The effects of E_σ on the characteristic ratio and on its temperature coefficient are shown in Figures 8 and 9, respectively. Dashed lines have been calculated for $\varphi_g = \pm 120°$, and solid lines for $\pm 112.5°$, the value indicated by the energy calculations. Values of E_ω are shown with each curve. Heavy-line portions of the curves in Figure 8 represent ranges of E_σ within which $-(\mathrm{d} \ln \langle r^2\rangle_0/\mathrm{d}T) \times 10^3 = 1.15 \pm 0.1$, in agreement with experiment.[10] Similarly, the heavy-line sections of curves in Figure 9 denote ranges over which the characteristic ratio matches the experimental value, 6.8 ± 0.3.[10,11]

Comparison of Figures 8 and 9 shows the temperature coefficient of $\langle r^2\rangle_0$ to be more sensitive than the magnitude of the characteristic ratio to both E_σ and E_ω (and therefore to both σ and ω). Changes in the rotation angle φ_g have a relatively small effect on the temperature coefficient (Figure 9).

Ranges of the conformational energies E_σ and E_ω affording agreement with experimental values for the characteristic ratio and its temperature coefficient are presented in Table III. The results for $\varphi_g = \pm 120°$ agree with the previous calculations of Hoeve.[6] The more realistic choice of $\pm 112.5°$ for φ_g suggests a value of E_σ less than 500 cal mole^{-1} and probably about 400 cal mole^{-1}. The uncertainty in φ_g, about $\pm 3°$, is alone sufficient to displace the value of E_σ required to match the experimental results for polymethylene by as much as 100 cal mole^{-1}. The experimental value of 500 cal mole^{-1} found for the lower n-alkanes is subject to an error of similar magnitude. The intimation in Table III of a discrepancy with this latter figure is not therefore significant.

Table III. Conformation Energies Consistent with Experimental Value for the Characteristic Ratio for Polymethylene at 140° and with Its Temperature Coefficient

	Energies, cal mole^{-1}		
φ_g, deg	E_σ	E_ω	$E_{g^+g^-} = 2E_\sigma + E_\omega$
120	430–590	1700–1900	2560–3080
112.5	260–450	1300–1600	1820–2500

The range of energy for $E_{g^+g^-}$ found with $\varphi_g = \pm 112.5°$ is 1800 to 2500 cal mole^{-1}. This result compares favorably with the figure of 3100 cal mole^{-1} calculated for the *perturbed* $g^+g_*^-$ minima in Figure 6. The agreement is improved if allowance is made for the adjustment of the energy required to compensate the artificial assignment of this paired state to the unperturbed locations for g^+g^-, *i.e.*, to φ_g, $-\varphi_g$.

Acknowledgment. This work was supported by the Directorate of Chemical Sciences, Air Force Office of Scientific Research, Contract No. AF49(638)-1341.

Random-Coil Configurations of Vinyl Polymer Chains. The Influence of Stereoregularity on the Average Dimensions

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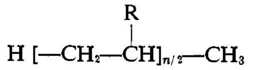
Contribution from the Department of Chemistry, Stanford University, Stanford, California. *Received October 8, 1965*

Abstract: The random-coil configurations of α-olefin polymers $(\text{-CH}_2\text{CHR-})_{n/2}$, where R = CH_3 or CH_2CH_3, etc., are treated in terms of three rotational states for each skeletal bond, the states being weighted as dictated by interactions between CH, CH_2, and R groups separated by three and by four C–C bonds. Interactions between these groups produce systematic displacements of the rotational states from symmetrical positions of 0 and $\pm 120°$ for *trans* and *gauche* conformations, respectively. The treatment is applied to isotactic, syndiotactic, and atactic chains, with proper account of the configurations of the asymmetric CHR centers in each instance. Characteristic ratios $\langle r^2\rangle_0/nl^2$ calculated for a perfect isotactic chain are much greater than observed by experiment (*ca.* 9 to 10). Also, a large negative temperature coefficient is predicted, contrary to observations. These large discrepancies are not diminished by adoption of a more realistic array of four rotational states for each bond, or by incorporation of refinements suggested by detailed calculations of the conformational energy of 2,4-dimethylpentane as a function of its internal rotation angles. Agreement can be achieved, however, by postulating the presence of *ca.* 5 to 10% of syndiotactic units in isotactic polymers of n-butene-1 and n-pentene-1. The high degrees of crystallinity and narrow melting ranges found for typical isotactic polymers can be reconciled with so large a proportion of heterotactic units only if these units are incorporated in the crystalline phase as imperfections. Effects on the crystalline structure are discussed. Positive temperature coefficients found for the corresponding atactic polymers are attributable to steric interactions of the β-CH_2 of R when the adjoining skeletal bonds of the chain are both *trans*.

In this paper we treat the random-coil configurations of vinyl polymers with emphasis on isotactic chains



$$\mathrm{H}[\text{—CH}_2\text{—}\overset{\displaystyle \mathrm{R}}{\overset{|}{\mathrm{C}}}\mathrm{H}]_{n/2}\text{—CH}_3$$

in which all, or most, of the asymmetric -CHR- groups have the same configuration as their immediate neighbors in the chain.[1] The presence on alternate skeletal carbon atoms of the substituent R (where for example R = CH_3 or C_2H_5) proliferates steric inter-

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[1] See P. J. Flory, J. E. Mark, and A. Abe, *J. Polymer Sci.*, B3, 973 (1965), for a preliminary report.

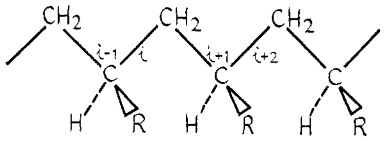

Figure 1. Schematic view of an isotactic chain in its planar conformation.

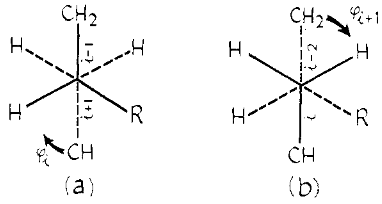

Figure 2. Diagrams illustrating nonbonded interactions dependent on a single rotation angle, φ_i in (a) and φ_{i+1} in (b).

actions in the vinyl chains as compared with polymethylene considered in the preceding paper.[2] The dependence of these interactions on the chain conformation is markedly affected by the stereochemical configurations of the asymmetric -CHR- groups of the chain. The interactions which arise, although increased in number, have their counterparts in the less hindered *n*-alkanes. Results of the preceding paper consequently can be drawn upon to advantage in the present one.

The interactions considered are the same as those dealt with in the preceding paper, namely, intrinsic bond torsion potentials, repulsions between nonbonded atoms, and, of lesser importance, dispersion attractions between nonbonded atoms. On the experimental side, the characteristic ratios for α-olefin polymers[3] are about 9 to 10 and hence are not much greater than that (6.8) for polymethylene.[4] Even more surprising is the evidence indicating little effect of stereoregularity on this ratio. The further observation that the temperature coefficient $d \ln \langle r^2\rangle_0/dT$ for isotactic polymers is zero, or possibly slightly positive, is strikingly at variance with results of theoretical treatment of the chain configuration.[3,5] Interpretation of these observations has been the principal motivation for this investigation.

General Treatment of Vinyl Chains

A portion of an isotactic chain in its planar, all-*trans* conformation is shown in Figure 1. As here represented, the substituent R groups are situated above the plane of the backbone and the H atoms attached to the tertiary carbon atoms lie below it. We shall designate this arrangement arbitrarily as the *d* form when viewed from left to right; the alternative situation of the R groups below the plane will be called the *l* form. The two are, of course, equivalent (in absence of distinguishable end groups), the one being converted to the other by rotation about an axis in the plane and perpendicular to the chain.[6] The main development will be carried out for a *d* chain thus defined. The transformation of results to those for an *l* chain, as required later, is easily effected by symmetry operations.

Let a configuration of the chain be generated by successively fixing the rotation angles φ_2, φ_3, . . ., φ_i, . . ., φ_{n-1} in the order from left to right. Each is to be assigned to one of three states, *t*, g^+, or g^-, in accordance with the rotational isomeric state scheme. In first approximation these three states may be considered to occur at $\varphi = 0$, 120, and $-120°$, respectively, the rotation angles being defined as in the preceding paper. However, allowance will be made for perturbing effects of nonbonded interactions which may displace the minima from these symmetric locations as further discussed below.

Interactions Dependent upon a Single Skeletal Rotation Angle. The rotation φ_i about bond *i* sets the position of the CH group between bonds $i + 1$ and $i + 2$ relative to the positions of preceding groups, *i.e.*, relative to groups occurring to the left of bond *i* in Figure 1. Confining attention at the outset to "three-bond" interactions[7] dependent upon a rotation about only one bond of the chain backbone, we focus therefore on the interaction of this CH group with the CH_2 group attached to bond $i - 1$ and with the intervening R group. This interaction is wholly dependent on rotation φ_i in the approximation of representing the participating groups as structureless domains, and hence of ignoring the precise positioning of their pendant H atoms. The interaction of the specified CH group with the CH preceding bond $i - 2$ depends on φ_{i-1} as well as on φ_i, and therefore falls in the category of a "four-bond" interaction dependent upon two rotation angles. Account of such interactions between groups separated by four C–C bonds will be taken up in the following section.

