Macromolecules **1990,** *23,* 1531–1539

Structure and Packing in Crystalline Aliphatic Polyesters

Wen-Bin Liau and Richard H. Boyd*

Department of Materials Science and Engineering and Department of Chemical Engineering, University of Utah, Salt Lake City, Utah 84112.

Received April 13, 1989; Revised Manuscript Received July 10, 1989

ABSTRACT: Crystalline aliphatic polyesters show an interesting structural effect. Some adopt, like polyethylene and their polyamide counterparts, planar zigzag conformations. However many have conformations that contain kinks made up of pairs of gauche bonds of opposite sense separated by one or more trans bonds. The unit cells are of a variety of types including both orthorhombic and monoclinic structures. Thus this family provides excellent test cases for methods for predicting crystal structures and packing via conformational energy calculations. We have examined six of the aliphatic polyesters by using a molecular mechanics method that simultaneously minimizes the intramolecular energy and the intermolecular packing energy and takes advantage of a newly parameterized force field for the ester group. The polar interaction energies are represented by a mutual induction polarization model that explicitly calculates the internal field at each bond rather than invoking a macroscopic dielectric constant for mediating the electrostatic interactions. Good calculated values of unit cell parameters were obtained. The kink conformation containing examples are found to be stable compared to trans counterparts because the intramolecular energy penalty for kink formation is modest and because the kink conformations pack well for some kink locations.

The aliphatic polyesters have an interesting history. They were the first polymers made by Carothers in his classic effort to make synthetic macromolecules of unequivocal structure by means of well-understood chemistry.[1] As a result, they were also among the first such molecules to have their structures studied by means of X-ray diffraction.[2] These X-ray studies revealed an interesting effect. The "*c*" axis cell dimensions of some members had values expected on the basis of the chain conformation being a planar zigzag. However many, if not most, of those studied had "*c*" axis dimensions significantly shortened from the planar zigzag values. Clearly, the chain conformations depart from the all trans planar zigzag. Later, specific torsional angle sequences were proposed as chain conformations that account for the shortening.[3,4] These involved the occurrence of a pair of gauche bonds of opposite sense separated by one or more trans bonds. We will call these entities "kinks". It is not at all clear from either an intermolecular packing or an intramolecular conformational point of view why structures containing kinks should be a favored over the all trans. In both polyethylene and the "nylon" aliphatic polyamide analogues all trans conformations are observed.

Conformational energy or "molecular mechanics" calculations provide one means for explaining the conformational and packing effects observed in polymers.[5–7] The aliphatic polyesters would seem to be an excellent testing ground for such approaches because of the abovementioned effects and also because a variety of unit cell types, including orthorhombic and monoclinic, are observed experimentally. In the present work, we have selected six members of the family for study using a recently developed methodology where the intramolecular conformational energy and the intermolecular packing energy are simultaneously minimized.[6]

Computational Methods

The method described by Sorensen et al.[6] was used. In that method, the simultaneously varied parameters in the energy minimization are the following. Intramolecularly, there are the "unrotated" Cartesian coordinates of the chain repeat unit atoms and the helix advance angle and distance, σ and "d". Intermolecularly, there are the unit cell dimensions "a" and "b" and angles α, β, and γ, a setting angle, θ_x, and a second chain offset, Z_o.

Some comments on these degrees of freedom are appropriate. In the methodology a helix is set up at the origin. A basic conformational repeat unit (CRU) is assumed that is repeated by the helix operations of rotation through the angle, σ, and the advance distance, d. In all the cases studied here, the CRU was taken to be identical with the chemical repeat unit of the polyester. The rotational orientation of the helix in the x–y plane (z is along the helix axis or c) is arbitrarily based on the first atom the CRU lying along the x axis. Then the actual helix orientation is generated by the setting angle rotation, θ_x, about z. The latter is a minimization variable. No constraints on the intramolecular geometry (all atom positions are free to adjust) are imposed, and σ and d are minimization variables. However when there is more than one chain per cell all further chain chains are assumed to be related to the first via symmetry operations experimentally (as the result of screw axes or glide planes) or constraints computationally. In the case of two chains per cell, in some cases, like polyethylene, these constraints conveniently take the form of placing the second chain at a fixed fractional cell position and with a setting angle related to that of the base chain. In other cases like some of those studied here, where the intramolecular symmetry is lower, it is necessary to explicitly introduce the glide plane or screw axes operations. This was done by performing reflections on the base helix and then moving the new helix to a fixed fractional cell position at a setting angle related to the base chain and at an arbitrary absolute z axis position, Z_o. The latter position is a variable in the minimization. A proper 2_1 screw operation would, in addition to two reflections to produce the rotation, correspond to $Z_o = c/2$ on minimization.

In the examples studied here, the experimental structures are reported to have the fiber repeat distances identical with the chemical repeat unit of the polyester. Thus the advance angles of the helices are experimentally reported as $\sigma = 360°$ and d = "c" cell dimension. As stated, we have allowed both σ and d to minimize and the above experimentally reported conditions do not necessarily have to result.

The electrostatic energy is calculated by using a mutual induction polarization model where a polarizability center is located in each bond and bond-centered permanent moments are located in polar bonds.[6,8,9] The permanent moments induce moments that can in turn induce further moments. The internal field is found by solving the set of linear equations that result for the induced moments. The electrostatic energy is then the energy of the permanent moments in the electric field local to each moment. In applying the mutual induction model to crystals, it is necessary to evaluate certain lattice sums in calculating Lorentz tensors.[10] Some elaboration was necessary to accomplish this for the case of nonorthogonal lattice vectors (monoclinic and triclinic cells), and this is described in the Ph.D. dissertation of W.B.L.[11]

Unfortunately, the mutual induction methodology does not lend itself to participating in the minimization process and the accompanying adjustment of atom positions. It is invoked after minimization, and the geometry has been determined, in calculating the electrostatic energy. During minimization, electrostatic effects are mimicked by means of fixed point charges. The electrostatic forces have relatively "soft" spatial dependence, and the steric or nonbonded forces are much more influential in determining the local geometry of packing or conformation. It is believed that the geometry determined this way does not differ greatly from that corresponding to minimum energy using the polarization model.[8] Most importantly, there is every reason to believe that the polarization model electrostatic energies are much more reliable than those from the fixed charge scheme. In implementing fixed charges in minimization, charges of $\pm 0.27e$ were placed on the C and O atoms of the $C{=}O$ bond and $\pm 0.063e$ on each of the two $C{-}O$ bonds in the ester group with the oxygen negative and an effective dielectric constant of 3 was invoked.

The force field parameters used are those presented in the companion paper.[12] The intramolecular energy and also the number of independent variables adjusted in minimization arising from the atom coordinates was based on one chemical repeat unit. However, when the intermolecular energy sums are performed, one chemical repeat unit in *each* of the chains per cell was taken as the basis for the energy. The sums for each chain extended over two packing shells around the chain, a total of 18 chains. The sums extended for three repeat units along each chain summed over.

