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Conformational and Packing Calculations on Crystalline Syndiotactic 1,2-Poly(1,3-butadiene)

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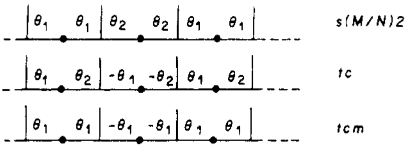
The role of intra- and intermolecular interactions in determining the conformation and mode of packing of various crystalline isotactic polymers was pointed out in previous papers.[1-5] Conformational calculations on syndiotactic polymers were also reported in past years;[6-8] some of us also performed calculations on the isolated chain of syndiotactic 1,2-poly(1,3-butadiene) (PB12) in comparison with analogous calculations on syndiotactic polypropylene.[9] In this paper we report more complete conformational energy calculations and packing energy calculations in order to predict the crystal structure of syndiotactic PB12.[10]

The conformational calculations reported here have been performed on the portion of the polymer chain represented in Figure 1 according to the equivalence principle,[11] that is, imposing the geometrical equivalence of the configurational repeating units (CRUs) along an axis. The potential functions used are those reported by Flory et al.,[8,12] as well as the method of calculation used by some of us in a previous paper.[13]

The map of the conformational energy as a function of the torsion angles[14] θ_1 and θ_2, reported in Figure 2, has been obtained with the following values for torsion and bond angles: $\theta(CH_2\text{-}C\text{-}CH{=}CH_2) = 61.975°$, so that the plane containing the double bond bisects the bond angle τ_1, $\tau_1 = 111°$, $\tau_2 = 113°$, $\tau(C\text{-}CH{=}CH_2) = 122°$, $\tau(C_{sp^3}\text{-}C_{sp^2}\text{-}H) = 119°$; a local C_{2v} symmetry has been imposed on the methylene groups.

Starting from the two nonequivalent A and B minima of the map, we have performed minimizations of the conformational energy for the possible line repetition groups[14] compatible with a syndiotactic polymer and according to the equivalence principle applied to one monomeric unit; they are *s*(*M*/*N*)2, *tc*, and *tcm*. These line repetition groups are realized with the following successions of torsion angles:



where the horizontal lines indicate the polymer chains, the vertical bars the lateral groups, and the points the methylene groups in the chains.

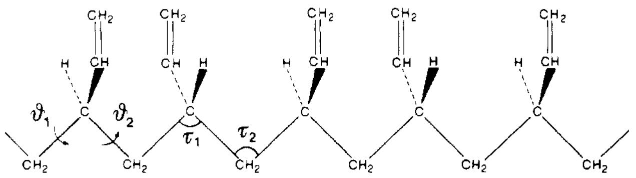


Figure 1. Section of the chain of syndiotactic PB12 used for the calculations of conformational energy.

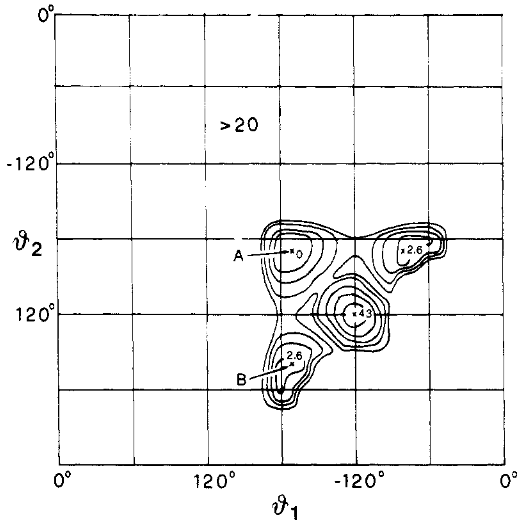


Figure 2. Internal energy map for helical conformations of a syndiotactic PB12 chain as a function of the torsion angles θ_1, and θ_2. According to ref 14, T and G± correspond to torsion angles of respectively 180° and ±60°. The curves are reported at intervals of 5 kJ/(mol of CRU) with respect to the minimum of the map assumed as zero.

Table I
Packing Energy and Values Assumed by the Parameters Varied in the Points of Minimum Energy for the Examined Space Groups[a]

space group	*E*, kJ/(mol of CRU)	*a*, Å	*b*, Å	Δx	Δy
$Pmc2_1$	−19.6	13.18	5.24	0.137	
*Pnc*2	−11.3	10.70	8.13	0.054	
Pccm	−20.7	12.88	5.24	0.140	
Pcam	−26.4	9.91	6.15		0.886

[a] Δx and Δy are the fractional coordinates of the carbon atom of the methylene group with the orientation of the chains as in Figure 3. The values of the experimental axes[10] are $a = 10.98$ Å, $b = 6.60$ Å, and $c = 5.10$ Å.

