involve the same type of γ-H atom, *e.g.*, primary H atoms. For the one other case observed in this study, that for primary H atoms in the n-C_3H_7 group and secondary H atoms in the R group of the n-C_3H_7COR molecule, $\Delta E = 1.3$ kcal/mole. Presumably a slightly higher value would apply for the case of t-H atoms in the γ position of the R group. N_a and N_b are the numbers of γ-H atoms of a given type in the n-C_3H_7 and R groups, respectively, and A_a and A_b are the preexponential factors related to the rate constants k_{IIa} and k_{IIb}, expressed as a rate per γ-H atom. Unless some peculiar geometrical configuration favors the type-II process or the singlet state is involved significantly as well as the triplet, one would expect $A_a = A_b$. With the exception of the n-butyl n-propyl ketone case this assumption seems warranted. It is gratifying but perhaps not surprising that an equation with so many parameters fits all of the data well. Compare the experimental and calculated values of ϕ_{IIa} and ϕ_{IIb} in Table III.

One may predict ϕ_{II} values for the 3130-A photolysis of some ketones not yet studied through an extrapolation of eq 1 and 2. Thus 4-nonanone, 4-decanone, etc., should have ϕ_{II} values equal to those for 4-octanone photolysis at 3130 A: $\phi_{IIa} \cong 0.035$, $\phi_{IIb} = 0.25$ (150°); $\phi_{IIa} \cong 0.024$, $\phi_{IIb} \cong 0.24$ (76°). Furthermore, one expects for 2,2-dimethyl-4-heptanone that $\phi_{IIa} \cong 0.05$ and $\phi_{IIb} \cong 0.15$, independent of temperature. For 7-methyl-4-octanone one anticipates that $\phi_{IIa} \leq 0.04$ and $\phi_{IIb} \geq 0.25$.

Obviously the type-II process involves a complex interaction of many structural effects, a few of which may be identified in this work. It is hoped that further studies of this sort will help delineate further the relations between the photochemistry and the molecular structure of the ketones.

Acknowledgment. The authors are grateful for the support of this work through a research grant from the National Center for Air Pollution Control, Bureau of Disease Prevention and Environmental Control, U. S. Public Health Service, Bethesda, Md. We wish to acknowledge the significant constructive criticism of the original manuscript by Drs. P. Ausloos, T. J. Dougherty, W. A. Noyes, Jr., R. Srinivasan, and P. J. Wagner.

Stereochemical Equilibrium in Chain Molecules

Paul J. Flory

Contribution from the Department of Chemistry, Stanford University, Stanford, California.

Received November 28, 1966

Abstract: A general theory of stereochemical equilibria in chain molecules possessing two or more asymmetric centers is presented. It is applied to vinyl polymers CH_3-$(CHR$-$CH_2)_x$-H and their low molecular homologs in the presence of a catalyst capable of effecting racemization of the -CHR- centers. The relative abundance of each stereoisomeric species is proportional to the sum of the statistical weights for all of its rotational conformers, *i.e.*, to the statistical mechanical configuration partition function Z for the species. The relevant partition function Z for the equilibrated system is the sum of the Z's for all stereoisomeric species. It is expressed without approximation in terms of statistical weight parameters for rotational isomeric states, with due account of neighbor effects. Equilibrium populations of various dyads, triads, and higher sequences are readily derived for chains of any length. The stereochemical configuration of a given unit in a chain of many units is shown to depend not only on the symmetries of its immediate neighbors, but also on centers many units removed. The theory departs therefore from the statistics for an Ising lattice with first-neighbor dependence. Dyad and triad compositions of dimeric and trimeric homologs cannot in general be construed as being representative of infinite chains, as is shown by trial calculations. In general, the statistical distribution of symmetries of consecutive asymmetric centers is neither Bernoullian nor Markoffian. Available experimental results are interpreted according to the theory.

A general treatment of the spatial configurations of vinyl polymer molecules of the type

$$CH_3\text{—(—}CHR\text{—}CH_2\text{—)}_x\text{—}H$$

I

was published recently by the author and his collaborators.[1] Local bond conformations were represented in the terms of the rotational isomeric state scheme, which has gained widespread usage in the analysis of spatial configurations of chain molecules.[2-4] Each bond was accorded three rotational states in keeping with the character of the rotational potentials applicable generally to C–C bonds. Potentials affecting rotations about a given bond are strongly dependent on rotational states of bonds which are first neighbors, and this circumstance was rigorously taken into account.

In typical vinyl chains for which the substituent group R is of a size commensurate with or larger than Cl or CH_3, most of the configurations of the chain are subject to prohibitive steric overlaps. Those which are free of severe repulsions between nonbonded atoms or groups are comparatively few in number. Which of the mani-

---

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

(2) S. Mizushima, "Structure of Molecules and Internal Rotation," Academic Press Inc., New York, N. Y., 1954.

(3) M. V. Volkenstein, "Configurational Statistics of Polymeric Chains," translated from the Russian edition by S. N. Timasheff and M. J. Timasheff, Interscience Publishers, Inc., London, 1963.

(4) T. M. Birshtein and O. B. Ptitsyn, "Conformation of Macromolecules," translated from the Russian edition (1964) by S. N. Timasheff and M. J. Timasheff, Interscience Publishers Inc., New York, N. Y., 1966.

fold of spatial configurations of a very long chain are acceptable on this score depends on the symmetries of the consecutive –CHR– groups. Thus, a syndiotactic chain in which the asymmetric centers can be represented as alternatingly *dldl*, etc., have at their disposal a greater number of conformations (alias configurations in the statistical mechanical sense) than an isotactic chain represented as *ddd*, etc. This fact is readily ascertained by examination of models, or from projection formulas. The numbers of conformations accessible to chains in which the asymmetric centers are disposed in some sequence of intermediate (atactic) character is not so easily reckoned. More elaborate mathematical methods are required to treat the enormous array of stereoisomeric species which can be generated through alteration of the symmetries of the asymmetric centers within a very long chain such as I.