Structural Results

Examples Studied. Six polyesters were studied. Adapting the nomenclature widely used for polyamides, the first digit refers to the number of carbons in the diol and the second to the number in the diacid; they are 2–4, 2–6, 2–8, 4–6, 6–6, and 6–10. They were selected as representing two degrees of chain shortening, resulting from two types of kinks, two examples where the kink placement is not known, and two non-shortened planar zigzags. Three of them (2–4, 2–6, 2–8) have had refined X-ray structures resulting in atom coordinates determined and three of them have only unit cell information. One of the latter, 4–6, has two polymorphs for which cell information is available and indicates one has a kinked chain conformation and the other a planar zigzag one. The selected polyesters are shown in Figure 1 along with the known or proposed locations of the kinks. In the cases where chain shortening through kink conformations occur, companion calculations for all trans planar zigzags were also carried out. The structural results are discussed first here, and then the question of stability of kink containing structures versus planar zigzag is taken up.

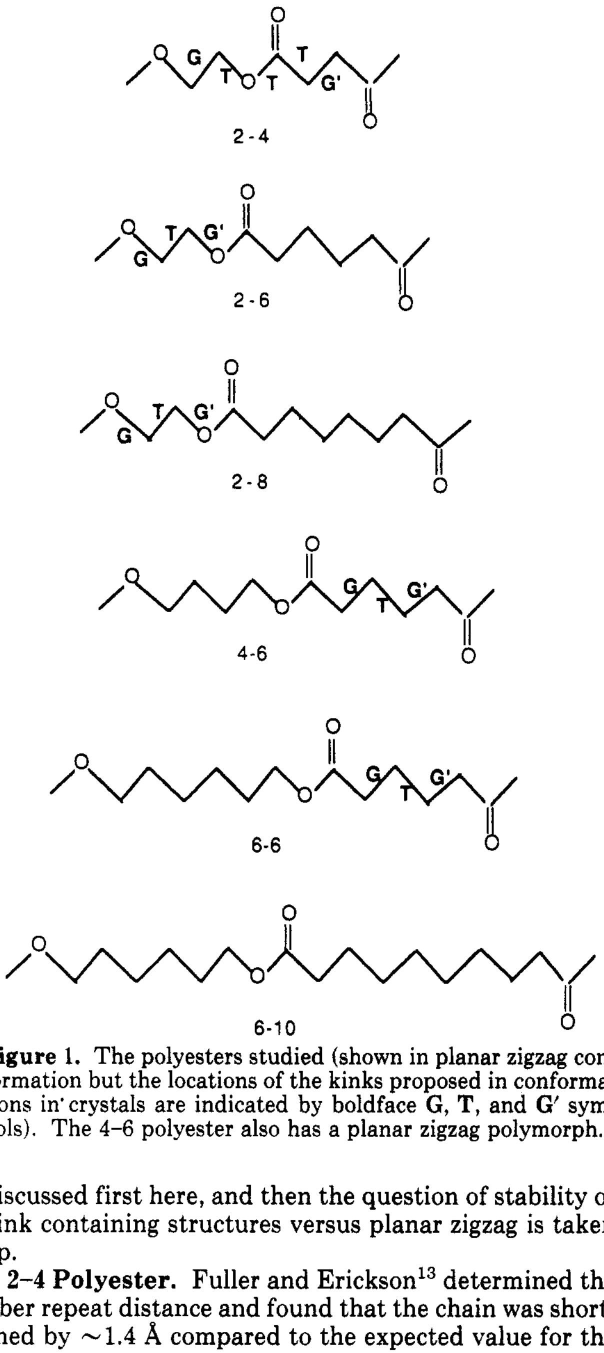

Figure 1. The polyesters studied (shown in planar zigzag conformation but the locations of the kinks proposed in conformations in crystals are indicated by boldface **G**, **T**, and **G′** symbols). The 4–6 polyester also has a planar zigzag polymorph.

2–4 Polyester. Fuller and Erickson[13] determined the fiber repeat distance and found that the chain was shortened by ~1.4 Å compared to the expected value for the planar zigzag conformation. They proposed a monoclinic unit cell. However, Ueda et al.[4] determined the cell as belonging to an orthorhombic space group with four chains per cell and reported a refined structure with the chain conformation containing the kink as located in Figure 1. In this structure, chain 2 is related to chain 1 by a glide by $a/2$ in a plane perpendicular to b at $b/4$. The third chain is related by a screw axis in the c direction at $a/4$, $b/2$ to the first one. The fourth chain is related to chain 3 by an $a/2$ glide along a plane at $-b/4$. Calculations based on this structure as a starting point and incorporating the constraints relating the chains by the above operations were carried out. Intramolecular symmetry relations resulting from 2-fold rotation axes in the space group were not imposed. The unit cell parameters are reported in Table I and projections of the structure in Figure 2a,b. The experimental unit cell parameters of Ueda et al. are also recorded in Table I. The torsional angles at the two gauche bonds marked in Figure 1 were reported by Ueda et al. to be 77° (diol section) and −65° (diacid section), and we find calculated

Table I
Calculated and Experimental Lattice Parameters[a]

polyester[b]		a	b	d	α	β	γ	σ[c]	θ_x[d]	Z_o	ref
2–4	exp	10.75	7.60	8.33	90	90	90				4
	kink	10.24	7.62	8.52	90.0	90.1	90.0	355.6	0.0	4.30	
	planar-1	4.99	6.87	9.65	90.0	87.6	90.0	360.0	0.0	0.0	
	planar-2	5.57	7.11	9.63	82.9	115.4	93.8	357.1	152.8	0.0	
2–6	exp	5.47	7.23	11.72	90	113.5	90				3
	kink	5.46	6.96	11.62	90.0	113.2	90.0	360*	124.7	0.0	
	planar-1	4.77	7.32	12.19	90.0	92.8	90.0	360.0	0.0	0.0	
	planar-2	5.50	7.21	12.18	102.2	106.2	90.7	354.4	160.8	0.0	
2–8	exp	5.51	7.25	14.28	90	114.5	90				3
	kink	5.49	6.98	14.16	90.0	114.1	90.0	360*	134.0	0.0	
	planar-1	4.73	7.45	14.74	90.0	93.1	90.0	360.0	0.0	0.0	
	planar-2	5.50	7.31	14.72	99.5	114.1	84.9	363.2	146.5	0.0	
4–6	α-exp	6.70	8.00	14.20	90	45.5	90				14
	kink	6.49	8.28	13.96	90.0	45.8	90.0	359.8	0.0	0.0	
	β-exp	5.05	7.36	14.65	90	90	90				14
	planar-1	4.74	7.44	14.73	90.0	86.9	90.0	360.0	180.	0.0	
	planar-2	5.33	7.17	14.72	90.0	108.6	90.0	360.0	141.9	0.0	
6–6	exp	10.08	7.32	16.83	90	90	90				16
	kink	10.57	7.29	16.61	90.0	91.6	90.0	360*	25.2	2.98	
	planar-1	4.72	7.51	17.28	90.0	86.8	90.0	360.0	180.	0.0	
	planar-2	5.37	7.18	17.27	90.0	111.7	90.0	360.0	140.2	0.0	
6–10	exp	5.52	7.40	22.15	90	115.0	90				17
	planar	5.35	6.98	22.34	90.0	106.3	90.0	360.3	138.8	0.0	
	kink	6.31	6.26	21.66	90.0	79.2	90.0	360.0	0.0	10.83	
PE[e]	exp RT	7.42	4.95	2.547	90	90	90		~45		18,19
	exp 0 K	7.15	4.91	2.546	90	90	90				
	calc	7.05	4.94	2.544	90.0	90.0	90.0	360.0	46.9	0.0	7

