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Vibrational Analysis of *trans*-1,4-Polypentadiene. 1. Single-Chain Model

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ABSTRACT: The vibrational spectrum of crystalline isotactic *trans*-1,4-poly(1,3-pentadiene) is compared with results of a normal-mode calculation of the isolated chain, using a set of force constants transferred from *trans*-1,4-polybutadiene. The dynamical equation of a vibrating chain is presented in terms of linear coordinates, and it can be easily extended to include interactions among different chains. Normal coordinates are obtained in terms of internal, translational, and rotational displacements for each repeat unit, and vibrational frequencies, computed for a wave vector $\mathbf{k} = 0$, are compared with observed data. Calculations are carried out for two possible conformations of the polymer chain and show a better agreement for a conformation characterized by side methyl groups in a skew arrangement with respect to the neighboring double bonds.

The infrared spectrum of isotactic *trans*-1,4-poly(1,3-pentadiene), hereafter referred to as ITPP, was first studied by Natta and co-workers,[1] who showed that the absorption pattern in the region 650–5000 cm^{-1} is little influenced by interactions between polymer chains in the crystal. The crystal structure was later determined by Bassi et al.,[2] who proposed a chain conformation in the crystalline state characterized by side methyl groups in a cis arrangement with respect to the neighboring double bonds. This conformation, hereafter referred to as the cis form, is schematically shown in Figure 1a while in Figure 1b a possible alternative form is given in which the side methyl groups are in a skew arrangement relative to the double bonds. It was suggested[3] that the energy difference between these two different conformations is small, and a skew form was in fact found for similar compounds (see discussion given in ref 2).

In the present paper we report the results of a vibrational analysis of a single polymer chain of ITPP, assuming, as stated in ref 1, that interchain interactions are relatively unimportant for this polymer. This assumption is supported by the observation that very few factor group splittings occur in the infrared spectrum, despite the presence of four monomers per unit cell, each belonging to a different chain. Besides, the spectrum of the crystal is very similar to that of the paracrystalline modification, obtained from the crystalline sample by melting and fast cooling, in which three-dimensional order does not exist. It must be pointed out, however, that the assumption of a crystal made up of noninteracting chains is an approx-

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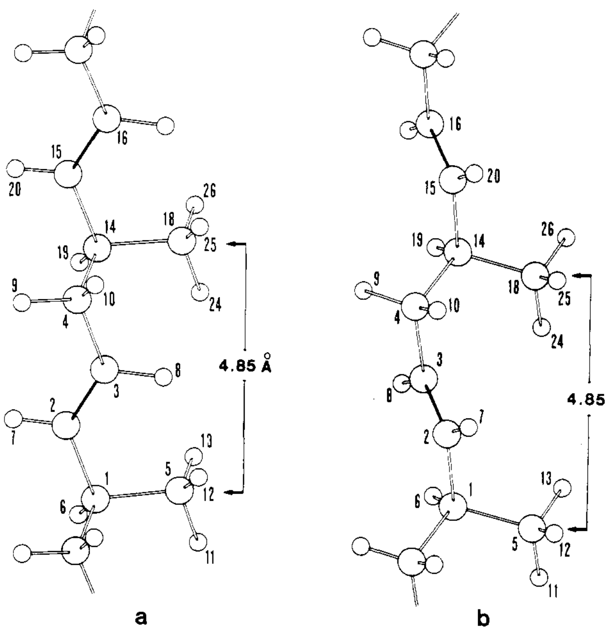

Figure 1. Possible conformations of an isolated chain of *trans*-1,4-poly(1,3-pentadiene). The side methyl groups are a cis (a) or skew (b) arrangement with respect to adjacent double bonds. Numbers from 1 to 13 identify atoms of a repeat unit (see description of internal coordinates).

imation and cannot account for frequency shifts due to crystal field effects which may be important even for bands which do not show appreciable factor group splitting. Thus, even if for ITPP a vibrational analysis based on the isolated chain model should lead to a good assignment of the normal modes, a satisfactory agreement between observed and calculated frequencies is not expected if interchain interactions are not taken into account.

Following this scheme, we present here the results based on the model of a polymer made of isolated chains and give a convenient description of the essential features of the infrared spectrum. Observed frequencies, obtained for the crystalline sample at liquid nitrogen temperature and for the melt, are compared with the values calculated by an internal force field previously adopted for *trans*-1,4-polybutadiene[4] and a vibrational assignment is proposed. Details of the calculation method are also given since, in contrast with previous work,[4] translational and rotational coordinates for each repeat unit are now used, allowing a better description of the normal modes and the potential energy matrix. A vibrational analysis extended to a three-dimensional crystal, including interactions among chains in terms of semiempirical atom-atom potentials, will be reported in a forthcoming paper. In this next paper we will also present infrared data on deuterio derivatives of ITPP which, when compared with the corresponding calculated values, should confirm the vibrational assignment proposed here for the polymer and give further spectroscopic evidence on the chain conformation.

Experimental Section

ITPP was obtained by stereospecific polymerization of *trans*-1,3-pentadiene through the use of $Al(C_2H_5)_3$–VCl_3 catalyst in *n*-heptane as described in ref 1. All operations were carried out at room temperature and under a N_2 atmosphere. After separation of the amorphous fraction, crystalline ITPP was extracted with benzene and kept under N_2 at low temperature and in the dark to prevent structural or chemical modification of the polymer. Samples for the infrared spectra were examined as solutions in CCl_4 and as films obtained either by hot pressing or by deposition from benzene solutions on KBr or CsI windows.

