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Journal:	*CrystEngComm*
Manuscript ID:	CE-ART-04-2015-000802.R1
Article Type:	Paper
Date Submitted by the Author:	09-Jun-2015
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CrystEngComm

ARTICLE

Received 00th January 20xx,
Accepted 00th January 20xx
DOI: 10.1039/x0xx00000x
www.rsc.org/

Chirality, Entropy and Crystallization in Polymers: Isotactic Poly(3-methyl-1-pentene) as Example of Influence of Chirality and Entropy on the Crystal Structure.

Claudio De Rosa,[a,*] Finizia Auriemma,[a] Chiara Santillo,[a] Rocco Di Girolamo,[a] Giuseppe Leone,[b] and Giovanni Ricci[b]

We report the synthesis and the crystal structure of isotactic poly((R,S)-3-methyl-1-pentene) (iP(R,S)3MP). A purely random achiral copolymer of two enantiomeric (R) and (S) 3-methyl-1-pentene monomers cannot be obtained by polymerization of the racemic mixture of the (R) and (S) monomers but has been obtained by stereospecific polymerization of 3-methyl-1,3-pentadiene to isotactic 1,2-poly(3-methyl-1,3-pentadiene) (iP3MPD12) and successive hydrogenation. The crystal structures of the achiral iP(R,S)3MP and of the chiral poly((S)-3-methyl-1-pentene) (iP(S)3MP) are different, indicating that polymer crystal structures may be driven by different entropic effects related to chirality and types of crystal disorder. The conformational disorder of the chiral lateral groups prevails in the chiral iP(S)3MP inducing crystallization of chains of one helical chirality, whereas the entropic effect due to the statistical substitution of chains of different helical chirality in the sites of the lattice prevails in the achiral iP(R,S)3MP.

Introduction

Crystallization of polymers in chiral crystals, even in the case of achiral polymers, is quite frequent and strictly related to the occurrence of helical conformations of the chains. Although chiral polymers are typically constituted by chemical repeating units containing true asymmetric centers, they can also be formed from achiral monomers.[1,2] In fact, helical conformations generally assumed by the polymer chains in the crystalline state are intrinsically chiral, even though the chemical repeat is achiral.[3] This is the case of monomeric units that present a stereoisomeric center which is not a true asymmetric carbon because it is linked to two undistinguishable chain segments. This occurs, for instance, in isotactic vinyl polymers (-CH_2-C*HR-)$_n$ that are chiral as long as the chain ends are distinguishable. In these polymers the chains form helical conformations, but right-handed and left-handed helices are equally probable since they are isoenergetic.[3,4] For this reason these polymers are called *chiral but racemic*, where the chirality is buried.[2,5,6] Chiral but racemic systems consisting of equally probable right and left-handed helices may crystallize either in non-chiral space groups where the helices of opposite handedness co-exist in the unit cell in equal amount (optical compensation in a unit cell or racemic compound),[4,7,8] or chiral space groups in which only helices of a given chirality are present in an individual polymer crystal. In the latter case, equal fractions of crystals of the enantiomorphous space groups will be present (intercrystalline compensation or conglomerate).[4,7,8] In principle, the formation of chiral crystals from achiral or racemic helical polymers may be related to the stability of the chiral modification or may be associated with kinetic factors.[9,10] It has been suggested that a hexagonal or pseudo-hexagonal arrangement of helical chains in the crystalline state promotes the chiral crystallization and is, in turn, favoured by clustering of isochiral helices.[10] When a given polymer forms both chiral and non-chiral modifications, the non-chiral structure is often the most stable one, whereas the chiral form develops under kinetic control.[10]

A second case of chiral single chain and achiral polymer, with optical compensation in a unit cell or racemic compound, occurs when the monomeric unit is chiral, each individual polymer molecule consists of isochiral monomers and the single chain is chiral but the macroscopic sample is a *racemate* and forms upon crystallization of a racemic mixture of chains having monomers with opposite absolute configurations.[4] Enantiomorphic forms made of chains having monomers with opposite absolute configurations form helices of opposite hand and the two enantiomorphous helices are blended in the unit-cell of the racemic compound. Since monomers of opposite configurations occur in equal number, right and left-

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Electronic Supplementary Information (ESI) available: [details of polymer synthesis, diffraction analysis, conformational and packing energy calculations]. See DOI: 10.1039/x0xx00000x handed helical chains are equiprobable. Unlike the case of *chiral but racemic* polymers where the helices of opposite chirality may in principle interconvert, in this case the helices of opposite chirality are not isoenergetic and cannot interconvert.[4]

