the annealed films, the SANS peak intensity in unannealed film is about half that in the annealed film. This could only mean that a small fraction of absorbed D_2O in unannealed film diffuses into the interlamellar region, while a large fraction of absorbed D_2O diffuses into the amorphous regions outside the lamellar stacks; only the first fraction contributes to neutron-scattering contrast and SANS intensity. Our conclusions are also consistent with the lamellar spacing obtained from SAXS and the crystallite size derived from WAXD. In one fiber sample in which 53% of the polymer was amorphous, the lamellar spacing was 71 Å and the lamellar thickness (crystallite size along the fiber axis, corrected for instrumental and microstrain broadening) was 62 Å.[9] Thus, the fraction of the amorphous polymer in the interlamellar region is 13%, about one-fourth of the total amorphous material.

Conclusion

We have shown that water molecules diffuse almost exclusively into the amorphous regions of nylon 6. Diffusion of water into the interlamellar regions swells this amorphous matrix, increases the lamellar repeat, decreases the unit cell volume in preexisting lamellae, and at elevated temperatures hydrolyzes the tie molecules. Diffusion of water into the amorphous region outside the lamellar stacks, which can be a significant fraction, lowers the glass-transition temperature, decreases the modulus, and crystallizes the polymer.

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Registry No. Nylon 6, 25038-54-4; water, 7732-18-5.

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Structural and Energetic Analyses of the α to β Phase Transition in Poly(butylene terephthalate)

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ABSTRACT: The crystal structure of the stressed β phase of PBT was refined by using intensity data from recently obtained high-quality X-ray fiber diffraction patterns. The crystallographic *c* axis was found to be tilted 1.5° away from the macroscopic fiber axis. This was manifested in determinable displacements of the reflections above and below their respective layer lines. These displacements were beneficial since they allowed several overlapping reflections to be resolved and they confirmed several indexing solutions. The reported structure is preferred over those reported earlier on the basis of better agreement with observed intensity data, Hamiltonian statistics of parameters refined, and potential energy calculations. The energy calculations also indicate that the α form, with its A^+TA^- tetramethylene conformation, is favored over the β phase (ttt conformation) predominantly due to intermolecular packing contributions.

1. Introduction

Poly(butylene terephthalate), PBT, is a member of the series of aliphatic terephthalate polyesters which includes such commercially successful materials as poly(ethylene terephthalate), PET. A great deal of interest in PBT has been generated recently because fibers of the polymer exhibit a reversible crystal–crystal phase transition when uniaxially drawn. This transition was first discovered by Boye and Overton in 1974.[1] The relaxed or α phase is exhibited when PBT is cooled from the melt. Upon stretching, this is converted to the strained, or β-phase, which upon removal of the stress reverts back to the α-phase. The major obvious distinctions between these two crystalline forms lies in the conformation of the tetramethylene segment and the crystallographic repeat dis-

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tance in the chain axis direction. This clear distinction between the phases is based on X-ray structure analysis which shows that the α phase tetramethylene segment is off-gauche–trans–off-gauche (A^+TA^-). The X-ray data are confirmed by infrared studied that report an appearance of methylene bands in the α form which do not occur in the β form nor in the amorphous polymer.[23,24]

The static and dynamic properties of this reversible phase transition have been studied by a variety of characterization techniques. These include infrared (IR) and Raman spectroscopy, nuclear magnetic resonance (NMR) spectroscopy, and wide-angle X-ray diffraction. A review of the work performed using the various techniques has been given by Perry.[2]

The study of the α to β phase transition in PBT has been complicated due to the lack of reliable detailed structural information on the β phase. Although several structures have been reported on this phase,[9-11] the quality and quantity of diffraction data have been somewhat deficient. Hence, the objective of this work was to refine the β phase structure by using recently obtained diffraction data of improved quality. In addition, the tilt of the crystallographic c axis away from the fiber axis has been considered. The structure reported by Hall and Pass[10] was chosen as a starting point for the refinement since it was regarded to be the most reliable.

