

There are several open questions concerning the formulation of theoretical energy functions. One concerns the form of the energy functions used and the representation of contributions to the energy by chain motions and lattice vibrations. Torsional contributions are generally represented as a constant factor, the magnitude of which is determined by the torsional angles of the molecule. Since the unit cell parameters of PTBD as a function of temperature are known,⁴ the potential energy can be calculated as a function of distance and can be compared to the energy obtained from experimental heat capacity measurements. The difference between the two can be used as an estimate of the contribution of the torsional modes.

A second important question which can be answered with PTBD is whether or not single-chain energy calculations can be used for describing the energy of a crystalline system. Some of the calculations to be described here are based on a three-dimensional lattice of identical unit cells. The energy minima and the lattice dimensions and chain orientation at these minima for the entire lattice can be compared with like values for the single chain and the unit cell. Since the single-chain intramolecular calculations occupy such a large part of the literature, this study should provide a critical evaluation of those calculations.

Having decided upon a classical potential function with suitable parameters, it is necessary to have a method for calculating thermodynamic properties from structure. Two well-known approaches are open to us. The first is the rotational isomeric state theory, developed by Volkenstein⁵ and by Flory,⁶ which is essentially a single-chain (intramolecular) calculation that does not take into account effects of packing within the unit cell of the crystal. It will be seen that these calculations are sufficient to predict statistical properties for PTBD such as the entropy, but inclusion of *intermolecular* effects, as Mark⁷ has pointed out, is necessary in order to predict the internal structure of the crystal itself.

An alternative approach to the energy function problem is the one largely developed by Scott and Scheraga in a series of papers.⁸⁻¹¹ This point of view is that when stereoregular polymers crystallize, they assume the conformation which achieves the minimum free energy of the system. The total conformational energy, U , is considered to be a sum of the energy due to nonbonded interactions (interactions among all the atoms not covalently bonded), U_{nb} , and the torsional energy (energy due to the ethane-like rotational barriers in the molecule), U_{tors} , where

$$U_{tors,i} = \frac{V_0}{2} (1 + \cos 3\omega_i) \quad (1)$$

where ω_i is the value of the i th dihedral angle. The value $V_0 = 2.0$ kcal/mol was used in all calculations of U_{tors} .

Two energy functions were used in this study. One was the Scott and Scheraga function and the second was that derived by Kitaigorodsky and others,^{12,13} which was parameterized from the Van der Waals radii collected from crystal lattice data, and does not consider the lattice

energy separately. Kitaigorodsky's equation is

$$V_{nb} = 3.5(8600 \exp(1-13z) - 0.04z^{-6}) \quad (2)$$

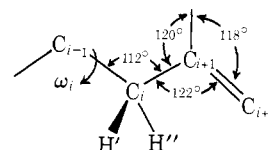
where r is the distance between two nonbonded atoms, R is the sum of their Van der Waals radii or contact distances, and $z = r/R$. V_{nb} is the energy of interaction in kcal/mole, and can obviously be negative (attraction) or positive (repulsion).

In this paper heat capacity measurements for PTBD from 50–130° are presented; the entropy change over part of this temperature range, as calculated from the heat capacity and the heats of transition and melting, is compared with that calculated using the rotational isomeric state approximation. Energies of the two crystal forms of PTBD are calculated as functions of structural parameters and it is concluded that *intramolecular* interactions are not sufficient to account for the internal structure of the crystal, but that it is necessary to include *intermolecular* interactions as well.

Experimental Section

The PTBD used was described previously (sample K).^{2a} The specimens used for heat capacity measurements were melt recrystallized single crystals prepared from heptane. Heats and entropies of transition and fusion for such samples were reported^{2b} earlier. Specific heat data were collected in the 50–130° temperature range with a Perkin-Elmer DSC-1B scanning calorimeter using a sapphire reference. This temperature range was divided into four stages in order to minimize the machine base-line drift, which was also measured in each range.

The main geometrical parameters of PTBD used in calculations are shown as



definition of structural parameters

Other relevant parameters are defined as follows, where the values of the angles are based on the experimentally determined structure: $\angle H_i' C_i H_i'' = 109.5^\circ$; $\angle H_i'' C_i C_{i-1} = \angle H_i' C_i C_{i-1} = \angle C_{i-1} C_i H_i' = 108.3^\circ$; $-C-C- = 1.54 \text{ \AA}$; $-C-H = 1.08 \text{ \AA}$; $-C=C- = 1.32 \text{ \AA}$; $=C-H = 1.08 \text{ \AA}$.

