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Chirality Constraints in Crystal−Crystal Transformations: Isotactic Poly(1-butene) versus Syndiotactic Polypropylene

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ABSTRACT: Solid-state crystal−crystal transformations in polymers are limited by conformational and steric constraints when helical hands are involved in the initial, final, or both stages of the transformation. The constraints are illustrated by (a) the phase II to phase I transformation in isotactic poly(1-butene), which preserves the chirality of the helices, and (b) the generation of unusual, *chiral* crystal phases of syndiotactic polypropylene when starting from an extended-chain crystal phase, whereas the stable structure is *fully antichiral*. In the latter case, the isochirality of the resulting helical phase indicates that the transformation is a *cooperative process*.

1. Introduction

Crystal−crystal transformations, if not widespread, are, nevertheless, relatively frequent among crystalline polymers. Some of them are spontaneous, but most are induced by specific treatments (in particular, mechanical, e.g., on stretching). From a conformational standpoint, the initial and final crystal phases may be based on identical conformations of the chain, as in the all-trans orthorhombic and monoclinic phases of polyethylene (PE),[1] in the α and β phases of poly(ethylene-*co*-carbon monoxide) (POK),[2] or in the α to δ transformation of poly(vinylidene fluoride)[3] (helices with $tgtg^-$ conformations). Alternatively, the crystal phases may involve different initial and final helical chain conformations, as in the well-known, spontaneous transformation of isotactic poly(1-butene) (PBu1) from phase II (11_3 helix) to phase I (3_1 helix).[4] Finally, the crystal phases may involve extended-chain conformations and helical ones, as in the transformation from phase III of syndiotactic polypropylene (sPP) (extended chain, all-trans conformation) to phases II and IV (helices based on t_2g_2 and $t_2g_2t_6g_2$ chain conformations, respectively).[5,6]

Crystal−crystal transformations which preserve the initial chain conformations and involve only chain rotations and/or shifts are not subject to any specific constraints. The relative orientations of initial and final crystal lattices as well as the nature of the "transition" planes reflect merely the best energetic pathway from one crystal lattice to the other. These relationships have been investigated in considerable detail and analyzed in terms of the Bevis model for crystal-phase transformations.[7,8]

Crystal transformations in which helical conformations are involved are subjected to more severe constraints. The major one is the need to preserve the initial helical hands during the transformation process: reversal of helical hand is indeed an unlikely molecular event (this statement certainly applies for polyolefins, but may suffer exceptions, as for the twin helix-reversal defects of poly(tetrafluoroethylene)[9] or also for some polypeptides, e.g., derivatives of poly(L-aspartate)[10] in which the helix envelope is little modified in the process). In the present paper, these constraints are recalled and/or discussed by taking two examples of the above-mentioned crystal−crystal transformations: the phase II to phase I transformation of PBu1 and the generation of the helical phases II and IV starting from the all-trans conformation (phase III) of sPP, which turns out to provide new insights into the "chirality" of the transformation process itself.

2. Transformation of Phase II of PBu1 into Phase I: Preservation of Helical Hands

The spontaneous transformation of phase II of PBu1 into phase I illustrates the constraints set by preservation of the helical hands (Figure 1). Phase II is a tetragonal packing of 11_3 helices with alternation of helical hands along both *a* and *b* axes: as a result, (110) layers are made of isochiral helices, with successive layers being antichiral. Phase I is a trigonal unit cell with 3-fold helices with, also, antichiral alternation of (110) layers made of isochiral helices. Upon transformation, it is observed that the (110) planes of the resultant trigonal unit cell are parallel to the (110) planes of the parent tetragonal unit cell (Figure 1).[11] This relative orientation, first established by Fujiwara,[12] illustrates most convincingly the requirement of preservation of the helical hands in the transformation: any other relative orientation of initial and final lattices would require reversal of helical hands of at least a fraction of the stems. In addition, the transformation is facilitated by a very fortunate near-matching (−5%) of interhelical distances in the two planes, which means that helix shifts are minimized during the transformation (but the contraction is nearly 20% in the orthogonal direction, with resultant development of cracks in the transformed crystal).[11] In other words, when the nomenclature introduced by Bevis is followed,[7] a favorable

