Communications to the Editor

First Detailed Determination of the Molecular Conformation and the Crystalline Packing of a Chiral Poly(3-alkylthiophene): Poly-3-(*S*)-2-methylbutylthiophene

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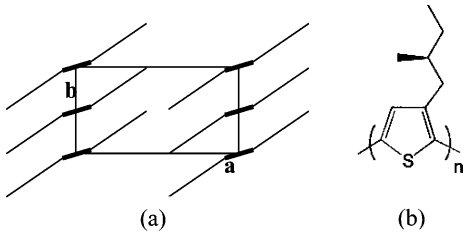
Substituted thiophene systems are a class of stable and processable polymers whose electronic properties can be tailored by monomer functionalization. The more studied are poly(3-alkylthiophenes) (P3AT's) whose basic crystalline organization features have been established by the work, often requiring nonstandard approaches, of many groups.[1−12] There is consensus on a model in which parallel stacks of polyconjugated main chains organize in layers, with the side chains running in the regions between the stacked main chains (Scheme 1a). Fitting the models to diffraction data in various instances required doubling the interlayer lattice periodicity (**a** in Scheme 1a).[2,7,9] However, disorder, poor regioregularity, and the scarce propensity to crystallization of the rigid polythiophene chain have so far prevented the actual solution and refinement of the crystal structures of these macromolecules.

When enantiopure side chains are attached to the thiophene rings, chiral polythiophenes are obtained, which are of interest because of their potential as nonlinear optical, circularly polarized luminescent and enantiosensor materials.[13,14] The optical activity of chiral polythiophenes is influenced by regioregularity, by the nature of chiral substituents, and by the modes of aggregation into chiral supramolecular structures, both in solution and in the solid state.[15,16] Meijer et al. found that chiral substituents can induce high optical activity in the $\pi-\pi^*$ transition of the backbone, when polymers are in aggregated, plausibly well-ordered, states. It was proposed that the strong chiroptical effects result from chiral intermolecular organization of the rigid polymer chains in ordered, possibly crystalline, domains. To our knowledge, however, the nature of the crystalline organization of the chiral aggregated states and the associated molecular conformations were discussed on the basis of the optical features[13] but never characterized in detail for any of the studied systems. Fundamental structural studies appear very desirable for P3AT's and even more so for the chiral systems.

Scheme 1. (a) Projection of the Packing Widely Accepted for P3AT's;[a] (b) Chiral Poly-3-(*S*)-2-methylbutylthiophene Monomer Unit



[a] In form I polymorphs chains organize in layers characterized by the *a* periodicity; within a layer the main chains (thick lines in projection) are stacked approximately parallel, with periodicity $^1/_2 b$.

In the present study we report the solution and detailed refinement of the crystal structure of chiral poly-3-(*S*)-2-methylbutylthiophene (PMBT, Scheme 1b). This represents, to our knowledge, the first instance in the case of a P3AT. We have recently described the synthesis and a broad characterization of highly regular, chiral PMBT, a polythiophene with a short, optically active alkyl substituent.[17] Combining absorption, emission, and vibrational spectroscopies with thermal characterization and X-ray diffraction, a transition between a disordered and an ordered three-dimensional assembling was evidenced. Remarkably PMBT, unlike other polyalkylthiophenes, shows only two condensed phases, i.e., the amorphous and what appears to be a single crystalline modification.

For the present investigation we have taken full advantage of the relatively simple phase behavior and of the chirality of poly-3-(*S*)-2-methylbutylthiophene. The latter feature limits possible chain symmetry and simplifies the space groups analysis. The high regioregularity, the small side chain dimension, and the substantial crystallinity of PMBT, which can be estimated by comparison with patterns of fully amorphous samples (see Figure 2 of ref 17), strongly suggest a well-ordered crystalline organization of the sample used for the crystal structure analysis. The powder X-ray diffraction data (Figure 1) allowed to propose an orthorhombic lattice with $a = 13.3$ Å, $b = 7.70$ Å, and c (chain axis) $= 7.76$ Å. With four monomer units, i.e., two chains, in the unit cell a calculated density of 1.27 mg/m^3 is obtained. These data are consistent with an approximate structural model of the kind suggested for form I polymorphs of P3AT's[2,7−9,11,12,17] with a somewhat expanded stacking periodicity (Scheme 1a).

The chiral side chain, under the equivalence postulate of chemical repeating units,[18] limits the symmetry of transoid crystalline chains to twofold screw conformations. Molecular models were obtained imposing the 2_1 symmetry with a 7.76 Å periodicity and exploring the potential energy surface of the infinite isolated main chain by molecular mechanics calculations (see Supporting Information). The torsion angle C(6)−C(5)−C(3)−C(1) between the backbone and the side chain (Figure

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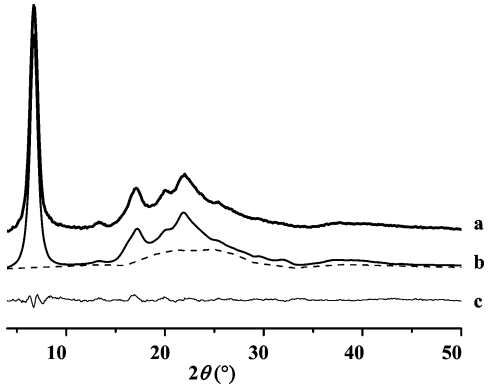


Figure 1. X-ray diffraction pattern of crystalline poly-3-(*S*)-2-methylbutylthiophene: (a) observed profile; (b) calculated profile in $C222_1$ and background profile (dashed line); (c) difference curve.

