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Conformational Properties of Polyisobutylene[1]

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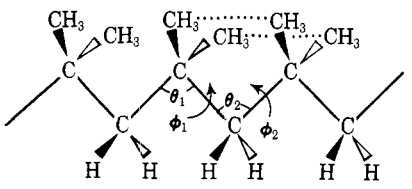
ABSTRACT: Polyisobutylene is a sterically strained and crowded macromolecule, yet it is an elastomer with a low glass temperature. In order to investigate the molecular structural basis for this fact, we have undertaken the calculation of the conformational properties of 2,2,4,4-tetramethylpentane, 2,2,4,4,6,6-hexamethylheptane, and 2,2,4,4,6,6,8,8-octamethylnonane. All of the atoms were allowed to move independently and such motions as cooperative interlocking methyl group rotations, steric repulsions of the methyl groups forcing the chain bond angles wider and distorting the chain rotational angles, were thus incorporated. The calculations were completely *a priori*, the parameters in the energy function minimized were taken from previous work. The calculations yield a most stable conformation, in agreement with the interpretation by Allegra, Benedetti, and Pedone of the X-ray diffraction of the crystal. A relatively simple conformational model gives a good representation of the conformations calculated and permits a statistical mechanical calculation of the characteristic ratio. Energy diagrams for bond rotation in tetramethylpentane and hexamethylheptane were generated, and on their basis, a suggestion regarding the origin of the elastomeric properties of polyisobutylene is made.

Vinylidene polymers, $-CH_2CX_2-$, are interesting from a structure–property point of view because they show a pronounced lowering of the glass temperature over their vinyl counterparts, $-CH_2CHX$. It is of interest to investigate to what extent this behavior can be related to the conformational properties and the energetics of bond rotation of these polymers. Polyisobutylene (PIB) is especially interesting because inspection of models shows it to be a sterically strained and crowded molecule, yet it is an elastomer with quite a low T_g.

PIB is characterized by crowding of the methyl groups in



polyisobutylene (PIB)

all conformations. Much of the previous work on PIB has been summarized.[2] It attempts to interpret its conformational properties in terms of the most stable conformation being an 8/5 helix as inferred from X-ray diffraction on the oriented crystalline form of the material. This implies[2,3] that the most stable conformation has both bond rotation angles at 98° (based on eclipsed as zero) or, in another interpretation,[2,4] one at 78° and another at 129°. However, Wasai, Saegusa, and Furukawa[5] suggested an 8/3 helix, and a recent paper by Allegra, *et al.*,[6] gives convincing evidence that the X-ray diffraction actually shows an 8/3 helix. In conjunction with conformational calculations, the latter have interpreted this helix in terms of an alternating distorted TG structure (203° and 313° bond rotation angles). In their conformational calculations on a monomeric unit, the methyl groups were considered fixed (no rotation about C–CH_3 bond) or as point force centers. Since the methyl crowding is alleviated by distortion of θ_2 to larger than tetrahedral values, the methyl···methyl potential parameters were adjusted to give a value of θ_2 (= 124°) in agreement with an X-ray diffraction study of 2,2,4,4-tetramethyladipic acid (θ_2 = 122.6°). With the chain constrained with each monomer unit in the same conformation ($\phi_1 = \phi_3 = \phi_5$, etc., $\phi_2 = \phi_4 = \phi_6$, etc.), and all bond angles and lengths except θ_1, θ_2, ϕ_1, and ϕ_2 (and their counterparts) fixed, a contour map was generated as a function of ϕ_1 and ϕ_2, with θ_1 and θ_2 adjusted to minimize the energy. The principal conclusion of their calculations was that methyl crowding is best alleviated when pairs of bonds (ϕ_1, ϕ_2) are distorted (about 20°) in the same sense from 60 and 180°; *i.e.*, T_+T_+, T_-T_-, T_+G_+, T_+G_+', T_-G_-, T_-G_-', etc. (see Table I for notation). For uniformly repeated sequences, Allegra, *et al.*,[6] found that T_-G_- pairs were more stable than T_+G_+ pairs. However, they did not consider the interaction between two pairs of bonds when the pairs were in different conformations.

(1) Presented at the 162nd National Meeting of the American Chemical Society, Division of Polymer Chemistry, Washington, D. C., Sept 12–17, 1971.

(2) P. J. Flory, "Statistical Mechanics of Chain Molecules," Interscience, New York, N. Y., 1969.

(3) A. M. Liquori, *Acta Crystallogr.*, **8**, 345 (1955).

(4) C. W. Bunn and D. R. Holmes, *Discuss. Faraday Soc.*, **No. 25**, 95 (1958).

(5) G. Wasai, T. Saegusa, and J. Furukawa, *Makromol. Chem.*, **86**, 1 (1965).

(6) G. Allegra, E. Benedetti, and C. Pedone, *Macromolecules*, **3**, 727 (1970).

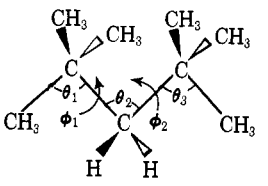
TABLE I
CONFORMATIONAL NOTATION

eclipsed = 0°
G = 60°, G_- < 60°, G_+ > 60°
T = 180°, T_- < 180°, T_+ > 180°
G′ = 300°, G_-' < 300°, G_+' > 300°

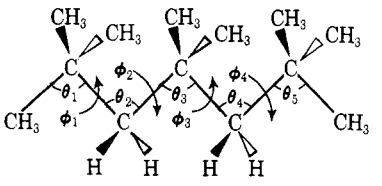
[a] Conformational sequences in which all plus signs are changed to minus signs and primed symbols to unprimed symbols (and *vice versa*) differ only in right- and left-handedness and have the same energy; *e.g.*, $T_+G_+ = T_-G_-'$.

Conformational Calculations and Results

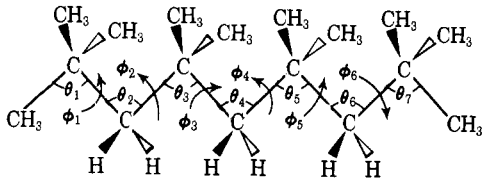
In the work reported here, we have made more detailed and sophisticated calculations on polyisobutylene, taking advantage of recently developed conformational calculation methods.[7-9] In particular, we have calculated in a completely *a priori* manner conformational properties of 2,2,4,4-tetramethylpentane ("monomer"), 2,2,4,4,6,6-hexamethylheptane ("dimer"), and 2,2,4,4,6,6,8,8-octamethylnonane ("trimer").