This is the case, for instance, of the crystals of poly(L-lactide)/poly(D-lactide) stereocomplex, which forms upon crystallization of a racemic mixture of poly(L-lactide) and poly(D-lactide). In the crystals of the stereocomplex right-handed threefold helical chains of poly(D-lactide) and left-handed threefold helical chains of poly(L-lactide) are intrinsically blended in the trigonal unit cell, according to the space group $R3c$ or $R\overline{3}c$.[11,12] Another example is provided by the form I of isotactic poly(*t*-butylethylene oxide), which presents chiral monomeric units giving two types of optical isomers, *Rectus* (*R*) and *Sinister* (*S*).[13] The tetragonal unit cell contains two left-handed 9/4 helical chains of the *Rectus* polymer and two right-handed 9/4 helical chains of the *Sinister* isomer,[13] giving a *racemic* compound and optical compensation.[14]

Finally, the third case is that of chiral polymers characterized by truly chiral monomeric repeating units, that is monomers containing a “true” asymmetric atom. In this case the chirality of the monomeric units favours the formation of helices of one specific helicity (right or left-handed). In fact, when the monomeric units are enantiomerically pure, helices of opposite chirality are not equivalent, since they have different conformational energies.[3,4,9,15,16] Poly(L-peptides) and polylactides fall in this class of chiral polymers. In particular, polylactides [-C*H(CH_3)-CO-O-]$_n$ have a true asymmetry and can be obtained in the two enantiomorphic forms, poly(L-lactide) and poly(D-lactide) (PLLA and PDLA). Each species adopts a specific helicity, imposed by the stereochemistry, left-handed for poly(L-lactide), right-handed for poly(D-lactide).[17-19] The case of chiral polyolefins bearing chiral side groups have been extensively investigated to study the effect of the presence of chiral atoms on the conformation of macromolecules and crystal packing,[15,20-24] and, more recently, in connection with a phenomenon described as a macromolecular amplification of chirality.[9] An example is the case of isotactic poly((S)-3-methyl-1-pentene) iP(S)3MP, where only 4/1 left-handed helical chains are present in the tetragonal unit cell according to the space group $I4_1$.[15,16]

Optical compensation for polymers with chiral monomeric units may occur when the racemic polymer consists of crystallites, each composed only of the rectus chains or only of the sinister polymer chains, and a same amount of optical antipodes crystallites are present. In general, for the various mentioned examples of racemic crystalline polymers where *R* and *S* polymers mix in a 1:1 ratio, three types of optical compensation should be considered.[13,14] Optical compensation in a unit cell (racemic compound), where the optical isomers are included in the unit cell pairwise, the compensation in a crystallite, where equal amount of *R* and *S* polymers are included in a crystallite randomly (solid solution), and the intercrystallite compensation, which is characterized by the presence of equal amounts of enantiomeric crystallites, each crystallite being composed only of *R* polymers or only of *S* polymers (conglomerate), and the bulk sample is optically inactive.[13]

Particularly interesting is the case of intramolecular compensation that may occur when the monomeric repeating unit is chiral, and the polymer chain is made by a random enchainment of the two enantiomeric *R* and *S* monomeric units. Different crystallization behaviour and different crystal structure are expected for this random copolymer of the two enantiomeric monomers, compared to those of the enantiopure homopolymers or of the racemate.

Isotactic poly(3-methyl-1-pentene) (iP3MP) is the ideal example of polyolefin that can be either chiral, containing a “true” asymmetric atom on the side group, with corresponding optical activity, or not chiral when the two enantiomeric *R* and *S* monomeric units are randomly enchained with compensation of the chirality of the lateral groups. This allows studying and comparing the effect of the chirality of the lateral groups and the effect of intramolecular chirality compensation on the conformation of the chains and the packing of chains in the crystals.

Both chiral monomer (*S*)-3-methyl-1-pentene ((*S*)3MP) and the racemic mixture (*R*,*S*)-3-methyl-1-pentene ((*R*,*S*)3MP) polymerize to isotactic polymers in the presence of Ziegler-Natta or metallocene catalysts.[15,25-26] The polymerization of the chiral monomer (*S*)3MP produces a chiral isotactic polymer, poly((S)-3-methyl-1-pentene) (iP(*S*)3MP). The polymerization of the racemic mixture (*R*,*S*)3MP gives an isotactic copolymer poly((*R*,*S*)-3-methyl-1-pentene) (iP(*R*,*S*)3MP), where the two enantiomeric monomers (*R*)3MP and (*S*)3MP should be enchained.[25] However, the polymer produced with Ziegler-Natta catalyst was separated into fractions having optical activity of opposite sign by adsorption chromatography on highly crystalline iP(*S*)3MP.[25] This has indicated that copolymers of the two enantiomeric monomeric units, with prevalence of *S* or *R* monomeric units in the optically active polymers were obtained,[25] due to the stereoselectivity of the polymerization by heterogeneous catalysts that gives rise to macromolecules formed prevailingly by one single monomeric antipode.[25] The same polymer was also obtained with single-center homogeneous metallocene catalysts.[26] Therefore, a purely statistical copolymer of the two monomeric antipodes was not obtained with heterogeneous or homogeneous stereoselective catalysts.

