [b] Energy, relative to the more stable modification, if available. [c] Hexagonality parameter (see text): $H = 1.00$ for hexagonal structures, 1.41 for tetragonal, and 1.73 for tricoordinated structures. [d] o.i. = optically active and respectively o.i. = optically inactive, i.e. racemic structures; note that similar considerations apply also to 1,4-*cis*-poly(2-methylpentadiene).

chemical repeat is achiral. This obviously does not apply to nonhelical molecules and to degenerate 2-fold helices (e.g. zigzag planar, *cis*–*trans* planar, or *glide* type) which also occur frequently but will not be discussed in this paper.

If individual identical monomers all share the same chirality then all helices in the sample will normally in their own turn share the same handedness (case 1). On the other hand, if the chemical repeat unit is nonchiral, right-handed and left-handed polymer helices will be equally probable (case 2). This is the well established consequence of the fact that the conformational energy of helices with opposite spiralization are generally different if individual chemical repeats are chiral, whereas helices of opposite handedness are isoenergetic if monomers are nonchiral. Poly(amino acids) or polysaccharides can be taken as examples of the chiral class, and stereoregular vinyl polymers are a classic case of the second type. An intermediate situation should be briefly considered wherein each individual polymer molecule consists of isochiral monomers but the macroscopic sample is a racemate (case 3): i.e. monomers with opposite absolute configurations occur in equal numbers and helices of opposite handedness are consequently equiprobable. The notable difference between this last instance and the one in which monomer units are achiral is that in the racemate case, in general helices of opposite chirality will not interconvert (i.e. they are not isoenergetic), while in the former instance, helices of opposite chirality can interconvert through a conformational rearrangement, although such a process will have a low probability as the chain approaches the crystalline organization.

If we analyze the available data concerning polymer crystal structures with the above considerations in mind, a large number of cases can be identified in which nonchiral systems (i.e. case 2 and 3 systems consisting of equiprobable right- and left-handed helices) also crystallize in a chiral space group in which only helices of a given chirality can exist within an individual polymer crystal; obviously, an equal weight fraction of crystals of the enantiomorphic space group will in general be present. In principle such a process can be the result of a thermodynamic or a kinetic drive. Cases where the former applies are reasonably straightforward, and their analysis will be postponed.

We will examine first some instances in which the packing of helices with opposite chirality within the same crystal is thermodynamically favored. This is sometimes[4] considered to be the "normal" situation and is a way to reformulate Wallach's rule[12,13] which states that racemic crystals are normally denser than the corresponding chiral ones. As previously noted,[13] the idea that racemic crystals are more stable than the corresponding chiral structures should be considered a reasonable hypothesis rather than an established fact. The rule however applies to the cases presented in Table 1: the relative energy, the density, and the melting temperature values clearly show a greater enthalpic stability for the racemic structures. The possibility of a thermodynamic drive toward chiral crystallization in the instances under consideration would rest on the assumption of a greater entropy value for the chiral crystalline structure, which seems rather unlikely as this phase in all the instances in Table 1 displays the lower melting point. Furthermore in the absence of substantially different degrees of dynamic disorder large entropy differences between polymorphs of a given substance are highly improbable.[13] For the cases presented in Table 1, excluding poly(*tert*-butylene sulfide, to account for the occurrence of the chiral crystalline phases, we remain with the kinetic explanation: if the idea of spontaneous segregation of molecules of a given chirality in the isotropic melt (or in solution) is rejected, the only alternative seems to be the development of an intermediate state, which could be a mesophase or a precrystalline nucleus, favoring somehow chiral crystallization.

Beyond the already discussed data, Table 1 reports for each structure an additional parameter: the hexagonality index H, defined as the ratio of the largest to the smallest distance between the axis of the reference chain and those of its six nearest neighbors. H is thus equal to 1.0, 1.41, and 1.73, respectively, for a hexagonal, a tetragonal, and a trigonal (i.e. tricoordinated) structure. It is interesting to note that in the examples in Table 1, for any given polymer, H attains its smallest value corresponding to the chiral structure, implying that the packing in the chiral structure will be significantly closer to an ideal pseudohexagonal arrangement. Since for the helical polymers in Table 1 the thermodynamic stability of the chiral crystalline modification appears to be lower than that of the nonchiral forms, the data in Table 1 could be accounted for with the 2-fold hypothesis that (i) the chiral structure should be favored by precrystallization factors, as anticipated previously, and (ii) the chiral structures derive from a precrystalline hexagonal chain packing, which tends to be maintained in the crystalline state.