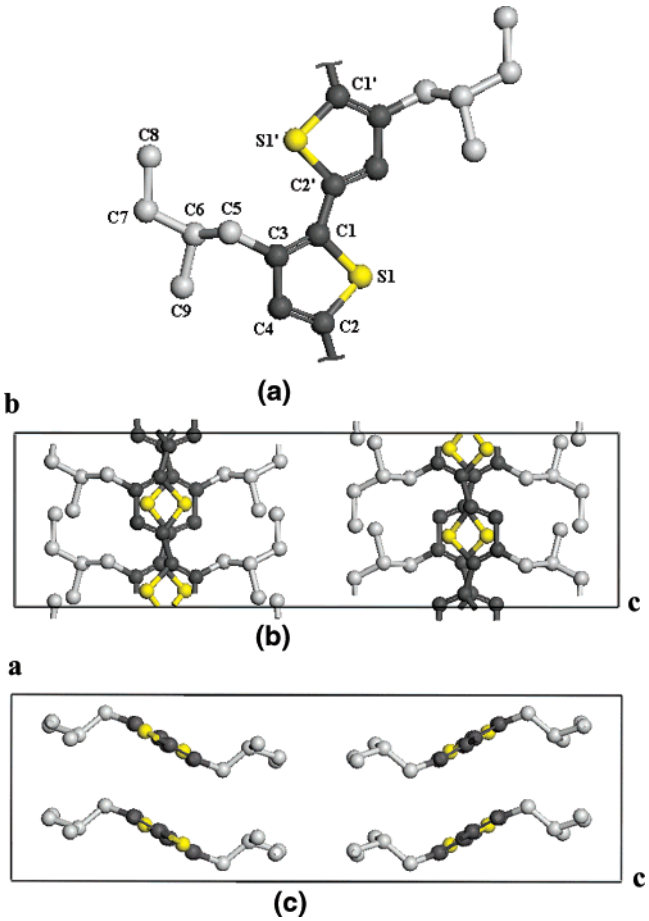
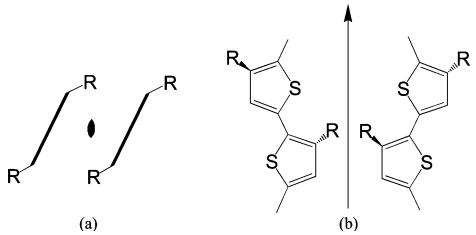


Figure 2. Crystal conformation of poly-3-(*S*)-2-methylbutylthiophene refined in $C222_1$ (a) and molecular packing viewed along the *a*-axis (b) and down the *b*-axis (c) (only non-hydrogen atoms are shown).

2a) shows low-energy areas around +90°, −90°, and 180°. The minimum in the +90° region is more stable by about 1 and 3 kcal/(mol cru) respectively than the −90° and the 180° minima. Side-chain conformations with the C(3)−C(5)−C(6)−C(7) and the C(5)−C(6)−C(7)−C(8) torsion angles respectively trans and gauche are marginally more stable than the tran−trans sequence.

To solve the structure, the working hypothesis that monomer units are crystallographically equivalent was adopted. Thus, all chains in the crystal must be isomorphous and adopt a side-chain conformation close to one of the identified minima. The chain axis must coincide with a crystallographic 2_1 axis, and the symmetry operators allowed for space groups of the orthorhombic or the monoclinic systems are only twofold axes

Scheme 2. (a) Projection View and (b) Side View of Intralayer Stacking in Space Groups $C222_1$ and $C2$[a]



[a] Chains are isodirectional because the intralayer symmetry operator is a 2 axis parallel to the chain axis.

whereas, in the present case, mirror planes and inversion centers are not allowed. Few monoclinic and orthorhombic space groups satisfy these constraints along with density requirements, without implying statistical orientational disorder of the chains. Considerations about the stacking of polythiophene chains in individual layers show the $C2$ and $C222_1$ space groups to be the most favorable. In the latter doubling of the interlayer axis, which conventionally becomes the *c*-axis, is required: a four-chain unit cell results with the chain axis parallel to *b*. In both these space groups chains in a given layer are isodirectional (Scheme 2) because the intralayer stacking symmetry operator is a twofold rotation axis parallel to the main chain axis. In $C222_1$ the interlayer symmetry operators are twofold axes orthogonal to the chain axis and antiparallel layers arise. On the contrary, in $C2$ successive layers result from lattice translations: all chains in a crystal would be isodirectional, making it nonplausible for crystals obtained from random chain orientation systems like melts or solutions.

