(22) s, d, t, and q stand for singlet, doublet, triplet, and quarted denoting the multiplicity of the peaks in the off-resonance spectrum.
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Crystal Structure of Isotactic *trans*-1,4-Poly(1,3-pentadiene). An Analysis by Conformational and Packing Energy Calculations

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ABSTRACT: Conformational and packing energy calculations have been performed on isotactic *trans*-1,4-poly(1,3-pentadiene). Two different minimum energy conformations in agreement with the experimental chain axis have been found. One of them corresponds to a chain having the side methyl groups in a skew arrangement and the other to a chain having the side methyl groups in a cis arrangement with respect to adjacent double bonds. The two chains have been independently packed in the space group $P2_12_12_1$ and two corresponding packing energy minima have been found. The calculations show that the skew arrangement, corresponding to the lowest conformational and packing energies, is preferred as opposed to the cis arrangement, even if the latter should be partially present in the crystal structure of oriented samples of the polymer.

Introduction

Structural data on isotactic *trans*-1,4-poly(1,3-pentadiene) (ITPP) were first reported by Natta et al.[1] who performed X-ray and IR investigations showing that this polymer may exist in two different modifications, a crystalline and a paracrystalline one. The crystal structure of ITPP was determined by X-ray fiber patterns by Bassi et al.;[2] the proposed unit cell is orthorhombic, space group $P2_12_12_1$, with $a = 19.80 \pm 0.20$ Å, $b = 4.86 \pm 0.05$ Å, $c = 4.85 \pm 0.05$ Å, and $d_{RX} = 0.97$ g·cm^{-3}. Bassi et al. showed that the best agreement between calculated and observed intensities is obtained when the polymer chain is assumed to have the side methyl groups in a cis arrangement with respect to the adjacent double bonds (henceforth denoted the cis model) rather than in a skew arrangement (henceforth denoted the skew model). Later Neto et al.[3,4] performed a vibrational analysis on unstretched samples of ITPP and concluded that the comparison between observed and calculated spectra indicates better agreement in the case of the skew model, both for the crystalline and for the paracrystalline modification. Recently Brückner et al.[5] reported the results of a X-ray diffraction analysis on a powder sample of ITPP, showing that the skew model is in good agreement with their experimental data. They concluded that the disagreement between the conformational model proposed in ref 2 and that proposed in the succeeding papers is due to the different samples of ITPP studied (stretched sample in the first case, unstretched samples in the succeeding works[3-5]).

In this paper a study of the crystal structure of ITPP as dictated by conformational and packing energy calculations is reported. The effectiveness of energy calculations in the prediction of the chain conformations and crystal structures of various polymers,[6-9] and in particular of polydienes,[10-13] was tested in preceding papers. Therefore it seems interesting to extend this kind of analysis to ITPP with the purpose of contributing to the elucidation of the above-mentioned disagreement concerning the polymer chain conformation in the crystalline state.

Table I
Bond Lengths and Bond Angles Used in the Calculations of the Conformational Energy Maps of ITPP

bond lengths/Å		bond angles	
C—C	1.53	C—Ĉ—C	111°
C=C	1.34	C—Ĉ=C	127°
C—H	1.10	C—Ĉ—H	109.5°
		C=Ĉ—H	116.5°
		H—Ĉ—H	108.9°

Conformational Energy Calculations

The conformational energy calculations have been performed on the portion of the polymer chain represented in Figure 1. According to the equivalence postulate,[14] the geometrical equivalence of successive constitutional repeating units (CRUs) has been imposed with the aim of obtaining results representative of the polymer chain in the crystalline field. The method of calculation has been reported in preceding papers.[11,12] The methyl group has been taken as a single unit in the calculations of the nonbonded interactions. The potential functions used are those of Flory et al.[15-17] Threefold intrinsic torsional potential with barriers of 11.7 and 4.2 kJ·mol^{-1} have been used for the rotations around skeletal —C$\overset{\curvearrowright}{}$C— and —C$\overset{\curvearrowright}{}$C= torsion angles, respectively. However, the actual barriers to the rotations around these torsion angles depend on the different nonbonded interactions of the lateral substituents (hydrogen atoms or methyl groups). The force constants for the bending at the C_{sp^2} carbon atom are those reported by Zerbi and Gussoni.[18]