2. Experimental Section

Commercially prepared fibers of PBT were obtained from Celanese Corp. Melt extruded and quenched monofilaments were drawn approximately 275% and annealed at 200 °C for 8 h without tension. The resulting α phase samples were converted to the β phase by cold drawing to 40% strain. The fibers were mounted under tension in a Statton camera evacuated to reduce air scatter. Nickel-filtered Cu Kα radiation (λ = 1.5418 Å) was used, and an accurate sample-to-film distance was calculated by using CaF_2 powder. Intensity data were obtained on Kodak DEF film at various distances by using multiple films and scaled accordingly. A computer-controlled Optronics P-1000 scanning photodensitometer was utilized in transmission mode to digitize the intensity values into a two-dimensional data array. The intensity arrays were analyzed on an AED 512 color graphics terminal.

3. Results and Discussion

3.1. Indexing. The coordinates of the center of the two-dimensional intensity map were determined by using the positions of several sets of off-meridional, off-equatorial reflections. In addition, the rotation of the pattern around an axis parallel to the X-ray beam direction was calculated. The intensity map was then corrected for background scatter by using a number of radial intensity profiles, which did not pass through any crystalline PBT reflections. These scans were averaged and radially subtracted from the original diffraction pattern. This procedure reduced the isotropic contributions due to air scatter, amorphous content, and CaF_2, if present. The d spacings of the Miller planes were determines by using this background-corrected pattern.

A schematic of the diffraction pattern is shown in Figure 1. It can be seen that the reflections do not lie exactly on layer lines; instead, they appear to be randomly displaced above and below them. This has been observed in the α phase of PBT and in other materials such as PET and poly(ethylene 2,6-naphthalenedicarboxylate).[3-5] The displacements have been attributed to a tilting of the crystallographic c axis away from the fiber axis. There are two immediate benefits to this occurrence. First, it can cause adjacent reflections, which would otherwise overlap, to be resolved and allow accurate intensity measurements to be obtained. Secondly, since the displacements can be calculated from a knowledge of the indexing and the tilting, indexing can be simplified, since improbable selections can be identified and eliminated.[6]

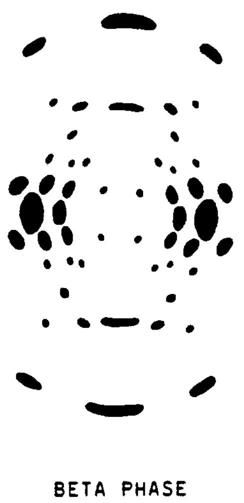


Figure 1. Schematic diagram of the fiber diffraction pattern of the β phase of PBT. Area of reflections is not indicative of relative intensities.

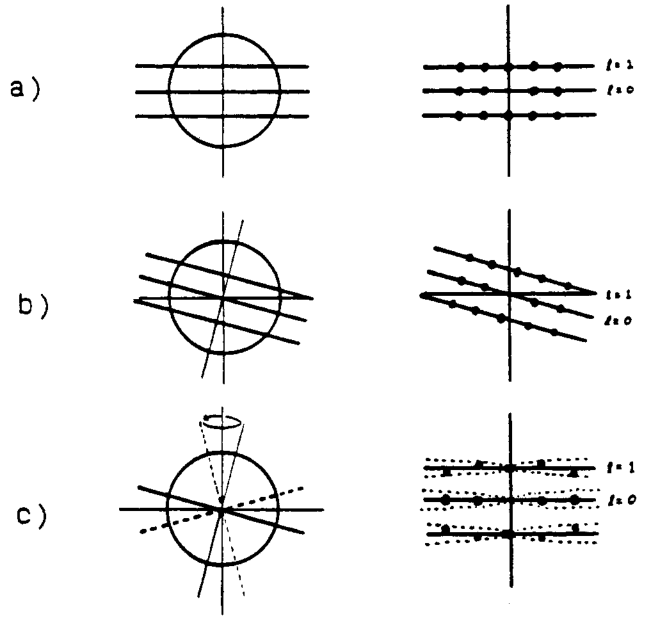


Figure 2. Relationships between the reciprocal lattice and the fiber axis (left) and the resulting diffraction patterns (right): (a) Fiber axis and c axis coincident and vertical, (b) fiber axis and c axis coincident but tilted from vertical, and (c) fiber axis vertical but c axis tilted.