Spectra for solid-state samples were obtained on a Perkin-Elmer Model 225 in the region 180–4000 cm^{-1} and run at various temperatures with films annealed in order to obtain a crystalline structure for the polymer.

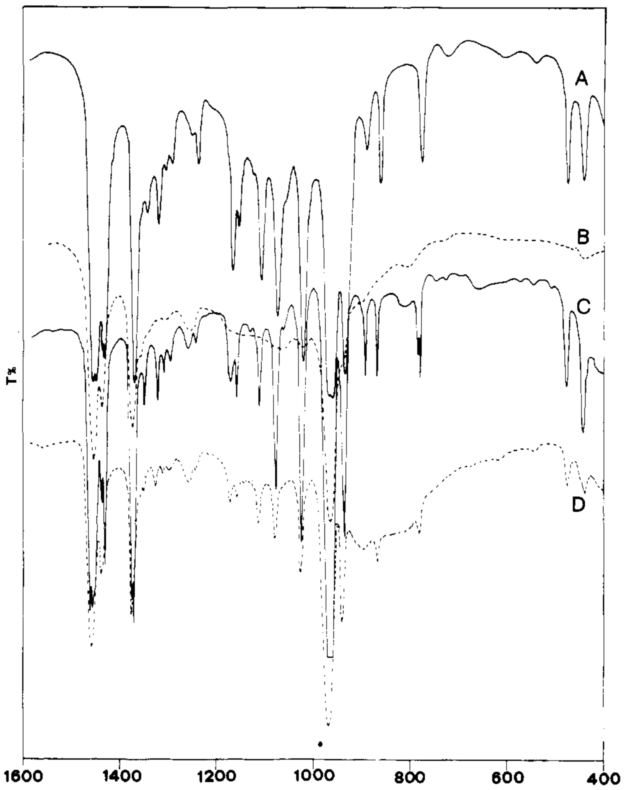

Figure 2. Infrared spectra of *trans*-1,4-poly(1,3-pentadiene): (A) crystalline sample at room temperature; (B) melted sample; (C) crystalline sample at liquid nitrogen temperature; (D) paracrystalline modification.

By melting and fast cooling, the crystalling samples were transformed into the paracrystalline modification and the results were controlled by means of X-ray fiber spectra. The infrared spectrum of ITPP in the region 400–1600 cm^{-1} is shown in Figure 2 for the crystalline sample at room and liquid nitrogen temperatures. In the same figure the spectrum of the paracrystalline sample is also reported and compared with the spectrum of the melt. The absorption spectrum below 400 cm^{-1} was obtained only for the crystalline sample at room temperature.

Method of Calculation

In this section we give a brief outline of the method used to set up the secular equation for an isolated polymer chain in terms of internal and external displacement coordinates. We consider a polymer chain made up of repeat units each containing N atoms such that X_{is}^n is, in a given space-fixed basis, the sth Cartesian component of a vector from the origin to atom i of the nth repeat unit. If ρ_k is a distance or an angle within the chain whose value is a known function of Cartesian coordinates, its expansion in a Taylor series about the equilibrium is

$$S_k \equiv (\rho_k - \rho_k^\circ) = \sum_{is}\sum_{n}\left(\frac{\partial \rho_k}{\partial U_{is}^n}\right)_0 U_{is}^n \qquad (1)$$

Here $U_{is}^n = m_i^{1/2}\Delta X_{is}^n$ are mass-weighted Cartesian displacements and, assuming very small displacements from equilibrium, the expansion is truncated to first order. According to eq 1, S_k are linear coordinates of the kind introduced by Wilson,[5] measure variations of bond lengths, interbond angles, etc., and involve atoms belonging either to the same repeat unit or to different units of a vibrating chain.

Although the set S_k is very convenient for expanding the potential energy V about the equilibrium, as is usually done for isolated molecules, for a polymer chain the dimensionality of the dynamical problem will usually exceed $3N$ even if local redundancies are absent or eliminated. For this reason we introduce here a set of $3N$ independent coordinates q_a^n for each repeat unit such that each q_a^n involves only atoms belonging to the nth repeat unit, according to an algebraical definition explicitly given in what follows. Since basic force constants are given in terms of displacements S_k, we need a transformation to coordinates q_a^n. Thus, under the assumption the potential function for the polymer chain is such that

$$(\partial V/\partial q_a^n)_0 = 0 \qquad \text{for all } a, n \tag{2}$$

force constants in terms of localized coordinates q_a^n are given by

$$\left(\frac{\partial^2 V}{\partial q_a^m \partial q_b^n}\right)_0 = \sum_{kl}\left(\frac{\partial^2 V}{\partial S_k \partial S_l}\right)_0 \sum_{is}\left(\frac{\partial S_k}{\partial U_{is}^m}\right)_0 \times \left(\frac{\partial U_{is}^m}{\partial q_a^m}\right)_0 \sum_{jt}\left(\frac{\partial S_l}{\partial U_{jt}^n}\right)_0 \left(\frac{\partial U_{jt}^n}{\partial q_b^n}\right)_0 \tag{3}$$