"monomer"



"dimer"



"trimer"

The potential function parameters of ref 8 were used. Energy minimization calculations were carried out which "automatically" converge on the local conformation of least energy from a starting approximation to those conformations inspired by inspection of models. All atoms of the three molecules (29, 41, and 53 atoms respectively) are allowed to move independently. Consequently, all bond lengths and angles can adjust to seek the minimum energy. This includes interlocking cooperative rotation of the methyl groups and distortion of the chain bond angles and bond rotation angles to accommodate the methyl repulsions. Nonbonded interactions between all atoms not in a bond angle interaction are included, ~1200 such interactions in the trimer.

Our calculations agree qualitatively, for the most part, with the conclusions of Allegra, *et al.*,[6] as far as the latter go. However, we find quantitative differences and, especially, differences in the model for representing the conformational calculations (see section on characteristic ratio). We find pairwise distortion (T_+T_+, T_+G_+, etc.) from the 60, 180, and 300° G, T, G′ bond rotation angles. In our calculations on monomer, the angles are distorted about 17° on either side of the above positions. The skeletal bond angle, θ_2, is calculated to be 122°, in agreement with the surmise[6] from the structure of 2,2,4,4-tetramethyladipic acid. A sensitive test of the overall success of the calculation is a comparison of the strain energy (from angle distortions and atom crowding) with that determined experimentally *via* the heat of formation. Table II makes this comparison. The agreement is very satisfactory, especially considering that the strain energy results primarily from angle distortions forced by nonbonded interactions. This is a situation particularly sensitive to the potential function parameters used.

TABLE II
COMPARISON OF CALCULATED AND EXPERIMENTAL STRAIN ENERGIES (SE) (KCAL/MOL) OF 2,2,4,4-TETRAMETHYLPENTANE

$-\Delta H_f°$, g (298°)			
Exptl[a]	Ref structure[b]	SE, exptl	SE, calcd, this work
−57.83	−64.46	6.6	7.4

[a] D. R. Stull, E. F. Westrum, Jr., and G. C. Sinke, "The Chemical Thermodynamics of Organic Compounds," Wiley, New York, N. Y., 1969. [b] Unstrained reference structure from group contribution. Group contributions from ref 8.

From the dimer, we are able to study the interaction between one pair of interior (to methyl-substituted carbons) bonds and another (ϕ_1, ϕ_2, with ϕ_3, ϕ_4). In the dimer there are no differences in conformation engendered by the stable positions of ϕ_1 and ϕ_4 other than plus or minus, and it is appropriate to label 1 and 4 as always trans conformation. In the trimer all conformations of the interior pair ϕ_3, ϕ_4 may be studied in addition to the interaction with neighboring pairs ϕ_1, ϕ_2 and ϕ_5, ϕ_6. Table III summarizes the results of calculations of all the conformations of the dimer and a number of those of the trimer. We have attempted to summarize these energies in terms of inherent conformational energies of an interior pair of bonds and the interaction energy with a neighboring pair. The parameters derived are given in Table IV. It may be seen that they do a satisfactory job of representing the conformational energies. It is to be noticed that although there are interaction energies between two pairs of bonds, there is no particular prejudice to + + pairs occurring next to − − pairs compared to all being of like sign. This is in agreement with the earlier conjecture of Pittsyn and Sharanov.[2,10] Since their calculations were on uniformly repeated sequences, Allegra, *et al.*,[6] did not study this point.

The physical significance of the deduced energy parameters is of interest. Owing to the large number of interactions and degrees of freedom, it is difficult to describe this precisely. However, the parameters can be rationalized either in terms of the number of cooperative interactions or simultaneous coordinations a methyl group must undergo or in terms of obvious long-range steric interferences generated by the backbone conformation. Reference to the idealized structure

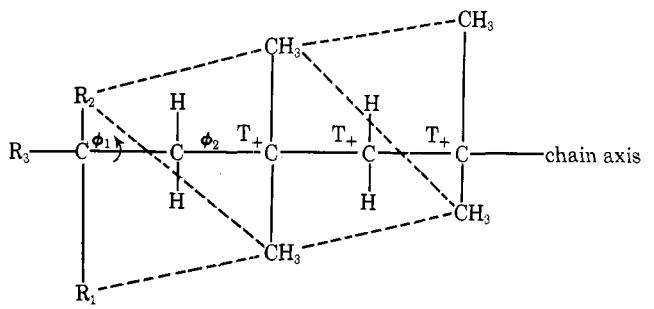
(7) R. H. Boyd, *J. Chem. Phys.*, **49**, 2574 (1968).
(8) S. Chang, D. McNally, S. Shary-Tehrany, M. J. Hickey, and R. H. Boyd, *J. Amer. Chem. Soc.*, **92**, 3109 (1970).
(9) R. H. Boyd, S. N. Sanwal, S. Shary-Tehrany, and D. McNally, *J. Phys. Chem.*, **75**, 1264 (1971).
(10) O. B. Pittsyn and I. A. Sharanov, *Zh. Tekhn. Fiz.*, **27**, 2744, 2762 (1957).