The displacement of reflections above and below the equator (or layer lines) can be calculated from the conditions of diffraction. By analogy to single-crystal diffraction, the fiber axis can be considered to be an axis of rotation, since there is radial symmetry of the crystallites around this axis. For the case of an untilted crystal, the a^*b^* reciprocal lattice planes are perpendicular to the rotation (fiber) axis. As the crystal, along with its reciprocal lattice planes, is rotated, the conditions for diffraction are satisfied when a reciprocal lattice point intersects the sphere of reflection (radius = $1/\lambda$). One can then construct a ray originating from the center of the sphere and continuing through the point–sphere intersection and onto the X-ray film, where it appears as a reflection for that particular reciprocal lattice point. As can be seen in Figure 2a, the reflections from an untilted crystal lie on parallel layer lines if a cylindrical camera is used. These are hy-

Table I
Unit Cell Parameters for the Different Phases Reported for PBT

	Mencik α	Hall/Pass β	present work β
a, Å	4.83	4.69	4.73
b, Å	5.96	5.80	5.88
c, Å	11.62	13.00	13.06
α, deg	99.9	101.9	103.3
β, deg	115.2	120.5	119.8
γ, deg	111.3	105.0	104.4
V, Å^3	260.0	269.0	277.0
tilt, deg	3.0–3.5[a]	2.0	1.5
rotatn	23.5	20–30	32
R factor	17.0	22.3	16.4

[a] Orientation (rotation) of c-axis tilt is measured clockwise from the b^* axis. The tilt in Mencik's α structure was determined by Stambaugh.[3]

perbolic in form (except the 0 layer) when using flat plate film cameras. The effect of tilting the coincident rotation and the crystallographic c axes together is illustrated in Figure 2b. This is identical with the former case, except that the diffraction pattern is rotated by the same angle as that of the tilting. For the present situation, where the c axis is tilted away from the rotation (fiber) axis, the c axis could be considered to be precessing about the rotation axis (see Figure 2c). The reciprocal lattice points, which lie on planes perpendicular to the c axis, will intersect the sphere of reflection at positions which can be determined from the coordinates of the reciprocal lattice points and the angle and orientation of tilt. The positions of reflections from this type of system can then be calculated and will be located within an envelope surrounding each layer line.

In order to determine the displacement of the reflection from the equator on the film (ζ, in reciprocal space), the coordinates of reciprocal lattice points were converted to Cartesian coordinates and rotated to account for c-axis tilt and orientation. The final equation for ζ is given elsewhere.[3] An iterative procedure was used until self-consistency was achieved between the tilt angle and orientation and the Miller indexing selections. Beginning with the unit cell for the β phase of PBT, as reported by Hall and Pass,[10] a least-squares approach was then taken to calculate the unit-cell parameters. Although the changes in the unit-cell parameters were relatively small (Table I), a statistical analysis of observed and calculated d spacings showed that they were significant.

3.2. Intensities. As was mentioned previously, the X-ray data was initially corrected for isotropic background scattering. In addition, the observed intensities required correction for Lorentz and polarization effects as well as the path length of the diffracted beam through the double sided emulsion film. These corrections could be applied individually to each integrated reflection; however, a more accurate point-by-point correction was made by using a series of computer programs written by Fraser et al.[7,8] and modified to run on a VAX 11/780. In addition to correcting the intensity, the data was converted from film coordinates to reciprocal cylindrical coordinates (R–Z map).

The intensity data from individual reflections were further corrected for the remaining local background scattering by the following procedure. The reflection was first isolated by drawing a rectangular box or an arcing sector around it. The intensity values along the perimeter of this window were fitted to the equation of a plane by using the method of least squares. The intensity at each point within the window was then determined by calculating the background value from the equation of the plane and subtracting from the intensity at that point. The total intensity for a particular reflection was finally obtained by summing the background-corrected intensities at each point within the window.

