tion of the strong nonbonded interaction energies involved in our system.

(c) Assuming, as a first approximation, that the energy map reported in Figure 3b still holds some validity after the changes in bond angles, ψ_1 and ψ_2 should be modified so that the representative point A moves toward the minimum of the potential energy function.

(d) From what has been said at the end of the previous section, ψ_3 may have any value in the range 65–95°.

(e) The d_m value must remain in the range 1.66 ± 0.05 Å, and the Θ angle must remain equal to 108° (see expression 3 and Figure 4).

On the basis of trial and error methods, the best agreement with the experimental X-ray distribution has been obtained with the model reported in Figure 4, where $\theta_1 = 112°$, $\theta_2 = 108°$, $\theta_2' = 123°$; $\psi_1 = 157°$, $\psi_2 = 59°$, $\psi_3 = 67°$. The full list of the geometrical parameters corresponding to the model of Figure 4 is reported in Table IV. Figure 5 shows the calculated X-ray profiles, and the observed X-ray intensities are also indicated in conventional notation. An isotropic thermal factor equal to 4 Å^2 has been applied to all atoms, hydrogens omitted. The agreement is clearly satisfactory.

Conclusions

The present study represents a characteristic example of a polymer conformational analysis where two different techniques—X-ray and potential energy calculations—are employed in an alternate sequence, leading to a progressive refinement of the chain model.

It also emphasizes the importance of considering the bond angle flexibility in crowded molecules. As a matter of fact, no improvement from model A of Figure 3b—unacceptable from the X-ray point of view—seems possible if this kind of molecular deformability is not taken into account. On the other hand, analysis of Table III is in itself sufficiently indicative of the possibility of achieving significant energy stabilization through bond angle deformation.

Acknowledgment. We want to thank Dr. Hung-Tsung Chen for his helpful discussions in formulating our program. We also wish to thank the National Institutes of Health for their support through Grant GM 08974.

Second and Fourth Moments of Vinyl Polymer Chains

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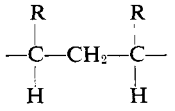
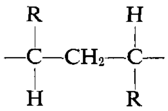
ABSTRACT: Configuration partition functions, z, and second and fourth moments, $\langle r^2\rangle_0$ and $\langle r^4\rangle_0$, of the end-to-end vector $\mathbf{r}$, for vinyl polymer chains are calculated as functions of chain length (n), of the statistical weight parameter (ω) representing steric repulsions between groups separated by four bonds, and of the average stereochemical configurations of dyads comprising the chain. For small steric repulsions in the aforementioned conformations, *i.e.*, for $\omega > 0.10$, the characteristic ratio $C_n = \langle r^2\rangle_0/nl^2$ in the limit of long chains is comparatively small (<7) and nearly independent of the degree of stereoregularity throughout the range from isotactic to syndiotactic. For stronger repulsions, *i.e.*, for $\omega \approx 0$, C_n is much larger for isotactic than for syndiotactic chains; for atactic chains, it is lower than for either of the stereoregular forms. Characteristics of chains varying in stereoregularity *from isotactic to atactic* are fairly well reproduced by calculations for isotactic chains with ω varied artificially in the range from 0 to 0.1. Anomalous behavior of the ratio $\langle r^4\rangle_0/\langle r^2\rangle_0^2$ for syndiotactic chains is traced to the suppression of nonplanar conformations for tetrahedrally bonded chains in the limit $\omega = 0$.

Two aspects of the structure of vinyl polymers $-CH_2CHRCH_2CHR-$, etc., set them apart from other kinds of long chain molecules. First, steric interactions involving the substituent R, assumed to be of the size of CH_3 or larger, severely limit the conformations available to the chain. Second, alternate skeletal atoms being asymmetric, the characteristics of the chain may depend decisively on the stereochemical configurations of these centers of asymmetry. The stereochemical configuration of the chain is appropriately defined through specification of the symmetry of each of its successive dyads, which may be either *meso* (m)



$$-\underset{\mathrm{H}}{\overset{\mathrm{R}}{\mathrm{C}}}-\mathrm{CH_2}-\underset{\mathrm{H}}{\overset{\mathrm{R}}{\mathrm{C}}}-$$

or racemic (r)



$$-\underset{\mathrm{H}}{\overset{\mathrm{R}}{\mathrm{C}}}-\mathrm{CH_2}-\underset{\mathrm{R}}{\overset{\mathrm{H}}{\mathrm{C}}}-$$

The two species of the mirror-image pair (*dl* and *ld*) comprising the latter form need not be differentiated for our purposes. The stereochemical configuration of a sequence is then adequately specified by . . . *mrrmr* . . . , for example.

Limitations on the spatial configuration of the chain molecule are markedly dependent on the *stereochemical* configurations of the asymmetric centers $-CHR-$. They are most severe in isotactic chains, which, if the ultimate in structural purity could be attained, would be exclusively *meso*. Interspersion of racemic dyads greatly increases the spatial configurations available, as measured by the configuration partition function, for example (*cf.* the following).

In effect, the racemic dyad has available two conformations free of severe steric overlaps, whereas the *meso* dyad has only one in an all-isotactic chain.

The effects of conformational interactions and of the stereochemical configuration on the characteristic ratio $C_n = \langle r^2\rangle_0/nl^2$, $\langle r^2\rangle_0$ being the mean-square end-to-end length of the unperturbed chain consisting of n bonds each of length l, were investigated by Mark and Abe[1] in collaboration with one of us. They showed that C_n, or C_∞ in the limit of a very long chain, would be very large for an all-isotactic chain and that its temperature coefficient should be negative and large. Magnitudes calculated for both quantities decrease rapidly with introduction of racemic dyads.

Characteristic ratios calculated for a wide range of statistical weight parameters are presented in this paper. Previous Monte Carlo calculations[1-3] for stereoirregular chains having Bernoullian distributions of *meso* and racemic dyads in various proportions are confirmed, and the effects of relaxing the suppression of disfavored conformations are examined in greater detail. Fourth moments $\langle r^4\rangle_0$ are calculated for isotactic and syndiotactic chains subject to various values of the steric exclusion parameter ω. By varying ω for an isotactic chain, the entire range from stiff, rodlike chains ($\omega = 0$) to very tortuous ("flexible") random coils ($\omega \approx 1$) can be covered. For $0 < \omega \ll 1$ the isotactic chain can be considered to represent a succession of helical segments whose average lengths (*i.e.*, numbers of bonds) depend inversely on $\sqrt{\omega}$. Thus, the calculations here presented may be regarded as illustrative of chains of variable "stiffness," in the sense of the foregoing distinctions. They are relevant also to the analysis of small-angle X-ray scattering and optical anisotropies of polymer chains treated in the following papers.[4,5]

Theory and Methods of Calculation

As in previous studies[1-3,6,7] the rotational isomeric state model is employed throughout the present series of papers, three rotational states being assigned to each bond. These will be taken at rotation angles $\varphi = 0°$, $120°$, and $-120°$ for *trans* (t), *gauche*$^+$ (g^+), and *gauche*$^-$ (g^-), respectively, except as noted otherwise.

