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Ordered Stacking of Regioregular Head-to-Tail Polyalkylthiophenes: Insights from the Crystal Structure of Form I′ Poly(3-*n*-butylthiophene)

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We report the synthesis, structural characterization, and features of the crystallization behavior of a highly regioregular head-to-tail poly(3-*n*-butylthiophene) (PBT) with average molecular weight $M_w =$ 10.2 kDa. The thermal behavior and the X-ray diffraction (XRD) patterns of our native PBT samples allow a crystal polymorph (form I′) to be identified, never previously discussed in the literature but closely related to the more common but more disordered form I. The crystal structure of form I′ PBT has been determined and refined by Rietveld analysis of XRD patterns from polycrystalline samples and has been confirmed by molecular mechanics (MM) calculations adopting a thiophene-specific force field developed in our group. Using such a combined approach we are able to show that the studied polymorph, in analogy with poly-3-(*S*)-2-methylbutylthiophene (PMBT), is well described by a limit-ordered orthorhombic model in space group $C222_1$ with refined lattice parameters $a = 7.64(1)$ Å, $b = 7.75(1)$ Å (chain axis), and $c = 24.97(8)$ Å, yielding a calculated density of 1.24 g/cm^3 in good agreement with the experimental value. The refined structure, which presents stacking and layering similar to form I, is shown by MM to be a local potential energy minimum. We also find lower energy structures with looser stacking periodicity of the polythiophene chains, consistently with data on PBT polymorphism. Both the form I′ PBT and the PMBT crystal structures, the only two poly(3-alkylthiophenes) (P3ATs) structures for which detailed models are presently available, confirm features of the inverse comb model of P3ATs by Prosa et al. (*Macromolecules*, **1992**, *25*, 4364). Our models also suggest important new aspects: isodirectional arrangements are preferred over antiparallel ones within tightly packed polythiophene stacks. This feature is incompatible with chain-folding occurring between chains within individual stacks. On the contrary crystal growth with chain-folding between chains in adjacent layers is compatible with the refined structures and in principle possible, although plausibly slow, as it requires disruption of preexistent π-stacking interactions. The molecular and crystal models we devised allow a more detailed understanding of the reasons causing crystallization to be slow and limited in extent, especially for high molecular weight P3ATs.

Introduction

Conjugated polymers are one of the most important classes of materials for organic electronics and have been the object of a growing body of investigations since their discovery three decades ago. The most notable properties of these materials result from electron delocalization along the polymer backbone and range from electrical conductivity to optical properties which can be made sensitive to environmental stimuli. In this context, polythiophenes are one of the most versatile and studied families of conjugated materials, whose appeal lies in the possibility to change and fine-tune their properties by playing with substituents, molecular weight distribution, regioregularity, doping, etc. The possibility of easy, low-cost manufacturing of active thin films by solution casting or printing technologies is another important feature for their application[1] in electroluminescent devices,[2] field-effect transistors,[3] solar cells,[4] photochemical resists, nonlinear optic devices,[5] sensors,[6] and batteries.[7] In particular poly(3-alkythiophene)s (P3AT) are materials with

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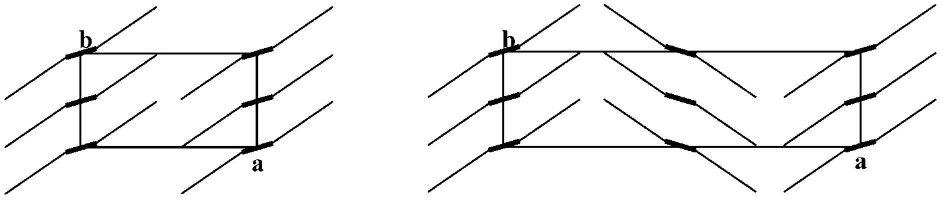

(a) (b)

Figure 1. (a) Projection of the widely accepted packing model for P3ATs (form I type polymorphs): chains organize in layers characterized by the *a* periodicity; within a layer the main chains (thick lines in projection) are π-stacked with periodicity *b*/2. (b) Alternative packing determined for example in the case of PMBT: in this case the lattice parameter *a* is twice the layer periodicity.

good solubility, processability, and environmental stability, showing some of the best transistor mobilities and remarkable performances as hole transporters in bulk-heterojunction plastic solar cells.[3,8] Their importance as active materials is evidenced also by the commercial availability of several of these polymers, with a number of fine chemical companies now offering both regioregular and regiorandom P3ATs in their catalogues. Polythiophenes may be rightly called the "workhorses of organic electronics".

The most interesting properties of P3ATs depend both on the conformation of the individual chains and their three-dimensional organization in the solid state. The former determines the conjugation length (roughly the number of consecutive coplanar thiophene rings within the polymeric backbone), the latter the interchain coupling of π-orbitals which is important for charge hopping and exciton formation. The relationship between chemical structure, solid state organization, and physical properties in this family of polymers is thus highly significant. The basic features of the crystalline organization, morphology, polymorphisms, and their relationship to the properties of P3ATs have been established with the contribution of many groups.[9−27] Concerning in particular their crystal structure, there is consensus on a model in which stacks of polyconjugated main chains organize in layers, with the side chains extending in the regions between the stacked main chains (Figure 1a). In some cases, fitting the models to diffraction data requires doubling the interlayer lattice periodicity (Figure 1b).[10,15,17] However, disorder, poor regioregularity, polymorphism, and the scarce propensity to crystallization imply that only poor quality diffraction data are generally available for these systems. These factors, along with difficulties encountered in obtaining well oriented P3AT samples with appreciable degrees of crystallinity and the relative complexity of thiophene units with long side chains, have so far prevented the identification of *well-defined* crystal structures (i.e., unit cell, space group, and atomic coordinates). The only exception is represented by poly-3-(*S*)-2-methylbutylthiophene (PMBT), a chiral polymer whose structure has been reported recently by our group.[27]