Each set of $3N$ coefficients $(\partial U_{is}^m/\partial q_a^m)_0$, for fixed a and m, may be viewed as components of a basic vector in $3N$-dimensional direct space. It follows that, in terms of components $(\partial q_a^m/\partial U_{is}^m)_0$ for the corresponding vector in reciprocal space, we have

$$\left(\frac{\partial U_{is}^m}{\partial q_a^m}\right)_0 = \sum_b\left[\sum_{jt}\left(\frac{\partial U_{jt}^m}{\partial q_a^m}\right)_0\left(\frac{\partial U_{jt}^m}{\partial q_b^m}\right)_0\right]\left(\frac{\partial q_b^m}{\partial U_{is}^m}\right)_0 = \sum_b \mathbf{G}_{ab}^{-1}\left(\frac{\partial q_b^m}{\partial U_{is}^m}\right)_0 \tag{4}$$

Here $\mathbf{G}^{-1}$ is the inverse of a matrix $\mathbf{G}$ whose elements are contravariant components of the metric tensor written as

$$\mathbf{G}_{ab} = \sum_{is}\left(\frac{\partial q_a^m}{\partial U_{is}^m}\right)_0\left(\frac{\partial q_b^m}{\partial U_{is}^m}\right)_0 = \sum_{is}\left(\frac{\partial q_a^n}{\partial U_{is}^n}\right)_0\left(\frac{\partial q_b^n}{\partial U_{is}^n}\right)_0 \tag{5}$$

where the last equality holds for all possible values of n and m just because of the translational symmetry of the polymer chain.

Thus, if a set of basic force constants is known for the polymer in terms of coordinates S_k given by eq 1, force constants (eq 3) in terms of independent coordinates can be easily obtained once the metric tensor is defined for the space of displacements q_a^n. This metric tensor factorizes in blocks of dimensionality $3N$ since we assumed that each q_a^n involves only atoms of the nth repeat unit. One obvious choice would be to take coordinates q_a^m coincident with Cartesian displacements in mass-weighted coordinates, such that $\mathbf{G} = \mathbf{E}$ and eq 3 simply gives force constants in terms of Cartesian coordinates, a procedure adopted, for instance, by Kobayashi[6] in formulating the dynamical matrix for molecular crystals or polymers.

However, a description in terms of displacements U_{is} is not convenient for discussing the vibrational assignment which can be better understood in terms of coordinates q_a^n, adopted in the present paper, which include internal displacements given as a linear combination of those coordinates S_k involving only atoms of a given repeat unit and external coordinates related to translations and rotations of the whole repeat unit. Thus if $R_1^m, R_2^m, ..., R_l^m$ is a subset of the whole set S_k of all internal coordinates involving only atoms of the mth repeat unit, $3N - 6$ independent coordinates q_r^m are defined for each unit such that

$$\left(\frac{\partial q_r^m}{\partial U_{is}^m}\right)_0 = \sum_p\left(\frac{\partial q_r^m}{\partial R_p^m}\right)_0\left(\frac{\partial R_p^m}{\partial U_{is}^m}\right)_0 \tag{6}$$

$$r = 1, 2, ... 3N - 6$$

For nonlinear repeat units the subset of R_p^m coordinates may contain more than $3N - 6$ elements only if redundancies are included.

In this case independent coordinates q_r^m are defined as a linear combination of displacements R_p^m, with constant coefficients given by $(\partial q_r^m/\partial R_p^m)_0$.

For nonlinear repeat units six external coordinates of translational and rotation types are defined as

$$\left(\frac{\partial T_\alpha^m}{\partial U_{is}^m}\right)_0 = \left(\frac{m_i}{M}\right)^{1/2}\Lambda_{s\alpha} \tag{7a}$$

$$\left(\frac{\partial \vartheta_\alpha^m}{\partial U_{is}^m}\right)_0 = \left(\frac{m_i}{I_\alpha}\right)^{1/2}\sum_t(\Lambda \mathbf{M}^\alpha \tilde{\Lambda})_{st}(X_{it}^m - X_{Bt}^m) \tag{7b}$$

$$\alpha = 1, 2, 3$$

In eq 7a M is the total mass of the repeat unit and Λ is a 3×3 real, orthogonal matrix, whose determinant is taken equal to $+1$, which diagonalizes the inertial tensor about the mass center for a repeat unit with eigenvalues I_α. In eq 7b X_{it}^m is the equilibrium value of the corresponding coordinate and X_{Bt}^m is a component for the mass center such the $\sum_i m_i(X_{it}^m - X_{Bt}^m) = 0$. Finally $\mathbf{M}^\alpha$ is a 3×3 skew-symmetric matrix which represents an infinitesimal rotational operator about the αth coordinate axis, such that $\mathbf{M}_{st}^\alpha = \delta_{\alpha ts}$ in terms of Levi-Civita density symbols. Thus ϑ_α^m is an infinitesimal rotation angle about the αth principal inertial axis of the mth repeat unit and, accordingly, T_α^m is a component for a translation of the whole repeat unit.

Because of definitions 7, if by q_α^m we mean any of the six external coordinates, metric tensor elements are such that

$$\mathbf{G}_{\alpha\beta} \equiv \sum_{is}\left(\frac{\partial q_\alpha^m}{\partial U_{is}^m}\right)_0\left(\frac{\partial q_\beta^m}{\partial U_{is}^m}\right)_0 = \delta_{\alpha\beta} \tag{8a}$$

$$\alpha, \beta = 1, 2, ..., 6$$

$$\mathbf{G}_{\alpha r} \equiv \sum_{is}\left(\frac{\partial q_\alpha^m}{\partial U_{is}^m}\right)_0\left(\frac{\partial q_r^m}{\partial U_{is}^m}\right)_0 = 0 \tag{8b}$$

$$\alpha = 1, 2, ..., 6$$

$$r = 1, 2, ..., 3N - 6$$

We recall that metric tensor components in reciprocal space are just elements of the Wilson's $\mathbf{G}$ matrix,[5] inverse to the kinetic energy matrix given by $\mathbf{G}^{-1}$ in eq 4, which is thus a constant quantity in block-diagonal form. It is not difficult to show that eq 8b corresponds, for each r, to the Malhiot and Ferigle conditions[7] on internal coordinates R_p^m written as

$$\sum_i \left(\frac{\partial R_p^m}{\partial X_{is}^m}\right)_0 = 0$$

$$\sum_{is} \left(\frac{\partial R_p^m}{\partial X_{is}^m}\right)_0 \sum_t \mathbf{M}_{st}^{\alpha} X_{it}^m = 0 \qquad (9)$$