Unlike those in Table 1, when the crystalline polymers reported in Table 2 adopt a nondegenerate helical chain conformation, the resulting crystal structure is chiral. Note that the list is by no means exhaustive and serves just as a series of examples. In the structures reported in Table 2, which are all chiral, the H index is found again to be very close to unity, except for the 7_2

Table 2. Data Relative to the Selected Polymer Displaying Only Chiral Crystalline Phases Where a Nontrivial Helical Conformation Is Adopted

polymer	phase	helix	H^a	ref
poly(tetrafluoroethylene)	triclinic	13_6	1.00	31
	"trigonal"	15_7	1.00	31
it-poly[(*S*)-4-methylhexene][b]	pseudotetragonal (tricl)	7_2	1.41	14
poly(isobutylene)	$P2_12_12_1$ (orth)	$\approx 8_3$	1.00	32
poly(oxymethylene)	trigonal (pseudohex)	9_5	1.00	33
	orthorhombic	2_1	1.05	34
poly(thiomethylene)	triclinic	17_9	1.00	35
poly(selenomethylene)	pseudohexagonal	21_{11}	1.00	36
	orthorhombic	2_1	1.00	37
it-poly(-5-methyl-1-hexene)	pseudohexagonal	3_1	1.00	38
it-poly[(*S*)-5-methyl-1-heptene][b]	pseudohexagonal	3_1	1.00	38
it-poly(*tert*-butyl acrylate)	pseudohexagonal	3_1	1.00	39
it-poly(isopropylethylene oxide)[b]	orthorhombic	2_1	1.01	40
poly(β-ethylpropiolactone)[b]	orthorhombic	2_1	1.36	41
poly(β-methylpropiolactone)[b]	orthorhombic	2_1	1.25	42
poly(diketene)	orthorhombic	2_1	1.04	43
poly(*p*-benzamide)	orthorhombic	2_1	1.01	44
poly(ethylene oxybenzoate)	orthorhombic	2_1	1.21	45
it-*cis*-poly(1,3-pentadiene)[b]	orthorhombic	2_1	1.08	46

[a] Hexagonality parameter (see text). [b] Optically active chemical repeat unit.

helix of *it*-poly[(*S*)-4-methylhexene].[14] This case is particularly relevant because, although the polymer presents an optically active carbon in the side chain, the structure consists of helices of opposite chirality as expected[4] (*vide infra*) for the pseudotetragonal packing implied by the value of the H index. In the other cases substantial differences from a pseudohexagonal packing occur only for certain 2-fold helices which present the more marked deviations from a continuous helix with a cylindrical envelope. We may add however that our analysis works better than could be expected for the generality of 2-fold helices (and even for "nonhelical" polymers), because the geometrical path of the chain bonds may provide physical reality to the helical description, which is missing in the abstract representation of the chain residues as pointlike objects. Table 2 in essence shows that if helical polymers adopt a pseudohexagonal packing (H close to 1) then individual crystallites are likely to consist of isochiral helices. The absence of data for the nonchiral packing of the corresponding helical molecules leaves us unable to make stability comparisons as carried out in Table 1. It is a hint suggesting that in the instances reported in Table 2 racemic packing of helices is unlikely to be favored.

Because of the packing specificity of individual molecules, the guidelines given above are by no means to be taken as strict rules. However counterexamples are rare and some of the few nonchiral structures with hexagonality indices close to 1.0 may involve statistical disorder[15,16] with respect to helix chirality. This in turn could be accounted for either by truly disordered structures or by chiral-domain structures. We are aware of only two cases[17,18] in which a pseudohexagonal packing has been established for regularly packed helices of opposite chirality.