3.3. Refinement. There have been three independent structures reported for the β phase of PBT.[9-11] Our approach was to select the most reliable one and refine that structure by using our intensity data. The structure reported by Yokouchi[9] was shown by Desborough[11] to be unsatisfactory for a variety of reasons. Most importantly, the unit cell provided calculated d spacings which did not correlate well to the observed ones. In addition, preliminary refinement models were produced by using a constrained intramolecular conformational energy approach and did not consider packing energy contributions. As a result, the refined structure was reported to have a methylene conformation of eclipsed–trans–eclipsed. There was strong evidence that this was incorrect. Infrared and Raman spectroscopies showed that the all trans methylene conformation is exhibited by the β phase of PBT.[12,13] The structure reported by Hall and Pass[10] was in agreement with the vibrational spectroscopy results. Bond lengths, bond angles, and torsion angles for the starting conformation were obtained from the structures of model compounds. Only those parameters that significantly reduced the structure factor residual were allowed to vary. A weighting scheme was used which allowed the weaker reflections to contribute more to the refinement. Stambaugh[14] suggested that increasing their contribution compounded the error in cases where a tilting of the c axis away from the macroscopic fiber axis is not considered, since the weaker reflections, which are usually assigned to more than one hkl plane, are the most imprecise. Desborough[11] reported a structure for the β phase similar to that of Hall and Pass, except for a 5° rotation of the molecule about the c axis. Intensity data was prepared by using the same weighting scheme as described above. However, evidence was presented which supported the treatment of the ($\bar{1}10$) and (100) reflections as an unresolvable overlapping pair and intensity was not apportioned between them. In consideration of the aforementioned differences, the structure reported by Hall and Pass was chosen as a starting point for the refinement. This was primarily due to the assumptions made, the statistical significance of refined parameters, and the correlation of structure to supplementary data.

Density measurements were carried out on the α phase by using a density column. These could not be performed on the β phase due to its existence only while under tension. A value of 1.398 g/cm^3 confirmed that there was one monomeric repeat unit per unit cell. It was assumed that the β phase also contained one molecular repeat per unit cell and this is shown in Figure 3.

Although more data have been obtained in the present work than by previous investigators, the quantity of data does not allow one to perform a complete structural analysis. However, several valid assumptions were made which reduced the number of parameters and, therefore, allowed a reliable structure analysis to be undertaken. The space group for the β phase has been determined to be $P\bar{1}$. This implies that centers of symmetry be placed as shown in Figure 3. The terephthaloyl section of the repeat unit contributes most to the scattering power of PBT, and it was assumed to be nearly planar. Tonelli has calculated that the barrier to rotation about the bond joining the carbonyl carbon and the aromatic carbon is relatively low.[15] Although this residue is planar in the relaxed α phase and in low molecular weight compounds, it has been reported

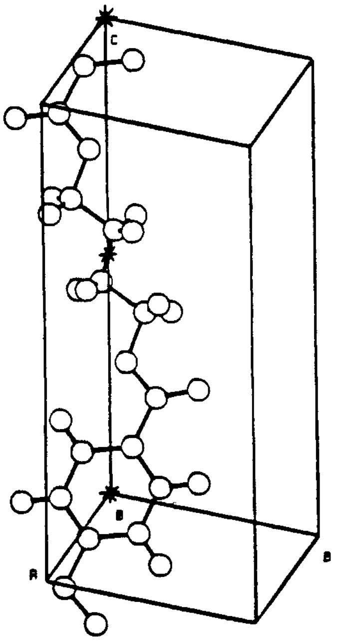


Figure 3. Ball and stick model of the refined β phase structure of PBT (the asterisk = center of symmetry).

that the carbonyl group is about 10° out of plane with the benzene ring in PET.[4] Since the intermolecular packing of this group may help to explain the stability of the α phase over the β phase, this parameter was allowed to vary during the refinement process.

The structure refinement process was carried out by varying structural parameters in such a way so as to minimize the sum of the squares of the difference between observed and calculated structure factors. The linked atom least squares (LALS) computer program, described elsewhere,[16,17] was used to perform the refinement. The linked atom concept is useful in instances where the amount of data is not sufficient to perform a full-matrix least-squares refinement. In many cases, this sparse diffraction data can be supplemented by applying various stereochemical constraints and restraints. The arrangement of atoms within a molecule can be defined by bond lengths, bond angles, and dihedral (torsional) angles. Since the great majority of organic molecules obey a fairly rigid set of rules with respect to the way its constituent atoms are linked together, a number of valid assumptions can be made with regard to bond lengths. As a result, the number of parameters to refine is greatly reduced and the ratio of data to parameters refined is large enough so that a structure refinement may be reliably undertaken.