The relevant atoms and groups involved in three-bond interactions dependent upon φ_i are shown in Figure 2a. These interactions are independent of neighboring bond rotations in the approximation that CH_2 and CH may be regarded as structureless domains. In the *trans* conformation shown in Figure 2a the CH group attached to bond $i + 1$ (shown as a dashed line) is close to the substituent R; in the g^+ state resulting from clockwise rotation of CH and the two H atoms subtended by dashed lines, the CH group is moved away from R and into corresponding proximity with CH_2; and in the g^- state CH is situated between CH_2 and R, where it is within range of interaction with both of them.

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[2] A. Abe, R. L. Jernigan, and P. J. Flory, *J. Am. Chem. Soc.*, 88, 631 (1966).

[3] J. E. Mark and P. J. Flory, *ibid.*, 87, 1423 (1965).

[4] R. Chiang, *J. Phys. Chem.*, 69, 1645 (1965).

[5] J. E. Mark and P. J. Flory, *ibid.*, 67, 1396 (1963).

[6] The conventional terms *meso* and *racemic* recommended for isotactic and syndiotactic chains, respectively, avoid the artificiality of distinctions between *d* and *l* and between *dld* and *ldl*, etc. This terminology is unsuited, however, to mathematical treatment of chains of intermediate degrees of tacticity. In a chain comprising several isotactic sequences alternately "*d*" and "*l*," for example, which of the sets of sequences is called "*d*" and which "*l*" is of course arbitrary. It is nevertheless essential for rigorous mathematical treatment to take cognizance of the existence of two classes of sequences and to differentiate those of one class from those of the other. Adoption of the term *meso* for both is therefore untenable, and we retain the arbitrary terms *d* and *l*, the absence of a basis for an absolute distinction notwithstanding.

[7] The terms "three-bond" and "four-bond" interactions will refer to groups separated by three and four C–C bonds, respectively, in keeping with previous usage.[2] See also P. J. Flory and J. E. Mark, *Makromol. Chem.*, 75, 11 (1964), and J. E. Mark and P. J. Flory, *J. Am. Chem. Soc.*, 87, 1415 (1965).

To the extent that CH may be considered the equivalent of CH_2, the interaction in the g^+ conformation corresponds to that for g^+ or g^- in the n-alkanes treated in the preceding paper.[2] A statistical weight σ might therefore be assigned to represent the contribution from three-bond interactions in this conformation, in keeping with the scheme applied[2] to the n-alkanes and to polymethylene. Similarly, τ could be chosen to represent the factor entering into the statistical weight from the corresponding interaction of CH_2 with R in the *trans* conformation. In the g^- state, CH is situated in proximity to both R and CH_2. If the t, g^+, and g^- states were symmetrically located at $\varphi = 0$, $2\pi/3$, and $-2\pi/3$, then these interactions should be the sum of those for the t and the g^+ states, and the statistical weight for g^- would be $\sigma\tau$. On this basis, the statistical weights for t, g^+, and g^- would be τ, σ, and $\sigma\tau$, respectively. Normalizing to a weight of unity for the g^+ state, we would have η, 1, and τ, where η replaces τ/σ. It will be convenient to incorporate these statistical weights in a diagonal matrix

$$D' = D(\eta,1,\tau) \qquad (1)$$

with elements as indicated.

The scheme of statistical weights expressed in eq 1 can be used irrespective of the angular locations of the rotational isomeric states, a matter to be considered below. To this end we shall let η and τ express the statistical weights for the respective rotational states, without regard for the formal definition $\eta = \tau/\sigma$, wherein σ is required to conform to some predetermined value.

A corresponding analysis of rotation about bond $i + 1$ (see Figure 2b) leads to

$$D'' = D(\eta,\tau,1) \qquad (2)$$

The distinction between g^+ and g^- in both eq 1 and 2 is an obvious consequence of the asymmetry of the CHR carbon. The relationship of eq 2 to 1 is consistent with the interconversion of the two superficial forms of the isotactic chain by the symmetry operation mentioned above.

If the substituent R is CH_2X, where X is neither bulky nor polar, then insofar as its involvement in three-bond interactions is concerned R should be equivalent to CH_2 in Figure 2. Hence, $\eta = 1$ and eq 1 and 2 may be replaced by

$$D' = D(1,1,\tau) \qquad (1')$$

$$D'' = D(1,\tau,1) \qquad (2')$$

Throughout the remainder of this paper, we shall take $\eta = 1$ and accordingly use eq 1′ and 2′ in place of eq 1 and 2.

If all bond angles are equal, and therefore symmetric tetrahedral, then the *trans* and *gauche* states unperturbed by three-bond interactions may be taken at equal intervals, *i.e.*, at 0, 120, and −120°. Actually, the CCC angles in these branched aliphatic hydrocarbons may be greater than tetrahedral by several degrees, and this necessarily introduces a displacement of the positions of the rotational minima. For example, if the value 112° is assigned to all CCC angles, including the one joining the side chain to the backbone, then geometrical requirements about secondary and tertiary carbons of the skeleton are met by taking: $\angle CCH = 106.8°$ at tertiary carbons and $\angle CCH = \angle HCH = 110°$ at secondary carbons. The *gauche* positions for symmetrical staggering of bonds will then occur at $\pm 126.8°$ instead of at $\pm 120°$. Throughout most of the discussion, however, we shall, in interests of simplicity, proceed in the approximation that the *gauche* states would occur at $\pm 120°$ if unperturbed by three- and four-bond interactions. That is, the positions of the various rotational states will be treated under the simplifying assumption of tetrahedral symmetry. This assumption will not, however, preclude adoption of a skeletal bond angle $\pi - \theta$ differing from the symmetrical angle in numerical calculations of the characteristic ratio.

Repulsions between the sterically interacting groups may be expected to alter the positions of the rotational minima after the manner noted in the preceding paper. As will be apparent from Figure 2a, the t and g^+ states about bond i may be shifted on this account to $\varphi' = \Delta\varphi$ and $2\pi/3 - \Delta\varphi$, respectively, $\Delta\varphi$ being taken positive; *i.e.*, the angles φ' for these two minima are brought somewhat closer to one another. In the approximation of steric equivalence of CH_2 and R, the position of g^- should remain unchanged at $-2\pi/3$, inasmuch as CH is here subject to symmetrically situated three-bond interactions with these groups. Similarly, the t and g^- rotational states about bond $i + 1$ (Figure 2b) should be altered to $\varphi_t = -\Delta\varphi$, and to $\varphi_{g^-} = -(2\pi/3 - \Delta\varphi)$, with φ_{g^+} unchanged. Alterations of the positions of the various rotational minima by three-bond interactions may therefore be specified by a single parameter $\Delta\varphi$, and equivalence requires that their positions be represented by[8]

$$\begin{aligned} \varphi_t' &= \Delta\varphi \\ \varphi'_{g^+} &= 2\pi/3 - \Delta\varphi \\ \varphi'_{g^-} &= -2\pi/3 \end{aligned} \qquad (3)$$

and

$$\begin{aligned} \varphi''_t &= -\Delta\varphi \\ \varphi''_{g^+} &= 2\pi/3 \\ \varphi''_{g^-} &= -2\pi/3 + \Delta\varphi \end{aligned} \qquad (4)$$

Calculations for n-butane presented in the preceding paper suggested a value of $\Delta\varphi$ between 5 and 10°. This alteration of angle φ was rendered favorable in part by adjustment of the rotation angles about the terminal C–C bonds of butane, or about the neighboring bonds $i - 1$ and $i + 1$ of polymethylene. Corresponding adjustments in the substituted isotactic chain presently under consideration precipitate other interactions. Inspection of models shows that the effects of these would be to diminish $\Delta\varphi$. However, considerations of higher-order interactions, which find analogy in 2,4-dimethylpentane to be discussed below, suggest larger values of $\Delta\varphi$ for the states of main interest.

According to the initial definitions of τ and σ introduced above, the equivalence of R to CH_2 would denote $\tau = \sigma$, with the latter parameter having the value found in the preceding paper.[2] This identification holds only for rotational states symmetrically situated at $\varphi =$

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(8) See T. M. Birshtein ann O. B. Ptitsyn, "Conformation of Macromolecules," Interscience Publishers, Inc., New York, N. Y., 1966, Chapter 3. The pattern of rotational states prescribed by eq 3 and 4 was adduced previously by these authors.

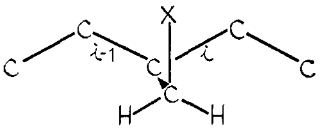

Figure 3. Conformation for a side chain situated between two skeletal bonds in *trans* conformations.

0, (2/3)π, and $-(2/3)\pi$. Alteration of these rotation angles in the manner set forth above reduces the interactions in the t and g^+ states for bond i, and correspondingly in t and g^- about bond $i + 1$. The pairs of interactions encountered in the g^+ and the g^- states for these respective bonds cannot be similarly alleviated, as noted above. It follows that τ should be much smaller than the σ for n-alkanes.[2] It is for this reason that we retain τ as a separate quantity which in general will be less than σ of the preceding paper.