In order to find the low-energy regions in the multidimensional conformational energy surface, preliminary maps of the energy as a function of the torsion angles ϑ_1 and ϑ_2 have been calculated. In these calculations bond lengths and bond angles have been fixed at the values reported in Table I. The value of ϑ_3 has been fixed at 180° (trans conformation) as has also the double bond (trans

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Table II
Values of Internal Parameters and Energies Obtained in the Minimizations of the Conformational Energy in the Regions near C and D in the Map of ITPP[a]

	τ_1	τ_2	τ_3	τ_4	τ_5	ϑ_1	ϑ_2	ϑ_3	E/kJ·(mol of CRU)$^{-1}$
C′	110.6°	128.8°	126.6°	110.9°	112.1°	103°	−104°	−178°	8.8
D′	109.9°	125.5°	125.6°	109.9°	113.2°	−116°	116°	180°	−3.0

[a] The corresponding conformations are indicated as C′ and D′.

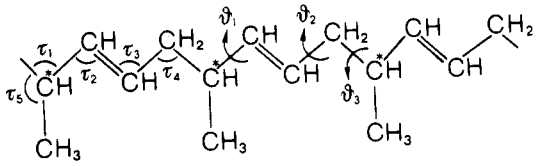

Figure 1. Portion of the chain of ITPP used in the conformational energy calculations, with indication of bond and torsion angles kept variable during the minimizations. The ϑ_i indicate the torsion angles defined with respect to the main chain. C* indicates asymmetric carbon atoms.

configuration). This condition produces a chain conformation sufficiently extended to be easily packed for each value of ϑ_1 and ϑ_2. Figure 2 shows the maps of the energy resulting both in the case of the asymmetric carbon atom having an *R* configuration (a) and in the case of the *S* configuration (b). The two maps are symmetric because each point of the first and the corresponding point of the second map refer to enantiomorphous conformations. The points indicated by A and C correspond to chain conformations similar to the skew model and the cis model, respectively, as reported in ref 2. The point indicated by D corresponds to a chain conformation similar to that reported in ref 5. Point C, near a relative minimum of the map, is higher in energy with respect to points A and D (absolute minima) because it corresponds to a conformation in which a noticeable repulsive nonbonded interaction arises between a skeletal carbon atom and the methyl group. Only conformations near points A, B, C, and D can give a chain axis repeat equal to the experimental one. The other minima of the maps correspond to chain conformations having axes very long with respect to the experimental value. For this reason, minimizations of the conformational energy have been effected only in the regions of the minimum D (enantiomorphous with A) and of the minimum near C (enantiomorphous with B) of the map computed for ITPP having C* atoms in configuration *S*. The minimizations have been effected under the constraint of maintaining the experimental value of the *c* axis (4.85 Å) and varying all the torsion angles (except that around the double bond) as well as the bond angles, but with the assumption of a local symmetry C_{2v} on the methylene groups. The values of the optimized conformational parameters and the energies corresponding to the two calculations are reported in Table II.

Packing Energy Calculations

The packing energy has been calculated 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. Each of the two chain conformations obtained by conformational energy calculations has been packed in the space group $P2_12_12_1$ proposed in both ref 2 and 5. The unit cell constants reported in ref 5, i.e., a = 19.802 Å, b = 4.801 Å, and c = 4.850 Å, have been fixed in the packing energy calculations of the