A different route for the synthesis of a purely random achiral copolymer iP(*R*,*S*)3MP could be the stereospecific polymerization of 3-methyl-1,3-pentadiene to isotactic 1,2-poly(3-methyl-1,3-pentadiene) and successive hydrogenation. The isotactic stereoregularity could be preserved after hydrogenation and a purely statistical copolymer of the two enantiomeric monomers with intramolecular compensation of chirality, could be obtained with this procedure.

In this paper we report the synthesis of a purely random achiral copolymer iP(*R*,*S*)3MP, by hydrogenation of isotactic 1,2-poly(*E*-3-methyl-1,3-pentadiene) (iP3MPD12). The obtained polymer iP(*R*,*S*)3MP resulted highly isotactic and crystalline and the crystal structure has been resolved by X-ray diffraction analysis. We found that the crystal structure of iP(*R*,*S*)3MP is different from that of the chiral iP(*S*)3MP. The reasons of the different crystallization behaviour are discussed in term of entropic effects related to the presence of different types of disorder included in crystals of the chiral and achiral polymers.

Results and Discussion

The precursor polydiene iP3MPD12 has been synthesized with a new class of catalysts based on cobalt phosphine complexes of the type $CoCl_2(PRPh_2)_2$ (with R = methyl, ethyl, *n*-propyl, isopropyl, cyclohexyl),[27] as described in ref. 28 (see supporting information). These complexes, in combination with methylaluminoxane (MAO), were found to be highly active and stereoselective for the 1,2 polymerization of various dienes (e.g., butadiene, 1,3-pentadiene, 1,3-hexadiene, 1,3-heptadiene, 1,3-octadiene and 5-methyl-1,3-hexadiene).[29] The same catalytic systems promote the polymerization of 3-methyl-1,3-pentadiene giving a polymer with essentially isotactic *E*-1,2 structure.[28] The isotactic content was found to depend on the type of catalyst used (i.e., type of phosphine ligand bonded to the cobalt atom). The polymers obtained with the catalytic systems having minimally hindered ligands (e.g., $PMePh_2$, $PEtPh_2$, $PnPrPh_2$) were found to be highly crystalline and highly isotactic ([*mm*] ≥ 90%).[28] iP(R,S)3MP has been prepared by hydrogenation of iP3MPD12 with *p*-toluenesulfonyl hydrazide in o-xylene as solvent, following the experimental procedure reported in ref. 30 (see supporting information). NMR data indicated that the high isotacticity of iP3MPD12 ([*mm*] ≥ 90%) is preserved after hydrogenation for the sample iP(R,S)3MP. Circular dichroism measurements on the sample of iP(R,S)3MP have shown no significant signal, indicating optical compensation and statistical presence of R and S monomeric units along the chains. X-ray diffraction and DSC analyses have shown that the obtained sample of iP(*R*,*S*)3MP is crystalline with melting temperature of 198 °C and glass transition temperature of 43 °C. The sample crystallizes from the melt by cooling at 10 °C/min at nearly 160 °C.

Samples of chiral iP(*S*)3MP has been prepared by polymerization of (*S*)3MP with standard Ziegler-Natta catalyst.[26]

The X-ray powder diffraction profiles of the samples of achiral iP(*R*,*S*)3MP and chiral iP(*S*)3MP are reported in Figure 1. The comparison of Figure 1 clearly shows that the racemic iP(*R*,*S*)3MP and the chiral iP(*S*)3MP give different X-ray diffraction patterns. The diffraction profile of iP(*R*,*S*)3MP presents two strong, sharp and very close reflections at 2θ = 9.5° and 10.4° and a strong reflection at 2θ = 16.6° (Figure 1a), whereas the diffraction of the chiral iP(*S*)3MP is characterized by a single strong reflection at 2θ = 9.3° (110 reflection), diffraction peaks at 2θ = 13.2° (200 reflection) and 18.7° (220 reflection) and a strong reflection at 2θ = 19.8° (211 reflection) (Figure 1b). This indicates that the crystal structure of the copolymer of the two enantiomeric monomeric units iP(*R*,*S*)3MP is different from that of the enantiopure iP(*S*)3MP.[15]

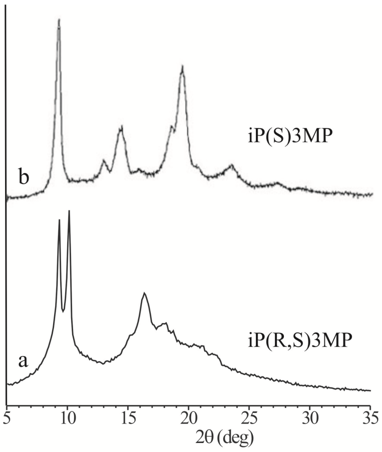


Figure 1. X-ray powder diffraction profiles of iP(*R*,*S*)3MP (a) and iP(*S*)3MP (b).