For the polymethylene (PM) chain we employ the statistical weight matrix

$$\mathbf{U}_i = \begin{bmatrix} 1 & \sigma & \sigma \\ 1 & \sigma & \sigma\omega \\ 1 & \sigma\omega & \sigma \end{bmatrix} \qquad (1)$$

which has found extensive use in previous studies.[8,9]

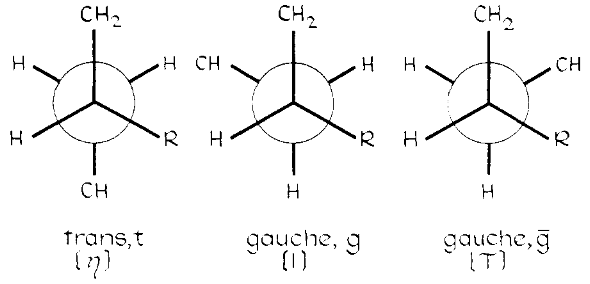


Figure 1. Newman projections for the three rotational isomeric states and their designation. Statistical weight parameters representing respective three-bond interactions are given in parentheses.

Rotational states are indexed in the order t, g^+, and g^-, those for bond $i - 1$ on the rows and those for bond i on the columns. The parameter σ represents the statistical weight of a *gauche* state relative to *trans* insofar as interactions of "first order" (*i.e.*, those dependent on only one bond rotation) are concerned. The additional factor ω applies to the "second-order" interactions associated with g^+g^- and g^-g^+ conformations for consecutive bond pairs.

Newman projections representing the rotational states for a skeletal bond of a vinyl polymer chain are shown in Figure 1. The states, or conformations, are here shown at intervals of 120°. Each diagram is intended to include its mirror image,[6] in which the asymmetric center is inverted and, in the case of a *gauche* (g or $\bar{g}$) conformation, the sign of the rotation is reversed as well. Accordingly, the states are designated[6] t, g, and $\bar{g}$ for the *trans* and the two kinds of *gauche* states, respectively. The chirality of the *gauche* state is not specified inasmuch as both left- and right-handed rotations may occur for either g or $\bar{g}$; the sign of the rotation for each of these states depends on the symmetry of the substituted carbon[6] as viewed in Figure 1. This designation of rotational states for vinyl chains departs therefore from the customary identifications with the signs of the rotations (as in eq 1 for polymethylene, for example), a scheme universally applicable to symmetric chains, *i.e.*, chains devoid of asymmetric centers.

The g state, in which CH is *syn* with respect to CH_2 (see Figure 1), is assigned a statistical weight of unity. The relative statistical weight for the t state in which CH is *syn* to R is expressed by η, and that for $\bar{g}$, in which CH is *syn* to both CH_2 and R, is represented by τ.[3,6,7]

The diagrams in Figure 1 represent only first-order interactions, these being solely dependent upon the rotation angle about one skeletal bond; such interactions involve groups separated by three bonds. Second-order interactions between groups separated by four bonds, and dependent therefore on two consecutive bond rotation angles, are especially important in restricting the configurations accessible to a vinyl chain.[1,3,6,7] They may be comprehended by examination of models or by study of diagrams like those in Figure 2 for a *meso* and for a racemic dyad, respectively. The various second-order interactions involve pairs of groups from the set comprising CH, CH_2, and R. Major steric overlaps occur when two such groups are

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(1) P. J. Flory, J. E. Mark, and A. Abe, *J. Amer. Chem. Soc.*, **88**, 639 (1966).

(2) A. Tonelli, Ph.D. Thesis, Stanford University, 1968.

(3) P. J. Flory, "Statistical Mechanics of Chain Molecules," Interscience Publishers, New York, N. Y., 1969, Chapter VI.

(4) Y. Fujiwara and P. J. Flory, *Macromolecules*, **3**, 288 (1970).

(5) Y. Abe, A. Tonelli, and P. J. Flory, *ibid.*, **3**, 294 (1970); A. Tonelli, Y. Abe, and P.J. Flory, *ibid.*, **3**, 303 (1970).

(6) P. J. Flory and Y. Fujiwara, *ibid.*, **2**, 315, 327 (1969).

(7) A. D. Williams and P. J. Flory, *J. Amer. Chem. Soc.*, **91**, 3111, 3118 (1969).

(8) A. Abe, R. L. Jernigan, and P. J. Flory, *ibid.*, **88**, 631 (1966); R. L. Jernigan and P. J. Flory, *J. Chem. Phys.*, **50**, 4165, 4178 (1969).

(9) See ref 3, pp 140-152.

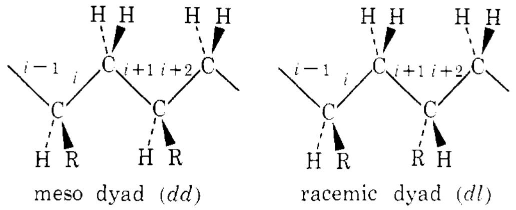

Figure 2. *meso* and racemic dyads of a vinyl chain.

in a situation corresponding to that of the terminal methyl groups of *n*-pentane in its g^+g^- and g^-g^+ conformations, where they would be at a distance of about 2.5 Å apart if the rotation angles were exactly ±120°. Consequently, the probability of occurrence of a consecutive bond pair in a conformation which places a pair of the foregoing groups in a corresponding situation is substantially reduced. For the purposes of the present series of papers, we assign a statistical weight factor ω for each such conformation, no distinction between the several kinds of pairs being required.[10]

The statistical weight matrices for vinyl polymer chains constructed from the parameters defined above are[11]

$$\mathbf{U}' = \begin{bmatrix} \eta\tau^* & 1 & \tau \\ \eta & \omega & \tau \\ \eta & 1 & \tau\omega \end{bmatrix} \tag{2}$$

$$\mathbf{U}_m'' = \begin{bmatrix} \eta\omega & 1 & \tau\omega \\ \eta & \omega & \tau\omega \\ \eta\omega & \omega & \tau\omega^2 \end{bmatrix} \tag{3}$$

$$\mathbf{U}_r'' = \begin{bmatrix} \eta & \omega & \tau\omega \\ \eta\omega & 1 & \tau\omega \\ \eta\omega & \omega & \tau\omega^2 \end{bmatrix} \tag{4}$$

The matrix $\mathbf{U}'$ refers to the first bond i of a dyad comprising bonds i and $i + 1$ as shown in Figure 2 for the case of a *meso* dyad in its *tt* conformation. The states t, g, and $\bar{g}$ of bond $i - 1$ are indexed on the rows of $\mathbf{U}'$, and those of bond i on the columns in the same order. The parameter τ^* is included[1,3] in order to take account of the steric repulsions associated with the *tt* conformation for the bond pair flanking the CHR group when R is an articulated substituent such as $-CH_2CH_3$, OCH_3, or $-CH(CH_3)_2$, etc. For the calculations to follow, τ^* has been set equal to unity.