The linear monomeric unit, $-CH_2CH=CHCH_2-$, contains four dihedral angles which must be specified. The central double bond of course is fixed at 180° for PTBD. The CH_2-CH_2 single bond has been observed at 180° in both solid-state forms.^{3,4} By symmetry, the two remaining CH_2-CH single bonds must have equal but opposite values, $\pm\omega$, to generate a helical structure. Hence a single parameter, ω , suffices to fix the geometry of the entire PTBD chain. The two crystalline forms of PTBD have dihedral angles, ω , equal to 109° (low temperature), and 80° (high temperature).^{3,4}

Results

Heat Capacity and Entropy Change. The heat capacity, C_p , of two melt recrystallized PTBD single crystal samples is shown in Figure 1 as a function of temperature. C_p rises very quickly at the transition, then drops to a value of about 0.4 cal/(g deg), and rises slowly until the melting point is reached. The entropy change in going from the crystalline solid in form I at the transition temperature to the melt at the final melting temperature can be calculated from the experimental results as follows

$$\begin{aligned} \Delta S_{exp} &= \Delta S_{tr} + \int_{T_{tr}}^{T_m} (C_p/T) dT + \Delta S_m = \\ &= 0.079 + 0.056 + 0.039 \quad (3) \\ &= 0.174 \text{ cal/(g deg)} = 9.38 \pm 1.8 \text{ cal/(mol deg)} \end{aligned}$$

where ΔS_{tr} and ΔS_m are experimental entropies of transi-

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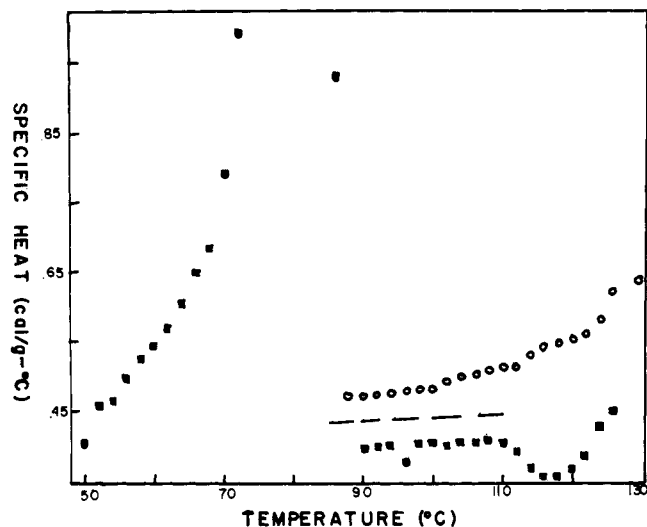


Figure 1. Experimental specific heat as a function of temperature for melt recrystallized PTBD: [■] sample 1; [○] sample 2.

tion and melting, respectively;^{2b} mean values of the experimental C_p values for the two samples studied (see Figure 1) were used to evaluate the above integral. T_{tr} and T_m are 73 and 139°, respectively.

To compute the error in ΔS_{exp} , we have added up the possible errors for the two transitions, plus the relative average deviation of three estimates of S_{90-122° , computed by taking each of two runs independently, plus a pooled data set.

Theoretical Calculation of Entropy of Fusion. A method for calculating the entropy of fusion of a polymer has recently been applied successfully by Tonelli¹⁴ to a variety of polymers, including poly(*cis*-butadiene).

The total entropy of fusion is believed¹⁵ to consist of two contributions, $(\Delta S_V)_{T(tr)}$ the entropy change at constant temperature due to volume expansion, and ΔS_a , the entropy gain due to the increase in conformational freedom. Kirshenbaum¹⁶ has demonstrated several useful approximations to $(\Delta S_V)_{T(tr)}$ for materials whose compressibility and expansion coefficients are not available. In particular, he states that use of $0.18 \Delta V_m$, where ΔV_m is the molar volume change on melting, should lead to errors no greater than 0.2–0.6 cal/(mol deg). Taking the volume change as the increase in the unit cell volume going from low- to high-temperature forms, and using the density data of Natta *et al.*¹⁷ ($V_l = 1.03 \text{ cm}^3/\text{g}$, $V_{II} = 1.08 \text{ cm}^3/\text{g}$), we find 0.43 cal/(deg mol) for $(\Delta S_V)_{T(tr)}$. According to Tonelli,¹⁴ the entropy change ΔS_a due to conformational freedom is calculated by the ordinary thermodynamic formula

$$\Delta S_a = R[\ln Z + (T/Z)(dZ/dT)] \quad (4)$$

where Z is the partition function of the polymer. To evaluate this quantity we employ the rotational isomeric state methods developed by Abe and Flory¹⁸ for PTBD. Some of the details of this calculation are given in Appendix I. By this method, the estimate of ΔS_a near the melting