A final remark is in order with respect to polymers which, always limiting our analysis to cases where a nondegenerate helical conformation is adopted, crystallize only in nonchiral crystals. A quick survey shows that in these cases tetragonal or tricoordinated chain arrangements are generally adopted, with an H index of 1.4 or greater. A large number of helical polymers with very bulky side groups, like more or less substituted isotactic-polystyrenes, involve tricoordinated structures often crystallizing in space groups $R3c$ or $R\bar{3}c$.[4]

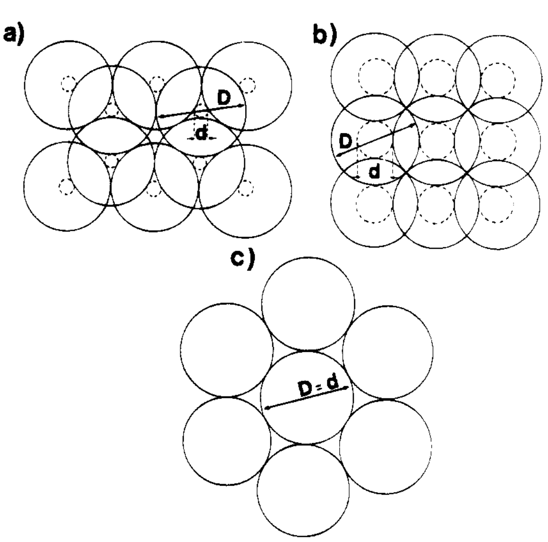

Figure 1. Different modes of packing of screwlike chains projected along the chain axis. D and d, respectively, represent the largest and the smallest diameter of the chains; (a)−(c) stand respectively for a "trigonal", a "tetragonal", and a "hexagonal" arrangement. The three modes are characterized by coordination numbers 3, 4, and 6, respectively.

Symmetry and Energy Consideration on Isochiral Chain Packing

At the onset of polymer crystallization, we may consider the following alternatives: (i) the process is slow enough as to be virtually at equilibrium, in which case the resulting crystalline structure may depart completely from the one existing in the precrystallization state; (ii) the crystallization process is so fast that equilibrium cannot be approached, and the resulting crystalline structure will closely resemble the one existing in the precrystallization state. Otherwise stated, points i and ii may be referred to respectively as the equilibrium and the kinetic viewpoints. In this section we shall present some considerations to show that a hexagonal or pseudohexagonal packing of chains having an approximately cylindrical shape gives both an equilibrium and a kinetic advantage to the presence of isochiral chains. We shall start from the equilibrium aspects.

Corradini[4] presented an interesting argument to suggest that, whenever the polymer chain may be approximated by a smooth impenetrable surface similar to a screw, a tetragonal packing of antichiral chains is favored if the ratio of the largest to the smallest screw diameter is in the vicinity of $1/(\sqrt{2} - 1) \cong 2.4$. In fact in this case a tight fitting of threads into grooves is achieved, each chain having four nearest neighbors of opposite chirality. If the ratio is substantially larger than 2.4, approaching the figure $\sqrt{3}/(2 - \sqrt{3}) \cong 6.5$, for the same reason a trigonal packing may arise, whereas the best space filling is obtained through a hexagonal arrangement if the ratio is much smaller than 2.4, tending toward unity (see Figure 1). It is this last case that forms the principal object of the present analysis.

From a crystallographic viewpoint, let us point out that it is not possible to pack two different types of chains, such as helices of opposite chirality, in a hexagonal arrangement and keep them symmetrically equivalent. In fact, the unit cell of a crystal consisting of close-packed cylindrical objects is bound to comprise either one or three or more such objects, but only in the first case are they equivalent. The obvious conclusion is that a hexagonal packing of nonisochiral chains