The matrices $\mathbf{U}''$ given by eq 3 and 4 refer to the second bond of the dyad pair, *i.e.*, to bond $i + 1$. States for bonds i and $i + 1$ are indexed on the rows and columns, respectively, in the order t, g, and $\bar{g}$ as above. The matrices $\mathbf{U}_m''$ and $\mathbf{U}_r''$ apply to *meso* and racemic dyads, respectively. When rows and columns are arranged as above, the two racemic forms, *dl* and *ld*, need not be distinguished.[3,6,7]

The matrices given by eq 1–3 are generally applicable to vinyl chains, subject only to the validity of disregarding differences between the several kinds of second-order interactions. Distinctions between these interactions may be included in the formulation, if desired.[10]

The configuration partition function for the chain as a whole is given by

$$Z = \mathbf{J}^*\left(\prod_{i=2}^{n-1} \mathbf{U}_i\right)\mathbf{J} \tag{5}$$

where i indexes the bonds in serial order, $\mathbf{U}_i$ is the statistical weight matrix appropriate for bond i, and

$$\mathbf{J}^* = [1 \quad 0 \quad 0]$$
$$\mathbf{J} = \begin{bmatrix} 1 \\ 1 \\ 1 \end{bmatrix} \tag{6}$$

In the case of a vinyl chain of the constitution $H(CH_2\text{-}CHR)_xCH_3$ comprising x units, and therefore $x - 1$ dyads, the partition function is conveniently expressed by

$$Z = \mathbf{J}^*\left(\prod_{k=1}^{x-1} \mathbf{U}_k^{(2)}\right)\mathbf{J} \tag{7}$$

where $\mathbf{U}_k^{(2)}$ is one or the other of the dyad matrices defined by

$$\begin{aligned} \mathbf{U}_m^{(2)} &= \mathbf{U}'\mathbf{U}_m'' \\ \mathbf{U}_r^{(2)} &= \mathbf{U}'\mathbf{U}_r'' \end{aligned} \tag{8}$$

Which of these is used is dictated by the symmetry of the kth dyad. Equations 5 and 7 are generally applicable to chains of virtually any description. In particular, eq 7 can be applied to any vinyl chain of specified stereochemical sequence. In the case of a stereoregular vinyl chain, we have

$$Z = \mathbf{J}^*(\mathbf{U}_s^{(2)})^{x-1}\mathbf{J} \tag{9}$$

where s is m for an isotactic chain and r for a syndiotactic one.

For the calculation of second and fourth moments[1,12,13] $\langle r^2\rangle_0$ and $\langle r^4\rangle_0$, we require the appropriate axis transformation matrices $\mathbf{T}_i$ for transforming the representation of a vector in the cartesian reference frame of bond $i + 1$ to its representation in the reference frame for bond i. In keeping with conventions now well established, we take the axis x_i along the skeletal bond i and in the direction from left to right.[3] The y_i axis is taken in the plane of bonds $i - 1$ and i, with its direction making an acute angle with bond $i - 1$. The direction of the axis z_i is so chosen as to complete either a right-handed or a left-handed coordinate system, the choice being dictated by rules to be elaborated below. For chains like PM having no asymmetric centers, right-handed coordinate systems are the natural choice. It follows that a vector expressed in coordinate system $i + 1$ is converted to its representation in coordinate system i by premultiplication with the matrix

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(10) Separate statistical weight factors may of course be introduced for each of the several pairs if desired, as Williams and Flory[7] have shown. Since all such factors ω are small, being only slightly greater than zero for the cases of main interest, we may, with negligible bias of results to follow, avoid the complications of a greater number of parameters by adopting a single ω to represent all of these interactions of "second order."

(11) The detailed derivation of matrices applicable to vinyl chains is given in ref 1 and 3. Their rearrangement to the present form is treated in ref 6.

(12) P. J. Flory and R. L. Jernigan, *J. Chem. Phys.*, **42**, 3590 (1965).

(13) See ref 3, Chapter IV.

$$\mathbf{T}_i = \begin{bmatrix} \cos\theta_i & \sin\theta_i & 0 \\ \sin\theta_i\cos\varphi_i & -\cos\theta_i\cos\varphi_i & \sin\varphi_i \\ \sin\theta_i\sin\varphi_i & -\cos\theta_i\sin\varphi_i & -\cos\varphi_i \end{bmatrix} \quad (10)$$

where θ_i is the supplement of the bond angle at skeletal atom i (marking the right-hand terminus of skeletal bond i) and φ_i is the angle of rotation about bond i measured in the positive, or right-handed, sense.

The second moment $\langle r^2\rangle_0$ of the end-to-end vector **r** for the unperturbed, free chain may be calculated according to methods set forth in detail elsewhere.[12,13] Briefly, it is obtained through serial multiplication of matrices

$$\mathcal{G}_i = \begin{bmatrix} \mathbf{U} & (\mathbf{U}\times\mathbf{l}^{\mathrm{T}})\|\mathbf{T}\| & (l^2/2)\mathbf{U} \\ \mathbf{0} & (\mathbf{U}\times\mathbf{E}_3)\|\mathbf{T}\| & \mathbf{U}\times\mathbf{l} \\ \mathbf{0} & \mathbf{0} & \mathbf{U} \end{bmatrix}_i \quad (11)$$

where $\mathbf{l}^{\mathrm{T}}$ is the row $[l\ 0\ 0]$ representing the bond vector for the ith bond in its reference frame, $\mathbf{l}$ is its column representation, $\|\mathbf{T}\|$ denotes the diagonal array of **T** matrices for the respective rotational states—t, g^+, and g^- in the case of a polymethylene chain; $\mathbf{E}_3$ is the identity matrix of order three; and $\times$ denotes the direct matrix product. The subscript i applies to all quantities **U**, **T**, and **l** within the brackets. All information pertaining to bond i is embodied in $\mathcal{G}_i$, with due account of the state of its predecessor, bond $i - 1$. Serial multiplication of such matrices, one for each bond, yields $\langle r^2\rangle_0$ according to the formula

$$\langle r^2\rangle_0 = 2Z^{-1}\mathcal{J}^*\left(\prod_1^n \mathcal{G}_i\right)\mathcal{J} \quad (12)$$

where $\mathcal{J}$ is the column having elements 00...0111, and $\mathcal{J}^*$ is the row with elements 100...0. For terminal bonds, $\mathcal{G}_i$ and $\mathcal{G}_n$ are formulated according to eq 11 with $\mathbf{U}_i = \mathbf{U}_n = \mathbf{E}_3$. Fourth moments $\langle r^4\rangle_0$ may be computed in an analogous manner using appropriately defined matrices $\mathcal{K}_i$ instead of $\mathcal{G}_i$.[12,13] Higher moments may be obtained by elaboration of these methods[14,15] but the computational labor is increased considerably.