Interactions Dependent upon Neighboring Pairs of Rotation Angles. The all-*trans* state of the isotactic chain is manifestly unsatisfactory because of the large overlaps of neighboring R groups in this conformation shown in Figure 1. These overlaps may be eliminated by rotations to other states. Such rotations may merely replace the offending R group with a CH_2, however, and for the kinds of substituents R under consideration do not therefore offer a preferable alternative. It will be apparent that repulsions between a pair of neighboring R groups can be abolished by a judiciously chosen rotation about either of the two intervening skeletal bonds. If the two R groups in question are those separated by skeletal bonds i and $i + 1$ of Figure 1, for example, then the relevant rotation angles are φ_i and φ_{i+1}. Four-bond steric conflicts can be avoided altogether through either a g^+ rotation about bond i, or a g^- rotation about bond $i + 1$. Whereas in the analysis of three-bond interactions the specification of R as being a group of structure CH_2X warranted treating it as equivalent to CH_2, interactions involving X may affect the pattern of four-bond interactions. This point will be elaborated in due course. At the outset we proceed on the premise that articulation of the side chain R = CH_2X beyond its α-methylene group can be ignored.

Let us first treat the four-bond interactions dependent upon a pair of rotation angles such as $i - 1$ and i. The associated three-bond interactions which depend upon rotation about only one of these angles having been taken into account as set forth in the preceding section, we ignore them in the present connection. The pendant atoms and groups to be considered are those connected *directly* to the skeletal carbon atoms separated by bonds $i - 1$ and i. Interactions of other groups to the right of the carbon at the terminus of bond $i + 1$, *e.g.*, interactions of the following R group, will be dealt with in the next step of the analysis concerned with rotations φ_i and φ_{i+1}. The relevant statistical weights for the bond rotation pair φ_{i-1} and φ_i may be presented in 3 × 3 array indexed in the order t, g^+, g^-, as follows

$$V' = \begin{bmatrix} 1 & 1 & 1 \\ 1 & 1 & \omega \\ 1 & \omega & 1 \end{bmatrix} \tag{5}$$

where ω denotes the relative statistical weight associated with a steric overlap corresponding to the g^+g^- (or g^-g^+) conformation of n-pentane.[2] The rows of V' are indexed to states of bond $i - 1$, the columns to those of bond i. The 2,3 and 3,2 elements of V$'$ represent the four-bond interactions associated with g^+g^- and g^-g^+ overlaps of skeletal CH_2 groups, precisely like those arising in the polymethylene chain.

The four-bond interactions associated with the bond pair i and $i + 1$ are more numerous. They are represented by

$$V'' = \begin{bmatrix} \omega & \omega & 1 \\ 1 & \omega & \omega \\ \omega & \omega^2 & \omega \end{bmatrix} \tag{6}$$

The factor ω^2 records the fact that two such interactions occur for the g^-g^+ rotational pair; one of these is between CH_2 and R and the other between R and CH_2, the respective groups being taken in left-to-right order. The statistical weight for this paired state may be presumed to be effectively zero and will be so regarded henceforth.

An articulated side group having a structure such as $-CH_2-CH_2-Y$ or $-CH_2-O-Y$, in which the atom or group β to the chain backbone is commensurate in size to CH_2, may be accommodated without difficulty provided that one, or both, of the skeletal bonds adjoining the substituted carbon atom is in a *gauche* conformation. Thus, if either bond $i - 1$ or bond i is $g^\pm$, an intervening R group of this kind will have available to it a conformation unencumbered by steric repulsions warranting a factor comparable to τ or ω. If, however, both of these skeletal bonds are *trans*, then the situation depicted in Figure 3 occurs. Here the α carbon of the substituent has been placed (arbitrarily) above the plane occupied by the sequence of the five skeletal carbons shown. Of the three rotational states for $-CH_2X$, only the one shown avoids a four-bond steric overlap between X and one or the other of the skeletal carbon atoms at the extremities of the sequence shown. Although the conformation shown in Figure 3 is free of overlaps of this severity, the group X is involved in three-bond interactions with both of the neighboring skeletal carbon atoms. The skeletal conformation shown in Figure 3 therefore requires a statistical weight factor commensurate with τ, but not necessarily equal to it in view of differences between the groups involved. We therefore designate this factor by τ^*. It is to be applied for each occurrence of a $t;t$ pair of bonds, one on either side of a -CHR- group. The semicolon is included to indicate that the pair of bonds whose states are specified adjoin a substituted chain atom. A pair of *trans* bonds between two consecutive -CHR- groups, designated tt, do not require a factor τ^*.

Introduction of τ^* in this manner can be accomplished by redefining V' as follows

$$V' = \begin{bmatrix} \tau^* & 1 & 1 \\ 1 & 1 & \omega \\ 1 & \omega & 1 \end{bmatrix} \tag{5$'$}$$

This revision is of little significance for perfect isotactic chains, where *trans* pairs are of rare occurrence. In syndiotactic and in atactic chains, $t;t$ pairs of the kind specified may readily occur; hence acknowledgment of the factor $\tau^* < 1$ assumes importance. If, however, $R = CH_2$, then we conclude that $\tau^* \cong 1$ irrespective of the stereosequence.[9]

Statistical Weight Matrices and the Partition Function. Interactions dependent upon more than two consecutive skeletal bonds may at most assume only a minor role, as we have emphasized previously.[2] Interactions of higher order (in this sense) may therefore be ignored, and statistical weights for various configurations of the chain can be generated from the 3×3 matrices $U' = V'D'$ and $U'' = V''D''$, respectively. Thus, from eq 1′, 2′, 5′, and 6 we have

$$U'_d = \begin{bmatrix} \tau^* & 1 & \tau \\ 1 & 1 & \tau\omega \\ 1 & \omega & \tau \end{bmatrix}; \; U''_{dd} = \begin{bmatrix} \omega & \tau\omega & 1 \\ 1 & \tau\omega & \omega \\ \omega & 0 & \omega \end{bmatrix} \tag{7}$$

The former statistical weight matrix is applicable to bonds which, like i, join CHR to CH_2, and the matrix U'' is applicable to bonds which, like $i + 1$, connect CH_2 with CHR. Each element of U' represents the factor entering into the total statistical weight when bond i is assigned to state φ_i, bond $i - 1$ having been assigned to state φ_{i-1}. Elements of U'' perform the analogous role with respect to bond $i + 1$. The subscripts d and dd have been appended in eq 7 to signify that these matrices refer specifically to the d chain as here defined. A single index suffices for U' inasmuch as the relevant section of the chain embraces only one asymmetric center; two indices are required for U'' since two CHR members are involved. When reference to the d chain is obvious, these subscripts will be omitted.

The corresponding statistical weight matrices for the all-*l* chain are given by

$$U'_l = \begin{bmatrix} \tau^* & \tau & 1 \\ 1 & \tau & \omega \\ 1 & \tau\omega & 1 \end{bmatrix}; \; U''_{ll} = \begin{bmatrix} \omega & 1 & \tau\omega \\ \omega & \omega & 0 \\ 1 & \omega & \tau\omega \end{bmatrix} \tag{8}$$

For *dl* and *ld* placements (syndiotactic) of the pair of asymmetric carbon atoms joined by bonds i and $i + 1$

$$U''_{dl} = \begin{bmatrix} 1 & \omega & \tau\omega \\ \omega & 1 & \tau\omega \\ \omega & \omega & 0 \end{bmatrix} \tag{9}$$

and

$$U''_{ld} = \begin{bmatrix} 1 & \tau\omega & \omega \\ \omega & 0 & \omega \\ \omega & \tau\omega & 1 \end{bmatrix} \tag{10}$$

The matrices for bond rotation φ_i are given by U'_d or by U'_l of eq 7 and 8, respectively. Except where otherwise noted, we shall assume an all-*d* chain, to which U' and U'' of eq 7 are applicable.

The partition function for a vinyl chain of n bonds conforming to the structure expressed by the formula in the introductory section is given by

$$Z = J^T \left[\prod_{i/2=1,2\ldots}^{n/2-1} U'_i U''_{i+1} \right] J \tag{11}$$

where J^T and J are the row and column matrices defined in the preceding paper,[2] and having all elements unity. Here U'_2 is the diagonal matrix which for a d configuration of the first unit is given by D' of eq 1′. Succeeding matrices U''_i with $i \geq 2$ and U'_i with $i > 2$ are those specified in eq 7 if all units are in the d configuration. Otherwise, the U' and U'' are those given by eq 7 to 10 for the stereochemical configurations of the pair of units relevant to the bond of index i.

If account were taken of the shifts $\Delta\varphi$ of preferred states from the symmetrically situated angles as prescribed by eq 3 and 4, some of the steric conflicts responsible for the factors ω would be partially alleviated, thus permitting assignment of larger values for some of the ω. None of the states thus affected would have its energy markedly lowered, however. It is possible to show that the effects of such revision of the locations of the rotational states by amounts $\Delta\varphi$ as specified by eq 3 and 4 can be taken into account in good approximation merely by altering the values of the parameters τ and ω without modifying the form of either U' or U''.[10] Hence, we shall adhere to the expressions for these matrices as given above, even when the angles of preferred states are altered by amounts $\Delta\varphi$.