[a] Units for a, b, and d cell parameters are Å, d = helical advance distance = unit cell c for $\sigma = 360°$; α, β, and γ in deg; σ = helical advance angle, θ_x = setting angle measured about z from projection on x axis in deg; Z_o = c axis offset of second chain, in Å. [b] exp = experimental values; kink = calculated values for chain conformation containing kink located as in Figure 1; planar = calculated values for planar zigzag chain conformation. [c] Asterisks indicate constrained values. [d] The setting angles for the kink structures are arbitrary and are not necessarily based on an average molecular plane. [e] PE = polyethylene, RT = room temperature, 0 K = low temperature.

values of 69.7° and −70.9°. Complete tables of calculated internal or valence coordinates for all of the polyesters calculated are given by Liau.[11]

Companion calculations of structures with all trans conformations were also carried out. A polyethylene-like orthorhombic structure was the starting point with two chains per cell and a ± setting angle for the plane of the zigzag relative to the x axis relating the two chains. It was found that two structures were obtained depending on the starting setting angle. One structure, called "planar-1", minimizes to a zero setting angle and has a nearly orthorhombic cell with the cell parameters shown in Table I and projections of the structure in Figure 3a,b. The chain conformation was almost exactly planar. The other structure, "planar-2", has a nonzero setting angle, but the cell is triclinic. The finding of two stable packing structures for planar zigzag conformations, one with parallel molecule planes and the other with rotated chains, much as in polyethylene, was found in general for the polyesters. The relative stability of these two packing arrangements will be discussed below.

2–6 and 2–8 Polyesters. Turner-Jones and Bunn[3] reported the unit cells in both polymers as monoclinic with two chains per cell and determined refined atomic structures which placed the kink at the C–O bond in the glycol unit as indicated in Figure 1. The space group relates the two chains by a glide of $a/2$ in the plane perpendicular to b at $b/4$. Calculations were carried out on this structure. The second chain was generated by the above operation and a setting angle invoked, but no intramolecular symmetry was imposed. On unconstrained minimization, it was found that the helical advance angle, σ, went to a value of ~310° rather than 360°. A calculation with the advance angle constrained to 360° converged to a lower energy, better packed structure. Attempts to converge to this structure without the constraint were not successful, apparently due to the energy surface being rather flat in this coordinate direction. Thus the constrained minimization structure was adopted as the calculated one. The calculated unit cell parameters are shown in Table I along with the experimental ones. Turner-Jones and Bunn[3] reported ±114° as the values of the torsion angles of the two gauche bonds (Figure 1) in both 2–6 and 2–8 polyesters whereas we find calculated values of ±83° in both. The setting angles in Table I for kink structures can be rather arbitrary since they are based on the first bond of the CRU rather on an average molecular plane. Structures may be reproduced, however, from the listed setting angles and the unrotated Cartesian coordinates of the CRU's listed by Liau.[11] Projections of the calculated structure of 2–6 polyester are shown in Figure 4a,b; the structure of the 2–8 is rather similar.

In the companion calculations of the all trans conformations, again as for 2–4, two stable crystal structures were found for both the 2–6 and 2–8 polyesters. One corresponds to a nearly orthorhombic unit cell with a setting angle of zero and the other to a triclinic cell with a nonzero setting angle. The cell parameters are listed in Table I. The 2–8 structure is similar but has somewhat different cell parameters and setting angle (Table I). The a, b projections of the packing of the nearly orthorhombic planar-1 forms is like that of Figure 3a; the triclinic planar-2 form for 2–8 polyester is shown in Figure 5. The orthorhombic zero setting angle forms have a nearly perfect planar zigzag conformation, but in the triclinic nonzero setting angle structures noticeable distortions of the chain from planarity are observed (Figure 5).

4–6 Polyester. Minke and Blackwell[14,15] reported the occurrence of two isomorphs. Annealed stretched films give the more stable α form which is monoclinic, $P2_1$,

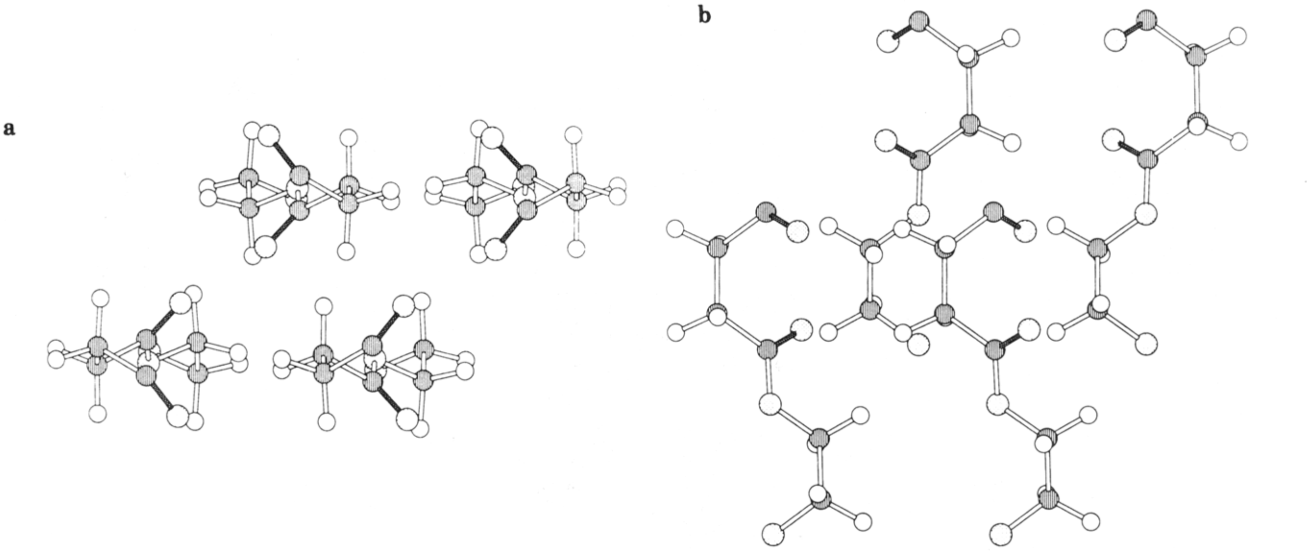

Figure 2. a. Calculated 2–4 polyester structure (a, b plane projection). There are four chains per cell: the second chain is at ($a/2$, 0) relative to the first chain at (0, 0), the third at ($a/4$, $b/2$), and the fourth at ($-a/4$, $b/2$). b. Calculated 2–4 polyester structure (a, c plane projection).