The signification of rotational states for vinyl polymers according to the scheme t, g, $\bar{g}$ defined above necessitates appropriate revisions in the formulation of the matrices $\mathcal{G}_i$, and of matrices used to calculate higher moments and other averaged quantities. It proves expedient to assign right-handed coordinate systems to skeletal bonds which when viewed in the direction from CHR to $\mathrm{CH_2}$ have their substituents arrayed as in Figure 1. For bonds presenting the opposite (mirror image) stereochemical configuration, a left-handed coordinate system is assigned, the direction of the z axis being the reverse of that for a right-handed coordinate system.[16] In harmony with the choice of a left-handed coordinate system, the rotation angle φ for the bond considered is measured in the negative (*i.e.*, left-handed) sense. With these conventions, which supersede those offered in ref 3, corresponding conformations of an enantiomorphic pair (*e.g.*, one of the diagrams in Figure 1 and its mirror image) are accorded rotation angles of the same sign. If, for example, rotational states are taken at equal intervals, $\varphi = +120°$ for a g state irrespective of whether or not the rotation in a given instance is positive (g^+) or negative (g^-); similarly, $\varphi = -120°$ for a $\bar{g}$ state without regard for the sign of the actual rotation.

According to arguments presented in greater detail elsewhere,[1,3] we may expect the rotational isomeric states for vinyl chains to be displaced somewhat from their symmetrical locations assumed above. The pattern of these displacements is simplified when expressed in the present scheme. We therefore reexamine them briefly.

The three-bond interaction between CH and R in the *trans* state shown in Figure 1 may be expected to displace the energy minimum by an amount $\Delta\varphi$, perhaps on the order of 10° (see ref 1 and 3). Thus, a more realistic location for the *trans* state is $\varphi_t = \Delta\varphi$. If the substituent R is comparable in size to $\mathrm{CH_2}$, then a similar displacement of opposite sign may be expected for the g state. Since in the $\bar{g}$ state the CH group is subject to three-bond impingements on both sides, the location of this state may be presumed to be unaltered in first approximation. On this basis the rotational isomeric states occur at angles as follows

$$\begin{aligned} \varphi_t &= \Delta\varphi \\ \varphi_g &= 120° - \Delta\varphi \\ \varphi_{\bar{g}} &= -120° \end{aligned} \quad (13)$$

This prescription is invariant with respect to enantiomorphs—a further advantage of the present scheme.[17]

It remains to consider the transformation matrices **T** to be used in the construction of the $\mathcal{G}$ matrices and their analogs for treatment of various average quantities. Premultiplication by the transformation matrix $\mathbf{T}'$ required to be used in conjunction with $\mathbf{U}'$ for the construction of $\mathcal{G}_i$ for a bond like bond i in the diagrams in Figure 2 must effect the transformation of the representation of a vector in the reference frame of bond $i + 1$ to that of bond i; this matrix depends on φ_i. Suppose the dyad to be *meso*, *dd* (Figure 2). According to the conventions enunciated above, the coordinate system for bond $i + 1$ is left handed (LH) and that for bond i is right handed (RH). Hence, the required transformation is

$$\mathrm{RH} \longleftarrow \mathrm{LH}$$

Observing that **T** expressed by eq 10 refers to

$$\mathrm{RH} \longleftarrow \mathrm{RH}$$

we note that the sense of φ_i is retained but that the direction of the axis z_{i+1} must be reversed. Accordingly, signs in the last column of eq 10 must be reversed, and the required transformation $\mathbf{T}'$ is[18]

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(14) R. L. Jernigan, Ph.D. Thesis, Stanford University, 1967.

(15) K. Nagai, *J. Chem. Phys.*, **48**, 5646 (1968).

(16) The device of using right- and left-handed coordinate systems in the treatment of vinyl chains was introduced by T. M. Birshtein and O. B. Ptitsyn, "Conformations of Macromolecules," Interscience Publishers, New York, N. Y., 1966, p 157. The present conventions governing the choice of one or the other coordinate system are not coincident with theirs, however.

(17) Compare ref 3, p 211.

(18) See ref 3, p 228.

$$\mathbf{T}_* = \begin{bmatrix} \cos\theta & \sin\theta & 0 \\ \sin\theta\cos\varphi & -\cos\theta\cos\varphi & -\sin\varphi \\ \sin\theta\sin\varphi & -\cos\theta\sin\varphi & \cos\varphi \end{bmatrix} \qquad (14)$$

For the case considered $\theta = \theta_i$ and $\varphi = \varphi_i$. If the *meso* dyad were *ll*, the transformation would be represented by

$$\mathrm{LH} \longleftarrow \mathrm{RH}$$

The sign of φ_i in eq 10 would be reversed and elements of the third row of **T** given by eq 10 would require multiplication by -1. The result is $\mathbf{T}_*$ given by eq 14. The distinction between *ll* and *dd* dyads is artificial; moreover, the identity of the transformations required for *dd* and *ll* follows directly from symmetry arguments pertaining to mirror reflection.[3]

If the dyad is racemic *dl*, the transformation is

$$\mathrm{RH} \longleftarrow \mathrm{RH}$$

and the appropriate transformation $\mathbf{T}'$ is **T** of eq 10. The same transformation applies to the racemic *ld* form, as follows from mirror symmetry.

The transformations $\mathbf{T}''$ relating the coordinate system for a pair of bonds such as $i + 2$ and $i + 1$ in Figure 2 necessarily involve coordinate systems of opposite chirality according to the convention adopted above. They depend only on the character of the *second* asymmetric center of the dyad. Thus, for *dd* and *ld* dyads we have

$$\mathrm{LH} \longleftarrow \mathrm{RH}$$

and for *ll* and *dl*

$$\mathrm{RH} \longleftarrow \mathrm{LH}$$

Both require $\mathbf{T}'' = \mathbf{T}_*$, as may easily be verified.[3]

The foregoing considerations lead to rules as follows for the formulation of $\mathcal{G}$ matrices according to eq 11

$$\begin{aligned} \mathcal{G}_m' &= \mathcal{G}(\mathbf{U}', \mathbf{T}_*, \mathbf{I}) \\ \mathcal{G}_r' &= \mathcal{G}(\mathbf{U}', \mathbf{T}, \mathbf{I}) \\ \mathcal{G}_m'' &= \mathcal{G}(\mathbf{U}_m'', \mathbf{T}_*, \mathbf{I}) \\ \mathcal{G}_r'' &= \mathcal{G}(\mathbf{U}_r'', \mathbf{T}_*, \mathbf{I}) \end{aligned} \qquad (15)$$

Serial indexes i, $i + 1$, etc., are omitted for simplicity. The several **U** matrices are given by eq 2–4; **T** and $\mathbf{T}_*$ are given by eq 10 and 14, respectively.

