Ordered Structures of Poly(*p*-hydroxybenzoic acid). 1. Nonbonded Interactions in Layers of Phenyl Rings Orthogonal to the Chain Axis

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ABSTRACT: An examination of the influence of the intermolecular energy in layers of phenyl rings perpendicular to the chain axis on the packing features and the feasibility of certain modes of motion is presented. It is a first step in an analysis of the packing of polymer chains in the structures of poly(*p*-hydroxybenzoic acid) (PHBA) that have so far been observed in experiments. Energy profiles and maps have been obtained based on empirically justified potential functions. Increased rotational freedom for phenyl rings is observed in the smectic-like high temperature structures as compared to the low temperature crystal modifications. The consideration of strongly correlated rotations assumed in the model of a perfect crystal shows the possibility of reorientational motion for crankshaft-like chain fragments in the high temperature modifications. This rotation of crankshaft-like fragments is proposed as being the origin of the reorientational disorder observed experimentally in the smectic-E-like phase of PHBA.

I. Introduction

Aromatic polyesters are stiff-chain polymers whose solid state properties are of current scientific and industrial interest. Poly(*p*-hydroxybenzoic acid) (PHBA) is the basic component for a family of random copolymers that show thermotropic liquid crystalline behavior. The structure of the homopolymer is of considerable significance for the understanding of the structures of these copolymers, but the nature of the crystallinity in PHBA itself has been subject to slightly controversial discussions in literature.[1-3]

At room temperature, two phases have been observed in various investigations of the crystalline state of PHBA by X-ray diffraction of bulk samples and electron diffraction of thin-sheared films. Phase I has an orthohombic unit cell with the cell parameters a = 7.47–7.62 Å, b = 5.67–5.7 Å, and c = 12.5–12.55 Å.[1,4,5] Phase II, which is also orthorhombic but will cell parameters a = 11.06–11.12 Å, b = 3.77–3.78 Å, and c = 12.89–12.9 Å,[3,4] is often observed in PHBA homopolymers with low degrees of polymerization. The proportions of phases I and II depend on the preparation conditions and the portion of phase II also decreases with chain growth.[6]

At increased temperatures, differential scanning calorimetry (DSC), thermal mechanical analysis (TMA), and X-ray investigations show the occurrence of two phase transitions.[1,2,4,5,7,8] At temperatures near 340 °C both crystalline low temperature modifications are converted to a phase III which is pseudohexagonal and has cell parameters a = 9.13–9.24 Å, b = 5.28–5.35 Å, and c = 12.49–12.5 Å. The unit cell volume increases significantly upon the transition from phase I to phase III due to the sharp increase of cell parameter a. However, according to experimental data, the differences of the periodicity along the chain between phase I and phase III are insignificant, and it can, therefore, be assumed that this transition involves no change of the larger scale conformation of the main chain. The occurrence of some conformational disorder of the type observed in the smectic-E phases[9] of small rodlike molecules has been proposed[5] for the structure of phase III. This kind of disorder involves a twofold axis of rotation through an angle π around the chain axis for each two-monomer repeat unit. According to dielectric measurements,[10] the nature of this twofold reorientational disorder is dynamic and the movements involved correlate strongly.

In addition to the transitions mentioned above, a further transition is observed[2,3,5,8,10] at ca. 440 °C which has been described as analogous to the smectic-E to smectic-B transition[11,12] of small molecules. As a result, phase III is transformed to a new hexagonal modification (phase IV) with cell parameters a = 9.31–9.35 Å, b = 5.36–5.40 Å, and c = 12.47–12.49 Å. It has been suggested that, as in the transition from phase I to phase III, no change of the larger scale conformation of the main chain is involved in this transition. However, a loss of the long range orthorhombic coherence of the packing of the phenyl rings is observed.[5,13]

Neither the crystal structure of the different phases of PHBA nor the mechanism of the structure transitions has yet been fully clarified. The goal of the present work is to contribute to the clarification of the crystal structures of the low and high temperature phases.

The PHBA chain consists entirely of an alternation of ester groups and *para*-linked phenyl rings. The phenylene moiety may rotate in PHBA chains as in the stiff-chain aramid PPTA[14] without significant effect on the larger scale chain conformation, but possibly with major impact on chain packing. According to the experimental data, the main changes of the crystal structure upon the structure transitions have been observed in the layers of the phenyl rings that are orthogonal to the chain axis. The focus of this paper is put on these structural differences in the

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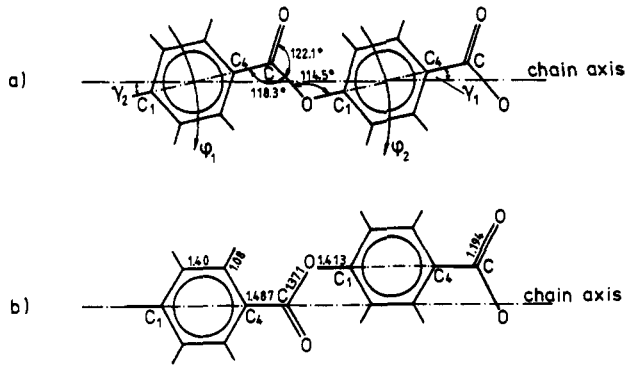

Figure 1. Segments of chains of poly(*p*-hydroxybenzoic acid) (PHBA) are depicted with a *trans* conformation (a) and a *cis* conformation for successive ester groups in the chain. φ_1 and φ_2 are the torsional angles for the rotation of a phenyl ring around the axis formed by the atoms C_1 and C_4. The values of the bond lengths and the valence angles have been taken from ref 15.

packing of all the ordered structures observed in experiments. The possibility of reorientational motion in such layers in the high temperature phases is explicitly investigated. As a first approach we considered the packing of the phenyl rings in one layer.