If the asymmetric centers of the polymer molecule I are subject to racemization, as in the presence of a suitable catalyst, a state of equilibrium can be envisaged in which all stereoisomeric species are represented. The proportions of each will be determined by the intramolecular configuration space (in the statistical mechanical sense) at its disposal; *i.e.*, the concentration of a given stereoisomer will be determined at equilibrium by the sum of the statistical weights associated with each of the spatial configurations accessible to it. The statistical-weight matrices formulated previously[1] for the purpose of interpreting the configurational statistics of vinyl polymer chains, in which the stereochemical arrangement of the asymmetric centers is fixed, are immediately applicable here.

The present problem is reminiscent of the simple, one-dimensional Ising lattice in which each element may adopt either of two states (+ and −, or, as here, *d* and *l*) with a mutual dependence between choices for elements which are first neighbors. The two problems turn out to be quite different, however. The one here considered derives its "cooperative" character from the conformational interdependence, which is indeed confined (in good approximation) to bonds which are first neighbors. This interdependence may transmit its effect for many units, however. The degree of preference of a given center for *d* over *l*, or *vice versa*, consequently will be found to depend not only on the character of its first neighbors but also on more remote asymmetric centers. Our treatment imposes no limit whatever on the range of this dependence.

The present theory will be seen to be suitable for application, with nominal revisions, to the more general problem of stereochemical equilibrium in a chain molecule of any kind having two or more asymmetric centers. Consider, for example, a molecule which can be represented as a sequence of units M, its formula being expressed schematically by

$$M_1M_2M_3\cdots M_x$$

II

The units M_i may or may not be alike in constitution. At least two of them bear asymmetric centers subject to racemization. The asymmetric centers must be sufficiently near in sequence along the chain to engender a mutual interdependence of the conformations of the units M in which they are situated; the bias imposed by their interdependence must depend on the stereochemical configuration of the pair of centers.

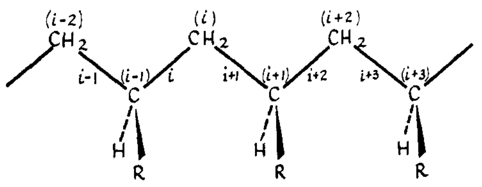


Figure 1.

All molecules of the specimen will be assumed to conform to the same formula I or II; the only differences between species will be those occasioned by different asymmetries of the respective asymmetric centers. In the case of a vinyl polymer I, this implies restriction to chains of specified length. If the molecule is a copolymer comprising units M_i of two or more kinds, these will be assumed to occur in precisely the same sequence in every species present in the specimen considered. Extension of the treatment to a sample comprising polymer chains differing in length and/or in composition could be accomplished by separately treating each representative member of the distribution of molecules, and then summing over the distribution.

Statistical-Weight Matrices for Vinyl Polymers

A portion of a vinyl chain is represented in Figure 1. Centers CHR having the configurations shown will be designated arbitrarily as *d* centers, their inverses obtained by mirror reflection as *l* centers. The distinction is genuine only if the ends of the chain are distinguishable. The assumption that this is the case will be removed in due course.

Bond rotation potentials are pairwise dependent as previously pointed out;[1] interdependences of higher order should be quite negligible. Hence, if three states, *trans* (*t*), *gauche*+ (g^+), and *gauche*− (g^-), are ascribed to each skeletal bond, the statistical weights associated with rotations about a given bond may be expressed in the form of a 3 × 3 matrix. Two such matrices are required, one for each of the alternating pairs of bonds CHR–CH_2 and CH_2–CHR. These matrices are, respectively

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

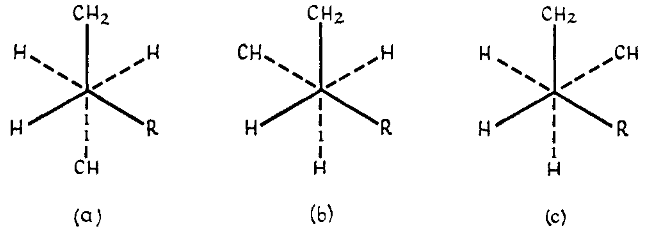
$$\mathbf{U}''_{dd} = \begin{bmatrix} \eta\omega & \tau\omega & 1 \\ \eta & \tau\omega & \omega \\ \eta\omega & \tau\omega^2 & \omega \end{bmatrix} \tag{2}$$

The former matrix refers to rotations about a bond such as i in Figure 1. The states of bond $i - 1$ are indexed on the rows of $\mathbf{U}'_d$ in the order t, g^+, g^-; states of bond i are similarly indexed on the columns. The matrix $\mathbf{U}''_{dd}$ presents the statistical weights for assignment of the state of bond $i + 1$, that of i being given by the row index.

The parameters η and τ represent factors contributed by interactions of groups separated by three bonds. These "first-order" interactions depend on only one rotation angle.[5] The parameter η denotes the statistical weight for the conformation shown in Figure 2a relative to that in Figure 2b. In the former, CH is in a *gauche*

---

(5) This is strictly true only if the internal structure of the groups is ignored, *e.g.*, if the locations of the H atoms in CH_2 and CH groups are ignored for a given distance of separation of the C atoms.



(a) (b) (c)

Figure 2.

position in relation to R; in the latter, CH is *gauche* to CH_2. Thus, η measures the interaction of CH with R relative to its interaction with CH_2. Depending on the nature of the substituent R, η may be either greater or less than unity.