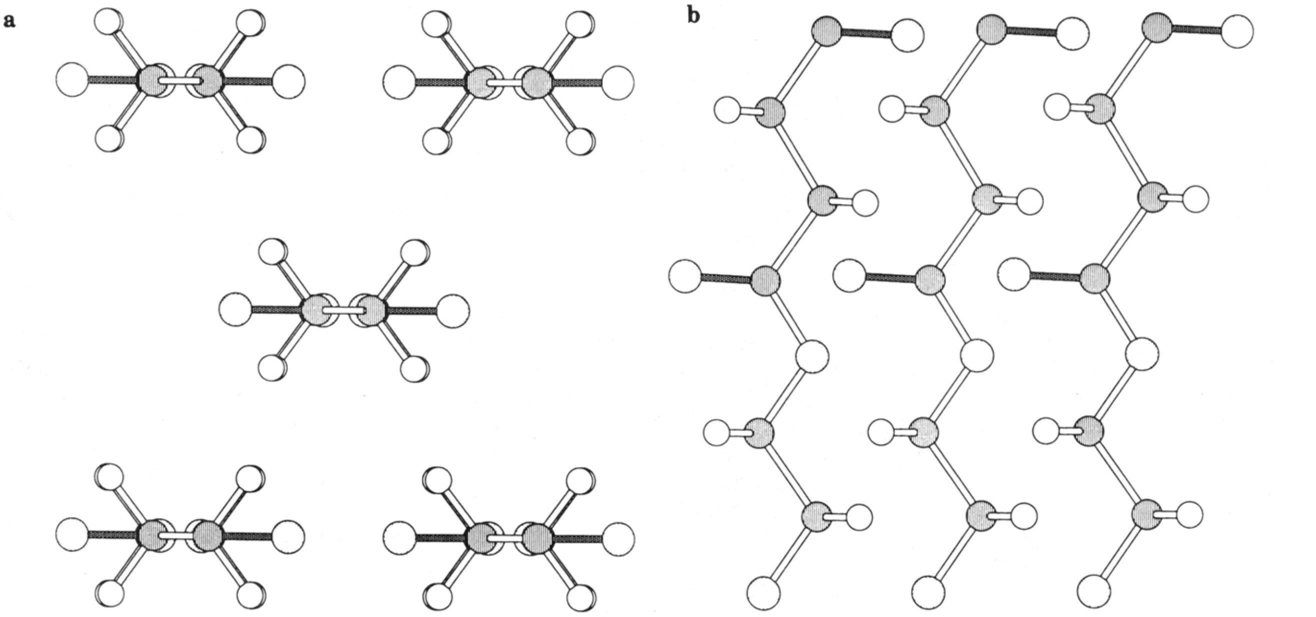

Figure 3. a. Calculated hypothetical 2–4 polyester planar-1 conformation structure (a, b projection). There are two chains per cell: the second is at ($a/2$, $b/2$), one shown, relative to the first at (0, 0), four shown. b. Calculated hypothetical 2–4 polyester planar-1 conformation structure (a, c projection).

with two chains per cell and chain shortening, indicating a kink-containing conformation. The β form was found in oriented films prepared from quenched melts. It is orthorhombic with two chains per cell and no chain shortening indicating an all trans structure.

Although no atom position refinement was attempted, Minke and Blackwell suggested that the kink in the α form might be in the diacid moiety and our calculations confirm this. In the calculation the two chains were related as in 2–6 and 2–8 polyesters above by a glide of $a/2$ in the plane perpendicular to b at $b/4$. The kink was placed in Figure 1. Starting from the reported cell parameters, the structure did minimize to a monoclinic one. The resulting optimized cell parameters are listed in Table I along with the experimental ones. It is seen that the calculated and experimental unit cell parameters, including the β angle = 45°, are in good agreement with the kink placed in the diacid section, indicating the correctness of this conjecture. Projections of the calculated structure are shown in Figure 6a,b. In addition, calculations were carried out on packing of a conformation where the kink was placed in the center of the diol section. It was found that the packing efficiency was definitely not as great as for the other position for the kink and the resultant cell parameters were not as good.

The two planar conformation structures found are shown in Table I and compared to the experimental results of Minke and Blackwell for the β form. The agreement for the nearly orthorhombic form is reasonable. However as will be seen below the more monoclinic one appears to be more stable by calculation.

6–6 Polyester. Aylwin and Boyd[16] reported the unit cell as orthorhombic with four chains per cell with chain shortening indicating a kink but did no further structural refinement. On the basis of the similarity of the cell with the 2–4 polyester, the chains were placed in the calculation with the same operations as in that structure. The kink however was assumed to be in the diacid

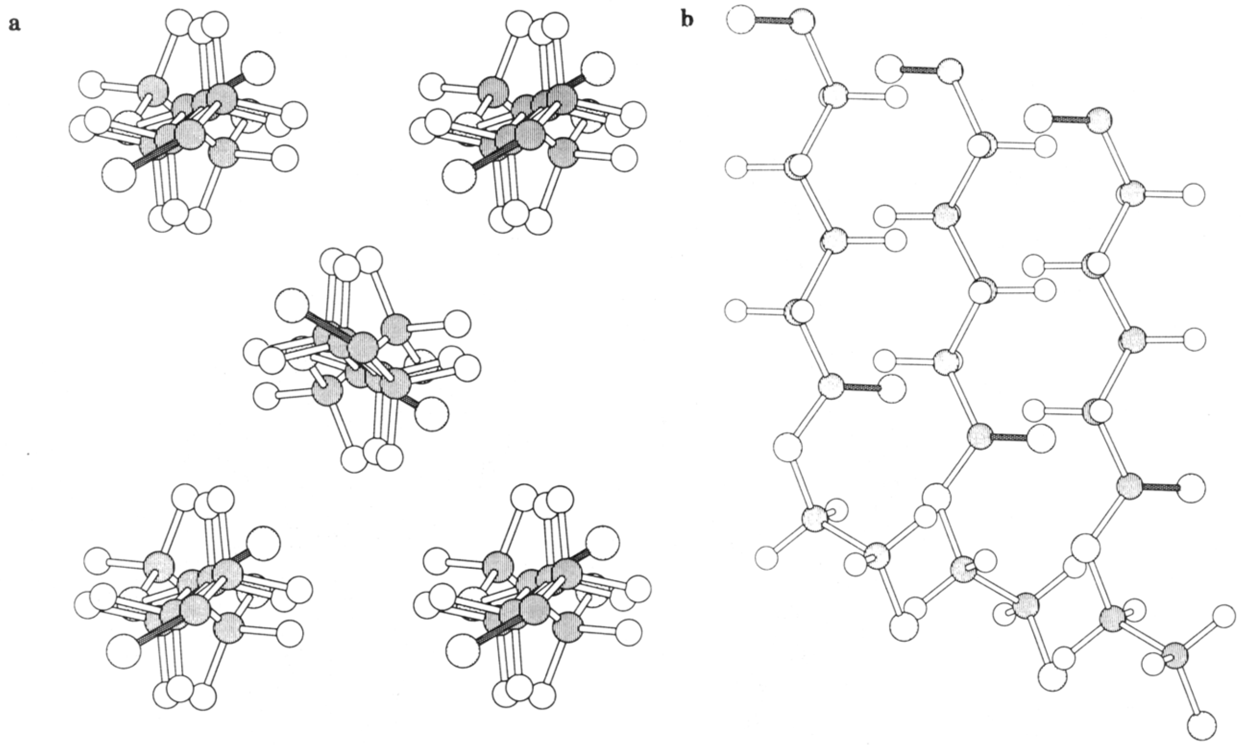

Figure 4. a. Calculated 2–6 polyester structure (*a*, *b* plane projection). Two chains per cell: (0, 0), four shown, and (*a*/2, *b*/2), one shown. b. Calculated 2–6 polyester structure (*a*, *c* plane projection).

