studies of ionomers functionalized by various complex metal salts with organic amine should serve to give us new information on the structure and properties of ionic clusters and are in progress in our laboratory.

Registry No. (EMAA·Zn)·BAC, 108644-30-0.

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Conformational and Packing Energy Calculations on Crystalline Isotactic 1,4-*trans*-Poly(2-methylpentadiene)

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ABSTRACT: Conformational and packing energy calculations have been performed on isotactic 1,4-*trans*-poly(2-methylpentadiene) in the crystalline field. The results have been compared with experimental structure by powder X-ray diffraction. Conformational energy calculations show that only one conformation is compatible with the experimental chain axis repeat. Packing energy calculations show that the best space group is $P2_1/a$, in agreement with experimental crystal structure. The results indicate that conformational polymorphism should not be observed for the studied polymer.

Introduction

The crystal structure of isotactic 1,4-*trans*-poly(2-methylpentadiene) (PMPD) has been recently determined through best fitting of the X-ray diffraction powder profile by Brückner et al.[1] The proposed unit cell is monoclinic, space group $P2_1/c$, with a = 4.819 Å (chain axis), b = 9.186 Å, c = 12.891 Å, β = 93.5°, and d_{RX} = 0.96 g·cm^{-3} (Z = 4). The authors have also outlined the convenience of the analysis of X-ray diffraction data from polymer powders when obtaining oriented fibers is problematic. On the other hand, in the case of isotactic 1,4-*trans*-poly(1,3-pentadiene) (ITPP), a polymer having the same configuration and a constitution like that of PMPD, two different conformations of the polymer chain have been proposed in the crystal structures determined by X-ray analysis of oriented and unoriented samples.[2,3]

An effective approach to the determination of the structure of polymers is provided by conformational and packing energy calculations. Predictions of the conformation and of the packing stability of the chains have been performed by energy calculations for various crystalline polymers.[4-9] Also predictions of the conformation and of the crystal structure of polymers having double bonds in the main chain have been reported.[10-16] Recently conformational and packing energy calculations have been performed on ITPP[17] with the aim of elucidating the above-mentioned disagreement between the proposed X-ray structures.

The purpose of this paper is to find the most stable crystal structure of PMPD by energy calculations starting from the experimental values of the axes of the unit cell[1] and to compare the results with those obtained by X-ray analysis. The theoretical approach seems to be particularly interesting in the case of PMPD for which, at variance with ITPP, results of X-ray study on oriented fibers have not been reported nor has conformational polymorphism been found.

Conformational Energy Calculations

The conformational energy calculations have been performed on the portion of polymer chain reported in Figure 1, applying the equivalence postulate[18] along successive constitutional repeating units (CRUs) with the aim of obtaining results representative of the polymer chain in the crystalline field. The parameters for the calculations of the bending energies, torsional energies, and nonbonded interactions are those of Flory et al.,[19-21] with the exception of the force constants for the bending at the C_{sp^2} carbon atoms which have been taken from Zerbi and Gussoni.[22] As far as the nonbonded interactions are concerned, each methyl group has been considered as a single interacting atom. The intrinsic torsional potential has been taken into

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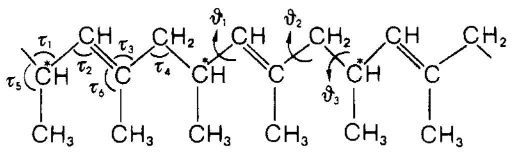


Figure 1. Portion of the chain of PMPD used in the conformational energy calculations, with indication of bond and torsion angles kept variable during the minimizations. Torsion angles ϑ_i are defined with respect to the main chain. C^* indicates asymmetric carbon atoms.

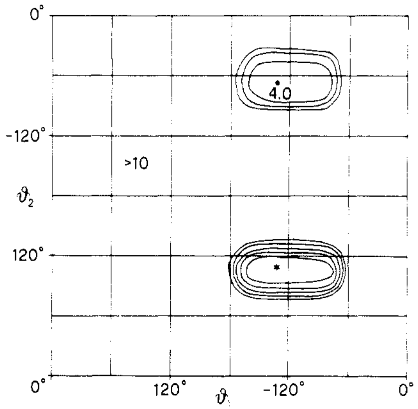


Figure 2. Map of the conformational energy of PMPD as a function of torsion angles ϑ_1 and ϑ_2. The curves are reported at intervals of 2 kJ·(mol of CRU)$^{-1}$ with respect to the absolute minimum assumed as zero and indicated by an asterisk.