For an isotactic chain the preferred conformations prescribed by the matrices given in eq 7 with $\omega < 1$ (and with $\tau\omega < 1$ in the unlikely event that $\tau > 1$) consist of sequences of either g^+t or of tg^- pairs of bonds occurring between consecutive substituted skeletal carbon atoms. Intercombination of one of these conformations with the other without introducing a factor $\omega < 1$ can occur only through $g^+t \rightarrow tg^-$. The reverse "transition" $tg^- \rightarrow g^+t$ would require at least one bond in a conformation of higher energy, and hence at least one factor ω. This will be apparent from multiplication of the U matrices in the order $U'U''U'$, etc., according to eq 11. Repetition of g^+t generates the

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(9) N. Borisova and T. M. Birshtein, *Vysokomolekul. Soedin.*, **5**, 279 (1963), and **6**, 1234 (1964), ascribe a value less than unity to τ^* (in our notation) even for $R = CH_3$ on the grounds that interactions of the methyl hydrogens with the *two* skeletal methylene groups occurring in close proximity to R in the $t;t$ conformation cannot be alleviated by rotation of the methyl group, whereas this is possible in $t;g^{\pm}$ for which interaction occurs with only one skeletal methylene group. While the effect may be real, we would expect it to be small, and certainly much less than the reduction of $\tau^* < 1$ for a group **X** substantially larger than H.

(10) Inspection of the various conformations will show that the effects of the $\Delta\varphi$ adjustments given by eq 3 and 4 can be represented by replacing ω with ω' ($\omega < \omega' << 1$) in those cases where the interaction is alleviated by alteration of *one* of the pair of rotation angles, and by $\omega''(\omega' < \omega'' << 1)$ in instances of alleviation by *both* rotation angles about the pair of consecutive skeletal bonds. (In no case do the prescribed adjustments enhance the overlap for $\Delta\varphi > 0$.) Then

$$U' = \begin{bmatrix} \tau^* & 1 & \tau \\ 1 & 1 & \tau\omega \\ 1 & \omega'' & \tau \end{bmatrix} \text{and } U'' = \begin{bmatrix} \omega'' & \tau\omega' & 1 \\ 1 & \tau\omega' & \omega'' \\ \omega' & 0 & \omega' \end{bmatrix}$$

The substitution $\tau = (\omega''/\omega')\tau'$, followed by multiplication of the third column of U' by ω'/ω'' and division of the third row of U'' by the same factor, yields

$$U' = \begin{bmatrix} \tau^* & 1 & \tau' \\ 1 & 1 & \tau'\omega \\ 1 & \omega'' & \tau' \end{bmatrix} \text{and } U'' = \begin{bmatrix} \omega'' & \tau'\omega'' & 1 \\ 1 & \tau'\omega'' & \omega'' \\ \omega'' & 0 & \omega'' \end{bmatrix}$$

This column and row multiplication has no effect on the results obtained by the subsequent application of these matrices to a perfect isotactic chain, apart from a trivial "end effect," inasmuch as U' and U'' are required to be multiplied in alternating succession. Except for the 2,3 element of U', these matrices differ in form from those given by eq 7 only in the replacement of τ by τ' and ω by ω''. This 2,3 element is of little importance owing to the low statistical weights of elements in the second column and the third row of U''. The second column of U'' contributes factors which must precede the 2,3 element $\tau'\omega$ of U', and the third row of U'' contributes factors which must succeed it in the statistical weight for a configuration of the molecule as a whole. Hence, changes in the rotational states resulting from $\Delta\varphi \neq 0$ have no sensible effect on the *form* of U' and U''. The value of ω may thereby be increased ($\omega'' > \omega$), but at the expense of a decrease in τ ($\tau' < \tau$).

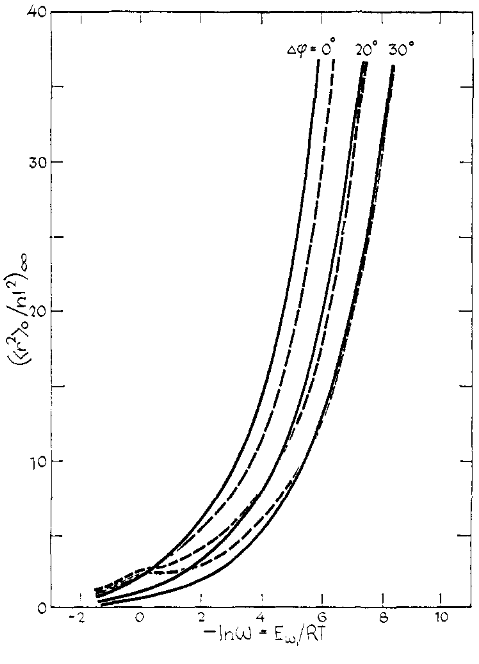

Figure 4. The characteristic ratio for a perfect isotactic chain as a function of $-\ln\,\omega = E_\omega/RT$. The solid and dashed curves are calculated for $\tau = 0.05$ and $\tau = 0.5$, respectively.

right-handed Natta–Corradini 3_1 helix;[11] the corresponding left-handed helix is generated by repetition of tg^-. Hence, as is generally recognized,[8] the conformations of lowest energy for the isotactic molecule as a whole are restricted to those comprising only two helical sections, one being right-handed and the other left. These can be represented as $(g^+t)_m$; $(tg^-)_{(n/2)-m}$. End-for-end rotation of the molecule as a whole merely reverses the order of the right- and left-handed helices, with the arbitrary *d* designation being replaced by *l*.

If the exclusion of states resembling the g^+g^- conformation of *n*-pentane is sufficiently stringent, *e.g.*, if $\omega = 0$, then the perfect isotactic chain can assume only these preferred configurations, $(n/2) + 1$ in number with $0 \leq m \leq n/2$. All of these configurations are highly extended. Each of them ($m = 0$ and $n/2$ excepted) contains one and only one $t;t$ pair. It is on this account that the value of the factor τ^* is of little importance for isotactic chains, and hence that its replacement by unity is permissible.

Stereoregular Isotactic Chains

Characteristic ratios $(\langle r^2\rangle_0/nl^2)_\infty$ were computed using the method of the preceding paper adapted to a chain of the type represented in the introductory section above. For such a chain

$$\langle r^2\rangle_0/nl^2 = 1 + (2/Znl^2)[J^T0\ldots0]\,\mathcal{G}_1 \prod_{i/2=2}^{n/2-1} \mathcal{G}'_i\mathcal{G}''_{i+1} \begin{bmatrix} 0 \\ 0 \\ 0 \\ J \times 1 \\ J \end{bmatrix} \qquad (12)$$

where $J \times 1$ is the column matrix defined in the preceding paper as the direct product of J with the column vector $\{l,0,0\}$; $\mathcal{G}'$ and $\mathcal{G}''$ correspond to $\mathcal{G}$ of the preceding paper but with U' and U'', respectively, replacing U. The matrix U_1 required for $\mathcal{G}_1$ is the identity E of the same order as U. Matrices U' and U'' required for the $\mathcal{G}'$ and $\mathcal{G}''$ factors within the product in eq 12 are identical with those entering the similar product in eq 11 for Z. Thus, for a perfect isotactic chain, which we may arbitrarily consider to consist of *d* units, $U'_2 = D(1,1,\tau)$ in $\mathcal{G}'_2$, and all U's required for the succeeding $\mathcal{G}'$ are $\mathcal{G}''$ are given by eq 7. Bond angles θ' and θ'' at CH_2 and at CHR were taken to be the same in expressing the two coordinate transformation matrices T' and T'' (see eq 5 of the preceding paper). A value of 68° was assigned to these angles.[12] Asymptotic values of $\langle r^2\rangle_0/nl^2$ for $n = \infty$ were obtained by successively squaring the $\mathcal{G}'\mathcal{G}''$ matrix product,[13] or by the eigenvalue method.[14–17] Results of representative calculations are shown in Figure 4 for several values of the parameter τ and for several sets of rotational states defined by $\Delta\varphi$ according to eq 3 and 4, the independent variable being $-\ln\,\omega = E_\omega/RT$ in each instance. In consideration of its trivial contribution for isotactic chains, τ^* was equated to unity for all of the calculations reported in this section of the paper. Monotonic increase of the characteristic ratio with E_ω, the energy obstructing four-bond overlaps, is apparent in Figure 4. The steep rise with $-\ln\,\omega$ leads to the prediction of a large negative temperature coefficient, contrary to observation. The same prediction follows from the interpretations given by Birshtein, Ptitsyn, and others,[14,18–20] and by Allegra, Ganis, and Corradini,[21,22] who have treated the isotactic chain in the approximation of 3_1 helical sequences interrupted by an occasional conformation other than the preferred one. The incidence of such other conformations entails a positive energy, probably of several kilocalories mole^{-1}, relative to the preferred one. On this basis therefore, the temperature coefficient should be negative and large. This conclusion is sustained by the more rigorous calculations shown in Figure 4.

According to extensive calculations of which Figure 4 is representative, a choice of parameters (ω in particular) which matches the approximate values (9 to 10) observed for the characteristic ratio predicates a large negative temperature coefficient. A temperature coefficient of zero can be realized by arbitrarily setting $\omega = \tau = 1$, or, with comparable disregard for reality, by taking $\omega = 0$. The former condition yields a char-

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[11] G. Natta, P. Pino, P. Corradini, F. Danusso, E. Mantica, G. Mazzanti, and G. Moraglio, *J. Am. Chem. Soc.*, **77**, 1708 (1955); G. Natta, *J. Polymer Sci.*, **16**, 143 (1955); G. Natta and P. Corradini, *Makromol. Chem.*, **16**, 77 (1955).

