

# CONFIGURATION-DEPENDENT PROPERTIES OF POLYMER CHAINS

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## ABSTRACT

Geometrical and spatial characteristics of macromolecular chains are determined by bond lengths, bond angles and hindrances to rotations about skeletal bonds as expressed by the conformational energies associated therewith. The presence of cyclic structures or of double bonds within the backbone may alter the configurational behaviour markedly. The structures of familiar polymeric substances present wide variations in these respects. Mathematical methods now available enable one to evaluate average properties of randomly coiled polymer chains of almost any description, full account being taken of all configurations of the molecule. These methods are exact, being subject only to the scheme adopted for describing bond conformations. The rotational isomeric scheme is generally applicable for this purpose, although more refined models may be employed for complicated chains such as the polypeptides and polynucleotides. The nature of the methods is described and configurational characteristics of representative chains are reviewed. Artificial models such as the freely jointed chain and the wormlike chain are incapable of representing the diversity of chemical structures that are of interest. These models tend to obscure rather than clarify the connections between properties and structure of polymeric chain molecules, which can now be treated in realistic fashion by newer methods.

## INTRODUCTION

The configuration of a chain molecule in space is determined by the lengths  $l$  of the bonds of the chain skeleton, by the angles  $\theta$  specifying the difference between the directions of successive bonds (i.e. the supplements of the conventional bond angle), and by the angles  $\varphi$  of rotation, or torsion, about these bonds. In general, the bond lengths  $l$  and bond angles  $\theta$  are fixed within narrow limits. It is permissible, therefore, to treat these quantities as predetermined geometrical parameters. The rotational angles, though subject to rotational potentials which may limit considerably the values they assume, are usually susceptible to much wider variations. One may therefore consider the spatial configuration of the chain molecule to be determined on the one hand by a set of fixed parameters  $\{l, \theta\}$  and, on the other, by the variable set  $\{\varphi\}$  comprising the rotational angles  $\varphi_2 \dots \varphi_{n-1}$  about each of the  $n - 2$  internal bonds,  $n$  being the total number of skeletal bonds in the chain.

Suppose the chain to consist of  $x$  identical repeat units, each of which comprises  $\xi$  bonds: then  $n = \xi x$ . If the same subset  $\{\varphi\}_\xi$  of rotation angles  $\varphi_{k+1}, \varphi_{k+2} \dots \varphi_{k+\xi}$  is assigned to the corresponding bonds of every unit ( $k$ )

in the chain, the configuration thus specified will be a regular one; in general it will be a helix of one sort or another. The regular conformation thus defined may not be a tenable one; if the steric domains of non-bonded atoms are forced to overlap excessively, or if torsional angle preferences are seriously violated, the energy may be inordinately large. For judiciously chosen values of the subset  $\{\varphi\}_\xi$ , however, steric conflicts may be avoided and torsional angle preferences may be respected, with the result that the energy will be low. Such conformations are the ones found in the crystalline state.

If, on the other hand, successive units are not constrained to adopt the same conformation specified above by  $\{\varphi\}_\xi$ , then the spatial configuration will, in general, be irregular. The aggregate of all such configurations (very large in number for a long chain) is collectively referred to as the set of random coil configurations. The stipulation that all repeat units shall be identical may be abandoned in this context; the discussion may embrace copolymers as well as homopolymers of identical units.

The capacity of the polymer chain to assume a great variety of configurations in space is the central feature, common to virtually all macromolecules, which sets them apart from other substances. The spatial extent of the polymer chain is prominently manifested in the properties—both equilibrium and dynamic—of its dilute solutions. The special behaviour of polymers under stress, and, in particular, the accommodation of very large compliances that characterizes the rubbery state, depend directly on configurational rearrangements. Even in a crystalline polymer, residual amorphous regions play an indispensable role in determining the physical and mechanical properties. An understanding of the spatial configurations of the long chains of consecutively connected atoms and groups that make up a polymer chain is therefore essential for the rational interpretation of their physical and chemical properties. Indeed, the spatial configuration embodies the nexus between the chemical structure and those properties which so clearly distinguish polymers from other classes of materials.

