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Configurational Statistics of Vinyl Polymer Chains

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Abstract: The primary chiral elements of a vinyl polymer chain $\text{CH}_3(\text{CRR}'\text{CH}_2)_x\text{H}$, in which $\text{R}' \neq \text{R}$, are the skeletal bonds rather than the substituted carbons as conventional terminology implies. The conformation in relation to any specified stereochemical configuration may be treated with full generality in terms of the chiralities of skeletal bonds. Statistical weight matrices are formulated in a parallel manner for both mono- ($\text{R}' = \text{H}$) and disubstituted chains, with emphasis on the latter. As an indirect consequence of the copious second-order interactions (involving groups separated by four bonds) when the sizes of both R and R' are commensurate with or larger than CH_3 , interactions of higher order (involving groups separated by as many as eight bonds) are not averted by interactions of second order, as is the case when $\text{R}' = \text{H}$. Significant interactions of longer range in disubstituted chains may introduce interdependence between consecutive pairs of skeletal bonds, the relevant pairs being the two that adjoin each substituted carbon. The complications thus arising are easily managed by resort to statistical weight matrices (of orders 7×7 for three states per bond) that relate the combined state of one such bond pair to that of the neighboring pair. Previous methods are adapted to the formulation of generator matrices suitable for calculation of configuration-dependent properties on the basis of these pair-pair statistical weight matrices. Simplifications for symmetric chains are introduced.

The spatial configurations of monosubstituted vinyl polymer chains, $\text{CH}_3[\text{CHRCH}_2]_x\text{H}$, are greatly restricted by steric interactions if, as is usual, the substituent R is comparable to or greater than CH_3 in size.^{1,2} The predominant interactions are those involving pairs of groups from the set CH_2 , CH , and R that are separated by four bonds. The distance between the centers of two groups thus related depends on the angles of rotation about the central pair of the sequence of four bonds; see Figure 1 with $\text{R}' = \text{H}$. Hence, following Birshtein and Ptitsyn,³ we refer to these as interactions of *second order*.² The mutual orientation of the two groups depends, of course, on the rotations about the two outer, or pendant, bonds of the set of four. In particular, for groups like CH_2 and CH_3 the mutual disposition of the peripheral hydrogen atoms, which are the atoms most directly involved in the interaction, depends on these rotations. To an approximation that is often adequate, groups such as these may be treated as spherical domains. Rotations about the outer two bonds of the sequence

usually are of secondary importance and often may be ignored altogether. It is appropriate, therefore, to consider the intensity of these "four-bond" interactions to be determined principally by rotations about the central pair of skeletal bonds, bond lengths and bond angles being assumed to be fixed.

Similar considerations apply to interactions between groups separated by three bonds, *e.g.*, between CH and R and/or between CH and CH_2 . The intensities of these interactions depend primarily upon the rotation about one skeletal bond and, hence, are classified as *first order*.^{2,3} For a quantitative estimation of the energy of interaction, however, the locations of individual atoms must be taken into account.

The preponderance of the skeletal conformations generated for a monosubstituted vinyl chain by arbitrary assignments of their rotation angles to the usual *trans* and *gauche* states (with or without displacements from staggered positions) are subject to steric interactions of second order as identified above.^{1,2} However, conformations which are free of these steric repulsions are accessible, although they are comparatively few in number. Which conformations are thus favored depends on the stereochemical configuration of the vinyl chain. In the case of an isotactic chain consisting exclusively of meso dyads, for example, the right- and left-handed Natta-Corradini helices generated by

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

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

(3) T. M. Birshtein and O. B. Ptitsyn, "Conformations of Macromolecules," translated by S. N. Timasheff and M. J. Timasheff, Interscience, New York, N. Y., 1966, p 76.

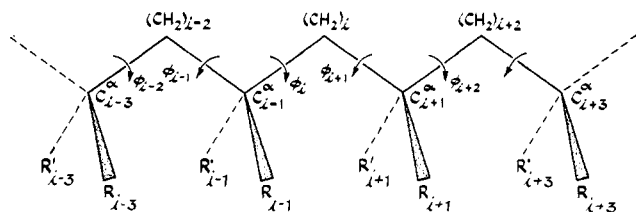


Figure 1. Schematic representation of an isotactic, or all-meso, vinyl chain in the trans or planar zigzag conformation. The substituents R and R' attached to the α -carbon atoms are assumed to differ; R' = H in the case of a monosubstituted vinyl chain. Indexes i , etc., enumerate the serial order of the skeletal atoms, the initial carbon atom (CH_2) being numbered zero.

assigning bonds alternately trans and gauche, *i.e.*, ... $\text{tg}^{\pm}\text{tg}^{\pm}$, etc., are the only ones free of second-order interactions.

In chain molecules in general, groups separated by five or more bonds may be brought within range of steric overlap by arbitrarily conforming the internal members (three or more) of the sequence of bonds. However, such a conformation for sequences of five to eight bonds invariably involves one or more second-order overlaps between intervening skeletal groups (*e.g.*, CH_2 or CH) and, hence, would be reduced to low incidence on this score alone, even if the interactions of higher order were somehow set aside. In good approximation, therefore, interactions beyond second order (four bond) may usually be ignored.^{1,2} Hence, it suffices to formulate statistical weight matrices comprising elements for pairs of bonds; the larger statistical weight matrices that would be necessary to accommodate statistical weights for longer sequences of bonds are not required.⁴

The intervention of second-order interactions in obviating the need to take account of interactions of higher order greatly simplifies the treatment of chain molecules in general, including monosubstituted vinyl polymers. Three different statistical weight matrices are needed for the latter: one, U' , for the pair of bonds flanking an α carbon (*i.e.*, a substituted carbon—CHR—), another, U_m'' , for the pair of bonds between successive α carbons of a meso dyad, and the third, U_r'' , for the corresponding bonds of a racemic dyad. These matrices form the basis for the calculation of various constitutive properties that depend on the conformation of a chain. Chains of any specified stereochemical sequence can be treated. The general formulation of these matrices^{2,5} and a number of applications of them to vinyl polymers have been given previously.⁵⁻⁹

In disubstituted vinyl chains, $\text{CH}_3[\text{CRR}'\text{CH}_2]_x\text{H}$, wherein both R and R' are large compared to H, severe second-order overlaps cannot be avoided in any conformation. In fact, two such interactions occur within each dyad in every staggered conformation. This is at once apparent from the diagrammatic representation

(4) P. J. Flory, *J. Polym. Sci., Part A-2*, **11**, 621 (1973).

(5) Y. Fujiwara and P. J. Flory, *Macromolecules*, **3**, 280 (1970); P. J. Flory and Y. Fujiwara, *ibid.*, **2**, 315 (1969).

(6) A. D. Williams and P. J. Flory, *J. Amer. Chem. Soc.*, **91**, 3111 (1969); P. J. Flory and C. J. Pickles, *J. Chem. Soc., Faraday Trans. 2*, **69**, 632 (1973); P. J. Flory, *J. Amer. Chem. Soc.*, **89**, 1798 (1967).

(7) P. J. Flory and Y. Fujiwara, *Macromolecules*, **2**, 327 (1969); Y. Fujiwara and P. J. Flory, *ibid.*, **3**, 43 (1970); P. J. Flory, *ibid.*, **3**, 613 (1970).

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

(9) A. Abe, *J. Amer. Chem. Soc.*, **90**, 2205 (1968); **92**, 1136 (1970).

of the structure of an all-meso chain in Figure 1. For the dyad centered at $(\text{CH}_2)_i$, the pairs of groups involved in second-order interactions involve one member from the set $(\text{CH}_2)_{i-2}$, R_{i-1} , and R_{i-1}' and the other from the set $(\text{CH}_2)_{i+2}$, R_{i+1} , and R_{i+1}' . The same holds for any stereochemical configuration. Various pairs of groups may be engaged in interaction through rotations about the consecutive pair of bonds flanking an α carbon, *e.g.*, bond pair $i - 1$, i in Figure 1.