The crystal structure of iP(*S*)3MP is characterized by chains in 4/1 helical conformation packed in a tetragonal unit cell with axis $a = b = 13.35$ Å, $c = 6.80$ Å,[15] according to the space group $I4_1$. Only left-handed 4/1 helices are included in the tetragonal unit cell resulting in a chiral structure.[15] A model of the structure of iP(*S*)3MS is shown in Figure 2.

The chirality of the monomeric units favours the formation of helices of one specific chirality.[15,16,31] since right-handed and left-handed 4/1 helices are no longer equivalent, as instead generally occurs for isotactic polymers.[4] In fact, two low energy conformations of the chiral lateral group are possible for the left-handed helix, with the methyl carbon atom in gauche or in trans conformations with respect to the methine carbon, while only the trans conformation is possible for the right-handed helix.[4,16] The left-handed helix of iP(*S*)3MS is, therefore, favoured over the right-handed one. In the crystal structure, the lateral groups of left-handed helices of iP(*S*)3MP included in the tetragonal unit cell, may take statistically both conformations of minimum energy.[15,16] The statistical conformational disorder of the side groups in the crystals provides a gain in entropy that favours the isochiral packing. Therefore, the chirality of the lateral groups induces the crystallization of isochiral helices.[4,15]

The chirality of the lateral group influences the conformation of the chain not only in the crystalline state. The experimental observation that vinyl polymers having optically active lateral groups show optical activity also in solution, and that the optical activities show non-linear relationships between the configurational enantiomeric characteristics of the monomeric units and the optical activity of the derived polymer,[20-23] suggests that a prevailing spiralization sense of the helical chains is present in solution. In the case of iP(*S*)3MP in solution or in the melt, local left-handed helical conformation should prevail in length over the right-handed one for entropic reason,[31] because of the higher numbers of possible low energy conformational states accessible to the lateral groups when the helical chains are left-handed. This entropic effect also induces crystallization of the isochiral helical structure.

The tetragonal crystal packing for iP(*S*)3MS is in agreement with the simple principle of packing of polymer chains in helical conformations s(*M*/*N*),[4] that is, *the principle of close-packing and the principle of conservation of the chain symmetry.*[4] Chains in 4/1 helical conformation are, indeed, generally packed in tetragonal lattices, where the local helical symmetry of the chains is maintained in the lattice as crystallographic symmetry. The packing of enantiomorphous chains with coordination number equal to 4 with high symmetry space groups $I4_1cd$ or $I4_1/a$ is generally favored.[4] In the case of iP(S)3MS, the chirality of the lateral groups induces isochiral packing (Figure 2),[15] even though the driving force toward the packing of enatiomorphous chains is generally very strong.[4]

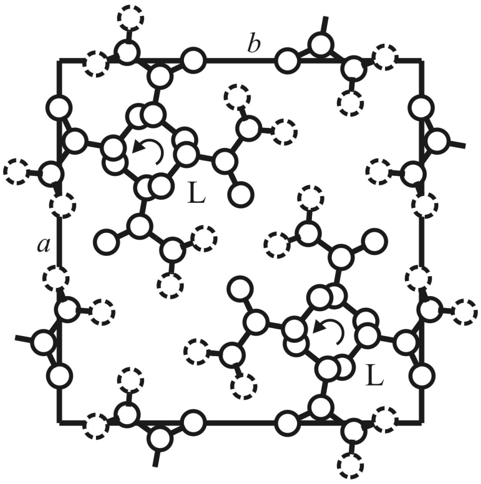


Figure 2. Model of the crystal structure of iP(*S*)3MP.[15] Chains in 4/1 helical conformation are packed in the tetragonal unit cell with axes *a* = *b* = 13.35 Å, *c* = 6.80 Å according to the space group $I4_1$. The unit cell contains two isomorphous left-handed (*L*) 4/1 helices in which the side groups assume statistically two different almost isoenergetic conformations. The dashed lines indicate the two statistical positions of the methyl carbon atoms, corresponding to the two possible low energy conformations of the side groups.