A straightforward scanning of configurational space has been applied in our calculations. The configurational space has been represented by a set of appropriate coordinates: the phenyl ring rotation angle and the chain rotation angle. In the interpretation of the results, we will concentrate on those areas of configurational space near the local, low energy minima.

II. Description of the Model

The repeat unit of the PHBA chain is depicted in Figure 1. In our model of crystalline PHBA, all bond lengths and valence angles are kept constant. The phenyl rings are completely rigid. The geometric parameters for the fixed bond lengths and valence angles are based on experimental observations. We used the data of Sun, Cheng, and Blackwell.[15] The rotation of the ring plane around the C_1–C_4 axis is possible by changing the torsional angles φ_1 and φ_2. This rotation can be performed independently from the helical structure of the chain.

The total energy V of a packing structure can be divided into the intramolecular and intermolecular contributions V_{INTRA} and V_{INTER}:

$$V = V_{INTER} + V_{INTRA} \tag{1}$$

Intramolecular contributions to the total energy were ignored in the calculations presented in this work. However, contributions of the torsional potentials of the ester group torsions[16,17] have been considered in the discussion, where it was appropriate.

The intermolecular interactions have been represented by a sum of two-body potentials (depending on the internuclear distance r_{ij}),

$$V_{INTER} = \frac{1}{2}\sum_{l}\sum_{i}\sum_{j} V_{ij}^{(pl)}(r_{ij}) \tag{2}$$

where all atoms in the chains are acting as force centers and only those contributions to the potential energy have been considered that arise from the interactions between the atoms i of the central chain segment p and the atoms j of the chains l in the shell of nearest neighbors (see Figure 2a), because this region contains the dominant contributions to the packing energy[14,18,19] that are responsible for the geometry of the structure.

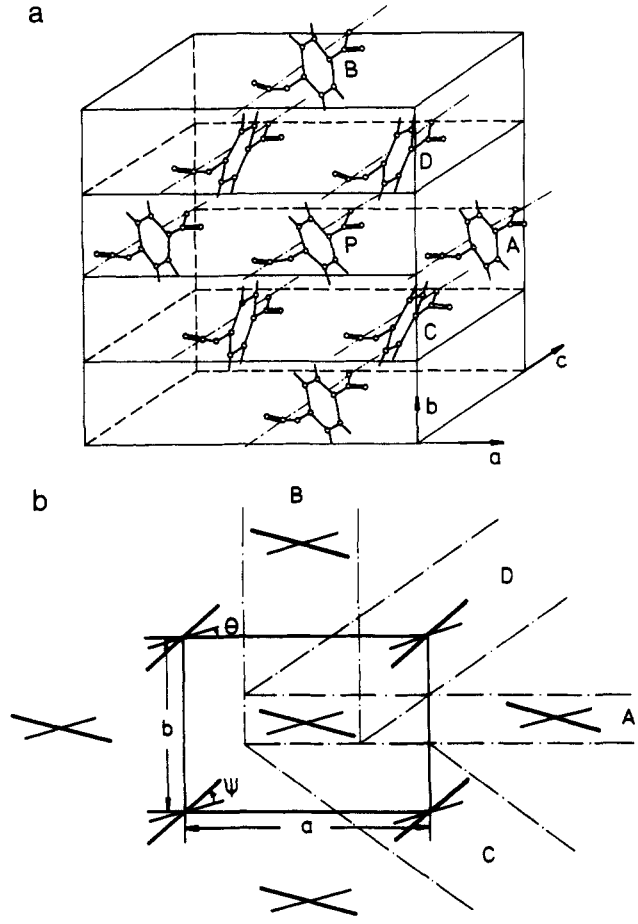

Figure 2. (a) Relative orientation of the chains with respect to the cell axes. The significance of the different interaction types A, B, C, and D between the atoms of the central reference chain segment P and the atoms of the chain segments A–D is explained in the text. (b) Schematic representation of the packing structure by a local domain in a plane orthogonal to the chain axis. Projections of the phenyl rings and ester groups are displayed as bold and thin lines, respectively. Dashed lines enclose the central reference chain segment and one of the neighboring chains to illustrate the different phenyl ring pairs corresponding to the interaction types. The rotation angle Ψ, defined as the angle between the plane of the phenyl ring and the plane of the ester groups, and the setting angle θ, defined as the angle between the plane of the ester groups and the crystallographic plane a–c, are displayed in this figure as well.

