TABLE VI
PEROXIDE TREATMENT OF POLY(2-PHENYLBUTADIENE)

Sample no.	Peroxide[a]	Molding temp, °C	Soluble material after molding, %	$\overline{M}_n$, g/mol × 10^{-3}	Nmr olefinic H/ aromatic H
4	0			77	0.29
4A	1 (dicumyl)	135	80	25	0.25
4B	2 (dicumyl)	135	68	18	0.17
4C	6 (dicumyl)	177	50	1.3	0.17
4D	6 (benzoyl)	91	100	4.5	0.25

[a] Parts per hundred parts polymer.

Peroxide Treatment of Poly(2-phenylbutadiene). It is well established that polybutadienes containing a high proportion of 1,2 structural units can be peroxide cured to hard thermosetting resins.[5] The cross-linking reaction is of very high efficiency, presumably because it occurs *via* a chain polymerization type mechanism in which several double bonds are consumed by each peroxide molecule.[17] Table VI lists the results obtained when a poly(2-phenylbutadiene) containing about 50% vinyl units is molded with various amounts of peroxide.

Sample 4 was not molded, but is listed in Table VI as a control. The characterization data for this polymer are listed in Tables II and III. The numbers in the fourth column of Table VI were obtained by extracting the molded samples with hot toluene overnight. The molecular weight values in column five were measured on the soluble portions of the molded polymers. When dicumyl peroxide was employed, dramatic decreases in molecular weight with increasing peroxide loadings were observed. In addition, the concentration of olefinic protons decreased with increasing peroxide levels. When benzoyl peroxide was used, no gel was obtained after molding. However, decreases in both molecular weight and olefinic proton concentration were noted. These results indicate that polymer degradation occurs readily during the peroxide molding of poly(2-phenylbutadiene). This is in sharp contrast to the peroxide treatment of high vinyl polybutadiene, which produces highly cross-linked thermosetting resins.[5]

Acknowledgment. The authors wish to thank Professors H. J. Harwood, R. A. Benkeser, and Dr. R. A. Hayes for helpful discussions during the course of this study. In addition, appreciation is extended to Dr. A. S. Hilton for the mass spectral analyses, Mrs. Jean Hackathorn for sample ozonolyses, and Dr. D. F. Lohr for monomer synthesis.

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Conformational Properties of Polypropylene[1]

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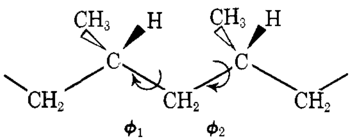
ABSTRACT: Conformational energy calculations have been carried out on 2,4,6-trimethylheptane as a model for polypropylene using energy minimization with all internal degrees of freedom allowed to participate. Previously developed energy functions were used. The conformational energies are well represented by a simple model (identical with one proposed by Flory, Mark, and Abe) with gauche main-chain interactions (E_g = 400 cal), skew methyl interactions (E_{SK} = 600 cal), and excess "pentane interference" interactions (E_ω = 1300 cal). The latter agrees well with both the experimental and our calculated value for the similar interaction in polyethylene. Calculations of characteristic ratio and its temperature coefficient are made over a range of values of E_ω (0–3000 cal) and over the complete range of tacticities (replication probability 0.0–1.0). The calculated characteristic ratios of isotactic and atactic polymer for the conformational energies deduced in our work are in good agreement with experimental values. We conclude that there is no necessity for assuming stereoirregularity in the isotactic form to obtain agreement with experiment for the characteristic ratio or its temperature coefficient. Profiles for the least energy path for bond rotation in the isotactic and syndiotactic forms were calculated.

The conformational properties of polypropylene have aroused considerable interest ever since the discovery of the stereospecific polymerization of propylene. Because of steric repulsions between methyl groups and methyl groups and the chain backbone, inspection of models leads to the expectation that there should be a marked preference for certain sequences of conformations of the skeletal bonds. For example, the isotactic form should prefer repeated TG sequences or repeated G'T sequences (see Table I) for bonds 1 and 2 of **1**. The syndiotactic form should prefer repeated TTTT, TTGG, or G'G'TT sequences for bonds 1,2,3, and 4 of **2**. These expectations are confirmed by the conformations in the crystalline forms of these polymers.[2,3] The degree



1
a meso dyad in polypropylene

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(1) Presented at the Meeting of the Division of Polymer Chemistry, American Chemical Society, April 9–14, 1972, Boston, Mass.

(2) G. Natta, P. Corradini, and P. Ganis, *Makromol. Chem.*, 39, 238 (1960).

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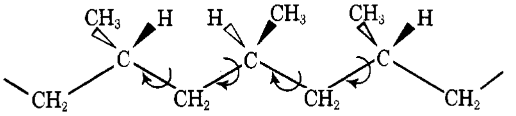
Table I
Conformational Notation

Eclipsed = 0° [a]
$G = 60°$, $G_- < 60°$, $G_+ > 60°$
$T = 180°$, $T_- < 180°$, $T_+ > 180°$
$G' = 300°$, $G_-' < 300°$, $G_+' > 300°$

[a] Rotational angles are measured as a clockwise rotation of the far bond from the near bond looking down the central bond in three-bond sequence.