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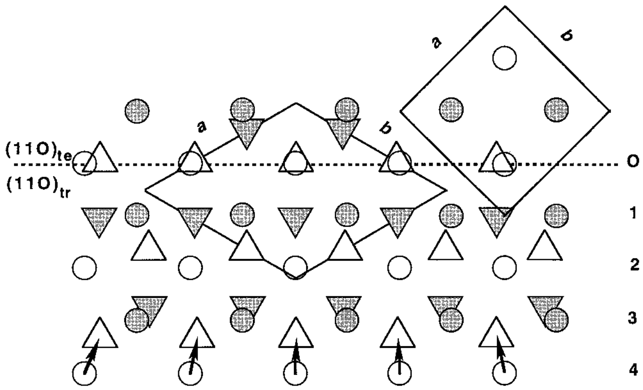

Figure 1. Scheme of the transformation mechanism of isotactic poly(1-butene) in its tetragonal form II to the trigonal form I. Helices of the two forms are represented as circles (for the 11_3 or 11_8 helix of the tetragonal form) and triangles (3-fold helices of the trigonal form), and the helical hands are differentiated by the shading. The "invariant plane" is $(110)_{te}$ for the tetragonal form and $(110)_{tr}$ for the trigonal form. Transformation in that plane (plane 0) takes place with limited lateral movements. As the transformation proceeds to planes 1, 2, 3, ..., movements (illustrated in plane 4) are amplified because of the ≈20% densification upon transformation, *but the helical hands are maintained in the process.* Adapted from ref 11 and reproduced from ref 10 with permission.

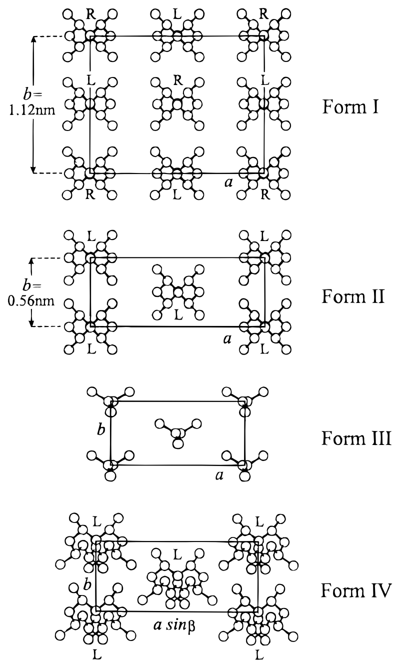

Figure 2. Different crystal modifications of sPP. The stable form I rests on a packing of antichiral helices (marked as R and L). The transformations under discussion start with phase III (extended chain, obtained on stretching) and yield the two chiral phases II and IV. Phase II has the same chain conformation but cell symmetry and cell dimensions (*b* axis halved) different from those of phase I. Note that the chain conformation of phase IV is not *stricto sensu* helical, but it has a right or left ("helical") hand, which is the feature of interest in the present analysis. Using a convenient shorthand, but loose terminology, we therefore describe it as a "helix".

(on geometric grounds) "invariant plane" which also meets the preservation of the helix chirality requirement happens to exist. In particular, the transformation proceeds across growth sector boundaries which exist in single crystals: the crystallographic constraints are much more important than the fold orientation requirement, which was at one time[3] thought to influence the transformation process. Finally, it should be noted that the transformation takes place between two "natural", spontaneous crystal modifications of PBu1, in sharp contrast with the situation described now for sPP.