The more promising models were refined using the Rietveld technique,[19] i.e., by the best fitting of the whole X-ray powder pattern profile. The agreement between calculated and observed diffraction patterns was much more encouraging below $2\theta = 20°$ for the $C222_1$ space group, on which subsequent work concentrated. The program "Debvin"[20] was used. In the $C222_1$ space group the lattice parameters refined to the following values: $a = 8.24(2)$ Å, $b = 7.75$ (1) Å, and $c = 27.00(2)$ Å yielding a calculated density of 1.18 g/cm^3. The refined fractional coordinates and nonstructural parameters are reported in the Supporting Information. The value of the final disagreement factor R_2' was 0.075 ($R_2' = \sum|I_{obs} - I_{calc}|/\sum I_{net}$, where $I_{net} = I_{obs} - I_{bkg}$) with an overall isotropic temperature factor B of 10. In Figure 1 the observed (a), calculated, and background (b) profiles are reported together with the difference curve (c). Bond lengths and bond angles values from the tetrahexylsexithiophene crystal structures by Destri et al.[21] were adopted allowing only minor adjustments.

In Table 1 the refined internal coordinates for PMBT are listed. All values are in the expected range. Views of the refined molecular conformation and of the packing are shown in Figure 2. Refinement of the structure with C(3)−C(5)−C(6)−C(7) and the C(5)−C(6)−C(7)−C(8) torsion angles respectively trans and gauche, corresponding to the lower energy conformation, gives a substantially better fit than trans−trans or gauche−trans sequences.

Intermolecular distances are acceptable, and the only one somewhat short contact (3.49 Å) involving non-hydrogen atoms occurs between methyl carbons of adjacent chains within a layer, while all others are above 3.60 Å. The setting angle formed by the (h00) lattice planes and the l.s. plane of the PMBT main chain is ∼40°, consistent with a longer than expected *a*-axis. Layers arise stacking isodirectional chains: noninterdigitation of the side chains of different layers is apparent in the refined

Table 1. Refined Internal Coordinates for Poly-3-(*S*)-2-methylbutylthiophene[a]

	Bond Lengths (Å)		
C1−S1	1.735	C2−S1	1.723
C1−C3	1.390[b]	C2−C4	1.370[b]
C3−C4	1.448	C3−C5	1.510[b]
C5−C6	1.530[b]	C6−C7	1.530[b]
C7−C8	1.530[b]	C6−C9	1.530[b]
C1−C2′	1.462		
	Bond Angles (deg)		
C1−S1-C2	92.7	S1−C1−C3	111.0[b]
S1−C2-C4	111.0[b]	C4−C3−C5	120.7
C3−C5-C6	113.8	C5−C6−C7	116.6
C6−C7-C8	113.6	C5−C6−C9	108.9
C2′-C1−S1	114.2	C2′−C1−C3	134.7
S1′-C2′-C1	119.1		
	Torsion Angles (deg)		
S1−C1-C3−C4	0.0	C1−C3-C4−C2	0.0
C1−C3-C5−C6	97.7	C3−C5-C6−C7	180.7
C5−C6-C7−C8	63.3	C3−C5-C6−C9	62.0
C2−C4-C3−C5	−188.6	S1′−C2′−C1−S1	−178.1
C2′-C1−C3-C5	6.3	S1′−C2′−C1−C3	4.5
C2′-C1−C3-C4	177.5		

[a] Estimated standard deviations vary between 0.3° and 1.0° for bond angles and between 1.0° and 2.0° for torsion angles. [b] Values not refined.

structure confirming a feature assumed in form I polymorphs of polythiophenes.[7,8,11,17] The small deviations from planarity of the polyconjugated main chain are hardly significant; however, the refined molecular model is clearly chiral since the ordered, optically active side chains create a chiral envelope around the main chain.

We conclude noting that the good agreement between calculated and observed XRD patterns confirms the adopted simplifying assumptions and suggests that for the PMBT crystal structure it is unnecessary to invoke complex disorder models. By integration of the calculated crystalline and amorphous pattern (see Figure 1) resulting from the refinement, a crystallinity of 65 ± 5% is obtained, quite high in the context of semicrystalline polymers. The simplicity of the refined structural model may result of key importance in the exploration by molecular dynamics of aggregation processes of polythiophenes as well as of disorder features and surfaces[22,23] in polythiophenes aggregates. Moreover, our results indicate that, among the models proposed to account for the chiroptical behavior of polythiophenes,[13] cisoid helical molecular structures can be ruled out in the present instance, whereas the likelihood of different chiral aggregate models may depend on morphology and needs further investigations.

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Supporting Information Available: Refined atomic coordinates and nonstructural parameters, along with the details of the structural refinement procedure. This material is available free of charge via the Internet at http://pubs.acs.org.

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