The severity of local steric interactions in all conformations of disubstituted vinyl chains is reflected in increases in the heats of formation by 6–8 kcal/mol of monomer unit^{10,11} and in the opening of the CCC bond angle at the methylene carbon by 10 to 15°. ^{12,13} As expected, the bonds at the α carbons appear to be little distorted from the symmetrical tetrahedral arrangement.¹³

Owing to the fact that no particular conformation or restricted set of conformations is decisively preferred as a result of interactions of first and second orders, those of third and fourth order may be important. This is in contrast to circumstances prevailing in monosubstituted vinyl polymers. Depending upon the nature of R and R', interdependence of conformations over as many as four bonds may therefore have to be taken into account, and the statistical weight matrices must be elaborated accordingly.

In this paper we generalize and extend the theory and methods for treating vinyl chains with particular emphasis on those which are disubstituted. The stereochemical character of the chain when $R' \neq R$ is treated according to a novel scheme for specifying the local chirality.

Chiral Character of Skeletal Bonds and the Specification of Conformation

The α -carbon atoms in a vinyl polymer chain in which $R' \neq R$ usually are cited as pseudoasymmetric centers; the stereochemical configuration is specified by reference to them. The actual loci of chirality are the skeletal bonds and not the α carbons. The chirality of the bond depends, of course, on the disposition of bonds about the α carbon, but the carbon center acquires chirality only if a criterion is introduced whereby the center is unambiguously associated with one of the two adjoining skeletal bonds. The bonds and not the carbon centers are the chiral elements.

Differentiation of the enantiomeric bonds is facilitated by viewing all bonds in the same direction, *e.g.*, from the α carbon to the methylene group, without regard for the direction of progression along the chain. Newman projections of the various conformations for bonds viewed in this manner are shown in Figure 2. We designate one of the enantiomeric forms *d* (dextro) and the other *l* (levo) as indicated. As a part of this convention, rotations φ about bonds of the former kind are assigned positive values when measured in the right-handed sense starting from the trans conforma-

(10) P. J. Flory, "Principles of Polymer Chemistry," Cornell University Press, Ithaca, N. Y., 1953, pp 249–256.

(11) R. M. Joshi, "Encyclopedia of Polymer Science and Technology," Vol. 13, Wiley, New York, N. Y., 1970, pp 788–821; R. M. Joshi and B. J. Zwolinski, *Macromolecules*, **1**, 25 (1968).

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

(13) E. Benedetti, C. Pedone, and G. Allegra, *Macromolecules*, **3**, 16, 727 (1970).

tion ($\varphi = 0$); rotations about the latter are measured in the left-handed sense. This is the signification of d and l ; it bears no relation whatever to optical rotation, or to the previous^{1,2} arbitrary differentiation of d and l centers at C^α . Under this convention the rotation angle φ is accorded the same sign, as well as magnitude, for equivalent conformations of enantiomeric bonds, the one being the mirror image of the other. It will be noted that the two skeletal bonds flanking a given α carbon are necessarily of opposite chirality. Thus, the bonds in a vinyl chain are equally divided between d and l forms, irrespective of its tacticity.

The application of the foregoing convention to the trans and gauche conformations is illustrated in Figure 2. Shown in the uppermost row are the trans conformations of the two enantiomeric forms, followed by the gauche, g , and the gauche \bar{g} , conformations. We choose to identify the conformer in which C^α is gauche relative to R' and CH_2 by g and the one in which C^α is gauche relative to R and CH_2 by \bar{g} . If $R' = H$, this convention accords with that introduced previously^{2,5} for monosubstituted vinyl chains. Each conformer is related by mirror reflection to the corresponding conformer (t , g , or \bar{g}) of its enantiomer. This relation is indicated in Figure 2 by the mirror plane separating conformations of enantiomer d from those of l . The g and \bar{g} conformers are obtained from the trans by rotations of $\varphi = +120$ and -120° , respectively. With φ measured as specified above, these stipulations apply alike to d and to l enantiomeric bonds. Although adherence to the g and \bar{g} designations as here defined obviates specification of the sense of rotation, we note that in the case of a d bond the g and \bar{g} conformations are generated from trans by right- and left-handed rotations, respectively; the opposite applies to an l bond.

The conformers may, of course, be assigned angles that depart from those indicated for perfect staggering, as appropriate in particular examples. A greater number of states may be chosen or the pattern may be otherwise altered. In any case, the requirements of symmetry can be met in a manner corresponding to that for bonds adhering to the three-state scheme.

A meso dyad comprises a pair of bonds of opposite enantiomeric character, *i.e.*, dl alias ld , and an isotactic sequence consists of an alternating succession $|dl|dl|$, etc., or its inverse $|ld|ld|$, etc. The vertical lines serve to indicate the locations of α carbons and hence denote the junctions between successive dyads. Racemic dyads comprise the enantiomeric pairs dd and ll ; a syndiotactic sequence consists of dyad pairs of alternating racemic character, $|dd|ll|dd|$, etc.

A scheme equivalent in its essentials to the one described above has been applied previously⁵ to monosubstituted vinyl chains. Recognition of the role of the skeletal bonds as the primary chiral elements facilitates establishment of correspondence between equivalent conformations of bonds of opposite chirality and thus eliminates the need to heed the sign of the rotation in addition to its t , g , and \bar{g} designations.

Statistical Weight Matrices for Interactions of First and Second Orders

In this section we formulate statistical weight matrices that take account of interactions that depend on

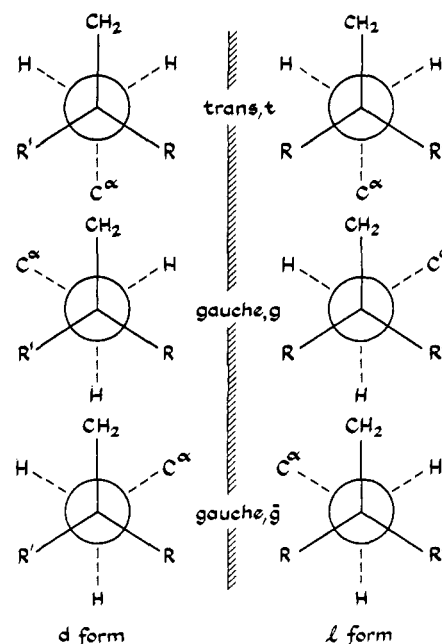


Figure 2. Newman diagrams for skeletal bonds viewed from C^α to CH_2 in the trans (t) and the two gauche (g and \bar{g}) conformations. Enantiomeric forms d and l are related by reflection through the plane indicated by the vertical line.

one or on two consecutive skeletal bond rotations, *i.e.*, interactions of first and second orders. Interactions of higher order are discussed in the following section.

Monosubstituted Vinyl Chains. In this case, $R' = H$ in Figures 1 and 2. Retaining the notation introduced previously,^{1,2,5} we let η , l , and τ represent the statistical weights for the first-order interactions depicted in Figure 2 for the t , g , and \bar{g} conformations, respectively. These may be presented as the elements of the diagonal matrix

$$U_1 = \text{diag}(\eta, l, \tau) \quad (1)$$

which is applicable alike to both d and l bonds.