3. Transformation of Phase III of Syndiotactic Polypropylene into Phases II and IV: An Isochiral Process

Figure 2 presents the various crystal phases known for sPP. The transformation of the extended all-trans phase III[13] of sPP into helical phases takes place either upon simple release of the applied tension (and generates a mixture reported to contain primarily phase II)[5] or upon exposure of the stretched sample to various solvent vapors (and generates predominantly phase IV).[6]

Both phases II and IV are based on packing of *isochiral* helices with conformations $(t_2g_2)_n$ or $(t_2g_2t_6g_2)_n$ into an orthorhombic[14] and a triclinic[6] (recently reinterpreted as monoclinic[15]) unit cell, respectively. The feature of interest in the present context is that *phase II of sPP is not the most stable phase* based on the t_2g_2 chain conformation: it is phase I, which has an orthorhombic cell also, but with a *b* parameter doubled to 11.2 Å (Figure 2), and rests on a packing of antichiral helices along both *a* and *b* axes.[16−18] Phase I is obtained in most of the crystallization range and in pure form at high crystallization temperatures. At lower T_c's, a packing typical of phase II sets in and introduces a structural disorder.[19,20] Indications of occasionaly "purer" phase II crystallization have been observed (in the form of (110) reflections characteristic of its C-centered chain packing) or in a more systematic manner upon quench precipitation from solution.[21] However, these (110) reflections are best evidenced in fiber X-ray diffraction patterns: indeed, the initial crystal structure determination was based on such diffraction patterns and led to the identification of phase II as the (at that time only) crystal structure of sPP.[14]

No similar comparison with an antichiral variant is possible for phase IV based on the $t_2g_2t_6g_2$ chain conformation. However, summing up the above analysis, we conclude that *the two crystal structures of sPP produced on transformation of the all-trans phase are both based on isochiral helices only*, even though, in one documented case at least, this structure is *less stable* than its antichiral counterpart.

The generation of isochiral helices during the transformation process may be rationalized by steric and conformational constraints. Generation of a helix structure requires the introduction of gauche$^+$ or gauche$^-$ bonds (hereafter g and g$^-$) in an all-trans chain:

$$\mathrm{ttttttt} \rightarrow \mathrm{ttggtttt} \rightarrow \mathrm{ttggttggtt...}$$

which imply a modification of chain direction and ultimately generation of a helix with a larger cross section than that of the initial conformation. Such processes also involve very major molecular readjustments, which, to take place, *must be cooperative ones.* A similar cooperativity, but on a much larger, almost macroscopic scale, is illustrated by kink bands in polyethylene (Figure 3).[22,23] On a molecular level, the kink bands correspond to g (or g$^-$) conformations which are concentrated at the same level (along the *c* axis) of

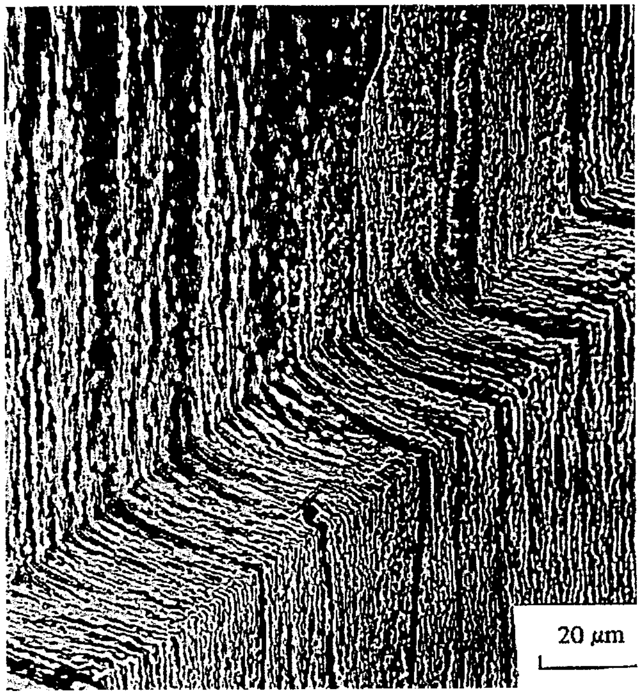

Figure 3. Optical micrograph of a kink band (acetate replica) produced by uniaxial compression of a fiber-oriented polyethylene initially annealed under anabaric conditions. Reproduced from ref 22, with permission.