2

two racemic dyads in polypropylene

to which these sequences of conformations are preferred over others has also been of interest and, particularly in the isotactic form, even aroused controversy. The preference for various conformations is conveniently and succinctly summarized in terms of the *characteristic ratio*[4]

$$Z = \langle R^2 \rangle / nb^2 \qquad (1)$$

where $\langle R^2 \rangle$ is the unperturbed average square of the end-to-end vector of a collection of identical isolated polymer chains, n is the number of bonds in a chain, and b is the length of one bond. The characteristic ratio can be conveniently predicted by statistical mechanics from a knowledge of the energetics of the conformations of a relatively short section of chain or of model compounds. It is also accessible to experimental measurement.[4] Several workers have undertaken the evaluation of the energies of local conformations using assumed potential functions for the steric (nonbonded) interactions between atoms and for the twisting of bonds. Natta, Corradini, and Ganis[2,3] calculated energy contour maps as functions of ϕ_1 and ϕ_2 for the isotactic polymer and $\phi_1 = \phi_2$ and $\phi_3 = \phi_4$ for the syndiotactic form. Allegra, Ganis, and Corradini[5,6] made conformational energy calculations and derived formulas for the characteristic ratio of isotactic and syndiotactic polymers. They concluded that in the isotactic polymer inclusion of one TT conformation for a dyad could be accomplished at no expense of energy

TG/TG/TT/G′T/G′T

and accomplished a reversal of the spiral. They also included the effect of insertion of meso G′G dyads and assigned them an excess energy of 2.7 kcal/mol. Borisova and Birshtein[7] calculated conformational energy maps of the isotactic polymer and concluded that dyads that interrupt the most stable TG (or G′T) helical sequences should have a "mean" excess energy of about 1.5 kcal/mol, which can be compared to the average of the two types considered by Allegra, *et al.*, or 2.7/2 = 1.35 kcal/mol. Birshtein and Ptitsyn[8] have discussed the implications of this for the resulting characteristic ratio and also the effects of the shape of the potential surfaces near the most stable conformations. In a study of the conformational properties of vinyl polymers, Flory, Mark, and Abe[9] made conformational energy calculations for 2,4-dimethylpentane as a model for the iso- and syndiotactic α-olefin polymers. They also analyzed the conformational energies of various conformations in terms of possible physical interactions. Statistical weight matrices for calculating the characteristic ratio of polymers with any (both configurational and conformational) sequence of dyads were set up in terms of parameters describing the physical interactions. The most critical parameter, which they denoted as E_ω, was that describing the excess energy of a methyl in interference with another methyl or with a chain $-CH_2-$ group. This interaction is very similar to the so-called "pentane interference" in polyethylene when a gauche (G) conformation is followed by a gauche (G′) of the opposite sense. For isotactic polymer the characteristic ratio was found to be very sensitive to $\omega = e^{-E_\omega/RT}$, with the characteristic ratio approaching infinity as ω approaches zero. The temperature coefficient of Z was predicted to be always negative and increasing in absolute value as ω decreases. Experimentally, the coefficients for two isotactic α-olefins, poly(*n*-butene-1) and poly(*n*-pentene-1), were found to be small but positive.[10] The characteristic ratio itself of isotactic polymers appeared to be quite modest, a value of $Z = 5.7$ being reported for polypropylene[11] and 9.2 for poly(*n*-pentene-1).[10] Flory, Mark, and Abe,[9] although they did not commit themselves to a definite predicted value of ω, concluded that values they deemed likely would lead to values of Z larger then experimental. Coupled with the conclusion that the temperature coefficients were experimentally small and positive, they concluded that the experimentally measured characteristic ratios and their temperature coefficients were inconsistent with the likely conformational properties of isotactic α-olefins. They proposed a resolution of this paradox through the results of calculations concerning the predicted effects of lack of perfect regularity of tacticity. They found that the combination of a large value of E_ω (5 kcal/mol) and the incorporation of some racemic dyads should lead to a temperature coefficient approaching zero and that the presence of racemic dyads would also limit the characteristic ratio itself to reasonable values. As a consequence they proposed that isotactic poly(*n*-butene-1) and poly(*n*-pentene-1) contain about 5–10% racemic dyads. By inference then, polypropylene would also have a large value of E_ω and consequently would require stereoirregularity to explain its modest characteristic ratio. Flory later commented[12] that 10–20% racemic dyads (and E_ω = 3–5 kcal/mol) would account for the experimental chain dimensions of isotactic polymers.

The above conclusions are at odds with the work of Heatley, Salovey, and Bovey,[13] on the 220-MHz proton nmr spectrum of isotactic polypropylene, who reported that their nmr results show their sample to contain only 2% racemic dyads; yet, the characteristic ratio was measured to be 4.75, slightly smaller than that reported by Kinsinger and Hughes.[11] Flory[14] has criticized the interpretation of the nmr spectrum by Heatley, *et al.*, and suggested that the resulting measurement of stereoregularity might be in error.

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(10) J. E. Mark and P. J. Flory, *ibid.*, **87**, 1423 (1965).

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(12) P. J. Flory, ref 4, p 237.

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TABLE II
CONFORMATIONAL ENERGIES AND GEOMETRIES

2,4,6-Trimethylheptane[a]

Conformation	ϕ_1	ϕ_2	ϕ_3	ϕ_4	E,[b] kcal/mol
TGTG	180.64	61.85	181.05	60.98	5.84 ($E_0 + 3E_{SK} + E_g = 5.85$)
TT$_-$TG	186.48	134.06	182.61	61.27	7.49 ($E_0 + 4E_{SK} + E_\omega = 7.35$)
T$_+$G′TG	222.02	300.78	186.81	62.15	7.92 ($E_0 + 4E_{SK} + E_g + E_\omega = 7.75$)
GG$_+$TG	66.06	98.48	189.30	63.57	7.58 ($E_0 + 4E_{SK} + E_g + E_\omega = 7.75$)
GT$_-$TG	59.31	134.75	183.38	61.34	7.82 ($E_0 + 5E_{SK} + E_\omega = 7.95$)
G′G$_+$TG	296.35	99.38	190.50	64.47	6.98 ($E_0 + 3E_{SK} + E_g + E_\omega = 7.15$)
G$_-$G′TG	260.60	293.77	188.40	62.36	7.96 ($E_0 + 4E_{SK} + E_g + E_\omega = 7.75$)
GT$_-$G′T	58.40	138.79	286.96	166.35	7.51 ($E_0 + 4E_{SK} + E_g + E_\omega = 7.75$)
G′TTG	299.62	175.27	185.28	60.31	5.97 ($E_0 + 4E_{SK} = 6.05$)
TGGG$_+$	184.14	55.61	60.62	93.96	7.45 ($E_0 + 3E_{SK} + 2E_g + E_\omega = 7.55$)
TGG$_-$′T	189.63	64.50	256.12	165.67	6.84 ($E_0 + 2E_{SK} + 2E_g + E_\omega = 6.95$)
T$_+$TT$_+$G′	222.71	174.26	228.32	301.30	9.56 ($E_0 + 5E_{SK} + 2E_\omega = 9.25$)
GG$_+$GG$_+$	65.98	99.61	66.90	100.42	9.50 ($E_0 + 4E_{SK} + 2E_g + 2E_\omega = 9.45$)
G$_-$′G′G$_-$′G	258.51	293.17	258.96	64.91	8.93 ($E_0 + 3E_{SK} + 2E_g + 2E_\omega = 8.85$)
TT$_-$G$_-$′G′	188.33	134.24	275.47	299.35	8.91 ($E_0 + 4E_{SK} + E_g + 2E_\omega = 9.05$)