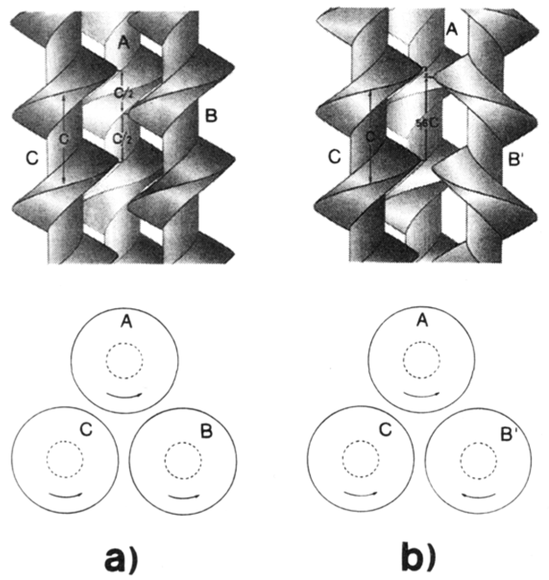

Figure 2. Two arrangements of groups of three helical chains packing in a hexagonal or a pseudohexagonal mode. The chains are represented by continuous screws. In (a) the three screws are isomorphous and facing points of neighboring screws are exactly midway along the axial coordinate. Conversely, in arrangement b the chain B′ is enantiomorphous with respect to both A and C and, if the axial displacement is fixed to optimize packing within pairs AC and AB′, the packing between C and B′ is bound to be less satisfactory.

cannot achieve the highest possible crystallographic symmetry. *A higher crystal symmetry, as noted by Corradini[4] following some general hints by Kitagorodsky,[1] implies wider minimum energy wells wherein atoms and molecules are located, and consequently a larger vibrational entropy.* Hence, a hexagonal crystal of isochiral chains should have an entropic advantage over one made of antichiral chains. [This observation will be even more relevant for high-entropy mesomorphic phases or precrystalline nuclei, with substantial implications on kinetically controlled crystallization.]

We now turn our attention to some general packing considerations. Disregarding cases where the chain has deep grooves and prominent bulges, which may favor a tetragonal or a trigonal arrangement as stated before,[4] we confine our attention to the hexagonal, or pseudohexagonal, chain packing. Each chain will be conveniently idealized as a continuous helix that connects the more peripheral atoms in the chain i.e. the atoms more distant from the chain axis. Our purpose is to compare the packing efficiency for parallel stem arrangements of helices (i) of a single chirality and (ii) of opposite chiralities. For either case Figure 2 shows the smallest significant fragment comprising three chains. In case a we see that the closest helix-to-helix contacts may be best relieved if the three chains are obtained from one another by a rigid lateral translation with a zero component in the axial direction; in fact, the axial coordinate of the helix point closest in projection to the axis of a neighboring chain is exactly midway between the axial coordinates of the more protruding points on the adjacent helix. This does not occur in (b) where simultaneous optimization of the contacts involving helix pairs AB′ and AC (B′ is enantiomorphic with respect to both A and C) produces close contacts between helices B′ and C, facing bulges being at nearly the same height. *We may conclude that arrangements of helices possessing the same chirality are favored in a pseudohexagonal packing.*

An additional stabilization factor may be provided by the common arbitrary rotation that all helices may undergo around their axes with virtually no change of the closest packing distances. In this respect, the basic invariance of the nonbonded interaction energy under an equal rotation of all chains around their axes, found by Giglio and D'Ilario[19] for crystalline poly(tetrafluoroethylene) (PTFE) for both the 13_6 and the 15_7 structures but not for the polyethylene planar zigzag structure, is a strong support to the present argument. Obviously enough, since the entropic gain amounts to a single degree of freedom per crystallite, on a single-chain basis the gain is larger, the smaller the number of chains within the crystallite.

Another relevant feature concerns the number of monomer units per helical repeat N in a N_M helix. In general, the larger N the more the chain atoms may be regarded as uniformly spread on an ideal helix, leading to a more closely cylindrical chain encumbrance. A similar but less compelling argument may apply also to the number of monomers N/M per helix turn and to the value of the helix repeat h. We should thus expect that for helices with comparatively large N and h values, pseudohexagonal arrangements will be frequently favored and isochiral packings should be relatively frequent. Again, in the case of PTFE, as N grows from 13 to 15 (M from 6 to 7 and h from 16.88 to 19.50 Å), the barrier to the rotation of a helix around its axis while keeping the six nearest neighbors chains fixed, has been shown to decrease significantly.[19] The disordering mode suggested by Clark and Muus for the 15_7 PTFE structure,[20] involving small statistical rotations of each chain around its axis, appears to take advantage of these features typical of the isochiral helix packing. On the other hand the case of poly(ethylene oxide) (PEO) indicates that these guidelines need to be applied with care: although the conformation of PEO is not far from a 7/2 helix with a periodicity h of 19.5 Å, it crystallizes in the centrosymmetric space group $P2_1/a$[21] with $H = 1.43$. The minimization of packing energy achieved with this pseudotetragonal arrangement causes apparently significant regular departures from the intramolecular helical symmetry, making this a borderline case for our analysis.