A glossary of properties of long-chain molecules that depend upon configuration is given in *Table 1*. Each property depends on a combination, or sum, of contributions from individual bonds or groups. The resultant must be averaged over all configurations of the random chain.

Mathematical methods<sup>1, 2, 5</sup> developed in recent years bring within easy reach the rigorous calculation of the characteristic properties of the unperturbed chain listed in *Table 1*. These methods are broadly applicable to chain molecules of any length and structure. They rest solely on the representation of the conformation of each bond by a discrete set of rotational states<sup>19, 20</sup>, appropriately chosen for the particular bond. This rotational isomeric state scheme has broad precedent in the treatment of small molecules. It should obviously be equally applicable to long chains. No further approximations are involved in the mathematical methods by means of which this scheme is adapted to macromolecules having very large numbers of bonds subject to rotational isomerization. Thus, the molecular properties of polymeric chains are susceptible to treatment with no greater compromise of exactness and rigour than is involved in treating corresponding properties of small molecules having at most only a few bonds capable of assuming different conformations.

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*Table 1.* Glossary of configuration-dependent properties

(Angle brackets enclosing various quantities appearing in this table denote averages taken over all configurations of the chain.)

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1. Chain dimensions<sup>1,2\*</sup>  
Measured by the mean-square length  $\langle r^2 \rangle$  or by the radius of gyration  $S_2 = (n+1)^{-1} \sum_{i < j} \langle r_{ij}^2 \rangle$
  2. The distribution function  $W(\mathbf{r})$  of the end-to-end vector<sup>3</sup>.  
Depends on  $\langle r^2 \rangle$  and, in better approximation, on higher moments  $\langle r^4 \rangle$ , etc., as well<sup>4,5</sup>.
  3. Cyclization equilibria\*.  
Depend principally on  $\langle r_m^2 \rangle$  for a ring of  $m$  bonds.
  4. Light scattering, and x-ray scattering at small angles<sup>\*,6</sup>.  
Depend on radius of gyration  $S_2$  and also on higher moments  $S_4 = (n+1)^{-2} \sum_{i < j} \langle r_{ij}^4 \rangle$
  5. Dipole moments<sup>\*,7</sup>.  
 $\langle \mu^2 \rangle$ ; calculable by methods for  $\langle r_{ij}^2 \rangle$ .
  6. Optical anisotropy\*  
Strain birefringence<sup>8,9</sup>,  $\langle \mathbf{r}^T \hat{\alpha} \mathbf{r} \rangle / \langle r^2 \rangle$ , where  $\hat{\alpha}$  is the traceless tensor representing the anisotropy of the molecular polarizability.  
Depolarized Rayleigh scattering<sup>10,11</sup>, trace  $(\hat{\alpha} \hat{\alpha})$ .  
Kerr effect<sup>12</sup>.
  7. Optical rotation<sup>13</sup>.  
Decisively dependent upon local conformation.
  8. The n.m.r. chemical shifts<sup>14,15</sup>.  
Depend directly on the average conformation in the vicinity of the resonant proton (or other nucleus), but this average conformation may acquire a long range dependence on structure owing to strong interdependence of neighbouring bond rotations.
  9. Strain dichroism<sup>16,17</sup>.  
Depends on preferential orientation of the transition moment  $\mathbf{m}$  as expressed by  $\langle \mathbf{r}^T (\mathbf{m} \cdot \mathbf{m}) \mathbf{r} \rangle$  where  $\mathbf{m} \cdot \mathbf{m}$  is the dyadic product
  10. Hydrodynamic properties of dilute solutions.  
Intrinsic viscosity.  
Translation friction constant (sedimentation and diffusion).  
Rotational diffusion.
  11. Thermodynamic properties of dilute solutions; the second virial coefficient in particular.
  12. Rubber elasticity; rotational isomerization under deformation<sup>18</sup>.
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\* Topics indicated by an asterisk are treated in ref. 1 and in some cases also in ref. 2. Original literature is cited in these references. For a generalization of the methods presented in ref. 1, which simplifies the formulation and computation of quantities of higher order, see ref. 5.