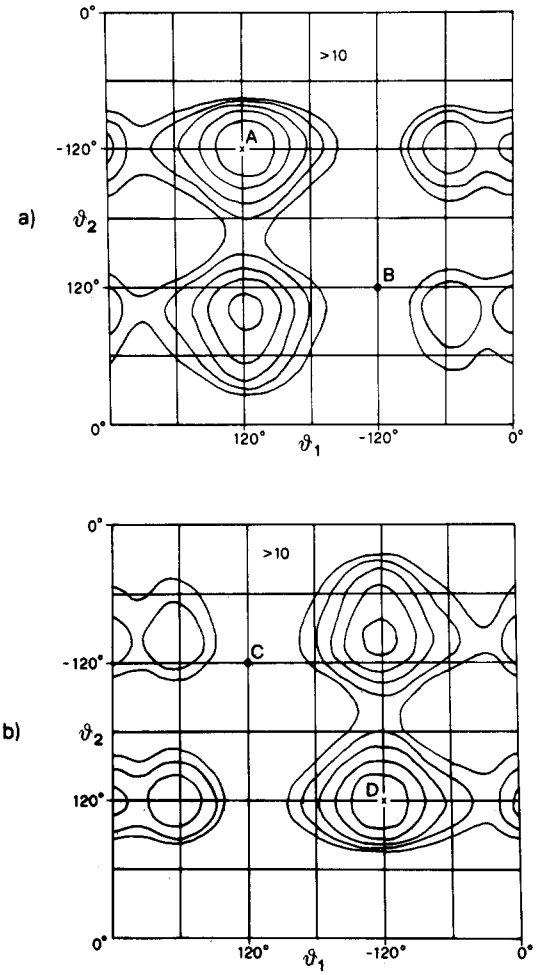

Figure 2. Map of the conformational energy of ITPP as a function of torsion angles ϑ_1 and ϑ_2: (a) with C* having configuration *R*; (b) with C* having configuration *S*. The curves are reported at intervals of 2 kJ·(mol of CRU)$^{-1}$ with respect to the absolute minimum assumed as zero and indicated by ×.

chains having conformation D′ (see Table II); the unit cell constants reported in ref 2 have been used in the packing energy calculations of the chains having conformation C′. The parameters that determine the relative positions of the chains in the unit cell according to the symmetry elements of the space group $P2_12_12_1$ have been used as variables in these calculations. They are defined in Figure 3.

As in the conformational calculations, preliminary maps of the energy have been calculated. These maps have been obtained by calculating the packing energy as a function of ω and Z for fixed pairs of values of x and y. The results show that lower energy values are obtained when x is bounded in the range 0.08–0.18; on the other hand, the energy is not strongly influenced by the value of y. Figures 4 and 5 show the maps calculated with x = 0.1 and y = 0.2 for the packing of chains having conformations D′ and C′, respectively. Minimizations of the packing energy as a function of the four previously defined parameters have been effected starting from the different minima of each map. The lowest energy values for each of the two packed

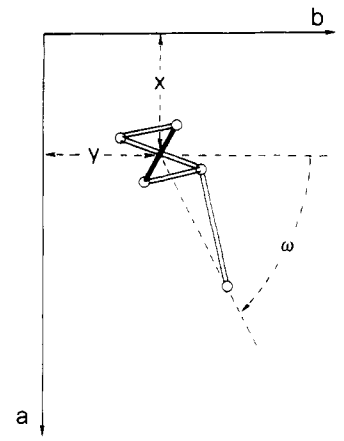

Figure 3. Definition of the parameters kept variable during the packing energy calculations with the projection along the c axis of a chain of ITPP in skew arrangement. Z is the height of the methyl group. x and y are the fractional coordinates of the mid point of the double bond. ω is positive for clockwise rotation.

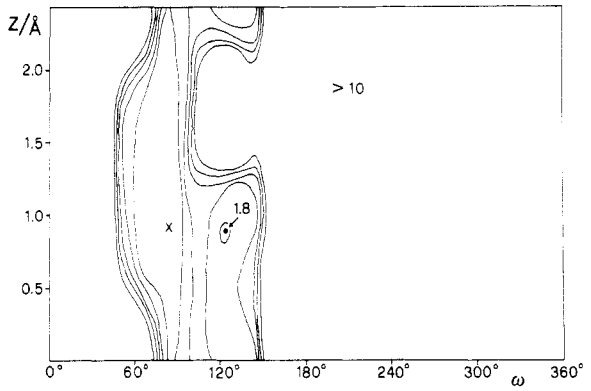

Figure 4. Map of the packing energy in the space group $P2_12_12_1$ of ITPP with chains having conformation D′ as a function of ω and Z, for $x = 0.1$ and $y = 0.2$. The curves are reported at intervals of 2 kJ·(mol of CRU)$^{-1}$ with respect to the absolute minimum of the map assumed as zero and indicated by ×.