Table I
Bond Lengths and Bond Angles Used in the Calculations of the Conformational Energy Map of PMPD

bond lengths, Å		bond angles			
C—C	1.53	C—$\hat{\mathrm{C}}$—C	111.0°	C—$\hat{\mathrm{C}}$—H	109.5°
C=C	1.34	C—$\hat{\mathrm{C}}_{sp^2}$—CH$_3$	115.0°	C—$\hat{\mathrm{C}}$(CH$_3$)—H	107.9°
C—H	1.10	C=$\hat{\mathrm{C}}$—C	127.0°	C=$\hat{\mathrm{C}}$—H	116.5°
		C=$\hat{\mathrm{C}}$(CH$_3$)—C	125.0°	H—$\hat{\mathrm{C}}$—H	108.9°
		C=$\hat{\mathrm{C}}$—CH$_3$	120.0°		

account by using threefold functions with energy barriers of 11.7 and 4.2 kJ·mol^{-1} for the rotations around skeletal —C$\curvearrowright$C— and —C$\curvearrowright$C= torsion angles, respectively. This set of potential functions, already used in previous papers,[9,12-17] has always given results in excellent agreement with experimental data both for vinyl and for diene polymers.

A preliminary map as a function of the torsional angles ϑ_1 and ϑ_2 has been calculated with the purpose of finding low-energy regions in the conformational energy multidimensional surface. In the calculation of the map, bond lengths and bond angles have been fixed at the values reported in Table I. In order to obtain chain conformations sufficiently extended to be easily packed for each pair of values of ϑ_1 and ϑ_2, the ϑ_3 value has been fixed at 180° (trans conformation) as has also the double bond (trans configuration). The asymmetric carbon atom has been chosen as having an S configuration. (If the asymmetric carbon atom has an R configuration the corresponding enantiomorphous (and therefore isoenergetic) conformations are obtained.)

Figure 2 shows the map of the conformational energy as a function of ϑ_1 and ϑ_2. The two minima of the map correspond to values of ϑ_1 and ϑ_2 near some of their torsional minima (anticlinal conformations[23]).

The greater steric hindrance of methyl groups with respect to hydrogen atoms causes the lack of the other conformational minima corresponding to torsional minima of the angles ϑ_1 and ϑ_2. This effect is apparent in the series of the following polydienes with 1,4 enchainment having the double bond in trans configuration: poly(*trans*-1,4-butadiene) (TPB) (having no lateral methyl group), poly(*trans*-1,4-isoprene) (TPI) (having a methyl group bonded to a C$_{sp^2}$ atom), ITPP (having a methyl group bonded to a C$_{sp^3}$ atom), and PMPD (having both a methyl group bonded to a C$_{sp^2}$ atom and a methyl group bonded to a C$_{sp^3}$ atom). Moreover, as far as ITPP and PMPD are concerned, some conformational minima are displaced from the torsional minima A toward G conformations. Table II shows the minimum-energy conformations and the corresponding energy values obtained by the maps for the above-mentioned polydienes.

Table II
Minimum-Energy Conformations and Corresponding Energy Values for Four Polydienes with 1,4 Enchainment[a]

	energy			
conformation	TPB[16]	TPI[16]	ITPP[17]	PMPD
A$^-$ (trans) A$^-$ T	0.0	0.0	1.2	
A$^-$ (trans) A$^+$ T	0.2	0.2	0.0	0.0
C (trans) A$^+$ T	5.6	6.0	5.5	
A$^+$ (trans) C T	5.6			
A$^-$ (trans) G$^-$ T				4.0
G$^+$ (trans) A$^+$ T			4.3	

[a] The conformations are referenced to successions of dihedral angles ϑ_1, (trans), ϑ_2, ϑ_3. For each polymer the energy values, reported in kJ·(mol of CRU)$^{-1}$, are referenced to the absolute minimum assumed as zero.