For vinyl chains it is convenient to define dyad matrices $\mathcal{G}^{(2)}$ in analogy to $\mathbf{U}_m^{(2)}$ and $\mathbf{U}_r^{(2)}$ (see eq 8). Thus

$$\begin{aligned} \mathcal{G}_m^{(2)} &= \mathcal{G}_m'\mathcal{G}_m'' \\ \mathcal{G}_r^{(2)} &= \mathcal{G}_r'\mathcal{G}_r'' \end{aligned} \qquad (16)$$

Then

$$\langle r^2\rangle_0 = 2Z^{-1}\mathcal{G}^*\left(\prod_{k=1}^{x-1}\mathcal{G}_k^{(2)}\right)\mathcal{G} \qquad (17)$$

Fourth moments and other quantities can be treated in like manner by formulating the appropriate matrices, $\mathcal{K}_m^{(2)}$ and $\mathcal{K}_r^{(2)}$, for example,[13] according to the same format.

The foregoing multiplication schemes are applicable to chains of virtually any description, and the computations are feasible for chains of any length of interest. For stereoirregular vinyl chains comprising both *meso* and racemic dyads statistically distributed in some specified manner, it is necessary to resort to Monte Carlo calculations.[1,8] Thus, a chain of x units is generated by numerical methods conforming to the statistical distribution of m and r dyads. Then both Z and the product

$$\prod_{1}^{x-1}\mathcal{G}_k^{(2)}$$

are calculated for the given Monte Carlo chain, and the value of $\langle r^2\rangle_0$ is obtained from their ratio (see eq 17). The calculations are repeated for each of a number of chains similarly generated, and the values of $\langle r^2\rangle_0$ are averaged. In all cases considered below, the sequence of m and r dyads is taken to be Bernoullian and governed therefore by the *a priori* probability f_r, or fraction of racemic dyads in the system.

Results and Discussion

Parameters. Values of η for oligomers of polystyrene and of poly(vinyl chloride) are *ca.* 1.4 and 3.5, respectively.[7] A larger substituent R should be expected to lower η below unity. For the illustrative calculations that follow, we have taken $\eta = 1.00$. In general, τ may be expected to occur in the range 0.2–1.0; a value of 0.5 has been adopted here. As noted earlier, we let $\tau^* = 1.0$.

The parameter on which we place main emphasis is ω. A value of $\omega \ll 1$ is to be expected for most vinyl polymers. We have explored the effect of variation of this parameter throughout the range 0–1, but have examined the range $0 \leq \omega \leq 0.1$ in greatest detail. Supplements θ of skeletal bond angles are taken to be 68° except as noted otherwise in Figure 9. Rotational states are taken at $\varphi = 0°, 120°, -120°$. The energy minima probably are displaced[1,8] some 10–20° from these values of the rotation angle, but in interests of simplicity, we have adopted the symmetrical locations for the purposes of the illustrative calculations that follow.

The same values of θ and φ have been used for the calculations on polymethylene presented here for comparison. The statistical weight parameters are assigned their "best values"[3,8] for a temperature of 140°, namely, $\sigma = 0.54$ and $\omega = 0.088$.

The Partition Function. In Figure 3 we show the mean partition function z per bond, *i.e.*, $z = Z^{1/n}$, as a function of the fraction f_r of racemic dyads for the several values of ω indicated, other parameters having been assigned the values stated above. The terminal points at $f_r = 0$ and 1 represent exact calculations carried out for stereoregular isotactic and syndiotactic chains, respectively, in the limit $n \rightarrow \infty$. Intermediate points are averages for five Monte Carlo chains, each of $x = 200$ units, or $n = 400$ bonds. The deviations from mean values due to statistical scattering are less than 1%. That the results for $n = 400$ may be construed as representing limiting values for infinite chains is confirmed by the fact that calculations for $n = 800$ or 1600 differ imperceptibly from those shown in Figure 3.

When $\omega = 0$, all conformations except the preferred

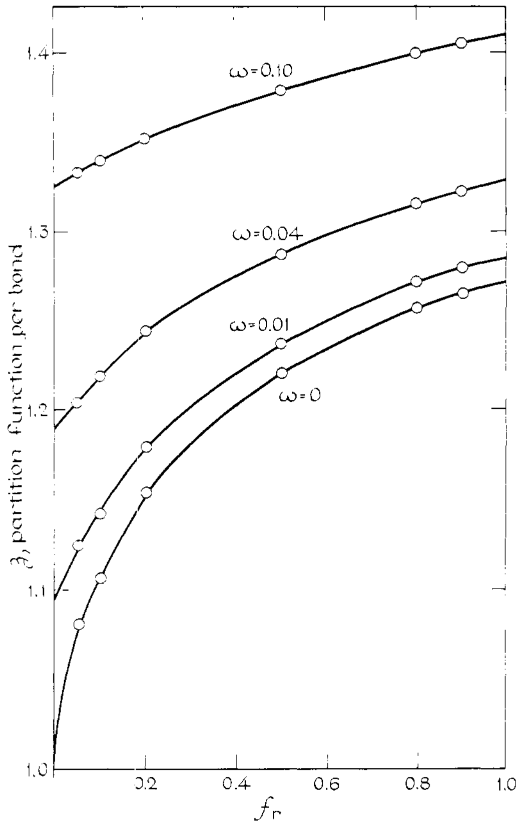

Figure 3. The average partition function per bond *vs.* the fraction f_r of racemic dyads in vinyl chains of 200 units.

ones (*i.e.*, those devoid of second-order steric overlaps) are suppressed. The contrast between isotactic ($f_r = 0$) and syndiotactic ($f_r = 1$) chains is then most striking. For the former, $z \rightarrow 1$ in the limit $n \rightarrow \infty$, the chain being forced to adopt the Natta-Corradini 3_1 helix throughout; the diversity of configurations accessible to the syndiotactic chain, on the other hand, yields a value substantially in excess of unity, namely, $z = 1.272$ per bond, or $z^{(2)} = 1.618$ per dyad. The rise in z with f_r is most rapid at $f_r = 0$, becoming more gradual as f_r approaches unity.

Values of $\omega > 0$ permit occurrence of conformations other than the preferred ones, and hence cause the partition function to increase. The effect, as expected, is most marked for the isotactic chain. Hence, the difference between z for syndiotactic and isotactic chains diminishes as ω is increased from 0 to 0.10.