In the preceding discussion we examined aspects promoting essentially equilibrium crystallization of isochiral chains. Let us now turn to a relevant factor helping the formation of small bundles of isochiral chains in the precrystallization state, namely twist deformation (see Figure 3). This type of cooperative distortion may help to explain the formation of isochiral crystals, whether hexagonal or not, from either bundle association or bundle accretion by surface deposition, even when the resulting crystals do not represent the most stable structure. This applies if the crystallization rate from the melt, a solution, or a mesophase is large enough and the final temperature sufficiently low as to hinder extensive molecular reorganization. Twist deformation, or cooperative spiralized deformation of all chains within a bundle, represents perhaps the most important departure from straight-chain packing, in that it preserves a compact filling of space; double and triple helices are to be regarded as particular cases of twist deformation. A semiquantitative argument for the larger entropic stability of isochiral bundles may be given as follows. As far as a single chain is concerned, twist deformation may be described as imparting a set of small changes to the rotation angles within each

Figure 3. Cooperative twist deformation of a bundle of three chains (see text). In the instance shown the regularity of the deformation gives rise to a triple helix.

monomeric unit, that we shall denote as $\{\Delta\theta\}$. We shall evaluate the statistical probability (i.e., the sum of the Boltzmann weights) of a bundle by assuming for sake of simplicity that (1) the bundle may only be twisted in two opposite ways (+ and −), and that (2) all the chains within the bundle undergo the same deformation angles $\{+\Delta\theta\}$ and $\{-\Delta\theta\}$, in the two respective cases. Two different possibilities will be considered, i.e., (i) the bundle comprises n chains all having the same chirality; (ii) of the n chains belonging to the bundle, n_1 chains are right-handed and n_2 are left-handed, with $n_1 + n_2 = n$. Let us remark that a right-handed chain with deformation angles $\{+\Delta\theta\}$ has the same conformational energy ϵ_1 as a left-handed helix with deformation angles $\{-\Delta\theta\}$, since the two objects are merely mirror images of one another; the same is true of a right- and left-handed helix with respective deformation angles $\{-\Delta\theta\}$ and $\{+\Delta\theta\}$, ϵ_2 being their common energy. For the two cases (i) and (ii), respectively, the statistical probability is

$$w_{(\mathrm{i})} = \exp[-n\epsilon_1/k_\mathrm{B}T] + \exp[-n\epsilon_2/k_\mathrm{B}T]$$

$$w_{(\mathrm{ii})} = \exp[-(n_1\epsilon_1 + n_2\epsilon_2)/k_\mathrm{B}T] + \exp[-(n_2\epsilon_1 + n_1\epsilon_2)/k_\mathrm{B}T] \quad (1)$$

After the substitutions

$$a_1 = \exp[-\epsilon_1/k_\mathrm{B}T] \qquad a_2 = \exp[-\epsilon_2/k_\mathrm{B}T] \quad (2)$$

we have, remembering $n = n_1 + n_2$,

$$w_{(\mathrm{i})} - w_{(\mathrm{ii})} = a_1^{\,n} + a_2^{\,n} - a_1^{\,n_1}a_2^{\,n_2} - a_1^{\,n_2}a_2^{\,n_1} = (a_1^{\,n_1} - a_2^{\,n_1})(a_1^{\,n_2} - a_2^{\,n_2}) \quad (3)$$

We see that, for any non-zero values (n_1, n_2), we always have $w_{(\mathrm{i})} > w_{(\mathrm{ii})}$ no matter what the energies ϵ_1 and ϵ_2 are. Therefore we conclude that the statistical probability of bundle twisting is always larger for isochiral chains than for chains distributed between the two opposite chiralities. The argument may be easily generalized for a continuous ensemble of twist angles as well as for chains undergoing different twist deformations, as required whenever their axes are at a different distance from the axis of the bundle.