The parameter τ will generally be less than unity.[1] It expresses the statistical weight for the conformation in Figure 2c relative to that in Figure 2b. Analysis of thermodynamic data for 2-methylbutane by Scott, *et al.*,[6] suggested an energy for the conformation corresponding to Figure 2c which exceeds that for Figure 2b by 2 kcal mole^{-1} or more. Thomas and Gwinn[7] arrived at a similar energy difference for the corresponding conformers of 1,1,2-trichloroethane, based on the dipole moment and its constancy with temperature. These estimates of conformational energy are somewhat larger than would have been expected. They clearly justify the assertion that $\tau < 1$, and suggest further that for R = CH_3, C_2H_5, etc., a value of *ca.* 0.1 or possibly less may be anticipated.

If a consecutive pair of bonds assumes either the g^+g^- or the g^-g^+ conformation, two skeletal members (CH or CH_2) are subjected to severe steric overlap. Similar repulsions, involving R groups as well, occur in a number of conformations. All of these are weighted by the factor ω in eq 1 and 2. Distinctions[8] between the various conformations of this character are here ignored, a single symbol being used for all of them. The refinement attainable by distinguishing the several ω's is not justified at the present level of approximation.

If the substituent $-R$ is of the kind $-CH_2-X$, where X is comparable in size to $-CH_3$ or larger, then the conformation *tt* for a bond pair such as $i - 1$, i in Figure 1 will entail a repulsion like that illustrated in Figure 3.[1] In the conformation shown, X occupies a position comparable to CH in Figure 2c. Alternative conformations of the side chain precipitate four bond overlaps of X with one or the other of the neighboring CH groups. The factor τ^* in $\mathbf{U}'_d$ takes account of these circumstances disfavoring the *tt* conformation for the pair of skeletal bonds adjoining a $-CHR-$ group. Assignment of either of these bonds to a *gauche* conformation permits the side chain to assume an acceptable conformation free of the dual *gauche* interaction shown in Figure 3. Hence, τ^* applies only to the single element in $\mathbf{U}'_d$.

If R = CH_3 or Cl, then we may take $\tau^* = 1$. For an articulated substituent $-CH_2-X$, a value of $\tau^* < 1$ may be expected. It is to be observed, however, that an articulated substituent of the first unit of the chain has open to it a conformation free of major steric repulsion. Thus, the absence of a skeletal CH group beyond the left-hand terminus (CH_3) of the chain I permits accommodation of X by rotation of 120° about the CH–CX bond, connecting the first substituent to the chain skeleton in Figure 3. The parameter τ^* should therefore be set equal to unity for the first unit.

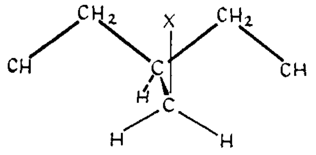


Figure 3.

The matrix $\mathbf{U}'$ depends on the asymmetry of one center only, *e.g.*, center $i - 1$ in Figure 1. The matrix $\mathbf{U}''$ depends on the asymmetries of both centers of a dyad, *e.g.*, centers $i - 1$ and $i + 1$ connected by bonds i and $i + 1$. Accordingly, a single subscript is appended to $\mathbf{U}'$, and two to $\mathbf{U}''$. For the *dl* dyad the double-primed matrix for a bond such as $i + 1$ is

$$\mathbf{U}''_{dl} = \begin{bmatrix} \eta & \omega & \tau\omega \\ \eta\omega & 1 & \tau\omega \\ \eta\omega & \omega & \tau\omega^2 \end{bmatrix} \qquad (3)$$

Statistical-weight matrices applicable to centers of other symmetries are readily obtained by suitably transforming the matrices given in eq 1–3. The elementary matrix for the inversion operation, namely

$$\mathbf{Q} = \begin{bmatrix} 1 & 0 & 0 \\ 0 & 0 & 1 \\ 0 & 1 & 0 \end{bmatrix} \qquad (4)$$

serves this purpose. Thus

$$\mathbf{U}'_l = \mathbf{Q}\mathbf{U}'_d\mathbf{Q} \qquad (5)$$

$$\mathbf{U}''_{ll} = \mathbf{Q}\mathbf{U}''_{dd}\mathbf{Q} \qquad (6)$$

$$\mathbf{U}''_{ld} = \mathbf{Q}\mathbf{U}''_{dl}\mathbf{Q} \qquad (7)$$

(compare ref 1). The transformation interchanges second and third rows and second and third columns.

It will be convenient to define products of statistical-weight matrices $\mathbf{U}'$ and $\mathbf{U}''$ for *meso* (isotactic) and for racemic (syndiotactic) dyads. To this end we let

$$\mathbf{U}'_d\mathbf{U}''_{dd} = \mathbf{U}_m^{(2)} \qquad (8)$$

$$\mathbf{U}'_d\mathbf{U}''_{dl} = \mathbf{U}_r^{(2)} \qquad (9)$$

Then

$$\mathbf{U}'_l\mathbf{U}''_{ll} = \mathbf{Q}\mathbf{U}_m^{(2)}\mathbf{Q} \qquad (10)$$

$$\mathbf{U}'_l\mathbf{U}''_{ld} = \mathbf{Q}\mathbf{U}_r^{(2)}\mathbf{Q} \qquad (11)$$

The relations expressed by eq 5–7, 10, and 11 are general. They follow from considerations of symmetry alone. They could be applied to any other consistent scheme of rotational isomeric states; if the number of these states exceeds three, **Q** would require obvious revision to higher order.

The Partition Function

The partition function for a chain molecule whose structure, including the symmetries of all asymmetric

---

[6] D. W. Scott, J. P. McCullough, K. D. Williamson, and G. Waddington, *J. Am. Chem. Soc.*, 73, 1707 (1951).