The Characteristic Ratio for Stereoregular Chains. The characteristic ratio is defined by

$$C_n = \langle r^2 \rangle_0 / nl^2 \qquad (18)$$

Its values for isotactic (I) and syndiotactic (S) chains in the limit $n \rightarrow \infty$ are plotted against log ω in Figure 4. Enforcement of the 3_1 helical conformation at $\omega = 0$ causes C_∞ to become infinite.[1,3] The characteristic ratio decreases rapidly with increase in ω, however.[1] For syndiotactic chains the dependence on ω is less marked.

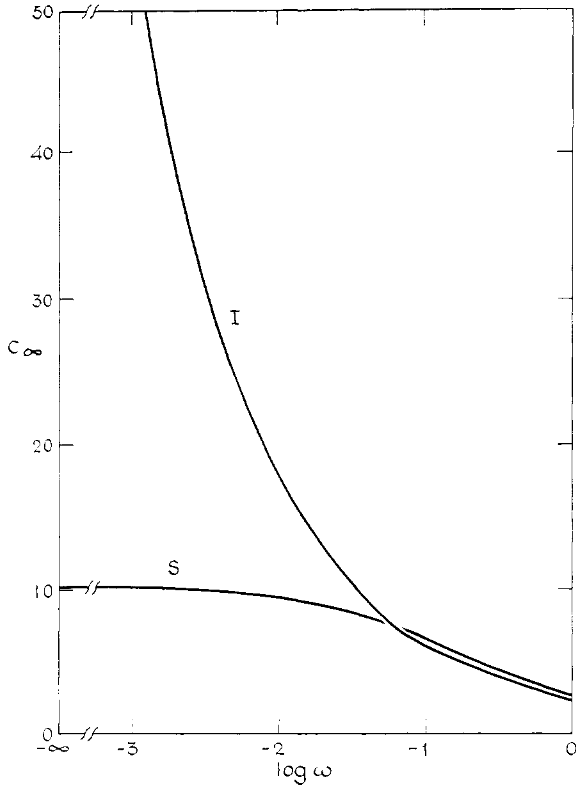

Figure 4. The characteristic ratio for isotactic (I) and syndiotactic (S) chains of infinite length as functions of log ω.

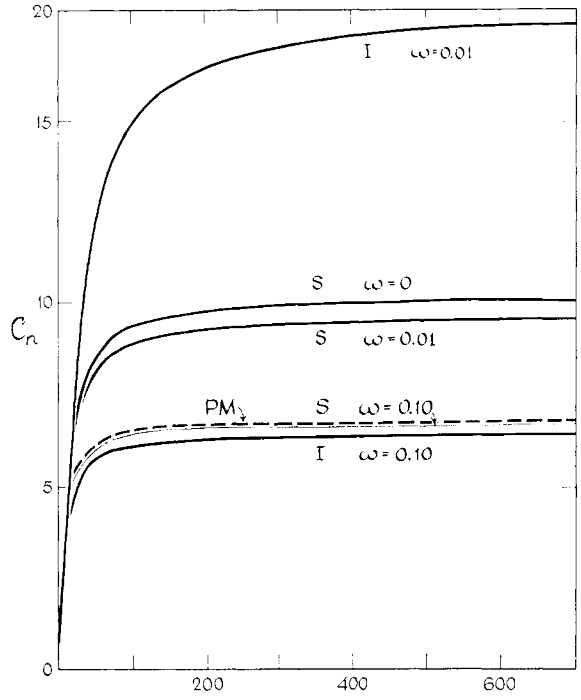

Figure 5. The dependence of the characteristic ratios on chain length for isotactic and syndiotactic chains for the several values of ω indicated. The curve for polymethylene (dashed) is included for comparison.

The dependence of the characteristic ratio on chain length n is shown in Figure 5 for stereoregular chains subject to the values of ω indicated. Also included for comparison is the dashed curve calculated for polymethylene chains (PM) using values of the parameters given above.[8] The same curves (with the exception of that for PM which very nearly coincides with the S, $\omega = 0.10$ curve) are replotted in Figure 6 against $1/n$. The curves are of course asymptotically linear at their

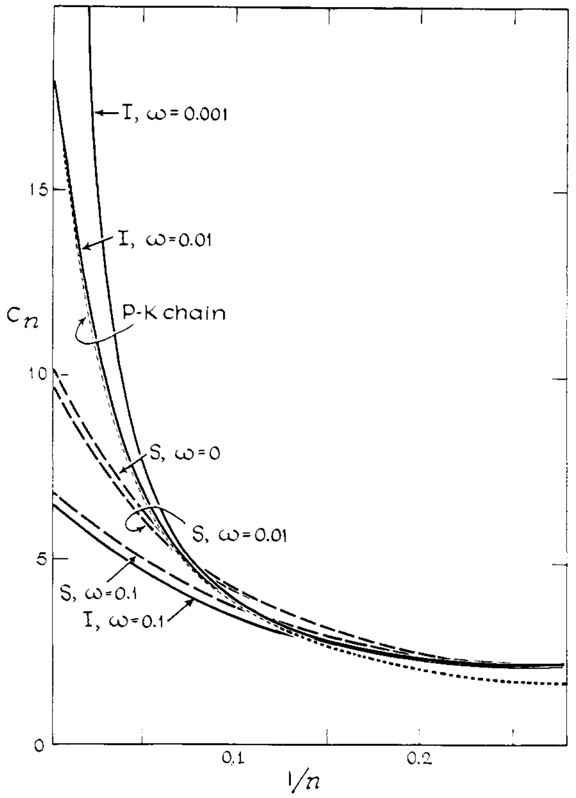

Figure 6. Characteristic ratios of Figure 5 plotted against the reciprocal of the chain length. Calculations for a Porod–Kratky chain, shown by the dotted line, also are included.

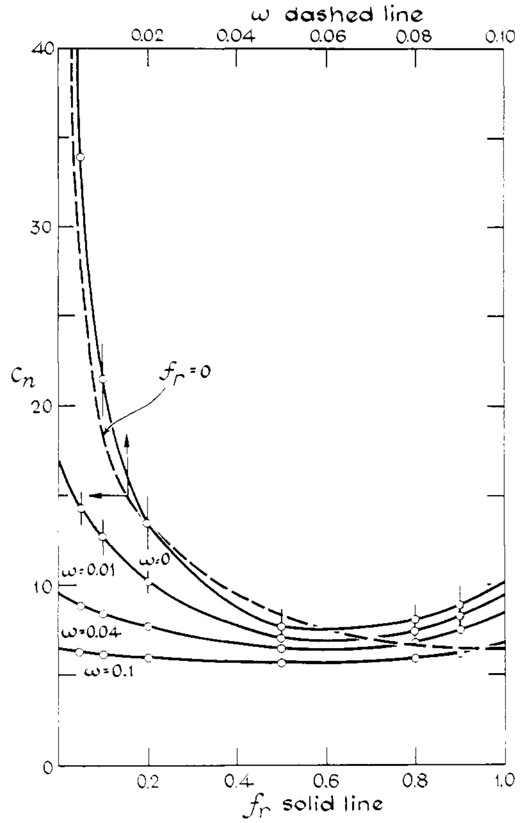

Figure 7. Dependence of C_n on the tacticity (solid curves), represented by f_r, according to Monte Carlo calculations on chains with $n = 400$. Vertical bars represent standard deviations for calculations on five chains in each instance. The dashed curve represents C_n for an isotactic chain ($f_r = 0$) as a function of ω, given on the upper margin.

ordinate intercepts, but the range of linearity is limited. The various curves cross in the range of small n.