In addition to the mean-square length  $\langle r^2 \rangle$ , higher even moments of chain vector  $\mathbf{r}$  at least up to  $\langle r^{12} \rangle$  can be computed by the methods referred to<sup>4,5</sup>. These even moments define the distribution function  $W(\mathbf{r})^{1-3}$ ; see item 2 in *Table 1*. They are pertinent also to cyclization<sup>1,21,22</sup> (item 3) and to radiation scattering (item 4)<sup>6</sup>. In fact, the essential invariants, or parameters, characterizing each of the properties cited in *Table 1* can be evaluated by the methods referred to.

## CONFORMATIONAL INTERACTIONS AND THE CONFIGURATION PARTITION FUNCTION

In the aforementioned approximation that the bond lengths and bond angles are fixed, but that the bond rotation angles are variable, the molecular

configuration partition function is expressed by

$$Z = \int \dots \int \exp [-E(\{\varphi\})] d\{\varphi\} \quad (1)$$

with integration extending over the  $n - 2$  rotation angles of the set  $\{\varphi\}$  for all skeletal bonds exclusive of terminal ones whose rotations are of no consequence. The rotational partition function for a skeletal bond may be defined by

$$z = Z^{1/(n-2)} \quad (2)$$

$$\approx Z^{1/n} \text{ for large } n \quad (2')$$

If the bond rotations are mutually independent so that the molecular energy can be replaced by a sum of energies, one for each bond, i.e. if

$$E(\{\varphi\}) = \sum_{i=2}^{n-1} E_i(\varphi_i) \quad (3)$$

then

$$z = \int \exp [-E(\varphi)] d\varphi \quad (4)$$

the index  $i$  specifying the particular bond being omitted in this equation for simplicity. If for a given chain such separation of the total energy does not obtain, then equation 4 cannot be used and we must rely on equations 1 and 2, or 2', for the definition of  $z$ .

Values of  $z$  calculated for various chains at a temperature of 300°C are given in Table 2. In the case of free rotation,  $z = 2\pi$  radians. Introduction

Table 2. Bond rotational partition functions  
 $T = 300^\circ\text{K}$

Chain	$z$	
	relative	in radians
Free rotation	—	6.28
3-fold, symmetric with a barrier of 3.4 kcal mole <sup>-1</sup>	(3.00)	1.41
t, g <sup>+</sup> , g <sup>-</sup> ; $E_g - E_t = 0.5$ kcal mole <sup>-1</sup>	1.86	0.87
Polymethylene ( $\omega = 0.035$ )	1.69	0.79
Vinyls, —CH <sub>2</sub> —CHR—(with $\omega = 0$ ):		
R = —CH <sub>3</sub> or —C <sub>6</sub> H <sub>5</sub> , isotactic	1.00	0.40
R = —CH <sub>3</sub> or —C <sub>6</sub> H <sub>5</sub> , syndiotactic	1.27	0.51
R = —CH(CH <sub>3</sub> )—CH <sub>2</sub> ...	1.00	0.40
or —CH <sub>2</sub> —CH(CH <sub>3</sub> )—CH <sub>2</sub> ...		
		} isotactic, } syndiotactic, } or atactic

of a threefold, symmetric potential like that in ethane greatly reduces  $z$ , which may be regarded as a measure of the configuration space effectively available per bond. In the second entry in Table 2 we have chosen a barrier height of 3.4 kcal per mole for the calculation of  $z$  according to equation 4. This is somewhat greater than the barrier (ca. 3.0 kcal mole<sup>-1</sup>) for ethane, but corresponds, approximately, to the barrier separating *trans* (t) and *gauche* (g)

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states in *n*-butane and in higher normal alkanes. In order to facilitate comparisons with other examples, the higher barrier has been adopted. The preponderance of the contribution to the integral in equation 4 comes from values of  $\phi$  near the minima; ranges of  $\phi$  near the maxima contribute negligibly. It is justified therefore to ascribe a contribution  $1.41/3 = 0.47$  radian to each minimum. In an equivalent way, we may assign an arbitrary statistical weight of unity to each minimum. On this basis, the *relative* value of  $z$  is three, as given in the penultimate column of the table.