An additional important obstacle to the resolution of crystal structures of polythiophenes is the fact that readily available, "precooked" all-purpose force fields have proven to be inadequate to devise or validate structural models by molecular modeling. This follows from the need to model accurately and consistently both intramolecular features (torsion potentials of the π-conjugated backbone and side chains) and intermolecular interactions (van der Waals and electrostatics). However, suitable modifications of these force fields have been recently proposed by some of us, which yield reliable results for various related thiophene oligomers.[28]

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As a further step in the structural characterization of regioregular P3ATs, we decided to tackle the solid state organization of the simplest member of the series for which all the features of processable polyalkylthiophenes are maintained, namely, poly(3-*n*-butylthiophene) (PBT). This polymer is receiving increasing attention: it has been shown to form stable nanowires, which can be used to produce highly efficient solar cells by blending with functionalized fullerenes,[4b] while appropriate solvent deposition and annealing techniques can lead in general to high levels of order,[29] influence its polymorphic behavior, and give rise to new modes of orientation[30,31] with respect to substrates. These features may turn out to be technologically very significant. From our own point of view, the following additional features make it a nearly ideal model to study crystallization of P3ATs: in the crystal structure of this system, (i) the number of parameters to be refined is kept to a minimum, (ii) the side chains, including the possible associated disorder, make a relatively small contribution to the diffraction data, and as a consequence, (iii) the main chain organization should stand out more clearly. We have also taken full advantage of the chain symmetry, devising conformational and packing models for which the crystallographic equivalence of monomer units is respected, and possible models are defined by appropriate space groups.

As a consequence of this approach, it has also been possible to test the best models devised from the analysis of the X-ray diffraction data by molecular mechanics (MM) using the specific force field developed in our group. The immediate goal of our study is to establish, at least for one polymorph of PBT, a reliable limit-ordered model[32] of the crystal structure. This can be used as reference for subsequent description of partially disordered systems, in terms of perturbations or departures from such a limit-ordered model. The broader perspective is to gain insight into the driving forces leading to crystallization and development of specific morphologies in P3ATs.

Experimental Section

Synthesis. Regioregular poly(3-*n*-butylthiophene) was prepared with 78% yield using the McCullough synthetic route, giving absolute regiocontrol at each coupling step in the polymerization.[33] NMR analysis of the polymer indicated more than 99% head-to-tail (HT) couplings.

The polymer was extracted in a Soxlet apparatus first with methanol and then with diethyl ether, to separate low molecular weight fractions. It was finally dissolved in boiling chloroform and was reprecipitated by relatively rapid solvent evaporation at 40 °C, to obtain a powder which was dried under vacuum at room temperature. The polymer was then stored for further use, in the dark at −18 °C.

The molecular weight distribution was obtained by a modular multidetector size exclusion chromatography system from Waters with UV−visible diode array detector, in THF using a calibration curve obtained with polystyrene standards. The average molecular weight was $M_w = 10.2$ kDa and the polydispersity was $M_w/M_n = 1.86$.

DSC. Differential scanning calorimetry (DSC) experiments were performed on a Perkin-Elmer DSC7 instrument equipped with a liquid nitrogen subambient device. The sample, typically 5 mg, was placed in a sealed aluminum pan, and the measurements were carried out using heating and cooling rates of 20 °C/min.

X-ray Diffraction. Minute polymer fragments (∼0.1−0.2 mg) were mounted on a glass fiber, and X-ray diffraction patterns were recorded using graphite monochromated Cu Kα radiation ($\lambda = 1.54179$ Å), on a Bruker P4 diffractometer equipped with a HiStar 2D detector. The sample-to-detector distance was about 10 cm. Samples were rotated during data collection around the angles ϕ and χ or around ϕ at $\chi = 54.7°$ (magic angle) to obtain diffraction patterns with random crystallite orientations. One-dimensional diffraction patterns were obtained by integrating 2D spectra over the azimutal angle χ at constant 2θ.

Modeling. Most MM calculations were carried out with the Tinker 4.2 molecular modeling package,[34] using our own force field for oligo- and polythiophenes.[28] Accelrys Materials Studio[35] was also employed for visualization and preliminary calculations. Details and tests of the force field, which differs in some important aspects from our original implementation[28c] and generalizes our parametrization for tetrathiophene,[28d] will be published elsewhere:[28e] here we only provide a brief overview. Bond lengths and angles were assigned standard values by comparison with available X-ray crystal structures[36] or ab initio calculations on short oligomers. The most critical parts of the force field are the nonbonded interactions and intramolecular torsion potentials. Lennard-Jones parameters were taken without further adjustments from the OPLS-AA force field.[37] Point charges on the backbone atoms, including also the C(sp^3) atom connecting the alkyl chains to the backbone, were obtained by fitting the electrostatic potential produced by the B3LYP/6-311G** electron densities of oligomer models, making small adjustments to the ab initio charges to ensure their transferability and electroneutrality of individual monomer units. Point charges on the alkyl side chains were borrowed from OPLS-AA for hydrocarbons. The inter-ring torsion angle within the polymer backbone was parametrized by fitting the results of high-level ab initio calculations (MP2/aug-cc-pVTZ) on the thiophene dimer.[28a] The torsion potentials of the alkyl side chains were taken from the OPLS-AA force field. The torsion potential for the C−C bond connecting the alkyl side chains to the thiophene backbone was computed ab initio by the B3LYP/6-311G** method.