For purposes of comparison to other investigators, unobserved reflections were omitted from the refinement process. Only observed reflections were used to calculate the structure factor residual, R:

$$R = \frac{\sum |F_c - F_o|}{\sum F_o}$$

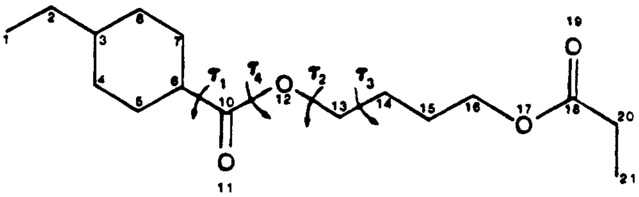
Thje values of the bond lengths, bond angles, and torsion angles from the refined structure of Hall and Pass were used for the initial model of the β phase. In consideration of the linked atom concept and the symmetry of the molecule, only four torsion angles (τ_1–τ_4) and three bond angles (θ_1–θ_3) may be expected to vary in the refinement (see Figure 4).

A number of combinations of these parameters can be calculated wherein one or more parameters are allowed to vary while the others are maintained at a fixed value. After eliminating those combinations which would not yield reasonable or consistent structures, each variation was allowed to refine by using the LALS approach, starting each one with the original structure reported by Hall and Pass. The rotation of the repeat unit about the c axis and the overall isotropic temperature factor were also allowed to vary as parameters in each of the refinement runs. By the use of Hamiltonian statistics,[18] which compares the final structure factor residual, R, with the number of refined parameters, the combination that exhibited the most significant change was identified and is reported below. The final structure had a residual more than 26% less than that reported by Hall and Pass.

The torsion angle τ_3 was found to refine from a initial value of 162.2° to −165.8°. This appears to be reasonable since the same angle in the α phase was determined to be −88.1° and it is unlikely that this angle would rotate through 180° into the positive regime upon the application of a simple stress. In addition, the bond angle, θ_1, simultaneously refined to 109.5° which is closer in agreement with the value associated with a tetrahedral carbon. A comparison of the stereochemical data of the phases is shown in Figure 4.

The interatomic distances of all paris of nonbonded atoms were compared with their sums of van der Waals radii. In order to make direct comparisons with the results of Hall and Pass, their values for van der Waals radii were used. Specifically, the radius of carbon was taken to be 1.7 Å, hydrogen was 1.0 Å, and oxygen was 1.4 Å. A listing of separations that are less than their sum of radii is shown in Table II. Comparisons of interactions in the β phase reported by Hall and Pass are also listed.

As was mentioned earlier, most of the scattering power of PBT originates from the terephthaloyl unit. As a result,



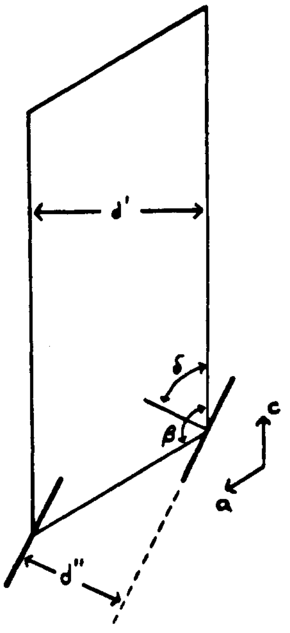
	Mencik α	Hall/Pass β	Present β
τ_1 (C5-C6-C10-O12)	174.8	172.9	172.9
τ_2 (C10-O12-C13-C14)	-90.6	-159.1	-159.1
τ_3 (O12-C13-C14-C15)	-88.4	162.2	-165.8
τ_4 (C6-C10-O12-C13)	177.5	-178.6	-178.6
θ_1 (C13-C14-C15)	105.	113.0	109.5
θ_2 (O12-C13-C14)	104.	105.0	105.0
θ_3 (C10-O12-C13)	119.	119.0	119.0

Figure 4. Stereochemical data for the different phases reported for PBT.