TABLE III
CONFORMATIONAL ENERGIES OF 2,2,4,4,6,6-HEXAMETHYLHEPTANE (DIMER) AND 2,2,4,4,6,6,8,8-OCTAMETHYLNONANE (TRIMER)

			E, kcal/mol[a]
		Dimer	
T_+T_+	T_+T_+, T_-T_-	T_-T_-	21.35 ($E_0 + E_\beta$ = 21.35)
T_+T_+	T_-T_-		21.48 ($E_0 + E_\beta$ = 21.35)
T_+T_+	G_+T_+, T_-T_-	$G_-'T_-$	20.30 (E_0 = 20.35)
T_+T_+	G_-T_-, T_-T_-	$G_+'T_+$	20.45 ($E_0 + E_\omega + E_\delta$ = 20.45)
T_+T_+	$G_+'T_+$, T_-T_-	G_-T_-	19.82 ($E_0 + E_\omega$ = 19.85)
T_+T_+	$G_-'T_-$, T_-T_-	G_+T_+	20.30 (E_0 = 20.35)
T_+G_+	G_+T_+, T_-G_-'	$G_-'T_-$	20.31 (E_0 = 20.35)
T_+G_+	G_-T_-, T_-G_-'	$G_+'T_+$	21.37 ($E_0 + E_\omega + E_\gamma$ = 21.15)
T_+G_+	$G_+'T_+$, T_-G_-'	G_-T_-	high
T_+G_+	$G_-'T_-$		high
T_+G_+'	$G_+'T_+$, T_-G_-	G_-T_-	high
T_+G_+'	G_-T_-		high
		Trimer	
T_+T_+	T_+T_+	T_+T_+	32.17 ($E_0 + 2E_\beta$ = 32.10)
T_+G_+	T_+G_+	T_+T_+	30.08 (E_0 = 30.10)
T_+T_+	G_+G_+'	T_+T_+	29.73 ($E_0 + E_\omega$ = 29.60)
T_+G_+'	T_+G_+'	T_+T_+	29.20 ($E_0 + 2E_\omega$ = 29.10)
T_+T_+	G_+G_+	T_+T_+	30.56 ($E_0 + 2E_\alpha$ = 30.50)
T_+G_+	G_+G_+	G_+T_+	29.99 (E_0 = 30.10)
T_+G_+	G_+G_+	T_+T_+	30.23 ($E_0 + E_\alpha$ = 30.30)
T_-G_-	T_+G_+'	T_+T_+	30.00 ($E_0 + E_\omega + E_\delta$ = 30.20)
T_+G_+'	T_+G_+'	T_-T_-	29.85 ($E_0 + 2E_\omega + E_\delta$ = 29.70)
T_+T_+	$G_+'G_+'$	T_+T_+	29.05 ($E_0 + 2E_\omega$ = 29.10)
T_+G_+	G_+G_+'	T_+T_+	29.50 ($E_0 + E_\omega$ = 29.60)
T_+G_+	G_-T_-	G_+T_+	30.68 ($E_0 + E_\omega + E_\gamma$ = 30.90)
T_+T_+	G_+G_+	T_-T_-	30.16 ($E_0 + E_\alpha$ = 30.30)
T_+G_+	G_+G_+	T_-T_-	30.07 (E_0 = 30.10)
T_+T_+	T_+G_+	T_+T_+	31.10 ($E_0 + E_\beta$ = 31.10)
T_+G_+	T_+T_+	T_+T_+	31.09 ($E_0 + E_\beta$ = 31.10)

[a] The values in parentheses are those constructed from the parameters of Table IV.

below is helpful. Conformations with R_1, R_2 = CH_3, R_3 = CH_2 correspond to $\phi_1\phi_2$ = $|T_+T_+|$; R_2, R_3 = CH_3, and R_1 = CH_2 correspond to $|G_+T_+|$; and R_1, R_3 = CH_3, and R_2 = CH_2 correspond to $|G_+'T_+|$. The E_β interaction arises because the maximum simultaneous right–left coordination of



methyl groups occurs when the $\cdots T_+/T_+\cdots$ or $\cdots T_-/T_+\cdots$ sequence is present (ϕ_2 = T_+ in the diagram). Each methyl on the $C(CH_3)_2$ group undergoes three close interactions in $\cdots T_+/T_+\cdots$, and one has four and the other two in $\cdots T_+/T_-\cdots$. However, if ϕ_1 in the diagram becomes G_+ or G_+' (and ϕ_2 = T_+), a methyl group (R_3) is "freed" in the sense that simultaneous right and left interactions are removed. Although it is involved in interactions with the next interior sequence to the left, it does not interact in the ϕ_1, ϕ_2 interior sequence on the right. The extra stability of G_+' (and G_-) relative to G_+ (and G_-'), the E_ω interaction, is a consequence of freeing the methyl that would have been R_2 in a trans conformation rather than R_1. The R_2 position undergoes two close interactions to the right, whereas R_1 has only one. This argument presupposes that the orientation of the hydrogens on the $-CH_2-$ is such that appreciable disturbance of the rotational conformation of the R_2–C (when ϕ_1 = G_+') or R_1–C bond (when ϕ_1 = G_+) which is involved in the interior pair to the left of ϕ_1, ϕ_2 is not necessary in order for the R_2 (or R_1) to coordinate efficiently with the $C(CH_3)_2$ on the right side of ϕ_1, ϕ_2. For ϕ_1 = G_+' and the R_2–C bond = T_+, this appears to be true. However, for the R_2–C bond = T_-, the $\cdots T_-/G_+'\cdots$ interaction (E_δ) arises. For ϕ_1 = G_+, the R_1 group interacts with only one methyl and is, therefore, less sensitive to the conformation of the R_1–C bond, and an interaction analogous to E_δ does not appear to arise directly. The relatively minor $G_+G_+/T_+\cdots$ interaction (E_α = 200 cal) appears to be real in terms of achieving a somewhat better fit of the conformational energies. It does not appear to have a ready explanation except that, perhaps, it is the ϕ_1 = G_+ analogy to $\cdots T_-/G_+'\cdots$ (the sign of T is proper for this) but somehow requires an additional G_+ group to bring it out.

When exterior bonds are in $\cdots G/G\cdots$ conformations, there is an interference between two $C(CH_3)_2$ groups that are separated by a $-CH_2C(CH_3)_2CH_2-$ sequence. This interference is intolerable when $\cdots G_+'/G_+'\cdots$ (or $\cdots G_-/G_-\cdots$) is present but alleviated to the E_γ interaction when present as $\cdots G_+/G_-\cdots$ ($=\cdots G_-'/G_+'\cdots$) and completely absent in $\cdots G_+/G_+\cdots$ (and G_-'/G_-'). When exterior bonds are $\cdots G/G'\cdots$, intolerable interferences take place in all +, − combinations.