The nonbonded, two-body interactions are represented by a Buckingham type potential:

$$V_{ij}(r_{ij}) = Ae^{-\beta r_{ij}} - Br_{ij}^{-6} \tag{3}$$

using different parameter sets; Corradini *et al.*[20] and Kitaigorodskii[21] specified their parameters on the basis of a wide range of crystallographic data of organic molecular crystals, while the parameter set of Dashevskij[22] is thought to be especially suitable for polymer molecules with heterocyclic or aromatic moieties.[23,24]

III. Structure Representation

It can be concluded from the available experimental data that the periodicity along the chain corresponds to *trans* (phase II) and *cis* conformations (phases I and III) for successive ester groups.[1,2,4,5,8] The *trans* conformation is rodlike in character, while the *cis* arrangement leads to crankshaft-like conformations (see Figure 1). The aromatic planes are nearly parallel to the chain axis for the

cis conformation, while for the *trans* conformation the C_1–C_4 axis of the phenyl rings is inclined to the chain axis (inclination angles of $\gamma_1 = 7.3°$ and $\gamma_2 = 10.1°$ for two successive monomers in the chain). Due to these differences in the inclination angles, the layers of phenyl rings orthogonal to the chain axis are not identical for the *cis* and *trans* conformations.

The orientation of the phenyl rings can be defined by the angle Ψ between the plane of the phenyl rings and the plane of the ester groups. This angle will be referred to as the rotation angle in the rest of this paper.

In the first part of this work we consider the packing possibilities for the phenyl rings in the crystal cell, discussing a placement of the ester groups in the crystallographic planes *a*–*c* and *b*–*c* only. In this part, the rotation angle $\Psi = 0°$ corresponds to a placement of the phenyl rings in the crystallographic plane *a*–*c*.

In the second part we introduce an additional degree of freedom with an angle θ, which is the angle of the orientation of the main chain (defined by the plane containing the ester groups) relative to the crystallographic planes. This angle will from hereon be referred to as the setting angle.

A longitudinal displacement of chains along the chain axis would reduce the rotational freedom of the phenyl rings due to the interchain neighborhood of ester groups, because the rotations of these two types of moieties are different. Phenyl rings can revolve around their axis, while changes of the main chain conformation are necessary for a rotation of the ester groups. Moreover, strong interactions between specific groups in polymer chains introduce a preference for a packing with layers of identical groups for polymers with specific groups in the chain, e.g. for polyamides.[14] Polyesters contain dipolar groups and a similar type of packing can be expected for them. Therefore, longitudinal displacements of the chains along their chain axis are not considered in the present work.

Considering the symmetrical requirements of the cell, Lieser[4] proposed a $P2_12_12_1$ space group for phase I of PHBA. He supposed that the unit cell consists of two antiparallel molecular chains with a 2/1 screw axis along the fiber direction. However, Sun *et al.*[15] investigated the possibilities arising from different polarities of the chains in the unit cell and they could not decide between parallel and antiparallel molecular chain packing. In this paper we assumed parallel packing of the chains. The comparison of parallel and antiparallel chains and their consequences will be discussed in detail in a subsequent paper.[25] The space groups of phases II to IV have not been discussed in the literature so far.

The experimental data fix the lattice types for our calculations—orthorhombic for the low temperature modifications, and pseudohexagonal and hexagonal at higher temperatures. There are some fluctuations in the experimental values for the cell parameters published so far. We averaged values in these cases. A body-centered placement of the phenyl rings in the two-dimensional layer orthogonal to the chain axis has to be applied, because the unit cell contains the dimer sections of two chains.

The layer perpendicular to the chain axis, which coincides with the crystallographic axis *c*, contains two independent sets of phenyl rings. One of these sets is formed by those on the lattice knots and the other set by the phenyl ring in the central position and by its periodic images. The rotation angle Ψ for these two sets may point in the same or in opposite directions. We will call these two possibilities synchronous and counterrotating.

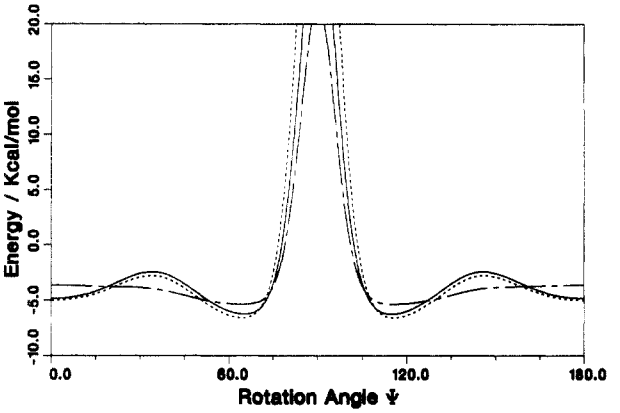

Figure 3. Profiles for the contributions of the intermolecular interactions of the phenyl rings to the energy of phase I (in kcal/mol) are displayed against the rotation angle Ψ (counterrotation). The different curves have been obtained using the parameter sets of Corradini *et al.*[20] (- - -), Kitaigorodskii[21] (– · –), and Dashevskij[22] (—).