n-Octane

Conformation	ϕ_1	ϕ_2	ϕ_3	ϕ_4	ϕ_5	E, kcal/mol
TTTTT	179.98	180.00	180.00	179.99	179.99	2.55
TTGTT	179.67	176.09	66.92	176.07	179.66	3.16
TGG$_-$′TT	174.39	63.82	262.11	177.08	179.95	5.06
TG$_-$′GTT	177.32	262.02	63.73	174.45	179.45	5.05

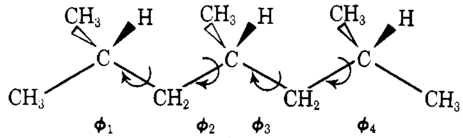
[a] The conformations of 2,4,6-trimethylheptane are named by designating one of the terminal methyl groups at each end to be main chain and the other as a side group and so that the all-trans structure is isotactic. Thus all the conformations are "isotactic" conformations. The naming could equally well have been "syndiotactic;" the helix-reversing G′TTG conformer above is the same as the TTTT syndiotactic conformer, for example. [b] E_{SK} = 600 cal (skew methyl interaction), E_g = 400 cal (gauche main-chain interaction), E_ω = 1300 cal (excess pentane interference interaction), E_0 = 3650 cal.

The present work was undertaken to provide a thorough investigation of the conformations of polypropylene as deduced from energy function calculations of the conformational properties of 2,4,6-trimethylheptane. These calculations benefit from several recent developments in quantitative conformational analysis. Rather than generate contour maps of conformational energies as a function of skeletal bond rotational angles with all other bond angles and lengths held fixed, it is now possible to use energy-minimum-seeking algorithms to find the optimum molecular geometry of various conformations with all degrees of freedom allowed to participate.[15-19] Furthermore, the use of such algorithms has permitted the wide testing of potential functions against a large body of experimental data of diverse types so that more reliable functions have become available.[20-23]

Another important goal of this work was to generate energy profiles for bond rotation. It is our belief that such profiles will be of great value in assessing the importance of internal rotation energetics *vs.* intermolecular hindrances in correlating polymer structure with the glass and other transitions in bulk polymers.

Conformational Calculations and Results

Using previously developed energy function parameters,[20] we have calculated by energy minimization[19] energies and geometries of a number of conformations of 2,4,6-trimethylheptane (**3**). This molecule is appropriate for studying the interactions within a dyad and between pairs of dyads. The calculated energies and skeletal bond rotational angles are reported in Table II. The conformations are labeled according to Table I and as if the planar zigzag structure above were the *lll* isotactic form. The bonds represented by ▽ are considered to go into the plane of the paper, and bonds represented by ▼ are considered to go out of the plane of the paper. The carbons of the terminal methyl groups coplanar with the chain in this conformation retain their designation as skeletal or main-chain carbons in all conformations. By reversing which of the two terminal methyls at each end is to be considered as the main chain, the conformations could have been labeled as appropriate for the *ldl* syndiotactic form.



3

The calculated energies can be rationalized in terms of a simple model based on previously well-recognized conformational interactions. A three-bond CH_2–CH–CH_2–CH– interaction is considered to give rise to a gauche energy, E_g, if the center bond is G or G′. A methyl group (either side chain or terminal in the model compound) is considered to give rise to a

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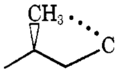
(23) A. Warshel and S. Lifson, *J. Chem. Phys.*, **53**, 582 (1971).

"skew methyl" energy, E_{SK}, for each gauche interaction it forms with the rest of the molecule



The repulsive interaction between two methyls or a methyl and –CH– is best relieved by unequal rotations of ϕ_1 and ϕ_2 to distorted values. For example, the strain in a TT dyad is best relieved by a large rotation of ϕ_2 to a distorted value and a minor one of ϕ_1 to TT_- or by a large rotation of ϕ_1 and a minor one of ϕ_2 to T_+T. This pentane interference energy, above that of the skew and gauche interactions present, is designated E_ω following Flory, Mark, and Abe.[9] Considering distortions of the above type to be the only allowed ones, all of the conformations of a dyad (TG = G′T, TT_- = T_+T, T_+G', GG_+, GT_-, $G'G_+$ = $G_-'G$, $G_-'G'$) are represented in Table II in the first seven conformations. The conformation $GT_-/G'T$ illustrates one of the above dyads coupled to G′T rather than to TG. The helix reversal pointed out by Allegra, Ganis, and Corradini[5] (see above) is represented by G′TTG. TG/GG_+ and TG/G'_-T illustrate the coupling between dyads when ϕ_2 and ϕ_3 are G or G′. Notice that it is possible to have G/G′ coupling between dyads provided one of them is distorted in the same manner as above. The remaining conformations test the validity of additive energies when distorted dyads are adjacent to each other and each conformation contains two ω interactions. Assigning values of E_g = 400 cal/mol, E_{SK} = 600 cal/mol, and E_ω = 1300 cal/mol, together with a base energy of 3650 cal/mol, results in excellent agreement between the conformational energies calculated by energy minimization and those estimated by counting interactions. The latter are listed in parentheses in Table II. The model chosen here for accounting for the conformational energies is essentially identical with that used by Flory, Mark, and Abe.[9] However, the latter as pointed out previously did not commit themselves to values of the conformational energy parameters, E_g, E_{SK}, and E_ω.

