Application of the Molecular Simulation Technique for Clarification of the $\alpha \leftrightarrow \beta$ Phase Transformation in Poly(butylene terephthalate)

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ABSTRACT: Poly(butylene terephthalate) (PBT) is known to undergo a stress-induced crystalline $\alpha \leftrightarrow \beta$ phase transition. The unit cells of each form have been simulated using a molecular mechanics energy minimization approach. Unit-cell parameters derived from the simulated cells compare favorably with those determined experimentally as do calculated X-ray diffraction patterns. From the simulated structures, it is clear that the change in c-axis length upon transforming from α to β can only be explained in terms of a conformational change of the tetramethylene units from a crumpled to extended state.

Introduction

Poly(butylene terephthalate) (PBT) copolymerized with other polyethers is one of the most widely-used thermoplastic elastomers as well as a subject of much academic interest. This prominence arises from its unusual crystal–crystal phase transition when undergoing uniaxial extension. Two crystalline modifications differing in both molecular conformation and crystalline packing have been postulated. The α phase is obtained when PBT is cooled from the melt. Upon uniaxial deformation (5–15% strain) the α phase is converted to a stretched, or β, form. The process is reversible as essentially all α crystals are recovered upon release of stress.

The two crystalline modifications have been studied through use of wide-angle X-ray scattering (WAXS),[1-7] infrared,[8-11] Raman,[3,8,12] and NMR.[13-15] WAXS, infrared, and Raman studies all suggest that the primary structural difference between the two forms lies in the conformation of the tetramethylene units. In the α form the tetramethylene units adopt a crumpled gauche–trans–gauche (gtg) conformation, while in the stressed β form they extend into an all-trans (ttt) conformation. Recently, however, the structural changes associated with this phase transformation have become a subject of contention. Interpretations of high-temperature solid-state NMR data, both broad-line ^{1}H and ^{13}C, dispute this conclusion and instead assert that the tetramethylene units are conformationally equivalent in both modifications, with the stress-induced conformational change associated with a conformational change in the terephthalate residue.[13,15]

In this study, the molecular-simulation technique was employed using molecular mechanics to examine the structures of several possible crystalline forms of PBT. Previous studies utilizing such a technique have defined the structures of crystalline polymers.[16-18] X-ray diffraction is perhaps the most definitive technique in assigning atomic placements within individual unit cells. With recent advances in simulation software, it is also possible to generate diffraction patterns from simulated crystalline structures. Comparison between calculated and experimental patterns should reveal structural differences of the α and β crystalline forms.

Simulation Technique Employed

The monomer repeat unit of PBT along with our atomic numbering scheme is shown in Figure 1. The computer program utilized is a material simulation package, POLYGRAF, provided by Molecular Simulations, Inc. The force field used in the POLYGRAF molecular mechanics and dynamics calculations has been previously described.[19] For our simulation study, the two crystalline forms were generated in a similar manner. Models proposed from fits to X-ray diffraction data were used as initial structures. These structures were then optimized by molecular mechanics. In order to account for long-range interactions, the periodic boundary condition is used in all cases. Two general methods were employed to reach the final crystalline state. One was to minimize the energy of an isolated chain and then *place* it into crystalline lattices using unit-cell parameters reported in the literature. It is also possible to seek the lowest energy states by simultaneously minimizing the chain and unit cells. In both cases no constraints were placed on either the chain or unit cell. The first method descended to the state of minimum energy more quickly than the second. The crystalline unit cells obtained were identical for both methods. The unit cells calculated for both the α and β forms are shown in Figures 2. The two chain conformations calculated are shown in Figure 3.

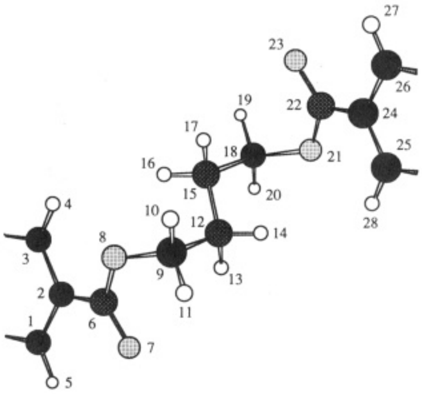

Figure 1. Calculated structure of α-PBT. The atom numbering scheme is used to define structural parameters shown in Table II.