On the other hand, conditions on the metric tensor can be also written for covariant components and in this case the set of equations, which are actually the counterpart of eq 8b in direct space, are just the well-known Sayvetz conditions.[8] Thus the metric tensor in the space of displacements is completely defined and, through the use of eq 3 and 4, force constants can be easily obtained in terms of independent molecular displacement coordinates q_a^m, of internal and external types, defined for each repeat unit in the polymer chain.

We conclude this section by introducing translationally symmetrized coordinates

$$Q_a(\mathbf{k}) = \frac{1}{L^{1/2}} \sum_n e^{2\pi i \mathbf{k}\cdot\mathbf{R}_n} q_a^n \qquad (10)$$

which are actually working coordinates for the polymer chain since they allow a factorization of the dynamical problem, for a chain made up of L repeat units, into blocks of dimensionality $3N$ for each value of the wave vector **k**. Strictly speaking for a polymer chain we have translations in only one direction; thus translations $\mathbf{R}_n$ in the direct lattice and wave vectors **k** reduce to scalars. However, the more general vector notation is applied since it turns out to be necessary when calculations are extended to a real three-dimensional polymer crystal.

In terms of coordinates defined by eq 10, elements of the potential energy matrix **F** are given by

$$\mathbf{F}_{ab} \equiv \left(\frac{\partial^2 V}{\partial Q_a(\mathbf{k}) \partial Q_b(-\mathbf{k})}\right)_0 = \sum_n e^{-2\pi i \mathbf{k}\cdot\mathbf{R}_n} \left(\frac{\partial^2 V}{\partial q_a^0 \partial q_b^n}\right)_0 \qquad (11)$$

while the kinetic energy matrix is not **k** dependent and each $3N \times 3N$ block is given by the **G** matrix previously discussed. Vibrational frequencies and eigenvectors, for the polymer chain and as a function of **k**, are thus very simply obtained through diagonalization of the complex matrix **G**·**F**, according to a general procedure.[5]

Table I
Internal Coordinates for *trans*-1,4-Poly(1,3-pentadiene) with Atoms Numbered as in Figure 1

r_1	5	11			C—H str (CH_3)
r_2	5	12			
r_3	5	13			
d_1	4	9			C—H str (CH_2)
d_2	4	10			
s	1	6			C—H str (CH)
l_1	2	7			C—H str (double bond)
l_2	3	8			
T_1	1	2			C—C str (skeletal)
T_2	3	4			
z	1	5			C—C str (CH_3)
D	2	3			C=C str
β_1	11	5	1		C—C—H bend (CH_3)
β_2	12	5	1		
β_3	13	5	1		
ϑ_1	9	4	3		C—C—H bend (CH_2)
ϑ_2	10	4	3		
η	6	1	2		C—C—H bend (CH)
χ	6	1	5		
ψ_1	7	2	1		C—C—H bend (double bond)
ψ_2	8	3	4		
φ_1	7	2	3		C=C—H bend
φ_2	8	3	2		
α_1	12	5	13		H—C—H bend (CH_3)
α_2	11	5	13		
α_3	11	5	12		
δ	9	4	10		H—C—H bend (CH_2)
π	5	1	2		C—C—C bend (CH_3)
ϵ_1	1	2	3		C=C—C bend
ϵ_2	2	3	4		
Γ_1	1	2	3	7	out-of-plane wagging
Γ_2	2	3	4	8	
τ_1	5	1	2	7	C—C torsion (skeletal)
τ_2	6	1	2	3	
τ_3	8	3	4	9	
τ_4	2	3	4	10	
τ_5	2	1	5	11	C—C torsion (CH_3)
τ_6	6	1	5	12	
τ_7	1	2	3	4	C=C torsion
τ_8	7	2	3	8	
R	4	14			C—C str (skeletal)
γ_1	9	4	14		C—C—H bend (CH_2)
γ_2	10	4	14		
ρ	19	14	4		C—C—H bend (CH)
ξ	4	14	18		C—C—C bend (CH_3)
ω	3	4	14		C—C—C bend (skeletal)
σ	4	14	15		
τ_1'	18	14	15	20	C—C torsion (skeletal)
τ_2'	19	14	15	16	
τ_9	4	14	15	16	
τ_{10}	2	3	4	14	
τ_{11}	10	4	14	19	
τ_{12}	3	4	14	15	
τ_{13}	9	4	14	18	
τ_5'	15	14	18	24	C—C torsion (CH_3)
τ_6'	19	14	18	25	
τ_{14}	4	14	18	26	