A herringbone type packing, i.e., counterrotation of the phenyl rings in the crystallographic plane *a*–*b* (depicted in Figure 2b) has been assumed in almost every experimental paper for the ordered low and high temperature structures of PHBA. On the other hand, the possibility of a synchronous rotation resulting in a parallel packing of the phenyl rings in this crystallographic plane has been proposed for the high temperature modification phase III.[8] For this reason synchronous and counterrotation of the phenyl rings in the crystal cell have been considered for the high temperature modifications in this work.

IV. Results

For the low temperature crystals of phase I, calculations have been performed with different sets of potential parameters. According to experimental data the PHBA chains in phase I are packed in a *cis* conformation, and the layer of phenyl rings has been composed on this basis. The total energies for the phenyl ring layer calculated with the parameters stated by Kitaigorodskii[21] (curve 1), by Corradini *et al.*[20] (curve 2), and by Dashevskij[22] (curve 3) are displayed in Figure 3 as functions of the rotation angle (counterrotating). Curves 2 and 3 do almost coincide, but curve 1 differs both in the depth of the minimum and in the height of the barrier, though these differences are not too strong. All curves have minima at rotation angles of $\Psi = 65°$ and $\Psi = 115°$. Additionally, curves 2 and 3 possess less deep minima at the rotation angle 0°. Curve 1 contains a small barrier (ca. 1 kcal/mol) for this position. The position of the deepest minimum is significant for the determination of the packing features. In our case these minima at 65 and 115° are in accordance with the experimental data (ca. 60°).[8,26]

When the main chain (defined by the plane of the ester groups) is placed in the crystallographic plane *a*–*c*, the rotation angle Ψ coincides with the torsion angle φ_1, while the placement of the main chain in the crystallographic plane *b*–*c* implies that the torsion angle φ_1 is equal to $\pi/2 - \Psi$. In both cases the intramolecular interactions should not shift the location of the minima significantly, because the intramolecular energy differences are comparably small; the intramolecular energy at the intermolecular energy minima is less than 1 kcal/mol higher than at the intramolecular minima (energy values taken from ref 17).

In the following discussions, we will center on the calculations performed with the Dashevskij[22] parameters (see Table 1), because these potentials have already been

Table 1. Nonbonded Parameter Set for Eq 3 and Corresponding Minimum Energy Distances R_0 Derived by Dashevskij[22] That Have Been Used in the Calculations of the Intermolecular Interactions of PHBA Structures Presented in This Paper[a]

atoms	A (Å^6 kcal/mol)	B (10^4 kcal/mol)	C (Å^{-1})	R_0 (Å)
H–H	40.1	2.86	5.2	2.43
C–C	476	3.77	3.513	3.70
O–O	354	9.65	4.333	3.00
C–H[b]	121	3.28	4.13	3.15

[a] Combination rules have been used to determine the parameters for non-like atom pairs (with the exception of C–H interactions). Geometric averages have been used for parameters A and B while arithmetic averages have been used for the minimum energy distances R_0. Parameter C is related to R_0 by the formula $C = 13/R_0$. [b] Independent determination.

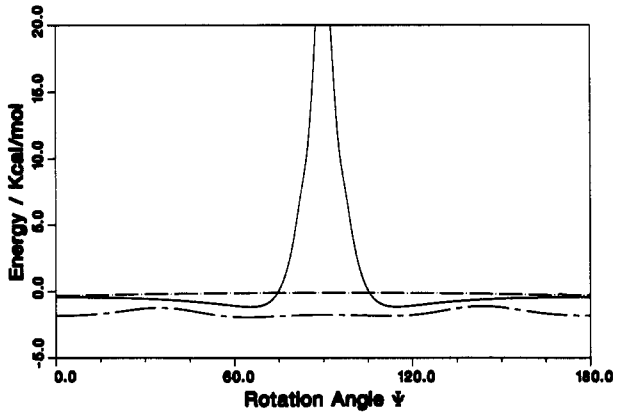

Figure 4. Contributions from the different interaction types A (-·-), B (—), C (- - -), and D (-··-) to the energy profile of phase I (in kcal/mol) using the Dashevskij parameter set[22] are displayed as a function of the rotation angle Ψ (counterrotation). The interaction types reproduce the interactions of pairs of phenyl rings in different relative positions. The contributions of interaction types C and D are identical for counterrotation. The definitions of the pairs are given in the text and in Figure 2.

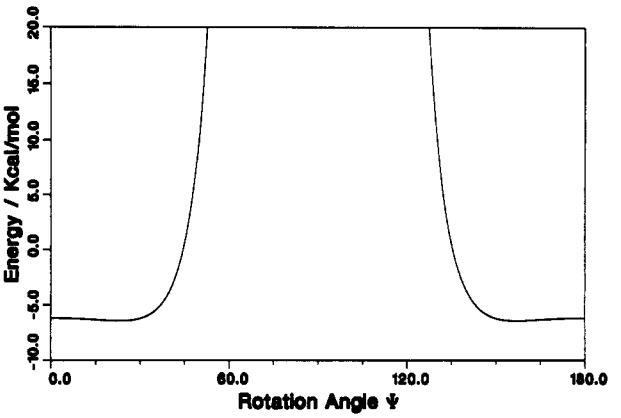

Figure 5. Profile for the contributions of the phenyl rings to the intermolecular part of the energy for phase II that is stable for shorter chain lengths (in kcal/mol) is displayed against the rotation angle Ψ (counterrotation).