Second-order interactions dependent upon the rotations about a pair of bonds flanking a substituted carbon (C^α); *e.g.*, bonds $i-1$ and i in Figure 1 involve the pendant pair of CH groups, *e.g.*, HC_{i-3}^α and HC_{i+1}^α . Gauche rotations of opposite sign, represented in the scheme here employed by $g|g$ and by $\bar{g}|\bar{g}$, bring these CH groups into close proximity. The resulting steric overlap is reminiscent of the $g^\pm g^\mp$ conformations encountered in polymethylene chains^{1,2} which, even after compromising bond rotations to minimize the energy, are reduced to an incidence which is marginally significant. In the vinyl chain, the $CH \cdots CH$ interaction is augmented by involvements of the substituents R . Although interactions between the substituents of this pair are, strictly speaking, of higher order, their inevitability justifies rejection of the second-order conformations that engender them. (Exceptions may occur when $R = F, OH, OR''$, or $OCOOR''$, wherein the van der Waals radius of the group attached directly to C^α is comparatively small. The statistical weights for $g|g$, and possibly for $\bar{g}|\bar{g}$, may then exceed zero to a significant extent; see eq 2 and 3.) In the $g|\bar{g}$ and $\bar{g}|g$ conformations (*i.e.*, $g^\pm|g^\mp$), the HC^α groups are sufficiently separated to eliminate the likelihood of appreciable interactions that may be

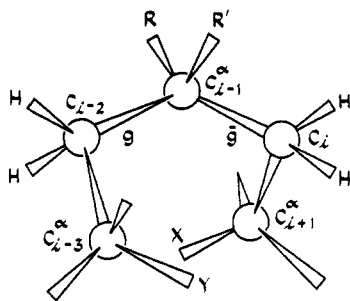


Figure 3. Six-bond interaction between any two groups, X and Y, attached to C_{i-3}^{α} and C_{i+1}^{α} , respectively, when the bond pair $i-1|i$ is $g|\bar{g}$ (or $\bar{g}|g$). The groups X and Y lie one above the other in the projection shown.

classified as second order. Hence, when $R' = H$ the matrix of second-order statistical weights can be represented by

$$U_{II'} = \begin{bmatrix} 1 & 1 & 1 \\ 1 & 0 & 1 \\ 1 & 1 & 0 \end{bmatrix} \quad (2)$$

(with the possible exceptions noted parenthetically above). The complete matrix of statistical weights for the stated bond pair is

$$U' = U_{II'} \cdot U_I = \begin{bmatrix} \eta & 1 & \tau \\ \eta & 0 & \tau \\ \eta & 1 & 0 \end{bmatrix} \quad (3)$$

For the pair of bonds between successive C^{α} 's, it is necessary to distinguish second-order interactions involving the three pairs of groups as follows: $CH_2 \cdots CH_2$, $CH_2 \cdots R$, and $R \cdots R$. Again, adhering to previous notation,^{1,6} we represent these interactions by statistical weights ω , ω' , and ω'' , respectively. Then, for the meso dyad, which may occur as $|dl|$ or in the reversed order $|ld|$

$$U_m'' = \begin{bmatrix} \omega'' & 1 & \omega' \\ 1 & \omega & \omega' \\ \omega' & \omega' & \omega\omega'' \end{bmatrix} U_I = \begin{bmatrix} \eta\omega'' & 1 & \tau\omega' \\ \eta & \omega & \tau\omega' \\ \eta\omega' & \omega' & \tau\omega\omega'' \end{bmatrix} \quad (4)$$

Similarly for a racemic dyad, which may be either $|dd|$ or $|ll|$

$$U_r'' = \begin{bmatrix} \eta & \omega' & \tau\omega'' \\ \eta\omega' & 1 & \tau\omega \\ \eta\omega'' & \omega & \tau\omega'^2 \end{bmatrix} \quad (5)$$

It may sometimes be advantageous to include all first-order interactions in the U'' matrix. Revisions to this end may be carried out by omitting the factor U_I in eq 3 and applying it instead as a premultiplier of U'' . Then U' will be replaced by $U' = U_{II'}$ (see eq 2), and

$$U_m'' = \begin{bmatrix} \eta^2\omega'' & \eta & \eta\tau\omega' \\ \eta & \omega & \tau\omega' \\ \eta\tau\omega' & \tau\omega' & \tau^2\omega\omega'' \end{bmatrix} \quad (6)$$

$$U_r'' = \begin{bmatrix} \eta^2 & \eta\omega' & \eta\tau\omega'' \\ \eta\omega' & 1 & \tau\omega \\ \eta\tau\omega'' & \tau\omega & \tau^2\omega'^2 \end{bmatrix} \quad (7)$$

Inasmuch as the matrices U' and U'' are multiplied in alternating succession for generation of the partition function and for other applications, it is obvious that reallocation of factors in the foregoing way can have no effect on the final results.

Normalization with respect to the $|tt|$ state for the racemic dyad may sometimes be preferred. This is easily effected through division of each element of both matrices by η^2 .

If the products $\tau\omega$, $\tau\omega'$, and $\tau\omega''$ are negligible compared to η , then the third rows and columns can be deleted from U' and U'' ; only the t and g states are required.^{1,4} For a planar substituent like C_6H_5 in polystyrene or $COOCH_3$ in poly(methyl acrylate), the \bar{g} state for bond i is suppressed by steric interactions between R_{i-1} and the groups R_{i+1} , $R_{i+1}' = H$, and $(CH_2)_{i+2}$ attached directly to C_{i+1}^{α} .¹⁴ Hence, $\tau = 0$ and deletion of third rows and columns as above is unambiguously indicated for a substituent of this nature.

Disubstituted Vinyl Chains. The same set of parameters, namely, η , 1, and τ (see eq 1) may be chosen to represent the first order interaction depicted in Figure 1 for $R' \neq H$. Their values may bear little relation to those for the monosubstituted chain ($R' = H$), and, of course, they depend on the nature of R' as well as on R .

With regard to second-order interactions associated with a bond pair like $i-1|i$ in Figure 1, we observe that steric overlaps occurring in the $g|g$ and $\bar{g}|\bar{g}$ conformations are proliferated by the presence of the second substituent (compare above). Hence, the suppression of these conformations is justified *a fortiori* in the present case.

The conformations $g|\bar{g}$ and $\bar{g}|g$ engender interactions, illustrated in Figure 3, between groups separated by six bonds. The particular groups involved, denoted noncommittally by X and Y, depend on the rotational states of bonds $i-2$ and $i+1$ as well as those of bonds $i-1$ and i . In the strict sense, therefore, these interactions are fourth order. If the substituents R and R' resemble CH_2 when involved in interactions of the type represented in Figure 3, then the various conformations for bonds $i-2$ and $i+1$ need not be distinguished; the same statistical weight ψ may then be assigned for the $g|\bar{g}$ and $\bar{g}|g$ states of bonds $i-1$ and i irrespective of the states of the adjoining bonds. With the adoption of this assumption as an approximation, the interactions under consideration reduce to second order. Relegating all first-order statistical weights to the U'' matrices, we have, therefore, that

$$U' = U_{II'} = \begin{bmatrix} 1 & 1 & 1 \\ 1 & 0 & \psi \\ 1 & \psi & 0 \end{bmatrix} \quad (8)$$

For tetrahedral bond angles and staggered conformations (rotation angles φ of $0, \pm 120^\circ$), the groups X and Y in Figure 3 are separated by a distance of only 2.5 Å. Opening the skeletal bond angles at the

(14) P. R. Sundararajan, D. Y. Yoon, and P. J. Flory, to be submitted for publication.

intervening methylene groups by 10–15° (see above) has only a small effect on this distance. It may be increased somewhat by decreasing the magnitudes of the gauche rotations. A fairly strong steric overlap persists nevertheless, and we anticipate, therefore, that ψ may be substantially smaller than unity. If $\psi \ll 1$, its precise value is not required, and the dependence of the interaction on the states of bonds $i - 2$ and $i + 1$ can be dismissed without reservation. The approximation introduced in the preceding paragraph gains support in these circumstances.