The dotted line in Figure 6 represents the Porod–Kratky (P–K) "wormlike" chain. The fully extended length in this instance was set equal to the length L of the 3_1 helical form, and the persistence length a was so chosen as to reproduce the values of C_∞ for the isotactic chain with $\omega = 0.01$. The agreement with the curve calculated for the latter chain is quite good for $n > 10$. For shorter chains the P–K curve gives values of C_n which are too low.

The foregoing identification of the fully extended length L with the axial length of the 3_1 helix is to some extent arbitrary, even for an isotactic chain subject to a small value of ω. For atactic and syndiotactic chains, this identification would be quite unjustified. Moreover, no other rational basis for assigning a value to L is apparent for such chains. Hence, we are obliged to treat both L/n and a as arbitrary parameters. With two parameters at one's disposal, the portions of the solid curves in Figure 6 for large values of n may be well reproduced by the P–K model. The parameters cannot be independently determined, however; they can only be established from calculations of the kind carried out here for a realistic model of the chain in question. Even with assignment of arbitrarily adjusted values to L/n and a, deviations from the P–K model may be substantial for small values of n.

The Characteristic Ratio for Stereoirregular Chains. Results of Monte Carlo calculations carried out on sets of five chains, each consisting of 400 bonds, are represented by the solid curves in Figure 7 for the several values of ω indicated. As shown previously,[1-3] the characteristic ratio depends critically on the degree of stereoregularity for predominantly isotactic chains. This dependence is diminished by an increase in ω.

The dashed curve in Figure 7 shows C_∞ for an isotactic chain as a function of ω plotted according to the scale shown on the upper margin. This curve is taken from Figure 4 and is reproduced here in order to compare the effect of an increase in ω, whereby second-order steric overlaps are rendered less severe, with the effect of stereoirregularity. For very small values of ω, *i.e.*, for $\omega < 0.01$, the incidence of departures from the preferred form can be shown to depend approximately on $\sqrt{\omega}$. That an increase in ω when $f_r = 0$ simulates the effect of increasing stereoirregularity in the range $f_r = 0.05$–0.50 is apparent by comparisons of the dashed curve with the solid curve for $\omega = 0$. Calculations for stereoregular isotactic chains carried out for various values of ω in the range 0–0.1 are used in the following papers to illustrate the effects of varying the tortuosity of a chain from the extreme case of a stiff rod ($\omega = 0$) to that of a chain comparable to polymethylene in its "flexibility" (see Figure 5).

The curve in Figure 7 for $\omega = 0$ agrees with earlier calculations by Flory, Mark, and Abe[1] and the more extensive calculations by Tonelli[2] for Monte Carlo chains of 400 units. These authors also examined the effects of rational adjustments in the angles φ for the rotational states according to eq 13. We ignore such adjustments here, inasmuch as the calculations pre-

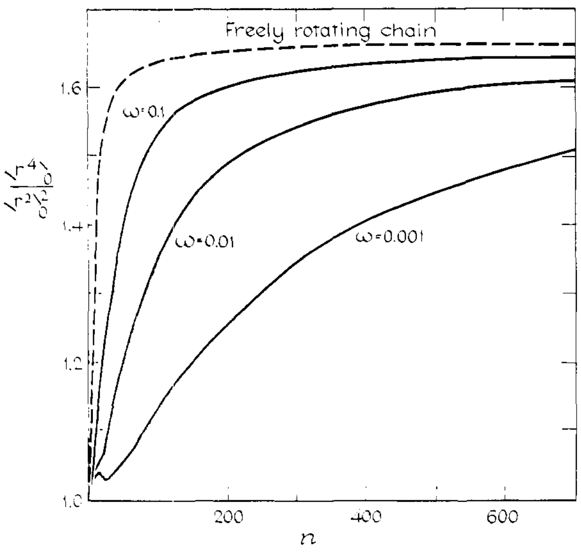

Figure 8. The ratio of the fourth moment to the square of the second moment *vs.* the chain length for isotactic chains (solid lines). The curve for a chain subject to free rotation is shown for comparison.

sented are intended to be illustrative of chains of varying tortuosity rather than literally representative of particular vinyl chains. It is to be noted, however, that refined representation of the rotational states of vinyl chains would modify the quantitative features, as was shown by previous calculations.[1,3]

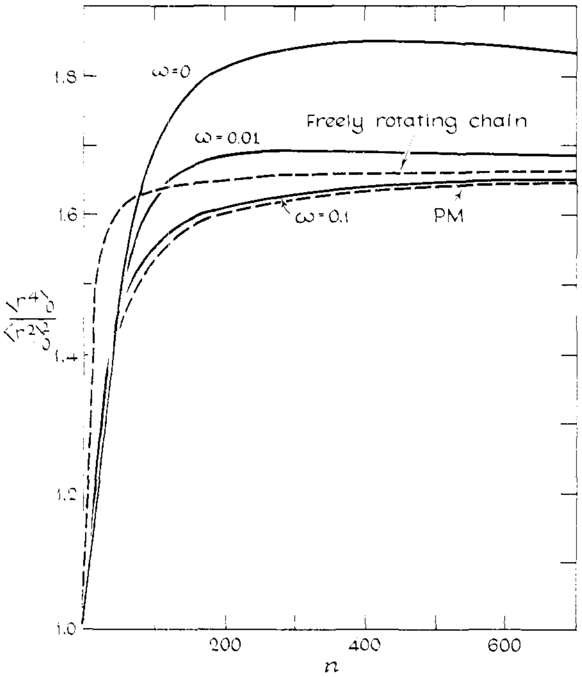

Figure 9. Fourth moment ratio for syndiotactic chains (solid curves) *vs.* n for the values of ω indicated. The freely rotating and PM chains are shown for comparison.

