serving the *c* axes dimensions and the unit cell symmetry the *a* axes dimensions change almost linearly with composition (see Figure 5) and are always comprised between the values corresponding to the two pure homopolymers.

The melting points of these copolymers are a function of composition and are always between the melting points of the two pure homopolymers (Figure 3B).

As in the preceding system, the behavior of the melting points of the homopolymer mixtures of isotactic PIPVE and of isotactic PSBVE is less clear, possibly owing to separation processes that occur at high temperatures.

Binary Mixtures Containing PMP and PIPVE, and PMHE and PSBVE. The chain conformations and the chain packings of the two poly(α-olefins) are very similar to the chain conformations and chain packings of the corresponding poly(alkyl vinyl ethers). The cross-sectional area in the crystalline state differs by about 12% in both systems. Starting these considerations, it seemed possible that also in these two systems the formation of solid solutions might take place. However, the trials we have conducted have shown that poly(α-olefins) and the corresponding poly(alkyl vinyl ethers) crystallize in separate unit cells in the full range of compositions. This fact may be tentatively attributed to the difference in polarity between the two classes of polymers.

Conclusions

The polymer system consisting of homo- and copolymers of 4-methyl-1-pentene and 4-methyl-1-hexene as well as that derived from isopropyl vinyl ether and *sec*-butyl vinyl ether represent interesting examples of the possible phenomena of isomorphous replacement, in macromolecular systems. Both copolymeric systems show isomorphism in the whole range of compositions. In the case of the homopolymer mixtures, the poly(alkyl vinyl ethers) show the same behavior, whereas the poly(α-olefins) yield isodimorphism, the limiting phases corresponding to about 25% of weight concentration of either component.

It is interesting to observe that only two cases of isomorphism among homopolymers had been previously described: polystyrene and styrene-*p*-methylstyrene copolymer (molar fraction 30% of *p*-methylstyrene[2,3]), poly(vinyl fluoride) and poly(vinylidene fluoride) system.[19] In these cases, in addition to the requisites of size and conformational analogy among the replacing units there is the additional feature of the chemical compatibility among the homopolymer chains. It seems that the last feature is also very important as in the systems consisting of poly(4-methyl-1-pentene) with poly(isopropyl vinyl ether) and of poly(4-methyl-1-hexene) with poly(*sec*-butyl vinyl ether) where, in spite of the over-all size of the chain conformation of the two types of macromolecules being very similar, no isomorphism phenomena have been observed.

Acknowledgment. The A. thank Dr. G. Gianotti for the melting point determinations.

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Configurational Statistics and Stereochemical Structure of Vinyl Polymers

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ABSTRACT: General methods are presented for the calculation of the average conformations of adjoining pairs of bonds in vinyl chains $(\text{—CH}_2\text{—CHR—})_x$ of any specified stereochemical configuration. Intramolecular interactions are characterized by a small set of statistical weight parameters, usually three in number. Those involving two groups (CH_2, CH, and/or R) separated by four bonds are dominant in discriminating between various possible conformations of the chain molecule. Numerical calculations are carried out to illustrate the role of the several kinds of interactions in stereoregular isotactic and syndiotactic chains. The average conformations of one, two, and three consecutive racemic dyads within an otherwise *meso* (isotactic) chain illustrate the effects of the stereochemical configurations of adjoining units. The average conformation of one racemic dyad, or of a pair of racemic dyads, in an atactic chain is subject to wide variation, depending on the stereochemical configurations of sequences of dyads adjoining the one(s) in question. This is demonstrated by generating sets of 100 Monte Carlo chains in which the average incidence of racemic dyads is specified but the sequence in which they occur is random, then carrying out calculations for racemic dyads situated in the chains thus generated. The steric interactions which severely limit the conformations of vinyl chains cause the conformation of a given skeletal bond to be strongly influenced by the conformations of adjoining dyads. This neighbor interdependence renders the average conformation of a given dyad dependent upon the stereochemical configurations of other dyads in the chain, including those removed some distance in the chain sequence.

The conformations accessible to a vinyl polymer chain depend in marked degree on the character of

$$\text{H—(CH}_2\text{—CHR—)}_x\text{CH}_3$$

the substituent R and on the configurations of the asymmetric centers CHR. If R is a group commensurate in size with or larger than methyl, the number of significant conformations for the chain as a whole is severely restricted by steric interactions between nonbonded atoms and groups. Those conformations which are

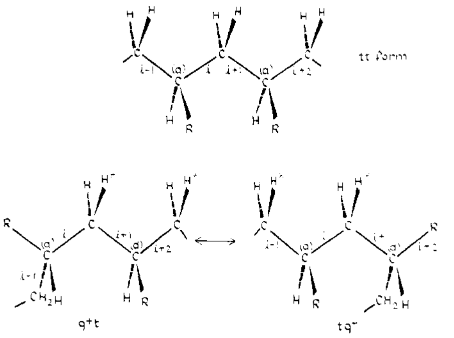

Figure 1. Conformations of a *meso* dyad.

sterically acceptable, and in particular the preferred ones, are readily deduced by assertion of the condition that major steric overlaps shall be avoided.[1-3] The elementary rules of conformational analysis suffice for this purpose; their application to vinyl polymer chains requires mathematical elaboration however.[3,4]

Consider an isotactic vinyl chain comprising x units, each having a single substituent R. Let the bonds of the chain skeleton be indexed $\ldots i-1, i, i+1$, etc., from left to right. A *meso* (*dd*) dyad of such a chain, together with adjoining bonds and attached skeletal CH_2 groups, is shown in Figure 1 in several conformations. A racemic (*dl*) dyad is shown similarly in Figure 2. It is expedient to introduce arbitrary definitions of d and l asymmetric centers. To this end, let the chain first be arranged in its all-*trans* conformation with all skeletal bonds coplanar, and let it be so rotated about the long axis as to place the CHR groups below that axis and the CH_2 groups above it. The *trans,trans* (*tt*) conformations of the two kinds of dyads are displayed in this manner in Figures 1 and 2. Asymmetric centers appearing with the substituent R forward from the plane of the adjoining skeletal bonds when the chain is so arranged are arbitrarily labeled *d;* those with R back of this plane are labeled *l*. These designations are arbitrary.[3,4] In fact, a *d* center thus defined is converted into an *l* center, and *vice versa*, by rotation about a vertical axis in the plane of the figure. While these designations are individually superficial, as well as arbitrary, the characters, *d* or *l*, of two or more of them are materially significant in relation to one another. For most purposes the conventional dyad designations *meso* and racemic will suffice.[1,3] They will replace the *d* and *l* designations in due course.

In the planar *trans* conformation the substituents R of the pair of asymmetric centers of the *meso* dyad are subject to major steric overlaps if R is methyl or a larger group. Similar steric interferences involving pairs of groups from the set CH, CH_2, and R, the members of the pair being separated by four bonds, are encountered in various conformations generated through rotations about the pairs of skeletal bonds $i-1$, i, and i, $i+1$.

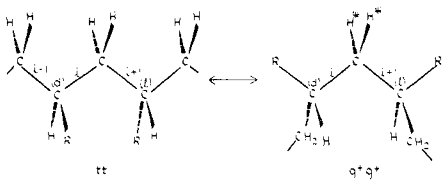

Figure 2. Preferred conformations for a *dl* racemic dyad.

One or more of these four-bond steric overlaps is operative in all staggered conformations for bond pair i, $i+1$ with the exception of the *gauche-trans* (g^+t) and the *trans,gauche* (tg^-) combinations shown in the lower portion of Figure 1. Perpetuation of either of these throughout an isotactic chain produces one or the other of its two preferred conformations. The two forms differ only in the sense of rotation, the one being right handed and the other left handed.[5] Together they represent the preferred conformations for isotactic polymers in the crystalline state, namely, the right- and left-handed 3_1 Natta–Corradini[6] helices.

With reference to the molecule when free of the constraints of packing in the crystal, the g^+t conformation is compatible with tg^- as its successor, but the reverse sequence in which tg^- is followed by g^+t juxtaposes g^- with g^+ and hence introduces a four-bond steric conflict between the adjoining pair of CH groups. Such conformations will therefore be of rare occurrence. On the basis of these rudimentary considerations, one is led to conclude that the preferred conformations for an isotactic vinyl polymer chain are described by[1-4]

$$(g^+t)(g^+t)\cdots(g^+t)(tg^-)\cdots(tg^-)$$

i.e., by

$$(g^+t)_k(tg^-)_{x-k-1}$$

with $0 \leq k \leq x-1$, where x is the number of repeat units in the chain. Parentheses are used to enclose pairs of skeletal bonds, such as i and $i+1$, occurring between successive substituted chain atoms. Thus, the preferred conformations of the free molecule comprise the highly restricted set consisting of two helical sections, one right handed and the other equivalent to it but having the opposite, or left hand, screw sense. Of course, the two sections may occur in reversed order, with the left-handed helical sequence preceding the right-handed one; this alteration merely requires end-for-end rotation of the chain in any given conformation specified by k.

For later reference, the methylenic hydrogen atoms of the dyad are distinguished in Figure 1 by labeling one of them with an asterisk. They are intrinsically nonequivalent as is well known. Specifically, the environments furnished by neighboring groups differ. In the preferred conformations g^+t and tg^-, the unlabeled H atom is *syn* to one neighboring R group and *anti* to the other; the atom H* is *syn* with respect to both R groups. The

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

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

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

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

(5) A right-hand rotation about a given bond is simply defined as one whose rotation vector is in the direction leading from the stationary to the rotated group joined by the bond. Thus defined, the sense of rotation is independent of which group is chosen for the stationary role. The ambiguities of "clockwork" definitions are thus avoided.