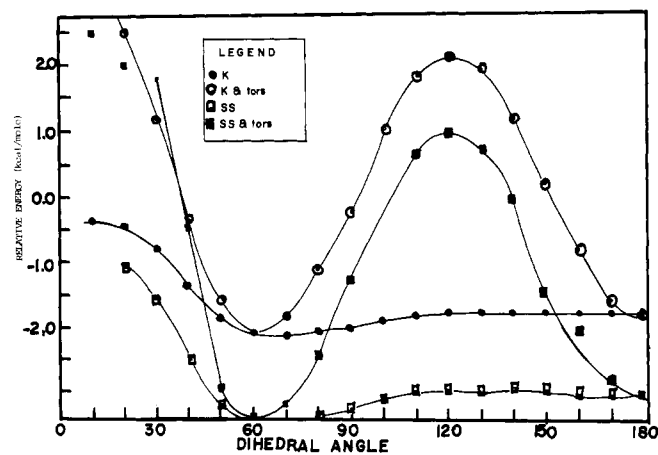


Figure 2. The energy of a single PTBD chain as a function of dihedral angle.

Table I
Calculated Energies of a PTBD Single Chain

Potential Function	Dihedral Angle (deg)	Energy (kcal/mol)
SS (no torsional term)	109	-63.198
	80	-68.001
K (no torsional term)	109	-37.726
	80	-41.781
SS (with torsional term)	109	-13.454
	80	-48.001
K (with torsional term)	109	-36.915
	80	-21.781

point ($T = 139^\circ$) is 5.3 cal/(deg mol). Therefore, the predicted entropy of fusion is $5.7 \pm 0.6 \text{ cal}/(\text{deg mol})$.

Considering first of all the approximation of the volume expansion contribution, ΔS_V , and secondly the fact that a rotational isomeric model by its very nature restricts the number of allowed states, of which the entropy is a measure, the theoretical value is in favorable agreement with experiment.

Single-Chain Energy Calculations. The results of energy calculations for a single PTBD chain 20 monomer units in length as a function of the dihedral angle ω appear in Figure 2. The graph shows that both the Scott and Scheraga (SS) function and the Kitaigorodsky (K) function without the torsional term predict that the chain has a poorly defined minimum energy at a dihedral angle of 60° but that all angles above 60° are energetically easily accessible to the chain. When the torsional term is added, the energy curves then take on a sinusoidal character and energy minima and maxima are clearly defined. The SS and K functions predict minima at 60° and maxima at 120°.

The effect of chain length on single-chain intramolecular energy calculations was studied, using the K function including the torsional term. The results indicated that a 20 monomer unit chain length is sufficient to overcome end effects on the chain energy. The calculated single-chain energies at the dihedral angles found experimentally for the two crystalline forms are of special interest and are given in Table I.

It can be seen that a calculation of the enthalpy of transition using energy values from Table I would yield a negative result, indicating that the low-temperature form is less stable than the high-temperature form, except when a torsional term is added to the K function.

Unit Cell Energy Calculations. Energies were calculated for the PTBD unit cell of the low- and high-temper-

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Table II
Comparison of the Value and Location of the Energy Minima

Potential Function	Temp Form	Lattice Energy (kcal/mol)	Energy of Unit Cell (kcal/mol)	Unit Cell Parameters	
				<i>a</i> (Å)	<i>b</i> (Å)
(a) Monoclinic Lattice and the Unit Cell					
SS	Low	-69.577 ^a	-11.146	8.70	9.60
		-67.544	-11.592 ^a	8.50	9.60
SS	High	-76.017 ^a	-12.146	9.85	8.50
		-75.654	-12.362 ^a	9.85	8.60
K	Low	-40.212 ^a	-6.942 ^a	8.65	9.50
		-39.449	-7.247 ^a	8.45	9.50
K	High	-43.289 ^a	-7.548	9.70	8.50
		-29.33	-8.625 ^a	9.10	8.70
Interchain Distance (Å)					

(b) Hexagonal Lattice and the Unit Cell

K	Low	-41.761 ^a	-7.090	4.60
		-41.559	-7.111 ^a	4.64
K	High	-42.788 ^a	-4.192	4.67
		-38.531	-6.273 ^a	4.94
K	High	-39.411	-6.225	4.90 ^b

^a Energy minima. ^b The experimental data indicate that the high-temperature form does not exist below an interchain distance of 4.90 Å. Thus only the local minimum, not the absolute minimum makes sense experimentally.