Features peculiar to the substituents R and R' must be taken into account in the formulation of the matrix of second-order interactions for a dyad pair, e.g., bond pair i and $i + 1$ in Figure 1. For the main purposes of the present paper, we proceed under the assumption that the substituents R and R' are cylindrically symmetric and, hence, that rotations about the C $^{\alpha}$ -C $^{\beta}$ bonds are inconsequential. Three illustrative cases are considered as follows: (i) R \neq R' \approx CH $_2$; (ii) R = R' \neq CH $_2$, and (iii) R = R' \approx CH $_2$. The general case where R \neq R' \neq CH $_2$, which may be treated by elaborating case i, is not discussed here.

Second-order statistical weights for the various pairs of interacting groups are specified for cases i and ii in Table I. Exact equivalence of R' to CH $_2$, insofar as

Table I. Second-Order Statistical Weight Parameters

Interacting pair	Case i	Case ii
	R \neq R' \approx CH $_2$	R = R' \neq CH $_2$
CH $_2$...CH $_2$	ω	ω
R...CH $_2$	ω'	ω'
R...R	ω''	ω''
CH $_2$...R'	ω	ω'
R...R'	ω'	ω''
R'...R'	ω	ω''

second-order interactions are concerned, is assumed in case i. For case iii all of the second-order parameters may be equated to unity. In case i the first-order parameter $\tau \approx \eta$, in case ii $\tau = 1$, and in case iii $\eta \approx \tau = 1$.

Poly(methyl methacrylate) treated in the following paper¹⁵ and poly(α -methylstyrene) might appear to be examples meeting the terms of case i. However, the substituents R = COOCH $_3$ and C $_6$ H $_5$, respectively, are not cylindrically symmetric and, hence, are formally excluded from the cases specifically considered here. Poly(vinylidene chloride) is an example of case ii, and polyisobutylene is illustrative of case iii.

Turning first to case i, the statistical weight matrices for bond pairs i and $i + 1$ within meso and racemic dyads are respectively

$$U_m'' = \begin{bmatrix} \eta^2\omega\omega'' & \eta\omega\omega' & \eta\tau\omega'^2 \\ \eta\omega\omega' & \omega^2 & \tau\omega\omega' \\ \eta\tau\omega'^2 & \tau\omega\omega' & \tau^2\omega\omega'' \end{bmatrix} \quad (9)$$

and

$$U_r'' = \begin{bmatrix} \eta^2\omega'^2 & \eta\omega\omega' & \eta\tau\omega\omega'' \\ \eta\omega\omega' & \omega^2 & \tau\omega\omega' \\ \eta\tau\omega\omega'' & \tau\omega\omega' & \tau^2\omega'^2 \end{bmatrix} \quad (10)$$

(15) P. R. Sundararajan and P. J. Flory, *J. Amer. Chem. Soc.*, **96**, 5025 (1974).

with states indexed in the order t, g, and \bar{g} as above. These expressions may be verified easily from Figure 1 and the corresponding diagram for a racemic chain. With states g and \bar{g} defined as above, the matrix U_r'' is directly applicable to both racemic dyad enantiomers.

In retaining η and τ as separate parameters in the present case (case i) in which $\tau \approx \eta$, we allow for possible (small) differences between the first-order interactions of R' and CH $_2$, although these groups are considered to be equivalent with regard to second-order interactions.

Normalization of eq 9 and 10 relative to the |tt| state for the meso dyad, accomplished through division of all elements in both matrices by $\eta^2\omega\omega''$, followed by the substitutions

$$\alpha = \omega'/\eta\omega'' \quad (11)$$

$$\beta = \omega'^2/\omega\omega'' \quad (12)$$

yields

$$U_m'' = \begin{bmatrix} 1 & \alpha & \beta\rho \\ \alpha & \alpha^2/\beta & \alpha\rho \\ \beta\rho & \alpha\rho & \rho^2 \end{bmatrix} \quad (13)$$

and

$$U_r'' = \begin{bmatrix} \beta & \alpha & \rho \\ \alpha & \alpha^2/\beta & \alpha\rho \\ \rho & \alpha\rho & \beta\rho^2 \end{bmatrix} \quad (14)$$

where τ/η is replaced by ρ in interests of simplifying these expressions and especially those appearing below. The number of parameters required for the U'' matrices is thus reduced from five to three. In all, four parameters are required for evaluation of U' and U'' . If it is permissible to set $\rho \equiv \tau/\eta = 1$, as case i suggests, the number is reduced to three.

In case ii $\tau = 1$, the chain is symmetric, the distinction between meso and racemic dyads vanishes, and the basis underlying the definition of g and \bar{g} states is voided. It is necessary, therefore, to revert to the use of g^+ and g^- states. We note that U' according to eq 8 requires indexing in the order t, g^- , and g^+ on the rows and t, g^+ , and g^- on the columns (or *vice versa*, since simultaneous interchange of the second and third rows and of the second and third columns leaves the matrix unchanged). The matrix U'' must be expressed correspondingly in order to be compatible with U' as given above; i.e., t, g^+ , and g^- for the rows and t, g^- , and g^+ for the columns (or *vice versa*). With states indexed according to this prescription

$$U_s'' = \begin{matrix} & \begin{matrix} t & g^- & g^+ \end{matrix} \\ \begin{matrix} t \\ g^+ \\ g^- \end{matrix} & \begin{bmatrix} \eta^2\omega''^2 & \eta\omega'\omega'' & \eta\omega'\omega'' \\ \eta\omega'\omega'' & \omega\omega'' & \omega'^2 \\ \eta\omega'\omega'' & \omega'^2 & \omega\omega'' \end{bmatrix} \end{matrix} \quad (15)$$

where the significations of the second-order parameters ω , ω' , and ω'' are given in the last column of Table I; the subscript s denotes "symmetric." Dividing through by $\eta^2\omega''^2$, we obtain

$$U_s'' = \begin{bmatrix} 1 & \alpha & \alpha \\ \alpha & \alpha^2/\beta & \alpha^2 \\ \alpha & \alpha^2 & \alpha^2/\beta \end{bmatrix} \quad (16)$$

where α and β retain their definitions given by eq 11 and 12. Thus, three parameters, inclusive of ψ in U' , are required for case ii.

In case iii all of the second-order parameters may be replaced by unity, and $\tau = 1$ as well. Hence, $\alpha = 1/\eta$, $\beta = 1$, and

$$U_s'' = \begin{bmatrix} 1 & \sigma & \sigma \\ \sigma & \sigma^2 & \sigma^2 \\ \sigma & \sigma^2 & \sigma^2 \end{bmatrix} \quad (17)$$

with σ replacing $1/\eta$. In this case $\sigma \approx 1$. The previous rendition of U' according to eq 8 applies.

On the assumption that interactions of higher order may be ignored, the configuration partition function Z for a vinyl chain conforming to the structure $\text{CH}_3\text{-(CRR}'\text{CH}_2)_x\text{H}$ and of given stereochemical sequence may be obtained as the serial product of U' and U'' matrices, taken in alternating succession, according to the expression^{2,5,16}

$$Z = U_0 \left(\prod_{k=1}^{x-1} U_k' U_k'' \right) U_x \quad (18)$$

where k indexes the dyads serially 1 to $x - 1$ in the chain consisting of x units for a total of $n = 2x$ skeletal bonds. Thus, the k th dyad comprises skeletal bonds $i = 2k$ and $i + 1 = 2k + 1$ in Figure 1. For all k in the range $0 < k < x$ the statistical weight matrix U_k' is given by eq 8; U_k'' is given by U_m'' of eq 13, by U_r'' of eq 14, or by U_s'' of eq 16 or 17, depending on the character of the k th dyad (meso, racemic, or symmetric); $U_0 = \text{row}(1, 0, 0)$ and $U_x = \text{col}(1, 1, 1)$. Averages of various configuration-dependent properties may be calculated by methods given previously using these statistical weight matrices.^{2,5,16,17}

Interactions of Higher Order

"Cyclic" conformations which would place groups separated by 5 to ca. 10 bonds at a distance within the range of strong steric repulsion invariably interpose one or more successive gauche rotations of opposite signs, $g^\pm g^\mp$, within the sequence of $m - 2$ internal bonds of the m -bond sequence.^{1,2} Hence, quite apart from whatever repulsions may be operative between the pair of groups separated by m bonds, the repulsions due to the intervening $g^\pm g^\mp$ pairs will discourage occurrence of the cyclic conformations for which $4 < m < \sim 10$. If the statistical weight for $g^\pm g^\mp$ is very small ($< \sim 0.05$) compared to other conformations of bond pairs, the m -bond interaction will be reduced to such low incidence by the second-order ($m = 4$) interactions as to obviate measures to take account of the higher order interaction. Hence, the latter may be ignored.