Results and Discussion

Thermal Behavior. The thermograms obtained from successive DSC scans are shown in Figure 2. First heating

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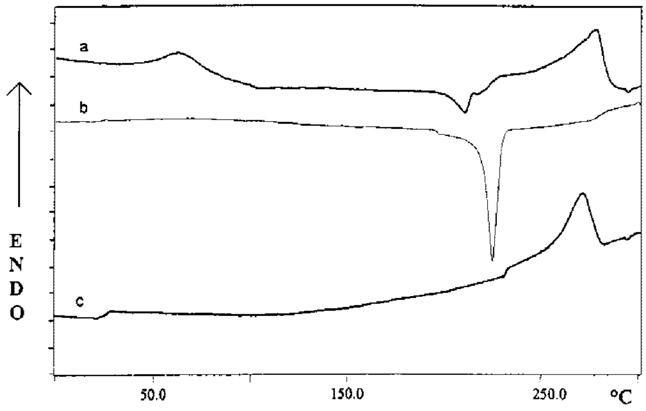

Figure 2. DSC thermograms of PBT with a heating and cooling rate of 20 °C/min: (a) heating of the native polymer; (b) cooling; and (c) subsequent heating of the sample cooled from the melt.

runs on native PBT samples (Figure 2, trace a) show an endothermic transition in the 50−80 °C range and centered at 63 °C, with a heat flow of 12 J/g. Heating further there is an exothermic transition at 210 °C (9.4 J/g) and an endothermic transition centered at about 277 °C with a heat flow of 26 J/g, due to final melting. The first endothermic peak in P3ATs is commonly associated with disordering of the side chains, giving rise, in the temperature range from this transition to the final melting endotherm, to a structure which can be described as 2D mesophase.[10,15,19,20] In the cooling scan from the melt (Figure 2, trace b) there is a sharp exothermic peak centered at 224 °C (transition enthalpy 26 J/g): the relative small undercooling at which recrystallization occurs, even at 20 °C/min, appears consistent with the formation of a mesomorphic phase. Figure 2 (trace c) shows a heating curve of PBT crystallized from the melt, presenting a single endothermic transition at ca. 269 °C ($\Delta H = 21$ J/g). There is evidence of a second-order transition at 25 °C, which could correspond to the T_g, and there are also hints of some crystallization at 230 °C.

Allowing for the higher regioregularity of our samples, these results compare reasonably well with other published data for PBT.[23,31] The low temperature transition occurring in the first run on native PBT samples is only scarcely commented.[23,30,31] The absence in the second (and successive) heating cycle of an endothermic peak below 100 °C is usually assumed to indicate that P3ATs do not attain complete side-chain order upon crystallization from the melt. The situation in our case does not change with hold times of a few minutes at room temperature, confirming that the 3D order of such samples should be limited. Both the final melting temperature and enthalpy in the second heating cycle are significantly lower than in the first one, even if they are substantially higher than any final melting values reported in the literature for other PBT samples originally in form I.[23,31] On the other hand, the final melting enthalpy of less regioregular samples originally in form II is 29 J/g,[31] which is significantly larger than our values, including that in the first heating scan. On the contrary, the final melting temperature of form II samples[31] is about 30 °C lower than that seen in the first heating of our native samples. Since thermal degradation is expected to play a minor role in the outlined behavior, the available data suggest that the disordered phase, which exists above the low temperature endotherm or in the second and successive heating cycles, may not be unique. In other words, there may be different mesophases with conformationally disordered side chains and different partially ordered packings of the main chains. Detailed investigation of such issues will be carried out in future work.

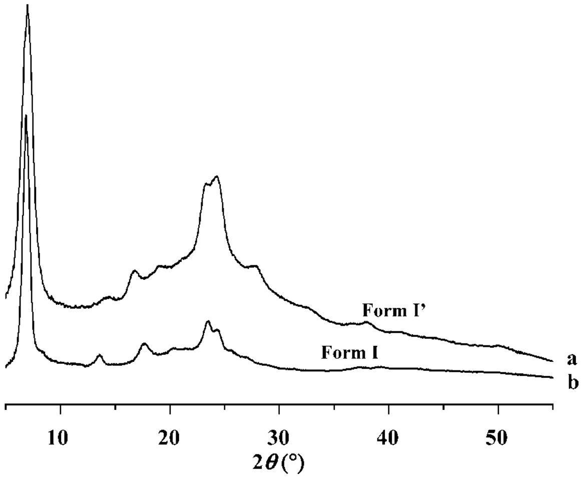

Figure 3. X-ray diffraction patterns of poly(3-*n*-butylthiophene): (a) native: form I′; (b) annealed at 180 °C and slowly cooled: form I.

In conclusion, our thermal data can be interpreted assuming that the initial crystalline phase, which we will name form I′ (vide infra), presents some analogies but also significant differences from the more disordered crystalline phase commonly obtained by crystallization from the melt (i.e., form I). Both form I and form I′ should be metastable at room temperature, since our comparison with the literature data concerning form II[31] indicates that the latter should be the thermodynamically stable phase. However, with our sample under the conditions we adopted, we do not have any evidence of form II crystallization.

X-ray Diffraction and Crystal Structure of Form I′. The thermal behavior of PBT is qualitatively similar to that found for other regioregular P3ATs.[20] It differs on the other hand from PMBT which shows, even in the native state, a single high temperature melting exotherm and presents, as far as it is known, only one crystal phase and no 2D-mesophase.[27] Consistently with the DSC observations, the X-ray diffraction patterns of our regioregular, randomly oriented polycrystalline PBT samples reveal two different crystal polymorphs. The modification stable below the 63 °C transition that we named form I′ in the thermal data discussion, has never been discussed in detail in the literature. It is present in the native samples, which are crystallized from $CHCl_3$ by solvent evaporation at 40 °C and gives rise to the diffraction pattern shown in Figure 3, trace a. Above the temperature of 63 °C, a different polymorph develops (Figure 3, trace b), which is identified in the literature as form I.[23,30,31] This modification crystallizes also upon cooling from the melt through the mesophase. The strong maximum at $2\theta \approx 6.9-7.0°$, which is present in both diffraction patterns and is normally indexed as (100) in the literature, corresponds to the characteristic periodicity between adjacent layers of chains with noninterdigitating side chains typical of form I type structures (see again Figure 1).[10,14,15,20] On the other hand, there are also significant differences in the

Table 1. List of the Observed Maxima in Powder Patterns of Form I′ and Form I

form I′		form I	
d (Å)	intensity	d (Å)	intensity
12.54	vs	12.87	vs
		10.50	w/m
6.15	w/m	6.52	m/s
5.28	m/s	5.03	m/s
4.65	m	4.39	w/m
4.17	w/m	4.13	w
3.81	s	3.80	s
3.66	s	3.64	s
3.20	m/s	3.49	w
2.73	w/m	3.31	w/m
2.36	w/m	3.05	vw
2.20	vw	2.40	w
2.04	vw	2.30	w
1.82	w		

two X-ray diffraction patterns, plausibly made more apparent by the fact that both were obtained from polycrystalline samples with random orientation. Comparing profiles a and b in Figure 3, we note a slight shift to higher angles of the first peak of form I′ as compared to form I, consistent also with the different positions of the higher order (h00) peaks. The recognition of two distinct polymorphs is further confirmed also by a number of other differences in peak intensity and location, involving the region of the diffraction patterns around $2\theta = 23.0-28.0°$. Pertinent data are summarized in Table 1. In the present paper we shall concentrate on form I′, leaving form I, form II, and issues concerning the disorder in high temperature phases to future investigations.