Table III
Energy Surface of Monoclinic PTBD Lattice around Minimum Calculated with Kitaigorodsky Function^a

		Low-Temperature Form ^a					High-Temperature Form		
		<i>a</i> → (Å)							
		8.60	8.65	8.70	8.75	8.80			
<i>b</i> ↓ (Å)	9.45	-40.170	-40.179	-40.158	-40.072	-39.920			
	9.50	-40.182	-40.212 ^b	-40.209	-40.126	-40.006			
	9.55	-40.115	-40.184	-40.203	-40.136	-40.020			
	9.60	-39.982	-40.087	-40.109	-40.070	-39.982			
	9.65	-39.820	-39.957	-39.985	-39.965	-39.860			
		9.30	9.40	9.50	9.60	9.70	9.80	9.90	10.00
<i>b</i> ↓ (Å)	8.10	-37.230		-39.288		-39.487		-38.852	
	8.20		-40.188		-41.332		-41.092		-40.323
	8.30	-39.468		-42.008		-42.441		-41.952	
	8.40		-41.501		-42.959		-42.957		-42.281
	8.50	-39.452		-42.559		-43.289 ^b		-42.947	
	8.60			-40.964	-42.881		-43.094		-42.524
8.70	-37.886		-41.610		-42.691		-42.530		

^a Energy in kcal/mole. ^b Energy minimum.

ature forms using the SS and K functions. In these calculations the dihedral angle was fixed and the *a* and *b* unit cell parameters varied. The minimum energies and the corresponding *a* and *b* parameters are given in Table II. The space group and unit cell parameters are not known for the high-temperature form of PTBD. However, it was shown⁴ earlier that in this form each chain is hexagonally surrounded by equidistant chains. Therefore, calculations were also carried out assuming a hexagonal lattice for which the unit cell energy was obtained as a function of interchain distance taking four monomer units per cell. The minimum energies calculated in this manner are shown in Table II.

Energy Calculations for a PTBD Crystal Lattice. Preliminary calculations were carried out on a lattice of 243 cells and a lattice of 125 cells. The energies were

found to be very close, indicating that interactions beyond three nearest neighbors did not appreciably affect the energy. All further calculations were carried out on a lattice of 125 unit cells. The same type of calculations carried out for the unit cell alone were done using the lattice of 125 unit cells. Some results of this minimum energy search appears in Tables III and IV and Figure 3. The tables consist of that portion of the energy surface that surrounds the energy minimum. The minimum energies are also given in Table II for comparison with the unit cell energy values.

The observed *a* and *b* unit cell parameters for the low-temperature form are given³ as *a* = 8.63 Å and *b* = 9.11 Å. The coordinates of the calculated energy minima for both functions are quite close to the experimental value. The lattice constants found by the SS function deviate

Table IV
Energy Surface of Monoclinic PTBD around Minimum Calculated with Scott and Scheraga Function^a

		Low-Temperature Form ^a					
		$a \rightarrow (\text{\AA})$					
		8.50	8.55	8.60	8.65	8.70	8.80
b	9.40			-68.175		-68.293	-67.879
	9.50				-69.293	-69.363	-69.091
\downarrow	9.60	-67.544		-69.041		-69.577 ^b	-69.459
(\AA)	9.70			-68.427		-69.201	-69.252

		High-Temperature Form					
		$a \rightarrow (\text{\AA})$					
		9.70	9.75	9.80	9.85	9.90	10.00
b	8.30			-74.896		-74.607	
	8.40			-75.584		-75.649	
\downarrow	8.50	-75.508		-76.014	-75.804	-75.904	-75.108
(\AA)	8.60		-75.861	-75.591	-75.654		-75.181

^a Energy in kcal/mole. ^b Energy minimum.