The geometrical results obtained for the skeletal bond angles and bond rotational angles are summarized in Table V. The variations in angles in the various minimum-energy conformations demonstrate the necessity for allowing all atoms to be able to move in arriving at realistic conformational energies. However, in the interest of simplifying statistical calculations, it is to be noticed that both types of skeletal bond angles (θ_1 and θ_2 in the PIB diagram) take on relatively uniform values of ~110 and 123° in the interior of most of the sequences of dimer and trimer, although deviations of as much as 5° can take place for θ_1. A further approximation that simplifies statistical mechanical calculations somewhat is that T_+, T_-, G_+, G_-, G_+', and G_-' conformations can be assigned values of the rotational angles, ϕ, independent of neighboring bonds. It can be seen that this is not a bad

TABLE IV
PARAMETERS FOR REPRESENTING CONFORMATIONAL ENERGIES[a]

Relative energies of bonds; each G_+' or G_- bond = E_ω = −500 cal (all others are zero)

Interaction energies of a pair of interior bonds with the neighboring pair

$\cdots T_+/T_+\cdots$, $\cdots T_+/T_-\cdots$ = E_β = 1000 cal
$\cdots T_+/G_-\cdots$, $\cdots T_-/G_+'\cdots$ = E_δ = 600 cal
$G_+G_+/T_+\cdots$, $G_-'G_-'/T_-\cdots$ = E_α = 200 cal
$\cdots T_+$ or T_-/any except above α, β, and δ types = 0
$\cdots G_+/G_-\cdots$, $\cdots G_-'/G_+'\cdots$ = E_γ = 1300 cal
$\cdots G_+/G_+\cdots$, G_-'/G_-' = 0
$\cdots G_+/G_+'\cdots$, $\cdots G_-'/G_-\cdots$, $\cdots G_+/G_-'\cdots$, $\cdots G_-'/G_+\cdots$, $\cdots G_+'/G_+'\cdots$, $\cdots G_-/G_-\cdots$, $\cdots G_+'/G_-\cdots$ = very high

E_0(dimer) = 20.35 kcal[a]
E_0(trimer) = 30.10 kcal[a]

[a] Base energy for calculation of absolute conformational energy.

TABLE V
GEOMETRICAL RESULTS (SKELETAL ANGLES) FOR CONSORMATIONS OF PIB[a]

Conformation	ϕ_1	ϕ_2	ϕ_3	ϕ_4	ϕ_5	ϕ_6	θ_1	θ_2	θ_3	θ_4	θ_5	θ_6	θ_7
2,2,4,4-Tetramethylpentane (Monomer)													
T_+T_+	192.41	195.27					106.45	122.30	111.84				
2,2,4,4,6,6-Hexamethylheptane (Dimer)													
$T_+T_+T_+T_+$	191.08	197.35	195.95	192.47			106.17	123.28	104.55	123.47	106.95		
$T_+T_+T_-T_-$	190.65	196.26	169.32	165.37			106.24	123.16	104.76	123.30	107.02		
$T_+T_+G_+T_+$	187.80	194.48	80.93	191.86			105.89	122.76	109.50	122.59	107.05		
$T_+T_+G_-T_-$	189.93	186.49	52.09	159.36			106.10	122.79	111.74	122.75	107.11		
$T_+T_+G_+'T_+$	192.94	194.96	307.74	194.50			106.18	122.70	111.18	122.69	107.12		
$T_+T_+G_-'T_-$	190.93	199.69	287.97	166.36			106.13	122.71	110.08	123.06	107.12		
$T_+G_+G_+T_+$	193.46	72.07	72.29	194.52			106.31	122.87	114.98	122.97	107.09		
$T_+G_+G_-T_-$	193.43	78.11	56.58	158.21			106.52	122.71	115.39	123.07	107.09		
2,2,4,4,6,6,8,8-Octamethylnonane (Trimer)													
$T_+T_+T_+T_+T_+T_+$	191.35	196.89	195.53	196.31	195.48	192.88	106.12	123.41	104.31	124.63	104.14	123.59	106.92
$T_+G_+T_+G_+T_+T_+$	192.96	81.73	191.71	78.12	192.14	189.84	106.50	122.53	108.53	123.41	109.16	122.93	106.99
$T_+T_+G_+G_+'T_+T_+$	187.64	194.10	84.10	306.96	189.61	196.94	105.92	122.89	109.88	123.27	110.47	122.92	106.99
$T_+G_+'T_+G_+'T_+T_+$	195.01	308.34	195.84	309.56	194.76	194.57	106.14	122.87	109.72	123.45	110.24	122.75	107.05
$T_+T_+G_+G_+T_+T_+$	188.33	194.83	80.16	80.69	193.29	190.66	106.12	122.90	109.57	123.26	109.20	123.10	106.94
$T_+G_+G_+G_+G_+T_+$	192.46	73.41	74.87	73.19	71.70	194.75	106.22	122.95	114.76	123.66	115.12	123.05	107.07
$T_+G_+G_+G_+T_+T_+$	193.85	71.69	71.69	82.47	192.12	190.09	106.28	122.94	115.08	123.53	108.89	123.05	106.97
$T_-G_-T_+G_+'T_+T_+$	159.98	52.09	186.65	307.53	195.89	193.69	106.43	123.09	110.25	123.63	110.71	122.86	107.01
$T_+G_+'T_+G_+'T_-T_-$	193.94	307.42	197.91	308.80	173.85	168.25	106.16	122.69	109.49	123.50	110.54	122.88	107.07
$T_+T_+G_+'G_+'T_+T_+$	192.86	195.03	310.09	309.88	193.98	194.58	106.11	122.81	111.52	123.36	110.31	122.83	107.03
$T_+G_+G_+G_+'T_+T_+$	193.86	72.28	75.38	308.59	193.93	194.46	106.29	122.93	115.34	123.64	110.54	122.85	106.97
$T_+G_+G_-T_-G_+T_+$	192.00	79.04	57.82	149.76	71.14	196.48	106.27	122.87	115.24	123.61	109.70	122.88	107.09
$T_+T_+G_+G_+T_-T_-$	187.71	193.64	82.38	71.93	158.13	169.65	106.06	122.82	109.58	123.50	109.55	123.12	106.93
$T_+G_+G_+G_+T_-T_-$	192.82	73.13	74.46	73.27	159.82	168.62	106.25	122.92	114.86	123.74	109.36	122.97	106.97
$T_+T_+T_+G_+T_+T_+$	192.62	195.70	195.99	80.79	193.62	189.27	106.12	123.43	104.48	123.75	109.06	122.94	107.00
$T_+G_+T_+T_+T_+T_+$	192.00	81.48	192.70	193.18	196.38	192.70	106.42	122.59	108.39	124.15	104.25	123.56	106.92

[a] See diagrams in text for designation of θ and ϕ angles.