Our success in the structure analysis of PMBT[27] encouraged us to follow a similar route, that is, we attempted to describe also the PBT form I′ structure by an asymmetric unit consisting of a single monomer, with a preference for lattices with the highest possible symmetry. Given the quality of the diffraction patterns, it would be otherwise difficult and possibly pointless to attempt to identify more complicated structural models with a large number of refinable parameters. Under the hypothesis that monomer units are crystallographically equivalent, all chains in the crystal must be isomorphous (or enantiomorphous) and adopt symmetry-related side-chain conformations. Preliminary molecular mechanics calculations show that the most plausible value for the torsion angle C(6)−C(5)−C(3)−C(1) between the backbone and the side chain is close to ±90° (see Figure 4). These minima are more stable by about 2.8 kcal/mol than the other low-energy region located around 180°. The most stable side-chain conformation has both the C(3)−C(5)−C(6)−C(7) and the C(5)−C(6)−C(7)−C(8) torsions in the trans state.

The most significant diffraction peaks in form I′ patterns (Figure 3, trace a, and Table 1), suggest a tentative orthorhombic lattice with $a = 7.63$ Å, $b = 7.76$ Å, and $c = 25.1$ Å, which are indeed close to those of PMBT. The space group choice is not as straightforward as in the case of PMBT, because a number of symmetry operators which are forbidden for PMBT become acceptable in PBT, due to the presence of a stereocenter in the side chain of the former and its absence in the latter. Under the postulate of equivalence of chemical repeating units,[32] the symmetry of crystalline *transoid* PBT chains is not limited to 2-fold screw conformations, as in the $C222_1$ space group of PMBT. Intramolecular glide planes can in principle be also adequate. Among intermolecular symmetry operators, also inversion centers become possible intrastack operators, implying different chain directionalities within the same layer (alternating up−down chains). Interlayer glide planes must also be considered. Thus, the larger number of allowed symmetry operators forces us to test a number of different space groups.

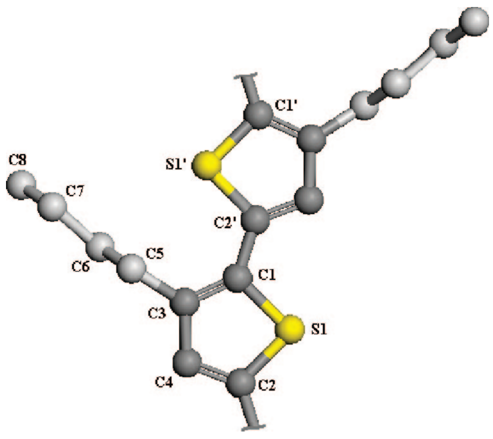

Figure 4. Numbering of the non-hydrogen atoms in a PBT chain. The isolated chain conformation depicted here corresponds to our final refined model in the form of I′ PBT crystals. The regioregular substitution pattern of the chain implies that the chain is directional, that is, two distinct orientations can be envisaged, sharing the same chain axis.

A series of orthorhombic space groups are compatible with the mentioned symmetry elements, along with density requirements, without implying statistical orientational disorder of the chains.[32,38] We decided to test also some monoclinic space groups notwithstanding their lower symmetry, because it is difficult to rule them out completely with the available diffraction data. The more plausible are $C222_1$, $P2_1/c$, $C2/c$, $Pca2_1$, and $Pbca$. In all these space groups, the different symmetry operators allow either intra- or interlayer antiparallel chains. Space groups like $C2$, Pc, and $P2_1$, with a single monomer asymmetric unit, involve chains with identical orientations. They were ruled out because, even though they might satisfy symmetry and packing requirements, we cannot envisage plausible physical mechanisms by which such crystals could form from the melt or from solution, where chains have random orientation.

Considerations about the stacking of polythiophene chains in individual layers and preliminary fitting (adopting the Material Studio suite of programs[35]) indicate the $C222_1$, the $C2/c$ with four chains in the unit cell, and the $P2_1/c$ with two chains as the most favorable space groups. In $C222_1$, which characterizes also PMBT, chains in a given layer are *iso*-directional because the intralayer stacking symmetry operator is a 2-fold rotation axis parallel to the main chain axis (Figure 5, a,b). Instead, in the $P2_1/c$ space group an intralayer antiparallel directionality results as a consequence of the inversion center (Figure 5c,d,e). In addition the interlayer packing produced by the symmetry operators of the $P2_1/c$ space group differs from the herringbone arrangement of $C222_1$ space group, as can be seen in Figure 1a. The $C2/c$ space group is somewhat intermediate between the

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(38) *International Tables For Crystallography*; Kopsky, V., Litvin, D. B., Eds.; IUCR/Kluwer Academic Publ.: Dordrecht, 2002; Vol. E.