Conclusions

The analysis developed in this paper suggests that, if a crystalline structure of helical macromolecules is nucleated from a hexagonal columnar mesophase or from precrystalline nuclei with a hexagonal arrangement of chains, it will have a high probability to be chiral. Furthermore a pseudohexagonal packing is energetically favored and frequently occurs both for chiral helical polymers and for chiral crystal structures of non-intrinsically-chiral helical polymers. Whether the crystal structure of a helical polymer is chiral or not can thus be very often predicted simply by examining the hexagonality index H of a given packing. H is the ratio of the largest to the smallest distance between the reference chain axis and its six nearest neighbors and will be relatively close to 1.0 for chiral structures while it will have normally values of 1.4 or higher for achiral packings. Counterexamples can occur as the idealized model of the continuous helix may not always apply strictly enough to actual polymer molecules. Some of the few exceptions we have identified may however involve statistical disorder with respect to helix chirality.[15,16] This could result as a consequence of true local statistical disorder or, alternatively, because of the occurrence of antiphase domains of opposite chirality. This second possibility would also bring these instances back within the framework of our treatment. On the other hand in the two cases[17,18] we identified where chains of opposite chirality pack pseudohexagonally in a regular mode, the interchain contacts are looser for isochiral than for antichiral chain pairs, consistent with our analysis. In short, polymer chains in a hexagonal arrangement have normally the lowest free energy if all the helices have the same handedness because (i) the isochiral arrangement has the largest vibrational entropy and the best chain-to-chain contacts and (ii) in the case of small bundles of chains, isochiral aggregates may undergo twist deformations with the largest statistical probability.

The reasons of the kinetic preference for chiral crystalline phases often occurring in polymers could be simply related to the fact that if the overall hexagonal packing normally found in the precrystalline state is maintained in a crystalline arrangement with hexagonality index close to 1.0, then chiral structures are preferred. In other words *in precrystalline states, if conformationally disordered chains which are roughly cylindrical and packed pseudohexagonally undergo an ordering process aimed at lowering their intermolecular potential energy, isochiral helices will tend to develop.* [This consideration may help us to understand why so many polymers which formally are "nonhelical" adopt chiral crystal structures with H indices close to 1.0.] Pseudohexagonal structures with regularly packed right- and left-handed helices are in other words extremely unlikely.

As shown by Corradini,[4] both the tetragonal and the tricoordinated arrangement (with hexagonality index H = 1.41 and 1.73, respectively) favor the copresence of antichiral helices. Since such arrangements (the more so the trigonal one) are substantially less attractive for disordered, approximately cylindrical chains, tetragonal and especially tricoordinated crystal structures will be kinetically less favored and will develop often very slowly, as in the case of isotactic polystyrene. These explanations allow a reasonable interpretation of the data in both Tables 1 and 2. Furthermore, the more pronounced tendency of polymers toward crystallization in chiral environments is accounted for. Finally, in some analogy with the argument put forward by Pratt Brock et al.[13] for low molecular weight substances, we can observe that, for any given polymer, *in order for both chiral and non chiral polymer structures to form, the racemate structure should be significantly more stable than the chiral ones, as otherwise chiral structures, favored by kinetic factors, will tend to occur.* Indeed, when both chiral and nonchiral polymer crystal structures are observed the nonchiral are likely to be the more stable ones while the chiral modifications develop under kinetic control.