Table III
Energy Values and Optimized Parameters As Obtained in the Packing Energy Minimizations for Chains Having Conformation D′ and C′

	x	y	z/Å	ω	E/kJ·(mol of CRU)$^{-1}$
D′	0.084	0.180	0.969	86°	−29.3
C′	0.099	0.318	0.324	100°	−25.5

chains as well as the optimized parameters are reported in Table III. The positions of the chains in the unit cell as obtained in these minimizations in comparison with those reported in ref 2 and 5 are indicated in Figure 6 by projections along the chain axis of the carbon atoms of the asymmetric unit.

Discussion

The conformational energy calculations show that the chain conformation having the methyl groups in a skew arrangement with respect to the adjacent double bonds (conformation D′) is preferred with respect to the chain conformation having the methyl groups in a cis arrangement (conformation C′). Moreover, a slight difference of the packing energies confirms the greater stability of conformation D′ in the crystalline field. The calculations give geometrical results in satisfactory agreement with the experimental data both for a polymer chain having the skew arrangement and for a polymer chain having the cis arrangement (see Figure 6). However, the resemblance

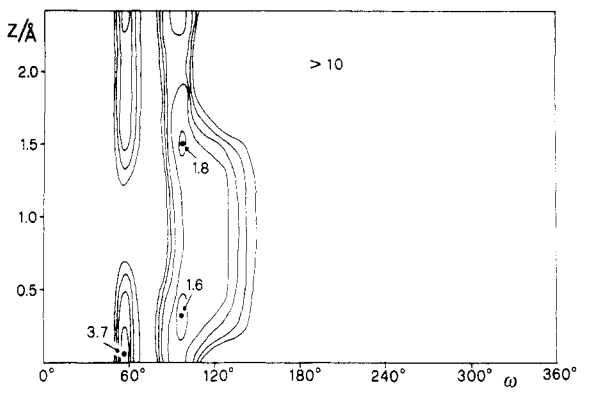

Figure 5. Map of the packing energy in the space group $P2_12_12_1$ of ITPP with chains having conformation C′ as a function of ω and Z, with $x = 0.1$ and $y = 0.2$. The curves are reported at intervals of 2 kJ·(mol of CRU)$^{-1}$ with respect to the absolute mimimum of the map of Figure 4.

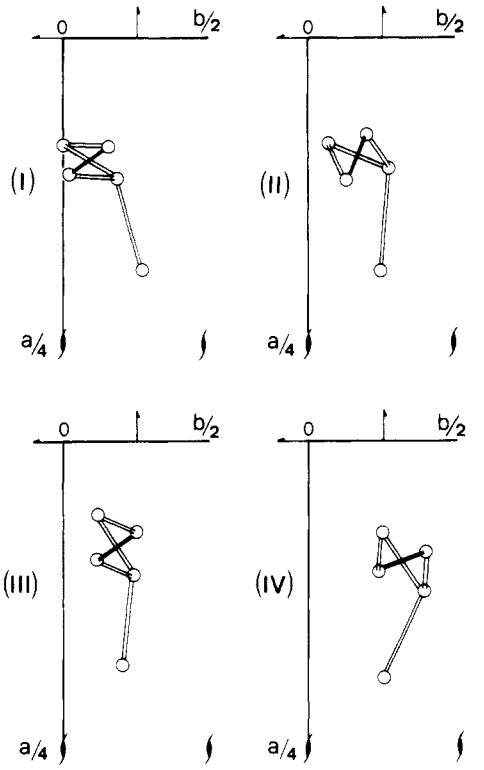

Figure 6. Projection along the chain axis of the carbon atoms of the asymmetric unit of ITPP; (I) skew model;[5] (II) cis model;[2] (III) chain having conformation D′; (IV) chain having conformation C′.