Table III
Values of the Conformational Parameters and Energy Obtained in the Minimization of the Conformational Energy of PMPD[a]

$\tau_1 = 111.2°$	$\tau_2 = 128.3°$	$\tau_3 = 124.3°$
$\tau_4 = 110.9°$	$\tau_5 = 112.5°$	$\tau_6 = 121.3°$
$\vartheta_1 = -100.7°$	$\vartheta_2 = 102.1°$	$\vartheta_3 = 176.0°$

energy = −1.8 kJ·(mol of CRU)$^{-1}$

[a] The energy value is referenced to the absolute minimum of the map of Figure 2.

The minimization of the conformational energy as a function of all the torsion angles (except that around double bond) and bond angles (with the assumption of a local symmetry C_{2v} on the methylene groups) has been effected by using an optimization routine developed by Buzzi Ferraris.[24] The minimization has been performed under the constraint of maintaining the experimental value of the chain axis (4.819 Å), starting from the absolute minimum of the map of Figure 2. The other minimum of the map has been neglected as it corresponds to a chain conformation having an axis repeat very far from the experimental value. The values of the optimized conformational parameters and the corresponding energy are reported in Table III.

Packing Energy Calculations

The packing energy has been evaluated as half of the sum of the nonbonded interactions between the atoms of one CRU with the atoms of the surrounding macromolecules within a sphere having a radius twice the sum of the van der Waals distances for each pair of atomic species considered. The calculations have been performed by using the same set of potential functions as in the conformational energy calculations. The minimum energy conformation chain, as obtained in the conformational calculations, has been packed in all the monoclinic space groups[25] with unique axis b compatibly with the presence of four monomeric units per cell. As in the conformational energy calculations, the assumption of the two chains with

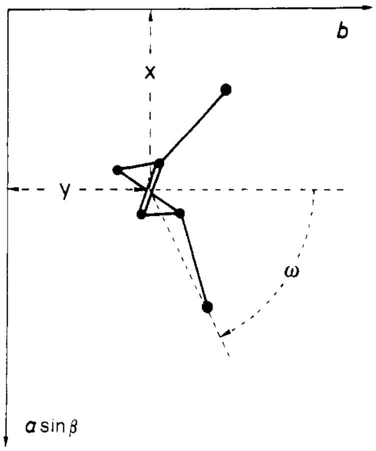


Figure 3. Definition of the parameters kept variable during the packing energy calculations with the projection along the chain axis of a chain of PMPD. Z is the height of the methyl group bonded to the C_{sp^3} carbon atom. x and y are the fractional coordinates of the middle point of the double bond. ω is positive for clockwise rotation.

the asymmetric carbon atoms having opposite configurations gives as results enantiomorphous and isoenergetic packings. The parameters that determine the relative positions of the chains in the unit cell for each space group considered have been kept as variables. They are defined in Figure 3. The experimental values of the parameters of the unit cell, i.e., a = 12.891 Å, b = 9.186 Å, c = 4.819 Å (chain axis), and β = 93.5°, have been fixed in these calculations for two reasons: (i) the best mode of packing of the chains is mainly related to the symmetry elements in the unit cell; (ii) the packing energy calculations performed by keeping as variables the parameters of the unit cell are indicative of the interchain distances at 0 K rather than at room temperature, as discussed in different papers.[6,12,26]

As in the conformational calculations, preliminary maps of the energy have been calculated for each space group. The maps have been obtained by calculating the packing energy as a function of ω and Z for fixed couples of values of x and y. Only short ranges of ω are of accessible energy for each space group as well as for each couple of values of x and y; on the contrary, the energy is not strongly influenced by the value of Z. Moreover, several values of x and y correspond, for suitable values of ω and Z, to low energies for some of the examined space groups. These results are in agreement with the expected influence of the bulky methyl groups on the packing mode of the chains.

Figure 4 shows, as an example, the map of the packing energy for space group $P2_1/a$ calculated for x = 0.20 and y = 0.05.