[12] The average bond angle ($\angle$CCC) for isotactic poly-α-olefins has been estimated to be 114° from X-ray diffraction studies on fibers [C. W. Bunn and D. R. Holmes, *Discussions Faraday Soc.*, **25**, 95 (1958)]. However, the spectroscopic value (111°) reported for isobutane [D. R. Lide, Jr., *J. Chem. Phys.*, **33**, 1519 (1960)] suggests a much smaller angle deformation at the tertiary carbon of the polymer main chain.

[13] P. J. Flory and R. L. Jernigan, *ibid.*, **42**, 3509 (1965).

[14] T. M. Birshtein and O. B. Ptitsyn, *Zh. Tekhn. Fiz.*, **29**, 1048 (1959).

[15] S. Lifson, *J. Chem. Phys.*, **30**, 964 (1959).

[16] K. Nagai, *ibid.*, **31**, 1169 (1959).

[17] C. A. J. Hoeve, *ibid.*, **32**, 888 (1960).

[18] T. M. Birshtein, Yu. Ya. Gotlib, and O. B. Ptitsyn, *J. Polymer Sci.*, **52**, 77 (1961); O. B. Ptitsyn, *Vysokomolekul. Soedin.*, **4**, 1445 (1962).

[19] N. P. Borisova and T. M. Birshtein, *ibid.*, **5**, 279 (1963).

[20] T. M. Birshtein, *ibid.*, **5**, 1675 (1963).

[21] P. Corradini and G. Allegra, *Atti Accad. Nazl. Lincei, Rend. Classe Sci. Fis. Mat. Nat.*, **30**, 516 (1961).

[22] G. Allegra, P. Ganis, and P. Corradini, *Makromol. Chem.*, **61**, 225 (1963).

acteristic ratio which is much too small, and the latter yields a dimension approaching full extension of the chain.

Failure to reconcile the foregoing treatment with experimental results led naturally to critical re-examination of the threefold potential model with the object of uncovering refinements which might bring out features not evident in the threefold approximation, the fact notwithstanding that the main characteristics of an impressive list of other chain molecules[2,7,23] have been treated successfully in this approximation.

Alteration of the positions of the rotational states by choosing $\Delta\varphi > 0$ should lower E_ω, and hence increase ω, as previously noted. Such adjustments have the effect[10] of *decreasing* τ, and this tends to compensate the effect of increasing ω, as will be apparent from the composition of the U's according to eq 7. The conclusion thus reached, and corroborated by calculations estimating nonbonded interactions, is that the g^- state for bond i (see U') and the g^+ state for bond $i + 1$ (see U'') occur so rarely as to make negligible contributions to the totality of chain configurations. The high conformational energies associated with these states cannot be circumvented by adjustments of rotation angles. The entire ranges of conformation represented by these states must therefore be abandoned.

In terms of the statistical weight matrices, the suppression of $(g^-)'$ follows from the small values of the elements in the third column of U' and in the third row of U''; the product of two elements, one from each set, is required for each occurrence of $(g^-)'$. The inevitably low value of the $\tau\omega$ elements (see above) of the second column of U'' suppresses $(g^+)''$. Thorough study of the model fails to reveal any rational basis for escape from these conclusions.

It follows that U' and U'' can be approximated, within the limitations of the three rotational state model, by the 2 × 2 matrices obtained by striking the second row and third column of U' and the third row and second column of U''. Then

$$U' = \begin{array}{c} \\ t \\ g^- \end{array}\!\!\begin{array}{c} \begin{array}{cc} t & g^+ \end{array} \\ \begin{bmatrix} 1 & 1 \\ 1 & \omega \end{bmatrix} \end{array}; \quad U'' = \begin{array}{c} \\ t \\ g^+ \end{array}\!\!\begin{array}{c} \begin{array}{cc} t & g^- \end{array} \\ \begin{bmatrix} \omega & 1 \\ 1 & \omega \end{bmatrix} \end{array} \qquad (13)$$

where τ^* has been replaced by unity. The main results of calculations carried out on the basis of eq 7 can be reproduced by eq 13.

At this juncture the possibility of significant contributions from other rotational states within the domain of t and g^+ for bond i and t and g^- for bond $i + 1$ of Figure 1 was explored. Alleviation of the four-bond g^+g^- conflict in n-pentane by rotation of one of the internal angles on the order of 40° as discussed in the preceding paper[2] suggested itself as a plausible basis for elaboration of the rotational state scheme represented by eq 13. The introduction of corresponding alternative states for 2,4-dimethylpentane, the monomeric prototype of the isotactic chain, requires a set of four rotational states for each bond, and 4 × 4 matrices to represent the associated statistical weights. These states occur at $\varphi' = 0$, 40, 80, and 120° for a bond of type i (see Figure 1) and at $\varphi'' = 0, -40, -80$, and $-120°$ for the succeeding bond, $i + 1$.

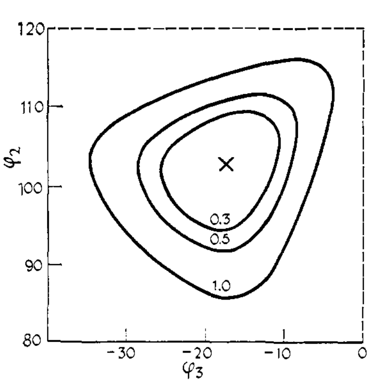

Figure 5. Energy contour diagram for 2,4-dimethylpentane in the neighborhood of its preferred conformation, calculated assuming tetrahedral symmetric bond angles ($\angle$CCC = 109.5°). Energies are indicated in kcal mole^{-1} with respect to the minimum marked by ×.

Let $U'(\varphi'',\varphi')$ and $U''(\varphi',\varphi'')$ represent the elements of the U matrices representing combinations of these bond rotational states. In analogy with the five-rotational-state scheme presented for n-pentane in the preceding paper,[2] each state with statistical weight ω in eq 13 is here replaced by a pair of states occurring at (or near) shallow minima of fairly high energy. These states are represented by the elements $U'(-80{,}120°)$, $U'(-120{,}80°)$, $U''(0,-40°)$, $U''(40{,}0°)$, $U''(80,-120°)$ and $U''(120,-80°)$, all of which can be approximated by ω^* of eq 4 of the preceding paper. Account must also be taken of the further reduction of the statistical weights of all states having rotation angles of 40 or 80° due to the bond torsional potentials. Weights for $U'(-80{,}80°)$, $U'(-120{,}120°)$, $U''(0{,}0°)$, $U''(40,-40°)$, $U''(80,-80°)$, and $U''(120,-120°)$ are effectively zero.

Computations carried out on this basis yielded larger values of $(\langle r^2\rangle_0/nl^2)_\infty$ and more negative temperature coefficients compared with those shown in Figure 4 for any reasonable set of parameters. Thus the disagreement with observations is not lessened by adoption of this more elaborate scheme.

Intramolecular conformational energies for 2,4-dimethylpentane calculated using the relationships given in the preceding paper for the various contributions to the rotational potentials suggested some latitude in the precise values of the angles describing the preferred state, *i.e.*, the g^+t (alias tg^-) helix. Contour maps for the energy in this region are shown in Figures 5 and 6. The former map was computed for tetrahedral angles. For the latter, $\theta' = \theta'' = 68°$, with other angles given in the legend as required for consistency with θ' and θ''. Figure 5 shows a displacement of the minimum for g^+t by $\Delta\varphi = 17°$ in each angle. This is considerably larger than was found for the n-alkane chains. Borisova and Birshtein[19] reached similar conclusions from an analysis of the conformation of isotactic polypropylene using somewhat different potentials for nonbonded atom pairs.

Distortion of the bond angles from their tetrahedral symmetric values alters the contour diagram considerably as shown by Figure 6. In this connection it should be recalled that the symmetrically staggered g^+ posi-

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[23] P. J. Flory, J. Crescenzi, and J. E. Mark, *J. Am. Chem. Soc.*, **86**, 146 (1964).

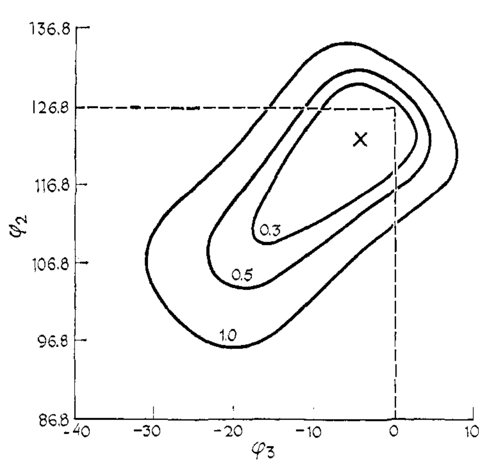

Figure 6. Energy contour diagram for 2,4-dimethypentane. All ∠CCC angles are taken to be 112°; ∠CCH = 106.8° and ∠HCH = 110°. Energies are indicated in kcal mole^{-1} relative to the minimum shown by X.

tion, unperturbed by three- and four-bond interactions, occurs at 126.8° as measured from the *trans* state having a planar backbone when $\theta = 68°$, instead of at 120° for tetrahedral valence angles. Relative to the $\varphi_2 = 126.8°$, $\varphi_3 = 0°$ position, the g^+t minimum now occurs at $\Delta\varphi = 5°$, *i.e.*, at $\varphi_2 = 121.8°$, $\varphi_3 = -5°$. This displacement is considerably less than that of Figure 5. However, Figure 6 displays a prominent "valley" along the line $\varphi_2 = 126.8° - \Delta\varphi$, and $\varphi_3 = -\Delta\varphi$. The computed energy is less than RT over a range of angle approximating 20°. This feature suggests a considerable latitude in conformation in the vicinity of the g^+t minimum. The tg^- region of the total diagram is of course equivalent to that for g^+t.