Oriented fibers of iP(*R*,*S*)3MP have been obtained by extrusion from the melt and stretching. The X-ray fiber diffraction pattern of iP(*R*,*S*)3MP is reported in Figure 3A. All the reflections observed in the fiber pattern of Figure 3A and in the powder diffraction profile of Figure 1a are listed in Table S1. The powder and fiber diffraction patterns of Figures 1a and 3A show the same reflections. It is apparent that the two strong reflections at 2θ = 9.5° and 10.4° observed in the powder profile (Figure 1a) are equatorial reflections (Figure 3A), whereas the strong reflection at 2θ = 16.6° is a first layer line reflection (Figure 3A and Table S1). From the fiber pattern of Figure 3A the value of the chain axis *c* = 6.87 Å has been evaluated for the chains of iP(*R*,*S*)3MP, similar to that of 6.80 Å of the chiral iP(*S*)3MP.[15] This indicates that chains of the achiral random copolymer iP(*R*,*S*)3MP assume the same 4/1 helical conformation of the chains of the chiral iP(*S*)3MP, but the two strong equatorial reflections at 2θ = 9.5° and 10.4° observed in the diffraction profile of iP(*R*,*S*)3MP (Figure 1a) indicate that the unit cell is different from the tetragonal cell of iP(*S*)3MP. The reflections observed in the fiber and powder patterns of iP(*R*,*S*)3MP are all accounted for by a monoclinic unit cell with parameters *a* = 10.02 Å, *b* = 18.48 Å, *c* = 6.87 Å and γ = 109.9°. The calculated density, with two chains in the cell is 0.932 g/cm^3 in agreement with the experimental value of the crystalline density of 0.89 g/cm^3. The indices *hkl* of the reflections according to this monoclinic unit cell are reported in Table S1. The systematic absence of *hk*0 reflections with *k* odd suggests that a possible space group, compatible with the presence of two chains in the unit cell, could be $P2_1/b$. As a consequence of the choice of this monoclinic space group, the 4/1 helical symmetry of the chains is not maintained in the lattice as crystallographic symmetry, as instead occurs for the chiral iP(*S*)3MP. The chains can be positioned in the unit cell with their chain axes coincident with the crystallographic 2_1 axes of the space group $P2_1/b$, so that they have only a local, non-crystallographic, 4/1 symmetry.

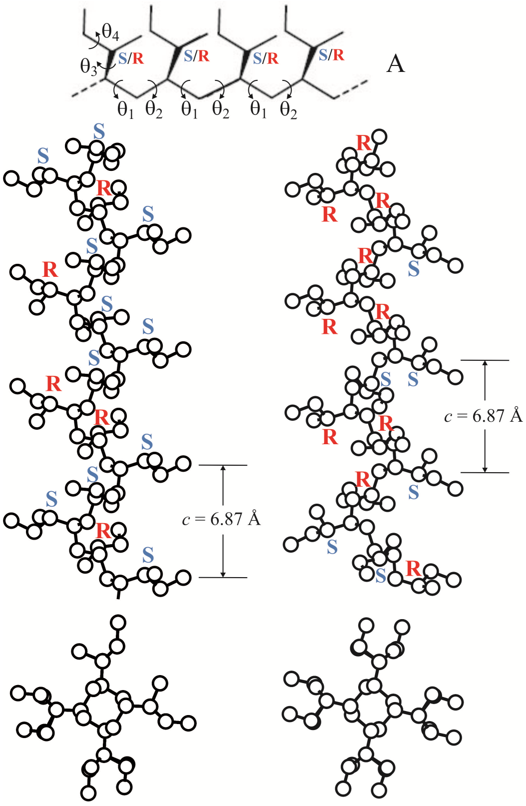

A) Experimental
B) Model of fig.5A
C) Model of fig.5B

Figure 3. X-ray fiber diffraction pattern of oriented fiber of iP(*R*,*S*)3MP (A) and calculated diffraction patterns for the models of packing of Figure 5A (B) and Figure 5B (B).

Possible models of packing of 4/1 helical chains in the monoclinic unit cell have been found performing calculations of the conformational and packing energy for the space group $P2_1/b$ and of diffraction patterns of the low energy models. The calculations of the conformational energy have been performed on portions of isolated chains of iP(R)3MP, iP(*S*)3MP and iP(*R*,*S*)3MP as a function of the torsion angles of the backbone θ_1 and θ_2 and of the side groups θ_3 and θ_4 (defined in Figure 4A), by assuming a s(*M*/*N*) symmetry and a sequence of the torsion angles...$\theta_1\theta_2\theta_1\theta_2$... (Figure 4A).[4]

For the same 4/1 helical conformation of the man chain, three low energy conformations of right and left-handed helix, corresponding to different conformations of the lateral groups, have been found for both enantiopure homopolymers iP(*S*)3MP and iP(*R*)3MP. For iP(*S*)3MP, two isoenegetic conformations of left-handed helix are possible, corresponding to side groups with $\theta_3 \approx$ T (trans) and $\theta_4 \approx$ T or G$^+$ (gauche) and only one conformation of the right-handed helix is possible for $\theta_3 \approx$ G$^+$ and $\theta_4 \approx$ T. For iP(R)3MP, two isoenegetic conformations of right-handed helix are possible, corresponding to side groups with $\theta_3 \approx$ G$^-$ and $\theta_4 \approx$ T or G$^-$, and only one conformation of the left-handed helix is possible for $\theta_3 \approx$ G$^+$ and $\theta_4 \approx$ T. For isolated chains of the enantiopure homopolymers, the left handed helix is favoured for iP(*S*)3MP and the right-handed helix is favoured for iP(*R*)3MP because of the entropy gain due to the two possible conformational states accessible to the lateral groups and the corresponding conformational disorder when the (*S*/*R*)chirality of the side groups and the (Right/Left)helical chirality are combined as *S*-left, *R*-right.