Table II
Intra- and Intermolecular Contact Calculations

	atom pair[a]	(sum of radii) − separation (Å) present work β	 Hall/Pass β
intra	O12–C7	0.35	0.38
	H7–O12	0.02	0.02
	O11–C13	0.41	0.42
	C10–H13	0.07	0.16
	C5–O11	0.25	0.25
	C16–H14	0.13	0.12
inter	H5–C7 (010)	0.14	0.18
	H5–C8 (010)	0.19	0.30
	H5–H8 (010)	0.09	0.20
	H14–H15 (100)	0.23	

[a] Numbers in parentheses refer to unit cell translations between molecules.



	Mencik α	Present β
d' (Å)	4.37	4.10
d" (Å)	3.64	3.86
tilt (δ)	73.7	87.2

Figure 5. Geometric relationships of aromatic rings within the unit cell.

this part of the repeat unit is probably the most accurately determined. As the α phase of PBT is strained to form the β phase, the benzene ring is aligned with the stress field. This is quantified by calculating the angle between the normal vector to the ring and the c axis which is 74.6° in the α phase and 87.2° in the β (see Figure 5). At this point, it should be noted that comparisons made here and below to Mencik's α structure have been made by using the correction for the short O–CH_2 bond as described by Stambaugh.[3] The perpendicular separation of adjacent benzene rings is then increased from 3.64 to 3.86 Å. This separation would be even larger if the unit-cell dimensions did not change during the transition; however, the changes cause the distance between adjacent chain axes to decrease from 4.37 to 4.10 Å. The transition from α to β also involves a rotation of the benzene ring normal vector around the c axis toward the b–c plane by an angle of 16.6°.

In an analogy to the structure reported by Hall and Pass, it can be shown that upon stressing PBT, changes in the unit cell parameters occur which maximize the packing efficiency of the new chain conformation.

3.4. Energy Calculations. The major difference between the structural repeat unit of the α and β phases of PBT is the conformation of the soft segment (tetramethylene residue). The phrase, soft segment, refers to the low barrier of rotation about bonds in this segment with respect to that in the more rigid aromatic ester fragment (hard segment). Since this conformation is nearly gauche–trans–gauche (A^+TA^-) in the α phase and nearly trans–trans–trans in the β phase, it would be expected that the β phase possesses a lower energy than the α as is shown to be true from the torsional energy calculations performed on the entire repeat unit using Allinger's[19] molecular mechanics program, MMP2 (Mencik α, 5.44 kcal/mol; Hall/Pass β, 2.60 kcal/mol; present work, β, 2.98 kcal/mol). This calculation, as well as the following ones, were carried out by using atomic coordinates from the X-ray refinement without further refining the geometry of the molecule by using energy minimization techniques. Other conformational energy calculations performed by using MMP2 were approximately the same between the two phases. On the basis of this conformational energy difference and the similarity between the β phase and other all trans polymers which are stable, the β phase might be expected to be stable. Since it is not, it has been suggested[9,10] that each phase represents a potential energy minimum. The energy of the α form is lower than that of the β form and the barrier between them is low enough that thermal activation can convert most of the PBT to the α phase at normal temperatures. The application of a stress has also been suggested to result in a reversal of the relative energies of these phases.

Table III
Results of the van der Waals Energy Calculations and the Analytical Form of the Buckingham Potential[a]

	Mencik α	Hall/ Pass β	present work β
intramolecular	19.94	17.62	15.18
intermolecular	−32.39	−12.24	−10.98
hard-segment contribution	52.9%	35.8%	49.9%
total	−12.45	5.38	4.20

[a] $V = K_v(2.9 \times 10^5 e^{-12.5r/r_v}) - 2.25(r_v/r)^6)$ for $r_v/r < 3.311$. $V = 336.176(K_v(r_v/r)^2)$ for $r_v/r < 3.311$. $K_v = (E_iE_j)^{1/2}$. E_i = hardness parameter for atom i. r_v = sum of the van der Waal radii. r = interatomic distance.