In the third example in *Table 2* the potential minima for the two *gauche* states at *ca.*  $\pm 120^\circ$  are raised  $500 \text{ cal mole}^{-1}$  above that of the *trans* state, the shapes of the three potential wells being unaltered. Thus, apart from their displacement in energy, the *gauche* wells are considered to be identical to that for the *trans*. Accordingly, the relative value of the partition function is given by

$$z_{\text{rel}} = 1 + 2 \exp(-500/RT) = 1.86 \quad \text{at } 300^\circ\text{K}$$

and

$$z = 1.86 \times 0.47 = 0.87 \text{ radian.}$$

This example is considered to correspond to *n*-butane. The energy, approximately,  $500 \text{ cal mole}^{-1}$ , for the *gauche* conformation relative to the *trans* is furnished by spectroscopic results and other evidence on *n*-alkanes in the liquid state<sup>1</sup>.

In the higher *n*-alkanes having two or more internal skeletal bonds account must be taken of the severe steric overlaps occurring when a pair of successive bonds is assigned to either of the combinations of states  $g^+g^-$  or  $g^-g^+$ . Owing to their high energy (*ca.*  $3 \text{ kcal mole}^{-1}$ )<sup>1,2,3</sup> such conformations are reduced to a much lower incidence than would hold if a commitment of energy no greater than that ( $1 \text{ kcal mole}^{-1}$ ) for two independent *gauche* states were required. Specification of these conformations involves two rotation angles; they cannot therefore be comprehended in terms of one bond alone. Hence, treatment according to equation 4 is precluded, and it is necessary to adopt a different mathematical approach. Appropriate methods to this end have been fully elaborated<sup>1,2</sup>. In effect, they generate a statistical weight factor (corresponding to the exponential which is the integrand in equation 1) for each configuration of the chain, and then take the sum of such factors for every configuration of the chain. This sum furnishes the molecular partition function  $Z$ . The mean factor  $z$  for one bond may then be obtained according to equation 2.

It is our intention to offer here only a descriptive account of the more prominent aspects of the mathematical methods to which reference has been made above. We note that the required set of statistical weights is generated by serial multiplication of matrices  $U_i$  of statistical weights for the states of each bond  $i$  in relation to those of its predecessor  $i - 1$ . Thus, we may write for a chain of  $n$  bonds

$$Z = \prod_1^n U_i \quad (5)$$

Inasmuch as only internal bonds, for which  $1 < i < n$ , are subject to rotations affecting the skeletal configuration, statistical weight matrices are not required for terminal bonds for which  $i = 1$  and  $n$ . It is convenient, however, to formulate  $U_1$  and  $U_n$  as the row and column matrices, respectively, to effect the required summation of terms. With the terminal matrices thus defined,  $Z$ , a scalar quantity, is given by equation 5. The principal feature of this equation is the expression of  $Z$  as a serial product of  $n$  factors (matrices), one for each bond.

Conformational energy calculations on the higher  $n$ -alkanes<sup>1,23</sup> confirm that the potential wells for the  $t$  and  $g^\pm$  states, apart from those associated with  $g^\pm g^\mp$  pairs, are equivalent to those for  $n$ -butane. The  $g^\pm g^\mp$  conformations occur so infrequently as to obviate a detailed account of the form of the energy minima associated with them. It is a legitimate approximation therefore to assume the shapes of the various energy minima to be the same. The minima for the  $g^\pm$  states are located 500 cal mole<sup>-1</sup> above the *trans* state in accordance with experimental evidence on the lower  $n$ -alkanes, and the  $g^\pm g^\mp$  pairs are further elevated by an additional 2000 cal mole<sup>-1</sup>. Calculations by the aforementioned methods yield  $z_{rel} = 1.69$ , a statistical weight of unity being assigned the *trans* state\*. Expressed in radians,  $z = 1.69 \times 0.47 = 0.79$ , as given in Table 2.