[7] J. R. Thomas and W. D. Gwinn, *ibid.*, 71, 2785 (1949).

[8] See footnote 10 of ref 1.

centers, is fully specified is given by

$$Z = \mathbf{J}^*\left(\prod_{i=2}^{n-1}\mathbf{U}_i\right)\mathbf{J} \tag{12}$$

where

$$\mathbf{J}^* = [1 \quad 0 \quad 0] \tag{13}$$

$$\mathbf{J} = \begin{bmatrix} 1 \\ 1 \\ 1 \end{bmatrix} \tag{14}$$

and $\mathbf{U}_i$ is the statistical-weight matrix applicable to the ith skeletal bond of the chain comprising n skeletal bonds in all. Equations 13 and 14 are expressed on the assumption that the bond rotations may be characterized by three rotational states. The scheme obviously is adaptable to any other finite number of states.

For a vinyl chain matching the formula I, the partition function can be written

$$Z = \mathbf{J}^*\left\{\prod_{k=1}^{x-1}\left(\mathbf{U}'_a\mathbf{U}''_{ab}\right)_k\right\}\mathbf{J} \tag{15}$$

where k indexes the kth dyad; a and b denote the symmetries, d or l, of the kth and $(k + 1)$th asymmetric centers, respectively. The various units may or may not be identical chemically, apart from their stereochemical configurations. If they differ, the various monomer units will be assumed to occur in a specified sequence. Given the stereochemical configurations of each of the x asymmetric centers (artificial labeling of one end of the chain being assumed for the present), eq 8–11 may be used to furnish the appropriate product $\mathbf{U}'_a\mathbf{U}''_{ab}$ for each dyad. Substitution of these expressions in eq 15, and cognizance of the necessity of identifying a for each dyad with b of its predecessor, leads to

$$Z = \mathbf{J}^*\left(\prod_{k=1}^{x-1}\mathbf{U}_k^{(2)}\right)\mathbf{J} \tag{16}$$

since $\mathbf{J}^*\mathbf{Q} = \mathbf{J}^*$, $\mathbf{QJ} = \mathbf{J}$, and $\mathbf{Q}^2 = \mathbf{E}$, where $\mathbf{E}$ is the identity matrix. The dyad matrix $\mathbf{U}_k^{(2)}$ in eq 16 is to be represented by $\mathbf{U}_m{}^{(2)}{}_k$ for *meso* and by $\mathbf{U}_r{}^{(2)}{}_k$ for racemic dyads. Equations 8 and 9 serve to define these matrices. The index k has been retained in order to take account of possible chemical differences between units (see above).

The artificial distinction between d and l centers has vanished in eq 16. It will suffice for the purposes of the present treatment to distinguish *meso* (isotactic) from racemic (syndiotactic) pairs. On the other hand, retention of the distinction between d and l centers, its artificiality notwithstanding, is a useful expedient for treatment of the mean-square end-to-end distance and other moments of chain molecules[1,9]—matters which we do not consider here. Such treatments involve use of coordinate transformation matrices, and observance of the differentiation of right- from left-handed transformations is obligatory.

Equilibrium Stereochemical Configurations.

A system consisting of N chain molecules of identical constitution except for the symmetries of their asymmetric centers is considered. Let a catalyst be introduced, which effectuates reversible racemization of the stereochemical configurations of all asymmetric centers, *e.g.*, –CHR–, without producing other changes. Inasmuch as the various molecular species in the system differ from one another only in the configurations of their asymmetric centers, the frequency of occurrence of each species at equilibrium will be proportional to the configuration partition function Z for that species. Let $\mathcal{Z}^N$ be the configuration partition function appropriate for a canonical ensemble of N molecule systems of the foregoing description. Then

$$\mathcal{Z} = \sum_{\{q\}} Z_{\{q\}} \tag{17}$$

where $\{q\}$ = *mrrm* etc., denotes the stereochemical configuration of the given species. The sum includes all stereoisomeric species thus specified.[10] Substitution of eq 16 in 17 gives

$$\mathcal{Z} = \mathbf{J}^*\sum_{\{q\}}\left[\prod_{k=1}^{x-1}\mathbf{U}_k^{(2)}\right]_{\{q\}}\mathbf{J} \tag{18}$$

The required sum of products may be generated identically by taking the serial product of the matrices

$$\mathcal{U}_k = (\mathbf{U}_m^{(2)} + \mathbf{U}_r^{(2)})_k \tag{19}$$

Hence

$$\mathcal{Z} = \mathbf{J}^*\left(\prod_{k=1}^{x-1}\mathcal{U}_k\right)\mathbf{J} \tag{20}$$

The index k has been retained in order to designate the kinds of units (apart from their asymmetries) occurring at each location in the chain sequence. For finite chains it is important to observe that $\tau^* = 1$ in $\mathcal{U}_1$ representing the first dyad. If all units of the chain are chemically identical, and we shall henceforth assume this to be the case, indexes k may be dropped, except that for the first unit, and we have

$$\mathcal{Z} = \mathbf{J}^*\mathcal{U}_1\mathcal{U}^{x-2}\mathbf{J} \tag{21}$$

where $\mathcal{U}_1$ is written separately to allow for $\tau^* = 1$ therein.