For any given $m > 10$, the cyclic conformation is statistically rare. On the other hand, the sum of such interactions for all $m > 10$ may affect the spatial configuration to a marked degree. Such interactions of longer range are appropriately treated as excluded volume effects and can be handled independently² and separately from the short-range interactions here considered.

The foregoing conditions regarding suppression of

$g^\pm g^\mp$ pairs must invariably be met in good approximation in monosubstituted vinyl chains. We have already discussed the justification for setting the elements of U' for $g|g$ and $\bar{g}|\bar{g}$ states (*i.e.*, $g^\pm g^\mp$) equal to zero. Even in cases included in the possible exceptions to this assignment (*e.g.*, for $R = F$ or OCH_3) the statistical weights for these elements must be very small. The relevant elements of U_m'' are $|gg|$ and $|\bar{g}\bar{g}|$; in U_r'' they appear as $|\bar{g}g|$ and $|g\bar{g}|$. The statistical weight ω for the $\text{CH}_2 \cdots \text{CH}_2$ interaction assures that these elements are small. Hence, to an approximation that will rarely entail significant error, we dismiss interactions of longer range in monosubstituted vinyl chains.

The prevalence of second-order interactions in all dyad conformations of disubstituted vinyl chains cancels the preferential avoidance of $|g^\pm g^\mp|$ states. Hence, interactions of longer range, *i.e.*, beyond second order, cannot be dismissed. The following discussion of interactions of higher order is addressed, therefore, to disubstituted vinyl chains.

We have pointed out earlier that suppression of $g|g$ and $\bar{g}|\bar{g}$ conformations for the bonds flanking an α carbon is assured in a disubstituted vinyl chain by interactions of higher order. Groups attached to the respective adjacent α carbons and separated by six bonds are involved in these interactions. As noted above, the $g|\bar{g}$ and $\bar{g}|g$ conformations may be subject to the interactions depicted in Figure 3, to which we have assigned the factor ψ in eq 18. These interactions also involve groups separated by six bonds but, like those above, may be treated as interactions of second order for reasons given earlier.

Inspection of all conformations that may introduce significant interactions between groups separated by eight or fewer bonds reveals only two other types that may not be precluded by steric overlaps of shorter range. These are illustrated in Figures 4 and 5 for tetrad sequences with a meso dyad at the center of each. The former figure depicts the interaction between groups X and Y separated by eight bonds when the sequence of four bonds centered about a meso dyad, *e.g.*, bonds $i - 1$, i , $i + 1$, and $i + 2$ in Figure 1, is in the $g|\bar{g}\bar{g}|g$ conformation; equivalent long-range interactions occur in the $\bar{g}|gg|\bar{g}$ state of the same bond sequence. In terms of the senses of rotation, these conformations are $g^-|g^-g^+|g^+$ and $g^+|g^+g^-|g^-$, respectively, for the enantiomorph represented in Figure 4. The group denoted by X may be any one of the pendant groups CH_2 , R, or R' on $C^{\alpha_{i-3}}$; Y denotes one of the corresponding groups attached to $C^{\alpha_{i+3}}$. The particular pair of groups engaged depends on the rotations about bonds $i - 2$ and $i + 3$ adjoining the four-bond sequence. If all bond angles were tetrahedral, with all bonds of identical length, then the centers of X and Y would coincide in this conformation. They are separated by opening the bond angles at the intervening methylene groups; the distance between them may be further increased by displacement of rotational states from their locations for perfect staggering: 0 and $\pm 120^\circ$. But for all adjustments within reasonable limits the overlap remains excessive. It is intolerable irrespective of the identities of X and Y. Rotations about bonds $i - 2$ and $i + 3$ are therefore immaterial and the interaction may be regarded as fourth (instead

(16) P. J. Flory and Y. Abe, *J. Chem. Phys.*, **54**, 1351 (1971); P. J. Flory, *ibid.*, **56**, 862 (1972).

(17) P. J. Flory, *Pure Appl. Chem.*, **26**, 309 (1971).

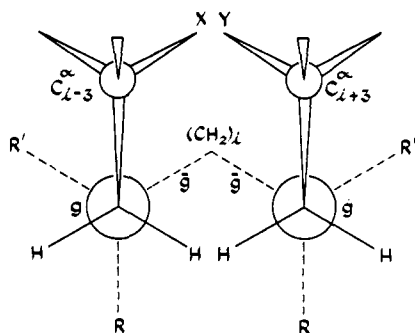


Figure 4. The $g|\bar{g}\bar{g}|g$ (or $g^-|g^-g^+|g^+$) conformation for the triad embracing bonds $i-1$, i , $i+1$, and $i+2$, the central dyad being meso, viewed along bonds $i-1$ and $i+2$. Interfering groups attached to C_{i-3}^α and C_{i+3}^α are indicated by X and Y, respectively. Equivalent interactions occur for $\bar{g}|\bar{g}\bar{g}|g$ (or $g^+|g^+g^-|g^-$).

of sixth) order. We shall assign it a statistical weight of zero.

As will be apparent from Figure 4, similar interactions occur in tetrads in which the central dyad is racemic for conformations of the four-bond sequence bearing the same designations when expressed according to the senses of rotation, *i.e.*, for each of the pair of conformations $g^\pm|g^\pm g^\mp|g^\mp$. These correspond to $\bar{g}|\bar{g}\bar{g}|g$ and its equivalent obtained by reversal of the sequence. (The conformers for the respective racemic enantiomers bear the same designations but are mirror related.)

The eight-bond interactions between X attached to C_{i-3}^α and both Y and Z attached to C_{i+3}^α occur in the conformations $g^+|g^+t|g^+$ and $g^-|g^-t|g^-$ and their inverses, as shown for the latter in Figure 5. These interactions are in addition to the six-bond interaction associated with $g^\pm|g^\pm$ (or $\bar{g}|\bar{g}$ and $\bar{g}|g$) cited above (Figure 3), which in Figure 5 involves X_{i-3} and R_{i+1} . The higher order conformations carry the designations $\bar{g}|\bar{g}t|g$ and $\bar{g}|\bar{g}t|g$ for a meso dyad; for a racemic dyad they are $\bar{g}|\bar{g}t|g$ and $\bar{g}|\bar{g}t|g$. The distance between pair X and Y or X and Z is *ca.* 2.9 Å if staggered conformations are assumed: $\angle C^\alpha(CH_2)C^\alpha$ is 122° , and $\angle CC^\alpha C = 109.5^\circ$. These steric overlaps, amounting to 0.8 to 1.0 Å for groups comparable in size to CH_3 , may be reduced by moderate departures of rotation angles from the locations for perfect staggering. We introduce a factor ξ for this interaction, with the expectation that $0 \ll \xi < 1$. In view of the marginal importance of this interaction, the same factors will be applied to all combinations X with Y and Z. On this basis, these eight-bond interactions are treated collectively as a single one of fourth order.