Calculations were also made (see Table II) on *n*-octane to provide a value of E_ω for polyethylene for comparison with the above value deduced for polypropylene. From Table II we see that the GG_-' (pentane interference) containing conformers possess 2500 cal energy above the all-trans. Noting that E_g = 610 and subtracting 2(610) cal for the gauche conformations, we arrive at 1280 cal for the extra energy equal to E_ω. This is essentially identical with the value found for polypropylene. Aside from the large body of molecular conformational energies and other properties already successfully calculated[20,24,25] with the energy function parameters and methods of ref 20, it is important to point out that the interaction energies derived here for polyethylene are very satisfactory. Abe, Jernigan, and Flory[26] quote ranges of E_g = 260–450 cal, E_ω = 1300–1600 cal, and $E_{GG'}$ = $2(E_g + E_\omega)$ = 1820–2500 cal for ϕ_G = 67.5° as leading to agreement of the calculated characteristic ratio and its temperature coefficient with experiment for polyethylene (also see below concerning the characteristic ratio). Since, as stressed by Flory[4,9] and confirmed by our calculations, the ω interactions should be similar in polyethylene and polypropylene, it is proper to conclude that the value calculated here for polypropylene (E_ω = 1300 cal) is also very satisfactory. The value of E_{SK} = 600 cal deduced is also in good agreement with the best recent estimates from heats of formation and other thermochemical evidence for hydrocarbons. Schleyer, *et al.*,[27] discuss the matter thoroughly and assign a value of 700 cal, a value which agrees well with other recent estimates cited by them. One of the present authors also assigned the value of E_{SK} = 600 cal in previous work.[20] In any event, the statistical calculations of dimensions are not highly sensitive to E_{SK},[4] and it seems warranted to regard E_g and E_{SK} as reasonably well known. Returning to E_ω, we do not believe that it would be possible to justify by conformational energy calculations or by other means such a large disparity between the ω interactions in polyethylene and polypropylene as implied by the values of E_ω selected by Abe, Jernigan, and Flory[26] and by Flory, Mark, and Abe.[9] We further suggest that any set of energy functions (bond twisting, nonbonded functions, etc.) that would lead to conformationally calculated values of E_ω as high as 3–5 kcal would give unsatisfactorily high calculated values of strain energies and heats of formation of the many hydrocarbon molecules available for test calculations.

Characteristic Ratio

Using the interaction energies derived above for polypropylene, statistical weight matrices may be set up for calculating the characteristic ratio. These matrices must express the stereochemical configurational (*d*, *l*) dependence of the conformational energies of various possible stereo sequences.[4,9] Although ϕ_1 and ϕ_2 in a dyad may individually take on only five rotational angles in the conformational model adopted, 7 × 7 matrices must be set up to render the latter conformable for arbitrary stereo sequences. The resulting matrices are presented in Table III. The matrices labeled superscript 1 or 2 refer to bond 1 or bond 2 in the structural diagrams **1** and **2** for polypropylene. The prohibition of conformational sequences within dyads was assigned to $\mathbf{U}^1$. Thus the $\mathbf{U}^1$ matrices have entries only for allowed conformations of bond 1 and bond 2, *e.g.*, TT_-, T_+T, etc., for *ll* dyads. The conformational energies are assigned to whichever bond is appropriate. Thus in TT_- a factor $\omega = e^{-E_\omega/RT}$ is assigned to $\mathbf{U}^2$, but for T_+T it is assigned to $\mathbf{U}^1$. The same is true for the E_g and E_{SK} energies. They are assigned to whichever matrix is appropriate for the bond in question. Due regard was given to the fact that the polymer has somewhat different interactions than the model compound (Table II) owing to the presence of methyl terminal groups in the latter. The subscripts on the **U** matrices refer to the stereo sequence. The convention of *l* assigned to the CH_3 bond into the plane of the paper and *d* to the CH_3 bond out of the plane in the diagrams **1**–**3** was used. In the above system of assigning statistical weights, $\mathbf{U}^1$ depends on the total configuration of the dyad, *i.e.*, *ll*, *dl*, *ld*, or *dd*, but $\mathbf{U}^2$ depends only on the configuration of the right-hand methyl-containing carbon in the dyad and requires only *l* or *d* as a subscript. Thus six matrices are required; the other three can be generated from those in Table III by changing primed to unprimed on G, + to −, and *d* to *l* and *vice versa*. Flory, Mark, and Abe[9] made calculations using matrices similar to these based on a three-state approximation using only T, G, and G′ rotational states. The same interactions and allowed sequences as here were used but the geometries of the distorted (+, −) states were approximated by the undistorted states in order to

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reduce the dimensions of the matrices. The matrices in Table III are generalizations of those 3 × 3 matrices and reduce to them with one exception if the + or − distorted states are entered under the undistorted T, G, and G′ headings without considering the latter to be degenerate. The exception is that we have excluded gauche coupling of opposite sense between dyads G/G′, etc., whereas Flory, *et al.*,[4,9] assigned a weight of ω to the interactions. The paragraphs below discuss this matter further. The notation used in ref 9 (τ, η, ω) is related to ours as $\tau = SK$, $\eta = SK/g$, and $\omega = \omega$. As an example of the correspondence between the matrices of ref 9 and Table III here, consider $\mathbf{U}_{ll}{}^1$ and $\mathbf{U}_l{}^2$. The ω interactions of $\mathbf{U}_l{}^2$ may be reassigned to $\mathbf{U}_{ll}{}^1$ by dividing a given row of $\mathbf{U}_l{}^2$ by ω and multiplying the corresponding column of $\mathbf{U}_{ll}{}^1$ by ω. Then, dropping the distinction between distorted and undistorted states but not regarding any state as degenerate, we obtain

$$\mathbf{U}_{ll}{}^1 = \begin{bmatrix} SK\cdot\omega & SK & SK\cdot\omega \\ g\cdot SK\cdot\omega & g\cdot SK\cdot\omega & 0 \\ g & g\cdot\omega & g\cdot\omega \end{bmatrix} \qquad (2)$$

and

$$\mathbf{U}_l{}^2 = \begin{bmatrix} SK & SK & SK \\ g & g & 0 \\ SK\cdot g & 0 & SK\cdot g \end{bmatrix} \qquad (3)$$

When row and column interchanges are made in each of the matrices of eq 2 and 3 to remove a difference in convention regarding the direction of sequences, these matrices are identical with the matrices $\mathbf{U}_{dd}{}''$ and $\mathbf{U}_d{}'$, respectively, of Flory,[28] with $\tau^* = 1$ and with the exception of the G/G′ sequences, as already noted. Flory, Mark, and Abe[9] also made calculations using a 2 × 2 matrix approximation based on $\omega\tau \ll 1$. They also describe generalizing the 2 × 2 matrices to 4 × 4 using distorted bond rotational states and mention making calculations with them.