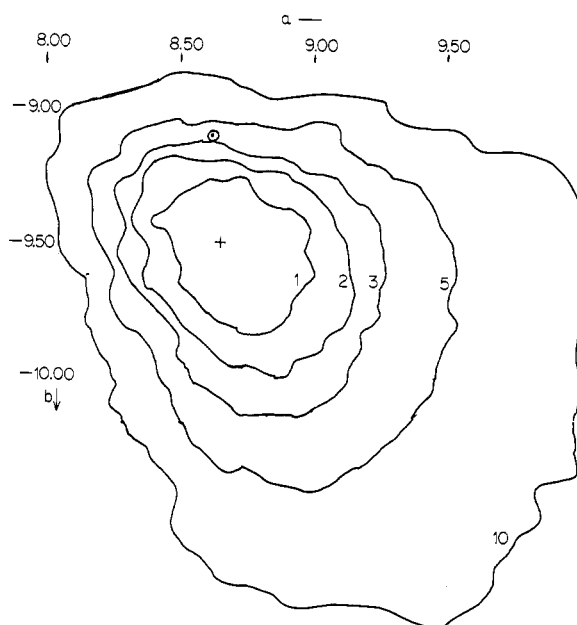


Figure 3. The energy of a monoclinic low-temperature PTBD lattice as a function of the a and b crystallographic parameters, calculated using the Kitaigorodsky potential function.

0.07 \AA for the a constant and 0.49 \AA for the b constant. The deviation of the a constant is 0.07 \AA and the b constant is 0.37 \AA for the minimum energy found with the K function.

Energy calculations were also made for a lattice containing the hexagonal array of chains; the results are given in Figures 4 and 5 for the low- and high-temperature forms, respectively; the minimum energies are given in Table II. From the figures it can be seen that there are clearly defined minima at 4.60 and 4.67 \AA for the low- and high-temperature forms, respectively. The observed interchain distance for the low-temperature form is the same as that found in the computer fit. The observed value⁴ for the high-temperature form of 4.90 \AA , however, deviates considerably from the fitted one.

Upon comparison of the values in Table II, it is seen that the energy of the lattice represents a structure that is well over six times as stable as the structure corresponding to the minimum value calculated for the unit cell. When the energy of the unit cell is compared with the energy calculated for four single chains, it is seen that the unit cell is in turn far more stable than the sum of the energies of the four chains, as shown in Table V.

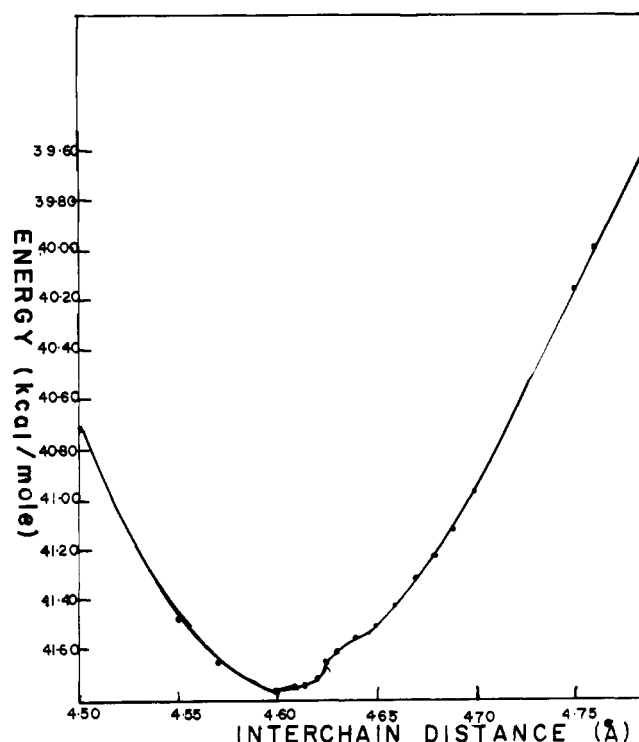


Figure 4. Energy of a hexagonal low-temperature PTBD lattice as a function of interchain distance calculated using the Kitaigorodsky potential function.

In the hexagonal lattice calculation the minimum energy for the unit cell in the high-temperature form occurs at an interchain distance of 4.94 \AA while the minimum for the lattice is at 4.67 \AA (see Table II). Thus, unlike the lattice, the coordinates of the minimum for the unit cell are very close to the experimentally observed interchain distance.⁴ The heat of transition calculated from the hexagonal lattice data given in Table II is in reasonable agreement with experiment. The difference between the energy minimum of the low-temperature form and the energy of the lattice at 4.90 \AA , the experimental interchain distance, is equal to 43.5 cal/g. If one uses the energy of the lattice at the coordinates of the calculated energy minimum for the unit cell (4.97 \AA), the heat of transition is found to be 59.8 cal/g. The heat of transition found experimentally^{2b} for melt recrystallized PTBD was 27 cal/g.