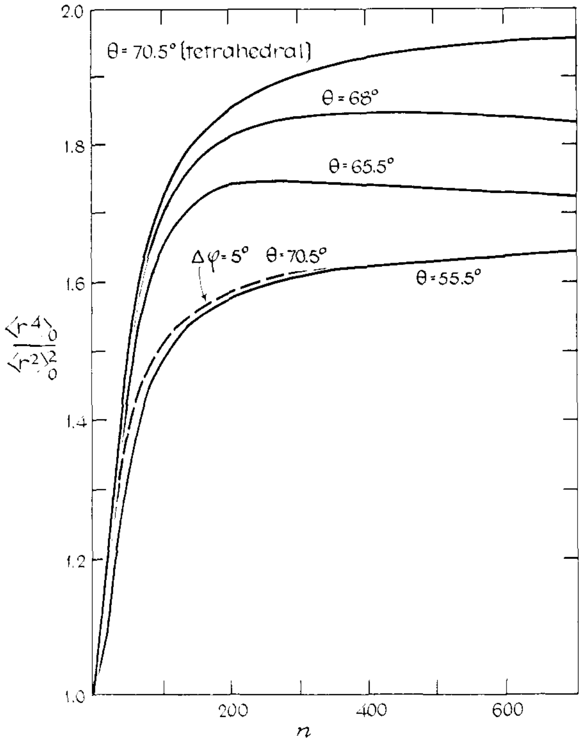

Figure 10. Fourth moment ratios for syndiotactic chains with $\omega = 0$, $\varphi = 0°$, $\pm 120°$ (solid curves) and θ equal to the values indicated. The dashed curve has been calculated with alteration of the rotational angles by $\Delta\varphi = 5°$ according to eq 13, and with $\theta = 70.5°$.

Fourth Moments. In light of the similar effect of an increase in ω to that of introduction of stereoirregularity into an isotactic chain, calculations of $\langle r^4\rangle_0$ were confined, in interests of simplifying computations, to stereoregular chains subject to various values of ω. Results for isotactic chains, expressed as the ratios $\langle r^4\rangle_0/\langle r^2\rangle_0^2$, are plotted against n in Figure 8 for the values of ω indicated. Also shown for comparison is the curve for the chain with free rotation. The curve for polymethylene[8] is virtually coincident with the one shown for $\omega = 0.10$, and therefore has not been reproduced separately. Convergence to the limiting value 5/3 is slower the smaller the value of ω, as should be expected.

Similar calculations carried out for syndiotactic chains and presented in Figure 9 show $\langle r^4\rangle_0/\langle r^2\rangle_0^2$ to pass through a maximum value with increase in n when ω is very small. As the chain length is increased further, the ratio decreases toward the limiting value of 5/3, to which any random chain in three dimensions must converge. The clue to this anomalous behavior is to be found in the geometric character of the preferred conformations of the syndiotactic chain, which alone may occur when $\omega = 0$. These conformations (*tt* and *gg*; see above) constrain the chain to spatial configurations which are propagated preponderantly in two dimensions. In fact, if valence angles are made exactly tetrahedral instead of 112°, as in the calculations presented, then all of the preferred conformations for the syndiotactic chain with rotational states at 0°, ±120° are two dimensional. The limiting value of $\langle r^4\rangle_0/\langle r^2\rangle_0^2$ for a random chain in two dimensions is two instead of five-thirds.

The solid curves in Figure 10 demonstrate the effect of the bond angle supplement θ on the dependence of the fourth moment ratio on n for syndiotactic chains.

The calculations were carried out for $\omega = 0$, and $\varphi = 0°, \pm 120°$, *i.e.*, for $\Delta\varphi = 0°$ in eq 13. The ratio for the tetrahedral chain ($\theta = 70.5°$) increases monotonically with n toward the limiting value of 2.00 for a two-dimensional chain. For small departures from the tetrahedral angle, the ratio passes through a maximum; the propensity for two-dimensional propagation of the chain over sequences of limited length is dominant for small or intermediate values of n, but, as n increases further, the small departures from strict confinement to two dimensions prevail, and the ratio diminishes eventually to a limiting value of five-thirds. For θ values less than about 60°, the maximum disappears.

The dashed curve in Figure 10 illustrates the effect of displacements of the rotational states by amounts $\Delta\varphi = 5°$, these displacements from the symmetrical positions adopted above being introduced according to eq 13. Even this small alteration of the rotational states suffices to eliminate the maximum.

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Small-Angle X-Ray Scattering by Polymer Chains in the Submolecular Range

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ABSTRACT: Functions describing the angular dependence of the intensity of radiation scattered by chain molecules are calculated on the basis of realistic rotational-isomeric-state models for polymethylene, and for both isotactic and syndiotactic vinyl chains. Numerical calculations are carried out for the submolecular range in which $\mu^2 = (4\pi/\lambda)^2 \sin^2(\vartheta/2)$ is much greater than the reciprocal square radius of the chain. The potentialities of small-angle X-ray scattering as a means of investigating the configurational characteristics of chain molecules are examined. The theoretical treatment is susceptible to major simplification owing to the virtual independence of the mean-square distance $\langle r_{ij}^2 \rangle$ between a pair of chain atoms separated by a given number m of bonds ($m = i - j$) on the position of the sequence i,j in the chain. However, values of higher even moments $\langle r_{ij}^4 \rangle$, etc., are required for an accurate representation of the scattering function for $\mu > 0.05$–0.10, *i.e.*, the range in which the scattering function is most sensitive to details of the chain configuration.

The theoretical treatment of Rayleigh scattering by chain molecules with realistic account of their structures has been reexamined recently[1,2] with the aid of new methods for treating the configurational characteristics of chain molecules. We have discussed in some detail the scattering function that is appropriate under conditions such that correlation between all pairs of groups, even including those which are most remote in sequence in the chain, are appreciably significant. In particular, Jernigan and one of us[1,2] have shown how the Debye equation for the scattering function, $P(\mu)$, or $P(\vartheta)$, for a freely jointed chain can be modified to render it applicable to real polymer chains. Further refinements can be achieved through computation of sums over the higher moments $\langle r_{ij}^4 \rangle$ of the distance between chain atoms i and j.[1,2] It was shown that corrections thus introduced often may be quite negligible.

Here we focus attention on radiation scattering under conditions, usually attainable only with X-radiation, such that the pairs of groups i,j whose correlations contribute most significantly to the scattering function are separated by numbers of bonds $m = i - j$ which are much less than the total length of the chain. This subject has been discussed extensively by Kratky[3,4] and by Kirste[5] and their coworkers. It is the purpose of this paper to bring into account the molecular structure of the chain in question, and its spatial configuration, in a realistic fashion without reliance on artificial models or assumptions lacking sound physical justification. The calculations here presented are intended to be indicative of the potentialities, and limitations as well, of small-angle X-ray scattering as a method for investigating the spatial configurations of chain molecules in general.

Theory

The dependence of the intensity of radiation scattered by a system of unoriented molecules on the angle ϑ from the incident beam and on the wavelength λ (in the scattering medium) is given by the well-known Debye equation[6]

$$P(\mu) = \sum_{i,j} f_i f_j (\mu r_{ij})^{-1} \sin(\mu r_{ij}) \Big/ \sum_{i,j} f_i f_j \qquad (1)$$

where f_i and f_j are the scattering factors for atoms or groups i and j, respectively; r_{ij} is the distance between groups i and j; and

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