The minimizations of the packing energy as a function of the four defined parameters have been performed starting from the absolute and the various relative minima of all the maps. The lowest energy values reached in the minimizations for each space group are reported in Table IV.

The values of the energy show that the packing of the chains of PMPD is not effective in the space groups having the mirror plane as a symmetry element. This is due to the repulsive interactions of the methyl groups related by a mirror plane in the unit cell. In contrast, low lattice energies were calculated also for the space groups containing m symmetry planes in the cases of polyacetaldehyde,[6] poly(*cis*-1,4-butadiene)[12] and syndiotactic 1,2-poly(1,3-butadiene),[27] but those calculations were performed keeping the axes of the unit cells (and therefore the interchain distances) as variables. However, the lattice energies for the space groups having the m symmetry element were higher with respect to those for the other examined space groups, with the exception of syndiotactic 1,2-poly(1,3-butadiene) which has planar and less bulky lateral groups and the m plane as a chain symmetry element.

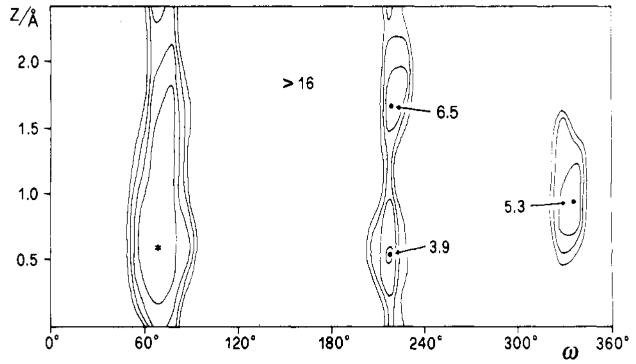


Figure 4. Map of the packing energy of PMPD in the space group $P2_1/a$ as a function of ω and Z, for x = 0.20 and y = 0.05. The curves are reported at intervals of 4 kJ·(mol of CRU)$^{-1}$ with respect to the absolute minimum of the map assumed as zero and indicated by an asterisk.

Table IV
Values of the Minimum Packing Energy Obtained for PMPD in the Examined Space Groups

space group[a]		energy,[b] kJ·(mol of CRU)$^{-1}$
short symbol	extended symbol	
$C2$	$C121$	1.6
	$A121$	2.7
	$I121$	1.4
Cm	$C1m1$	80.2
	$A1m1$	very high
	$I1m1$	80.7
Cc	$C1c1$	2.2
	$A1n1$	2.4
	$I1a1$	1.6
$P2/m$	$P12/m1$	80.1
$P2_1/m$	$P12_1/m1$	79.8
$P2/c$	$P12/c1$	1.4
	$P12/n1$	0.8
	$P12/a1$	1.8
$P2_1/c$	$P12_1/c1$	0.8
	$P12_1/n1$	0.1
	$P12_1/a1$[c]	−0.1

[a] For the space groups $C2$, Cm, Cc, $P2/c$, and $P2_1/c$ three different cell choices (with unique axis b) are possible; they are indicated by different extended symbols.[25] [b] The energy values are referred to the absolute minimum of the map of Figure 4. [c] Shortly indicated in this paper as $P2_1/a$.

The values of the optimized parameters in the space group having the lowest energy, i.e., $P2_1/a$, are reported in Table V together with the fractional coordinates of the carbon atoms of the asymmetric unit.

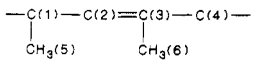
In order to confirm the validity of the results obtained in the above-reported packing energy calculations, energy minimizations have been also performed starting from the minima of Table IV for the space groups having lower energies and keeping as variables both the previously defined parameters and the parameters of the unit cell. As expected, the optimized axes of the unit cell are lower than the experimental values and the space group $P2_1/a$ emerges again as that of the lowest energy (Table VI). Only for the space groups $A121$ and $A1n1$ the calculated values of the b axis are slightly higher than the experimental value; however, also for these space groups the volumes of the unit cell are lower than that obtained by X-ray data.