Calculation of Heat Capacity. In order to get a theoretical estimate of the heat capacity, it is necessary to

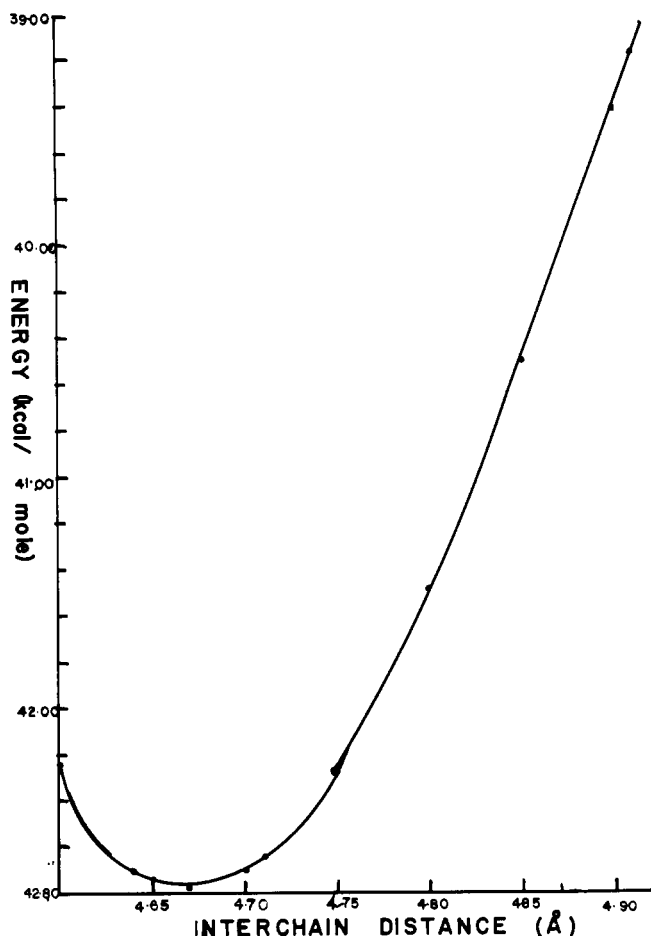


Figure 5. Energy of a hexagonal high-temperature PTBD lattice as a function of the interchain distance calculated using the Kitaigorodsky potential function.

know the lattice energy as a function of temperature. The lattice energy as a function of the interchain distance given in Figures 3 and 4 can be converted to plots of energy *vs.* temperature, through use of the X-ray crystallography data of Suehiro and Takayanagi.⁴ The results of this transformation are given in Figure 6. The high-temperature portion of curve is linear, and its slope, the heat capacity, C_V is 0.13 cal/(g deg). This differs from the experimental C_p value by about 0.3 cal/(g deg).

Discussion

The entropy change, calculated using the isomeric state approximation is that for a perfect crystal going to the melt. Since final melting of PTBD takes place from the highly disordered high-temperature form,⁴ it is not expected that ΔS_{calcd} will equal ΔS_m . However, ΔS_{calcd} should agree with the entropy change on taking the crystal from the low-temperature form at the transition temperature to the melt *via* the high-temperature form. As noted above, it is found that ΔS_{calcd} underestimates the entropy change by a factor of two. Therefore, a single-chain model suffices to approximate a statistical property such as the entropy.

On the other hand the single-chain model is not sufficient for calculation of the energy. Even when torsional energy terms are included, the conformations predicted to be the most stable are not those found experimentally for the crystal lattice. If the energy is calculated taking intermolecular interactions into account, then the unit cell parameters which are found at the energy minimum for the low-temperature form are in close agreement with those from X-ray analysis. This close agreement for form I indi-

Table V
Calculated Energies of a Unit Cell and Four Single Chains

Function	Min Energy Unit Cell (cal/g)	Energy of Four Chains (cal/g)
Low Temperature		
SS	-11.592	-4.618
K	-7.247	-2.602
High Temperature		
SS	-12.363	-5.041
K	-8.625	-2.887