Vinyl polymer chains bearing substituents  $R$  on alternate skeletal carbon atoms are subject to numerous interactions between non-bonded atoms or groups. If the size of  $R$  is as great as or greater than that of  $CH_3$ , the steric interactions of  $R$  with other groups effectively suppress most of the conformations that would otherwise be accessible to the chain. These interactions, which are of overriding importance, involve a given  $R$  with another group,  $CH_2$  or  $R$ , separated from it by four bonds. They depend therefore on two bond rotations, and are analogous to the 'second order' interactions between  $CH_2$  groups precipitated in  $n$ -alkane chains by a  $g^\pm g^\mp$  bond pair. The principal interactions occurring in vinyl polymer chains are not unlike those in simple alkane chains and in polymethylene of high molecular weight in particular. They are more numerous, of course, and consequently restrictions on the conformations accessible to the chain are much more limiting in their combined effect. Vinyl chains are nevertheless susceptible to a treatment quite as exact as that for polymethylene chains<sup>1</sup>. The theory of vinyl chains<sup>1,24</sup> is necessarily more elaborate. It must take cognizance of the two-bond repeat unit, and hence of two kinds of consecutive bond pairs, namely, pairs flanking a  $CHR$  and pairs flanking a  $CH_2$  skeletal group, respectively. Furthermore, the  $-CHR-$  groups are pseudo-asymmetric; hence, *meso* and racemic dyads  $-CHR-CH_2-CHR-$  must be distinguished.

Partition functions  $z$  for vinyl chains are included in Table 2. These have been calculated in the approximation that all conformations involving second order steric conflicts (in which groups separated by four bonds are involved; see above) are suppressed. Relaxation of this approximation through replacement of  $\omega = 0$  for the disallowed conformations with a physically more realistic value in the range 0.01 to 0.03 would raise the values of  $z$  slightly. In the approximation ( $\omega = 0$ ) that all conformations entailing second order

\* For a long chain,  $z_{rel}$  is given by the largest eigenvalue of the statistical weight matrix.

steric conflicts are suppressed, the only conformations accessible to a perfect isotactic chain are those designated by

$$(g^+t)_k(tg^-)_{x-k} \quad 0 \leq k \leq x$$

$x$  being the number of units. The state symbols within parentheses refer to a dyad pair of bonds between successive CHR groups and  $(g^+t)_k$  denotes  $k$  consecutive dyads in the indicated conformation. All such dyads are *meso* in the isotactic chain. The conformations designated above consist of two  $3_1$  helical sequences, one right-handed and the other left-handed, comprising  $k$  and  $x - k$  units, respectively. There are  $x + 1$  such conformations corresponding to all values of  $k$  from 0 to  $x$ ; hence  $Z = x + 1$ . Since the number of bonds  $n = 2x$ ,

$$z_{rel} = (x + 1)^{2x}$$

and in the limit  $x \rightarrow \infty$

$$z_{rel} = 1$$

Conformational energy calculations show the energy minima, when unencumbered by second order interactions (e.g. the  $g^+$  or the  $t$  state for the respective bonds of a *meso* dyad), to be only a little narrower than the minima in  $n$ -alkane chains. Numerical estimates yield 0.40 radian for the mean contribution of a minimum in the vinyl chain. Values of  $z$  given in the final column are obtained from  $z_{rel}$  on this basis.

A greater variety of conformations is available to a syndiotactic chain consisting of racemic dyads. These are typified by

$$(tt)_{k_1}(g^\pm g^\mp)(tt)_{k_2}(g^\pm g^\mp) \text{ etc.}$$

where  $k_1, k_2, \text{ etc.} \geq 1$ , and the signs of the  $gg$  rotational states depend on the symmetry character of the given racemic dyad. This greater variety is reflected in the substantially larger value of  $z_{rel}$ .

A. Abe<sup>13, 25</sup> has pointed out that branched sidechains  $R$  having a substituent (e.g.  $\text{CH}_3$ ) attached to either the first or the second carbon of the sidechain (see final entries in *Table 2*) further reduce the conformations of the chain skeleton. The branched sidechains impose interactions of second order which obstruct the  $tt$  conformation for the pair of skeletal bonds flanking a CHR group. In the approximation that all conformations subject to such interactions are suppressed completely, the isotactic chain is forced to adopt one helical form throughout (i.e.  $k = 0$  or  $x$  in the typical conformation expressed above), and, what is more important, the syndiotactic chain is restricted to the helix

$$(tt)(g^+g^+)(tt)(g^+g^+)$$

and its left-handed counterpart. Moreover, every intermediate (atactic) stereochemical structure comprising both *meso* and racemic dyads is restricted to a unique conformation. Hence,  $z_{rel} = 1$  irrespective of stereochemical structure. This rule, though subject to partial relaxation if  $\omega \neq 0$ , may be of far-reaching importance with regard to the properties of vinyl chains in which  $R$  is a bulky group.