the chain, as in

ttttttttttttttttttttttgttttttttttttg^-ttttttttttttttttttttttt

ttttttttttttttttttttttgttttttttttttg^-ttttttttttttttttttttttt

ttttttttttttttttttttttgttttttttttttg^-ttttttttttttttttttttttt

In PE, these gauche conformations are actually a little staggered along the chain and are located in a plane indexed as (012).[24] Any *single* (012) plane can contain only g or g^- conformations, since different chain orientations would be created. The next family of gauche conformations must be “segregated” in a neighboring (012) plane, where it generates the second component of the kink band, thus restoring the initial chain orientation. Figure 3 provides a most spectacular illustration of this cooperativity and segregation of like gauche conformers in a kink band produced by compression along *c* of a fiber-oriented polyethylene annealed under anabaric conditions.[22,23]

The cooperativity of the generation of gauche bonds illustrated by the kink bands of PE should also apply to the phase transformations which involve as the initial state the extended-chain phase of sPP. In particular, formation of right- and left-handed helices mixed on a molecular scale (i.e., as in the phase I crystal structure) appears sterically most unlikely since it would result in two transient, local stem orientations which would “diverge” on opposite sides of the initial extended chain (as shown in Figure 3 for the two different kink bands). On this basis, it appears that the generation of *isochiral* phases II and IV from the all-trans phase III of sPP *reflects steric constraints of the transformation mechanism itself: the generation of helical structures from an all-trans chain is, for steric reasons, an isochiral process.* The cooperativity described for one gauche bond is expected to apply at other levels of the chain, again as in the case of the kink band. When “travelling” in unison along the extended sPP chains, it creates an isochiral domain, in view of the interchain cooperativity just discussed.

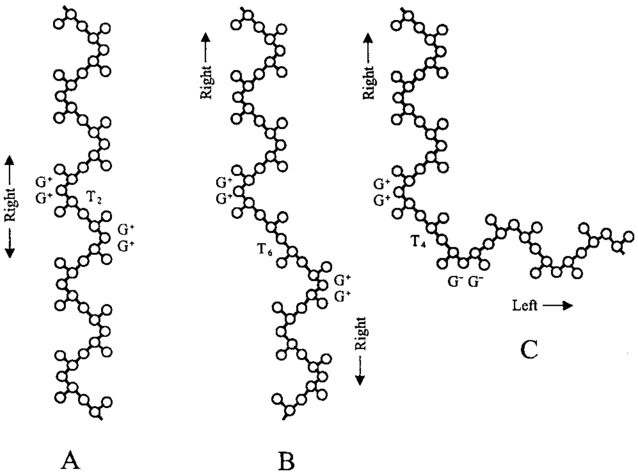

Figure 4. Model chains and structural defects for sPP: (A) A $(t_2g^+_2)_n$ right-handed helix representative of phases I and II. (B) Two right-handed portions of a chain connected by a t_{4n+2} ($n = 1$) defect. Note that whereas this model as a whole corresponds to a structural defect in phase II, the central $g_2t_6g_2$ sequence plus one neighbor t_2 conformations correspond to the structural repeat unit of phase IV. (C) Right-handed (top) and left-handed (bottom) portions of chains connected by a t_{4n} (with here $n = 1$) defect.

When examined at the individual chain level, the generation of gauche bonds in sPP is submitted to intrachain conformational constraints which help to understand the specificity of the transformation process, as well as acceptable and unacceptable structural disorders, with the latter being linked with “wrong” sequences of trans and gauche bonds.