If the distinction between $\mathcal{U}_1$ and $\mathcal{U}$ may be ignored, and it will always be legitimate to do so for sufficiently long chains, then the partition function $\mathcal{Z}$ may be expressed in terms of the eigenvalues λ_ζ of $\mathcal{U}$ as follows

$$\mathcal{Z} = \sum_{\zeta,\eta=1}^{\nu} A_{1\zeta}\lambda_\zeta^{x-1}B_{\zeta\eta} \tag{22}$$

where the $A_{1\zeta}$ are elements of the matrix $\mathbf{A}$ of eigenvectors of $\mathcal{U}$, and the $\mathbf{B}_{\zeta\eta}$ are elements of $\mathbf{B} = \mathbf{A}^{-1}$; the number of rotational states is given by ν (*e.g.*, $\nu = 3$). For long chains the approximation

$$\mathcal{Z} \cong \lambda_1^{x-1} \tag{23}$$

may be adopted, where λ_1 is the largest eigenvalue of $\mathcal{U}$. We shall make use of this relationship later on.

---

(9) P. J. Flory and R. L. Jernigan, *J. Chem. Phys.*, **42**, 3509 (1965).

(10) Enumeration of species in this fashion ignores the fact that if the initial center is d, the stereochemical configuration specified by *mrrm*, etc. (*i.e.*, *ddldd*, etc.) is not, in general, identical with that obtained by designating the first center to be l. If the ends of the chain were distinguishable, then indeed eq 17 would include only half of the species. If, however, they are indistinguishable in keeping with formula I (and this implies a symmetry number of two, without regard for stereochemical asymmetries), then each of this larger set of stereochemical configurations would be redundant with one other member of the set. Equation 17 therefore gives the correct partition function sum.

The preceding analysis is easily generalized to chain molecules of types other than that represented by formula I. The statistical weight matrices given explicitly for vinyl polymers by eq 1–3 have been presented by way of illustration and for later use; the treatment is not limited to them. A different set of rotational states, consistent with considerations of symmetry, might be required for other types of chain molecules. Revision to admit a greater number ν of rotational states is straightforward, as previously noted.

A Priori Probabilities of Dyad and Triad Sequences

Through the adoption of a device frequently used in statistical mechanics, we find for the fraction of isotactic (or *meso*) dyads in chains of any length

$$f_{\text{iso}} = 1 - f_{\text{syn}} = (x-1)^{-1}\mathbf{U}_m{}^{(2)}\partial \ln \mathcal{Z}/\partial \mathbf{U}_m{}^{(2)} \qquad (24)$$

The expansion of the derivative as a sum of terms can be condensed to[11]

$$f_{\text{iso}} = (x-1)^{-1}\mathcal{Z}^{-1}\,[1\;0\ldots0]\hat{\mathcal{U}}_1\hat{\mathcal{U}}^{x-2}\begin{bmatrix}\mathbf{0}\\ \mathbf{J}\end{bmatrix} \qquad (25)$$

with

$$\hat{\mathcal{U}} = \begin{bmatrix}\mathcal{U} & \mathcal{U}'\\ \mathbf{0} & \mathcal{U}\end{bmatrix} \qquad (26)$$

where

$$\mathcal{U}' = \mathbf{U}_m{}^{(2)}\partial\mathcal{U}/\partial\mathbf{U}_m{}^{(2)} = \mathbf{U}_m{}^{(2)} \qquad (27)$$

The matrix $\hat{\mathcal{U}}_1$ differs from $\hat{\mathcal{U}}$ through assignment of $\tau^* = 1$ in the former. The f's may be regarded as *a priori* probabilities averaged over all dyads of the chain.

The fractions, or *a priori* probabilities, F_{I}, F_{H}, and F_{S} of triads which are isotactic (*ddd* alias *lll*), heterotactic (*ddl* alias *dll* and *lld* alias *ldd*), and syndiotactic (*dld* alias *ldl*) may be obtained by an extension of the foregoing procedure. Let a matrix be constructed from the statistical weights in such a way as to take account of the characters of *two* consecutive units. A matrix meeting this requirement is the following

$$\mathcal{W} = \begin{array}{r|cc} & \begin{matrix}dd\\ \text{or}\\ ll\end{matrix} & \begin{matrix}dl\\ \text{or}\\ ld\end{matrix}\\ \hline dd \text{ or } ll & \mathbf{U}_m{}^{(2)} & \mathbf{U}_r{}^{(2)}\\ dl \text{ or } ld & \mathbf{U}_m{}^{(2)} & \mathbf{U}_r{}^{(2)}\end{array} \qquad (28)$$

Rows are labeled to denote the characters of the two preceding dyads, $k-2$ and $k-1$; column indexes refer likewise to dyads $k-1$ and k. Also let

$$\hat{\mathcal{W}}_1 = [\mathcal{W}_1\;\mathbf{0}] \qquad (29)$$

and

$$\hat{\mathcal{W}}_{\text{I}} = \begin{bmatrix}\mathcal{W} & \mathcal{W}_{\text{I}}'\\ \mathbf{0} & \mathcal{W}\end{bmatrix} \qquad (30)$$

where the $\mathbf{0}$'s are of order $2\nu \times 2\nu$, and

$$\mathcal{W}_{\text{I}}' = \begin{bmatrix}\mathbf{U}_m{}^{(2)} & \mathbf{0}\\ \mathbf{0} & \mathbf{0}\end{bmatrix} \qquad (31)$$

where $\mathbf{0}$'s are of order $\nu \times \nu$. Then the fraction of triads which are isotactic (*i.e.*, *ddd* alias *lll*) at stereochemical equilibrium is

$$F_{\text{I}} = \mathcal{Z}^{-1}(x-2)^{-1}[\mathbf{J}^*\;\mathbf{0}]\hat{\mathcal{W}}_1\hat{\mathcal{W}}_{\text{I}}{}^{x-2}\begin{bmatrix}\mathbf{0}\\ \mathbf{0}\\ \mathbf{J}\\ \mathbf{J}\end{bmatrix} \qquad (32)$$

where $\mathbf{0}$ in the pre-multiplying row is of order $1 \times \nu$, and the $\mathbf{0}$'s in the post-multiplying column are of order $\nu \times 1$. If the 3×3 forms of $\mathbf{U}_m$ and $\mathbf{U}_r$ are used (*i.e.*, if $\nu = 3$), then $\hat{\mathcal{W}}_{\text{I}}$ is of order 12×12.