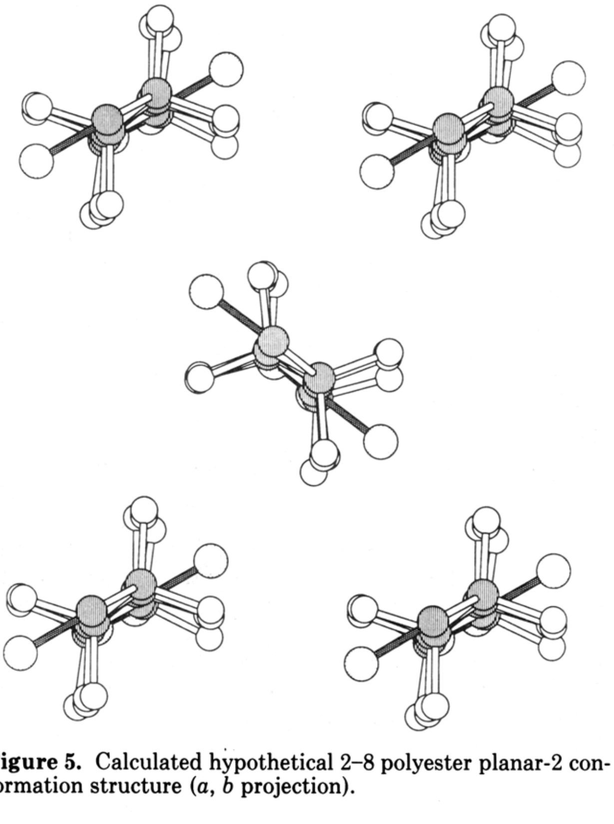

Figure 5. Calculated hypothetical 2–8 polyester planar-2 conformation structure (*a*, *b* projection).

segment. The structure minimized to nearly orthorhombic at several setting angles. The lowest energy one was found with the helix advance angle constrained to 360°. The *c* axis offeset does not correspond to a screw axis at the position in the 2–4 structure. The calculated and experimental cell parameters are reported in Table I. Projections are shown in Figure 7a,b. The companion all trans conformation calculation results are also listed in Table I.

6–10 Polyester. Kanamoto and Tanaka[17] reported the unit cell as monoclinic with two chains per cell and very little chain shortening, indicating an all trans planar conformation. In the calculation a polyethylene-like structure with a nonzero setting angle minimized to monoclinic. The conformation was closely exactly trans. This latter observation is somewhat different from the similar "planar-2" structures for other polyesters (Figure 5). There, noticeable distortions from exact planarity could be noticed. The calculated and experimental cell parameters are in Table I. Projections of the structure are shown in Figure 8a,b.

For purposes of stability comparison, companion calculations were carried out for a conformations containing kinks. One was arbitrarily placed symmetrically in the center of the diacid segment. A number of packing arrangements were attempted. The most stable one resulted from a two chains per cell placement similar to the 2–6, 2–8, and 4–6 structures above. The structural results are listed in Table I. Calculations with the kink placed symmetrically in the diol section were also carried out. Stable structures could also be found here but were not more stable energetically and no results are listed.

Polyethylene. In the limit of long aliphatic segments, the structures of the polyesters approach polyethylene. For this reason, the structural results for this polymer have been included in Table I. Another important reason is that unit cell dimensions are temperature-dependent, and most data, including all of that for the polyesters, are at room temperature, but the calculations are appropriate for 0 K. For polyethylene both room-temperature and low-temperature unit cell dimensions have been determined[18,19] and the comparison gives some idea of the temperature effects.

Energetics and Relative Stabilities

The energies of the various structures summarized in Table I are presented in Table II. For each structure

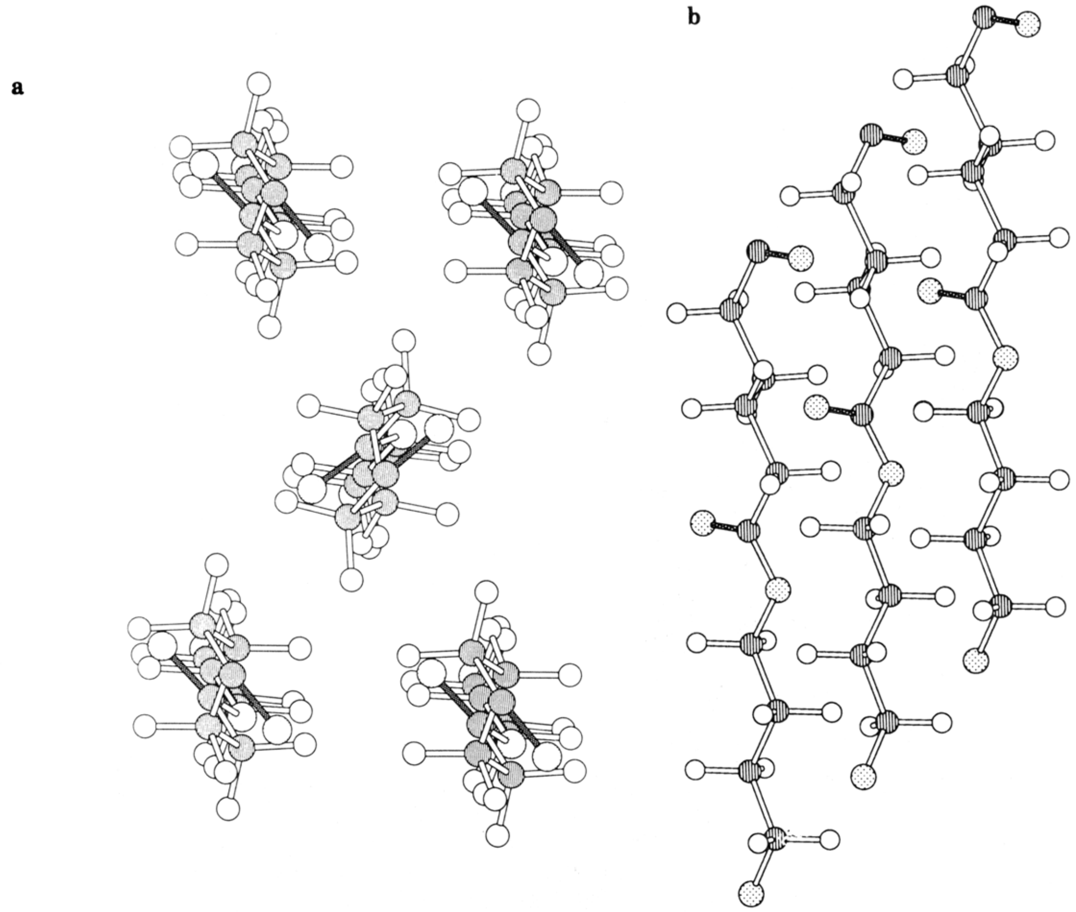

Figure 6. a. Calculated α 4–6 polyester structure (a, b plane projection). Two chains per cell: (0, 0), four shown, and (a/2, b/2), one shown. b. Calculated α 4–6 polyester structure (a, c plane projection).

they are broken down into the intramolecular energy (contributions from distortion of bond lengths, valence angles, torsional angles, and intramolecular nonbonded interactions), the intermolecular nonbonded energy, and the electrostatic energy.

In addition to the resolution of the packing energetics into intra- and intermolecular plus electrostatic contributions in Table II, it is also of interest to further resolve the electrostatic energy into contributions. Before presenting this, a comment is necessary since this is not totally straightforward. The electric field, $\mathbf{E}(i)$, at each each bond polarizability center, i, is calculated via the mutual induction model. The electrostatic energy contribution, $U_{\mathrm{ES}}(i)$ of the bond, i, is[6]

$$U_{\mathrm{ES}}(i) = -(1/2)\mu^0(i)\cdot\mathbf{E}(i) \tag{1}$$

where $\mu^0(i)$ is the *permanent* moment at bond, i. The total moments, both permanent and induced, at all other bonds contribute to the field $\mathbf{E}(i)$ at i, but only the permanent moments, and thus only the polar bonds, contribute to the electrostatic energy through eq 1.