The calculations in *Table 2* illustrate the effects of various constraints

acting to restrict rotation about skeletal bonds of chain molecules. There is first of all the threefold potential characteristic of the C—C bond, and also of C—O and C—N single bonds. It reduces the range of rotation angle  $\varphi$  effectively available by a factor of about four. Next, the higher energy of the *gauche* states for C—C bonds in alkane chains lowers  $z$  by nearly 40 per cent. Second order interactions which nearly suppress  $g^+g^-$  pairs bring about a further reduction. Finally, the profusion of steric interactions in vinyl chains, due to their substituents R, reduces the effective range of  $\varphi$  to only 6 to 8 per cent of that for free rotation.

The bond partition function may be looked upon as a measure of 'chain flexibility' in a certain sense of this much-abused term. Its use in this connection pertains of course to the *equilibrium* flexibility exclusively. One may with good reason contend that the term 'flexibility' should be reserved for dynamic, as opposed to equilibrium, behaviour. However, the confusion of meanings of this term is already well entrenched through the widespread identification of high extension (e.g. a large characteristic ratio  $\langle r^2 \rangle / nl^2$ ) with chain stiffness, and small extension with flexibility. In fact, extension of the chain in space is not a reliable measure of chain stiffness in either an equilibrium or a dynamic sense. This is a point which is elaborated in the discussion to follow.

### AVERAGE PROPERTIES; THE POLYMETHYLENE CHAIN

The equilibrium properties of a chain molecule depend not only on the extent of the accessible configuration space, as measured by  $Z = z^{n-2}$ , but also on the particular regions of this space that are accessible to the chain. The partition function alone does not determine the average properties of the random chain such as its mean dimensions for example. These properties depend on the particular conformations that are favoured and on the structural geometric parameters: bond lengths and bond angles. The mean dimensions of a chain subject to a threefold symmetric potential (second entry in *Table 2*), for example, are identically equal to those for the freely rotating chain, the bond lengths and bond angles being the same. The values of  $z$  differ markedly, however. Other instances may be cited in which location of the preferred conformation in the configuration space has a marked effect on the chain dimensions (cf. following).

Let  $p$  denote a characteristic property of the chain molecule which depends on its spatial configuration. For example,  $p$  may be the squared end-to-end length  $r^2$ , or it may be any other characteristic cited in *Table 1*. Then  $\langle p \rangle$  will denote its statistical mechanical average. The summation of contributions from constituent bonds, or units and the averaging over all configurations may be performed simultaneously through serial multiplication matrices  $\mathcal{P}_i$ , one for each bond  $i$ , followed by division by the molecular configuration partition function  $Z^{1,5}$ . That is,

$$\langle p \rangle = Z^{-1} \prod_{i=1}^n \mathcal{P}_i \quad (6)$$

The matrix  $\mathcal{P}_i$  incorporates all required information pertaining to bond  $i$ ,



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or to bond pair  $i - 1, i$ . It includes the geometrical parameters  $l_i$  and  $\theta_i$ , the statistical weights applicable to bond pair  $i - 1, i$  as embodied in the statistical weight matrix  $U_i$ , and the specific contribution of bond  $i$  to the property  $p$ ; e.g. if  $p$  represents the mean-square dipole moment  $\mu^2$ , then the moment  $\mu_i$  associated with bond  $i$  will appear in  $\mathcal{P}_i$ , and in  $\mathcal{P}_i$  only. In analogy with equation 5 for  $Z$ , the terminal factors  $\mathcal{P}_1$  and  $\mathcal{P}_n$  for the chain of  $n$  bonds may take the form of a row and a column, respectively, and thus yield the required sum of terms comprising contributions to property  $p$  from all configurations of the chain as a whole, the contribution of each configuration being multiplied by the statistical weight for that configuration.