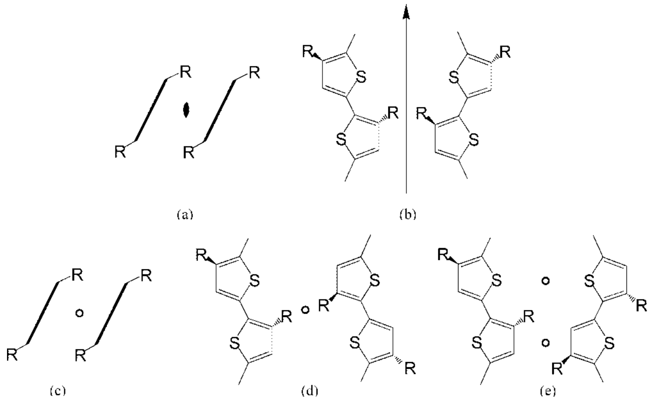

Figure 5. Schematic (a) projection view and (b) side view of intralayer chain stacking in space groups $C222_1$ and $C2/c$: chains are isodirectional because the intralayer symmetry operator is a 2 axis parallel to the chain axis (similar to PMBT[13]); schematic (c) projection view and (d,f) side views of intralayer chain stacking in space groups $P2_1/c$ and *Pbca*: chains possess different directionality because the intralayer symmetry operator is a inversion center (unviable in the case of PMBT[27]).

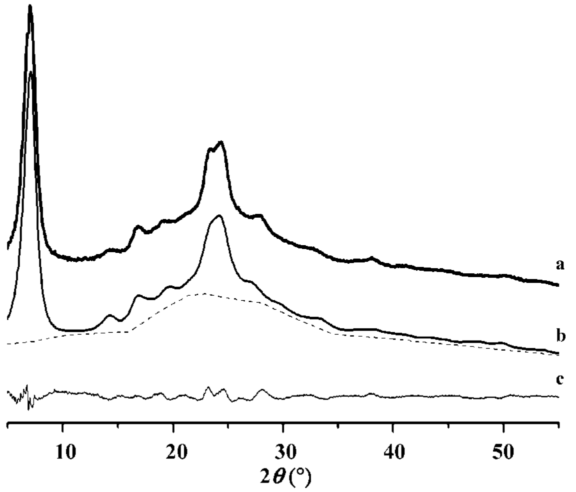

Figure 6. X-ray diffraction pattern of form I′ poly(3-*n*-butylthiophene): (a) observed profile; (b) calculated profile in $C222_1$ and background profile (dashed line); (c) difference curve.

previous two. The same intralayer *iso*-directionality of $C222_1$ chains is produced by the 2-fold rotation axis parallel to the main chain axis, while inversion centers as interlayer symmetry operators forms neighboring layers with different directionality but not a with a herringbone arrangement.

The more promising models were refined by the Rietveld method,[39] optimizing the fit to the whole X-ray powder pattern profile with the "Debvin" program.[40] A detailed investigation, considering both the agreement between calculated and observed diffraction patterns in the 5−25° range of 2θ and packing distances, induced us to concentrate our efforts on $C222_1$, the only remaining orthorombic space group. For both monoclinic groups, that is, $P2_1/c$ and $C2/c$, notwithstanding the additional degree of freedom involved in the optimization of the monoclinic angle, a poorer fit resulted in the 16−20° range of 2θ because of systematic absences and, for $P2_1/c$, also due to halving the c lattice periodicity. In the latter case, characterized by intralayer *antiparallel*-directionality, attempts to optimize the Rietveld fit gave also rise to a series of overshort intralayer packing distances. Energy minimizations by molecular mechanics were also carried out on the best fit structures obtained for each of these groups. The results, which will be discussed shortly, confirmed the preference for the $C222_1$ model.

The observed, calculated, and background profiles are reported together with the difference curve in Figure 6, for the $C222_1$ space group. Bond lengths and bond angle values were adopted from the crystal structure of tetrahexylsexithiophene.[36] Only very minor adjustments were allowed for bond lengths whereas bond angles were refined under elastic restraints to the values found in the tetrahexylsexithiophene crystal structure.[36] The refined lattice parameters are $a = 7.64(1)$ Å, $b = 7.75(1)$ Å, and $c = 24.97(8)$ Å, yielding a calculated density of 1.24 g/cm^3. Considering the degree of crystallinity of the sample (45 ± 5%, obtained by integration of the crystalline pattern and of the background profile), the calculated density is in good agreement with the experimental value of 1.18 ± 0.02 g/cm^3 determined by floatation. The value of the final disagreement factor R_2' was 0.093 ($R_2' = \Sigma I_{\text{obs}} - I_{\text{calcd}}/\Sigma I_{\text{net}}$ where $I_{\text{net}} = I_{\text{obs}} - I_{\text{bkg}}$) with an overall isotropic temperature factor B of 8. The background profile resulting from the Rietveld refinement differs from diffraction patterns of fully amorphous melt quenched PBT samples (see the Supporting Information). Such patterns are hardly ever used as background in polymer crystal structure refinements to account for the noncrystalline components to the scattering. This is due to experimental difficulties (e.g., minor differences in sample supporting systems), and because the amorphous structure may vary to some degree as a consequence of the crystallization of a substantial portion of the polymer. The pattern of the fully amorphous polymer is often not a viable refinement background also because of difficulties modeling short-range crystalline disorder in semicrystalline systems or due to the presence of minor amounts of other polymorphs or semiordered phases. The latter issue is likely to be particularly relevant to this refinement, as it is difficult to rule out the presence of small but significant percentages of other form I family crystalline or mesomorphic phases. Details of the background, if kept within reason, influence in negligible ways the refined model, which in our case is highly constrained. The disagreement factor between calculated and observed spectra is obviously affected by the adopted background, but in the present case it is extremely satisfactory. The refined fractional coordinates are listed in Table 2, while nonstructural parameters are reported in the Supporting Information.

The refined internal coordinates for PBT (form I′) are listed with estimated errors in Table 3. Views of the refined molecular conformation and of the packing are shown in Figures 4 and 7. Intermolecular distances are acceptable: the only somewhat short contact involving non-hydrogen atoms occurs between the C8 methyl carbon and the C7 methylene carbon of a chain from an adjacent layer (3.59 Å), while all others are well above 3.60 Å. The chain setting angle, that is, the angle between the (h00) lattice planes and the least-

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(40) Bruckner, S.; Immirzi, A. *J. Appl. Crystallogr.* **1997**, *30*, 207.

