Conformational and packing energy calculations on the two crystalline modifications of poly (*trans*-1,4-butadiene)

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Conformational and packing energy calculations have been performed on the two crystalline modifications of poly(*trans*-1,4-butadiene), and the results have been compared with experimental data. The conformational energy calculations predict the chain axis and conformation of the modification that is stable below 76°C, without any *a priori* assumption. Packing energy calculations on this modification show that the best space group is $P2_1/a$ and the position of the chains is in good agreement with X-ray data. Conformational energy calculations on the modification that is stable above 76°C predict that the lowest energy conformation is a statistical sequence with a random distribution of the three minimum torsion angles around the single bonds adjacent to the double bond, with a *trans* conformation around the other single bond.

(Keywords: conformational calculations; packing energy; poly(*trans*-1,4-butadiene); crystal structure; potential functions)

INTRODUCTION

The role of intra- and intermolecular interactions in determining the conformation and mode of packing of various crystalline polymers has been shown in previous papers[1-5]. Some of the present authors have already performed conformational and packing energy calculations on three of the four crystalline polymers of 1,3-butadiene, isotactic[6] and syndiotactic[7] 1,2-poly(1,3-butadiene) and poly(*cis*-1,4-butadiene)[8]. In this paper, we extend these calculations to poly(*trans*-1,4-butadiene) (PTBD).

Two crystalline modifications of PTBD were found and studied[9,10]. One of them (LT) is stable at temperatures below 76°C; the other (HT) is stable at higher temperatures. The transformation between the two modifications is a reversible solid–solid transition. The complete crystal structure of the LT modification was reported by Iwayanagi *et al.*[11]: the unit cell is monoclinic with $a = 8.63$ Å, $b = 9.11$ Å, $c = 4.83$ Å, $\beta = 114°$, and the proposed space group is $P2_1/a$. A structural study on the HT modification reported by Suehiro and Takayanagi[12] shows that the crystal lattice is hexagonal with $a = 4.95$ Å and $c = 4.66$ Å. The purpose of this paper is to compare the crystal structures of the two modifications of PTBD with the predictions of conformational and packing energy calculations.

CONFORMATIONAL CALCULATIONS

The conformational energy E_{conf} has been calculated as the sum of three terms:

$$E_{\text{conf}} = E_{\text{tor}} + E_{\text{ben}} + E_{\text{nb}} \qquad (1)$$

Here

$$E_{\text{tor}} = (E_0/2)(1 \pm \cos 3\theta) \qquad (2)$$

represents the contribution of torsional potential energy around single bonds with E_0 the barrier height,

$$E_{\text{ben}} = (k/2)(\tau - \tau_0)^2 \qquad (3)$$

represents the energy contribution due to bond angle deformation and k is the corresponding force constant, and

$$E_{\text{nb}} = Ar^{-12} - Br^{-6} \qquad (4)$$

is the energy contribution due to the interactions between atoms separated by more than two bonds. Parameters for the energy terms are from *Flory et al.*[13-15] and are reported in *Table 1*. Force constants k for the bending at the C_{sp^2} carbon atom are reported by Zerbi and Gussoni[16]. The calculations have been performed for the portion of polymer chain reported in *Figure 1*, imposing the equivalence principle[17] to configurational repeating units (CRUs)[18].

In order to find low-energy conformations, we have obtained preliminary maps as a function of the torsion angles θ_1 and θ_2, for θ_3 values corresponding to those of torsional minima (i.e. 180° and ±60°). Bond angles were fixed to the values $\tau_1 = \tau_4 = 111°$ and $\tau_2 = \tau_3 = 127°$. The hydrogen atom bonded to C_{sp^2} was fixed in such a way to bisect the concave C—C=C angle; a C_{2v} local symmetry was assumed on the C_{sp^3} atom. *Figure 2a* shows the map of the conformational energy of PTBD for $\theta_3 = 180°$. *Figure 2b* shows the corresponding map for $\theta_3 = 60°$. The map obtained for $\theta_3 = -60°$ is symmetric with respect to that of *Figure 2b*. The map of *Figure 2a* shows three non-equivalent minima: two of them are almost isoenergetic and correspond to the chain conformations†

(a) $(A^+ \; trans \; A^+ \; T)_n \equiv (A^- \; trans \; A^- \; T)_n$

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† The definitions of A, T and C are according to ref. 18.