TABLE VI
STATISTICAL WEIGHT MATRIX[a]

↑		T_-	G_-	G_-'	T_-	G_-	G_-'	T_-	G_-	G_-'	T_+	G_+	G_+'	T_+	G_+	G_+'	T_+	G_+	G_+'
→		T_-	T_-	T_-	G_-	G_-	G_-	G_-'	G_-'	G_-'	T_+	T_+	T_+	G_+	G_+	G_+	G_+'	G_+'	G_+'
T_-	T_-	β	β	β	1	1	1	1	1	α	β	β	β	1	1	1	δ	δ	δ
T_-	G_-	ω	ω	ω							$\delta\omega$	$\delta\omega$	$\delta\omega$	$\gamma\omega$	$\gamma\omega$	$\gamma\omega$			
T_-	G_-'	1	1	1				1	1	1	1	1	1				γ	γ	γ
G_-	T_-	$\beta\omega$	$\beta\omega$	$\beta\omega$	ω	ω	ω	ω	ω	$\alpha\omega$	$\beta\omega$	$\beta\omega$	$\beta\omega$	ω	ω	ω	$\delta\omega$	$\delta\omega$	$\delta\omega$
G_-	G_-	ω^2	ω^2	ω^2							$\delta\omega^2$	$\delta\omega^2$	$\delta\omega^2$	$\gamma\omega^2$	$\gamma\omega^2$	$\gamma\omega^2$			
G_-	G_-'	ω	ω	ω				ω	ω	ω	ω	ω	ω				$\gamma\omega$	$\gamma\omega$	$\gamma\omega$
G_-'	T_-	β	β	β	1	1	1	1	1	α	β	β	β	1	1	1	δ	δ	δ
G_-'	G_-	ω	ω	ω							$\delta\omega$	$\delta\omega$	$\delta\omega$	$\gamma\omega$	$\gamma\omega$	$\gamma\omega$			
G_-'	G_-'	α	α	α				1	1	1	1	1	1				γ	γ	γ
T_+	T_+	β	β	β	δ	δ	δ	1	1	1	β	β	β	1	α	1	1	1	1
T_+	G_+	1	1	1	γ	γ	γ				1	1	1	1	1	1			
T_+	G_+'	$\delta\omega$	$\delta\omega$	$\delta\omega$				$\gamma\omega$	$\gamma\omega$	$\gamma\omega$	ω	ω	ω						
G_+	T_+	β	β	β	δ	δ	δ	1	1	1	β	β	β	1	α	1	1	1	1
G_+	G_+	1	1	1	γ	γ	γ				α	α	α	1	1	1			
G_+	G_+'	$\omega\delta$	$\omega\delta$	$\omega\delta$				$\gamma\omega$	$\gamma\omega$	$\gamma\omega$	ω	ω	ω						
G_+'	T_+	$\beta\omega$	$\beta\omega$	$\beta\omega$	$\delta\omega$	$\delta\omega$	$\delta\omega$	ω	ω	ω	$\beta\omega$	$\beta\omega$	$\beta\omega$	ω	$\alpha\omega$	ω	ω	ω	ω
G_+'	G_+	ω	ω	ω	$\gamma\omega$	$\gamma\omega$	$\gamma\omega$				ω	ω	ω	ω	ω	ω			
G_+'	G_+'	$\delta\omega^2$	$\delta\omega^2$	$\delta\omega^2$				$\gamma\omega^2$	$\gamma\omega^2$	$\gamma\omega^2$	ω^2	ω^2	ω^2						

[a] $\alpha = e^{-E\alpha/RT}$, $\beta = e^{-E\beta/RT}$, etc. See Table IV for values of E_α, E_β, etc.

approximation, but deviations of 5° or so from average values of $T_+ = 195°$, $T_- = 165°$, $G_+ = 74°$, $G_- = 53°$, $G_-' = 286°$, and $G_+' = 307°$ are not uncommon.

Our calculations predict G_+' (or G_-) containing structures to possess added stability and either of the repeating conformations $T_+G_+'\ T_+G_+'\cdots$ or $T_+T_+\ G_+'G_+'\cdots$ to be the most stable conformations of the chain. It is interesting to note that the analysis of the X-ray diffraction by Allegra, *et al.*,[6] leads to $\cdots T_+G_+'\ TG_+'\cdots$ as the chain conformation in the crystal. Their deduced geometry of $\theta_1 = 110°$, $\theta_2 = 124°$, $\phi_1 = 203.3°$, $\phi_2 = 312.5°$ compares very favorably with our calculated values of $\theta_1 = 110°$, $\theta_2 = 123°$, $\phi_1 = 195°$, $\phi_2 = 310°$ for $T_+G_+'\ T_+G_+'(T_+T_+)$ (see Table V).

Characteristic Ratio

With the model of a pair of bonds that is distorted in the same sense from T, G, or G′ as the basic unit of the chain and further interacts with its next neighbor pair, a statistical weight matrix may be constructed from the parameters of Table IV. This matrix is presented in Table VI. The char-

TABLE VII
CALCULATED AND EXPERIMENTAL CHARACTERISTIC RATIOS ($Z = \langle R^2 \rangle / nl^2$) FOR POLYISOBUTYLENE[a]

	Z		d ln Z/dT × 10³	
T, °K	Calcd	Exptl[b]	Calcd	Exptl[b]
298	4.59	6.6	−0.12	−0.20 ± 0.20

[a] Using the energy parameters and statistical weight matrix of Tables IV and VI, respectively. Geometric parameters used were $T_+ \phi = 195°$; $G_+ \phi = 74°$; $G_+' \phi = 307°$; $T_- \phi = 165°$; $G_- \phi = 53°$; $G_-' \phi = 286°$, $\theta_1 = 110°$, $\theta_2 = 123$. [b] See ref 2.