(6) G. Natta and P. Corradini, *Makromol. Chem.*, **16**, 77 (1955); *J. Polym. Sci.*, **39**, 29 (1959); *Nuovo Cimento, Suppl.*, **15**, 9 (1960).

respective protons retain this distinction in passing from conformation g^+t to tg^-. The effect of transition from one of these conformations to the other is to convert the environment of each proton into its mirror image. These features are relevant to the interpretation of nmr spectra of the methylenic protons in *meso* and racemic dyads, as discussed in the following paper.[7]

A stereoregular syndiotactic chain is less restricted in the conformations it may adopt without engendering severe steric interferences. The *dl* racemic dyad shown in Figure 2 has available to it two quite different conformations free of four-bond overlaps, namely, *tt* and g^+g^+. The corresponding conformations for an *ld* racemic dyad are *tt* and g^-g^-. In a stereoregular syndiotactic chain these conformations are subject to the following combining rules: a *tt* dyad shall be succeeded by either *tt* or *gg*, but *gg* shall be followed (or preceded) only by *tt*. Violation of the latter rule would juxtapose *gg* pairs of opposite sign, *i.e.*, $(g^+g^+)\,(g^-g^-)$ or $(g^-g^-)\,(g^+g^+)$, depending upon the sequence *dld* or *ldl* of asymmetric centers; either conformation entails a four-bond overlap of the outer pair of CH groups for the triad. The two preferred *regular* conformations are therefore (i) the all-*trans* form and (ii) the right- and left-handed pair, $\cdots (tt)\,(g^+g^+)\,(tt)\,(g^+g^+) \cdots$ and $\cdots (g^-g^-)\,(tt)\,(g^-g^-)\,(tt) \cdots$. Both i and ii have been identified amongst the crystalline forms of syndiotactic chains.[8] The preferred conformations for the isolated syndiotactic chain comprise the array of intermediate conformations sanctioned by the rules stated.

The two methylenic protons of the racemic dyad are situated in equivalent environments in each of the two conformers in Figure 2. Their environments in the respective conformers differ, however. In the *tt* form the protons are in a situation like that of the unlabeled H atom in Figure 1, *i.e.*, each is *syn* to one neighboring R group and *anti* to the other. In the *gg* conformer the methylenic protons are *syn* to both R groups; hence, asterisks are applied to denote the resemblance to the environments of the similarly labeled protons in Figure 1. If interactions with more distant groups are ignored and if strict adherence to staggered conformations is assumed (*i.e.*, if bond rotation angles of 0, 120, and −120° are assumed for conformers of both *meso* and racemic dyads), then the correspondences between methylenic protons indicated by the labeling in Figures 1 and 2 are exact. Departures from strict adherence to bond staggering may be expected to vitiate the correspondence quantitatively, but not qualitatively. The environments of the methylenic protons depend also on rotations of bonds adjoining the dyad in question, as we point out in the following paper.[7]

The foregoing description of the preferred conformations of vinyl chains is authenticated by spectroscopic studies (ir and nmr) on low molecular analogs.[9,10] It is further supported by investigations on stereochemical equilibria in such model compounds.[11,12] The rules presented in brief above afford the basis for a complete analysis of the conformations in vinyl polymer chains if they are of perfect stereoregularity, and if all conformations involving severe four-bond steric overlaps may be assumed to be forbidden. If one or the other or both of these conditions does not hold, a more elaborate analysis is required. Methods are at hand, however, for treating chains of any stereochemical description.[3,4] Moreover, assessment of nonbonded interactions in the greater detail required when less favored conformations make an appreciable contribution to the total array of spatial configurations does not complicate the treatment unduly. In this paper we present calculations on the effects of less favored conformations and of stereoirregularity on the configurational statistics of vinyl chains. These calculations are intended to be illustrative of the consequences of conformational constraints in vinyl polymer chains in general, without reference to particular examples such as polypropylene, polystyrene, etc.

Owing to the intensity of the interdependence of rotations about neighboring skeletal bonds in vinyl chains, the influence of the conformation of a given bond may be transmitted successively from one neighbor to the next over a sequence of many bonds. The particular form of the constraints imposed by the conformation of a bond on its neighbors depends of course on the stereochemical configurations of the adjoining asymmetric centers. Thus, the nature of the correlation of the conformations of a pair of bonds depends on the stereochemical configurations of the intervening centers, and it may be of long range in the sense that the influence of the stereochemical configuration of a dyad may be transmitted over many bonds. The time averaged conformations of a given dyad may depend therefore not only on its own stereochemical character, but also on the configurations of neighboring asymmetric centers, possibly including those some distance removed in sequence. Especially to be noted is the influence of the stereochemical configurations of neighboring units on a racemic dyad. If it is situated within long *meso* sequences, the *tt* form will be strongly favored, as may be shown to follow from the rules set forth above. The degree to which the *tt* form (as opposed to *gg*) is preferred depends therefore on the kinds of dyads surrounding the one in question. The situations of different racemic dyads within the chains of a stereoirregular vinyl polymer may vary widely in this respect, owing to the statistical distributions of *meso* and racemic dyads along the polymer chains. The average conformations of the racemic dyads will reflect this statistical distribution. Such effects are demonstrated by the calculations presented below and their probable magnitude is indicated.

Theory

Statistical Weight Matrices and the Partition Function. The detailed derivation of statistical weight matrices for

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[7] P. J. Flory and Y. Fujiwara, *Macromolecules*, **2**, 327 (1969).

[8] G. Natta and P. Corradini, *J. Polym. Sci.*, **20**, 251 (1956); G. Natta, *Makromol. Chem.*, **35**, 93 (1960).

[9] T. Shimanouchi, *Pure Appl. Chem.*, **12**, 287 (1966); D. Doskočilová, J. Štokr, E. Vatavová, B. Schneider, and D. Lím, *J Polym. Sci., Part C*, **16**, 2225 (1967).

[10] U. Johnsen, *J. Polym. Sci.*, **54**, S6 (1961); W. C. Tincher, *ibid.*, **62**, 5148 (1962); D. Doskočilová, *ibid.*, *Part A-2*, 421 (1964); Y. Fujiwara, S. Fujiwara, and K. Fujii, *J. Polym. Sci., Part A-1*, **4**, 257 (1966); F. A. Bovey, F. P. Hood, III, E. W. Anderson, and L. C. Snyder, *J. Chem. Phys.*, **42**, 3900 (1965).

[11] P. J. Flory, *J. Amer. Chem. Soc.*, **89**, 1798 (1967).

[12] A. D. Williams, J. I. Brauman, N. J. Nelson, and P. J. Flory, *ibid.*, **89**, 4807 (1967).

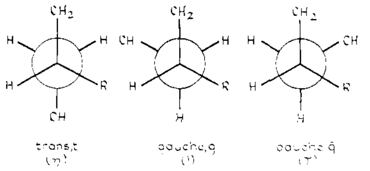

Figure 3. Newman projections showing the conformations about a bond of index *i* (see Figures 2 and 3) following an asymmetric center CHR presented in the (arbitrary) *d* configuration.

the characterization of the array of chain conformations of vinyl polymers is given elsewhere.[3,4] Here we shall summarize the analysis only to the extent necessary to underscore the meaning and significance of each of the several parameters involved. The essential matrices will be revised in the interests of achieving a more rational representation.

The statistical weights appropriate for a given conformation may be resolved into factors for interactions of first order, which depend upon rotation about one skeletal bond only and involve groups separated by three bonds, and second-order interactions dependent upon rotations about two consecutive bonds. The latter involve groups separated by four bonds. Interactions of first order may be comprehended through use of Newman diagrams as in Figure 3, where the three staggered conformations are shown. These diagrams represent a bond, such as bond *i* in Figure 1 or 2, that follows a center of the *d* configuration defined above. They also represent a bond preceding an *l* center, when viewed in the reverse direction. The designations *g* and *ḡ* correspond in these cases to *gauche* rotations g^+ of 120° and g^- of −120° from *trans* (*t*), respectively. The mirror images of the configurations in Figure 3 represent skeletal bonds following an *l* center or preceding a *d* center. For such bonds *g* and *ḡ* correspond to g^- and g^+, respectively,[13] the designations *t*, *g*, and *ḡ* being construed to include the mirror images. Thus interpreted, the diagrams in Figure 3 comprehend all situations.

(No significance is to be attached to the italicizing of *ḡ* throughout this paper and the one following, in contrast to the use of Roman letters for g, g^- and g^+. The unintended distinction is at variance with our usage elsewhere.)

We assign a statistical weight factor of unity for interactions of first order in the conformation *g* in Figure 3, in which CH is *syn* to CH_2. A factor η is introduced for the conformation (*trans*) in which R is *syn* to CH, and a factor τ for the *ḡ* conformation in which CH is *syn* to both CH_2 and R. These statistical weight factors apply identically to the mirror images of the respective configurations depicted in Figure 3. Depending upon R, the value of η may exceed or be less than unity. In general, we may expect $\tau < 1$.

Second-order (*i.e.*, four-bond) interactions centered about the pair of bonds $i - 1$ and i flanking the CHR group of *d* configurations occur only for the combinations g^+g^- and g^-g^+. We shall assign them a statistical weight ω, presumed to be much smaller than unity. Additionally to be considered if R is an articulated side chain such as $-CH_2-CH_3$, $-CH_2-C_2H_5$, or $-O-CH_3$, are the unfavorable interactions between the β group of the side chain and the chain skeleton when *both* adjoining skeletal bonds ($i - 1$ and i) are *trans*.[4] Assigning a factor $\tau^* < 1$ for an articulated side chain in this situation, we have for the matrix of factors for second-order interactions dependent jointly upon the rotations about the two consecutive bonds

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

the three states being given in the order *t*, g^+, and g^-, with states of bond $i - 1$ indexed on the rows and those for bond *i* on the columns. For a substituent such as CH_3 or Cl, and probably also for C_6H_5, we may take $\tau^* = 1$. Numerical calculations which follow are confined to this case. In the interests of generality, and without appreciable complication, we shall retain the factor τ^* in the following development. In any case, $\tau^* = 1$ for the first unit of the chain.

Multiplication of this matrix by the statistical weights for the first-order interactions in diagonal array yields the complete statistical weight matrix U' for bond *i* in relation to its predecessor in the chain. We thus obtain

$$\mathbf{U}_d' = \mathbf{V}_d'\mathrm{diag}(\eta, 1, \tau) \qquad (2)$$

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

The columns and rows are indexed *t*, g^+, and g^-, and in the order stated.