Table 2. Refined Atomic Parameters of Non-Hydrogen Atoms in Form I′ Poly(3-*n*-butylthiophene)

	x	*y*	*z*	*B* (Å^2)
C1	0.2550	0.4758	0.2600	8.0
C2	0.2499	0.1538	0.2570	8.0
C3	0.2715	0.4007	0.3099	8.0
C4	0.2684	0.2166	0.3076	8.0
C5	0.3021	0.5018	0.3607	8.0
C6	0.1410	0.5705	0.3894	8.0
C7	0.1805	0.6882	0.4365	8.0
C8	0.0165	0.7543	0.4642	8.0
S1	0.2360	0.3208	0.2111	8.0

Table 3. Refined Internal Coordinates for PBT (Form I′)[a]

	bond lengths (Å)		
C1−S1	1.719	C2−S1	1.732
C1−C3	1.380[b]	C2−C4	1.360[b]
C3−C4	1.428	C3−C5	1.510[b]
C5−C6	1.520[b]	C6−C7	1.520[b]
C7−C8	1.520[b]	C1−C2′	1.444
	bond angles (deg)		
C1−S1−C2	92.7	S1−C1−C3	110.7[b]
S1−C2−C4	110.7[b]	C4−C3−C5	123.7
C3−C5−C6	116.9	C5−C6−C7	114.5
C6−C7−C8	113.0	S1′-C2′-C1	121.1
C2′−C1-S1	117.1	C2′−C1-C3	132.2
	torsion angles (deg)		
S1−C1−C3-C4	0.0	C1−C3−C4-C2	0.0
C1−C3−C5-C6	86.4	C3−C5−C6-C7	−173.3
C5−C6−C7-C8	180.0	C2−C4−C3-C5	−176.0
C2′−C1−C3-C4	179.5	S1′-C2′−C1-S1	178.8
C2′−C1−C3-C5	−4.5	S1′-C2′−C1-C3	−0.7

[a] Estimated standard deviations vary between 0.3 and 1.0° for bond angles and between 1.0 and 2.0° for torsion angles. The numbering of the atoms is given in Figure 4. [b] Values not refined.

squares planes of the PBT main chains, is only a few degrees, at variance with PMBT.

The refined structure confirms that also in the case of form I′ the side chains of different layers do not interdigitate, as already found in form I of PMBT and as proposed for various unrefined poly(alkylthiophenes) structures in the literature.[10,14,15,20]

Molecular Modeling. The best candidate structures obtained by Rietveld fitting of the X-ray powder profile were also tested by MM minimization of their potential energy. In a first set of calculations, the energy of a crystal structure was minimized with respect to both atomic coordinates and lattice parameters but keeping the full symmetry of the original space group. In a second set of calculations, we repeated the same minimizations after switching off all symmetry constraints ($P1$ space group). As a consequence, triclinic distortions of the original monoclinic or orthorhombic cells were also allowed by this procedure. The main results are collected in Table 4.

Minimization of the $C222_1$ unit cell produces very minor structural alterations. Both the lattice parameters and chain conformation (in particular the C6−C5−C3−C1 torsion angle connecting the side-chain to the backbone) stay very close to their original values. There is no difference between the symmetry-constrained and the unconstrained $P1$ structures. Thus, we can state that the refined $C222_1$ cell discussed previously corresponds to a genuine minimum-energy structure. Note that the relative arrangement of the π-stacked thiophene rings within a layer corresponds to the absolute minimum-energy structure identified by Tsuzuki et al.[41] by high-level ab initio calculations on thiophene and 3-methylthiophene van der Waals dimers.

On the contrary, minimization of best candidate structures from the $C2/c$ and the $P2_1/c$ space groups leads to very large distortions, which are further amplified after removal of the symmetry constraints in the case of $C2/c$ symmetry. The final potential energies after $P1$ minimizations are actually slightly lower than the energy of the $C222_1$ structure. This correlates with the fact that their final $P1$ densities are also slightly higher and is consistent (vide ante) with the experimental observation that tightly stacked form I′ and form I structures are metastable crystalline phases. However, the changes in the lattice parameters are so large as to make these final structures incompatible with the experimental X-ray diffraction profile. The conformation of the side-chains changes significantly, too. In the $P1$ minimization of the $C2/c$ structure there is actually a complete loss of the intramolecular symmetry, including a significant distortion of the conjugated backbone from planarity. The S1−C1−C2′−S1′ dihedrals, which are equal to 180° in all starting structures, become ±134.5° and ±140.7° in this case.

Summarizing, $C222_1$ is the only one of the three investigated packing modes which preserves the stacking at about 3.8 Å of the polythiophene chains, even after removal of the symmetry constraints. The other candidate structure with stacked layers of isodirectional chains, namely, $C2/c$, maintains the stacking as long as symmetry constraints are retained. Stacks with antiparallel chains, generated by application of the inversion center in the $P2_1/c$ space group, expand significantly even when the symmetry constraints are preserved. Both the relaxed $C2/c$ and $P2_1/c$ models lead to a stacking distance reminiscent of the value found in form II PBT and are marginally more stable than form I′,[30,31] but they are incompatible with the PBT form I′ diffraction pattern.

Concluding Remarks

Combining Rietveld analysis of powder X-ray diffraction data, differential scanning calorimetry, and molecular mechanics calculations, we have studied the crystallization behavior and structure of a highly regioregular head-to-tail poly(3-*n*-butylthiophene) (PBT). In particular, we have identified and solved the structure of a new crystal polymorph (form I′), obtained in the native state by solvent evaporation at approximately 40 °C and never previously discussed in the literature.