Results and Discussion

Several groups have proposed molecular structures for both the α and β crystalline forms.[1,4,5,7] While there is some variance in structural details, i.e. values of valence and dihedral angles, the central idea remains the same in that structural differences between α to β forms are due

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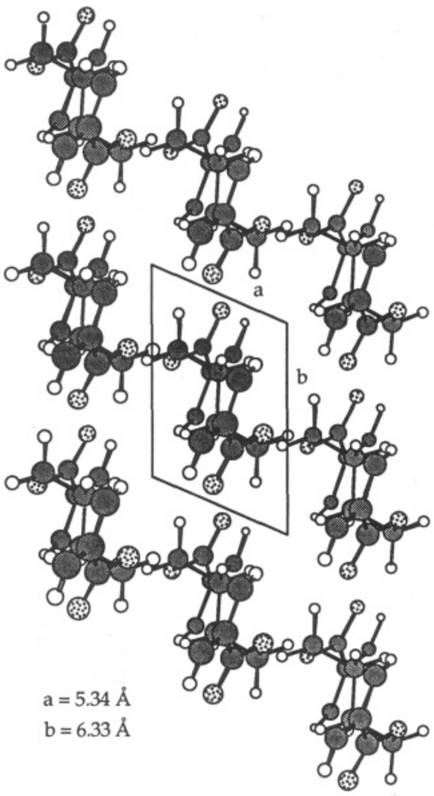

Figure 2. Crystalline unit cell calculated for α-PBT.

to differences in the tetramethylene segment. Models based on the NMR results have not been presented in detail. The unit-cell parameters calculated in this study are presented along with the average unit-cell values reported experimentally in Table I. The agreement between our calculated β unit cell and that reported experimentally is extremely good with differences on the order of 2–3%. The comparison between the calculated α cell and that reported experimentally is not as favorable, with maximum errors, however, in the range of 6–9%. It has been proposed that the driving force behind the reversible transition is the enhanced packing efficiency of the terephthalate groups in the α phase.[7] From WAXS measurements the density of the α phase has been determined to be 1.40 g/cm^3 versus 1.32 g/cm^3 for the β form. For our simulated structures, densities of 1.37 g/cm^3 and 1.35 g/cm^3 were calculated for the α and β phases, respectively.

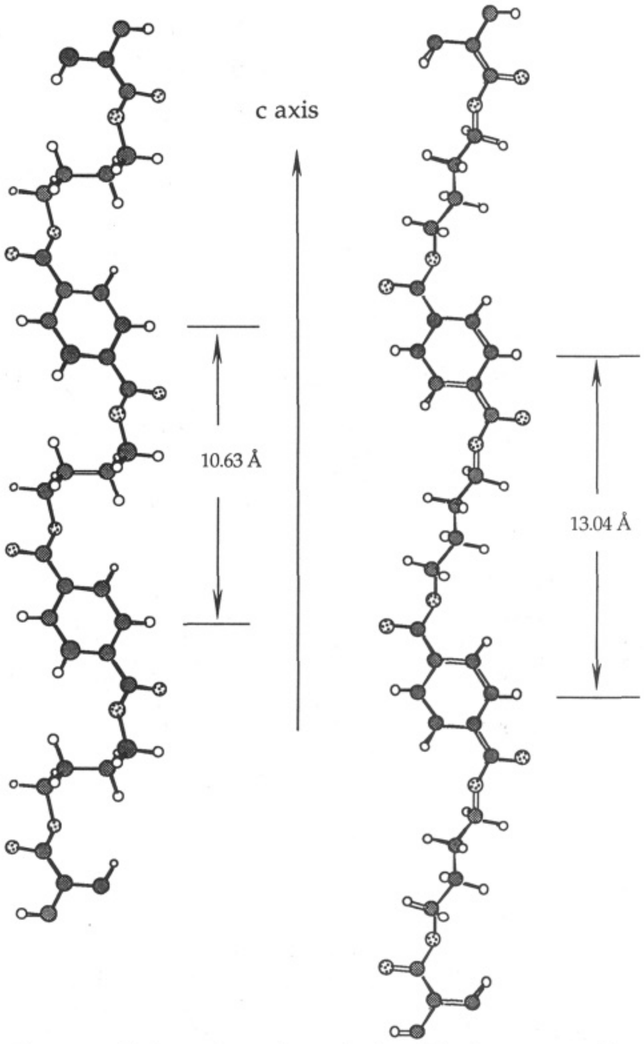

Figure 3. Chain conformations calculated for the two crystalline forms of PBT: left, α structure; right, β structure.