Statistical Weight Matrices Embracing Interactions of Higher Order

The significant higher order interactions cited above and represented in Figures 4 and 5 introduce conformational interdependence between successive *pairs* of bonds. In particular, it is the bond pair flanking an α carbon that is influenced by the rotational state of the pair affiliated with the preceding α carbon. It is essential to observe that the alternative sets of bond pairs, namely, those between successive α carbons, are not subject to *pair-pair* interdependence according to the analysis presented above.¹⁸ The conformational interdependence spans a range of four bonds for a sequence

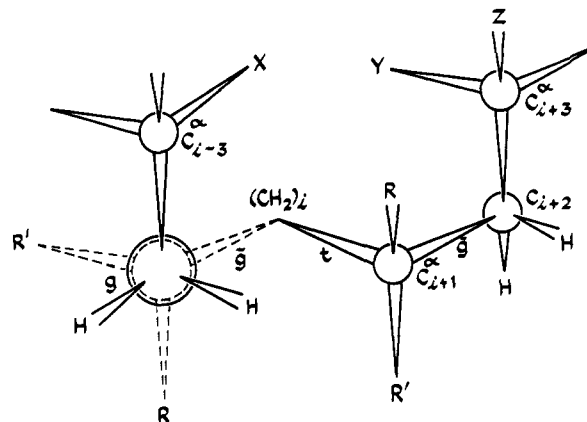


Figure 5. The $g|\bar{g}t|g$ (or $g^-|g^-t|g^-$) conformation for bonds $i-1, \dots, i+2$ centered about a meso dyad, as viewed along bond $i-1$. For tetrahedral bond angles and staggered conformations, groups Y and Z are equidistant from X. Equivalent interactions occur for $\bar{g}|\bar{g}t|g$ (or $g^+|g^+t|g^+$).

like $i-1$ to $i+2$ in Figure 1; *i.e.*, the conformation of bond $i+2$ depends on that of bond $i-1$ and also of i , according to the "rules" deduced above. However, the range of dependence is not uniform for all bonds; the conformation of bond $i+1$ is influenced only by the states of the preceding pair $i-1$ and i and not by that of bond $i-2$.

(In general, fourth-order interactions linking the state of *every* bond with the combined states of the three preceding bonds require statistical weight matrices whose elements relate the combined state of any sequence of three bonds, *e.g.*, bonds $j-1$, j , and $j+1$, to that of the three-bond sequence displaced by one bond, *e.g.*, of bonds $j-2$, $j-1$, and j . The resulting (sparse) matrix is of square order ν^3 , where ν is the number of states accessible to each bond. For polymers having a two-bond repeat unit, two such matrices would be required.)

Higher order interactions manifested in a pair-pair dependence of the kind described above for the disubstituted vinyl chain can be treated in relatively simple fashion by the device of representing the conformation in terms of states of the relevant bond pairs. Thus, the combined states for the bond pair flanking a given α carbon are $t|t$, $t|g$, $t|\bar{g}$, $g|t$, \dots , $\bar{g}|\bar{g}$. The required statistical weight matrix, which we denote by W_k , will relate the pair of bonds flanking the $(k+1)$ th α carbon to the pair flanking the k th α carbon, the former pair being indexed on the columns and the latter on the rows of W_k . Thus, the bonds represented in W_k are centered on the k th dyad. Only one such matrix will be required for each dyad.

As a first step, we construct the pair-pair matrix W_k^0 for the k th dyad with disregard of interactions of higher order. This may be achieved through operations expressed algebraically as follows

$$W_k^0 = (\text{diag } U_k')(J \otimes E_3)(U_k'' \otimes J^T) \quad (19)$$

(18) R. H. Boyd and S. M. Breiting, *Macromolecules*, **5**, 1 (1972), have treated polyisobutylene on the basis that interactions of long range impose an interdependence between bond pairs within successive dyads, rather than between the pairs of bonds flanking successive α carbons. They take no account of the long-range interactions considered here, the only ones of significance according to our analysis, which may be confirmed readily by examination of the model. They present a matrix relating successive bond pairs that superficially resembles our eq 19. It refers, however, incorrectly in our opinion, to the alternative set of bond pairs.

for $0 < k < x$. In this equation and those that follow \otimes denotes the direct product, \mathbf{E}_3 is the identity of order three, $\mathbf{J} = \text{col}(1, 1, 1)$ and its transpose is \mathbf{J}^T , and $\text{diag } \mathbf{U}_k'$ is the diagonal matrix of the elements of \mathbf{U}' taken in "reading order," i.e., $t|t, t|g, t|\bar{g}, g|t, \dots, \bar{g}|\bar{g}$. As before, matrices \mathbf{U}_k'' take on the character, meso or racemic, as dictated by the stereochemical configuration of the k th dyad. Terminal matrices for the chain $\text{CH}_3(\text{CRR}'\text{CH}_2)_x\text{H}$ are the row

$$\mathbf{W}_0^0 = \mathbf{U}_0 \otimes \mathbf{J}^T \quad (20)$$

and the column

$$\mathbf{W}_x^0 = \mathbf{J} \otimes \mathbf{U}_0^T \quad (21)$$

with \mathbf{U}_0 retaining the definition given previously in conjunction with eq 18. The assumption that the terminal methyl groups are equivalent to methylene in their interactions is implicit in these formulations of the terminal matrices.

The corresponding matrices \mathbf{W}_k that include higher order interactions are obtained by introducing statistical weight factors into the elements affected by such interactions. The appropriate factors deduced above are zero and ξ for the conformations of the kinds shown in Figures 4 and 5, respectively. In this way we obtain for a meso dyad, case i

$$\mathbf{W}_{m,k} = \begin{array}{c} \begin{array}{cccccccc} t|t & t|g & t|\bar{g} & g|t & g|\bar{g} & \bar{g}|t & \bar{g}|g \\ \left[\begin{array}{cccccccc} 1 & 1 & 1 & \alpha & \alpha & \beta\rho & \beta\rho \\ \alpha & \alpha & \alpha & \alpha^2/\beta & \alpha^2/\beta & \alpha\rho & \alpha\rho \\ \beta\rho & \beta\rho & \beta\rho & \alpha\rho & \alpha\rho & \rho^2 & \rho^2 \\ 1 & 1 & 1 & \alpha & \alpha\xi & \beta\rho & \beta\rho \\ \beta\rho\psi & \beta\rho\psi & \beta\rho\psi\xi & \alpha\rho\psi & \alpha\rho\psi & \rho^2\psi & 0 \\ 1 & 1 & 1 & \alpha & \alpha & \beta\rho & \beta\rho\xi \\ \alpha\psi & \alpha\psi\xi & \alpha\psi & \alpha^2\psi/\beta & 0 & \alpha\rho\psi & \alpha\rho\psi \end{array} \right]_k \end{array} \end{array} \quad (22)$$

with $0 < k < x$, and $\rho = \tau/\eta$ as above. We have deleted the $g|g$ and $\bar{g}|\bar{g}$ rows and columns; the latter are null and the former, therefore, are of no consequence when the matrices are multiplied serially as required to generate the partition function and other quantities (see below).

The matrices for terminal units, being unaffected by long-range interactions, are given by eq 20 and 21 with deletion of fifth and ninth rows and columns to conform with eq 22. Thus

$$\mathbf{W}_0 = \mathbf{W}_0^0 = [1 \ 1 \ 1 \ 0 \ 0 \ 0 \ 0] \quad (23)$$

no designations of stereochemical configuration (m or r) being required, and

$$\mathbf{W}_x = \mathbf{W}_x^0 = \text{col}(1, 0, 0, 1, 0, 1, 0) \quad (24)$$

The fact that $\mathbf{W}_{m,1}$ as given by eq 22 takes account of long-range interactions that are inoperative in the first dyad is of no consequence. When used in conjunction with \mathbf{W}_0 , only the first three rows of $\mathbf{W}_{m,1}$ are required (see eq 26) and this automatically eliminates all elements affected by interactions of longer range.