Bond angles and other information required for calculation of the energies are not known with sufficient accuracy to justify a choice between the diagrams shown in Figures 5 and 6. These calculations suggest, however, that (i) the optimum location for the preferred g^+t (or tg^-) conformation may differ by a $\Delta\varphi$ of as much as 15 or 20° affecting both angles, and (ii) permissible fluctuations about the minimum may be fairly large. In view of the uncertainty in the calculations, each must be regarded only as a plausible possibility. They are not, of course, mutually exclusive.

In further consideration of possibility ii, it is to be observed that the suggested variations in rotation angles would introduce distortions of the Natta–Corradini helix, and thus impart random-coil character to the preferred conformation. The narrowness of the valley in Figure 6 shows that $\Delta\varphi$ for bond $i + 1$ must be very close to $\Delta\varphi$ for bond i; this deduction can be verified by examination of the model. The choice of $\Delta\varphi$ for the next bond pair ($i + 2$ and $i + 3$) should, in first approximation, be independent of the value of $\Delta\varphi$ for the preceding pair (i and $i + 1$). Thus, the $\Delta\varphi$ values for successive pairs can be treated as independently variable.

In order to explore the effects of this departure from the conformation of the 3_1 helix, a two-state model was considered. One of the states for a given bond pair was assigned angles of $\varphi' = 0°$ and $\varphi'' = 120°$, and for the other $\varphi' = -\Delta\varphi$ and $\varphi'' = 120° - \Delta\varphi$. Each bond pair was treated as independent of its neighbors. For $\Delta\varphi = 20°$, $(\langle r^2\rangle_0/nl^2)_\infty = 114$, and, for $\Delta\varphi = 30°$, the result was 38. Even the latter is well above the range found by experiment. Variability of rotation angles about the preferred state may nevertheless be a significant factor acting to limit the extension of the perfect isotactic chain. It is to be noted that the flexibility thus introduced does not entail a commitment of appreciable energy. Hence, the temperature coefficient should be insensitive to this feature, to whatever extent it may be important. In fact, there is no suggestion whatever of an asymmetry in the potential which could compensate the large negative temperature coefficient which would be implicit in the frequent occurrence of conformations of energy E_ω.

Stereoirregular Chains

The evident futility of accounting for experimental observations on the configurational dimensions of so-called isotactic chains in terms of a realistic model for these polymers led to consideration of the effects of departures from perfect regularity in the steric configurations of successive units.[1]

Let p_r represent the incidence of isotactic units in a system of vinyl polymer molecules. That is, p_r is the probability that the stereochemical configuration of the asymmetric center -CHR- of any given unit corresponds to that of its predecessor in the chain; $1 - p_r$ is the probability of a syndiotactic placement. It is assumed that p_r can be treated as a constant, the same for all molecules of the sample, and throughout a given molecule irrespective of the length of the isotactic sequence preceding the unit in question. In this sense, the distribution of isotactic and syndiotactic units is assumed to be Bernoullian.

The mean-square length $\langle r^2\rangle_0$ for chains which are subject to statistical variations in structure cannot be calculated by use of averages for the factors (*i.e.*, the $\mathcal{G}_i$) involved.[24] It is necessary instead to compute $\langle r^2\rangle_0$ for representative structures; the same stereosequence must be used to compute Z by eq 11 as is used to compute the product of the $\mathcal{G}_i$ in the numerator of the second term of eq 12. To average Z and this numerator separately over the population of molecules, and then to divide these averages, would be tantamount to equating the average of a ratio to the ratio of two averages, and the result thus obtained could be seriously in error. We have therefore carried out exact computations of $\langle r^2\rangle_0$ on Monte Carlo chains of 100, and in a few cases of 200, monomer units for given values of p_r. A series of 100, or 200, random numbers in the range 0 to 1 was generated.[25] Each random number less than p_r specifies a unit of the same stereochemical configuration as its predecessor; each random number exceeding p_r specifies a syndiotactic unit. That the sequences thus generated are representative of the chain structures considered follows from the assumed Bernoullian character of replication of the stereochemical configuration in the course of polymerization.

The matrices $\mathcal{G}'$ and $\mathcal{G}''$ appropriate for the various pairs, *dd*, *dl*, *ld*, and *ll*, were obtained according to eq 7 of the preceding paper[2] from the corresponding U matrices, *i.e.*, from $U'_d \equiv U'_{dd} = U'_{dl}$ and $U'_l \equiv U'_{ll} = U'_{ld}$ of eq 7 and 8, and from U''_{dd}, U''_{dl}, U''_{ld}, and U''_{ll} of eq 7 to 10. The four-matrix prod-

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[24] P. J. Flory, *Proc. Natl. Acad. Sci. U. S.*, 51, 1060 (1964).

[25] Stanford Computer Center Library Program No. 7.

ucts $(\mathcal{G}'\mathcal{G}'')_{\lambda,\delta}$ where $\lambda,\delta = l$ or d, required for eq 12 were thus obtained by taking products of the indexed combinations of $\mathcal{G}'$ and $\mathcal{G}''$ matrices. The partition function Z for the given Monte Carlo chain was computed according to eq 11 by taking the product of the U matrices stipulated by the specified stereosequence of the chain. The product in eq 12 was similarly computed from the $(\mathcal{G}'\mathcal{G}'')$ products for the same stereosequence. The characteristic ratio of the Monte Carlo chain was then obtained by combining these results as dictated by eq 12. The computation was repeated for another Monte Carlo chain, generated with the same value of p_r, etc.

Calculations for R = CH$_3$. Incorporation of syndiotactic units in the chain raises the incidence of $t;t$ bond pairs. The statistical weight factor τ^* cannot then be ignored, and, for the reasons presented earlier and illustrated in Figure 3, it becomes necessary to draw a distinction between chains bearing a simple substituent typified by CH$_3$ and those in which R is an articulated group such as CH$_2$CH$_3$. Chains bearing substituents of the latter kind are treated in the following section. Here we identify R with CH$_3$, in which case τ^* may be replaced by unity in the statistical weight matrices of eq 7 and 8.

Results for a representative Monte Carlo chain for which $p_r = 0.90$ and $n/2 = 100$, computed on the basis of the threefold potential with $\Delta\varphi = 0$, 10, and 20°, are plotted against $-\ln\,\omega$ in Figure 7. Calculations are included also for a chain generated with $p_r = 0.50$ and $n/2 = 100$ with $\Delta\varphi = 0$. Solid and long dashed curves were calculated using the three-rotational-state scheme, the former with $\tau = 0.05$ and the latter with $\tau = 0.50$. The effect of τ is small. The curves for $p_r = 0.90$ reach asymptotes at $-\ln\,\omega \cong 8$. The value of the characteristic ratio diminishes with increasing $\Delta\varphi$ as expected.

At the asymptotes of the curves in Figure 7, ω is sufficiently small to force each sequence of isotatic units into a preferred helical conformation. A given sequence then comprises two helical sections of opposite sense, as specified above. For $\Delta\varphi = 0$, these are the familiar 3$_1$ helices; the directions of the axes of the two helical sections differ by the supplement θ of the bond angle. A fairly large energy $E_\omega = -RT\ln\,\omega$ is required for reaching this limiting situation in order to overcome the considerable statistical advantage of the larger array of conformations having one or more four-bond repulsions (of weight ω) within a given isotactic sequence.

The initial steep rise of $\langle r^2\rangle_0/nl^2$ with $-\ln\,\omega$ signifies a large negative temperature coefficient. By the same token, constancy of the characteristic ratio for larger values of $-\ln\,\omega$ predicates a temperature coefficient near zero. A possible basis for explanation of the experimental observations on "isotactic" poly(n-butene-1) and poly(n-pentene-1) is evident in this feature of the curves in Figure 7. Thus we are led to the hypothesis that the temperature coefficient is rendered small by a large steric energy E_ω; increase of the characteristic ratio is curtailed by the presence of syndiotactic units, or possibly by other heterotactic units,[26] which obstruct perpetuation of the preferred helix for a perfect isotactic chain.