The *a priori* probabilities F_{H} and F_{S} for heterotactic and for syndiotactic triads are given by equations identical with eq 32 except for the replacement of $\hat{\mathcal{W}}_{\text{I}}$ by $\hat{\mathcal{W}}_{\text{H}}$ and by $\hat{\mathcal{W}}_{\text{S}}$, respectively, where

$$\hat{\mathcal{W}}_{\text{H}} = \begin{bmatrix}\mathcal{W} & \mathcal{W}_{\text{H}}'\\ \mathbf{0} & \mathcal{W}\end{bmatrix} \qquad (33)$$

with

$$\mathcal{W}_{\text{H}}' = \begin{bmatrix}\mathbf{0} & \mathbf{U}_r{}^{(2)}\\ \mathbf{U}_m{}^{(2)} & \mathbf{0}\end{bmatrix} \qquad (34)$$

and

$$\hat{\mathcal{W}}_{\text{S}} = \begin{bmatrix}\mathcal{W} & \mathcal{W}_{\text{S}}'\\ \mathbf{0} & \mathcal{W}\end{bmatrix} \qquad (35)$$

where

$$\mathcal{W}_{\text{S}}' = \begin{bmatrix}\mathbf{0} & \mathbf{0}\\ \mathbf{0} & \mathbf{U}_r{}^{(2)}\end{bmatrix} \qquad (36)$$

Obviously, $F_{\text{I}} + F_{\text{H}} + F_{\text{S}} = 1$. The incidence of various tetrads and of sequences of higher order could be found by elaboration of this procedure.

Equations 20, 21, and 24–36 inclusive are applicable to chains of *any length* whose bonds are characterized by any (finite) number ν of rotational states. In the limit of large x, eq 23, expressing the partition function $\mathcal{Z}$ in terms of the largest eigenvalue λ_1 or $\mathcal{U}$, may be used, and the fraction f_{iso} of isotactic units at stereochemical equilibrium may be deduced by taking appropriate derivatives of λ_1 according to familiar procedures.

Application to Vinyl Polymers

For vinyl polymers, both ω and τ will generally be much less than unity. Without significant limitation on the scope or accuracy of the results obtained, it is permissible therefore to let $\tau\omega = 0$. Taking note of the requirement that the second asymmetric center of one dyad furnishes the first member of the next, we observe that the $\mathbf{U}$ matrices used to generate Z by sequential multiplication and defined by eq 1–3 and 5–7 can be reduced to 2×2 order when $\tau\omega = 0$. The thus simplified matrices are

$$\mathbf{U}'_d = \mathbf{U}'_l = \begin{bmatrix}\eta\tau^* & 1\\ \eta & \omega\end{bmatrix} \qquad (37)$$

$$\mathbf{U}''_{dd} = \mathbf{U}''_{ll} = \begin{bmatrix}\eta\omega & 1\\ \eta & \omega\end{bmatrix} \qquad (38)$$

and

$$\mathbf{U}''_{dl} = \mathbf{U}''_{ld} = \begin{bmatrix}\eta & \omega\\ \eta\omega & 1\end{bmatrix} \qquad (39)$$

In adopting these forms we abandon distinctions between g^+ and g^- states, as is permissible for the purposes of the present paper. On this basis

---

(11) R. L. Jernigan and P. J. Flory, unpublished.

$$\mathbf{U}_m^{(2)} = \begin{bmatrix} (\eta^2\tau^*\omega + \eta) & (\eta\tau^* + \omega) \\ (\eta^2\omega + \eta\omega) & (\eta + \omega^2) \end{bmatrix} \quad (40)$$

$$\mathbf{U}_r^{(2)} = \begin{bmatrix} (\eta^2\tau^* + \eta\omega) & (\eta\omega\tau^* + 1) \\ (\eta^2 + \eta\omega^2) & (\eta\omega + \omega) \end{bmatrix} \quad (41)$$

and

$$\mathcal{U} = (1 + \omega)\begin{bmatrix} \eta(1 + \eta\tau^*) & (1 + \eta\tau^*) \\ \eta(\eta + \omega) & (\eta + \omega) \end{bmatrix} \quad (42)$$

Adopting eq 40 and 41 for the dyad statistical-weight matrices, we define the matrix

$$g\mathbf{U}_m^{(2)} + \mathbf{U}_r^{(2)} = \begin{bmatrix} (1 + g\omega)\eta^2\tau^* + (g + \omega)\eta & (1 + g\omega) + (g + \omega)\eta\tau^* \\ (1 + g\omega)\eta^2 + (g + \omega)\eta\omega & (1 + g\omega)\omega + (g + \omega)\eta \end{bmatrix} \quad (43)$$

where g is a factor introduced for reasons which will be apparent below. The secular determinant of this matrix is

$$\psi(g,\lambda) = |g\mathbf{U}_m^{(2)} + \mathbf{U}_r^{(2)} - \lambda\mathbf{E}| = \lambda^2 - [(1 + g\omega)(\eta^2\tau^* + \omega) + 2(g + \omega)\eta]\,\lambda + (g^2 - 1)(1 - \omega^2)(1 - \tau^*\omega)\eta^2 \quad (44)$$

Let $\lambda_1(g)$ and $\lambda_2(g)$ be the eigenvalues obtained by equating eq 44 to zero, with $\lambda_1(g) > \lambda_2(g)$. For $g = 1$, these are the eigenvalues of the matrix $\mathcal{U}$; they are given by

$$\begin{aligned} \lambda_1 &= (1 + \omega)(2\eta + \eta^2\tau^* + \omega) \\ \lambda_2 &= 0 \end{aligned} \quad (45)$$