Table V
Values of the Optimized Parameters and Fractional Coordinates of the Carbon Atoms of the Asymmetric Unit[a] Obtained in the Minimizations of the Packing Energy of PMPD for the Space Group $P2_1/a$

packing params $\omega = 73.1°$ $x = 0.1908$ $y = 0.0454$ $Z = 0.6575$ Å

	fractional coordinates		
	x	y	z
C(1)	0.2248	0.0878	0.0519
C(2)	0.2205	0.0242	0.7580
C(3)	0.1612	0.0667	0.5346
C(4)	0.1627	−0.0044	0.2476
CH_3(5)	0.3378	0.1081	0.1605
CH_3(6)	0.0851	0.1939	0.5502

[a]



$$-\underset{\displaystyle CH_3(5)}{C(1)}-C(2)=\underset{\displaystyle CH_3(6)}{C(3)}-C(4)-$$

Table VI
Values of the Minimum Packing Energy Obtained for PMPD in the Calculations Performed by Keeping as Variables Also the Parameters of the Unit Cell[a]

space group		energy, kJ·(mol of CRU)$^{-1}$	a, Å	b, Å	β	V, Å^3 [b]
short symbol	extended symbol					
$C2$	$C121$	0.5	12.110	8.895	94.0°	517.8
	$A121$	0.7	11.990	9.197	93.5°	530.4
	$I121$	0.0	12.477	8.893	95.6°	532.2
Cc	$C1c1$	−1.8	12.478	9.056	113.9°	497.9
	$A1n1$	−0.8	11.685	9.274	91.4°	522.1
	$I1a1$	−1.2	12.106	9.056	90.5°	528.3
$P2/c$	$P12/c1$	−0.5	11.844	9.014	93.8°	513.4
	$P12/n1$	−0.8	11.753	9.095	93.1°	514.4
	$P12/a1$	0.5	12.520	9.108	100.0°	541.2
$P2_1/c$	$P12_1/c1$	−0.8	11.921	9.010	93.5°	516.6
	$P12_1/n1$	−3.5	12.105	8.893	102.6°	506.3
	$P12_1/a1$	−4.1	12.105	8.630	93.4°	502.5

[a] The energies are referenced to the absolute minimum of the map of Figure 4. The optimized values of the parameters and the volume of the unit cell are also reported. [b] V is the volume of the unit cell; the experimental value is 569.6 Å^3.

Conclusions

The conformational energy calculations show that the chain of PMPD with the asymmetric carbon atoms having an S configuration assumes in the crystalline field a low-energy conformation having torsion angles $\vartheta_1 = A^-(\sim)$, $\vartheta_2 = A^+(\sim)$, and $\vartheta_3 = T(\sim)$, like that observed in the experimental crystal structure.[1] (If the asymmetric carbon atoms have an R configuration the enantiomorphous conformation, having $\vartheta_1 = A^+(\sim)$, $\vartheta_2 = A^-(\sim)$ and $\vartheta_3 = T(\sim)$, is obtained.) In contrast, the calculations effected on ITPP,[17] a polymer showing two different experimental crystal structures, and on TPB[14] and TPI,[15] polymers showing more experimental crystal structures, gave as results more than one low-energy conformation. These results suggest that PMPD can have only one conformation in the crystalline field, as up to now observed. Therefore it can be concluded that the most stable conformation of PMPD in the crystalline field should be maintained also in fiber samples (at variance with ITPP) and at high temperature (at variance with TPB and TPI).

The packing energy calculations performed by the analysis of different space groups show that the lowest energy is obtained in the case of the space group $P2_1/a$; this space group is equivalent to $P2_1/c$ proposed by the X-ray analysis with a different choice of the chain axis.[1] The position of the asymmetric unit in the cell as obtained by these calculations is different from that reported in ref 1. However, it should be outlined that the calculations refer to an ideal crystal structure; moreover, in the space group $P2_1/a$ many low-energy modes of packing are possible and the calculated packing energy corresponding to the experimental structure is only 1.7 kJ·(mol of CRU)$^{-1}$ higher than the absolute minimum.

In conclusion, the results of the calculations reported in this paper are in substantial agreement with the experimental crystal structure of PMPD and give the indication that conformational polymorphism should not be observed for this polymer.

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