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Table 1 Parameters used in the enefgy calculations

Bond angle	k (kJ mol^{-1} deg^{-2})	τ_0 (deg)
C_{sp^3}–C_{sp^3}–C_{sp^2}	0.184	109.47
C–C_{sp^3}–H	0.121	109.47
H–C_{sp^3}–H	0.100	109.47
C_{sp^3}–C_{sp^2}–C_{sp^2}	0.174	125
C_{sp^2}–C_{sp^2}–H	0.101	117.5
C_{sp^3}–C_{sp^2}–H	0.098	117.5

Torsion angle	E_0 (kJ mol^{-1})	Sign in equation (2)
C–C–C–C	11.7	+
C–C–C=C	4.2	–

Interacting pair	$A\times10^{-3}$ (kJ mol^{-1} Å^{12})	B (kJ mol^{-1} Å^6)	Σr_w[a] (Å)
C_{sp^3}, C_{sp^3}	1666.4	1532	3.60
C_{sp^3}, C_{sp^2}	2595.9	1867	3.75
C_{sp^3}, H	238.7	536	3.10
C_{sp^2}, C_{sp^2}	4065.6	2311	3.90
C_{sp^2}, H	393.6	666	3.25
H, H	30.6	197	2.60

[a] Σr_w represents for a given pair of atomic species the sum of the van der Waals radii assumed to minimize the corresponding E_{nb}

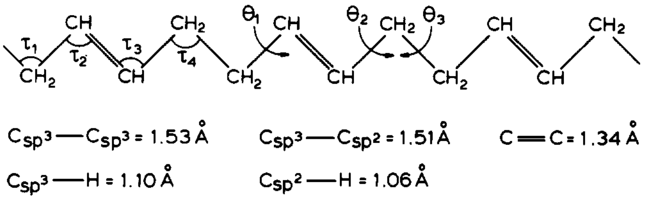

Figure 1 Portion of the chain of PTBD used for the conformational energy calculations. The bond lengths and the parameters kept variable during the minimization are also indicated

and

(b) $(A^-\ trans\, A^+\ T)_n \equiv (A^+\ trans\, A^-\ T)_n$

The other minimum, corresponding to the chain conformation

(c) $(C\ trans\, A^+\ T)_n \equiv (C\ trans\, A^-\ T)_n \equiv$
$(A^+\ trans\, C\ T)_n \equiv (A^-\ trans\, C\ T)_n$

is higher in energy. The map of *Figure 2b* shows three non-equivalent minima, the lowest being isoenergetic with the absolute minimum of *Figure 2a*.

Starting from the three non-equivalent minima of *Figure 2a*, we have optimized the internal energy with respect to all the bond angles (maintaining the local C_{2v} symmetry on the methylenic groups) and torsion angles. A subroutine developed by Buzzi Ferraris[19] was used as in our previous papers[4–8] in order to optimize the energy. The resulting minimum energy conformations of the polymer chain correspond to the line repetition groups[18] $s(M/N)2$, ti, $s(M/N)$ for the conformations (a), (b) and (c), respectively. The differences in energy between the three minima remain substantially unchanged with respect to those of the maps. Only the conformation (b) has a chain axis ($c = 4.85$ Å) equal to that found experimentally. The conformations (a) and (c), as well as those corresponding to the minima of the map of *Figure 2b*, give helical symmetries not found experimentally. The results of the minimizations are reported in *Table 2*. The value of the torsion angle θ_1 ($= -\theta_2$) in the minimum energy conformation (b) is $-117°$, in better accordance with the value* $\phi = 60°$ rather than $\phi = 71°$, both proposed by Iwayanagi *et al.*[11].

Moreover, we have investigated the possibility of reproducing a polymer chain having a c axis equal to 4.66 Å, as found in the HT modification. We have

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* In paper 11, ϕ is defined as $\phi = 180° - |\theta|$.