As will be apparent from the kind of argument leading to eq 24

$$f_{\text{iso}} = (\partial \ln \lambda_1(g)/\partial g)_{g=1} = -\lambda_1^{-1}[(\partial\psi/\partial g)/(\partial\psi/\partial\lambda)]_{g=1,\psi=0} \quad (46)$$

in the limit $x = \infty$. From eq 44 it follows that

$$f_{\text{iso}} = (2\eta + \eta^2\tau^*\omega + \omega^2)\lambda_1^{-1} - 2\eta^2(1 - \tau^*\omega)(1 - \omega^2)\lambda_1^{-2} \quad (47)$$

in the same limit. If $\omega = 0$

$$\lambda_1 = \eta(2 + \eta\tau^*) \quad (48)$$

and

$$f_{\text{iso}} = 2(1 + \eta\tau^*)/(2 + \eta\tau^*)^2 \quad (49)$$

A priori probabilities for triads in infinite chains may be treated similarly. For the deduction of F_{I} in this limit, we define a matrix

$$i(\mathbf{U}_m^{(2)})^2 + \mathbf{U}_m^{(2)}\mathbf{U}_r^{(2)} + \mathbf{U}_r^{(2)}\mathbf{U}_m^{(2)} + (\mathbf{U}_r^{(2)})^2 \quad (50)$$

The secular determinant of this matrix is treated as a function of λ and i, and F_{I} is obtained by the methods applied above to the deduction of f_{iso}. Similar procedures yield F_{H} and F_{S}. For the case $\omega = 0$, we find, again in the limit $x = \infty$

$$F_{\text{I}} = (3\eta\tau^* + 2)/(\eta\tau^* + 2)^3 \quad (51)$$

$$F_{\text{H}} = 2[2(\eta\tau^*)^2 + 3\eta\tau^3 + 2]/(\eta\tau^* + 2)^3 \quad (52)$$

$$F_{\text{S}} = 1 - [4(\eta\tau^*)^2 + 9\eta\tau^* + 6]/(\eta\tau^* + 2)^3 \quad (53)$$

The *a priori* probabilities for infinite chains are functions of $\eta\tau^*$ when $\omega = 0$, according to eq 49 and 51–53.

It is of interest to compare these equations for infinite chains with results obtained for short chains according to the methods of eq 24–36, with $\omega = 0$ throughout. For $x = 2$, *i.e.*, for a molecule consisting of a single dyad, we readily find

$$(f_{\text{iso}})_2 = 2\eta/(1 + \eta)^2 \quad (54)$$

and for $x = 3$ (two dyads, or one triad)

$$(f_{\text{iso}})_3 = (1 + \eta + \eta\tau^*)/(1 + \eta)(2 + \eta\tau^*) \quad (55)$$

$$(F_{\text{I}})_3 = \eta(2 + \tau^*)/(1 + \eta)^2(2 + \eta\tau^*) \quad (56)$$

$$(F_{\text{H}})_3 = 2(1 + \eta^2 + \eta^2\tau^*)/(1 + \eta)^2(2 + \eta\tau^*) \quad (57)$$

$$(F_{\text{S}})_3 = \eta(2 + \eta^2\tau^*)/(1 + \eta)^2(2 + \eta\tau^*) \quad (58)$$

Generation of algebraic expressions for longer chains is tedious. Numerical results for chains of any length may readily be computed however by use of eq 24 to 36.

Numerical Results

Comparisons of numerical results for dimeric and trimeric molecules with those for indefinitely long chains are presented in Table I for three arbitrary sets of values of η and τ^*, with $\omega = 0$ as required for eq 49 and 51–58 to apply. Results for $x = 2$ and 3 for the first choice of parameters suggest a random distribution of dyads without bias in favor of either isotactic or syndiotactic forms. The relations

$$\begin{aligned} F_{\text{I}} &= f_{\text{iso}}^2 \\ F_{\text{H}} &= 2f_{\text{iso}}(1 - f_{\text{iso}}) \\ F_{\text{S}} &= (1 - f_{\text{iso}})^2 \end{aligned} \quad (59)$$

which should hold if the dyads were independent (Bernoullian sequence distribution), are indeed obeyed for the populations of dimers and trimers in this example. This result is atypical; it does not hold for other values of η and τ^*, as the second and third examples show. Even for the first example, departures occur for larger values of x as indicated by the results for $x = \infty$.

Table I. Equilibrium Stereoisomeric Composition ($\omega = 0$)

	Dyad composition[a]	Triad composition			
x	f_{iso}	F_{I}	F_{H}	F_{S}	$F_{\text{I}}/F_{\text{S}}$
		$\eta = 1, \tau^* = 1$			
2	1/2				
3	1/2	1/4	1/2	1/4	1
∞	4/9	5/27	14/27	8/27	5/8
		$\eta = 2, \tau^* = 1$			
2	4/9				
3	5/12	1/6	1/2	1/3	1/2
∞	3/8	1/8	1/2	3/8	1/3
		$\eta = 2, \tau^* = 1/4$			
2	4/9				
3	7/15	1/5	8/15	4/15	3/4
∞	12/25	28/125	64/125	33/125	28/33

[a] Results for f_{iso} in the initial example were first derived by Dr. A. Abe.