On this basis, the transformation from extended-chain to (right-handed) helix in sPP amounts to generating a ...ttggttggtt... conformational sequence (Figure 4A) when starting from an all-trans sequence. It is worth noting, however, that such phase transformations are often associated with the onset of some conformational disorder. Most prominent among these disorders is the occurrence of “kink bands” of the type examined for PE (but on a much more local scale) which involve various lengths of trans sequences. This disorder has been observed in phase II obtained by quench crystallization of sPP solutions.[21,27] From a conformational standpoint, such defects are *by necessity* composed of $4n + 2$ trans conformations of the chain and link, again by design, two *isochiral* helical stretches of the chain which in addition have parallel helix axes (cf. Figure 4B). By the same token, the possible occurrence of both right- and left-handed stretches along the same stem as a result of generation of g^- and g^+ bonds appears unlikely. It would link stretches separated by $4n$ bonds and would result in antichiral helical stretches oriented at right angles to each other (Figure 4C).[25,26] This defect appears incompatible with a solid−solid transformation process of a syndiotactic polymer (although close association of g^+ and g^- bonds in a g^+tg^- sequence is a standard feature in so-called molecular “crankshafts” of linear polymers).

On a more global scale, a third type of disorder must exist: in the transformation, the “nucleation sites” themselves are chiral. Depending on the nucleation frequency, whole crystallites may “become” isochiral or may be made of different antichiral domains. In any case, the overall structure as a whole is racemic, since it is composed of domains (or crystallites) made of right-handed helices and others made of left-handed helices.

The transformation is also subjected to additional, larger scale geometric (steric) constraints, as best illustrated by the changes in cross section upon generation of a helix. Interestingly, such constraints *do not apply* for the phase II to phase I transformation in PBu1, since the cross section *shrinks* by nearly 20%. As already indicated, this shrinking mainly takes place in a direction normal to the invariant (110) plane and results in the development of multiple cracks parallel to the invariant plane in transformed single crystals.[11] *In contrast, the formation of helical structures from initial all-trans phases* increases *the cross section and, therefore, is constrained for geometric reasons*. For sPP, the cross section of the initial, extended phase III is nearly 30 Å^2 (29.15 Å^2) as opposed to 40.3 and 40.5 Å^2 for the final phases II and IV, respectively.

At any rate, the present hypothesis of isochiral transformation of the extended-chain phase of sPP helps rationalize the early assignment of phase II as the structure of sPP.[14] It is indeed tempting to consider that since the crystal structure was determined on *oriented* samples, they may have experienced generation of the all-trans phase as a result of stretching, which has thereafter *relaxed into the isochiral phase II*: this process has indeed been monitored recently.[5] Also, the conspicuous presence of phase II in these fibers may be taken as a *"structural marker"* which reveals the occurrence of a phase III to phase II transformation process with its associated steric constraints. The isochiral phase II is actually *highly suited* as a marker since it displays characteristic differences from the antichiral phase I, especially in cell symmetry.[16−18] In addition, since the differences with phase I rest on helix chirality, phase II cannot transform to phase I (for reasons developed above in the case of isotactic poly(1-butene)) and therefore becomes a *permanent structural memory of the transformation process from an extended-chain to a helical phase.* This structural memory is "lost" only upon annealing and melting−recrystallization, which leads to the more stable phase I.[17]

4. Conclusion

Steric and conformational constraints cannot be ignored in crystal−crystal transformations, since the latter necessarily take place in a "confined" solid. For polymers, these constraints may be brought to light by the rules that control the hand of constituent helices. For most (but not all) crystal−crystal transformations between two helical phases, the transformations maintain the initial helical hands in the final structures. This rule is illustrated and documented by the preservation of the antichiral alternation of isochiral planes of helices in phase II and resultant phase I of isotactic poly(1-butene) documented in earlier investigations.[11,12]

Additionally, in the present paper, the helical hand has been shown to be a *marker* of the steric constraints associated with the *generation* of a helical structure starting from an initial all-trans phase. Specifically, the transformation of phase III of syndiotactic polypropylene to *chiral* phases II and IV suggests that *cooperativity* imposed by steric constraints governs the generation of the gauche bonds needed to form helical structures. *This cooperativity leads to formation of crystal structures based on isochiral helices,* even when packing of chiral helices is less favorable than that of antichiral structures obtained under normal growth conditions: *the transformation of a crystal structure based on an extended-chain conformation to a helical one is a chiral process*. Since the steric constraints considered here are of general character, it is probable that most similar transformations generate crystal structures based on isochiral helices.

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