The statistical weights for first-order interactions associated with rotation about a bond such as $i + 1$ in Figure 1, *i.e.*, a bond *preceding* a *d* center, are expressed by

$$\mathrm{diag}(\eta, \tau, 1)$$

with elements indexed in the order above. Second-order interactions dependent upon rotations about the bond pair *i*, $i + 1$ of the *dd* dyad are more numerous than those for the preceding bond pair. These involve one or more pairs of the groups CH_2 and R. If R is commensurate with CH_2 in size, or if it is a group of the type $-CH_2-R'$, all of these interactions entail very small statistical weight factors and they should be similar in magnitude to ω assigned above for the second-order interaction of two CH groups. Simplifying the argument by ascribing the same factor ω to each second-order interaction, we have for the bond pair *i*, $i + 1$ between two *d* centers

$$\mathbf{V}_{dd}'' = \begin{bmatrix} \omega & \omega & 1 \\ 1 & \omega & \omega \\ \omega & \omega^2 & \omega \end{bmatrix} \qquad (4)$$

as may readily be confirmed. Combining these results, we have for the statistical weight matrix for this *meso dd* bond pair

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[13] A scheme of state designations equivalent to our *t*, *g*, and *ḡ* has been used by D. Doskočilová and coworkers, *J. Polym. Sci., Part C*, **16**, 215 (1967). See also T. Yoshino, *et al.*, *J. Phys. Chem.*, **70**, 1059 (1966), and D. Doskočilová, *et al.*, *J. Polym. Sci., Part C*, **23**, 365 (1968). Our *ḡ* replaces the *g′* used by these authors.

$$\mathbf{U}_{dd}'' = \mathbf{V}_{dd}''\mathrm{diag}(\eta, \tau, 1) \tag{5}$$

$$= \begin{bmatrix} \eta\omega & \tau\omega & 1 \\ \eta & \tau\omega & \omega \\ \eta\omega & \tau\omega^2 & \omega \end{bmatrix} \tag{6}$$

with rows and columns again indexed in the order t, g^+, g^-.

The configurational partition function of the isotactic chain, being the sum of statistical weights for all molecular conformations of the vinyl chain consisting of x units, is [3]

$$Z_{\mathrm{iso}} = \mathbf{J}^*(\mathbf{U}_d'\mathbf{U}_{dd}'')_1(\mathbf{U}_d'\mathbf{U}_{dd}'')^{x-2}\mathbf{J} \tag{7}$$

where

$$\left.\begin{array}{l} \mathbf{J}^* = [1 \quad 0 \quad 0] \\[2ex] \mathbf{J} = \begin{bmatrix} 1 \\ 1 \\ 1 \end{bmatrix} \end{array}\right\} \tag{8}$$

The factor for the first dyad is separated in eq 7 in recognition of $\tau^* = 1$ therein.

Interchange of second and third rows in $\mathbf{U}_d'$ and second and third columns in $\mathbf{U}_{dd}''$ yields the matrices

$$\mathbf{U}' = \begin{array}{c|ccc|} & t & g & \bar{g} \\ t & \eta\tau^* & 1 & \tau \\ g & \eta & \omega & \tau \\ \bar{g} & \eta & 1 & \tau\omega \end{array} \tag{9}$$

$$\mathbf{U}_m'' = \begin{array}{c|ccc|} & t & g & \bar{g} \\ t & \eta\omega & 1 & \tau\omega \\ g & \eta & \omega & \tau\omega \\ \bar{g} & \eta\omega & \omega & \tau\omega^2 \end{array} \tag{10}$$

where the row and column designations t, g, $\bar{g}$ correspond to their usage in Figure 3. The connections between $\mathbf{U}_d'$ and $\mathbf{U}'$ and between $\mathbf{U}_{dd}''$ and $\mathbf{U}_m''$ are expressed by

$$\left.\begin{array}{l} \mathbf{U}_d' = \mathbf{Q}\mathbf{U}' \\[2ex] \mathbf{U}_{dd}'' = \mathbf{U}_m''\mathbf{Q} \end{array}\right\} \tag{11}$$

where $\mathbf{Q}$ given by

$$\mathbf{Q} = \begin{bmatrix} 1 & 0 & 0 \\ 0 & 0 & 1 \\ 0 & 1 & 0 \end{bmatrix} \tag{12}$$

is the operator effecting the foregoing row and column interchanges. For bonds adjoining l centers, we have

$$\left.\begin{array}{l} \mathbf{U}_l' = \mathbf{U}'\mathbf{Q} \\[2ex] \mathbf{U}_{ll}'' = \mathbf{Q}\mathbf{U}_m'' \end{array}\right\} \tag{13}$$

as may easily be verified. In keeping with these relations, t, g, and $\bar{g}$ are construed to include also the mirror images of the conformations in Figure 3. Hence, the row and column designations in eq 9 and 10 hold irrespective of the symmetries of adjoining asymmetric centers.

Since $\mathbf{QQ} = \mathbf{E}$, where $\mathbf{E}$ is the identity matrix, and since also $\mathbf{J}^*\mathbf{Q} = \mathbf{J}^*$ and $\mathbf{QJ} = \mathbf{J}$, we find by substitution of eq 11 in eq 7 that $\mathbf{U}'$ and $\mathbf{U}_m''$ may replace $\mathbf{U}_d'$ and $\mathbf{U}_{dd}''$ in eq 7. The result thus obtained can be expressed as

$$Z_{\mathrm{iso}} = \mathbf{J}^*(\mathbf{U}_m^{(2)})^{x-1}\mathbf{J} \tag{14}$$

where

$$\mathbf{U}_m^{(2)} = \mathbf{U}'\mathbf{U}_m'' \tag{15}$$

is the matrix for a *meso* dyad; τ^* is to be set equal to unity in the factor for the first dyad. The identical result is obtained for an isotactic *l* chain (*i.e.*, an isotactic chain so oriented as to present its asymmetric centers in the *l* configuration as arbitrarily defined above) by substituting $\mathbf{U}_l'$ and $\mathbf{U}_{ll}''$ given by eq 13 in place of $\mathbf{U}_d'$ and U_{dd}'' in eq 7.

For a racemic chain the *dl* and *ld* dyads are nonsuperposable; they are related by mirror reflection, and hence a formal distinction must be maintained. They are of course subject to equivalent interactions, but the signs of the associated rotations differ. For a *dl* dyad, $\mathbf{U}'$ is again given by eq 3. For $\mathbf{U}_{dl}''$, we have

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

with rows and columns indexed in the order t, g^+, g^-. This matrix may also be represented by

$$\mathbf{U}_{dl}'' = \begin{array}{c|ccc|} & t & g & \bar{g} \\ t & \eta & \omega & \tau\omega \\ g & \eta\omega & 1 & \tau\omega \\ \bar{g} & \eta\omega & \omega & \tau\omega^2 \end{array} = \mathbf{U}_r'' \tag{16}$$

The matrix $\mathbf{U}_{ld}''$ is obtained by interchanging second and third rows and columns, *i.e.*

$$\mathbf{U}_{dl}'' = \mathbf{Q}\mathbf{U}''\mathbf{Q}_r \tag{17}$$

The partition function for a syndiotactic chain is given by

$$Z_{\mathrm{syn}} = \mathbf{J}^*\mathbf{U}_d'\mathbf{U}_{dl}''\mathbf{U}_l'\mathbf{U}_{ld}''\cdots\mathbf{J}$$

By substitution from eq 11, 13, 16, and 17 we obtain

$$Z_{\mathrm{syn}} = \mathbf{J}^*(\mathbf{U}_r^{(2)})^{x-1}\mathbf{J} \tag{18}$$

where

$$\mathbf{U}_r^{(2)} = \mathbf{U}'\mathbf{U}_r'' \tag{19}$$

The foregoing results admit of generalization to a vinyl chain of any specified stereochemical sequence.[3,11] Thus, in general

$$Z = \mathbf{J}^*\left(\prod_{k=1}^{x-1}\mathbf{U}_k^{(2)}\right)\mathbf{J} \tag{20}$$

where k indexes the dyads 1 to $x - 1$ in the chain of x units. Which of the matrices $\mathbf{U}_m^{(2)}$ or $\mathbf{U}_r^{(2)}$ is to be substituted for each factor $\mathbf{U}_k^{(2)}$ depends on the symmetry character of the kth dyad. Chains of any stereochemical sequence can be treated in terms of two dyad matrices derived from three primary statistical weight matrices for individual skeletal bonds, namely, $\mathbf{U}'$, $\mathbf{U}_m''$,

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(14) The scheme developed here for generation of the partition function of a vinyl chain is equivalent to that given in ref 3, Chapter VI. The matrices $\mathbf{U}'$, $\mathbf{U}_m''$, and $\mathbf{U}_r''$ as redefined in this paper differ from those of ref 3 through reordering of rows and columns.

and U_r''.[14] These latter matrices are defined by eq 9, 10, and 16, respectively. The arbitrary designations *d* and *l* do not appear in these and related equations.

According the the foregoing reductions, mirror image configurations, or inversion antipodes, can be accommodated within the general scheme without interchanging rows and columns of the various statistical weight matrices. The form of the matrices cited above may be treated as invariant to the configurational inversion by mirror reflection, or the inversion symmetry operation. Only if the directions of the bond rotations are explicitly required is it necessary to translate g and $\bar{g}$ into the g^+ and g^- significations. Connections between the former and the latter depend on the character, *d* or *l*, of the associated asymmetric center. Rules for this purpose have been stated above with reference to Figure 3.

Identification of states by the t, g, $\bar{g}$ designations, without regard for the symmetry of the dyad apart from its *meso* or racemic character, will prove convenient in most circumstances, and sufficient as well. In this way a quantity bearing given indexes may be defined to include corresponding conformational states of mirror image dyad pairs. For example, gg will include both g^+g^+ for *dl* and g^-g^- for *ld* dyads; these states are equivalent in the respective dyads, and they carry the same statistical weight. Similarly, tg for a *meso* dyad will represent the tg^- state if the dyad is *dd* and the tg^+ state if it is *ll*. These states differ intrinsically only in sense of rotation; they are mirror images and are accorded the same statistical weight. The disfavored states tg^+ and tg^- for these dyads, respectively, are comprehended by $t\bar{g}$.