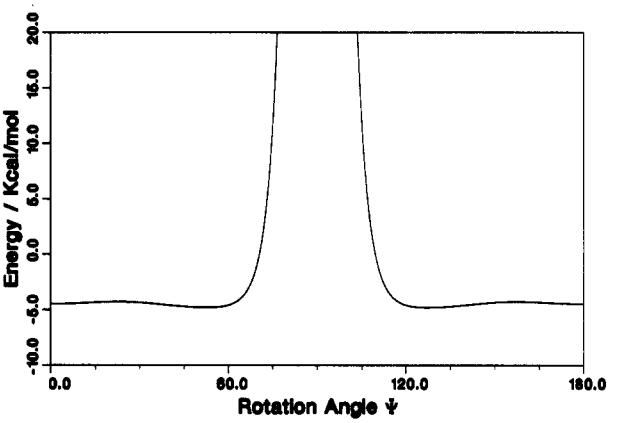

Figure 6. Profile for the contributions of the phenyl rings to the intermolecular part of the energy for the smectic-E-like high temperature phase III (in kcal/mol) is displayed as a function of the rotation angle Ψ (counterrotation).

used to obtain reasonable results for polymer molecules with heterocyclic and with aromatic moieties in the chain.[24]

Strong restrictions to the rotational freedom of the phenyl rings in phase I can be concluded from the curves in Figure 3. Figure 4 shows the contributions to this total packing energy from the energies of interactions between phenyl rings in different lattice positions. There are four different "pair" interactions of phenyl rings in the crystal cell to be considered (see Figure 2b). Types A and B are the interactions between the central phenyl ring ($^1/_2,^1/_2,0$) and its periodical images at ($^3/_2,^1/_2,0$) and ($^1/_2,^3/_2,0$), and types C and D are the interactions between the central phenyl ring and the phenyl rings on the lattice knots at (1,0,0) and (1,1,0). Strong restrictions to the rotational freedom of the phenyl rings are introduced by interaction type B. For the other "pairs", the barrier heights for the rotation angle are not very high. Interaction type B is directed along the crystallographic axis b. The most important changes upon the structure transition from phase I to phase III are observed in cell parameter a, and the less important restrictions in this direction can be a possible explanation for this fact.

PHBA chains have *trans* conformations in phase II. The calculations on the crystals of phase II were performed using the inclination angles γ_1 and γ_2 for the *trans* conformation. The differences in the interaction energy due to the change in the inclination angle do not exceed 0.3 kcal/mol according to the evaluations that we have made. This difference is rather insignificant compared to the differences in the total interaction energy in our system, and therefore, in this paper, only the results obtained for the inclination angle 10° are presented.

The simulation of phase II results in extremely large regions where repulsion is predominant. Minima surrounded by flat regions are observed at $\Psi \approx 0°$ and $\Psi \approx 180°$ (Figure 5); i.e., the phenyl rings have a tendency to lie close to the crystallographic plane a–c. A placement of the main chain in the crystallographic plane b–c is impossible due to the small value of cell parameter b (3.77–3.78 Å) which, in combination with the inclination angle, causes an overlap of the oxygen atoms of the ester groups of adjacent chains in the direction of the crystallographic axis b (distance: 1.658 Å).

Both synchronous and counterrotation of the phenyl rings had to be considered for the high temperature phase III. According to experimental data, the PHBA chains in phase III are packed in a *cis* conformation as in phase I. Some *trans* conformations may occur in this high temperature phase, but the aim of the present study is the description of a minimum structure without any distortions, and therefore an all-*cis* configuration was used in the calculations.

The total packing energy for counterrotation (Figure 6) shows a region of strong repulsions which is slightly wider in comparison with phase I. The slope of the total energy curve is small in the region of the minima, and therefore the phenyl rings possess a larger rotational freedom in the high temperature modifications than in phase I.

The possibility of parallel packing for the phenyl rings in the layer orthogonal to the chain (synchronous rotation)

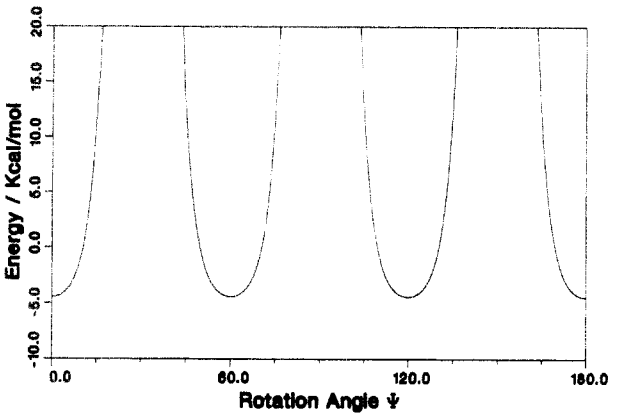

Figure 7. Profile for the contributions of the phenyl rings to the intermolecular part of the energy for the smectic-E-like high temperature phase III (in kcal/mol) is displayed as a function of the rotation angle Ψ (synchronous rotation).