In our force field parameterization here only the C═O, O—C, and C—O bonds at the ester groups are considered polar, i.e. as containing permanent moments. Thus all of the electrostatic energy can be considered as associated with the ester groups, and (i) in eq 1 ranges only over the above three bonds in each of the two ester groups. However the magnitude of the energy depends on all other bonds, as indicated, through the internal field $\mathbf{E}(i)$. It is possible to consider decomposition of $\mathbf{E}(i)$ into its contributions from the other bonds individually. This is not directly possible in the formalism used since in evaluating the internal field a lattice summation method is invoked that subverts identification with particular lattice translations of a given bond. However, the induced moments at all other bonds are readily deduced. Then from the induced and the permanent moments at a given remote bond the contribution to the field at (i) can be constructed. In this way the electrostatic energy was decomposed into the contributions displayed in Table III. Since direct finite summations of energies of bond types were involved, the totals in Table III do not necessarily agree exactly with the electrostatic energies in Table II.

It obviously is of interest to compare the stabilities calculated for the experimentally observed kink-containing structures with those calculated for planar conformation ones. Before doing this it is in order to first comment on the relative stabilities of the two planar forms found, "planar-1" versus "planar-2". It may be seen in Table II that on a steric packing basis, represented by the sub-total column, that the two forms tend to be competitive energetically. The nonrotated planar-1 structures are slightly more stable intramolecularly because there is some distortion from exact planarity in effecting optimized packing in the rotated planar-2 structures. However when the electrostatic energy is included, the planar-2, rotated, forms are more stable. From Table III it may be noted that the intermolecular ester–ester interaction energy and, to some degree, the intermolecular ester-induced dipole energy are more favorable for the chain-rotated structures.

Turning to comparison of the kink conformation structures with the hypothetically competitive planar ones (now determined to be planar-2), it is useful to separately discuss the contributions of the relative intramolecular energies, intermolecular nonbonded energies, and electro-

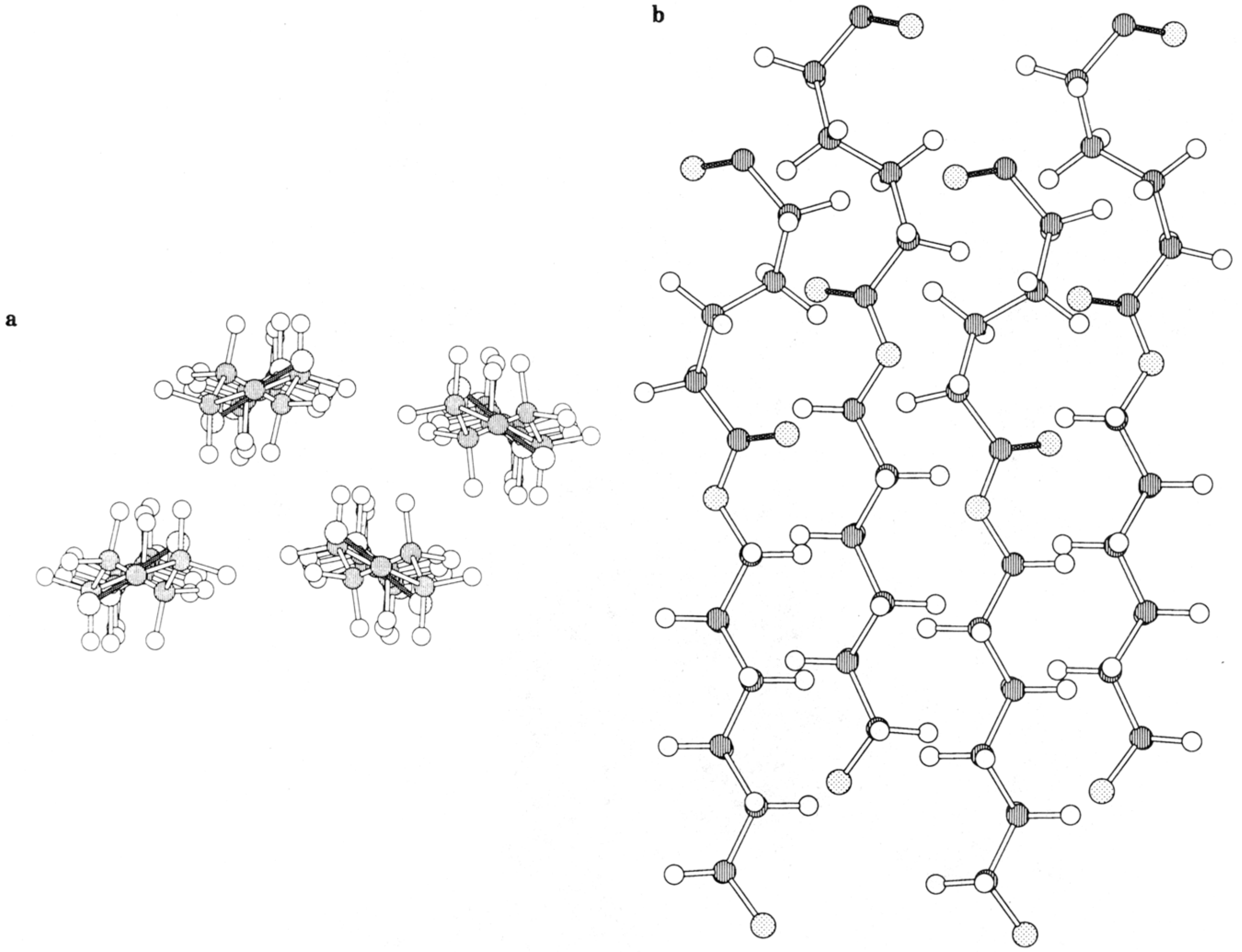

Figure 7. a. Calculated 6–6 polyester structure (*a*, *b* plane projection). There are four chains per cell, located as in Figure 2a. b. Calculated 6–6 polyester structure (*a*, *c* plane projection).

Table II
Packing Energetics[a]

polyester		intrachain	interchain-nonbonded	subtotal	electrostatic	total
2–4	kink	19.0	−64.3	−45.3	19.6	−25.7
	planar-1	21.4	−65.3	−43.9	26.4	−17.5
	planar-2	21.5	−64.1	−42.6	19.4	−23.2
2–6	kink	25.8	−88.8	−63.0	19.6	−43.4
	planar-1	23.7	−78.7	−55.0	34.1	−20.9
	planar-2	24.4	−72.6	−48.2	21.2	−27.0
2–8	kink	28.5	−105.0	−76.5	19.3	−57.2
	planar-1	26.3	−93.3	−67.0	34.5	−32.5
	planar-2	28.6	−92.6	−64.0	20.1	−43.9
4–6	kink	31.9	−88.9	−57.0	28.4	−28.6
	planar-1	26.3	−92.8	−66.5	36.1	−30.4
	planar-2	28.4	−92.4	−64.0	22.0	−42.0
6–6	kink	37.3	−100.9	−63.6	17.8	−45.8
	planar-1	29.2	−107.6	−78.4	35.9	−42.5
	planar-2	32.2	−109.3	−77.1	22.3	−54.8
6–10	planar	38.1	−142.0	−103.9	24.8	−79.1
	kink	43.7	−127.7	−84.0	33.8	−50.1

[a] Units are kJ/(mol chemical repeat unit); intrachain = energy from bond length, valence angle and torsional angle distortion, and intramolecular nonbonded interactions; electrostatic energy as calculated from mutual induction polar model.