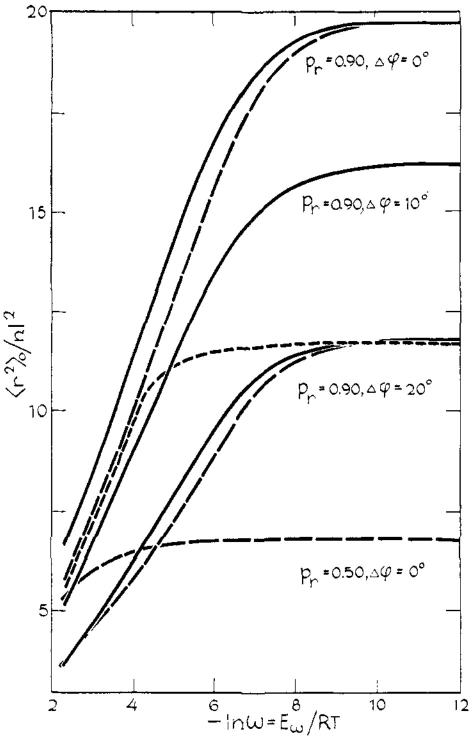

Figure 7. The characteristic ratio *vs.* $-\ln\,\omega = E_\omega/RT$ for a moderately isotactic and an atactic Monte Carlo vinyl chain. The solid and long dashed curves represent $\tau = 0.05$ and 0.5, respectively, the calculations having been carried out using the equations for three rotational states. The short dashed curve was computed using the four-state scheme for $p_r = 0.90$ and $\Delta\varphi = 20°$.

The value of $-\ln\,\omega$ at approach to the asymptotes for the solid and long dashed curves in Figure 7 suggests an energy $E_\omega \geq 5$ kcal mole^{-1} (for room temperature), which exceeds estimates of the energy E_ω for analogous conformations in n-pentane.[2] The comparison is obscured, however, by inaccuracies in the representation of these high-energy conformations by the three-state model and also by the greater complexity of interactions in the substituted vinyl chains. Calculations carried out on the basis of the more realistic four-state model briefly described above (and corresponding approximately to the five-state model for n-pentane[2]) did in fact display more rapid attainment of the limiting value of $\langle r^2\rangle_0/nl^2$ with increase in $-\ln\,\omega$. The short dashed curve in Figure 7 is illustrative. In this instance ω has been chosen to represent the combination of statistical weight factors for occurrence of one of the high-energy conformations departing from the preferred helical sequence. The associated energy, $-RT\ln\,\omega$, at the asymptote is comparable to that of the higher minima in Figure 6 of the preceding paper, but again quantitative comparisons are of limited significance.

Asymptotic values of the characteristic ratios for various Monte Carlo chains of 100 units, and in several instances of 200 units, are plotted against p_r in Figure 8. These were calculated using the U matrices given by

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(26) The appearance of a peak in the nmr spectrum which cannot be attributed to the structures arising from iso- or syndiotactic placements of units has been noted by W. C. Tincher, *Makromol. Chem.*, 85, 34 (1965). From studies on deuterated samples of polypropylene, Tincher suggested that the anomalous peak may be due to occasional heterotactic units which enter the chain by 1,3 addition, rather than to head-to-head and tail-to-tail addition, or to chain branching.

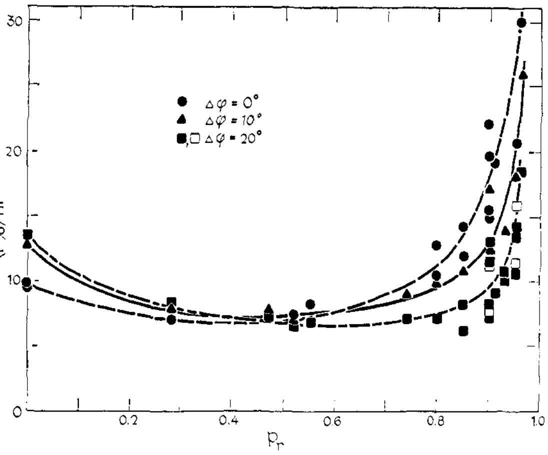

Figure 8. Variation of characteristic ratio with the replication probability p_r, calculated for a chain sequence of 100 monomer units using the three-state scheme with $\omega = 0$. Results obtained for 200 monomer units ($\Delta\varphi = 20°$) are also included and shown by *open* squares. Points for $\Delta\varphi = 0$, 10, and 20° are represented by the dashed, solid, and chain (—-—-—) curves, respectively.

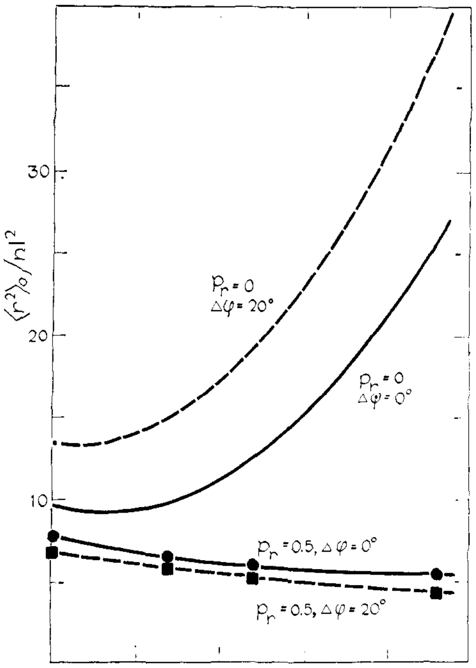

Figure 9. The characteristic ratio as a function of $-\ln \tau^* = E_{\tau*}/RT$ for syndiotactic ($p_r = 0$) chains, and for atactic ($p_r = 0.5$) chains of 100 monomer units. All calculations were carried out according to the three-state scheme with $\omega = 0$. Solid circles and squares indicate the mean value of $\langle r^2\rangle_0/nl^2$ for five different Monte Carlo chains of 100 units each.

eq 7–10 with $\omega = 0$. The parameter τ is eliminated from the computation when $\omega = 0$, as may be verified from the U matrices,[27] and the calculated temperature coefficient is zero.

Points in Figure 8 for different Monte Carlo chains generated for the same value of p_r scatter increasingly as p_r approaches unity. The scatter is due to the small number of configurations available to a given chain when $\omega = 0$. The resulting uncertainty in the location of the curves notwithstanding, a sharp decrease in the characteristic ratio with $1 - p_r$ is clearly demonstrated. The decrease is more precipitous the larger $\Delta\varphi$. Over the remainder of the diagram, the ratio is fairly insensitive to p_r, although it increases somewhat from atactic ($p_r = 0.5$) to syndiotactic ($p_r = 0$) chains. The effect of $\Delta\varphi$ on syndiotactic chains is the reverse of that noted above, *i.e.*, $\langle r^2\rangle_0/nl^2$ increases with $\Delta\varphi$.

According to these calculations, the experimental value of about 10 for the characteristic ratio can be reproduced by $p_r = 0.90$ to 0.93 if $\Delta\varphi = 20°$. Asymmetric fluctuations from discrete rotational states would lower this ratio somewhat. Other unaccounted refinements may affect it as well.

Calculations for an Articulated Substituent. A substituent such as CH_2CH_3 requires a value of $\tau^* < 1$ for the reasons given above. This revision is of no consequence for isotactic chains, but can be predicted to diminish the characteristic ratio for atactic polymers. This prediction was verified by computations carried out for five Monte Carlo chains of 100 units generated for $p_r = 0.50$ with τ^* varying from 1.0 to 0.1 and $\omega = 0$. The results were erratic between the several chains and became increasingly so for small values of τ^* owing to drastic reduction in the number of configurations. For each chain, however, $\langle r^2\rangle_0/nl^2$ decreased monotonically with a decrease in τ^* over this range. Mean values for these five chains are plotted in Figure 9 for $\Delta\varphi = 0$ and 20°. The slopes of these curves in the vicinity of $-\ln \tau^* = 1$ indicate a *positive* contribution to the temperature coefficient amounting to *ca.* 0.5×10^{-3} deg^{-1} as calculated from $d \ln \langle r^2\rangle_0/dT = (\partial \ln \langle r^2\rangle_0/\partial \ln \tau^*)(d \ln \tau^*/dT)$.

Similar computations for $p_r = 0.90$ were indecisive owing to large variations from one Monte Carlo chain to another.

Characteristic ratios computed for syndiotactic chains with $\omega = 0$, also shown in Figure 9, reveal an indifference to $-\ln \tau^*$ in the range 0 to 1, and an accelerating increase beyond $-\ln \tau^* = 1$. Syndiotactic chains having articulated substituents for which $\tau^* << 1$ should therefore exhibit large negative temperature coefficients. The physical basis for these results is readily apparent: as τ^* decreases, the syndiotactic chain is forced toward the helical conformation represented by $(g^+g^+)(tt)(g^-g^-)(tt)(g^+g^+)(tt)$, etc.

The calculations summarized in Figure 9 offer a plausible explanation for the prevalence of positive temperature coefficients among atactic vinyl polymers,[28] $(\text{-}CH_2CHR\text{-})_{n/2}$. They are also consistent with the observations of larger positive temperature coefficients for the atactic polymers of *n*-butene-1 and *n*-pentene-1 than for the corresponding isotactic polymers.[3]

Discussion

Analysis of models for isotactic chains, supplemented by the calculations for 2,4-dimethylpentane, indicate a mean value in the range of 10 to 20° for $\Delta\varphi$. If ω is assumed to be very small as required to account for the observed temperature coefficient, it follows from the calculations summarized in Figure 8 that p_r must be in the range 0.90 to 0.93 in order to account for the observed magnitude of the characteristic ratio. A high degree of accuracy for the model cannot be claimed.

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[27] These matrices may be reduced to order 2 × 2 in analogy to eq 13. The $\mathcal{G}$ matrices required in eq 12 are then of order 10 × 10.