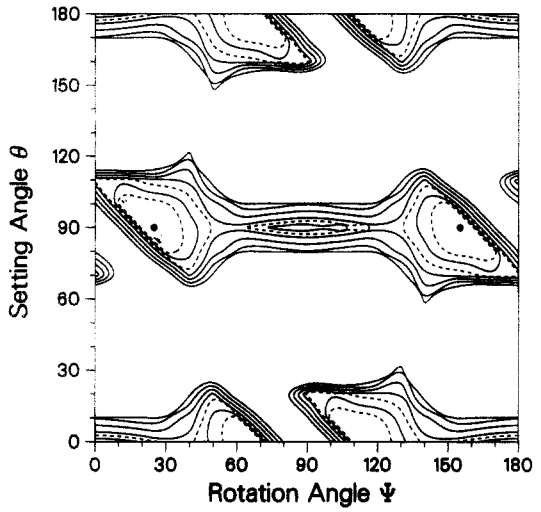

Figure 8. Contour map for cooperative rotation of chains in the low temperature phase I. The values for the rotation angle Ψ and the setting angle θ are given in degrees. The location of the deepest minima is indicated by dots. The energy for these configurations has been chosen as the zero-point energy. The energy difference between two neighboring, continuous lines in the plot is 2 kcal/mol. Dashed lines have been introduced for energy levels of 1 and 3 kcal/mol. Regions with energies higher than 10 kcal/mol are displayed as white areas.

was also investigated. Figure 7 shows that in this case four minima are observed at 0 and 180° as well as at 60 and 120°. These minima are extremely narrow and consequently a parallel packing of the phenyl rings is hardly probable. Therefore, the analysis of the phenyl ring interactions in the layer orthogonal to the chain axis demonstrates that the phenyl rings have to form herringbone packing in all crystal modifications.

So far we have discussed one-dimensional energy profiles. However, it seems appropriate to consider the setting angle θ as an additional degree of freedom, because the possibility of concerted chain rotations is of importance in connection with the question of the origin of the reorientational disorder observed experimentally for the high temperature modifications of PHBA.

Figure 8 shows the interaction energy of the fragments containing the phenyl ring and the two ester groups for phase I as a function of the rotation angle of the phenyl rings and of the setting angle θ. The rotational freedom of the chains is strongly limited to narrow regions near setting angles $\theta = 0°$ and $\theta = 90°$. These angles correspond to a placement of the ester groups in the crystallographic planes a–c and b–c, respectively. This restriction occurs

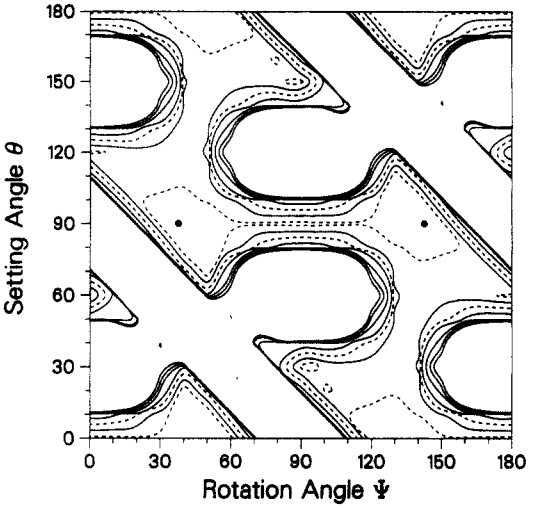

Figure 9. Contour map for the dependence of the energy on the rotation angle Ψ and the setting angle θ in the smectic-E-like high temperature modification phase III. The energy difference between two neighboring, continuous lines in the plot is 2 kcal/mol.

due to the strong steric hindrance of the phenyl ring rotation for intermediate setting angles.

The corresponding plot for the interaction energy of phase III is displayed in Figure 9. The figure shows the existence of a possibility for chain reorientation with a very low intermolecular energy barrier (ca. 2 kcal/mol) for this high temperature crystal modification. However, the consideration of intramolecular interactions is important for setting angles $\theta \approx 90°$ and rotation angles $\Psi = 90°$, as the conformational energy barrier for the torsional angle $\varphi_1 = 90°$ is ca. 5 kcal/mol.[16,17]

We have used the setting angle θ to describe reorientational motion of the whole polymer chain. Therefore it would seem that the simultaneous reorientation of long chain fragments was necessary, which is, of course, energetically and entropically very unfavorable. However, it has already been pointed out that the *cis* conformations of successive ester groups observed in phases I and III correspond to a crankshaft-like conformation. The rotation of a crankshaft-like fragment consisting of one phenyl ring and two ester groups around an axis defined by the C_1–C_4 axes of the successive phenyl rings of the neighboring layers is possible without changing the conformation of the whole chain. Therefore, the angle θ from our calculations corresponds to the rotation of a crankshaft-like fragment. The intramolecular activation energy of such a fragment includes the contributions from the ester groups on both sides of the central phenyl ring since the rotation of the crankshaft-like fragment takes place with respect to both chain ends. These intramolecular contributions to the barrier are more significant for the reorientational motion than for the intermolecular part.