If it is permissible to take $\omega = 0$, then all states $\bar{g}$ are suppressed and, as we have shown previously, the statistical weight matrices may be reduced to 2 × 2 order as[3,4]

$$\mathbf{U}' = \begin{array}{c|cc} & t & g \\ \hline g & \eta\tau^* & 1 \\ t & \eta & 0 \end{array} \qquad (21)$$

$$\mathbf{U}_m'' = \begin{array}{c|cc} & t & g \\ \hline t & 0 & 1 \\ g & \eta & 0 \end{array} \qquad (22)$$

$$\mathbf{U}_r'' = \begin{array}{c|cc} & t & g \\ \hline t & \eta & 0 \\ g & 0 & 1 \end{array} \qquad (23)$$

$$\mathbf{U}_m^{(2)} = \begin{bmatrix} \eta & \eta\tau^* \\ 0 & \eta \end{bmatrix} \qquad (24)$$

$$\mathbf{U}_r^{(2)} = \begin{bmatrix} \eta^2\tau^* & 1 \\ \eta^2 & 0 \end{bmatrix} \qquad (25)$$

These equations reaffirm the sets of preferred conformations designated in the beginning of this article for isotactic and for syndiotactic chains. They go further in prescribing statistical weights for each of the admissible conformations, exclusive of those suppressed by four-bond interactions.

The partition for the isotactic chain according to eq 14 and 24 (with $\tau^* = 1$ for the first unit) is given by

$$Z_{\text{iso}} = (x - 2)\tau^*\eta^{x-1} + 2\eta^{x-1} \qquad (26)$$

The first term represents those conformations $(gt)_k(tg)_{x-k-1}$ comprising a right- and a left-handed helical sequence for which $1 \leq k \leq x - 2$; the second term represents the two conformations with $k = 0$ and $k = x - 1$, respectively; each of these comprises a helix of uninterrupted sense.

The general expression for the partition function for a syndiotactic chain subject to the condition $\omega = 0$ is rather more complicated and is best elucidated through the eigenvalues of $\mathbf{U}_r^{(2)}$. With $\mathbf{U}_r^{(2)}$ given by eq 25, these are

$$\lambda_{1,2} = (\eta/2)[\eta\tau^* \pm \sqrt{(\eta\tau^*)^2 + 4}] \qquad (27)^{15}$$

The partition function Z_{syn} may be expressed in terms of these eigenvalues. It will suffice for our purposes to treat only the limiting case of a very long chain, for which it is permissible to adopt the familiar approximation

$$Z \approx \lambda_1^{x-1} \qquad (28)$$

λ_1 being the larger of the two eigenvalues. This equation holds for *any* stereoregular chain in the limit $x \rightarrow \infty$. It is not limited to the case $\omega = 0$ here considered.

A Priori **Probabilities.** Let β and γ denote indexes from the set t, g, $\bar{g}$. The expectation, or *a priori* probability, $p_{\beta\gamma;k}''$ that the pair of skeletal bonds within the kth dyad are in rotational states β and γ, respectively, is just the ratio of the sum of statistical weights for molecular conformations meeting this condition to the sum Z of the statistical weights for all conformations. It is given by[16]

$$p_{\beta\gamma;k}'' = Z^{-1}\mathbf{J}^*\left(\prod_{h=1}^{k-1}\mathbf{U}_h^{(2)}\right)(\mathbf{U}_k'\mathbf{U}''_{(\beta\gamma)k}) \times \left(\prod_{h=k+1}^{x-1}\mathbf{U}_h^{(2)}\right)\mathbf{J} \qquad (29)$$

where $\mathbf{U}_{(\beta\gamma)k}''$ is the matrix representing the second bond of the kth dyad with all elements except $u_{\beta\gamma}''$ replaced by zero. It will be formulated from eq 10 if the kth dyad is *meso*, and from eq 16 if it is racemic. Similarly, for the bond pair flanking the kth asymmetric center (*i.e.*, the CHR group on the left of the kth dyad) we have

$$\rho_{\alpha\beta;k}' = Z^{-1}\mathbf{J}^*\left(\prod_{h=1}^{k-1}\mathbf{U}_h^{(2)}\right)(\mathbf{U}_{(\alpha\beta)k}'\mathbf{U}_k'')\left(\prod_{h=k+1}^{x-1}\mathbf{U}_h^{(2)}\right)\mathbf{J} \qquad (30)$$

where $\mathbf{U}_{(\alpha\beta)k}'$ is the matrix $\mathbf{U}'_k$ (see eq 9) with all elements except $u_{\alpha\beta}'$ replaced by zero. In these equations and others to follow the serial indexes h, k will carry the significations m or r according to the character, *meso* or racemic, of the indexed dyad.

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(15) Strict adherence to a consistent notation would require these eigenvalues to be designated by $\lambda_1^{(2)}$ and $\lambda_2^{(2)}$, where the superscripts acknowledge that they represent two bonds of the chain. We shall deal with eigenvalues of this character only. Hence, superscripts are omitted from the λ's in interests of simplification of notation.

(16) See ref 3, Chapter III.

Let $p_{\alpha\beta}'$ represent the corresponding mean probability averaged over all bond pairs of the specified kind. That is

$$p_{\alpha\beta}' = (x - 1)^{-1}\sum_{k=1}^{x-1} p_{\alpha\beta;k}' \tag{31}$$

Similarly, for bond pairs within dyads

$$p_{\alpha\beta}'' = (x - 1)^{-1}\sum_{k=1}^{x-1} p_{\alpha\beta;k}'' \tag{32}$$

These mean probabilities, as may readily be shown,[16] are given by

$$p_{\alpha\beta}' = (x - 1)^{-1}Z^{-1}[1\ \ 0\cdots 0]\left(\prod_{k=1}^{x-1}\hat{\mathbf{U}}_{(\alpha\beta)k}{}^{(2)\prime}\right)\begin{bmatrix}0\\0\\0\\1\\1\\1\end{bmatrix} \tag{33}$$

where

$$\hat{\mathbf{U}}_{(\alpha\beta)k}{}^{(2)\prime} = \begin{bmatrix}\mathbf{U}^{(2)} & \mathbf{U}_{(\alpha\beta)}{}'\mathbf{U}'' \\ \mathbf{O} & \mathbf{U}^{(2)}\end{bmatrix}_k \tag{34}$$

The matrices $\mathbf{U}^{(2)}$ and $\mathbf{U}''$ shall by identified as *meso* (*m*) or as racemic (*r*) according to the character of dyad *k*. The mean probability $p_{\beta\gamma}''$ is given by an equation like eq 33 but with $\hat{\mathbf{U}}_{(\alpha\beta)k}{}^{(2)\prime}$ replaced by

$$\hat{\mathbf{U}}_{(\beta\gamma)k}{}^{(2)\prime\prime} = \begin{bmatrix}\mathbf{U}^{(2)} & \mathbf{U}'\mathbf{U}_{(\beta\gamma)}{}'' \\ \mathbf{O} & \mathbf{U}^{(2)}\end{bmatrix}_k \tag{35}$$

Singlet probabilities $p_{\beta;k}'$ and $p_{\gamma;k}''$, and the corresponding averages p_β' and p_γ'' as well, may be obtained by the foregoing methods. To this end a matrix $\mathbf{U}_{(\beta)k}'$ is defined with all columns null except the column of index β which is retained from the parent matrix $\mathbf{U}_k'$.[17] A matrix $\hat{\mathbf{U}}_{(\beta)k}{}^{(2)\prime}$ is then formulated from $\mathbf{U}_{(\beta)k}'$ after the manner of eq 34. For the calculation of p_γ'' matrix $\hat{\mathbf{U}}_{(\gamma)k}{}^{(2)\prime\prime}$ is similarly formulated by replacing columns of U_k'' by null vectors and by combining matrices according to eq 35.

The scheme above is applicable at once to stereoregular chains, with the simplification however that the product in eq 33 may be replaced by the appropriate matrix, *e.g.*, $\hat{\mathbf{U}}_{(\alpha\beta)m}{}^{(2)\prime}$, raised to the power $x - 1$. The serial products in eq 29 and 30 may be replaced similarly by powers of matrices $\mathbf{U}_m{}^{(2)}$ or $U_r{}^{(2)}$.

If x for the stereoregular polymer is very large, then

$$\left.\begin{aligned} p_{\alpha\beta}' &= p_{\alpha\beta;k}' \\ p_{\beta\gamma}'' &= p_{\beta\gamma;k}'' \end{aligned}\right\} \tag{36}$$

where $1 \ll k \ll x$. In this case further simplifications are possible as follows. From eq 29, for example, we have (see also eq 20)

$$p_{\beta\gamma;k}'' = \frac{\mathbf{J}^*(\mathbf{U}^{(2)})^{k-1}(\mathbf{U}'\mathbf{U}_{(\beta\gamma)}{}'')(\mathbf{U}^{(2)})^{x-k-1}\mathbf{J}}{\mathbf{J}^*(\mathbf{U}^{(2)})^{x-1}\mathbf{J}} \tag{37}$$

where $\mathbf{U}^{(2)}$ and $\mathbf{U}_{(\beta\gamma)}{}''$ are to be represented by the indicated matrices for a *meso* dyad if the stereoregular polymer is isotactic, and by those for a racemic dyad if it is syndiotactic. Let **A** and **B** be the eigenvector and eigenrow matrices (mutually normalized) of $\mathbf{U}^{(2)}$, and Λ the diagonal matrix of its eigenvalues. Then

$$\mathbf{U}^{(2)} = \mathbf{A\Lambda B} \tag{38}$$

Substitution in eq 37 yields

$$p_{\beta\gamma;k}'' = \frac{\mathbf{J}^*\mathbf{A\Lambda}^{k-1}\mathbf{BU}'\mathbf{U}_{(\beta\gamma)}{}''\mathbf{A\Lambda}^{x-k-1}\mathbf{BJ}}{\mathbf{J}^*\mathbf{A\Lambda}^{x-1}\mathbf{BJ}}$$