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References and Notes

(1) Kitagorodsky, A. J. *Molecular Crystals and Molecules*; Academic Press: New York, 1973.
(2) Frank, F. C.; Keller, A.; O'Connor, A. *Phil. Mag.* **1959**, *4*, 200.
(3) Noether, H. D. *J. Polym. Sci., Part C* **1967**, *16*, 725.
(4) Corradini, P. The Robert A. Welch Foundation Conferences on Chemical Research. X. Polymers, Houston, TX, 1966; Corradini, P. In *The Stereochemistry of Macromolecules, Part III*; Ketley, A. D., Ed.; Marcel Dekker Inc.: New York, 1968.
(5) Wunderlich, B. *Macromolecular Physics*; Academic Press: New York, 1973; Vol. 1.
(6) See for example: Klug, H. P.; Alexander, L. E. *X-ray Diffraction Procedures*; Wiley: New York, 1974.
(7) Ungar, G. *Polymer* **1993**, *34*, 2050
(8) Allegra, G. *J. Chem. Phys.* **1977**, *66*, 5453. Allegra, G. *Ferroelectrics* **1980**, *30*, 195.
(9) Chau, K. W.; Geil, P. H. *J. Macromol. Sci., Phys.* **1983**, *B22*, 543.
(10) Meille, S. V. *Polymer* **1994**, *35*, 2607.
(11) Ballauff, M.; Schmidt, G. F. *Makromol. Chem., Rapid Commun.* **1987**, *8*, 93. Adam, A.; Spiess, H. W. *Makromol. Chem., Rapid Commun.* **1990**, *11*, 249.
(12) Wallach, O. *Liebigs Ann. Chem.* **1895**, *286*, 90.
(13) Pratt Brock, C.; Schweizer, W. B.; Dunitz, J. D. *J. Am. Chem. Soc.* **1991**, *113*, 9811.
(14) Bassi, I. W.; Bonsignori, O.; Lorenzi, G. P.; Pino, P.; Corradini, P.; Temussi, P. A. *J. Polym. Sci., Polym. Phys. Ed.* **1971**, *9*, 193.
(15) Farmer, B. L.; Lando, J. B. *J. Macromol. Sci., Phys.* **1974**, *B10*, 403.
(16) Kusanagi, H.; Tadokoro, H.; Chatani, Y. *Macromolecules* **1976**, *9*, 531.
(17) Lind, M. G.; Geller, S *J. Chem. Phys.* **1969**, *51*, 348.
(18) Corradini, P.; Ganis, P.; Petraccone, V. *Eur. Polym. J.* **1970**, *6*, 281.
(19) D'Ilario, I.; Giglio, E. *Acta Crystallogr.* **1974**, *B30*, 372.
(20) Clark, E. S.; Muus, L. T. *Z. Kristallogr.* **1962**, *117*, 119.
(21) Takahashi, Y.; Tadokoro, H. *Macromolecules* **1973**, *6*, 672.
(22) Natta, G.; Corradini, P. *Nuovo Cimento Suppl.* **1960**, *15*, 40. Ferro, D. R.; Brückner, S.; Meille, S. V.; Ragazzi, M. *Macromolecules* **1991**, *24*, 1156.
(23) Turner-Jones, A.; Aizlewood, A.; Beckett, D. R. *Makromol. Chem.* **1964**, *75*, 134. Meille, S. V.; Ferro, D. R.; Brückner, S.; Lovinger, A.; Padden, F. J. *Macromolecules* **1994**, *27*, 2615. Lotz, B.; Kopp, S.; Dorset, D. *Compt. Rend.* **1994**, *319*, 187.
(24) Natta, G.; Corradini, P.; Bassi, I. W. *Nuovo Cimento Suppl.* **1960**, *15*, 52.
(25) Turner-Jones, A. *J. Polym. Sci.* **1963**, *B1*, 455. Petraccone, V.; Pirozzi, B.; Frasci, A.; Corradini, P. *Eur. Polym. J.* **1976**, *12*, 323.
(26) Cojazzi, G.; Malta, V.; Celotti, G.; Zannetti, R. *Makromol. Chem.* **1976**, *177*, 915; Dorset, D. L.; McCourt, M.; Kopp, S.; Wittmann, J. C.; Lotz, B. *Acta Crystallogr.* **1994**, *B50*, 201.