Table III
Contributions to the Electrostatic Energy[a]

polyester		intra	inter/ester	inter/nonester	total
2–4	kink	33.3	−7.4	−6.2	19.7
	planar-1	34.7	−8.7	0.4	26.4
	planar-2	35.2	−14.1	−1.6	19.5
2–6	kink	35.3	−13.9	−1.4	20.0
	planar-1	37.2	−3.6	1.5	35.1
	planar-2	30.7	−5.0	−4.2	21.5
2–8	kink	34.4	−12.9	−1.8	19.7
	planar-1	36.7	−2.6	1.8	35.9
	planar-2	34.0	−9.7	−3.8	20.5
4–6	kink	33.3	−3.5	−1.2	28.6
	planar-1	37.6	−1.6	0.7	36.7
	planar-2	37.6	−13.5	−1.8	22.3
6–6	kink	26.4	−2.7	−5.7	18.0
	planar-1	37.1	−1.1	0.5	36.5
	planar-2	37.0	−12.3	−2.0	22.7
6–10	planar	38.6	−12.6	−0.9	25.1
	kink	38.8	−7.0	2.2	34.0

[a] The electrostatic energy of the polar ester groups is decomposed into contributions from the permanent and induced moments of the other bonds in the same chain = intra, from the permanent and induced moments of the ester groups in other chains = inter/ester and, from the induced moments of other bonds in the other chains = inter/nonester. Units are kJ/(mol chemical repeat unit).

static energies to the overall stabilities. It may be seen in Table II for the cases where the kink is in the diol segment and for 4–6 and 6–6 as well, the intramolecular energy is rather competitive between the kink and planar forms. Since the kinks contain gauche bonds that carry some energy penalty, perhaps this is somewhat surprising and deserves comment. For 2–6 and 2–8 polyesters, where the kink is in the diol segment, the gauche bonds are at rotations about $C(sp^2)$–O–C–C bonds. In the force field parameterization[12] the gauche/trans energy difference at one such bond is only ~0.8 kJ/mol. The

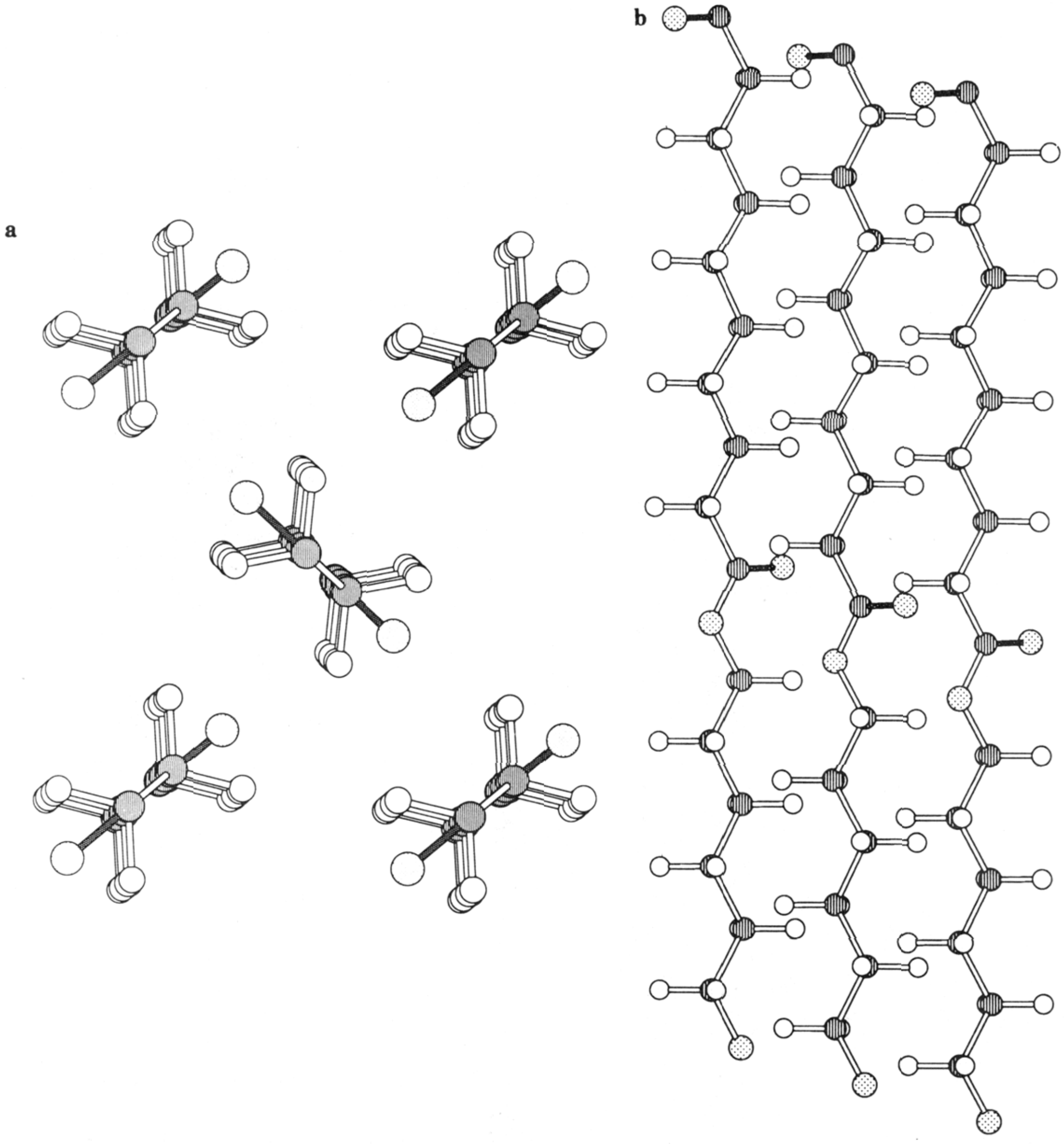

Figure 8. a. Calculated 6–10 polyester structure (*a*, *b* plane projection): two chains per cell: (0, 0), four shown, and (*a*/2, *b*/2), one shown. b. Calculated 6–10 polyester structure (*a*, *c* plane projection).

intramolecular energies of Table II are consistent with this for these two cases when a small contribution from the fact that the "planar-2" form is not exactly planar (cf. Figures 3a and 5) is considered. For 2–4 polyester, the kink conformer actually has an intramolecular energy that is slightly less than for the planar one. This arises from reduced nonbonded interactions in the diol segment. In the cases of 4–6 and 6–6 polyesters where the kink is postulated here to be in the diacid section there is somewhat more of a penalty for the gauche bonds than for the 2–6, 2–8 case. The contribution from the gauche bonds is approximately that for two gauche bonds in a C–C–C–C sequence, but in the comparison with the planar-2 conformation this somewhat offset by the deviation form exact planarity of the latter.