Normal-Mode Calculation

Geometric parameters used for normal-mode calculations on a single chain of ITPP are those given in ref 2 with the exception of the C=C—C angle, here taken equal to 122°15′, rather than 120°, to reproduce the repeat period of 4.85 Å as determined from X-ray data. A discussion of the possible conformations of the polymer chain may benefit from a simple analysis[9] based on the assumption that only staggered conformations are allowed and that distances between hydrogen atoms cannot be shorter than van der Waals radii. This analysis is reported in Figure 3, where possible different situations are shown for the three single bonds between two consecutive double bonds. Since the polymer contains groups of the type =CH—CH(CH_3)—CH_2— and the tertiary carbon atom is actually asymmetric, a given S configuration was selected in Figure 3. The skew form for the polymer corresponds to a sequence A = $G^+G^-G^+$ and this apparently does not show an internal energy greater than that of the cis form, given by a sequence B = G^-G^-C. Other conformations with higher internal energies are possible and their approximate order of stability is given by

$$A \simeq B > C = D \gg E > F \gg G > H$$

This analysis cannot be used to establish a cis or skew form as the more stable conformation for the polymer chain in the crystal since it does not take into account interchain forces which may favor a packing of chains in a cis form, as reported in ref 2. However, it justifies the procedure used in this work, which consists of performing frequency calculations for the two most probable conformations using a force field transferred, without unnecessary adjustments, from similar molecules. A comparison of the calculated spectrum with the observed data should give spectroscopic evidence on the chain conformation, but this, however, needs to be confirmed by further calcula-

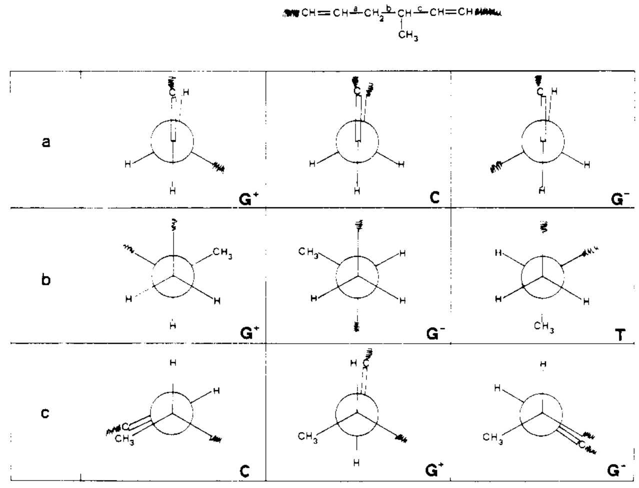

Figure 3. Conformational analysis for chain single bonds between two consecutive double bonds. The asymmetric carbon atom is in the S absolute configuration. For bonds b and c the nomenclature refers to the methyl group. The conformations are labeled as follows: A = $G^+G^-G^+$, B = G^-G^-C, C = G^+G^-C, D = $G^-G^-G^+$, E = G^+TC, F = G^+TG^+, G = G^-TC, H = G^-TG^+.

Table II
Set of 3*N* Independent Coordinates per Repeat Unit[a]

$q_1 = r_1$
$q_2 = r_2$
$q_3 = r_3$
$q_4 = d_1$
$q_5 = d_2$
$q_6 = s$
$q_7 = l_1$
$q_8 = l_2$
$q_9 = T_1$
$q_{10} = T_2$
$q_{11} = z$
$q_{12} = D$
$q_{13} = (1/\sqrt{12})(2\beta_1 - \beta_2 - \beta_3 + 2\alpha_1 - \alpha_2 - \alpha_3)$
$q_{14} = (1/\sqrt{2})(\beta_2 - \beta_3 + \alpha_2 - \alpha_3)$
$q_{15} = (1/\sqrt{2})(\beta_1 - \alpha_1)$
$q_{16} = (1/\sqrt{2})(\beta_2 - a_2)$
$q_{17} = (1/\sqrt{2})(\beta_3 - \alpha_3)$
$q_{18} = (1/\sqrt{6})(2\epsilon_1 - \varphi_1 - \psi_1)$
$q_{19} = (1/\sqrt{6})(2\epsilon_2 - \varphi_2 - \psi_2)$
$q_{20} = (1/\sqrt{2})(\varphi_1 - \psi_1)$
$q_{21} = (1/\sqrt{2})(\varphi_2 - \psi_2)$
$q_{22} = \vartheta_1$
$q_{23} = \vartheta_2$
$q_{24} = \eta$
$q_{25} = \chi$
$q_{26} = \delta$
$q_{27} = \pi$
$q_{28} = \Gamma_1$
$q_{29} = \Gamma_2$
$q_{30} = (1/\sqrt{2})(\tau_1 + \tau_2)$
$q_{31} = (1/\sqrt{2})(\tau_3 + \tau_4)$
$q_{32} = (1/\sqrt{2})(\tau_5 + \tau_6)$
$q_{33} = (1/\sqrt{2})(\tau_7 + \tau_8)$
q_{34} = translation along X
q_{35} = translation along Y
q_{36} = translation along Z
q_{37} = rotation about X
q_{38} = rotation about Y
q_{39} = rotation about Z

$\tau_D = (1/\sqrt{2})(\tau_7 + \tau_8) = q_{33}$ $\tau_R = (1/\sqrt{3})(\tau_{11} + \tau_{12} + \tau_{13})$
$\tau_T^{\,1} = (1/\sqrt{3})(\tau_1' + \tau_2' + \tau_9)$ $\tau_Z = (1/\sqrt{3})(\tau_5' + \tau_6' + \tau_{14})$
$\tau_T^{\,2} = (1/\sqrt{3})(\tau_3 + \tau_4 + \tau_{10})$

[a] X, Y, and Z refer here to the three principal inertial axes of the repeat unit. Group torsions are defined in terms of isolated torsions as given in Table I.