acteristic ratio,[2] Z ($=\langle R^2 \rangle / nl^2$, where $\overline{R^2}$ is the mean-square end-to-end distance and l is the skeletal bond length), was calculated using this matrix. The further approximation was made that bond rotation angles can be assigned to conformations of individual bonds rather than pairs, as implied by the statistical weight matrix. In other words, a value for ϕ for T_+, etc., was assumed that is independent of the conformation of its neighboring bond (see preceding section). The details of this calculation are given in the Appendix. The results are shown in Table VII and compared with experimental values. The agreement is fairly good although not quantitative, the calculated value being significantly smaller than the experimental. The rather small temperature coefficient of Z for PIB is reproduced satisfactorily. The calculated value of Z is rather insensitive to the values of the energy parameters derived and depends mostly on the pattern of exclusion of certain bonds following a bond in the preceding interior pair (the "very high" energies in Table IV.) We do not anticipate a calculation that could lead to values as high as the experimental.

Allegra, *et al.*,[6] calculated the characteristic ratio on the basis of a three-state idealization (T, G, and G′) of the conformation of the molecule and with energy parameters inferred from the calculations on uniformly repeated sequences of bond pairs. Half of the $\cdots T/G \cdots$ sequences (the slash refers to bonds exterior to methyl carbon; see Table IV) were given an energy of 1–2 kcal, and all $\cdots G/G \cdots$ sequences were assigned an energy of 2–4 kcal. The former type is suppressed more severely than our conformational calculations indicate. We find an interaction only of the type $\cdots T_+/G_- \cdots$, and Allegra, *et al.*, did not study +, − combinations. In our model, the difference among T_+G_+'/T_+G_+', etc., and T_+G_+/TG_+, etc., sequences is ascribed to greater stability of the G_+' conformation compared with G_+ rather than to a difference between $\cdots T_+/G_+' \cdots$ and $\cdots T_+/G_+ \cdots$. The $\cdots G/G \cdots$ sequences are also suppressed more heavily than in our model since we assign no *a priori* prejudice to one-third of this type, completely suppress one-third, and assign a weight corresponding to 1300 cal to one-third. As a result, Allegra, *et al.*, obtain a somewhat higher characteristic ratio (in the range of 6.4–6.75) than our calculation indicates. Their value is in better agreement with experiment. However, we believe that our calculations demonstrate adequately the actual nature of the relative stability of T_+T_+/T_+T_+, T_+G_+/T_+G_+, and T_+G_+'/T_+G_+' sequences. Furthermore, the lack of extra steric hindrance in $\cdots G_+/G_+ \cdots$ sequences is apparent even in inspection of models. Thus, we are of the opinion that our model gives a more realistic representation of the conformational properties of the molecule.

Energetics of Internal Rotation

In order to elucidate the kinetic flexibility of PIB, the energetics of bond rotation was investigated. Because of the cooperative nature of the bond interactions in conformational changes, there is no unique rotational energy diagram analogous to that of ethane or polyethylene. However, paths of least energy between selected conformational states can be determined. We have generated the paths between the conformations obtained by arbitrarily rotating an interior chain bond through 360° and allowing the rest of the molecule to take up the minimum-energy conformation. This was done for both monomer and dimer by rotating the angle ϕ_2. The molecules were started in the all T_+ conformation, and the appropriate bond rotated in steps of ~2° by using an artificially high barrier for that bond and a false minimum corresponding to the desired bond rotational angle. The energy was minimized using this artificial potential for the "driving" bond at each step and corrected for the energy that the driving bond actually possessed for the angle of that step. The final converged coordinates of each step served as the initial coordinates of the first iteration of the next step so that the process could be carried out stepwise in a single computer run. The energies (and geometries) of stable conformations as indicated by minima in the energy curves thus generated agreed well (generally to ~100 cal) with the energies in Table III found by starting approximations to what appeared to be reasonable stable conformations from inspection of models. This gives confidence in the reality of the uniqueness of the conformations found by both methods. The results for the energy of the monomer are shown in Figure 1. The response of the angle ϕ_1 to changes in ϕ_2 along the minimum energy path are shown in Figure 2. The energy of the dimer is plotted in Figure 3, and the responses of ϕ_2 and ϕ_3 are shown in Figure 4. For comparison, the rotational energy diagram of *n*-hexane (polyethylene model) calculated here using the same potential function parameters as the PIB calculations is shown in Figure 5. The highly cooperative nature in PIB of the response of the other angle (ϕ_1) in an interior pair to changes in the one being driven (ϕ_2) is particularly apparent in Figures 2 and 4. The existence of the pairwise −, − or +, + distortion of pairs of interior bonds manifests itself in almost discontinuous shifts in ϕ_1 from $- \leftrightarrows +$ in response to ϕ_2 changes as a $- \leftrightarrows +$ barrier is traversed. In contrast, the angle ϕ_3 in Figure 4 shows much more modest meanderings characteristic of the relative independence of two pairs of interior bonds (when not sterically prohibited) and whose interaction can be represented by the pair interaction energies of Table IV.

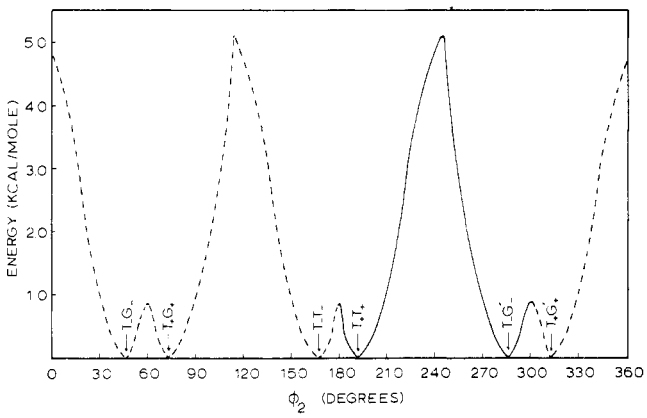


Figure 1. "Monomer." Rotational energy diagram along the least energy path. Although ϕ_2 is labeled as proceeding through G, T, and G′, by symmetry there are no differences among G, T, and G′ states. The portions of the curve constructed by symmetry are shown as dashed lines.