Our calculations correspond to a simultaneous reorientational motion for all fragments in one layer. Such a movement is of course impossible, but smaller nonreorientational movements of the surrounding chains are quite probable and they could be sufficient to keep the system near its energetic minimum. Therefore, our calculations show that the reorientational motion in phase III of PHBA can be explained as concerted motion of crackshaft-like fragments of adjacent chains in the same layer, orthogonal to the chain axis, which is contrary to suggestions[5,8] that a chain segment consisting of two monomers is necessary for the reorientational motion. The exact nature of these correlations, though, has to be the task of further

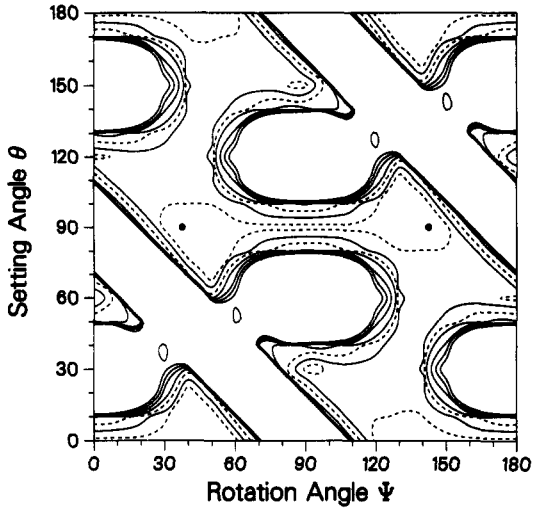

Figure 10. Contour map for the dependence of the energy on the rotation angle Ψ and the setting angle θ in the smectic-B-like high temperature phase of PHBA observed above 440 °C. The energy difference between two neighboring, continuous lines in the plot is 2 kcal/mol.

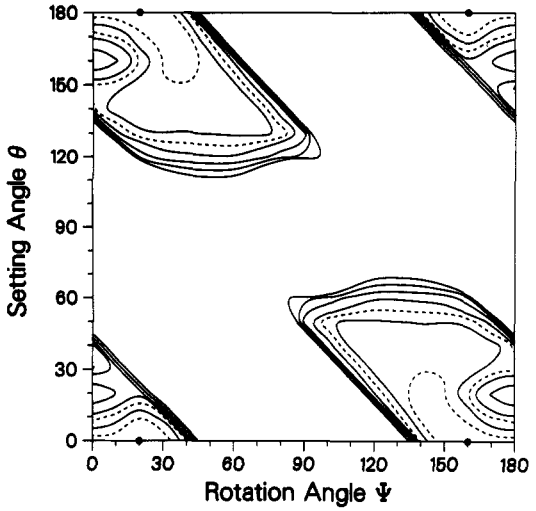

Figure 11. Contour map for the dependence of the energy on the rotation angle Ψ and the setting angle θ in phase II stable for lower degrees of polymerization. The energy difference between two neighboring, continuous lines in the plot is 2 kcal/mol.

investigations, applying a different molecular modeling approach.

We assume that the change of lattice type from orthorhombic to pseudohexagonal in the thermal structure transition at 340 °C is related to this new rotational degree of freedom. The lattice symmetry of the low temperature modifications seems to be the most suitable for the packing of phenyl rings. The pseudohexagonal lattice seems to be more appropriate for the packing of crankshaft-like fragments. Therefore the additional rotational degree of freedom plays a leading role in the formation of the high temperature phase.

A comparison of results for the smectic-B-like high structure observed at temperatures above 440 °C (Figure 10) with the results of the smectic-E-like structure of phase III (Figure 9) shows changes only for setting angles near 90°. The path for a possible reorientation has widened.

The second low temperature modification (phase II) exists for polymer chains with a low degree of polymerization. The probably strong interactions between ester groups in adjacent chains due to the small value of parameter *b* are the reason for the fact that the main chain cannot lie in the crystallographic plane *b*–*c* (see above). The calculations of the chain fragment consisting of the phenyl ring and the two ester groups are displayed in Figure 11. Our calculations show that there are very strong restrictions for the phenyl rings and the chain rotations in the highly ordered crystal structure of phase II, which points to instability of this phase at higher temperatures, as it should be entropically unfavorable. This result is supported by the observation of a partial or complete conversion of phase II to phase I at 260 °C reported by Lieser.[4] However, a quantitative evaluation of the free energy of the crystal would be necessary to confirm this assumption.

V. Conclusions

We presented in this paper an analysis of the packing features for all the experimentally observed, ordered structures of PHBA. The energies due to the intermolecular interactions were calculated for layers of phenyl rings orthogonal to the chain axis, as experimental results had shown that the significant changes mainly occur in these layers.