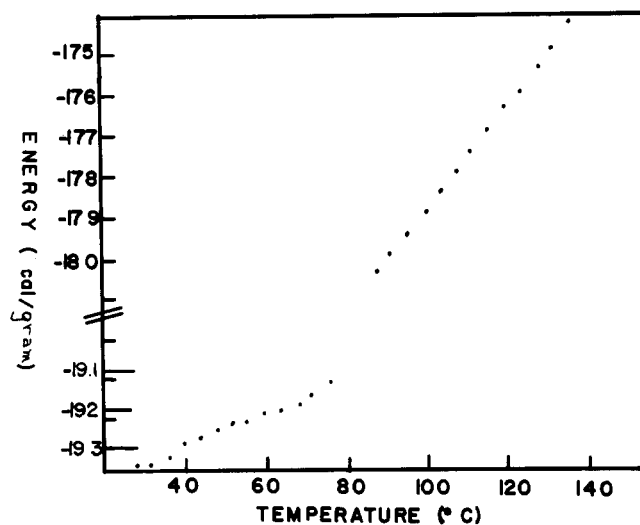


Figure 6. Energy as a function of temperature for PTBD.

cates that the potential energy function may be used with confidence to study other properties. Why then does it not appear to predict the structure of form II? One possibility is simply that the proposed structure of form II is incorrect (*i.e.*, some other set of internal angles exists which give the same repeat distance of 4.67 Å). What is more likely is the following. The conformation of the macromolecules at equilibrium is that for which the free energy is a minimum. But the free energy, ΔG , has two thermodynamic components, the enthalpy, ΔH , and entropy, $T\Delta S$. Minimizing the potential energy deals only with the enthalpic contribution to the free energy while totally ignoring the entropic term. This contribution, as experimental results show,^{2,19} is quite large and certainly not negligible, when form II is considered. Thus it is necessary to examine the entropy itself, and also the heat capacity, which measures the accessibility of conformational states of the polymer.

The difference of 0.28 cal/(g deg) or 60 cal/(mol deg) between theoretical and experimental heat capacity-temperature plots suggests that about two-thirds of the heat capacity of the high-temperature form is due to lattice motions. If, as a first approximation, one uses the law of Dulong and Petit for an estimate of the heat capacity due to lattice motions, about 54 cal/(mol deg) are left for low-energy vibrations. The Dulong-Petit value of 6 cal/(mol deg) is an estimate for monatomic crystals and probably underestimates the energy of the modes of a polymer lattice. However, the approximate value of 54 cal/(mol deg) indicates the probability of finding several chain vibrations below 200 cm^{-1} in the far-ir spectrum.

The fact that the Kitaigorodsky function accurately predicted the interchain distance of form I indicates that

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it is a "good" energy function for the system, and that models can be inferred from these calculations with reasonable confidence. Using the K function, minimum energies for a monoclinic and a hexagonal lattice were calculated, and the difference in energies for these structures is 1.549 kcal/mol for form I and 0.501 kcal/mol for form II. In the case of the high-temperature form, the difference in energy is less than kT at experimental temperatures, indicating that both forms are energetically accessible in the crystal, and justifying our use of the Suehiro-Takayanagi temperature data in constructing our energy-temperature plots.

The energy minima for PTBD are actually quite shallow in comparison with other materials for which lattice energy minimizations such as these have been performed. For example, Ahmed, Kitaigorodsky, and Mirskaya¹² calculated the energies of tetraphenyltin as a function of two orientation parameters and observed that a change in only 0.39 Å in one lattice parameter gave rise to a 10-kcal/mol energy change near the minimum. Tetraphenyltin, as well as many other molecules, has a much deeper energy well than does PTBD.

The shallowness of the energy well indicates that PTBD has considerable freedom of motion, even at the configuration corresponding to the potential minimum, because the energy barriers between configurations are comparatively low. Thus even with an energy difference of about $2kT$ for form I, both the hexagonal and monoclinic structures are energetically accessible, and much interconversion between these forms and various other configurations can be expected. This could explain the "pseudohexagonal" crystal structure attributed to PTBD in the X-ray investigation. It could also explain the difficulty in obtaining a specific crystallographic space group for the high-temperature form. The interconversion between the two lattices may be so great as to make it extremely difficult to obtain a clear pattern.