The matrices in Table III are inadequate in describing the conformational behavior of polypropylene in that they prohibit all sequences involving the coupling of dyads with G and G′ (including distorted bond rotations). The calculations in Table II, however, indicate that for *lll* pairs of dyads, for example, the sequences TG/G₋′T and TG₊/G′T have energies comparable to other allowed sequences containing one ω interaction. However only the T conformation of both terminal bonds is allowed. Similar considerations hold for other stereo sequences. The next-neighbor interactions inherent in the matrices of Table III are not adequate to describe the above situation. We have chosen to approximate this situation by excluding all G/G′ sequences. Since the characteristic ratio can be expected to be somewhat sensitive to the inclusion or exclusion of G/G′ sequences, we expect the calculated characteristic ratio to be slightly too high relative to those that would be obtained using the allowed G/G′ sequences.

TABLE III

STATISTICAL WEIGHT MATRICES[a]

$\mathbf{U}_{ll}{}^1$

	T₋	T	T₊	G	G₊	G₋′	G′
T₋	0	0	0	0	0	0	0
T	SK	0	0	SK	0	0	0
T₊	0	$SK\cdot\omega$	0	0	0	0	$SK\cdot\omega$
G	$g\cdot SK$	0	0	0	$g\cdot SK$	0	0
G₊	0	0	0	0	0	0	0
G₋′	0	0	0	$g\cdot\omega$	0	0	$g\cdot\omega$
G′	0	g	0	0	g	0	0

$\mathbf{U}_l{}^2$

	T₋	T	T₊	G	G₊	G₋′	G′
T₋	$SK\cdot\omega$	$SK\cdot\omega$	$SK\cdot\omega$	$SK\cdot\omega$	$SK\cdot\omega$	$SK\cdot\omega$	$SK\cdot\omega$
T	SK	SK	SK	SK	SK	SK	SK
T₊	$SK\cdot\omega$	$SK\cdot\omega$	$SK\cdot\omega$	$SK\cdot\omega$	$SK\cdot\omega$	$SK\cdot\omega$	$SK\cdot\omega$
G	g	g	g	g	g	0	0
G₊	$g\cdot\omega$	$g\cdot\omega$	$g\cdot\omega$	$g\cdot\omega$	$g\cdot\omega$	0	0
G₋′	$SK\cdot g\cdot\omega$	$SK\cdot g\cdot\omega$	$SK\cdot g\cdot\omega$	0	0	$SK\cdot g\cdot\omega$	$SK\cdot g\cdot\omega$
G′	$SK\cdot g$	$SK\cdot g$	$SK\cdot g$	0	0	$SK\cdot g$	$SK\cdot g$

$\mathbf{U}_{ld}{}^1$

	T₋	T	T₊	G	G₊	G₋′	G′
T₋	0	0	0	0	0	0	0
T	0	SK	0	0	0	SK	0
T₊	0	0	0	$SK\cdot\omega$	0	0	$SK\cdot\omega$
G	0	0	$g\cdot SK$	0	0	$g\cdot SK$	0
G₊	0	0	0	0	0	0	0
G₋′	0	$g\cdot\omega$	0	$g\cdot\omega$	0	0	0
G′	0	0	g	0	0	0	g

[a] $SK = e^{-E_{\mathrm{SK}}/RT}$, $g = e^{-E_g/RT}$, $\omega = e^{-E_\omega/RT}$.

The calculation of the characteristic ratio was carried out in a manner similar to that already described by us.[29] For use with the matrices of Table III, the infinite-chain equation (eq A-5) of ref 29 was altered appropriately for polypropylene to

$$\langle R^2\rangle/nb^2 = \sum_{m=0}^{M-1} \mathbf{h}^{\mathrm{T}}\mathbf{B}^{\mathrm{T}}\mathbf{U}_1\mathbf{U}_2\ldots\mathbf{U}_k\mathbf{U}_{k+1}(\mathbf{T}+\mathbf{I})(\mathbf{UT})^m \times \mathbf{U}_{k+2+m}\mathbf{U}_{k+3+m}\ldots\mathbf{U}_{k+1+m+l}\mathbf{Bh}/\mathbf{b}^{\mathrm{T}}\mathbf{U}_1\ldots\mathbf{U}_{k+1+m+l}\mathbf{b} \qquad (4)$$

where $(\mathbf{UT})^m = \mathbf{I}$, $m = 0$; $= \mathbf{U}_{k+2}\mathbf{T}$, $m = 1$; $= \mathbf{U}_{k+2}\mathbf{T}\mathbf{U}_{k+3}\mathbf{T}$, $m = 2$ etc., and $\mathbf{I}$ is the identity matrix. Each term in eq 4 represents the average of the projection of a bond vector $\bar{l}_j$ on a selected vector $\bar{l}_i$, $\langle\bar{l}_i\cdot\bar{l}_j\rangle/b^2$. This average also depends on the conformations of bonds external to the sequence *i* through *j*. The "end effect" as represented by the integers *k* and *l* was found to be adequately represented by taking $k = l = 12$. The number of bonds, *M*, required for convergence of eq 4 was taken to be 36 and was found to be adequate. Calculations were made on a stereoirregular polymer by generating stereo sequences from probabilities of replicating the previous stereo sense of the methyl-substituted carbon in the manner described by Flory, *et al.*[9] The characteristic ratios resulting from a number of sequences with the same replication probability (P_r) were then averaged. Calculations were also made using conformational energy parameters in addition to those derived here from conformational energy calculations. Values of E_ω spanning the range 0–3000 cal were used (along with E_g = 400 cal and E_{SK} = 600 cal) in addition to the value of E_ω =

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(28) P. J. Flory, ref 4, p 216.