(27) Carazzolo, G. *Chim. Ind. (Milan)* **1964**, *46*, 525. Perego, G.; Melis, A.; Cesari, M. *Makromol. Chem.* **1972**, *169*, 525. Brückner, S.; Meille, S. V.; Porzio, W. *Polymer* **1988**, *29*, 1586.
(28) Meille, S. V.; Brückner, S.; Lando, J. B. *Polymer* **1989**, *30*, 786. Ferro, D. R.; Brückner, S.; Meille, S. V.; Ragazzi, M. *Macromolecules* **1990**, *23*, 1676.
(29) Matsubayashi, H.; Chatani, Y.; Tadokoro, H.; Dumas, P.; Spassky, N.; Sigwalt, P. *Macromolecules* **1977**, *10*, 996.
(30) Cabassi, F.; Porzio, W.; Ricci, G.; Brückner, S.; Meille, S. V.; Porri, L. *Makromol. Chem.*, **1988**, *189*, 2135. Brückner, S.; Meille, S. V.; Porzio, W.; Ricci, G. *Makromol. Chem.* **1988**, *189*, 2145. Ferro, D. R.; Brückner, S.; Meille, S. V.; Ragazzi, M. *Macromolecules* **1992**, *25*, 5231.
(31) Sperati, C. A.; Starkweather, H. W., Jr. *Adv. Polym. Sci.* **1961**, *2*, 465. Bunn, C. W.; Howells, E. R. *Nature* **1954**, *174*, 549. Clark, E. S.; Muus, L. T. *Z. Kristallogr.* **1962**, *117*, 119. Corradini, P.; Guerra, G. *Macromolecules* **1977**, *10*, 531. Yamamoto, T.; Hara, T. *Polymer* **1982**, *23*, 521.
(32) Tanaka, T.; Chatani, Y.; Tadokoro, H. *J. Polym. Sci., Polym. Phys. Ed.* **1974**, *12*, 515.
(33) Tadokoro, H.; Yasumoto, T.; Murahashi, S.; Nitta, I. *J. Polym. Sci.* **1960**, *44*, 266. Carazzolo, G. *J. Polym. Sci. A* **1963**, *1*, 1573. Uchida, T.; Tadokoro, H. *J. Polym. Sci., Polym. Phys. Ed.* **1967**, *5*, 63.
(34) Carazzolo, G.; Mammi, M. *J. Polym. Sci., Part A* **1963**, *1*, 965.
(35) Carazzolo, G.; Valle, G. *Makromol. Chem.* **1966**, *90*, 66.
(36) Carazzolo, G.; Valle, G. *J. Polym. Sci. A* **1965**, *3*, 4013.
(37) Carazzolo, G.; Mammi, M. *Makromol. Chem.* **1967**, *100*, 28.
(38) Natta, G. *Makromol. Chem.* **1960**, *35*, 93. Corradini, P.; Martuscelli, E.; Montagnoli, G.; Petraccone, V. *Eur. Polym. J.* **1970**, *6*, 1201.
(39) Natta, G.; Corradini, P. *Chim. Ind. (Milano)* **1963**, *35*, 299.
(40) Takahashi, Y.; Tadokoro, H.; Hirano, T.; Sato, A.; Tsuruta, T. *J. Polym. Sci., Polym. Phys. Ed.* **1975**, *13*, 285.
(41) Yokouchi, M.; Chatani, Y.; Tadokoro, H.; Tani, H. *Polym. J.* **1974**, *6*, 248.
(42) Cornibert, J.; Marchessault, R. H. *J. Mol. Biol.* **1972**, *71*, 735. Yokouchi, M.; Chatani, Y.; Tadokoro, H.; Teranishi, K.; Tani, H. *Polymer* **1973**, *14*, 267. Brückner, S.; Meille, S. V.; Malpezzi, L.; Cesaro, A.; Navarini, L.; Tombolini, R. *Macromolecules* **1988**, *21*, 967.
(43) Yokouchi, M.; Chatani, Y.; Tadokoro, H. *J. Polym. Sci., Polym. Phys. Ed.* **1976**, *14*, 81.
(44) Tashiro, K.; Kobayashi, M.; Tadokoro, H. *Macromolecules* **1977**, *10*, 413.
(45) Kusanagi, H.; Tadokoro, H.; Chatani, Y.; Suehiro, K. *Macromolecules* **1977**, *10*, 405.
(46) Meille, S. V.; Barnasangiin, P.; Allegra, G.; Italia, S.; Porri, L.; Ricci, G. Paper in preparation.

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