Table I
Calculated and Observed Structural Parameters for α-PBT and β-PBT

	average experimental data	simulated structure
	α-PBT	
a (Å)	4.86 ± 0.03	5.343
b (Å)	5.97 ± 0.03	6.340
c (Å)	11.62 ± 0.10	10.631
α (deg)	99.7 ± 0.5	98.22
β (deg)	116.2 ± 0.8	117.13
γ (deg)	110.8 ± 0.5	114.32
volume (Å^3)	260.6 ± 4	266.6
	β-PBT	
a (Å)	4.78 ± 0.07	4.874
b (Å)	5.80 ± 0.08	6.053
c (Å)	12.98 ± 0.05	13.048
α (°)	102.2 ± 1.0	104.65
β (°)	120.4 ± 1.0	125.04
γ (°)	103.6 ± 2.0	103.06
volume (Å^3)	276.4 ± 8.0	269.47

A comparison of the calculated molecular structures from molecular mechanics with those derived from diffraction data is useful. The torsional angles along the tetramethylene segment are defined in Figure 1 for several of the previously proposed models, and the results derived in this simulation study are shown in Table II. The agreement between the previous models and the simulated structures is qualitatively good. It can be seen that the α phase tetramethylene units are in a gauche–trans–gauche conformation, while those in the β form are in an essentially all-trans conformation. An unusual point is the nonplanarity of the terephthalate unit, with the carbonyl bonds being ±11.57° out of plane of the benzene ring. From model studies, most previous studies have assumed a planar structure. However, since interchain interactions are expected to play a significant role in determining the molecular conformation, departures from the idealized planar structure may be expected. Theoretical calculations suggest that while planarity between the carbonyl and phenyl ring is the minimum energy state, the curvature of the potential well about this minima is quite gradual.[20] A ±20° rotation of the carbonyl units increases energy by only ~0.05–0.1 kcal/mol. We found this small change in dihedral angle contributes only 0.013 Å to the overall change in *c*-axis dimension upon conversion of the α to β form.

The molecular geometries of the simulated crystalline structures shown in Figure 3 clearly indicate that the

Table II
Comparison of Observed and Calculated Torsional Angles for α-PBT and β-PBT

torsion angle (deg)	Yokouchi et al.[5]	Hall and Pass[4]	Menick[1]	Grasso[7]	simulated
		α-PBT			
C(1)–C(2)–C(6)–O(8)	174	179	175		164
C(1)–C(2)–C(6)–O(7)	2	−1	−5		−12
C(2)–C(6)–O(8)–C(9)	178	−178	178		152
C(6)–O(8)–C(9)–C(12)	−88	−94	−91		−68
O(8)–C(9)–C(12)–C(15)	−66	−79	−88		−61
C(9)–C(12)–C(15)–C(18)	180	180	180		180
		β-PBT			
C(1)–C(2)–C(6)–O(8)	179	173		173	−175
C(1)–C(2)–C(6)–O(7)	−3	−7			−1
C(2)–C(6)–O(8)–C(9)	179	−179		−179	−129
C(6)–O(8)–C(9)–C(12)	−179	−159		−159	175
O(8)–C(9)–C(12)–C(15)	113	162		−166	177
C(9)–C(12)–C(15)–C(18)	180	180		180	180

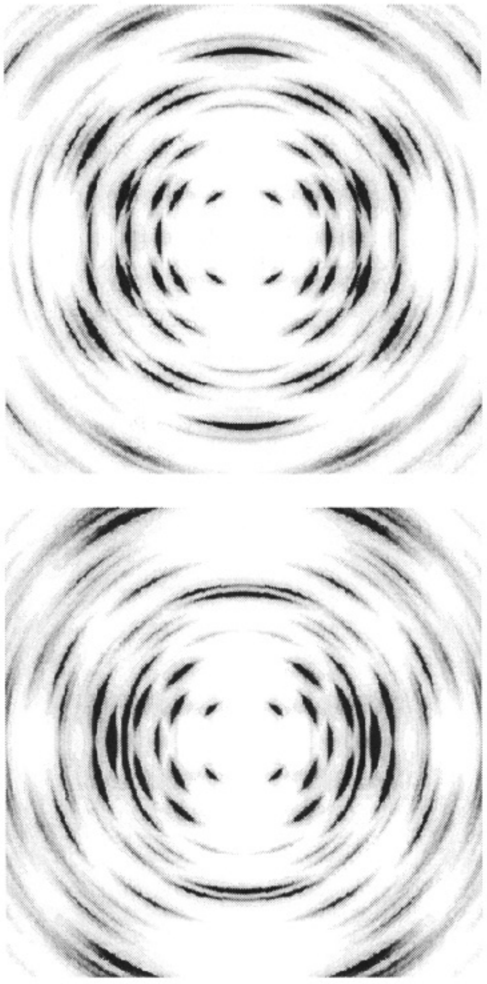

Figure 4. X-ray diffraction patterns simulated for highly oriented PBT fibers: (a, top) α-PBT; (b, bottom) β-PBT. The angular deviation from perfect orientation is ~5°.