Similarly to poly-3-(*S*)-2-methylbutylthiophene (PMBT), form I′ PBT adopts the orthorhombic space group $C222_1$ characterized by the absence of interdigitation of the side chains belonging to different layers. Other important features of the inverse comb model[15] for form I poly(3-alkylthiophenes), like the stacking periodicity, the setting angle, and the side chain orientation, are also confirmed in the case of form I′ PBT. However, significant new information emerges: in our *limit-ordered* models the symmetry elements imply

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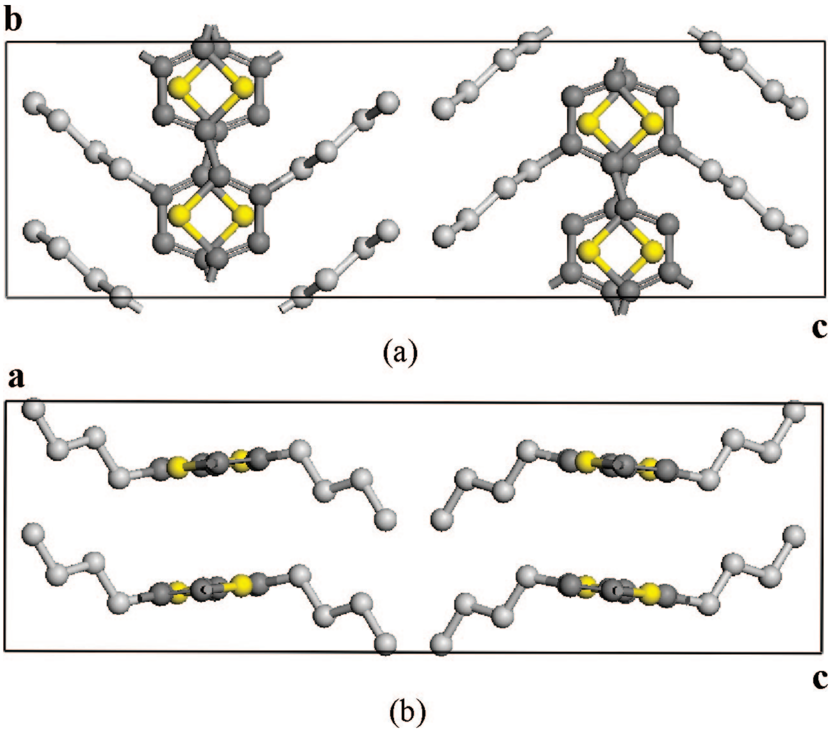

Figure 7. Crystal packing of PBT chains refined in $C222_1$, viewed along the *a* axis (a) and along the *b* axis (b). Only non-hydrogen atoms are shown. The conformation of the individual chains is also shown in Figure 4.

Table 4. Comparison of the crystal structures obtained by Rietveld refinement and by subsequent molecular mechanics minimizations

$C222_1$ space group		
Refined lattice parameters	Minimization in $C222_1$	Minimization in P1
a = 7.64 Å	7.61 (−0.46%)	7.61 (−0.46%)
b = 7.75 Å	7.81 (+0.77%)	7.81 (+0.77%)
c = 24.97 Å	25.29 (+1.29%)	25.29 (+1.29%)
		$\alpha = 90.0°$; $\beta = 90.0°$; $\gamma = 90.0°$
Density = 1.24 g/cm^3	1.22 (−1.57%)	1.22 (−1.57%)
C6−C5−C3-C1 torsion angles: 86.4°	84.6°	84.6°
Pot. Energy per monomer (kcal/mol)	−10.76	−10.76
*C*2/*c* space group		
Refined lattice parameters	Minimization in *C*2/*c*	Minimization in P1
a = 7.58 Å	7.32 (−3.40%)	9.75 (+28.6%)
b = 7.75 Å	7.81 (+0.68%)	7.82 (+0.82%)
c = 24.24 Å	26.03 (+7.41%)	23.79 (−1.85%)
$\beta = 90.0°$	$\beta = 90.0°$	$\alpha = 109.6°$; $\beta = 103.1°$; $\gamma = 114.5°$
Density = 1.29 g/cm^3	1.23 (−4.27%)	1.31 (+1.25%)
C6−C5−C3-C1 torsion angles: ± 76.6°	±93.3°	±72.5°; ± 73.8°; ± 93.3°; ± 97.9°
Pot. Energy per monomer (kcal/mol)	−10.70	−10.91
$P2_1/c$ space group		
Refined lattice parameters	Minimization in $P2_1/c$	Minimization in P1
a = 12.84 Å	10.81 (−15.8%)	10.81 (−15.8%)
b = 7.75 Å	7.80 (+0.61%)	7.80 (+0.61%)
c = 7.58 Å	9.13 (+20.4%)	9.13 (+20.4%)
$\beta = 106.67°$	$\beta = 104.9°$	$\alpha = 90.0°$; $\beta = 104.9°$; $\gamma = 89.9°$
Density = 1.27 g/cm^3	1.23 (−2.84%)	1.23 (−2.84%)
C6−C5−C3-C1 torsion angles: ± 84.2°	±91.6°	±91.6°
Pot. Energy per monomer (kcal/mol)	−11.19	−11.19

that within a given layer chains are isodirectional, whereas in adjacent layers they have opposite orientation. Both the main chains and the side chains of contiguous layers display a herringbone arrangement, which molecular mechanics shows to be particularly compatible with a tight stacking of isodirectional, parallel chains. Modeling results are also consistent with the fact that form I′ and a fortiori the closely related, more disordered form I are not the thermodynamically stable phases at room temperature.

The identification for regioregular PBT of an ordered form I′, along with the more common disordered form I, correlates with recent results on the polymorphism of regioregular poly(3-hexylthiophene) (PHT).[26] Using low molecular weight samples upon directional epitaxial solidification, formation of an ordered, highly crystalline modification of the form I family, apparently different from the usual form I, was observed by Brinkmann et al.[26] The new polymorph is characterized by high crystallinity and extended-chain crystallization. With molecular weights above 7−10 kDa and the onset of chain-folding, sample crystallinity and order drop, and the usual form I apparently occurs. Other authors,[25] under different crystallization conditions, indicate that chain-folding does not occur below about 10−12 kDa for PHT.