Table III
Valence Force Constants[d] **for *trans*-1,4-Poly(1,3-pentadiene)**[a]

force const	value	force const	value	force const	value
K_r	4.699[b]	H_Γ	0.199	$F_{\varphi\psi}$	0.027
K_d	4.524	τ_D	0.328	$F_{\vartheta\gamma}$	0.015
K_s	4.588[b]	τ_T	0.021	$F_{\beta\beta}$	−0.012[b]
K_l	4.947	τ_R	0.024	$F_{\eta\chi}$	0.012[b]
K_T	4.384	F_{rr}	0.043[b]	$F_{\omega\vartheta}$	−0.028
K_z	4.387[b]	F_{dd}	0.004	$F_{\epsilon\varphi}$	−0.029
K_D	8.702	F_{TR}	0.122	$F_{\sigma\pi}$	−0.041
H_β	0.645[b]	F_{Rz}	0.101[b]	f_t	0.120
H_ϑ	0.668	F_{TD}	0.094	f_g	−0.012
H_γ	0.664	$F_{T\vartheta}$	0.341	f_t'	0.008
H_η	0.657[b]	$F_{T\psi}$	0.333	f_g'	0.029
H_ψ	0.480	$F_{R\gamma}$	0.348	f_t''	−0.014[b]
H_φ	0.500	$F_{D\varphi}$	0.355	f_g''	−0.006
H_α	0.524[c]	$F_{z\beta}$	0.328[b]	$f_{\gamma\xi}{}^t$	0.049[b]
H_δ	0.518[c]	$F_{T\gamma}$	0.066	$f_{\gamma\xi}{}^g$	−0.045
H_π	1.084[b]	$F_{T\varphi}$	0.075	$f_{\omega\sigma}{}^t$	0.080
H_ω	1.049	$F_{T\omega}$	0.419	$f_{\epsilon\omega}{}^g$	0.012
H_ϵ	0.910	$F_{\vartheta\vartheta}$	−0.032		

[a] Numerical values are transferred from ref 4 except where otherwise noted. [b] Force constants obtained from saturated hydrocarbons.[10] [c] Force constants modified from their original value of 0.540. The force field is described for the skew form; for the cis form only the interactions enclosed in parentheses change: thus, for the cis form it must be that $f_{\eta\psi} = f_g$, $f_{\eta\varphi} = f_g'$, $f_{\varphi\chi} = f_t''$, $f_{\psi\pi} = f_{\gamma\xi}{}^t$. Symbols such as f_t, f_g, f_t', and f_g' are closely related to those used in ref 4. Stretching constants are in units of mdyn/A, stretch–bend interactions are in units of mdyn/rad, and bending constants are in units of (mdyn A)/(rad)². [d] $K_T = K_R$, $H_\eta = H_\chi = H_\rho$, $H_\pi = H_\xi = H_\sigma$, $\tau_R = \tau_z$, $F_{TR} = F_{Tz}$, $F_{T\vartheta} = F_{T\eta}$, $F_{\omega\vartheta} = F_{\omega\gamma} = F_{\sigma\rho} = F_{\sigma\eta} = F_{\xi\rho} = F_{\xi\chi} = F_{\pi\eta} = F_{\pi\chi}$, $F_{R\gamma} = F_{R\rho} = F_{z\chi}$, $F_{\eta\chi} = F_{\eta\rho} = F_{\rho\chi}$, $F_{T\gamma} = F_{T\chi} = F_{T\rho} = F_{R\vartheta} = F_{R\eta} = F_{R\chi} = F_{z\eta} = F_{z\rho}$, $F_{T\varphi} = F_{D\psi}$, $F_{\vartheta\vartheta} = F_{\gamma\gamma}$, $F_{\epsilon\varphi} = F_{\epsilon\psi}$, $F_{T\omega} = F_{T\pi} = F_{T\epsilon} = F_{T\sigma} = F_{D\epsilon} = F_{R\omega} = F_{R\xi} = F_{R\sigma} = F_{z\pi} = F_{z\xi}$, $F_{\sigma\pi} = F_{\sigma\xi} = F_{\pi\xi}$, $f_t = f_{\beta\chi} = f_{\gamma\rho} = f_{\varphi\varphi} = f_{\vartheta\psi} = (f_{\eta\psi})$, $f_g = f_{\beta\chi} = f_{\gamma\rho} = f_{\vartheta\psi}$, $f_g' = f_{\beta\eta} = f_{\beta\rho} = f_{\vartheta\varphi} = f_{\gamma\psi} = f_{\gamma\eta}$, $f_t' = f_{\beta\eta} = f_{\beta\rho} = f_{\vartheta\rho} = f_{\vartheta\varphi} = f_{\gamma\psi} = f_{\chi\psi} = f_{\varphi\psi} = f_{\gamma\eta} = f_{\gamma\chi} = (f_{\rho\psi}) = (f_{\eta\varphi})$, $f_t'' = f_{\vartheta\chi}$, $f_g'' = f_{\vartheta\chi} = f_{\rho\varphi} = f_{\psi\psi} = f_{\gamma\varphi} = f_{\vartheta\eta} = (f_{\varphi\chi})$, $f_{\gamma\xi}{}^t = f_{\beta\pi} = f_{\beta\xi}$, $f_{\omega\sigma}{}^t = f_{\epsilon\epsilon}$, $f_{\gamma\xi}{}^g = f_{\beta\pi} = f_{\beta\xi} = f_{\gamma\sigma} = f_{\vartheta\epsilon} = f_{\varphi\epsilon} = f_{\eta\epsilon} = f_{\psi\omega} = f_{\rho\omega} = f_{\psi\sigma} = (f_{\psi\pi})$, $f_{\epsilon\omega}{}^g = f_{\epsilon\pi} = f_{\epsilon\sigma} = f_{\omega\xi}$.

tions which include interaction among chains.