The conformational energy has been optimized with respect to all the torsion angles, the bond angle τ_2 (maintaining the local C_{2v} symmetry on the methylene group), and all the bond angles around the methine carbon atom. The results of these minimizations are very similar to those reported in ref 9; the minimum obtained for the *tcm* line repetition group, not reported in ref 9, is slightly higher in energy with respect to that for *tc*. However, the minima obtained for the three line repetition groups with conformations $\theta_1 \simeq$ T and $\theta_2 \simeq$ T are lower in energy than the minimum with $\theta_1 \simeq$ T and $\theta_2 \simeq$ G⁺, which is compatible with the *s*(*M*/*N*) 2 line repetition group. The latter, which corresponds to a chain conformation having a *c* axis far from the experimental one, has been neglected in the following.

In order to obtain the best conformations of the isolated chain to be used for calculations of the packing energy, we have also optimized the energy under the constraint of maintaining the experimental *c* axis at the value of 5.1 Å for the three line repetition groups. As a result, the three conformations degenerate into the same conformation having *tcm* symmetry with the following chain parameters: $\tau_1 = 113.3°$, $\tau_2 = 113.8°$, $\theta_1 = -173.5°$; the other chain parameters remain practically unchanged with respect to those used in the calculation of the map of Figure 2.

On the hypothesis that the glide plane of the chain is also a crystallographic element of symmetry, we have considered the possibility of the packing of syndiotactic PB12 in all the orthorhombic space groups having a *c* glide plane[15] and in accordance with the experimental datum of two chains in the unit cell. They are $Pmc2_1$, *Pcc*2, $Pca2_1$, *Pnc*2, *Pccm*, and *Pcam*. The space groups *Pcc*2 and $Pca2_1$ are different from the space groups *Pccm* and *Pcam*, respectively, because the latter contain mirror planes per-

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Table II
Fractional Coordinates of the Carbon Atoms of the Asymmetric Unit of Syndiotactic PB12 in the Space Group *Pcam* Obtained in the Minimization of the Packing Energy in Comparison with Experimental Ones[a,d]

	our calculations			exptl[b]			exptl[c]		
	x/*a*	*y*/*b*	*z*/*c*	*x*/*a*	*y*/*b*	*z*/*c*	*x*/*a*	*y*/*b*	*z*/*c*
C1	0	0.886	0	0	0.896	0	0	0.916	0
C2	0.007	0.022	0.250	0	0.030	0.250	0.014	0.050	0.250
C3	0.134	0.156	0.250	0.117	0.164	0.250	0.136	0.143	0.250
C4	0.131	0.374	0.250	0.117	0.364	0.250	0.143	0.342	0.250

[a] Reference 10. [b] Obtained with a trans-planar backbone chain. [c] Obtained with nonplanar backbone chain. [d] C1, C2, C3, and C4 indicate respectively the carbon atoms of CH_2 and of CH in the main chain and of CH and CH_2 of the side group.

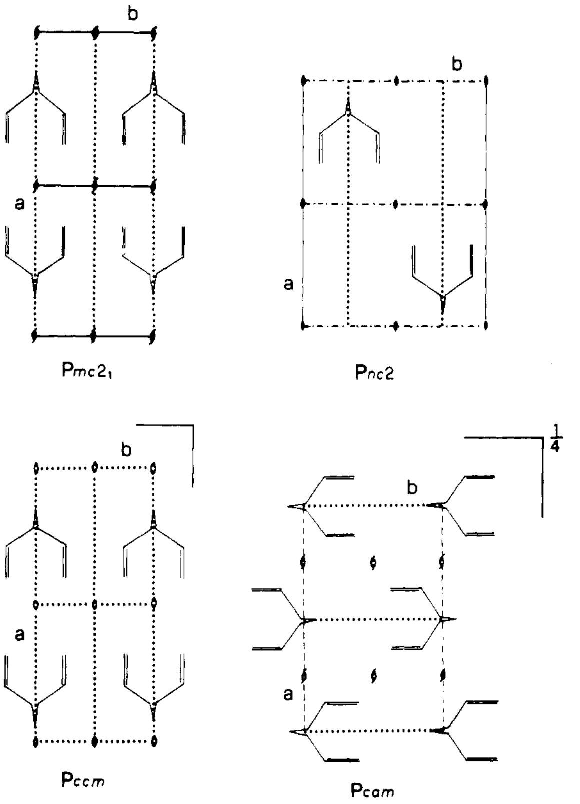

Figure 3. Projection along the chain axis of the contents of the unit cells of syndiotactic PB12 for the space groups $Pmc2_1$, $Pnc2$, $Pccm$, and $Pcam$, with the indication of the symmetry elements.[15]