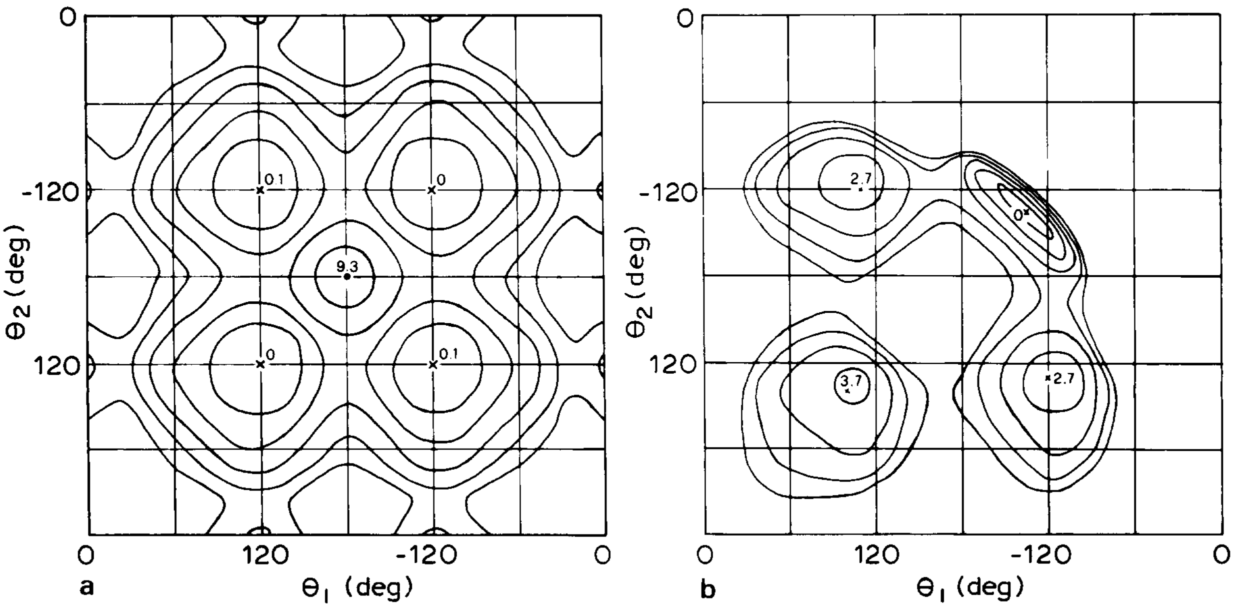

Figure 2 Map of the internal energy of PTBD as a function of θ_1 and θ_2 for (a) $\theta_3 = 180°$ and (b) $\theta_3 = 60°$. The curves are reported at intervals of 2 kJ mol^{-1} CRU with respect to the absolute minima of the maps assumed as zero

therefore optimized the energy of the isolated chain under the constraint of maintaining the experimental *c* axis. The resulting energy is ~3.5 kJ mol^{-1} CRU higher with respect to the minimum of the conformation (b). The angle θ_1 $(=-\theta_2)$ is $-91°$ and the bond angles of the main chain are $\tau_1=109.1°$ and $\tau_2=124.6°$, slightly lower than those generally found in analogous polymers. On the other hand, an energy calculation performed using the parameters reported by Suehiro and Takayanagi[12] gives an energy ~8.5 kJ mol^{-1} CRU higher than that of conformation (b).

Considering the three non-equivalent minima of the map of *Figure 2a*, it is possible to observe that a statistical sequence of torsion angles θ_1 and θ_2 produces a polymer chain sufficiently extended to be easily packed, provided the double bonds are *trans* and the torsion angle θ_3 is consistently in the *trans* conformation. The chain axis would be nearly the average of the distances between the carbon atoms at the end of the CRUs, which are 4.84 Å for the four conformations of the kind (a) and (b), and 4.48 Å for the four conformations of the kind (c), respectively. The value of the chain axis is in good agreement with that found experimentally for the HT modification and the energy resulting from the average of the single conformation energies is ~2.5 kJ mol^{-1} CRU higher with respect to that of conformation (b). These results are in accordance with the model proposed by Corradini[20] and with the X-ray spectrum of the HT modification, which is very diffuse[12].