The polymer repeat unit is defined by atoms numbered from 1 to 13 in Figure 1, while those identified by numbers from 14 to 26 are translated by one repeat distance along the chain axis such that atom 14 is translationally equivalent to 1, 15 to 2, etc. Internal displacement coordinates, each involving 2–4 atoms numbered as in Figure 1, are given in Table I, where we note that the first 40 coordinates are defined for a repeat unit and are thus of the kind R_p^0, according to the nomenclature given in the previous paragraph. All other coordinates involve atoms of two different repeat units and are needed, together with translated coordinates R_p^1, to describe the valence force field adopted here for the polymer chain, which obviously includes interactions among repeat units.

Local redundancies, for the double bond and CH_3 group, are eliminated through orthogonal transformations of coordinates R_p^0 such that one linear combination corresponds exactly to the first-order redundancy condition. Independent coordinates q_a^0 are thus those shown in Table II, where the last six coordinates are translations and rotations, defined according to eq 7, about inertial axes of the repeat unit. We note that, for $\mathbf{k} = 0$, a suitable choice would lead only to two external coordinates, i.e., two rotations, for a polymer chain, but this simplification is not used here in view of the extension of the normal-mode calculation to the three-dimensional crystal. Coordinates from q_{30} to q_{33} refer to group torsion but do not necessarily coincide with torsional coordinates used to describe the force field. Since force constants used for the present calculations were basically transferred from *trans*-1,4-polybutadiene,[4] group torsions must be defined accordingly. For this reason corresponding force constants were defined in terms of group torsions reported at the bottom of Table II which, with the exception of τ_D which coincides with q_{33}, represent linear combinations of individual torsions which may involve atoms belonging to two different repeat units. Thus diagonal force constants for group torsions give contributions to the whole dynamical equation of the polymer chain through a transformation of the kind in eq 3.

Table IV
List of Observed Frequencies for Crystalline Samples of *trans*-1,4-Poly(1,3-pentadiene) at Different Temperatures[a]

room temp	liq N_2 temp	room temp	liq N_2 temp
197 vw		1155 m	1155 m
261 w		1168 s	1170 m
330 w		1240 w	1240 vw
442 m	444 m	1260 w	1260 vw
476 m	476 m		1263 vw
548 vw	551 vw	1294 vw	1294 vw
777 m	777 m	1310 vw	1311 w
	782 w	1320 w	1324 m
862 m	863 m	1344 vw	1347 w
890 w	893 m	1374 vs	1374 vs
935 s	935 s		1377 vs
	937 s	1437 vs	1435 s
965 vs	965 vs		1439 s
1022 s	1025 vs	1456 vs	1456 vs
1074 s	1075 s		1458 s
1109 m	1111 m	1459 vs	1462 vs

[a] vw = very weak, w = weak, m = medium, s = strong, vs = very strong.

The internal force field in terms of general displacements S_k is described in Table III, with numerical values taken from ref 4 and, for the CH_3 group, from saturated hydrocarbons.[10] The validity of the polybutadiene force field[4] was confirmed for similar polymers as, for instance, *trans*-1,4-polychloroprene,[11] and even the inclusion of interchain potential for *trans*-polybutadiene[12] does not require changes in the intrachain potential; hence it is reasonable to foresee satisfactory results even for ITPP. No attempt was made to modify, through a refinement procedure, the existing force field with the exception of the H–C–H bending force constants H_α and H_δ. Their common value of 0.540, as taken from ref 4, produced bending frequencies consistently higher than the experimental values; thus H_α and H_δ were slightly lowered to 0.524 and 0.518. The force field applies to both the cis and skew forms of ITPP since only few interaction terms differ in the two cases, as indicated in Table III.

Results and Discussion

A list of observed frequencies with relative intensities is given in Table IV for the spectra in the region 200–1500 cm^{-1} of crystalline samples of ITPP at room and liquid nitrogen temperatures. Calculated values of vibrational frequencies are reported in Table V for both the cis and skew forms and compared with experimental data obtained from the infrared spectrum at room temperature for the crystalline sample in the region 180–4000 cm^{-1}. In the same table an approximate description of each normal mode is given in terms of quantities a_k defined as

$$a_k = (L_{ki}^2 F_{kk}/\lambda_i) \times 100$$

where λ_i is the ith calculated frequency, **L** is the matrix of the eigenvectors of the secular equation, and **F** is the