Given that $1 \ll k \ll x$, the index k on the left is immaterial (see eq 36), and only terms in the largest eigenvalues λ_1 of $\mathbf{U}^2$ need to be retained. It follows that in the limit of an infinite chain

$$\begin{aligned} p_{\beta\gamma}'' &= \frac{\mathbf{J}^*\mathbf{A}_1\lambda_1{}^{k-1}\mathbf{B}_1{}^*\mathbf{U}'\mathbf{U}_{(\beta\gamma)}{}''\mathbf{A}_1\lambda_1{}^{x-k-1}\mathbf{B}_1{}^*\mathbf{J}}{\mathbf{J}^*\mathbf{A}_1\lambda_1{}^{x-1}\mathbf{B}_1{}^*\mathbf{J}} \\ &= \mathbf{B}_1{}^*\mathbf{U}'\mathbf{U}_{(\beta\gamma)}{}''\mathbf{A}_1/\lambda_1 \end{aligned} \tag{39}$$

where $\mathbf{A}_1$ and $\mathbf{B}_1{}^*$ are the eigencolumn and eigenrow corresponding to λ_1. Equation 39 can be written

$$p_{\beta\gamma}'' = \left(\sum_\zeta B_{1\zeta}u_{\zeta\beta}'\right)u_{\beta\gamma}''A_{\gamma1}/\lambda_1 \qquad x \rightarrow \infty \tag{39'}$$

where $B_{1\zeta}$, $u_{\zeta\beta}'$, etc., are elements of the respective matrices. Similarly

$$\begin{aligned} p_{\alpha\beta}' &= \mathbf{B}_1{}^*\mathbf{U}_{(\alpha\beta)}{}'\mathbf{U}''\mathbf{A}_1/\lambda_1 \qquad x \rightarrow \infty &(40) \\ &= (B_{1\alpha}u_{\alpha\beta}'/\lambda_1)\sum_\zeta u_{\beta\zeta}''A_{\zeta1} \qquad x \rightarrow \infty &(40') \end{aligned}$$

Singlet *a priori* probabilities p_β' and p_γ'' for stereoregular polymers may be formulated similarly; *e.g.*

$$p_\gamma'' = \mathbf{B}_1{}^*\mathbf{U}'\mathbf{U}_{(\gamma)}{}''\mathbf{A}_1/\lambda_1 \qquad x \rightarrow \infty \tag{41}$$

where $\mathbf{U}_\gamma''$ denotes the matrix $\mathbf{U}''$ in which only the elements of column γ are retained, others being null.[17] This result lends itself to alternative expression as follows

$$p_\gamma'' = \mathbf{B}_1{}^*\mathbf{U}'\mathbf{u}_\gamma''A_{\gamma1}/\lambda_1 \qquad x \rightarrow \infty \tag{41'}$$

where $\mathbf{u}_\gamma''$ is the column of index γ from $\mathbf{U}''$.

The *a priori* triplet probability for a sequence of bonds indexed $i - 1, i, i + 1$ in Figures 1 or 2 is given by[18]

$$\begin{aligned} p_{\alpha\beta\gamma}'' &= \mathbf{B}_1{}^*\mathbf{U}_{(\alpha\beta)}{}'\mathbf{U}_{(\beta\gamma)}{}''\mathbf{A}_1/\lambda_1 \\ &= B_{1\alpha}u_{\alpha\beta}'u_{\alpha\gamma}''A_{\gamma1}/\lambda_1 \qquad x \rightarrow \infty \end{aligned} \tag{42}$$

This result can be put in a form better suited to its use in the following section by resort to the following primary expression

$$p_{\alpha\beta\gamma;k}'' = \frac{\mathbf{J}^*(\mathbf{U}^{(2)})^{k-2}(\mathbf{U}'\mathbf{U}_{(\alpha)}{}''\mathbf{U}_{(\alpha\beta)}{}'\mathbf{U}_{(\beta\gamma)}{}'')(\mathbf{U}^{(2)})^{x-k-1}\mathbf{J}}{\mathbf{J}^*(\mathbf{U}^{(2)})^{x-1}\mathbf{J}}$$

which is the analog of eq 37. The columns of $\mathbf{U}''$ rendered superfluous by postmultiplication by $\mathbf{U}_{(\alpha\beta)}{}'$ have been made null. This alteration is arbitrary. Thus, the subscript α could be deleted either from $\mathbf{U}_{(\alpha)}{}''$ or from $\mathbf{U}_{(\alpha\beta)}{}'$, but it serves our purpose to retain

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(17) A single state index, *e.g.*, β or γ enclosed in parentheses and subscripted on $\mathbf{U}'$ or $\mathbf{U}''$, will invariably denote the column retained. Correspondingly, a single state index on p' or p'' will denote the state of the bond in question, without regard for the state of its predecessor.

(18) Here and elsewhere the final index of a sequence $\alpha\beta\gamma$ applies to a bond of the character indicated by the superscript prime or double prime. Other indexes apply to bonds preceding this one in serial order.

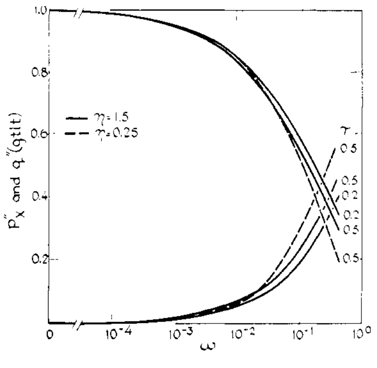

Figure 4. Average conformations of dyads in an infinite isotactic vinyl chain plotted against log ω. The lower set of curves represents the *a priori* probabilities $p_X'' = 1 - 2p_{gt}''$ of nonpreferred conformations (see eq 48) for the several values of τ and η indicated. Conditional probabilities $q_{(gt|t)}''$ of perpetuation of the preferred conformation *gt* from one dyad to the next are represented by the upper set of curves.

it on both factors. By the foregoing method we obtain in the limit $x \to \infty$

$$p_{\alpha\beta\gamma}'' = \mathbf{B}_1^*\mathbf{U}'\mathbf{U}_{(\alpha)}''\mathbf{U}_{(\alpha\beta)}'\mathbf{U}_{(\beta\gamma)}''\mathbf{A}_1/\lambda^2$$

$$= \mathbf{B}_1^*\mathbf{U}'\mathbf{u}_\alpha''u_{\alpha\beta}'u_{\beta\gamma}''A_{\gamma_1}'/\lambda^2 \qquad x \to \infty \qquad (42)$$

Conditional Probabilities. The most rudimentary conditional probabilities express the expectation that a given bond is in state β when its predecessor is known to be in a state α. Thus, if the bond in question is the one following an asymmetric center in the vinyl chain, we have for this conditional probability

$$q_{(\beta|\alpha)k}' = p_{\alpha\beta;k}'/p_{\alpha;k-1}'' \qquad (43)$$

Similarly, for a bond preceding an asymmetric center

$$q_{(\gamma|\beta)k}'' = p_{\beta\gamma;k}''/p_{\beta;k}' \qquad (44)$$

The quantities on the right-hand side of the expressions are furnished by relations given in the preceding section. If $1 \ll k \ll x$, the indexes k and $k - 1$ may be dropped.

The conditional probabilities of greater interest here are those representing the expectation of given states for the pair of bonds of dyad k, given the states of the bonds of dyad $k - 1$. Thus, in the case of an isotactic chain we may wish to know the probability that dyad k is in state *gt*, or *tt*, etc., given that dyad $k - 1$ is in the preferred state *gt*. Inasmuch as the present formulation rests on the premise that interdependence of rotational potentials does not extend beyond first neighbors, only the state of the bond which is the immediate predecessor of the dyad in question needs to be specified. Thus, for example

$$q_{(\beta\gamma,x\alpha)k}'' = q_{(\beta\gamma,\alpha)k}'' = p_{\alpha\beta\gamma;k}''/p_{\alpha;k-1}'' \qquad (45)$$

Or, if $1 \ll k \ll x$

$$q_{(\beta\gamma,\alpha)}'' = p_{\alpha\beta\gamma}''/p_\alpha'' \qquad (46)$$

From eq 42′ and 41′ (with α replacing γ), we have

$$q_{(\beta\gamma,\alpha)}'' = u_{\alpha\beta}'u_{\beta\gamma}''A_{\gamma_1}/\lambda_1 A_{\alpha_1} \qquad x \to \infty \qquad (47)$$

Numerical Calculations and Discussion

Isotactic Chains. Let p_X'' represent the fraction of dyads in conformations other than the preferred ones; *i.e.*, let

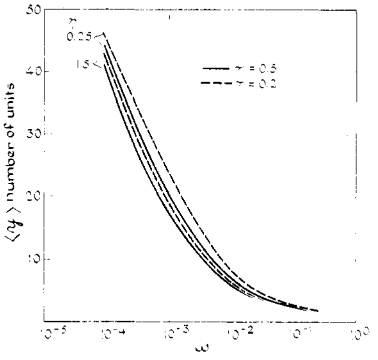

Figure 5. Average number of units $\langle y \rangle$ for sequences of the preferred conformation, *tg* or *gt*, in a stereoregular isotactic chain plotted against log ω for the values of η and τ indicated.

$$p_X'' = 1 - p_{gt}'' - p_{tg}'' = 1 - 2p_{gt}'' \qquad (48)$$

Results of calculations of this quantity carried out for infinite chains according to eq 39′ are shown as a function of ω by the lower set of curves in Figure 4. The several values of η and τ used in these illustrative calculations are indicated in the figure. Here and throughout all other calculations, we have taken $\tau^* = 1$. Only the preferred conformations *gt* and *tg* are permitted for $\omega = 0$. As ω is increased, other conformations are increasingly prevalent. The effect of decreasing τ parallels, approximately, the effect of a proportionate decrease in ω. The occurrence of nonpreferred conformations is augmented by an increase in η at low values of ω; the effect is opposite at comparatively large ω. The effect of η is small throughout the range.

The individual contributions of various nonpreferred conformations have not been separately considered. They could be readily determined if desired by the methods given above.