pendicular to the *c* axis. Since the chain symmetry used for the calculation of the packing energy is *tcm*, the space group $Pcc2$ is equivalent to $Pccm$ and the space group $Pca2_1$ to $Pcam$ if the *m* planes of the chains are assumed as crystallographic elements of symmetry. Hence we have effected calculations of the packing energy for the space groups $Pmc2_1$, $Pnc2$, $Pccm$, and $Pcam$.

The calculations of the packing energy have been performed with the fixed conformation of the chain having the *tcm* symmetry obtained from the minimization of the energy of the isolated chain under the constraint of maintaining the experimental *c* axis. The energy has been evaluated by taking into account the interactions between the atoms of one CRU and all the other atoms within spheres with a radius twice the sum of the van der Waals radii for each pair of atoms; the potential functions used for packing-energy calculations are the same as those used for the isolated-chain conformational calculations.

We have optimized the packing energy using as the variable a parameter that defines the position of the chains in the unit cell compatibly with the considered space groups, leaving the *a* and *b* axes fixed to the experimental values. These calculations show that the only space group having low energy is *Pcam*. We then performed minimizations of packing energy also with respect to the *a* and *b* axes of the unit cell for the various space groups. These calculations give information about the best symmetry elements with which the chains pack and also give an approximate value of the axes of the unit cell near 0 K.[4,5,13] The results are reported in Table I. The lowest energy is obtained for the space group *Pcam*, that is, the one experimentally proposed.[10] Moreover the values of the *a* and *b* axes obtained for the space group *Pcam* are in good agreement with the experimental ones, and only for this space group are they in accordance with the general trend of a lowering of the axes of the unit cell near 0 K.

Figure 3 shows the projection along the chain axis of the contents of the unit cells, as calculated by us, together with the symmetry elements[15] of the examined space groups. The best mode of packing along a direction perpendicular to the *c* glide plane and the chain axis is obtained with a 2_1 axis or with a glide plane, while in a direction contained in the *c* glide plane and perpendicular to the chain axis it is obtained with a simple translation. These conditions are both realized only in the space group *Pcam*.

In Table II we report the fractional coordinates of the asymmetric unit in the packing of minimum energy for the space group *Pcam*. They are in good accordance with those experimentally found;[10] small deviations are due to a slightly different conformation of the polymer chain.

The results of our calculations confirm the effectiveness of the method of conformational and packing-energy analysis to predict the crystal structure also for syndiotactic polymers.

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Registry No. Syndiotactic poly(1,3-butadiene) (homopolymer), 31567-90-5.

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Unperturbed Dimensions of Poly(2-chloroethyl methacrylate)

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In a study[2] of the characteristic ratios of various long side group *n*-alkyl methacrylate polymers we had occasion to prepare a series of fractionated samples of poly(2-chloroethyl methacrylate) (PCEM). The molecular weights of these samples were measured via osmometry and low-angle laser light scattering, and their dilute solution viscosities were measured under Θ conditions and in a good solvent. The Θ-solvent data allow the determination of unperturbed dimensions in an unambiguous fashion. Since this has not been previously done for poly(2-chloroethyl methacrylate), these results are the topic of this note.

Experimental Section

The monomer was obtained from Polysciences. After purification by fractional distillation under reduced pressure (measured purity >99%), the monomer was polymerized in benzene solution under vacuum-line conditions. AIBN was the initiator of choice. Polymer fractionation was accomplished by the procedures given elsewhere.[2] The PCEM tacticity was determined via ^1H and ^{13}C NMR measurements. 1,3,5-Trichlorobenzene at 105 °C was the solvent for the ^1H NMR measurements while $CDCl_3$ at 23% was used for the ^{13}C NMR analysis. These tacticity findings are given in Table I. The listed values are in essential agreement with those previously reported[4] for poly(chloromethyl methacrylate).

Polymer molecular weights and the heterogeneity indices were determined by a combination of low-angle laser light scattering (Chromatix KMX-6), membrane osmometry (Hewlett-Packard 503), and size exclusion chromatography (Waters Ana-Prep). The light scattering measurements were done in tetrahydrofuran at 30 °C while toluene at 37 °C was used for the osmometric evaluations. The relatively low A_2 values ($\leq 10^{-4}$ mL mol g^{-2}) found from the osmometry measurements indicate that toluene is a moderately poor solvent at 37 °C.