(29) R. H. Boyd and S. M. Breitling, *Macromolecules,* **5**, 1 (1972).

TABLE IV
CALCULATED CHARACTERISTIC RATIOS,[a] $Z = \langle R^2 \rangle / nb^2$

	P_r, replication probability[c]						
	1.0	0.90	0.75	0.50	0.25	0.10	0.0
Polypropylene[b] $E_\omega = 1300$ cal[d]							
Z	5.80	5.47	5.30	5.03	5.29	5.57	5.98
		(0.13)	(0.14)	(0.14)	(0.17)	(0.16)	
$-\mathrm{d} \ln Z/\mathrm{d}T \times 10^3$	0.99	0.78	0.70	0.56	0.75	0.95	1.21
		(0.08)	(0.11)	(0.12)	(0.12)	(0.10)	
$E_\omega = 0$ cal							
Z	4.50	4.45	4.39	4.25	4.23	4.22	4.23
		(0.03)	(0.04)	(0.05)	(0.04)	(0.04)	
$-\mathrm{d} \ln Z/\mathrm{d}T \times 10^3$	−0.47	−0.36	−0.31	0.06	0.30	0.40	0.53
		(0.05)	(0.05)	(0.08)	(0.07)	(0.06)	
$E_\omega = 2000$ cal							
Z	7.68	6.80	6.44	5.68	5.99	6.47	7.18
		(0.30)	(0.32)	(0.27)	(0.27)	(0.25)	
$-\mathrm{d} \ln Z/\mathrm{d}T \times 10^3$	2.30	1.70	1.45	0.75	0.79	1.03	1.33
		(0.21)	(0.25)	(0.19)	(0.13)	(0.12)	
$E_\omega = 3000$ cal							
Z	12.31	9.94	7.78	6.56	6.47	7.36	8.55
		(0.44)	(0.55)	(0.46)	(0.39)	(0.22)	
$-\mathrm{d} \ln Z/\mathrm{d}T \times 10^3$	3.43	2.45	1.37	0.58	0.45	0.65	0.91
		(0.24)	(0.24)	(0.28)	(0.15)	(0.07)	
Polyethylene[e]							
Z		7.05 (calcd)			6.7 ± 0.1 (exptl)[f]		
$-\mathrm{d} \ln Z/\mathrm{d}T \times 10^3$		1.30 (calcd)			1.1 ± 0.2 (exptl)[f]		

[a] Values in parentheses for Z and $-\mathrm{d} \ln Z/\mathrm{d}T \times 10^3$ are a measure of variance $= 2\sigma/\sqrt{N}$, where σ is the standard deviation and N is the number of sequences generated to average over in Monte Carlo calculations ($N = 36$ for all calculations here, except $N = 99$ for $E_\omega = 3000$ cal and $P_r = 0.90$ and 0.10). The measure used would be approximately 95% confidence limits if the calculated characteristic ratios for various sequences were normally distributed. [b] $E_{SK} = 600$ cal, $E_g = 400$ cal, $\phi_{T-} = 135°$, $\phi_T = 180°$, $\phi_{T+} = 225°$, ϕ_G 60°, $\phi_{G+} = 100°$, $\phi_{G-}' = 260°$, $\phi_G' = 300°$. Temperature = 145°, C–C–C valence angle = 112°. [c] $P_r = 1.0$, perfectly isotactic polymer; $P_r = 0.5$, completely atactic polymer; $P_r = 0.0$, perfectly syndiotactic polymer. [d] Value of the excess "pentane interference" energy derived from the conformational calculations of the present work. [e] Five-state model, $E_g = 610$ cal, $E_\omega = 1300$ cal, $\phi_G = 67°$, $\phi_{G+} = 98°$, $\phi_{G-}' = 262°$, $\phi_G' = 293°$. Temperature = 140°, C–C–C valence angle = 112°. [f] Reference 4.

1300 cal found in this work. The results of all these calculations are presented in Table IV. The experimental determinations of characteristic ratio and temperature coefficient from the literature are summarized in Table V.

From comparison of Tables IV and V, it is apparent that the calculated characteristic ratios of both atactic and isotactic polypropylene using the energy parameters deduced from the conformational energy calculations of the present work ($E_\omega = 1300$ cal) are in the range of the experimental values. The same is true for syndiotactic polymer when our calculated value is corrected to 45° using our calculated temperature coefficient (resulting in $Z = 6.7$). The calculated temperature coefficients are less negative than the value derived from measurements in several Θ solvents. However, Flory[14] has criticized experimental values based on this method as being unreliable. Our value for isotactic polypropylene is well within the limit of less negative than -1.50×10^{-3} quoted by Flory.[14] We conclude therefore that our values of Z and $\mathrm{d} \ln Z/\mathrm{d}T$ for isotactic polypropylene derived from conformational energy calculations are in satisfactory agreement with experiment. Thus we observe that there is no necessity to invoke stereoirregularity in order to obtain agreement.