In phases I and II, which are stable at room temperature, the rotation of phenyl rings is strongly restricted. The relatively large intermolecular energy differences during the rotation confirm the applicability of an approach that neglects intramolecular energy contributions to these phases. The results for the preferential orientation of the phenyl rings in the crystal cell in phase i are in accordance with experimental data. The possibilities for an orientation of the chain, i.e. the plane with the ester groups, relative to the crystallographic planes are restricted to the planes *a*–*c* and *b*–*c*. We suppose that phase II, which is observed in low molecular weight samples of PHBA, is unstable at higher temperatures due to entropy reasons since there are especially strong restrictions to the orientational freedom of the phenyl rings and the chains in the crystal lattice.

Conversely, in the high temperature modifications (phases III and IV), the rotational freedom of the phenyl rings is increased. The system acquires the possibility to reorient crankshaft-like chain fragments consisting of a phenyl ring and the two adjacent ester groups. The present model results in a very low intramolecular barrier for this reorientation. However, an improved model that considers the behavior of neighboring chains in a more realistic way will have to be presented to confirm this result. Nevertheless, the crankshaft-like fragment is a suitable moiety for reorientational motion and we believe, therefore, that the rotation of the these fragments is the origin of the reorientational disorder observed experimentally for these phases.

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References and Notes

(1) Geiss, R.; Volksen, W.; Tsay, J.; Economy, J. *J. Polym. Sci., Polym. Lett. Ed.* **1984**, *22*, 433.
(2) Hanna, S.; Windle, A. H. *Polym. Commun.* **1988**, *29*, 236.
(3) Liu, J.; Geil, P. H. *J. Macromol. Sci., Phys.* **1992**, *B31*, 163.
(4) Lieser, G. *J. Polym. Sci., Polym. Phys. Ed.* **1983**, *21*, 1611.
(5) Yoon, D. Y.; Masciocchi, N.; Depero, L. E.; Viney, C.; Parrish, W. *Macromolecules* **1990**, *23*, 1793.
(6) Kricheldorf, H. R.; Schwarz, G. *Makromol. Chem.* **1983**, *184*, 475.

(7) Economy, J.; Volksen, W.; Viney, C.; Geiss, R.; Siemens, R.; Karis, T. *Macromolecules* **1988**, *21*, 2777.
(8) Coulter, P. D.; Hanna, S.; Windle, A. H. *Liq. Cryst.* **1989**, *5*, 603.
(9) Field, N. D.; Baldwin, R.; Layton, R.; Frayer, P.; Scardiglia, F. *Macromolecules* **1988**, *21*, 2155.
(10) Kalika, D. S.; Yoon, D. Y. *Macromolecules* **1991**, *24*, 3404.
(11) Lavelut, D. S.; Doucet, J.; Lambert, M. *J. Phys. (Les Ulis, Fr.)* **1974**, *35*, 773.
(12) Doucet, J. In *The Molecular Physics of Liquid Crystals*; Luckhurst, G. R., Gray, G. W., Eds.; Academic Press: London, 1979; Chapter 14 and references therein.
(13) Kalika, D. S.; Yoon, D. Y.; Iannelli, P.; Parrish, W. *Macromolecules* **1991**, *24*, 3413.
(14) Rutledge, G. C.; Suter, U. W. *Macromolecules* **1991**, *24*, 1921.
(15) Sun, Z.; Cheng, H. M.; Blackwell, J. *Macromolecules* **1991**, *24*, 4162.
(16) Jaffe, R. L.; Yoon, D. Y.; McLean, A. D. In *Computer Simulation of Polymers*; Roe, R. J., Ed.; Prentice-Hall: Englewood Cliffs, NJ, 1991; p 1.
(17) van Ruiten, J.; Meier, R. J.; Hahn, C.; Mosell, T.; Sariban, A.; Brickmann, J. *Macromolecules* **1993**, *26*, 1555.
(18) Tripathy, S. K.; Hopfinger, A. J.; Taylor, P. L. *J. Phys. Chem.* **1981**, *85*, 1371.
(19) Zubkov, B. A.; Milevskaya, I. S. *J. Struct. Chem. (Engl. Transl.)* **1985**, *26*, 29.
(20) Corradini, P.; Avitabile, G. *Eur. Polym. J.* **1968**, *4*, 385.
(21) Kitaigorodskii, A. I. *Dokl. Akad. Nauk* **1961**, *137*, 116.
(22) Dashevskij, V. G. *Conformazii Organitoheskih Molecul*; Khimia: Moscow, 1974; p 111.
(23) Lukasheva, N. V.; Milevskaya, I. S., Baklagina, Yu. G. *Vysokomol. Soedin.* **1989**, *31*, 426.
(24) Kozlovich, N. N.; Beriketov, A. S.; Davydov, G. A.; Lukasheva, N. V.; Milevskaya, I. S.; Gotlib, Yu. Ya. *Vysokomol. Soedin.* **1990**, *32*, 1989.
(25) Lukasheva, N. Y.; Mosell, T.; Sariban, A.; Brickmann, J., in preparation.
(26) Economy, J. *Mol. Cryst. Liq. Cryst.* **1989**, *189*, 1.