Similar calculations have been performed for model chains of the disordered copolymer iP(*R*,S)3MP with disordered enchainment of *R* and *S* monomeric units and similar results have been obtained for the lowest energy conformations.



B) iP(R,S)3MP - Right
S units: $\theta_3 = G^+$, $\theta_4 = T$
R units: $\theta_3 = G^-$, $\theta_4 = T$

C) iP(R,S)3MP - Left
S units: $\theta_3 = T$, $\theta_4 = T$
R units: $\theta_3 = G^+$, $\theta_4 = T$

Figure 4. A) Scheme of chain of iP(*R*,*S*)3MP with definition of the torsion angles θ_1, θ_2, θ_3 and θ_4 and showing the sequence of torsion angles according to the s(*M*/*N*) line symmetry group. B,C) Low energy models of right-handed (B) and left-handed (C) 4/1 helical conformation of the copolymer iP(*R*,*S*)3MP where the lateral groups of *S* and *R* monomeric units assume different conformations depending on the chirality and handedness of the helical chain.

Models of left-handed and right-handed 4/1 helical conformation of the disordered achiral copolymer iP(*R*,*S*)3MP are shown in Figure 4. The side groups of S monomeric units assume conformations with $\theta_3 \approx T$ and $\theta_4 \approx T$ in the left-handed helix and $\theta_3 \approx G^+$ and $\theta_4 \approx T$ in the right-handed helix, whereas the side groups of R monomeric units assume conformations with $\theta_3 \approx G^+$ and $\theta_4 \approx T$ in the left-handed helix and $\theta_3 \approx G^-$ and $\theta_4 \approx T$ in the right-handed helix. The models of Figure 4 indicates that, in spite of the configurational disorder, due to the statistical enchainment of monomeric units of opposite R and S chirality, and of the disorder in the conformations assumed by the chiral side groups in different helical stretches, straight helical chains of the achiral copolymer iP(*R*,*S*)3MP of low conformational energy that maintain the chain axis periodicity of 6.87 Å, are possible. This also explains the observed crystallization of the disordered copolymer iP(*R*,*S*)3MP. Moreover, these results indicate that the random enchainment of *S* and *R* monomeric units in iP(R,S)3MP and the compensation of chirality makes the left-handed and right-handed 4/1 helices equivalent, and explain the experimental X-ray diffraction data that indicate a packing of enantiomorphous helices, according to the centrosymmetric space group $P2_1/b$, rather than an isomorphous packing, as in the case of iP(*S*)3MP of Figure 2.

Possible models of packing for the crystals structure of iP(*R*,*S*)3MP have been found performing calculations of the packing energy of the disordered chains of the random copolymer having conformation as in Figure 4, for the space group $P2_1/b$. The disorder present in the crystals of iP(*R*,*S*)3MP, due to configurational disorder in the sequence of *R* and *S* monomeric units along the chains of crystallizable stretches, conformational disorder of the lateral groups, and the presence of structural disorder in the packing of chains, has been modelled by assuming that each site of the crystalline lattice may be occupied with different probabilities by the different chains of the enantiopure homopolymers iP(*R*)3MP and iP(*S*)3MP, having different chirality of the side groups, different handedness of the helical conformation, different up/down orientations and different conformations of the lateral groups.

A good agreement between calculated and experimental diffraction data has been obtained for limit disordered models characterized by disorder in the random substitution in the sites of the lattice of chains having opposite helical handedness and opposite chirality of the lateral groups, as in the model of Figure 5A. In this model each site of the crystalline lattice with space group symmetry $P2_1/b$ is occupied with the same probability by a right-handed chain of iP(*S*)3MP with $\theta_3 = G^+$ and $\theta_4 = T$, and a left-handed chain of iP(*R*)3MP with $\theta_3 = G^+$ and $\theta_4 = T$, having opposite chirality in the helical hand (right-handed and left-handed), opposite *S* and *R* chirality of the lateral groups, and opposite up and down orientation (anticlined chains). As shown in the Figure 5A, the two models of chains that occupy statistically the lattice sites have identical projections in the *ab* plane, well simulating the disordered chain of the copolymer iP(*R*,*S*)3MP of Figure 4.

A comparison between the experimental X-ray powder diffraction profile of iP(*R*,*S*)MP of Figure 1a and the powder diffraction profile calculated for the model of Figure 5A is shown in Figure 6, whereas the 2D-fiber diffraction pattern calculated for the model of Figure 5A is shown in Figure 3B and compared with the experimental fiber diffraction pattern of Figure 3A. The structure factors calculated (F_c) for the limit disordered model of Figure 5A for the space group $P2_1/b$ are reported in Tables S4 and S5 of the supplementary information, and compared with the observed structure factors (F_o), evaluated from the X-ray powder diffraction profile of Figure 1a and the fiber diffraction pattern of Figure 3A, respectively. It is apparent that a very good agreement has been obtained. This indicates that in the crystals of iP(*R*,*S*)3MP *chain stretches of sequences of monomeric units with prevailing S configuration tend to assume a right-handed helical conformation, whereas those of prevailing R configuration tend to assume a left-handed helical conformation*. The prevailing combination of (*S*/*R*)chirality-(Right/Left)helical chirality are, therefore, *S*-right, *R*-left. Disorder originates from the random substitution of helical stretches of opposite *R* and *S* configuration and helical handedness provided that they are also anticlined, that is, one up and the other down. In this model the possible disorder in the conformation of the lateral groups is not present and both *S* and *R* monomeric units are characterized by conformation of the side groups with $\theta_3 = \mathrm{G}^+$ and $\theta_4 = \mathrm{T}$.