Conditional probabilities $q_{(gt|gt)}'' = q_{(gt|t)}'' = q_{(tg|g)}''$ of perpetuation of the preferred form are represented by the upper set of curves in Figure 4 for the same values of η and τ. These calculations have been carried out according to eq 47, which in this case reduces to

$$q_{(gt|t)}'' = \eta/\lambda_1 \qquad (49)$$

The average number of units in a sequence of preferred dyad conformations (either *gt* or *tg*) given by

$$\langle y \rangle = 1/[1 - q_{(gt|t)}''] \qquad (50)$$

is plotted as a function of ω in Figure 5. The spatial configuration of the chain can be viewed as a succession of helical segments of average length $\langle y \rangle$.

A priori probabilities for the preferred conformations *gt* and *tg* for the *k*th dyad in an isotactic chain consisting of $k + 50$ dyads are represented in Figure 6 as functions of k. The lower set of curves express the dependence of $p_{tg;k}''$ on k over the range 1–50 for $\tau = 0.5$, $\eta = 0.5$, and for the values of ω indicated. The sum of $p_{gt;k}''$ and $p_{tg;k}''$ for corresponding values of the parameters is given by the upper set of curves; the dashed curve is for $\tau = 0.5$, $\eta = 1.5$, and $\omega = 0.1$. Differences between corresponding curves from the respec-

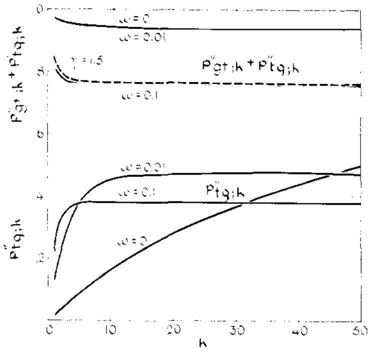

Figure 6. The *a priori* probabilities for the kth dyad in an isotactic chain consisting of $k + 50$ dyads, shown as a function of k over the range 1–50. The upper margin represents $p_{gt;k}'' + p_{tg;k}''$ for $\omega = 0$. The opposite end of the chain is represented by the converse of this diagram with roles of gt and tg reversed. $\tau = 0.50$; $\eta = 0.50$ for solid curves; $\eta = 1.50$ for dashed curves.

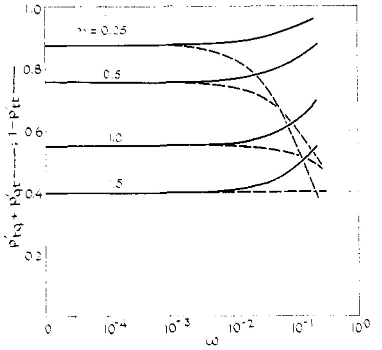

Figure 7. *A priori* probabilities for the pair of bonds flanking an asymmetric center —CHR— in an infinite stereoregular syndiotactic chain (*e.g.*, bonds $i - 1$ and i in Figure 2). Differences between solid ($p_{tg}' + p_{gt}'$) and dashed ($1 - p_{tt}'$) curves represent nonpreferred forms. $\tau = 0.50$ throughout.

tive sets furnish $p_{gt;k}''$. Other conformations are represented by differences between the upper margin of the figure and the upper set of curves. The roles of tg and gt are reversed at the opposite end of the chain.

The curves in Figure 6 show the state gt to be strongly favored over tg for the initial dyad. Persistence of this preference to the midpoint in the chain when $\omega = 0$ is an obvious consequence of the exclusion of all but the preferred conformations which comprise a sequence $(gt)_k$ followed by a sequence $(tg)_{x-k-1}$.

Relaxation of the suppression of nonpreferred conformations through adoption of $\omega > 0$ diminishes the range of the "end effect," owing to occurrence of conformations which interrupt perpetuation of the gt conformation from the beginning of the chain and of tg from its opposite extremity.

Syndiotactic Chains. In the limit $\omega = 0$ the 2 × 2 matrices given by eq 21, 23, and 25 are applicable and the expressions for the *a priori* probabilities for infinite chains reduce to simple algebraic form. The principal eigencolumn and eigenrow of $\mathbf{U}_r'^{(2)}$ as represented by eq 25 are

$$\mathbf{A}_{1;r} = \begin{bmatrix} \lambda_1/\eta^2 \\ 1 \end{bmatrix} \qquad (51)$$

$$\mathbf{B}_{1;r}{}^* = (2 + \tau^*\lambda_1)^{-1}[\lambda_1,\ 1]$$

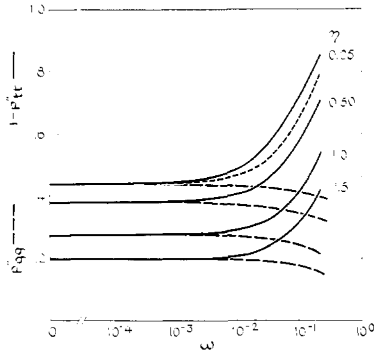

Figure 8. *A priori* probabilities for bond pairs within dyads of a syndiotactic chain (*e.g.*, bonds i and $i + 1$ in Figure 2). $\tau = 0.50$ for solid and long-dashed curves; $\tau = 0.20$ for short-dashed curve.

where λ_1 is the larger eigenvalue given by eq 27.[19] It follows from eq 39,′ 40,′ and 27 that

$$p_{gg}'' = 1 - p_{tt}'' = 1/(2 + \tau^*\lambda_1) \qquad (52)$$

$$= 2/[4 + (\eta\tau^*)^2 + \eta\tau^*\sqrt{4 + (\eta\tau^*)^2}] \qquad (52')$$

$$p_{tg}' = p_{gt}' = (1 - p_{tt}')/2 = p_{gg}'' \qquad (53)$$

The latter result follows also from the rules enunciated in the beginning of this article. Other conformations are forbidden for $\omega = 0$. These equations may be derived alternatively by differentiation of the principal eigenvalue λ_1 in the familiar manner.

For nonzero values of ω the statistical weight matrices do not reduce to 2 × 2 order, the secular equation is cubic, and one is obliged to calculate *a priori* probabilities by numerical methods according to eq 39′ and 40′. Results thus obtained are plotted against log ω in Figures 7 and 8 for several values of η, with $\tau = 0.5$ in all cases with the exception of the short dashed curve in Figure 8 for which $\tau = 0.20$. The dashed lines representing $p_{tg}' + p_{gt}'$ in Figure 7 converge in the limit $\omega \rightarrow 0$ to the solid lines representing $1 - p_{tt}'$. Similarly, those for p_{gg}'' converge to $1 - p_{tt}''$ in Figure 8. With increase in ω, other conformations are permitted to occur; their combined amounts are indicated by the differences between solid and dashed curves. Limiting values of the *a priori* probabilities for $\omega = 0$ depend on η according to eq 52′ with $\tau^* = 1$.

Racemic Dyads in Otherwise Isotactic Chains. Consider first a single racemic dyad situated between long sequences of *meso* dyads, a situation represented symbolically by $m_{k-1}\, r\, m_{x-k-1}$. If $k \gg 1$ and $\omega \ll 1$, *meso* dyad $k - 1$ will be tg with high probability. Similarly, if $x - k \gg 1$, *meso* dyad $k + 1$ on the right-hand side of the racemic dyad will almost certainly be gt. Interactions of the racemic dyad with each of its neighbors in the stated conformations cause p_{tt}'' to be very near unity. The average conformations for a racemic dyad thus situated may depart markedly from that for a racemic dyad in a stereoregular syndiotactic chain.[20]

A priori probabilities for a racemic dyad r^* isolated between infinite sequences of *meso* dyads may be cal-

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(19) The matrix $\mathbf{U}_m'^{(2)}$ given by eq 24 for a *meso* dyad when $\omega = 0$ is irreducible. Hence, methods corresponding to those represented by eq 51–53 are not available for isotactic chains.

(20) P. J. Flory and J. D. Baldeschwieler, *J. Amer. Chem. Soc.*, **88**, 2873 (1966).

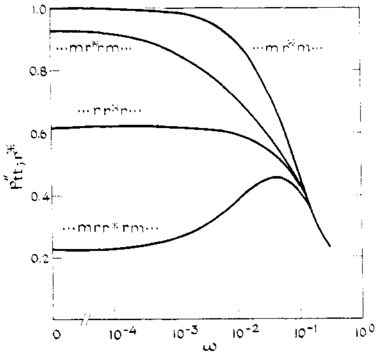

Figure 9. *A priori* probabilities $p_{tt;r^*}''$ for a racemic dyad situated within an infinite isotactic chain in the manner indicated, the dyad considered being marked by an asterisk. All calculations are for $\tau = 0.50$ and $\eta = 0.50$.

culated by obvious extension of methods introduced above. Thus

$$p_{\beta\gamma;r^*}'' = \mathbf{B}_1^*(\mathbf{U}'\mathbf{U}_{(\beta\gamma)}'')_r\mathbf{A}_1/\mathbf{B}_1^*\mathbf{U}_r^{(2)}\mathbf{A}_1 \tag{54}$$

$$= \Big(\sum_{\zeta}\mathbf{B}_{1\zeta}u_{\zeta\beta}'\Big)u_{\beta\gamma}''A_{\gamma 1}/\mathbf{B}_1^*\mathbf{U}_r^{(2)}\mathbf{A}_1 \tag{54'}$$

where $\mathbf{A}_1$ and $\mathbf{B}_1^*$ are the principal eigenvector and eigenrow of $\mathbf{U}_m^{(2)}$ for a *meso* dyad, and $\mathbf{U}'$ and $\mathbf{U}''$ refer to the racemic dyad. Similarly, the components of **A** and **B** appearing in eq 54′ refer to the *meso* dyad, whereas the elements of $\mathbf{U}'$ and $\mathbf{U}''$ are for a racemic dyad; subscripts denoting these distinctions have been omitted for simplicity. Probabilities $p_{tt;r^*}''$ calculated according to eq 54′ with $\tau = 0.50$ and $\eta = 0.50$ are represented by the uppermost curve in Figure 9, which may be compared with values calculated for the dyad of a stereoregular syndiotactic chain represented by the next-to-lowest curve in the figure. The dyad under consideration, *i.e.*, the *k*th dyad, is identified by an asterisk in the sequence designations in Figure 9.