In regard to the alternative of invoking large values of E_ω and some stereoirregularity, it can be concluded from Table IV, in agreement with Flory, Mark, and Abe,[9] that values of E_ω in excess of 3000 cal and 10–20% racemic dyads would be required to reduce the temperature coefficient to small absolute values and to limit the characteristic ratio. However, it is to be noticed that for polypropylene the characteristic ratio is higher than the experimental at all values of E_ω in excess of 2000 cal and that there is no combination of a large value of E_ω and replication probability that will give a characteristic ratio in agreement with experiment. Furthermore, we have already justified in the previous section the reasonableness of a much lower value of E_ω in the range of 1300 cal. We believe that the assumption of extreme values approaching 5000 cal for polypropylene is in conflict with the conformational origin of the interaction involved. We regard the question of the slightly positive value of the temperature coefficients for isotactic poly(*n*-butene-1) and poly(*n*-pentene-1) as moot until such time as conformational energy and characteristic ratio calculations are carried out that properly express the interaction of the flexible (through-bond rotation) side groups with the main chain. The use of a single "skew" interaction[9] for the side group or more elaborate but still oversimplified schemes to take into account the stereochemistry of side groups[30] could well lead to signifi-

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(30) A. Abe, *J. Amer. Chem. Soc.*, **90**, 2205 (1968).

TABLE V
EXPERIMENTAL VALUES OF CHARACTERISTIC RATIO, Z, AND TEMPERATURE COEFFICIENT, d ln Z/dT

Polymer	Temp, °C	Z	Method[a]	d ln Z/dT	Method[b]
Isotactic polypropylene	125	6.35[c]	IV		
	143	5.93[c]	IV		
	183	4.73[c]	IV	-4.0×10^{-3}	TIV
	145	5.78[d]	IV		
	145	4.73[e]	IV		
				"Less negative than -1.5×10^{-3}"	[f]
Atactic polypropylene	74	7.0[d]	IV		
	92	6.8[d]	IV		
	153	5.3[d]	IV	-3.3×10^{-3}	TIV
Syndiotactic polypropylene	45	6.7[i]	IV		
Isotactic poly-(n-butene-1)				0.09×10^{-3} [g]	FT
Atactic poly-(n-butene-1)				0.50×10^{-3} [g]	FT
Isotactic poly-(n-pentene-1)	62[g]	9.2	IV	0.34×10^{-3}	FT
Atactic poly-(n-pentene-1)				0.53×10^{-3} [g]	FT
Polyethylene	140[h]	6.7	IV	-1.1×10^{-3}	FT

[a] IV = intrinsic viscosity in Θ solvent. [b] TIV = intrinsic viscosity in the series of Θ solvents listed; FT = force–temperature curves. [c] A. Nakajima and A. Saijyo, *J. Polym. Sci., Part A-2*, **6**, 735 (1968). [d] Reference 11. [e] Reference 13. [f] Unpublished work of Hamada, quoted in ref 14. [g] Reference 10. [h] Reference 4, p 40. [i] H. Inagaki, T. Miyamoto, and S. Ohta, *J. Phys. Chem.*, **70**, 3420 (1966).

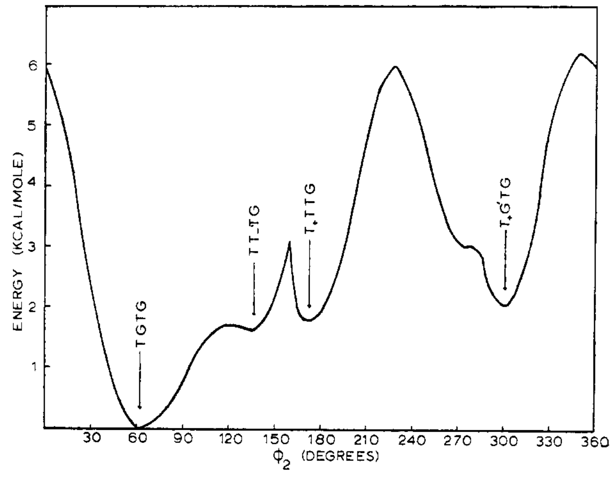

Figure 1. The energy profile for bond rotation along the least energy path for 2,4,6-trimethylheptane labeled as isotactic polymer.

cant inaccuracies in the calculated temperature coefficient. In summary, we conclude that the characteristic ratios of both isotactic and atactic polypropylene are well accounted for by the conformational energy parameters calculated here. The characteristic ratio of polypropylene is predicted in our work, in agreement with experiment, to be rather insensitive

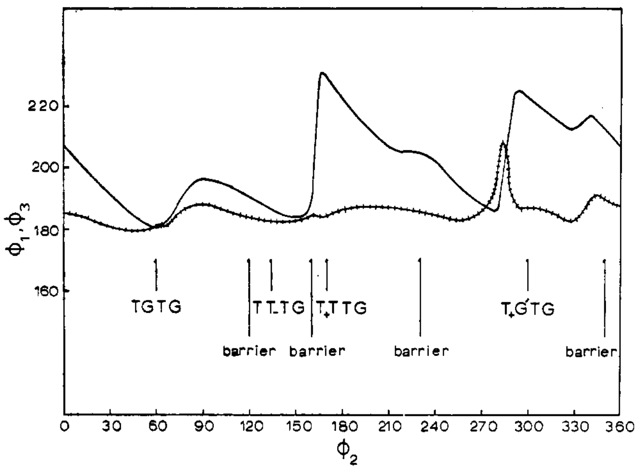

Figure 2. Response of angles ϕ_1 and ϕ_3 to changes in ϕ_2 along the least energy path (see Figure 1) (+++++, ϕ_3).

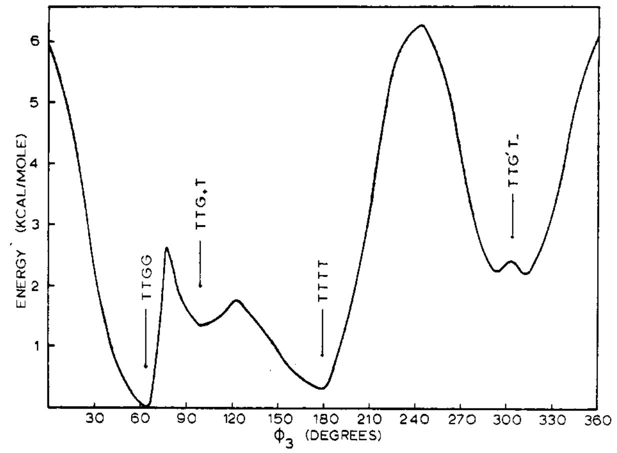

Figure 3. The energy profile for bond rotation along the least energy path for 2,4,6-trimethylheptane labeled as syndiotactic polymer.