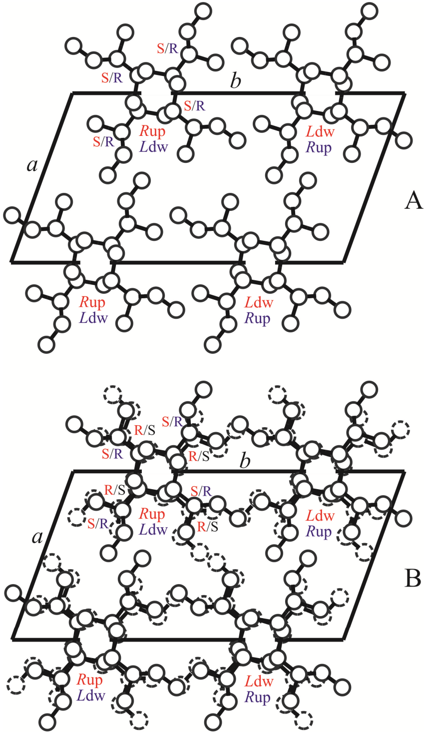


Figure 5. Limit disordered models of packing of iP(*R*,*S*)3MP in the monoclinic unit cell with axes *a* = 10.02 Å, *b* = 18.48 Å, *c* = 6.87 Å and γ = 109.9° according to the space group $P2_1/b$. In the model A each site of the crystalline lattice is occupied with the same probability by right-handed (up) chains of iP(*S*)3MP and left-handed (down) chains of iP(*R*)3MP, having opposite chirality in the helical hand (right-handed and left-handed), opposite *S* and *R* chirality of the lateral groups, and opposite up and down orientation (anticlined chains). Both chains have lateral groups in conformation with $\theta_3 = \mathrm{G}^+$ and $\theta_4 = \mathrm{T}$ and have identical projections in the *ab* plane. In the model B, each site of the lattice is occupied by the same two chains as in A (*S*-right and *R*-left) plus a left handed (down) chain of iP(*S*)3MP and a right-handed (up) chain of iP(*R*)3MP (*S*-left and *R*-right, respectively) (dashed lines), with lateral groups in conformations $\theta_3 = \mathrm{T}$, $\theta_4 = \mathrm{T}$ and $\theta_3 = \mathrm{G}^-$, $\theta_4 = \mathrm{T}$, respectively. *R*up and *L*dw indicate right-handed helix with up orientation and left-handed helix with down orientation, whereas *S*/*R* indicates the chirality of the methine carbon atoms of the lateral groups.

However, as in model of the chain of Figure 4, disorder in the conformation of the lateral groups is possible and disorder in the combination (*S*/*R*)chirality-(Right/Leflt)helical chirality may be present. This means that sequences of *S* monomeric units may also assume left-handed helical conformation and sequences of *R* monomeric units may also assume right-handed helical conformation (combination *S*-left and *R*-right). This disorder has been modelled assuming that each site of the lattice is occupied by the same two chains as in A (*S*-right and *R*-left) plus a left-handed down chain of iP(*S*)3MP and a right-handed up chain of iP(*R*)3MP (*S*-left and *R*-right, respectively), with lateral groups in conformations $\theta_3 = \mathrm{T}$, $\theta_4 = \mathrm{T}$ and $\theta_3 = \mathrm{G}^-$, $\theta_4 = \mathrm{T}$, respectively, as in the model of Figure 5B. It is apparent that the projection of the chains that occupy the lattice sites in Figure 5B is similar to the projection of the disordered chain of iP(*R*,*S*)3MP of Figure 4C, indicating that the model of Figure 5B well simulate the structure of the disordered random copolymer iP(*R*,*S*)3MP.