Table V
Observed and Calculated Frequencies for Both Cis and Skew Forms of *trans*-1,4-Poly(1,3-pentadiene) and Approximate Description in Terms of Potential Energy Distribution[a]

	calcd		potential energy distribution																		
obsd	cis form	skew form	r	d	s	l	T	z	D	$\alpha\beta$	$\epsilon\varphi\psi$	$\varphi\psi$	ϑ	$\eta\chi$	δ	π	Γ	τ_T	τ_z	τ_D	rot
3025	3027	3027				97															
	3009	3009				99															
	2961	2961	99																		
2959	2961	2961	99																		
2920	2919	2919		94																	
2902	2903	2904			94																
2874	2882	2882	99																		
2841	2844	2845		99																	
1660	1658	1661					14		66			14									
1459	1460	1460								95											
1456	1459	1459								99											
1437	1437	1437											14		83						
1374	1387	1385								74				14							
1344	1357	1352						10		28				39							
1320	1351	1326										21	24	35							
1310	1279	1315										25	30	25							
1294	1277	1284					10		14		31	12	11	10							
1260	1261	1261											32	37							
1168	1191	1174					33			18	11	11				11					
1155	1157	1157								28	14	10									10
1109	1094	1108					12	47													
1074	1075	1090					23					37	15	15							
1022	1022	1022					45						15								
965	983	983															39	16		43	
935	944	944					26			45				10							
890	896	917								45			10	17				12			
862	862	860						29					11				32	11			
777	755	759															76	11			
548	613	561									31						14				24
476	467	457									29			12			11	13			19
442	402	436														58	15				
330	318	330									10							35			47
261	222	211									12					11	13	24	12		23
197	193	192																	60		15
	173	177																80			16

[a] $r = a_1 + a_2 + a_3$, $d = a_4 + a_5$, $s = a_6$, $l = a_7 + a_8$, $T = a_9 + a_{10}$, $z = a_{11}$, $D = a_{12}$, $\alpha\beta = a_{13} + a_{14} + a_{15} + a_{16} + a_{17}$, $\epsilon\varphi\psi = a_{18} + a_{19}$, $\varphi\psi = a_{20} + a_{21}$, $\vartheta = a_{22} + a_{23}$, $\eta\chi = a_{24} + a_{25}$, $\delta = a_{26}$, $\pi = a_{27}$, $\Gamma = a_{28} + a_{29}$, $\tau_T = a_{30} + a_{31}$, $\tau_z = a_{32}$, $\tau_D = a_{33}$, rot $= a_{37} + a_{38} + a_{39}$ (see text).

potential energy matrix in terms of q coordinates. For the sake of simplicity, contributions less than 10% have been omitted from the potential energy distribution which refers to the calculation performed for the skew form. Similar results would be obtained from the cis form and have not been reported here.

The overall agreement between observed and calculated frequencies is satisfactory for both the cis and skew forms and this reflects the overall conformational similarity between the two forms. We note, however, that the average error $|\nu_i^{\text{calcd}} - \nu_i^{\text{obsd}}|$ is equal to 12.3 cm^{-1} for the cis form and 8.0 cm^{-1} for the skew form and marked differences are observed only for few bands. Calculations for both the cis and skew forms allow an unambiguous assignment of the CH stretching motions, of the C=C stretching at 1660 cm^{-1}, and of the CH_2 bending motions in the region 1460–1370 cm^{-1} due to CH_2 and CH_3 groups. Marked differences in the values calculated for the two forms occur between 1350 and 1260 cm^{-1}, the agreement between calculated and observed frequencies being much better for the skew rather than the cis form in this region. The normal modes involved show a marked character of (CH_3)–C–H bending according to the potential energy distribution, and, looking at conformations C and G^+ in Figure 3 for the c bond, we see that vibrations of just this type are expected to be sensitive to the position of the side methyl group. A much better agreement for the skew form, rather than the cis form, is also found for frequencies observed at 442 and 548 cm^{-1}, although the low intensity of the latter observed peak may put doubts on its character of fundamental band.

The vibrational assignment, as derived from Table V, must be consistent with the observed spectrum in the sense that it must also correctly account for bands observed in the spectra of crystalline and paracrystalline samples but absent in the spectrum of the melt. Since three-dimensional order is absent in the paracrystalline modification, such bands are considered to be characteristic of the regularity of the polymer chain while those observed even for the melt are clearly due to vibrations of local chemical groups insensitive to the chain conformation. From Figure 2 we see that the strong bands at 1168, 1155, 1109, 1074, 1022, 935, 862, 777, 476, and 442 cm^{-1} completely disappear in going from the solid, crystalline or paracrystalline, to the melt; this is consistent with their character of "skeletal" vibrations since, according to data of Table V, they involve C–C stretchings or torsions about single bonds of the main chain or rotations. This is not the case of the band at 965 cm^{-1} which maintains intensity even in the melt and should be thus attributed to a group vibration not affected by the regularity of the chain. The assignment of this band as CH out-of-plane wagging is confirmed by the potential energy distribution, and this is a test on the accuracy of the prediction based on normal-mode calculations for an isolated chain. Bands observed at 330 and 261 cm^{-1} should be highly characteristic of the chain conformation, but it was not possible to obtain experimental data at different temperatures in the region below 400 cm^{-1}; thus no direct comparison is possible. The band at 197 cm^{-1} is instead described as a methyl torsion and should not depend on the chain conformation as shown by the fact that its calculated value does not differ in going from the cis to the skew form.

Some observed frequencies, and most remarkably the band at 261 cm^{-1}, are not well reproduced by any of the two calculated spectra; this can be explained if we assume that interchain forces play a role in the crystal and cause a shift toward higher frequencies. The role of interchain forces is, on the other hand, evident from splittings observed for the bands at 777 cm^{-1} and in the CH_2 bending region, as can be seen in the spectrum at liquid nitrogen temperature. Effects of the crystal field are considered in a forthcoming paper in which interchain potential will be introduced in terms of interactions among atoms of different chains. Here we may simply conclude that the vibrational spectrum of crystalline ITPP is well accounted for by a single-chain model with a skew arrangement of the methyl group relative to adjacent double bonds.

These conclusions will be checked through similar calculations carried out on deuterio derivatives of ITPP to see whether better agreement for the skew form is also obtained for these polymers.

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