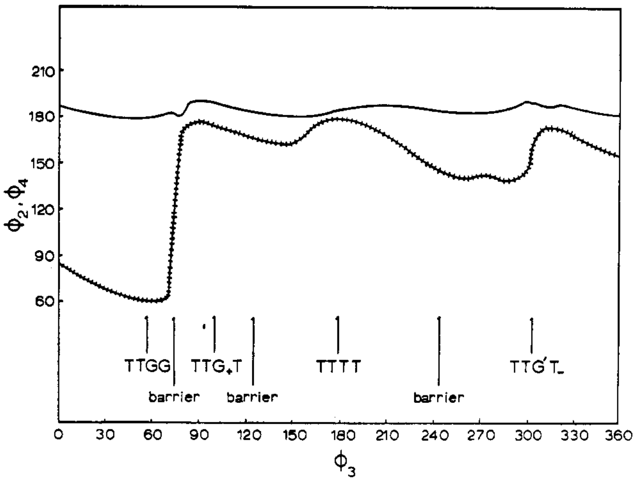

Figure 4. Response of angles ϕ_2 and ϕ_4 to changes in ϕ_3 along the least energy path (see Figure 3) (+++++, ϕ_4).

to tacticity. We also conclude that comparisons of experimental and calculated values is at present not a good way of studying the tacticity of polypropylene.[31]

Energetics of Internal Rotation

An energy profile for bond rotation in trimethyheptane starting from the most stable conformation appropriate for isotactic polymer (TGTG) was generated by the method previously described.[29] For each position of the bond, ϕ_2 (see **3**), the rest of the internal coordinates of the molecule are in a minimum-energy configuration. Thus the path generated is a least energy or "reaction coordinate" path. This profile is shown in Figure 1. The response of ϕ_1 and ϕ_3 to changes in ϕ_2 along the least energy path are plotted in Figure 2. Similarly, a path for trimethylheptane starting from the conformation appropriate to the most stable one of syndiotactic polymer (TTGG, labeled as syndiotactic) was also generated. The bond ϕ_3 was the "driving" bond. This profile is shown in Figure 3 and the response of ϕ_2 and ϕ_4 along the path to changes in ϕ_2 is shown in Figure 4. There is apparently considerable geometrical flexibility in some of the ω interaction containing states, since the TTG$'$T$_-$ state of the syndiotactic polymer was found in the bond rotation profile to have another state of equal energy nearby. However, this was the only such case to show up, and in general the states generated by bond rotation agreed very well with the state found by initial guesses based on inspection of models. We defer comment on the significance of these profiles to the dynamics of chain motion in bulk polymers to a later time.

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(31) One of the reviewers has suggested that since the constant-volume entropy of fusion may be sensitive to the conformational properties,[32-34] a comparison with the conformational entropy based on our conformational energy parameters might be in order. It appears that the two are in agreement, but owing to the theoretical uncertainties in the comparison and the experimental uncertainties in the constant-volume entropy of fusion, the comparison is not highly meaningful.

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(33) A. E. Tonelli, *J. Chem. Phys.*, **52**, 4749 (1970).

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Solution Conformation of Evolidine

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ABSTRACT: A computer search for low-energy cyclic conformations has been conducted for the cyclic heptapeptide evolidine *cyclo*-Ser-Phe-Leu-Pro-Val-Asn-Leu. All of the cyclic conformations generated possess individual low-energy residue conformations which are consistent with the vicinal amide to α-proton coupling constants reported by Kopple in a recent solution nmr study of evolidine. The two lowest energy cyclic conformations generated are both consistent with the nmr evidence, but are distinguishable from each other by the cis or trans conformation of the Leu–Pro peptide bond. The conformation containing the cis peptide bond is similar to one proposed by Kopple on the basis of building space-filling molecular models. Infrared spectroscopy is suggested as an experimental means of choosing between these two proposed conformations.

Kopple[1] has recently reported a 220-MHz proton nmr study of the naturally occurring[2] cyclic heptapeptide evolidine[3] in dimethyl sulfoxide. He was able to associate each amide proton resonance with a specific residue (save differentiating between the two Leu NH's) and measure its coupling constant to the α proton in the same residue, the temperature coefficient of its chemical shift and its rate of exchange with deuterium. (Kopple employed homonuclear spin-decoupling techniques to assign the observed resonances to individual amino acid residues. N–H resonances were related to those of the α protons, and the α-proton resonances to those of the β protons. Because the β protons of both the Phe$_2$ and Asn$_6$ residues appear near 3 ppm, it is not possible to use the chemical shifts of the β protons to differentiate between these two residues. Instead, Kopple relied on the difference in the absolute values of the geminal β–β proton couplings observed in phenylalanine peptides (13–14 Hz) and in asparagine and aspartic acid peptides (15–16 Hz). On the basis of the greater relative uncertainty in the assignment of resonances to the Phe$_2$ and Asn$_6$ residues, we allowed for the possibility that the correct assignment of resonances to these two residues may be the reverse of Kopple's assignment, when searching for cyclic evolidine conformations.)

Construction of space-filling molecular models of cyclic conformations with H–N–C$^\alpha$–H$^\alpha$ dihedral angles φ' which are consistent with the measured coupling constants according to a "Karplus-like" relation[4]

$$J_{N\alpha} = 7.5 \cos^2 \varphi' - 1.9 \cos \varphi' + 1.7 \sin^2 \varphi' \qquad (1)$$

resulted in Kopple's proposal of a cis Leu–Pro peptide bond conformation for evolidine in solution. He was unable to find any all-trans peptide bond conformations which were also consistent with his nmr findings.

Because the conformation proposed by Kopple possesses a cis Leu–Pro peptide bond and is of relatively high intramolecular conformational energy, it was decided to conduct a more extensive search for cyclic conformations which are not only consistent with his nmr data, but which also have low intramolecular conformational energies. Instead of molecular model building, we used a computer in the search for low-energy cyclic conformations.

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