[28] A. Ciferri, *J. Polymer Sci.*, **A2**, 3089 (1964).

Moreover, the experimental results[3] for $\langle r^2\rangle_0/nl^2$ are subject to an error of about 10%. These considerations suggest 5 to 10% as the proportion of heterotactic units required to account for the relevant experimental observations. The lower value matches the upper limit for syndiotactic units in isotactic polypropylene, as estimated by Stehling[29] from the nmr spectra of the deuterated polymer. A reliable value of $\langle r^2\rangle_0/nl^2$ for a polypropylene of comparable stereoregularity is not available. The experimental results[3] cited above are for the higher homologs of this polymer. Direct comparison of our estimate for the proportion of heterotactic units with appropriate analytical data is not possible at present.

Much evidence has accumulated indicating insensitivity of the characteristic ratio to stereoregularity.[30-33] These observations are well explained by the present hypothesis in conjunction with Figure 8. The characteristic ratio changes rather little over the range p_r = 0 to 0.9.

In the case of an R group such as CH_2CH_2Y, however, the characteristic ratio for the atactic polymer may be lowered to an undetermined extent as a consequence of interactions of the β-methylene group in the conformation of the chain skeleton shown in Figure 3. These same interactions offer a plausible explanation for the positive temperature coefficients generally observed for atactic vinyl polymers.[28] If sufficiently strong, they should raise the characteristic ratio for the syndiotactic polymer and render its temperature coefficient negative. These interactions are absent in polypropylene, and a null temperature coefficient may be expected for both atactic and syndiotactic varieties.

It remains to consider the implications[1] of the presence of a substantial proportion of heterotactic units with respect to properties of crystalline isotactic polymers. The high degrees of crystallinity of isotactic polymers,[34-37] their comparatively narrow melting ranges, the formation of spherulites[34,38] under suitable conditions of crystallization from the melt, and the formation of single crystals[39,40] of the usual layer thickness from dilute solutions are irreconcilable with exclusion of even 5% of heterotactic units from the crystalline phase. Instead of acting in this respect like ordinary copolymeric units which are excluded from the crystal,[41,42] these units evidently are tolerated by the crystalline phase, albeit as defects, without irreparable distortion of the lattice. We next consider how this may occur.

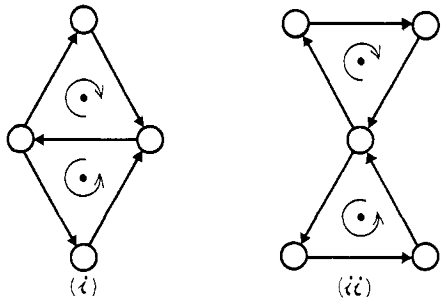

Figure 10. End views of 3_1 isotactic helices separated by a syndiotactic unit in the conformations described in the text.

A possible conformation for two successive sequences of isotactic units and the intervening syndiotactic placement is the following

$$(g^+t)(g^+t)\ldots(g^+t)(g^\pm t)^*(g^-t)\ldots(g^-t) \qquad \text{(i)}$$

where bond pairs between substituted atoms (CHR) are joined within parentheses, and the asterisk denotes the location of the syndiotactic pair. In the arbitrary terminology used above, units to the left of the asterisk are *d* and those to the right are *l*. Let $\Delta\varphi = 0$. Then both helices are 3_1. The one on the left is right-handed; the one on the right is left-handed. Their axes are parallel, but not colinear (*cf.* below). Their helix screw senses may be reversed by choosing the alternative conformations (tg^-) and (tg^+) for the respective isotactic sequences. The conformation at the syndiotactic point precipitates a four-bond interaction, and hence it entails an energy E_ω.

Expenditure of an energy E_ω may be avoided by adoption of the following alternative conformation at the syndiotactic unit

$$(g^+t)\ldots(g^+t)(tt)^*(g^-t)\ldots(g^-t) \qquad \text{(ii)}$$

Again, the axes of the two helical segments are parallel (if $\Delta\varphi = 0$) but not colinear.

Parallel axes for successive helical segments are an obvious requirement for their incorporation into the lattice. A necessary and sufficient condition is the presence of an odd number of *trans* bonds separating *gauche* members of the respective helices. For an even number of *trans* bonds, the two helix axis directions differ by the bond angle θ. (It follows incidentally to this conclusion that a given isotactic sequence must retain the same helix screw sense throughout. The kind of reversal discussed above requires a sequence like $(g^+t)(tg^-)$, etc., which would alter the helix direction by angle θ within the sequence.) Thus, conformations like i and ii above are the only eligible ones, and both require *a reversal of helix sense at the syndiotactic placement.*

The helix axis displacement for conformations i and ii are 0.82 and 1.64 Å, respectively, as shown in Figure 10. The *a* spacing of the hexagonal lattice for crystal-

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line 3_1 helical poly(n-butene-1) is 17.7 Å,[43] which corresponds to the width of two molecules. The shifts in helix axes required by both conformations i and ii are small by comparison. Either presumably could be accommodated without excessive distortion of the crystal. Moreover, the calculated displacements of the helix axis may be diminished by compromising bond rotation angles from those stipulated above.

Conformation i entails a smaller displacement of axis but requires a commitment of several kilocalories per mole. The enthalpy of fusion of isotactic poly(n-butene-1) is about 1500 cal/mole of C_4 units.[36,37] Even the presence of one syndiotactic unit in ten would appropriate only about one-fifth of the molar heat of fusion for an isotactic sequence of average length. Conformation ii does not require a contribution to the intramolecular energy, but it involves a larger "fault" in the crystal.

The reversal of helix screw sense at each interruption of a succession of isotactic units by a syndiotactic unit implies that the senses of rotation of neighboring chains in the crystal lattice must be random. Only in this respect is the present interpretation at variance with the structures proposed for crystalline isotactic polymers by Natta, Corradini, and their co-workers[34,43] on the basis of their pioneering investigations. They considered neighboring chains to be enantiomorphous, *i.e.*, of opposite helical screw sense. On the other hand, they concluded that oppositely directed helices of a given screw sense (*i.e.*, g^+t and tg^+ for right-handed and tg^- and g^-t for left-handed helices) probably locate at random in the crystal, their directions thus being essentially uncorrelated with those of their neighbors. Placement of all R groups of neighboring helices at the same level in the crystal then requires corresponding (random) axial translations of the helices by distances of one bond length. Skeletal bonds of neighboring bonds are not then in register.

It is worthy of note that both isotactic and syndiotactic poly(methyl methacrylate) are highly crystalline despite the presence of *ca.* 20% of heterotactic units in each.[44,45] The possibility of accommodating heterotactic units within the crystalline phase was pointed out long ago by Bunn and Peiser.[46]

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The Thermochemistry of the Gas Phase Equilibrium $I_2 + C_6H_5CH_3 \rightleftarrows C_6H_5CH_2I + HI$ and the Heat of Formation of the Benzyl Radical[1]

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Abstract: With the aid of a Cary spectrophotometer, modified for use with high-temperature gas systems, the equilibrium constant for the reaction $C_6H_5CH_3 + I_2 \rightleftarrows C_6H_5CH_2I + HI$ has been measured over the temperature range 210–390°. From a plot of log K_{eq} against $1/T$(°K), the following thermodynamic values were calculated: $\Delta H°_{573} = +10.30 \pm 0.17$ kcal/mole and $\Delta S°_{573} = 2.65 \pm 0.27$ gibbs/mole. When corrected to room temperature using an independent estimate of $\overline{\Delta C}_p° = 1.6 \pm 1.0$ gibbs/mole, these become: $\Delta H°_{298} = +9.86 \pm 0.32$ kcal/mole and $\Delta S°_{298} = +1.59 \pm 0.71$ gibbs/mole. This latter is in excellent agreement with an independent estimate based on bond additivity of $+1.0 \pm 1.0$ gibbs/mole, and the former, when combined with known values[2] of the heats of formation of $C_6H_5CH_3$, HI, and I_2, yields a value for $\Delta H_f°(C_6H_5CH_2I(g))$ of $+30.43 \pm 0.32$ kcal/mole. Crude kinetic data were also obtained within the temperature range 210–270°. Assuming the rate-controlling step in the initial stages of reaction to be that shown in eq ii in the text the following Arrhenius parameters were calculated: $\log k_4 = 8.43 \pm 1.22 - (14.4 \mp 2.9)/\theta$. From this activation energy, and an assumed value of $E_3 = 1.5$ kcal/mole, it may be shown that $\Delta H_f°(C_6H_5CH_2\cdot(g)) = 44.1 \pm 3.1$ kcal/mole and $DH°_{298}(C_6H_5CH_2–H) = 84.2 \pm 3.1$ kcal/mole, in good agreement with values from recent kinetic studies.

Using a spectrophotometric technique, it has been shown[3] that the kinetic parameters and equilibrium constants of reactions of the type $RH + I_2 \rightleftarrows RI + HI$ may be conveniently and accurately determined in the temperature range 200–400°, even though the extent of reaction is small and the equilibria are well to the left. We have previously used the technique[3] to obtain an accurate value for $\Delta H_f°(CH_3I(g))$ and to

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[1] This investigation was supported in part by Public Health Service Research Grant AP-00353-01 from the Air Pollution Division, Public Health Service.

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