PACKING ENERGY CALCULATIONS

The packing energy calculations have been performed on the LT modification of PTBD using the same set of potential functions as in the conformational energy calculations. The energy has been calculated as one-half of the sum of the nonbonded interactions between the atoms of one CRU and the atoms of all the surrounding chains within spheres having radii twice the van der Waals distance for each pair of atoms. The minimum energy conformation chain, as obtained in the conformational calculations, has been packed in the space groups $P2_1/a$, $P2_1/c$ and $P2_1/n$, which are those examined in the X-ray structure analysis. We have used as variables the parameters that determine the relative positions of the chains in the unit cell for each space group considered; they are defined in *Figure 3*. Preliminary maps of the packing energy as a function of ω and Z were obtained for $X=0.25$ and $Y=0.125$, with the purpose of delimiting the region of low energy. The maps of packing energy for the space groups $P2_1/a$ and $P2_1/n$ are reported in *Figures 4* and *5*, respectively. For the space group $P2_1/c$ the packing energy is always high when $X=0.25$ and $Y=0.125$, but low energies are found for values of Y very close to 0. The lowest energy is ~5 kJ mol^{-1} CRU higher with respect to the minimum of the map of *Figure 4* and the corresponding mode of packing is not pseudohexagonal as is the experimental one. The optimization of the packing energy as a function of the four previously defined parameters has been effected starting from the different low-energy regions of the maps, and using the same method of minimization as for the conformational energy calculations. In *Table 3*, we report the values of the variable parameters and the energies obtained in the optimizations for the three space groups examined. The lowest energy value is reached for the space group $P2_1/a$, that is the experimental one, and the position of the chains in the unit cell is in good agreement with that obtained by X-ray analysis, as reported in *Table 4*.

DISCUSSION

The conformational energy calculations performed on the isolated chain of PTBD show that the best conformation in the crystalline field can be predicted. The minimum energy conformation reproduces without any constraint the experimentally observed *c* axis for the LT modification, the internal parameters being very similar to those which give a best fit with the structure factors reported by Iwayanagi *et al.*[11].

The chain conformation of the HT modification is in better accordance with a random distribution of sequences ... *C trans* $A^{\pm}$ *T*... and ... $A^{\pm}$ *trans* $A^{\pm}$ *T*... rather

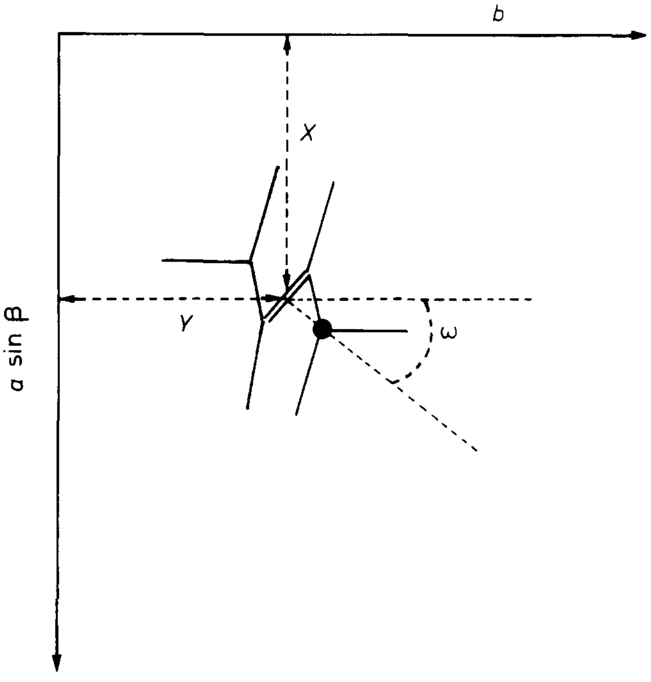

Figure 3 Definition of the parameters kept variable during the packing energy calculations with the projection along the *c* axis of the LT modification chain of PTBD in the unit cell. Z is the height of the carbon atom indicated with ●. *X* and *Y* are expressed in this paper as fractional coordinates

Table 2 Minimum energy conformations with corresponding internal energy and parameters for the isolated chain of PTBD

Chain conformation	τ_1 (deg)	τ_2 (deg)	τ_3 (deg)	τ_4 (deg)	θ_1 (deg)	θ_2 (deg)	θ_3 (deg)	Energy (kJ mol^{-1} CRU)
(a) $(A^+$ *trans* A^+ $T)_n$	110.3	126.0	–	–	116	–		−3.3
(b) $(A^-$ *trans* A^+ $T)_n$	110.3	126.0	–	–	−117	–		−3.1
(c) $(C$ *trans* A^+ $T)_n$	110.3	125.7	128.3	113.7	1	116	180	1.6