Since the conformational energies of the phases do not appear to explain what is seen experimentally, packing energies were considered to be the major contributing factor. This statement is in agreement with the change in calculated density from 1.40 to 1.32 g/cm^3 for the α and β phases, respectively. The higher density of the unstressed α form indicates a more efficiently packed structure. This is also confirmed by the increase in the perpendicular separation of adjacent benzene rings upon stressing the PBT, which was discussed earlier.

The packing energy was determined by using a van der Waals function which depends only on interatomic distances. Steric interactions between atoms bonded to each other or to a common atom are excluded from the calculation. The analytical form of the potential is known as the Buckingham potential or the "exponential minus six" expression and is shown in Table III. The use of the second expression at small interatomic distances ($r_v/r > 3.311$) is necessary since the "exponential minus six" expression deviates from the Morse curve and becomes binding at very small r.[20] Interactions involving hydrogens were calculated after shifting the centers of the hydrogen atoms 8.5% along the C–H bond toward carbon in order to approximate the center of electron density.[20-22] Values for the empirical hardness parameters and the van der Waals radii were taken from the MMP2 program.

The results of the van der Waals energy calculations show that on the basis of the intramolecular interactions, the energies of the three structures considered are roughly similar, with β phases exhibiting an average of a few kilocalories/(mole of repeat unit) less repulsive interactions than the α. The results of the van der Waals energy calculation, which account for only the intermolecular interactions of one repeat unit with its eight nearest neighbors, are also listed along with the total van der Waals energy which puts these calculations into perspective. It is apparent that the conformation of the α phase of PBT allows for a much more efficient packing of the chain with its neighbors than the β phase allows. In fact, the decrease in internal packing energy of the α phase is so favorable that it exceeds the intramolecular contributions of the steric and torsional factors.

In an attempt to understand which part of the molecular repeat is governing the chain packing process, the contribution of the hard segment to the intermolecular van der Waals energy was isolated. The hard segment was defined as that part of the repeat unit which includes the aromatic ring and the carbonyl group (C=O). It was found that the hard segment in the present β phase contributes 11.65 kcal/mol less to the intermolecular van der Waals energy than that in the α phase. The contribution from the analogous segment in Hall and Pass's β structure is 12.75 kcal/mol less than the α. Considering only the aromatic ring, the percent contribution that this functional group makes to the total intermolecular energy was calculated to be 45.3 and 37.7% for the α phase and the presently reported β phase, respectively. The value for Hall and Pass's structure was found to be 25.8% and is compensated by a large tetramethylene contribution. This may be a result of the previously discussed differences in the conformation of the soft segment. These isolated functional group energy calculations suggest that it is the intermolecular packing of the aromatic rings which favor the α structure over that of the β phase (see Figure 5).

It is informative to make several comparisons between the two reported β phases at his point. It is interesting to note that the intramolecular van der Waals energy of the β phase reported here is about 2.4 kcal/mol less than that reported by Hall and Pass. However, the intermolecular van der Waals energy is approximately 1.25 kcal/mol higher. It would appear that the structure reported here differs from that of Hall and Pass in that the energy detriment obtained from intermolecular packing (predominantly from a reduction in the soft segment contribution) is overcompensated by the benefit gained by intramolecular packing. The resulting total van der Waals energy for the present structure is 1.18 kcal/mol lower than the structure of Hall and Pass. This packing energy appears to favor the present structure even when torsional contributions are considered.

From these static calculations, it is clear that the structure reported here for the β phase is favored over that of Hall and Pass with respect to the packing energies. More importantly, it is in better agreement with the observed X-ray data as evidenced by the decrease in the structure factor residual. This confidence in the β phase structure allows the authors to conclude that it is the intermolecular packing of the PBT chains which allows the A^+TA^- methylene conformation of the α phase to be favored over that of the ttt conformation of the β phase.

As a final consideration, these energy calculations may assist in explaining the experimental fact that the α phase is more stable than the β. However, it should be noted that energy calculations for stability comparisons should be based on free energy which considers the entropic contribution.

Registry No. PBT (copolymer), 26062-94-2; PBT (SRU), 24968-12-5.

References and Notes

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