Clark[12] has reported preliminary results on stereochemical equilibria in lower homologs of several series

---

[12] H. G. Clark, *J. Polymer Sci.*, in press. The author is indebted to Dr. Clark for making available a copy of his manuscript in advance of publication.

of esters represented by formula I with R = COOR′. His results for the dimeric and trimeric methyl esters, equilibrated in methanolic NaOH at 25°, are compared in the first and second rows of Table II with compositions calculated according to eq 54–58 with $\eta = 1.85$ and $\tau^* = 0.50$. Also included are the values calculated for the infinite chain using eq 49 and 51–53 and the same parameters. Only two of the quantities for the trimer in the second row of the table are independent. In effect, three independent compositions, that of the dimer included, are calculated on the basis of a choice of two parameters. The agreement, while satisfactory, cannot be offered as conclusive confirmation of theory. The values of the parameters are reasonable, however.

Table II. Stereochemical Equilibria for Poly(methyl acrylate) Homologs, CH_3-[$CH(COOCH_3)$-CH_2]-H[a]

	f_{iso}		F_I		F_H		F_S	
x	Calcd	Obsd	Calcd	Obsd	Calcd	Obsd	Calcd	Obsd
2	0.456	0.455						
3	0.453	0.453	0.195	0.198	0.516	0.509	0.289	0.293
∞	0.450		0.191		0.519		0.290	

[a] Experimental equilibria determined by Clark[12] in methanol at 25°. Calculations for $\tau^* = 0.50$ and $\eta = 1.85$.

The smaller size of the -CO—O- group compared with CH_3, and the favorable interaction between O and CH_2 found in other chains,[13,14] indicates that η should exceed unity. For an articulated substituent R such as the one considered, the value of τ^* should be less than unity, as pointed out earlier.

Independent support for values of η and τ^* approximating those suggested above is provided by recent investigations of Doskočilová, Sýkora, Pivcová, Obereigner, and Lím[15] on the conformer populations in the individual species of these dimers and trimers. They deduced the rotational isomer compositions on the basis of coupling constants as applied to the interpretation of the CH_2 spin system in the nmr spectra of these compounds dissolved in *o*-dichlorobenzene. Their results are summarized in Table III, where they are compared with calculations carried out for $\eta = 1.43$ and $\tau^* = 0.60$. The experimental results clearly require values of $\eta > 1$ and $\tau^* < 1$, and in this respect the analysis confirms the independent deductions from the equilibrium composition of chemical species.

Table III. Comparison of Calculated with Observed Conformations of Lower Poly(methyl acrylate) Homologs[a]

Species		Conformation	Statistical wt	Mole fraction Calcd	Mole fraction Obsd[15]
$x = 2$:	iso (m)	tg and gt	η	1.00	1.00
$x = 2$:	syndio (r)	tt	η^2	0.67	<0.60
		gg	1		
$x = 3$:	I (mm)	$tgtg$	1	0.385	0.40
		$gttg$	τ^*	0.23	0.20
		$gtgt$	1	0.385	0.40
$x = 3$:	H (mr)	$tgtt$	η^2	0.48	0.43
		$gttt$	$\eta^2\tau^*$	0.29	0.32
		$gtgg$	1	0.23	0.25
$x = 3$:	S (rr)	$tttt$	$\eta^2\tau^*$	0.38	0.38
		$ttgg$	1	0.31	0.31
		$ggtt$	1	0.31	0.31

[a] Experimental results quoted are those of Doskočilova, *et al.*[15] Calculated values are for $\eta = 1.43$ and $\tau^* = 0.60$.

Discussion

The smaller proportions of isotactic as compared with syndiotactic dyads and triads in long chains reflects the greater number of spatial configurations made possible by syndiotactic placements. The degree of preference depends of course on the values of the parameters. For $\tau^* = 0$, $(f_{iso})_\infty = (f_{syn})_\infty = {}^1/_2$, the two kinds of units being subject to equally severe conformational constraints. Values of $(f_{iso})_\infty$ and of the ratio F_I/F_S decrease with increasing τ^* and η.

The stereochemical constitution of a long chain cannot be treated adequately and rigorously in terms of its dyad composition, or for that matter in terms of triads or any longer, but finite, sequences. Owing to the interdependence of conformations of neighboring units, the statistical weight (*i.e.*, Z) for the chain as a whole cannot be factorized into separate contributions for its respective units, or its dyads. The effect of altering the symmetry of one asymmetric center, -CHR-, is not therefore a matter which can be resolved within the locale of the unit in question; conformations of neighboring units are also influenced by its symmetry. Conversely, the neighbor dependence of conformational states causes the stereoisomeric character of a dyad to depend, at equilibrium, on the symmetries of units some distance removed as well as on those of its immediate neighbors. It is on this account that the sequence distribution is neither Bernoullian, as would be required for eq 59 to hold, nor Markoffian.

If the sequence of dyads were Markoffian, then the conditional probabilities for triads, *e.g.*, F_I/f_{iso}, should be independent of the chain length x. Examination of the numerical results for each of the three examples in Table I illustrates the dependence of the conditional probabilities on x. The physical basis for this generalization is to be found in the dependence of the stereochemical configuration of a given unit (or sequence of units) on its neighbors on *both* sides, and not merely on its predecessors as in a Markoffian chain.

Acknowledgment. The author takes pleasure in acknowledging the collaboration of Dr. Akihiro Abe in preliminary considerations of stereochemical equilibria in polymer chains. This work was supported by the Directorate of Chemical Sciences, Air Force Office of Scientific Research, Contract No. AF49(638)-1341.

---

(13) J. E. Mark and P. J. Flory, *J. Am. Chem. Soc.*, **87**, 1415 (1965); **88**, 3702 (1966).

(14) P. J. Flory, J. A. Semlyen, and D. A. Brant, to be published.

(15) D. Doskocilová, S. Sýkora, H. Pivcová, B. Obereigner, and D. Lím, paper presented at the International Symposium on Macromolecular Chemistry, Tokyo–Kyoto, 1966.