In considering the intermolecular nonbonded packing energy contributions to the relative stabilities of the kink form versus planar-2, it may be seen in Table II that for the 2–4 polyester they are very close and that for 2–6 and 2–8 polyesters the kink structures are definitely favored over the planar. The reasons for this are not obvious but ultimately rest on the fact that the kink containing chains do fit together well and that the ester group does interfere with efficient polyethylene-like packing in the planar conformation. For 4–6 and 6–6 polyesters the planar structures are now favored but only to a very small degree in the former and to a modest degree for the latter. In 6–10 polyester the difference has become fairly substantial.

The electrostatic contributions to the stability are almost the same for the kink versus the planar-2 structures for 2–4, 2–6, and 2–8 polyesters. For 4–6 polyester, the planar-2 electrostatic energy is lower than for the kink, and in 6–6 the kink is more stable compared to planar-2. In 6–10 the planar form is lower energy electrostatically.

Finally, the above contributions together lead to the conclusion from the calculations that the overall stability of the kink structure is very slightly higher than the planar for the 2–4 polyester and markedly higher for the 2–6 and 2–8. In 6–10, the situation is reversed, the planar structure is calculated to have substantially lower energy. All of these observations agree with the structures observed. In the case of 4–6, where polymorphism is found, the planar-2 form is calculated to have lower energy than the kink form and also planar-1. However it is the latter that is closer in its calculated cell parameters to being orthorhombic as observed for the planar form. It is difficult to know whether these calculated values for the kink and planar forms are close enough to permit polymorphism. They apply to the energy difference at 0 K as opposed to the free energy difference at somewhere in the region of room temperature. The energy difference of 13.4 kJ/(mol repeat) corresponds to ~1 kJ/(mol chain atom) and about 13% of the calculated lattice dissociation energy. In the case of 6–6 polyester, the calculations place the planar-2 form as 9 kJ/(mol repeat) more stable energetically than the kink structure, the latter representing the experimentally observed one. This amounts to ~0.6 kJ/(mol chain atom) and about 8% of the lattice dissociation energy. This is probably near the level of reliability of the calculations.

In summary, it can be concluded that the kink containing structures are stable because, in the appropriate examples, the energy penalty for forming them compared to the planar counterparts is modest and they pack competitively or better than the planar forms. By the time aliphatic lengths of those in 6–10 polyester are reached the packing in planar form is less perturbed by the ester groups, the packing is favored in the latter, and the intramolecular penalty for kink formation is apparent.

Acknowledgment. We are indebted to the Polymers Program, Division of Materials Research, National Science Foundation, for financial support of this work. They are also grateful to the San Diego Supercomputer Center for a grant of computer time.

References and Notes

(1) *Collected Papers of W.H. Carothers on High Polymeric Substances*; Mark, H., Whitby, G. S., Eds.; Interscience: New York, 1940; Vol. I.
(2) Fuller, C. S. *Chem. Rev.* **1940**, *26*, 143.
(3) Turner-Jones, A.; Bunn, C. W. *Acta Crystallogr.* **1962**, *15*, 105.
(4) Ueda, A. S.; Chatani, Y.; Tadokoro, H. *Polym. J.* **1971**, *2*, 387.
(5) Tripathy, S. K.; Hopfinger, A. J.; Taylor, P. L. *J. Phys. Chem.* **1981**, *85*, 1371.
(6) Sorensen, R. A.; Liau, W. B.; Boyd, R. H. *Macromolecules* **1988**, *21*, 194.
(7) Sorensen, R. A.; Liau, W. B.; Kesner, L.; Boyd, R. H. *Macromolecules* **1988**, *21*, 200.
(8) Boyd, R. H.; Kesner, L. *J. Chem. Phys.* **1980**, *72*, 2179.
(9) Boyd, R. H.; Kesner, L. *Macromolecules* **1987**, *20*, 1802.
(10) Colpa, J. H. P. *Physica* **1971**, *546*, 185, 205.
(11) Liau, W. B. Ph.D. Dissertation, University of Utah, 1989.
(12) Smith, G. D.; Boyd, R. H. *Macromolecules*, preceding paper in this issue.
(13) Fuller, C. S.; Erickson, C. L. *J. Am. Chem. Soc.* **1937**, *59*, 344.
(14) Minke, R.; Blackwell, J. *J. Macromol. Sci., Phys.* **1979**, *B16*, 407.
(15) Minke, R.; Blackwell, J. *J. Macromol. Sci., Phys.* **1980**, *B18*, 233.
(16) Aylwin, P. A.; Boyd, R. H. *Polymer* **1984**, *25*, 323.
(17) Kanamoto, T.; Tanaka, K. *J. Polym. Sci., Part A-2* **1974**, *9*, 2043.
(18) Swan, P. R. *J. Polym. Sci.* **1962**, *56*, 403.
(19) Tadokoro, H. *Structure of Crystalline Polymers*; Wiley-Interscience: New York, 1979.

Registry No. (Ethylene glycol)(butanedioic acid) (copolymer), 25569-53-3; (ethylene glycol)(butanedioic acid) (SRU), 25667-11-2; (ethylene glycol)(adipic acid) (copolymer), 24938-37-2; (ethylene glycol)(adipic acid) (SRU), 24937-05-1; (ethylene glycol)(octanedioic acid) (copolymer), 25776-26-5; (ethylene glycol)(octanedioic acid) (SRU), 26762-06-1; (adipic acid)(1,4-butylene glycol) (copolymer), 25103-87-1; (adipic acid)(1,4-butylene glycol) (SRU), 24936-97-8; (adipic acid)(1,6-dihydroxyhexane) (copolymer), 25212-06-0; (adipic acid)(1,6-dihydroxyhexane) (SRU), 24937-10-8; (1,6-dihydroxyhexane)(sebacic acid) (copolymer), 26745-88-0; (1,6-dihydroxyhexane)(sebacic acid) (SRU), 26762-10-7; polyethylene, 9002-88-4.

Polymorphism in Melt Crystallized Syndiotactic Polystyrene Samples

Gaetano Guerra, Vincenzo M. Vitagliano, Claudio De Rosa,
Vittorio Petraccone, and Paolo Corradini

Dipartimento di Chimica, Università di Napoli, via Mezzocannone 4, I-80134 Naples, Italy.
Received June 6, 1989; Revised Manuscript Received July 24, 1989

ABSTRACT: Both the crystalline forms containing zigzag planar conformations (pure or mixed) can be obtained by melt crystallization of syndiotactic polystyrene. Some of the factors that influence the polymorphic behavior in samples crystallized on cooling from the melt are described: the cooling rate from the melt, the crystalline form of the starting material, the maximum temperature of the melt, the time of residence in the melt at that temperature, and, in some cases, also the heating rate to reach melting. A possible interpretation of the observed polymorphic behavior in melt crystallizations for moderate cooling rates is that when a memory of α-form crystals remains in the melt, the acquisition of the α form is favored, otherwise the β form is obtained. The formation of the α form, also by quenching from the melt or by annealing from the amorphous phase, could be a kinetically controlled process.

Introduction

The polymorphic behavior of syndiotactic polystyrene (s-PS) is very complex. Two crystalline forms containing molecular chains in a zigzag planar conformation (with an identity period of 5.1 Å)[1] and two crystalline forms containing molecular chains with $s(2/1)2$ symmetry and an identity period close to 7.7 Å have been very recently described.[2,3] For the chains with $s(2/1)2$ symmetry a conformation TTGG was proposed on the basis of energy calculations.[3]

Although the preparation by melt crystallization is described in the literature for only one form, a careful