We do not know for certain if our form I′ PBT samples are chain-folded or not. The M_w value of 10.2 kDa (PS based), considering that it is plausibly overestimated by 50%,[42] implies a DP_w of about 50 and an average chain length of approximately 200 Å. The crystallite coherence length resulting from the structural refinement (see Supporting Information) is ~50 Å along the main chain axis. Together, these data may be compatible with a limited degree of chain-folding in the case of our form I′ PBT samples. On the other hand regioregular poly-3-(*S*)-2-methylbutylthiophene (PMBT) with a M_w value of 25 kDa, crystallizing in same $C222_1$ space group as form I′ PBT, is more likely to present significant degrees of chain-folding.[27]

It is apparent from the above discussion that the $C222_1$ space group model (adopted by both the regioregular PBT form I′ and the PMBT crystal structures) is incompatible with chain-folding within a π-stacked layer because, at variance with the constraints imposed by the space group, it would require adjacent chains to be antiparallel (unless a chain defect is located within a fold, but this is unlikely due to the high regioregularity of our samples). Quite independently, we can state that tight chain-folding of P3ATs along stacks of form I type structures, with chain axes less than 4 Å apart, can be expected to be extremely unlikely. Tight chain-folding requires sequences of five consecutive thiophene units with cis interring torsion angles[43] (see Figure 8) and hence an axial separations of 9 Å or more between the connected stems. Folds between closer crystalline stems would involve longer noncrystalline segments, decreasing their likeliness because of the associated energetic and steric requirements.

We have seen that the refined crystal structures of PBT and PMBT, along with simple independent considerations, indicate that chain-folding within a single P3AT stack is unlikely if not impossible. However, both in the melt and in solution, aggregation of polythiophene chains is generally thought to involve some degree of local π-stacking of thiophene rings.[44] The intramolecular component of these aggregates implies the formation of loops or loose folds, whose relevance increases with molecular weight. Our analysis suggests that, in order to crystallize, such aggregates with loose folding and interstem π-stacking interactions need to be disrupted and reorganized with stacking and fold patterns compatible with the final crystal structure. Thus, π-stacking of thiophene rings is both an important driving force and an obstacle in the orderly assembly of semicrystalline P3ATs. The relevance of the above comments is apparent specifically for crystallization of P3ATs from mesomorphic phases which, according to the current interpretations, show π-stacking interactions involving plausibly orientationally disordered main-chains, in microphase-separated structures with disordered side chains. Chain-folding and π-stacking mutually influence each other in ways which are specific to P3ATs and are likely to limit crystallinity and order, particularly in P3AT crystallized from the melt or through mesophases.

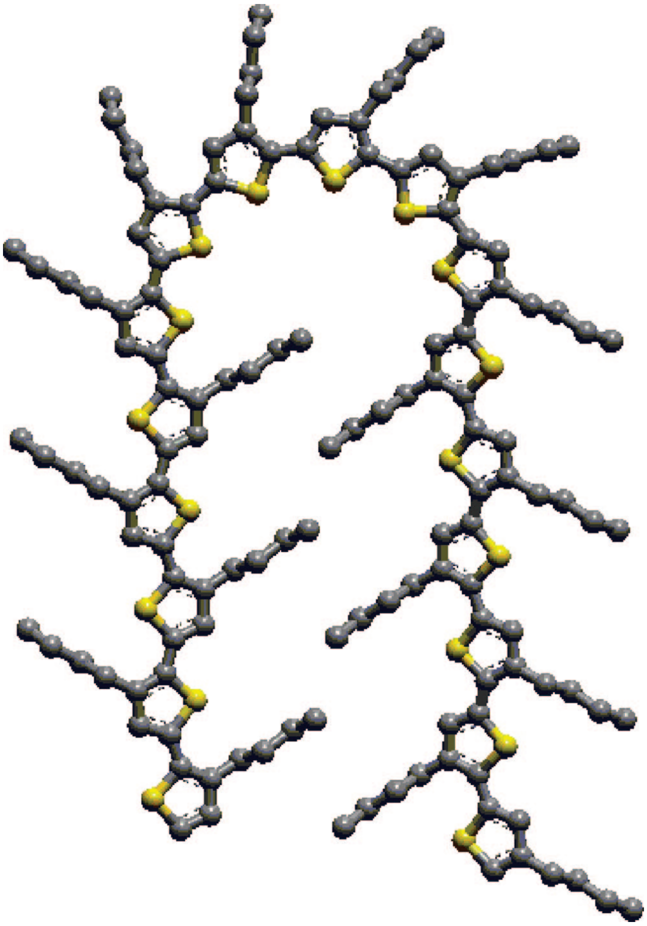

Figure 8. Chain folding model of a PBT chain with stem separation 12.5 Å (interlayer distance in the refined $C222_1$ structure). Notice that chain folding requires the *cisoid* conformation of five consecutive inter-ring bonds. Folding with the stem separation of 3.7 Å (intralayer π-stacking distance in the refined $C222_1$ structure) would require a substantially longer noncrystalline chain portion.

Compared to PMBT, the more complex polymorphism of PBT does not have simple explanations at this stage: we can only speculate that for PMBT the thermodynamically stable crystalline phase is also kinetically favored, at least for the relatively low molecular weights that were investigated,[27] while this is not the case with PBT.[30,31] The structural analysis and modeling studies are expected to help us to understand the remarkable differences between these polymers. Molecular dynamics simulations are currently under way to clarify the mesophase structure of PBT and the reasons for its absence in PMBT.

The results of the present work encourage us to extend the approach devised here to the other polymorphs of PBT, as well as polythiophenes with longer side chains or different substitution patterns. The crystal structures of PMBT and of form I′ PBT should be useful as detailed reference models, with the broader aim of gaining general insights into the structural properties, the crystallization mechanisms, and the

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development of specific morphologies in polyalkylthiophene-based materials, including, for example, blends with electron acceptors (e.g., fullerenes) in organic solar cells.

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Supporting Information Available: Refined nonstructural parameters, along with the details of the structural refinement procedure (PDF) and crystallographic information (CIF). This information is available free of charge via the Internet at http://pubs.acs.org. Crystallographic data for the structure reported in this paper have also been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC- 681386.

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