both in the steric encumbrance and in the position in the unit cell of the chain having conformation D′ with the chain corresponding to the cis model of ref 2 should be emphasized. This resemblance is evidenced also by a comparison of the calculated intensities of the reflections in the structure corresponding to the packing of chains having conformation D′ with the observed intensities reported in ref 2. The agreement in this structure is better than in the structure reported in ref 5, even though in both cases the calculated intensities of the (201) reflection are too low with respect to the observed intensity. On the other hand, in the structure corresponding to the packing of chains having conformation C′, higher in energy, the calculated intensity of the (201) reflection is in good agreement with the observed intensity.

These results suggest that the polymer chains of ITPP in the crystal structure assume a conformation having a skew arrangement of the methyl groups with respect to the

adjacent double bonds. This conformation, the lowest in energy, is in good agreement both with the conformation proposed by Brückner et al.[5] and with the spatial positioning of the chains in the unit cell proposed by Bassi et al.[2] The orientation of the polymer sample can produce at least a partial conformational change from the skew to the cis arrangement, higher in energy. This change can be explained by the relatively low energy barrier to rotation around bonds adjacent to double bonds. By analogy, in *cis*-1,4-polyisoprene, the structure of which can be interpreted on the basis of a statistical succession of two different conformations along the chain,[19] a change from one of the two conformations to the other (having slightly different energy) is influenced by external stress.[20] For ITPP the difference in energy between skew and cis arrangements is high and therefore the skew arrangement, the most probable in unoriented samples, should prevail also in oriented samples.

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Charge-Mosaic Membrane from a Polymer Blend with a Modulated Structure

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ABSTRACT: A charge-mosaic membrane was prepared from the solution-cast film of the polymer blend of chloromethyl polystyrene (CMPS) with poly(acrylonitrile-*co*-styrene) (SAN). The membrane was prepared as follows: (1) each polymer was dithiocarbonated to introduce a photo-cross-linkable site (a few mole percent in the polymer); (2) the dithiocarbonated polymers were solution cast to thin films with regularly phase-separated co-continuous structure (modulated structure); (3) this precursor film was cross-linked by UV radiation; (4) the CMPS phase was quaternized with bis(dimethylamino)hexane; (5) the SAN phase was sulfonated with chlorosulfonic acid. The film thus modified exhibited negative osmosis and selective permeability, i.e., permeable to salt but not to nonelectrolyte, as expected for a charge-mosaic membrane. The high salt permeability seems to originate from the characteristic two-phase structure in the precursor film.

Introduction

A charge-mosaic membrane consists of a set of anion and cation exchange elements arranged in parallel, each element providing a continuous pathway from one bathing solution to the other. When a gradient of electrolyte concentration is established across the membrane, anions and cations can flow in parallel through their respective pathways without a violation of macroscopic electroneutrality, resulting in a circulation of current between the individual ion-exchange elements. As a result of current circulation, the charge-mosaic membrane shows negative osmosis and salt permeability much greater than its permeability to nonelectrolytes.[1]

Since Weinstein and Caplan[2] prepared a model membrane by embedding cation-exchange beads and anion-exchange beads in a silicone rubber matrix, many attempts have been performed to prepare the charge-mosaic membrane.[3] Some are by chemical modifications of two-phase polymer systems, i.e., polymer blends, graft copolymers, and block copolymers. Among them, the most effective membrane was made by Fujimoto et al.[4,5] As a precursor polymer, they prepared a specially designed pentablock copolymer, poly(isoprene-*block*-styrene-*block*-isoprene-*block*-(4-vinylbenzyl)dimethylamino-*block*-isoprene), and chemically modified the solution-cast film of the block copolymer. Our studies in this article are along the same line as theirs, but we have employed a different precursor which is more easily available and the morphology of which may be more desirable for the charge-mosaic membrane.

In our recent article,[6] we found the development of a regularly phase-separated structure in solution-cast films of polymer blends. Characteristic features of the structure are periodicity and dual connectivity of phases, as schematically shown in Figure 1. We call this a modulated structure. The blended film with modulated structure is

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