We conclude the following. The calculated minimum energy configuration for form I coincides with the observed X-ray structure. Increasing the temperature of form I leads to an increase in interchain distance and intramolecular conformational freedom. Above the solid-solid transition temperature, the possibilities of many different configurations of approximately equal energy leads to a variety of conformations for the individual chains. Mandelkern¹⁵ has pointed out that "hexagonal packing allows a greater amount of rotational freedom about the chain axis and thus an increased entropy in the crystalline state." This is in fact what is observed for PTBD. This large increase in entropy contributes a major portion of the crystalline free energy, and explains the fact that minimization of ΔH (rather than ΔG) cannot predict the molecular structure for form II. However, the entropy change is approximated by a rotational isomeric state (single-chain) calculation.

Appendix I

The partition function for a chain of x butadiene units, $\text{CH}_3\text{CH}=(\text{CHCH}_2\text{CH}_2\text{CH}=\text{CH})_{x-1}\text{CHCH}_3$, is given by

$$Z = \prod_{k=1}^{x-1} z_k^{(4)} = (z^{(4)})^{x-1} \quad (5)$$

where $z^{(4)}$ is the partition function for a single unit consisting of four bonds: $[\text{CHCH}_2\text{CH}_2\text{CH}=\text{CH}]$. Consideration of rotational isomerism about each of the four bonds within

the unit leads to assignment of statistical weights, ρ , β , and σ , related to the relative conformational energies by expressions such as $\rho = \exp(-E_\rho/RT)$. E_ρ is the energy difference between skew and cis forms of the single bonds adjacent to the double bonds. E_σ is the amount by which the gauche conformation exceeds trans about the central bond, and E_β is the energy factor bias against $\text{Cg}\neq\text{C}$ conformations, corresponding roughly to E_w in alkanes.¹⁸ In view of experimental results and prior computational successes, Abe and Flory¹⁸ assigned the values: $E_\sigma = 0$ -200 cal/mol, $E_\rho = 300$ cal/mol, and $E_\beta = 2000$ cal/mol. The unit partition function is then equal to

$$z^{(4)} = U_a U_b U_c U_d \quad (6)$$

where

$$U_a = [\rho \ 1 \ 1] \quad (7)$$

$$U_b = \begin{bmatrix} 1 & 0 & 0 & \sigma & 0 & 0 & \sigma & 0 & 0 \\ 0 & 1 & 0 & 0 & \sigma & 0 & 0 & \sigma & 0 \\ 0 & 0 & 1 & 0 & 0 & \sigma & 0 & 0 & \sigma \end{bmatrix} \quad (8)$$

$$U_c = \begin{bmatrix} \rho & 1 & 1 \\ \rho & 1 & 1 \\ \rho & 1 & 1 \\ \rho\beta & \beta & \beta \\ \rho\beta & 1 & 1 \\ \rho\beta & 1 & 1 \\ \rho\beta & \beta & \beta \\ \rho\beta & 1 & 1 \\ \rho\beta & 1 & 1 \end{bmatrix} \quad (9)$$

$$U_d = \begin{bmatrix} 1 \\ 1 \\ 1 \end{bmatrix} \quad (10)$$

To calculate $z^{(4)}$, we multiply out the matrices and obtain

$$z^{(4)} = (2 + \rho)^2 + 2\sigma(4 + 4\rho\beta + \rho^2\beta) \quad (11)$$

The temperature derivative for a single unit is then

$$RT^2 \frac{dz^{(4)}}{dT} = 2(2 + \rho)\rho E_\rho + 2[\sigma\rho\beta[4(E_\sigma + E_\rho + E_\beta) + \rho(3E_\rho + E_\beta)] + 4\sigma E_\sigma] \quad (12)$$

and that for the polymer is

$$dZ/dT = (x - 1)[z^{(4)}]^{x-2} dz^{(4)}/dT \quad (13)$$

Finally, eq 5 and 13 are evaluated and the resulting values of Z and dZ/dT substituted into eq 4 for the conformational entropy change. In the computer program, the number of monomer units is increased in successive calculations until ΔS_a does not change with increased x .

The value of ΔS_a thus found was 5.68 eu/mol, with $E_\sigma = 0$; increasing E_σ to 200 cal/mol changed ΔS_a by less than 0.02 eu/mol. Because the low-temperature form ($\omega = 108^\circ$) differs from the energy minimum for a single chain by 0.171 kcal/mol, a zero-point entropy correction term of $171/412 = 0.42$ eu/(mol monomer unit) is to be subtracted, giving $\Delta S_a = 5.26$ eu/mol.