Table III
Comparison of Observed and Calculated d Spacings and Scattered Intensities for α-PBT and β-PBT

h	*k*	*l*	observed d spacing[5] (Å), d_o	calculated d spacing (Å), d_c	observed intensity,[5] I_o	calculated intensity, I_c
				α-PBT		
0	−1	1	5.46	5.64	31	19
0	1	0	5.13	5.27	42	76
1	0	−1	4.32	4.83	25	18
1	−1	−1	4.32	4.69	25	28
0	1	1	3.94	3.86	25	25
1	0	0	3.79	4.00	56	73
1	−1	−2	3.68	3.76	31	25
1	−1	1	3.49	3.63	48	100
1	0	1	3.05	3.03	20	21
1	1	−3	2.90	2.91	18	12
1	−2	0	2.86	3.10	17	19
1	−1	2	2.77	2.76	30	44
1	−3	0	1.95	2.07	20	9
				β-PBT		
0	−1	1	5.55	5.88	44	60
0	1	0	5.19	5.18	44	37
0	1	−2	4.62	4.80	12	15
1	−1	−1	4.00	4.19	46	54
1	−1	0	3.71	3.88	90	27
0	1	1	4.00	3.82	46	27
1	0	0	3.71	3.53	90	100
1	−1	−2	3.64	3.76	18	12
1	−1	1	3.30	3.19	37	42
1	−1	2	2.76	2.55	16	9

Table IV
Energetic Analysis of PBT Crystalline Forms

	α form	β form
total energy (kcal/mol)	23.0531	19.1976
internal energy (kcal/mol)	15.5286	12.1604
bonds	3.9610	3.5361
angles	9.0875	5.5177
torsions	2.3162	2.8156
inversions	0.1639	0.2550
nonbonded energy (kcal/mol)	7.5245	7.0372
van der Waals	3.9639	3.4136
electrostatic	3.5606	3.6236

principal difference between the two phases is in the conformation of the methylene units and the adjoining C–O bond. The conformation changes from ggtgg (68°, 61°, 180°, −61°, −68°) in the crumpled α form to an all-trans conformation (170°, 176°, 180°, −176°, −170°) in the extended β form. There are also small bond length and valence angle changes about the backbone ester oxygen, but these appear to arise principally from packing constraints as they are invariant in simulated isolated single-chain structures. There is also a ~6° reorientation of the terephthalate group, contributing ~10% to the *c* axis length change (0.3 Å). The possible structural differences calculated for the terephthalate unit do not explain the difference in the unit cell *c* axis length change (2.42 Å) associated with the α to β transformation as suggested from the NMR data.

X-ray diffraction patterns calculated using CERIUS satisfactorily reproduced those obtained experimentally. The simulated patterns of highly oriented α- and β-PBT fibers are shown in Figure 4. A tabulation of the most intense experimentally determined reflections in both forms are compared with calculated reflections in Table III. Due to significant differences in unit cell dimensions of the two crystalline forms, wide-angle X-ray reflections characteristic of either form have been identified. The intense [1

$-1\ 1]$ reflections in the α form are much weaker in the β form. The *c* axis repeat length increase on transformation from α to β is evidenced by a general increase in the d spacings associated with the $[0\ 1\ k]$ reflections.

Upon construction of crystalline unit cells, an energetic analysis can be readily performed. The β form was found to have a lower total energy than the α form. The β form is expected to possess a lower intramolecular energy than the α form because of its more extended conformation, and this is indeed the case as shown in Table IV. The internal energy of the β form is calculated to be about 3 kcal/mol lower than that of the α form. The total energy of the β form is roughly 4 kcal/mol higher than the α form even though packing is more efficient in the α phase as evidenced by its slightly higher density. The α form is most stable at room temperature in the absence of stress. One need thus recall that these are purely enthalpic energy calculations, with no consideration of entropic effects. In order to truly assess stability as a function of deformation, the relative free energies need be compared. The structures deduced in this calculation correspond to those at 0 K with no entropic contribution. It should also be stated that these energy minimization calculations, as well as WAXS, Raman, and infrared experiments, afford only a *static* molecular view whereas NMR allows one to probe mobility and dynamics. NMR measurements indicate that the tetramethylene units undergo rapid or large amplitude motions and the relation between this mobility and entropy may figure prominently in the relative stability of the two phases. NMR data obtained for PBT model compounds have been assigned based on the differences in the tetramethylene chain conformation.[21] The ^{13}C solid–state NMR measurements are usually carried out at elevated temperatures; the point has been raised whether PBT samples remain in the same state after these NMR measurements.[22] This, in fact, may contribute to the uncertainty in their interpretation.

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