For a racemic dyad in case i

$$\mathbf{W}_{r,k} = \begin{array}{c} \begin{array}{cccccccc} t|t & t|g & t|\bar{g} & g|t & g|\bar{g} & \bar{g}|t & \bar{g}|g \\ \left[\begin{array}{cccccccc} \beta & \beta & \beta & \alpha & \alpha & \rho & \rho \\ \alpha & \alpha & \alpha & \alpha^2/\beta & \alpha^2/\beta & \alpha\rho & \alpha\rho \\ \rho & \rho & \rho & \alpha\rho & \alpha\rho & \beta\rho^2 & \beta\rho^2 \\ \beta & \beta & \beta & \alpha & \alpha & \rho & \rho\xi \\ \rho\psi & \rho\psi\xi & \rho\psi & \alpha\rho\psi & 0 & \beta\rho^2\psi & \beta\rho^2\psi \\ \beta & \beta & \beta & \alpha & \alpha\xi & \rho & \rho \\ \alpha\psi & \alpha\psi & \alpha\psi\xi & \alpha^2\psi/\beta & \alpha^2\psi/\beta & \alpha\rho\psi & 0 \end{array} \right]_k \end{array} \end{array} \quad (25)$$

for $0 < k < x$. Equations 23 and 24 furnish \mathbf{W}_0 and \mathbf{W}_x , respectively.

The partition function may be generated by serial multiplication according to

$$Z = \prod_{k=0}^x \mathbf{W}_k \quad (26)$$

it being understood that the matrix \mathbf{W}_k for $0 < k < x$ is to be selected according to the character of the relevant dyad.

For symmetric chains conforming to cases ii and iii, the distinction between meso and racemic vanishes, and the matrix $\mathbf{W}_{s,k}$ obtained from eq 16 according to the procedure for the formulation of $\mathbf{W}_{m,k}$ and $\mathbf{W}_{r,k}$ is

$$\mathbf{W}_{s,k} = \begin{array}{c} \left[\begin{array}{cccccccc} 1 & 1 & 1 & \alpha & \alpha & \alpha & \alpha \\ \alpha & \alpha & \alpha & \alpha^2/\beta & \alpha^2/\beta & \alpha^2 & \alpha^2 \\ \alpha & \alpha & \alpha & \alpha^2 & \alpha^2 & \alpha^2/\beta & \alpha^2/\beta \\ 1 & 1 & 1 & \alpha & \alpha\xi & \alpha & \alpha \\ \alpha\psi & \alpha\psi & \alpha\psi\xi & \alpha^2\psi & \alpha^2\psi & \alpha^2\psi/\beta & 0 \\ 1 & 1 & 1 & \alpha & \alpha & \alpha & \alpha\xi \\ \alpha\psi & \alpha\psi\xi & \alpha\psi & \alpha^2\psi/\beta & 0 & \alpha^2\psi & \alpha^2\psi \end{array} \right]_k \end{array} \quad (27)$$

The states are indexed in keeping with eq 8, 16, and 19; the order is $tt, tg^+, tg^-, g^-t, g^-g^-, g^+t$, and g^+g^+ . In case iii, the second-order parameters reduce to unity, $\alpha = \sigma \equiv 1/\eta$, and $\beta = 1$ according to eq 11 and 12.

For symmetric chains in general, states with opposite rotational senses but of the same magnitude $|\varphi|$ may be combined according to procedures given elsewhere.^{16,19,20} The order of $\mathbf{W}_{s,k}$ may be reduced in this way from 7×7 to 4×4 .

If, in a particular example, it is legitimate to let $\psi = 0$, then the fifth and seventh rows in eq 22, 25, and 27 are null. These rows and the corresponding columns may then be deleted, whereupon factors for long-range interactions are eliminated, and the order of \mathbf{W} becomes 5×5 . (For symmetric chains represented by eq 27, the order may be further reduced to 3×3 by combining states of the same magnitude of rotation $|\varphi|$.) Computations are correspondingly simplified. If $\psi = 0$, one may, alternatively, revert to use of the pair of matrices, \mathbf{U}' and \mathbf{U}'' , of orders 3×3 (for symmetric chains 2×2), in which long-range interactions are ignored.

(19) K. Nagai, *J. Chem. Phys.*, **42**, 516 (1965).

(20) P. J. Flory, *Macromolecules*, in press.

Configuration-Dependent Properties

Treatment of the mean-square end-to-end length will be illustrative of the procedures^{2,16,20} applicable to various configuration-dependent properties such as dipole moments, optical anisotropies, squared radii of gyration, and higher moments $\langle r^4 \rangle_0$, etc., of the chain vector \mathbf{r} .

For a specified conformation of the chain, the square of the magnitude of its chain vector is given by^{16,20}

$$r^2 = \prod_{i=1}^n \mathbf{G}_i \quad (28)$$

where i indexes the bonds serially from 1 to n , and

$$\mathbf{G}_i = \begin{bmatrix} 1 & 2\mathbf{l}^T\mathbf{T} & \mathbf{l}^2 \\ \mathbf{0} & \mathbf{T} & 1 \\ \mathbf{0} & \mathbf{0} & 1 \end{bmatrix}_i \quad (29)$$

$$1 < i < n$$

\mathbf{l} being the bond vector (column) and \mathbf{l}^T its transpose (row); \mathbf{T}_i is the transformation relating the Cartesian coordinate system (see below) affixed to bond $i+1$ to that affixed to bond i . The initial and final factors \mathbf{G}_1 and \mathbf{G}_n of the serial product in eq 28 consist of the first row and final column, respectively, of matrices \mathbf{G} formulated according to eq 29 for the first and last bonds of the chain. The subscript i appended to the matrix in eq 29 signifies that all quantities within are selected to represent bond i .

The bond-based coordinate systems are defined in the conventional manner as follows. The x_i axis is taken parallel to the direction of the bond i , and the y axis is in the plane defined by bonds $i-1$ and i , its direction being chosen to make an acute angle with bond $i-1$. As an addendum to the convention defining d and l bonds (see Figure 2), we take the z axis in the direction to complete a right-handed coordinate system if the bond i is a d bond, and in the opposite direction as required to complete a left-handed system in the case of an l bond. As earlier stipulated, the torsional angle φ_i is to be measured in the corresponding sense.

If bonds $i+1$ and i are both of genus d , so that \mathbf{T}_i operates between two right-handed reference frames and φ_i is measured from the trans conformation in the right-handed sense according to the convention adopted earlier, then the transformation \mathbf{T}_i that, by premultiplication, transforms a vector in reference frame $i+1$ to its representation in reference frame i is of the form

$$\mathbf{T} = \begin{bmatrix} \cos \theta & \sin \theta & 0 \\ \sin \theta \cos \varphi & -\cos \theta \cos \varphi & \sin \varphi \\ \sin \theta \sin \varphi & -\cos \theta \sin \varphi & -\cos \varphi \end{bmatrix} \quad (30)$$

where θ is the angle between the bond vectors, e.g., between bond vectors i and $i+1$ (or axes x_i and x_{i+1}). If the bond i and its successor are both l , the third row and third column of \mathbf{T} are to be multiplied by -1 on account of the reversal of directions of both z axes. At the same time the sign of φ_i is reversed, with the result that \mathbf{T} is restored to its expression given by eq 30. If the pair is either dl or ld , the net effect of the required alterations is a reversal of signs in the third column of

\mathbf{T} . Hence, for such pairs the appropriate transformation is

$$\mathbf{T}^* = \mathbf{T} \text{diag}(1, 1, -1) \quad (31)$$

For the case of a vinyl chain, eq 28 may be written

$$r^2 = \mathbf{G}_0 \left(\prod_{k=1}^{x-1} \mathbf{G}_k' \mathbf{G}_k'' \right) \mathbf{G}_x \quad (32)$$

where \mathbf{G}_k' and \mathbf{G}_k'' are defined according to eq 29 and refer to the first and second bonds of the k th dyad. The terminal matrices retain the definitions given above, \mathbf{G}_0 (appearing as \mathbf{G}_1 in eq 28) being the first row of \mathbf{G} (eq 29) for the first bond in the chain and \mathbf{G}_x the last column of \mathbf{G} for the final bond.