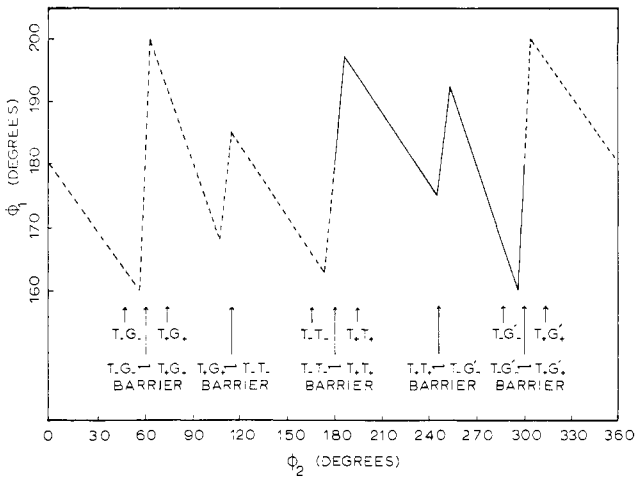


Figure 2. "Monomer." Response of the angle, ϕ_1 (see diagram in text) along the least energy path to changes of the angle, ϕ_1.

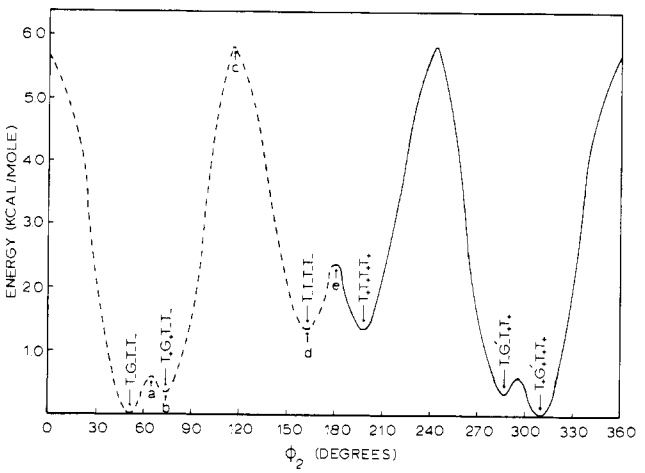


Figure 3. "Dimer." Rotational energy diagram as a function of ϕ_2 along the least energy path. Dashed portions were constructed by symmetry. $E_a = 0.63$, $E_b = 0.38$, $E_c = 5.85$, $E_d = 1.35$, and $E_e = 2.35$ kcal/mol.

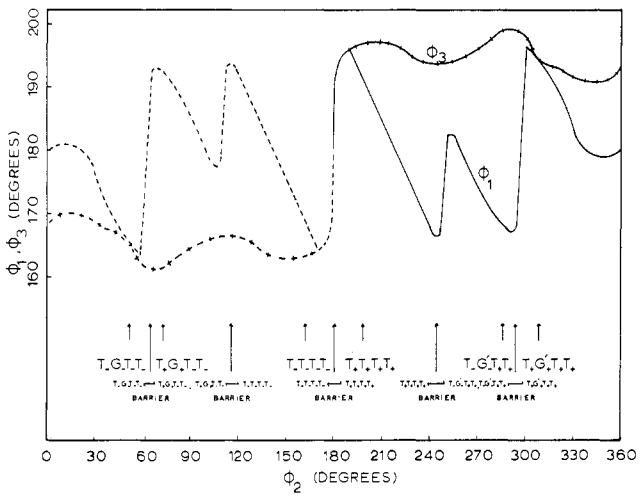


Figure 4. "Dimer." Response of the angles ϕ_1 and ϕ_3 (see diagram in text) along the least energy path to changes in the angle ϕ_2: — — —, ϕ_1; + — +, ϕ_3. Dashed portions were constructed by symmetry.

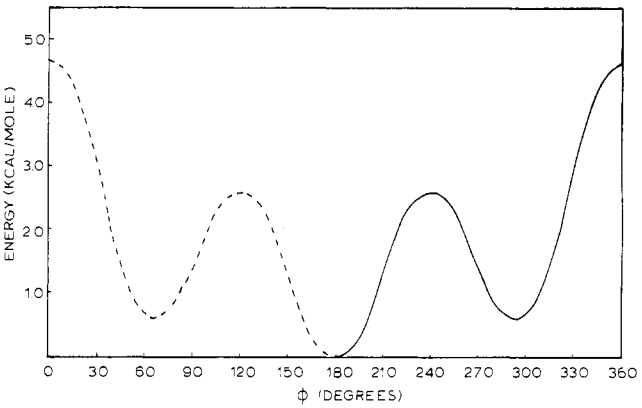


Figure 5. *n*-Hexane (polyethylene model). Rotational energy diagram for comparison with PIB using same potential function parameters.

The energy diagram of Figure 3 for the dimer should be representative of that for similar conformational changes for the long-chain polymer. It is to be noticed that the barrier for transitions between T, G, and G′ states is rather high, considerably higher than the lower of the two barriers (T ⇌ G) in polyethylene (Figure 5). This does not suggest high internal kinetic flexibility for PIB. However, rather than abandoning the hypothesis that such is necessary for elastomeric behavior at relatively low temperatures, we point out that another possibility is present. Transitions between neighboring + + and − − states, ($T_-G_- \rightleftharpoons T_+G_+$, for example) have low barriers and should occur relatively easily. Furthermore, these transitions are accompanied by fairly respectable rotational angle changes, ~30° for each bond in the internal pair. It may be that these changes are sufficient to impart rubberlike elasticity at relatively low temperatures. In other words, PIB at low temperature (but above T_g) might be considered in some approximation as a mixture of molecular chains each containing various sequences of T, G, G′ in which no (or few) transitions occur between T, G, and G′ but in which +, − transitions take place readily. The population of each type of sequence would no doubt be rather thermodynamically stiff but might well behave in a rubbery manner. The calculations of Treloar[11] using the Langevin distribution indicate that rather thermodynamically stiff chains can have typical stress–elongation curves at cross-link densities characteristic of typical elastomers.