Table I
Tacticity of Poly(2-chloroethyl methacrylate)

NMR method	triads mm	mr + rm	rr
$^1H^a$	6	37	57
$^{13}C^b$	7	37	56

[a] The triad concentrations were determined by the intensity of the methyl group protons. [b] The triad concentrations were determined by the intensity of the carbonyl carbon.

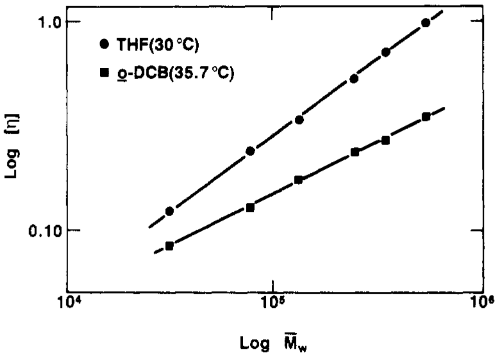

Figure 1.

The d*n*/d*c* for PCEM in tetrahydrofuran was found to be 0.0957 (±0.001) mL g^{-1} at 633 nm (Chromatix KMX-16). The Θ solvent was *o*-dichlorobenzene at 35.7 °C. The Θ temperature was taken as that temperature at which the light scattering second virial coefficient was zero. This was determined with the Sofica PGD photometer.

The glass transition temperature for PCEM was measured for the four highest molecular weight samples with the use of Du Pont 990 instrument. The value of 67 (±2) °C is based on extrapolation to the zero heating rate. The glass transition was the only transition found over the temperature range of ~0–150 °C.

Results and Discussion

Table II gives the pertinent data for the six poly(2-chloroethyl methacrylate) samples. The usual log–log plots of [*η*] against $\bar{M}_w$ (Figure 1) yield the following constants for the Mark–Houwink–Sakurada (M–H–S) equations for the good solvent tetrahydrofuran (30 °C) and the Θ solvent *o*-dichlorobenzene (35.7 °C).

$$[\eta]^{30°C}_{THF} = 6.83 \times 10^{-5}\bar{M}_w^{0.72} \quad \text{(corr coef = 0.999)}$$

$$[\eta]^{35.7°C}_{o\text{-DCB}} = 4.73_8 \times 10^{-4}\bar{M}_w^{0.50} \quad \text{(corr coef = 0.999)}^5$$

The characteristic ratio[3]

$$C_\infty = \lim_{n\to\infty} [\langle r^2\rangle_0/nl^2] = \lim_{n\to\infty}\left[\frac{\langle r^2\rangle_0\bar{M}_w^{-1}}{(n'/M)l^2}\right]$$

can be obtained by the use of the familiar relation

$$K_\theta = \Phi(\langle r^2\rangle_0/\bar{M}_w)^{3/2}$$

where $\Phi = 2.5\ (\pm 0.1) \times 10^{21}$[6-13] for intrinsic viscosities expressed in dL g^{-1}, l^2 is the mean-square average bond length, *n* is the number of chain bonds, *n′* is the number of bonds per monomer unit, and *M* is the monomer molecular weight.

Table II
Molecular Characteristics of Poly(2-chloroethyl methacrylate)

sample	$\bar{M}_n \times 10^{-4}$	$\bar{M}_w \times 10^{-4}$	$\bar{M}_w/\bar{M}_n{}^a$	$\bar{M}_z/\bar{M}_w{}^b$	$\bar{M}_z/\bar{M}_w{}^b$	$[\eta]^{30°C}_{THF}$, dL g^{-1}	$k_H{}^c$	$[\eta]^{35.7°C}_{o\text{-DCB}}$, dL g^{-1}	$k_H{}^c$
1	40.7	53.9	1.3_2	1.2_2	1.3_1	0.97_2	0.15	0.34_4	0.43
2	28.0	34.6	1.2_4	1.1_5	1.2_2	0.72_6	0.11	0.27_0	0.72
3	19.8	24.5	1.2_4	1.2_6	1.2_1	0.53_3	0.34	0.23_5	0.87
4	10.5	13.2	1.2_6	1.1_6	1.2_3	0.33_6	0.39	0.17_5	0.63
5	6.5_4	7.7_5	1.1_9	1.1_2	1.1_7	0.24_2	0.21	0.12_8	0.80
6	2.6_0	3.1_9	1.2_3	1.1_8	1.3_2	0.12_6	0.18	0.08_9	0.55

[a] Via absolute measurements. [b] Size exclusion chromatography; Ana-Prep. [c] Huggins coefficients.

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