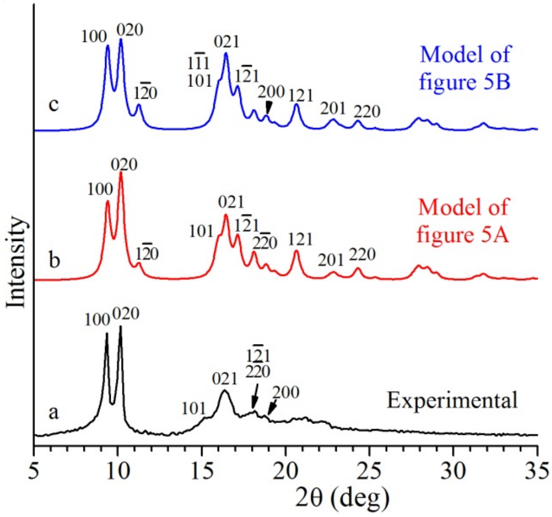


Figure 6. Comparison between the experimental X-ray powder diffraction profile of iP(*R*,*S*)3MP of Figure 1b after subtraction of the amorphous halo (a) and diffraction profiles calculated for the limit disordered models of packing of Figure 5A (b) and Figure 5B (c) for the space group $P2_1/b$.

The calculated diffraction profile for the model of Figure 5B is shown in Figure 6c, whereas the calculated fiber diffraction pattern is reported in Figure 3C. The comparison between observed structure factors (F_o), evaluated from the X-ray powder diffraction profile of Figure 1a and the fiber diffraction pattern of Figure 3A, and structure factors calculated (F_c) for the model of Figure 5B are reported in Tables S4 and S5, respectively, of supplementary information. A good agreement with the experimental powder profile (Figure 6a) and the fiber diffraction patter (Figure 3A) has been obtained for a disordered model of Figure 5B where chains are characterized by the presence of stretches of left-handed 4/1 helices of a prevailing *R* configuration or right-handed 4/1 helices of a prevailing *S* configuration with 80% probability (prevailing combination *R*-left, *S*-right), and stretches of left-handed 4/1 helices of a prevailing S configuration or right-handed 4/1 helices of a prevailing R configuration with 20% probability (combination *S*-left, *R*-right), and different conformations of the lateral groups. As in the model of Figure 5A, the presence of disorder in the statistical substitution of right and left handed helices in each site of the lattice is the key feature.

Conclusions

The synthesis and the crystal structure of achiral purely random copolymer iP(*R*,*S*)3MP have been reported. A novel synthetic strategy has been used based on the stereospecific polymerization of 3-methyl-1,3-pentadiene to isotactic 1,2-poly(3-methyl-1,3-pentadiene) and successive hydrogenation. This route has allowed for the synthesis of an isotactic 1,2-polydiene with a functional group in the side chain, then successive hydrogenation provides for the first time a polymer with random enchainment of *R* and *S* units. This random copolymer provides intramolecular optical compensation (an intramolecular racemic mixture), different from the case of crystallization of a racemic mixture of the two enantiopure chains having monomers with opposite absolute configurations (racemate).

We show that iP(*R*,*S*)3MP is able to crystallize, in spite of the configurational disorder due to the statistical enchainment of 3MP monomeric units of opposite *R* and *S* chirality. Crystallization is driven by the fact the macromolecules of iP(*R,S*)3MP maintain a regular backbone 4/1 helical conformation even in the presence of high degree of intramolecular disorder. The structure is different from that of the chiral enatiopure iP(*S*)3MP. The presence of both enantiomeric R and S monomeric units in the chains of the random achiral copolymer iP(*R*,*S*)3MP produce a change of the crystal packing from the tetragonal crystal structure of the chiral iP(*S*)3MP to a lower symmetry monoclinic structure. In iP(*S*)3MP the entropic effect arising from the two possible conformational states assumed by the chiral lateral groups prevails and induces crystallization of isochiral helices. In the case of the achiral random copolymer iP(*R*,*S*)3MP the intramolecular compensation of chirality makes the enantiomorphous helices equivalent and even though statistical disorder in the conformation of the side groups is still present, the entropic effect due to the statistical substitution of chains of different helical chirality and clinicity prevails and induces crystallization of the antichiral monoclinic structure. The crystal structures of chiral and achiral iP3MP provide a unique example of the relevant effect of entropy and disorder on the crystallization of polymers. The different packing modes in the chiral and achiral isomers are, indeed, driven by different entropic effects related to different types of disorder.

The proposed monoclinic model for iP(*R,S*)3MP is also an example of *symmetry breaking*,[4] because the crystal symmetry is lower than that expected for the structure of polymer chains in 4/1 helical conformation,[4] that generally are packed in a tetragonal lattice according to the energy principle of *close-packing,*[4] *and the entropic principles of conservation of the chain symmetry and of entropy-driven phase formation*,[4] which states that *a molecule in a crystal tends to maintain its symmetry elements, provided that this does not cause a serious loss of density*.[4] In a more symmetric position a molecule has a greater freedom of vibration, that is, the structure corresponds to a wider energy minimum.[4] In the monoclinic structure of iP(*R*,*S*)3MP the local 4/1 helical symmetry of the macromolecules is lost in the lattice as crystallographic symmetry achieving a tight packing of highly disordered helices in the lower symmetric lattice.

Acknowledgement

Financial support from MIUR (project Prin 2010-2011 and project PON-DIATEME 2007-2013) is gratefully acknowledged.

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