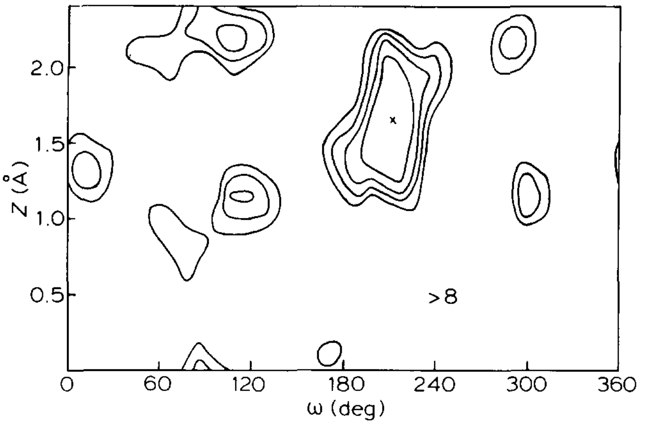

Figure 4 Map of the packing energy for the LT modification of PTBD in the space group $P2_1/a$, as a function of ω and Z. The curves are reported at intervals of 2 kJ mol^{-1} CRU with respect to the absolute minimum of the map assumed as zero and indicated with ×

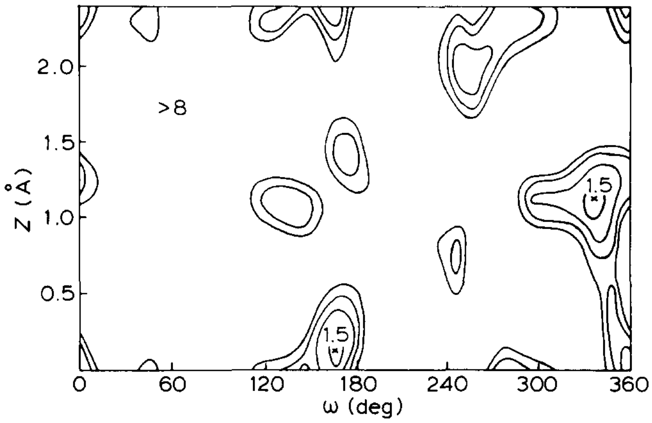

Figure 5 Map of the packing energy for the LT modification of PTBD in the space group $P2_1/n$, as a function of ω and Z. The curves are reported at intervals of 2 kJ mol^{-1} CRU with respect to the absolute minimum of the map of *Figure 4*

Table 3 Packing energy and values assumed by the variable parameters at the points of minimum energy for the space groups examined for the LT modification of PTBD

Space group	Energy (kJ mol^{-1} CRU)	ω (deg)	X	Y	Z (Å)
$P2_1/a$	−31.6	213	0.250	0.126	1.75
$P2_1/n$	−30.2	164	0.256	0.124	0.13
$P2_1/c$	−26.7	167	0.250	0.001	1.74

Table 4 Experimental fractional coordinates of the asymmetric unit and setting angle (defined in ref. 11) for the LT modification of PTBD in comparison with those obtained in our calculations for the space group $P2_1/a$

	Experimental			Calculated		
	x	y	z	x	y	z
C(1)	0.208	0.186	0.826	0.211	0.177	0.828
C(2)	0.288	0.145	0.161	0.290	0.148	0.164
C(3)	0.205	0.106	0.331	0.209	0.103	0.332
C(4)	0.283	0.062	0.673	0.288	0.074	0.667
Setting angle (deg)		120			123	

than with a regular sequence $(A^- \textit{trans}\ A^+\ T)_n$. The first is lower in energy and in better accordance with the very diffuse X-ray spectrum; moreover its cylindrical hindrance fits the observed hexagonal packing better. A statistical succession of different conformations has already been found in the crystal structure of poly(*cis*-1,4-isoprene)[21] and poly(methyl sorbate)[22]. It is interesting to observe that in these polymers, as in PTBD, the statistical succession concerns the single bonds adjacent to the double bond. In fact, the three torsional minima are easily accessible for these bonds, due to the relatively low energy barriers.

The packing energy calculations show that the lowest-energy space group for the LT modification of PTBD is $P2_1/a$, as given by the X-ray structure. For this space group, there are many low-energy regions corresponding to different physical situations, as shown in *Figure 4*. The absolute minimum is only 3 kJ mol^{-1} CRU lower than the others and its physical situation corresponds to that obtained by X-ray analysis. This means that even small differences in the packing energy are quite significant.

These results confirm that the methods of conformational analysis are helpful in the interpretation of experimental data and are effective in predicting the crystal structure of polymers.

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