If the process of "stereospecific" polymerization yielding a predominantly isotactic chain is guided by catalyst sites each of which favors one form (*d* or *l*) or the other, and if departures from perfect stereoregularity are contingent upon occasional errors at the catalyst site, then a typical stereochemical sequence is represented by ··· *dddlddd* ···. Incidence of departure from perfect regularity is marked by the occurrence of *two* racemic dyads, and the chain may be represented by ··· *m-m-r-r-m-m* ···. The first racemic dyad is subject to the influence of the preceding *meso* dyad; it is not directly coupled to the first *meso* dyad of the following sequence. The reverse holds of course for the second racemic dyad. If the *meso* sequence adjoining the given racemic dyad is very long, the *tt* state will be favored for this dyad. Inasmuch as each racemic dyad is subject to such influence from one side only, the constraints affecting it are less severe than those operative in the situation discussed in the paragraph above.

The *a priori* probability $p_{tt;r^*}''$ for one racemic dyad of a pair isolated in an otherwise isotactic chain of infinite length is shown by the second curve from the top of Figure 9. It has been calculated according to the following relationship for this case

$$p_{\beta\alpha;r^*}'' = \mathbf{B}_1^*(\mathbf{U}'\mathbf{U}_{(\beta\gamma)}'')_r\mathbf{U}_r^{(2)}\mathbf{A}_1/\mathbf{B}_1^*(\mathbf{U}_r^{(2)})^2\mathbf{A}_1 \tag{55}$$

Again $\mathbf{A}_1$ and $\mathbf{B}_1^*$ refer to $\mathbf{U}_m^{(2)}$ for a *meso* dyad; the

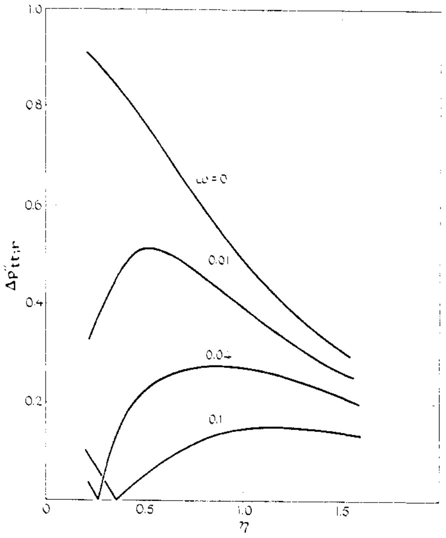

Figure 10. Differences $\Delta p_{tt;r^*}''$ for a racemic dyad r^* in ···*mr*m*··· and in ···*mrr*rm*··· plotted as functions of η for several values of ω. *meso* sequences are infinitely long.

U matrices represent racemic dyads as indicated by the subscript *r*.

The lowermost curve in Figure 9 represents the central member of three consecutive racemic dyads in an otherwise isotactic chain. It has been calculated according to

$$p_{\beta\gamma;r^*}'' = \mathbf{B}_1^*\mathbf{U}_r^{(2)}(\mathbf{U}'\mathbf{U}_{(\beta\gamma)}'')_r\mathbf{U}_r^{(2)}\mathbf{A}_1/\mathbf{B}_1^*(\mathbf{U}_r^{(2)})^3\mathbf{A}_1 \tag{56}$$

In this case the long isotactic sequences tend to favor *tt* states for the first and third racemic dyads, leaving the central member of the triplet free to choose between *gg* and *tt* without restraint from the likelihood that one of its neighbors may be *gg*. Hence, for small values of ω the central racemic dyad enjoys a much greater opportunity to assume the *gg* state than is afforded a dyad in an all-racemic chain (for which $p_{gg}'' < 0.50$ if $\omega = 0$ and $\eta > 0$; see above).

As these simple examples show, the average conformations of a racemic dyad may depend markedly on its environment, *i.e.*, on the stereochemical configurations of its neighbors. This dependence extends much beyond first neighbors. Thus, if the adjoining *meso* sequences were reduced to finite lengths, the average conformations of the racemic dyads in the situations explicitly treated here would be modified. Pursuit of these influences in detail would require that account be taken of the characters of dyads over greater ranges, even including those beyond the termini of adjoining *meso* sequences.

The examples chosen represent extreme cases. Differences between them are indicative of the range of variation of the average conformations of racemic dyads in various circumstances. With this in mind, in Figure 10 we have plotted differences $\Delta p_{tt;r^*}''$ between $p_{tt;r^*}''$ for ··· *mr*m* ··· and for ··· *mrr*rm* ··· as a function of η for the various values of ω indicated with each curve. If $\omega = 0$, then for reasons given above the racemic dyad in ··· *mr*m* ··· will of necessity be *tt* in an infinite chain, but r^* in ··· *mrr*rm* ··· may occur either as *tt* or as *gg*, with $p_{tt;r^*}''$ for this central racemic dyad determined by η. A small value of η disfavors the *trans* conformation

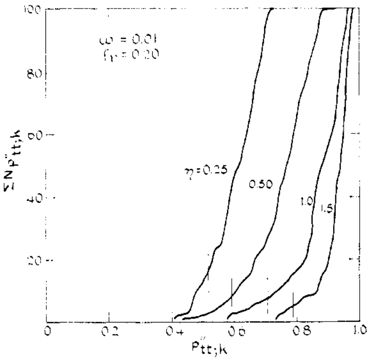

Figure 11. The effect of η on the integral distribution over conformational probabilities $p_{tt;k}''$ for racemic dyad $k = 51$ situated between Monte Carlo sequences of 50 units each; see text. Vertical lines denote values for a stereoregular syndiotactic chain.

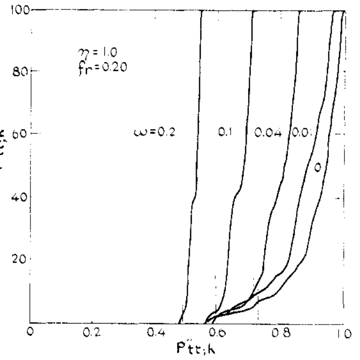

Figure 12. The effect of ω on the integral distribution of conformational probabilities for a racemic dyad situated between Monte Carlo sequences of 50 units each. Vertical lines denote values for a syndiotactic chain.

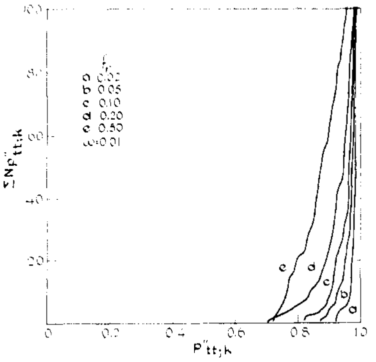

Figure 13. The effect of f_r on the integral distribution of conformational probabilities for a racemic dyad situated between Monte Carlo sequences of 50 units each; $\eta = 1.50$.

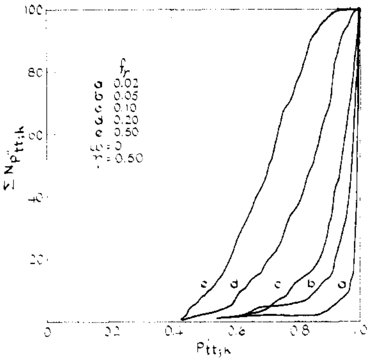

Figure 14. The effect of f_r on the integral distribution of conformational probabilities for a racemic dyad situated between Monte Carlo sequences of 50 units each; $\eta = 0.50$.

(see eq 9 and 16). It follows that $p_{tt;r*}'' \rightarrow 0$ as $\eta \rightarrow 0$ when $\omega = 0$. But $p_{tt;r*}''$ for an isolated racemic dyad in the sequence $\cdots mr^*m \cdots$ is unity for all $\eta > 0$. Hence, $\Delta p_{tt;r*}'' \rightarrow 1.0$ in the limit $\eta \rightarrow 0$ when $\omega = 0$. As Figure 10 shows, $\Delta p_{tt;r*}''$ decreases rapidly with increase in η owing to the increase in $p_{tt;r*}''$ for $\cdots mrr^* rm \cdots$, as pointed out above.

For values of $\omega > 0$, the restriction on the conformations of terminal dyads of the *meso* sequences is eased, and the disparity between conformations of the dyad r^* in the two extreme situations consequently is diminished for any value of η. The steady decrease of $\Delta p_{tt;r*}''$ with η which holds throughout the range of η when $\omega = 0$ also prevails for larger values of η when $\omega > 0$. The situation is rather more complicated at small values of η, where the occurrence of the *tt* conformation for the isolated racemic dyad is directly disfavored by a factor η^2 (see eq 9 and 16), while at the same time the *gg* conformation is opposed indirectly by the small value of ω, which tends to enforce *tg* and *gt* conformations on the respective adjoining *meso* dyads. With increase in η, commencing at $\eta = 0$, the value of $\Delta p_{tt;r*}''$ at first decreases, but subsequently increases. The location of the discontinuous change in slope depends of course on the magnitude of ω.

Racemic Dyads in Stereoirregular Chains. Each dyad of a stereoirregular chain is subject to the environment furnished by the stereochemical configurations of other dyads that are proximate to it in the chain. The configurations surrounding dyads of a given kind are variable to a degree determined by the random character of the succession of *meso* and racemic dyads produced in the synthesis of the polymer. These variations will be reflected in the average conformations of the individual dyads, as the preceding discussion serves to indicate. Since the preferred conformations *tt* and *gg* for a racemic dyad differ essentially whereas those of a *meso* dyad are related by mirror reflection, we confine the following analysis to racemic dyads.

In order to explore the variability of the average conformation, *e.g.*, of $p_{tt;k}''$, for the kth racemic dyad in a stereoirregular chain, we have generated "Monte Carlo" chains consisting of 101 dyads with the 51st ($k = 51$) designated as racemic. The stereochemical character, *meso* or racemic, of each of the preceding and following dyads was assigned subject to *a priori* probabilities $1 - f_r$ and f_r for the respective forms by resort to familiar methods involving generation of random numbers. A chain thus generated comprises two blocks of 50 dyads subject to the average stereochemical composition factor f_r and separated by a racemic dyad with index $k = 51$. Calculations to determine $p_{tt;k}''$ for each of 100 chains generated in this manner were performed according to eq 29. The partition function Z was computed in like manner for each chain through use of eq 20.