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Appendix. The Calculation of the Characteristic Ratio for PIB

The calculation of the characteristic ratio of an infinite-chain polymer from the statistical weight matrix by matrix averaging can be reduced to an eigenvalue problem.[12] In order to do this, the largest eigenvalue of the statistical weight matrix and its (column) eigenvector along with the corresponding (row) eigenvector of the inverse of the characteristic matrix of the statistical weight matrix are required. For the matrix in Table VI it was found that only a few of the eigen-

(11) L. R. G. Treloar, "The Physics of Rubber Elasticity," 2nd ed, Oxford University Press, London, 1958, Chapter VI.
(12) S. Lifson, *J. Chem. Phys.*, **30**, 964 (1959).

values and eigenvectors exist, and therefore, the inverse of the characteristic matrix does not exist. Rather than seek transformations that reduce the matrix to one that can be diagonalized, we proceeded to evaluate the characteristic ratio by direct matrix averaging. The method used is outlined below.

The mean-square end-to-end distance of a chain consisting of n bond vectors $\mathbf{l}_i$

$$R^2 = (\sum \mathbf{l}_i)(\sum \mathbf{l}_j) = nl^2 + 2\sum_{i>j} \mathbf{l}_i \cdot \mathbf{l}_j \quad (1)$$

if of the type illustrated by the PIB diagram in the text, may be approximated with increasing accuracy as n increases by

$$R^2 \cong nl^2 + (n-1)\mathbf{l}_1 \cdot \mathbf{l}_2 + (n-1)\mathbf{l}_2 \cdot \mathbf{l}_3 + (n-2)\mathbf{l}_1 \cdot \mathbf{l}_3 + (n-2)\mathbf{l}_2 \cdot \mathbf{l}_4 + \ldots \quad (2)$$

where $\mathbf{l}_1$, $\mathbf{l}_2$, and $\mathbf{l}_3$ refer to bond vectors of typical bonds in the chain, as indicated by the diagram. The vector dot products can be reformulated in matrix form[2,12] and the following equation in the limit of large n results

$$R^2/nl^2 = \left[1 + \sum_{m=0}^{\infty} \mathbf{h}^T(\mathbf{t}_2\mathbf{t}_1 + \mathbf{t}_1)(\mathbf{t}_2\mathbf{t}_1)^m\mathbf{h} + \sum_{m=0}^{\infty} \mathbf{h}^T(\mathbf{t}_1\mathbf{t}_2 + \mathbf{t}_2)(\mathbf{t}_1\mathbf{t}_2)^m\mathbf{h}\right] \quad (3)$$

where $\mathbf{t}_1$ and $\mathbf{t}_2$ are the transformation matrices[12] for projecting bonds of types 1 and 2 in the PIB diagram on the preceding bond. The matrix $\mathbf{h}$ is

$$\mathbf{h} = \begin{pmatrix} 0 \\ 0 \\ 1 \end{pmatrix} \quad (4)$$

Superscript T refers to the transpose of the matrix in question. The average of R^2 may be found by matrix averaging[2,12] and, from eq 3

$$\langle R^2\rangle/nl^2 = 1 + \sum_{m=0}^{\infty} [\mathbf{h}^T\mathbf{B}^T\mathbf{U}^k\mathbf{U}(\mathbf{T}_2\mathbf{T}_1 + \mathbf{T}_1)(\mathbf{U}\mathbf{T}_2\mathbf{T}_1)^m\mathbf{U}^k\mathbf{B}\mathbf{h} + \mathbf{h}^T\mathbf{B}^T\mathbf{U}^k\mathbf{U}(\mathbf{T}_1\mathbf{T}_2 + \mathbf{T}_2)(\mathbf{U}\mathbf{T}_1\mathbf{T}_2)^m\mathbf{U}^k\mathbf{B}\mathbf{h}]/\mathbf{b}^T\mathbf{u}^k\mathbf{u}^{m+1}\mathbf{u}^k\mathbf{b} \quad (5)$$

where k is a large fixed integer (representing the ends of the molecule exterior to the sequence considered), $\mathbf{u}$ is the statistical weight matrix from Table VI, $\mathbf{b}$ is a single-column matrix with elements equal to 1 and with the number of rows equal to the number of conformational states (=18 for PIB, the number of states of a pair of bonds; see Table VI).

$$\mathbf{b} = \begin{pmatrix} 1 \\ \cdot \\ \cdot \\ \cdot \\ 1 \end{pmatrix} \quad (6)$$

The matrices $\mathbf{T}$ and $\mathbf{U}$ are the "supermatrices" constructed from $\mathbf{t}$ and $\mathbf{u}$ in the manner of Lifson.[12] The matrix $\mathbf{B}$ is the supermatrix constructed from $\mathbf{b}$ as

$$\mathbf{B} = \begin{pmatrix} \mathbf{b} & 0 & 0 \\ 0 & \mathbf{b} & 0 \\ 0 & 0 & \mathbf{b} \end{pmatrix} \quad (7)$$

Its dimensions are 54 × 3 for PIB, the zeroes being repeated as necessary. Since the numerator and denominator of each term in the sum in eq 5 are scalars and thus equal to their traces when considered a matrix, the cyclic permutation property of the trace of a product of matrices leads to

$$\text{typical term of eq 5} = \text{trace}[\{\mathbf{U}(\mathbf{T}_2\mathbf{T}_1 + \mathbf{T}_1)(\mathbf{U}\mathbf{T}_2\mathbf{T}_1)^m\{\mathbf{U}^k\mathbf{B}\mathbf{h}\mathbf{h}^T\mathbf{B}^T\mathbf{U}^k\}\}]/\text{trace}[\mathbf{b}\mathbf{b}^T\mathbf{u}^{2k+m+1}] \quad (8)$$

It is a relatively simple matter by means of a digital computer to evaluate the numerator and denominator of eq 8 for increasing values of m by multiplying the matrices used for the numerator and denominator of the preceding value of m by $\mathbf{U}\mathbf{T}_2\mathbf{T}_1$ and $\mathbf{u}$, respectively. In practice, it was found that eq 5 approaches a geometrical series. About 10–15 terms were required to accomplish this with high accuracy, that is, for a given term to differ from that predicted from the preceding ones as a geometric series by 1 part in 10^5. The remainder of the series at the point of approach to a geometric series was computed as the latter. The remainder was typically several parts in a thousand of the sum of the series.