According to relations developed previously,^{2,7,16} the unperturbed mean-square length of the chain vector is given by

$$\langle r^2 \rangle_0 = \mathbf{Z}^{-1} \mathbf{G}_0 \left(\prod_{k=1}^{x-1} \mathcal{G}_k' \mathcal{G}_k'' \right) \mathcal{G}_x \quad (33)$$

where

$$\mathcal{G}_k' = (\mathbf{U}_k' \otimes \mathbf{E}_5) \|\mathbf{G}_k'\| \quad 0 < k < x \quad (34)$$

Here \mathbf{E}_5 is the identity of order five and $\|\mathbf{G}_k'\|$ is the diagonal array of the \mathbf{G}' matrices for each of the several rotational states t , g , and \bar{g} . The matrix \mathcal{G}_k'' is similarly defined. The terminal matrices are the row

$$\mathcal{G}_0 = \mathbf{U}_0 \otimes \mathbf{G}_0 \quad (35)$$

and the column

$$\mathcal{G}_x = \mathbf{U}_x \otimes \mathbf{G}_x \quad (36)$$

In order to formulate \mathcal{G} matrices appropriate for various stereochemical configurations, we consider the four possible dyad sequences $l|d|d$ or $d|d|l$, meso, and $l|dd|l$ and $d||l|d$, racemic. The first two (meso) are, of course, identical; the latter two (racemic) are mirror images of one another. We observe that the matrices \mathcal{G}' require the statistical weight matrix \mathbf{U}' for the bond pair flanking the C^α denoted by the first vertical line in each sequence above, together with the matrix \mathbf{T}' or $\mathbf{T}^{*'}$ for the transformation from the coordinate system of the second bond of the dyad pair between vertical lines to the first. Whether \mathbf{T}' of the form given in eq 30 or $\mathbf{T}^{*'}$ of eq 31 is required depends on the character of the dyad according to the rule deduced above. Similarly, \mathcal{G}'' involves \mathbf{U}'' for the dyad pair and the transformation matrix relating the pair of bonds flanking the second C^α of the sequence. Since this pair is necessarily $d|l$ or $l|d$, the required transformation is $\mathbf{T}^{*''}$.

We thus arrive at the following prescriptions⁵ for \mathcal{G} matrices for meso and racemic dyads

$$\begin{aligned} \mathcal{G}_m' &= \mathcal{G}(\mathbf{U}', \mathbf{T}^{*'}) \\ \mathcal{G}_r' &= \mathcal{G}(\mathbf{U}', \mathbf{T}') \\ \mathcal{G}_m'' &= \mathcal{G}(\mathbf{U}_m'', \mathbf{T}^{*''}) \\ \mathcal{G}_r'' &= \mathcal{G}(\mathbf{U}_r'', \mathbf{T}^{*''}) \end{aligned} \quad (37)$$

It will be understood that \mathbf{T}' and $\mathbf{T}^{*'}$ depend on the bond angle θ' between bonds of the dyad pair and on rotational states φ_t' , φ_g' , and $\varphi_{\bar{g}}'$. Similarly, $\mathbf{T}^{*''}$ depends on the angle θ'' between the pair of bonds flanking the second α carbon of the given dyad and on φ_t'' ,

$\varphi_{g''}$, and $\varphi_{g''}$ for the second bond of the same dyad. If the chain is "copolymeric" in the sense that various units may differ chemically as well as stereochemically, then the quantities (*i.e.*, **U**, **T**, and **l**) entering into \mathcal{G}_k' and \mathcal{G}_k'' must represent the chemical character of the *k*th unit.

Extension of this scheme to cases in which long-range interactions necessitate use of the pair-pair matrix \mathbf{W}_k is straightforward. This matrix relates the bond pair $i + 1|i + 2$ to the $i - 1|i$ pair where $i = 2k$. The matrix $\mathbf{G}_k' \equiv \mathbf{G}_i'$ associated with bond rotation $\varphi_{i'}$ depends, through the transformation \mathbf{T}_i' , on the symmetry character of the *k*th dyad; $\mathbf{G}_k'' \equiv \mathbf{G}_{i+1}''$ associated with bond rotation φ_{i+1}'' depends also on the character of the same dyad. The matrices \mathbf{G}_i' for the various rotational states of the bond *i* may be introduced in conformity with the state of bond *i* denoted by the second-row index of \mathbf{W}_k through premultiplication of \mathbf{W}_k by the diagonal array of \mathbf{G}' matrices

$$\|\mathbf{G}'\|_{\mathbf{W}} = \text{diag}(\mathbf{G}_t', \mathbf{G}_g', \mathbf{G}_g^-, \mathbf{G}_t', \mathbf{G}_g^-, \mathbf{G}_t', \mathbf{G}_g') \quad (38)$$

Fifth and ninth pseudoelements \mathbf{G}_g' and \mathbf{G}_g^- are omitted in consonance with the rendering of \mathbf{W} above. If these elements were included the pseudodiagonal matrix of 45×45 (instead of 35×35) order could be defined succinctly by

$$\|\mathbf{G}'\|_{\mathbf{W}} = \mathbf{E}_3 \otimes \|\mathbf{G}'\|$$

where

$$\|\mathbf{G}'\| = \text{diag}(\mathbf{G}_t', \mathbf{G}_g', \mathbf{G}_g^-)$$

The required introduction of matrices \mathbf{G}'' keyed to the first column index ($i + 1$) of \mathbf{W}_k may be achieved through postmultiplication by the pseudodiagonal

matrix

$$\|\mathbf{G}''\|_{\mathbf{W}} = \text{diag}(\mathbf{G}_t'', \mathbf{G}_t'', \mathbf{G}_t'', \mathbf{G}_g'', \mathbf{G}_g'', \mathbf{G}_g'', \mathbf{G}_g'') \quad (39)$$

which is obtained from the diagonal development $\|\mathbf{E}_3 \otimes \mathbf{G}''\|$ by deletion of fifth and ninth pseudoelements. We thus obtain

$$\mathcal{G}_k^{(2)} = \|\mathbf{G}_k'\|_{\mathbf{W}}(\mathbf{W}_k \otimes \mathbf{E}_3)\|\mathbf{G}_k''\|_{\mathbf{W}} \quad (40)$$

for $0 < k < x$. Thus eq 33 is replaced by

$$\langle r^2 \rangle_0 = Z^{-1} \mathcal{G}_0 \left(\prod_1^{x-1} \mathcal{G}_k^{(2)} \right) \mathcal{G}_x \quad (41)$$

where the terminal matrices are redefined (compare eq 35 and 36) as follows

$$\mathcal{G}_0 = \mathbf{W}_0 \otimes \mathbf{G}_0 \quad (42)$$

$$\mathcal{G}_x = \mathbf{W}_x \otimes \mathbf{G}_x \quad (43)$$

with \mathbf{G}_0 and \mathbf{G}_x retaining their previous definitions.

Symmetric chains, *i.e.*, cases ii and iii, may be treated in a corresponding manner with \mathbf{W}_k given by eq 27. Equations 38 and 39 require revision to the states *t*, g^+ , and g^- . In all other respects, the same formulation applies. The order of the generator matrix \mathcal{G}_k may be reduced by resort to procedures generally applicable to symmetric chains.^{16,19,20}

The foregoing treatment has been presented for three rotational states. It could be extended to a larger number if required.

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