Calculations according to this plan were carried out for various values of f_r and of the statistical weight parameters η and ω. We have taken $\tau^* = 1.00$ and $\tau = 0.50$ throughout; calculations above show τ to have no significant effect which cannot be compensated by a

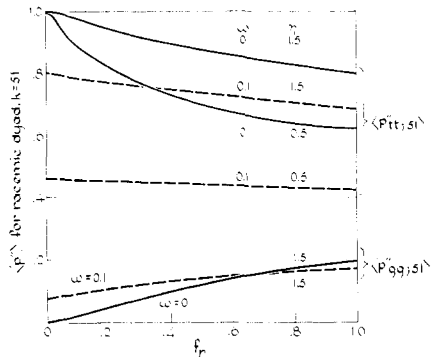

Figure 15. Mean values of $p_{tt;k}''$ and $p_{gg;k}''$ for racemic dyad $k = 51$ in sets of 100 Monte Carlo chains of 101 dyads, generated as described in the text and plotted against f_r for the several values of ω and η indicated.

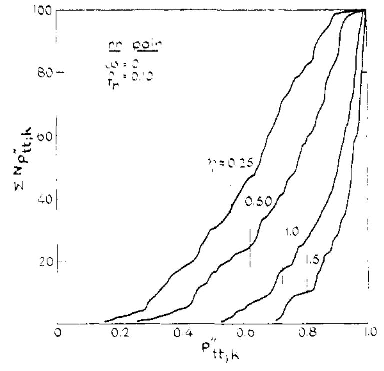

Figure 16. The effect of η on integral distributions of $p_{tt;k}''$ for one of a pair of racemic dyads rr situated between Monte Carlo sequences of 50 units each. Vertical lines indicate values for a syndiotactic chain.

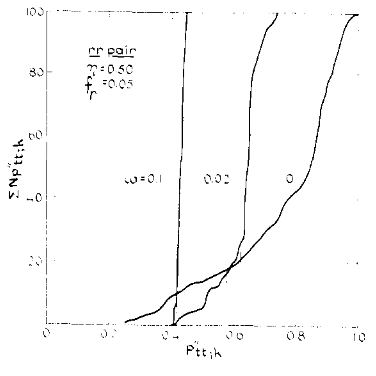

Figure 17. The effect of ω on integral distributions of $p_{tt;k}''$ for one of the racemic dyads between Monte Carlo sequences of 50 units each. Vertical lines denote values for syndiotactic chains.

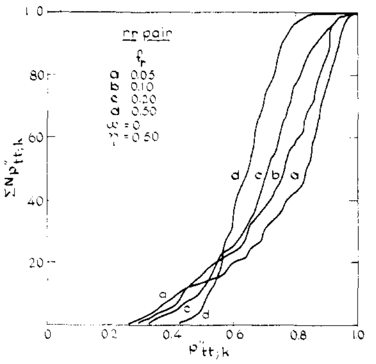

Figure 18. Integral distributions for several values of the Monte Carlo sequence probability f_r.

small change in ω. Results are plotted as integral distributions over $p_{tt;k}''$ in Figures 11–14. More specifically, the number of chains, designated by

$$\sum N p_{tt;k}''$$

for which $p_{tt;k}''$ is less than the value on the abscissa is plotted against $p_{tt;r}''$ in each figure. The effects of η and ω are shown in Figures 11 and 12, respectively, for $f_r = 0.20$. Vertical lines in Figures 11 and 12 locate values of p_{tt}'' for a stereoregular racemic chain subject to the same statistical weight parameters. The influence of f_r is illustrated in Figures 13 and 14. Mean values of $p_{tt;k}''$ for sets of 100 Monte Carlo chains are represented as functions of f_r by the upper group of curves in Figure 15. Also shown in Figure 15 are average values of $p_{tt;k}''$. Proportions of nonpreferred conformers are obtained as the difference between unity and the sum of values for the pair of corresponding curves from the two groups. The results shown in Figures 11–15, obtained for chains of 101 units constituted as described, can be accepted as representative of racemic dyads in infinite chains of the specified degrees of stereoirregularity; effects of longer range are negligible.

That the average conformation of a given racemic dyad, as represented by $p_{tt;k}''$, is subject to wide variation depending on the stereochemical environment of the dyad in question is well demonstrated in Figures 11–14. For the majority of the dyads $p_{tt;k}''$ exceeds its value, indicated by vertical lines in Figures 11 and 12, for the syndiotactic chain ($f_r = 1.0$) subject to the same values of ω and η. However, the distribution includes as well a minority of dyads which are less favorably disposed toward the tt conformation than are those of an all syndiotactic chain.

The breadth of the distribution varies with ω, η, and f_r. It diminishes with increase in ω, becoming quite sharp for $\omega > 0.10$ (see Figure 12). This observation is in keeping with the attenuation of effects of long range as the inhibitions implied by $\omega = 0$ are relaxed. The distribution appears to become narrower with increase in η (Figure 11). However, the change relative to the displacement of the mean value of $p_{tt;k}''$ is not decisive. The breadth of the distribution is maximal for intermediate values of f_r within the range of the values included for the calculations shown in Figures 13 and 14.

Analogous calculations for chains comprising Monte Carlo sequences of 50 dyads on either side of a central pair of racemic units (rr) are shown in Figures 16–18. The values of $p_{tt;k}''$ refer to either member of this pair. The distributions for $\omega = 0$ are broader than those presented above for a single racemic dyad. With increase in ω, the distribution narrows, becoming quite sharp for $\omega = 0.10$ (Figure 17). The curves in Figure 18 display a decrease in breadth of the distribution with increase in

f_r. This appears to be a reflection of the pronounced effect, when $\omega = 0$, of a decrease in length of the isotactic sequence adjacent to the racemic dyad.

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Conformations of Tetrads in Vinyl Polymers and Nuclear Magnetic Resonance Spectra of the Methylenic Protons

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ABSTRACT: The environment of a methylenic proton in a vinyl polymer is affected in major degree by the occurrence of the conformation *gt* for the pair of main-chain bonds preceding the methylene group, and similarly by the *tg* conformation for the following bond pair. These conformations are suggested as being of overriding importance in determining the nmr chemical shifts of the methylenic protons in polypropylene in which the substituent CH_3 resembles CH_2. Probabilities of these conformations are calculated for the several kinds of tetrads situated either in stereoregular chains or in atactic chains generated for various dyad compositions. The probabilities depend on the stereochemical configurations of dyads comprising the sequences adjoining the tetrad, and on this account the proton nmr resonances for tetrads of given character may be distributed over a range of frequencies (*ca.* 0.05 ppm) commensurate with the displacement (0.05–0.10 ppm) of their mean position from the resonances of tetrads of other kinds. The proton nmr spectra of poly(1,2,3,3,3-propylenes-d_5) are interpreted on this basis. The breadth of the range of resonances for racemic dyads in various stereochemical situations may obscure their detection in predominantly isotactic chains.

Rotations about the two skeletal bonds within a dyad —CHR—CH_2—CHR— of a vinyl chain determine the locations of the substituent groups R with respect to the methylenic protons. If the dyad is *meso*, the preferred conformations are g^+t and its mirror image tg^-, or *gt* and *tg* in the terminology introduced in the preceding paper (I).[1] In each of these equivalent conformations the methylenic hydrogen atom H* in Figure I-1 is *syn* to both R groups; the other methylenic hydrogen atom H is *syn* to one of the R groups only. If $\omega \ll 1$, as is usually the case, then this conformational pair is overwhelmingly preferred over all others.[1] This preference, expressed by values of $p_{gt}'' + p_{tg}''$ near unity according to calculations presented in the preceding paper,[1] is little affected by the stereochemical configurations of neighboring dyads. It follows that the chemical shielding of the respective methylenic hydrogens *by the substituents R* should be about the same for all *meso* dyads, irrespective of the stereochemical configurations of neighboring dyads of the chain.

The methylene protons of a racemic dyad are equivalent (if symmetries of neighboring dyads are ignored; *cf.* the following), but the environments differ for the two preferred conformations, *tt* and *gg*. In the former conformation, both protons of the methylene group of the racemic dyad are in situations corresponding to that of *one* of the *meso* protons (H in Figure I-1) when the *meso* dyad is in either of its preferred conformations. In the *gg* conformation, the two racemic protons are situated like the other proton (H* in Figure I-1) of the *meso* dyad. The distances between the respective protons and the pendant R and CH_2 groups in the two kinds of dyads (*meso* and racemic) are the same in these corresponding situations, and the directions of bonds CH—R and CH—CH_2 relative to the methylenic C—H bond are also equivalent. Hence, the space-averaged magnetic shielding of the protons by these groups in the corresponding situations should be approximately the same. (This equivalence may be vitiated if the substituent R is nonsymmetric about the CH—R bond axis, and in particular if its magnetic susceptibility tensor is not cylindrically symmetric with respect to this axis. Such effects are assumed to be small for the kinds of R groups of main interest.) On this basis, the chemical shift for the (equivalent) methylenic protons of a racemic dyad should be intermediate between those for the nonequivalent protons of the *meso* dyad. Its location within this range should depend on the proportions p_{tt}'' and p_{gg}'' of the two conformers. These proportions are strongly influenced by the stereochemical configurations of neighboring dyads, and this influence may persist over a considerable range of units[1] if $\omega \ll 1$. Hence, if the anisotropy of the magnetic shielding tensor for R differs markedly from that of the group, CH_2, which it replaces in the *gauche* (*g*) conformation, then the chemical shift for the methylenic protons of a racemic dyad must depend on the stereochemical configurations of neighboring dyads.[2]

Connections between chemical shifts and chain configuration cannot be interpreted solely on the foregoing limited basis, however. Effects of groups further removed from the dyad must be taken into account as well. Consider the preferred conformations shown in Figure 1 for a *meso* dyad and adjoining bonds. These conformations may be designated $g(tg)_m$ and $(gt)_m g$, respectively, the conformations of the pair of bonds

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(1) P. J. Flory and Y. Fujiwara, *Macromolecules*, **2**, 315 (1969), designated I in this paper.

(2) P. J. Flory and J. D. Baldeschwieler, *J. Amer. Chem. Soc.*, **88**, 2873 (1966).