Full details on the formulation of matrices here represented generally by  $\mathcal{P}_i$  are given elsewhere<sup>1, 5</sup>. The methods briefly described yield results which are free of mathematical approximations. Only the physical model, i.e. the rotational isomeric state scheme, stands as an approximation to the real chain<sup>19, 20</sup>. Errors associated with this idealization can be made quite small<sup>1, 20</sup>.

Table 3 presents a comparison of calculations of the mean-square end-to-end distance, expressed as the characteristic ratio  $\langle r^2 \rangle / nl^2$  evaluated in the limit  $n \rightarrow \infty$ , according to various models. Parameters are chosen to be representative of the polymethylene chain; calculations have been carried out for a temperature of 140°C. Experimental results for this temperature are quoted at the foot of the table.

Table 3. Characteristic ratios and their temperature coefficients calculated for various chain models compared with experimental results on polymethylene at 140°C

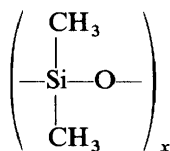
Model	$\langle r^2 \rangle_0 / nl^2$	$d \ln \langle r^2 \rangle_0 / dT$
Freely jointed chain	1	0
Free rotation, $\theta = 68^\circ$	2.2	0
Threefold symmetric potential	2.2	0
Rotational isomeric states: $t, g^+, g^-$ .		
Neighbouring rotations independent; $E_g - E_t = 500 \text{ cal mole}^{-1}$	3.4	$-1.15 \times 10^{-3}$
Same with neighbour dependence; $\Delta E_{g^+g^-} = 2000 \text{ cal mole}^{-1}$ .	6.8	$-1.15 \times 10^{-3}$
Experimental, 140°C	6.7 ( $\pm 0.3$ )	$-1.1 (\pm 0.1) \times 10^{-3}$

For the hypothetical freely jointed chain,  $\langle r^2 \rangle = nl^2$  and the characteristic ratio is unity. Fixing the bond angle at  $\theta = 68^\circ$ , the value for an  $n$ -alkane chain, while maintaining free rotation, raises the ratio to 2.2. Introduction of a symmetric threefold potential has no effect, as noted above. (The same holds for any  $m$ -fold symmetric potential with  $m \geq 2$ , as will be apparent.) However, if the energy of the *gauche* minima is raised by 500 cal mole<sup>-1</sup> above the *trans*, then the ratio increases to 3.4. Repression of  $g^+g^-$  states through adoption of the scheme for interdependent rotational states doubles the ratio. Incorporation of this latter feature of the real chain into the treatment has a considerably greater effect on the characteristic ratio than might have been anticipated from its effect on the configuration partition function

(compare *Table 2*). The fact that the temperature coefficient is unaffected by repression of  $g^{\pm}g^{\mp}$  pairs is fortuitous. It is possible to show<sup>23</sup> that agreement between theoretical and experimental values of both the characteristic ratio and the temperature coefficient cannot be achieved without taking account of rotational interdependence; a comparatively large value of  $\Delta E_{g^{\pm}g^{\mp}}$  is required, whereby  $g^{\pm}g^{\mp}$  states are reduced to very low incidence. The value adopted for  $E_g - E_t$  is independently supported by results on the lower *n*-alkanes as pointed out above; that for  $\Delta E_{g^{\pm}g^{\mp}}$  finds partial substantiation in conformational energy calculations<sup>23</sup>.

### OTHER CHAINS WITH UNINTERRUPTED ROTATIONAL INTERDEPENDENCE

Interdependence of rotational states plays an important role in other typical polymer chains including, for example, those of polyoxymethylene<sup>26</sup>  $(\text{CH}_2\text{—O—})_x$ , polyoxyethylene<sup>27</sup>  $(\text{CH}_2\text{—CH}_2\text{—O—})_x$ , and polyphosphates<sup>28</sup>  $(\text{PO}_3^-\text{—O—})_x$ . In the first of these three examples, the *gauche* conformation is preferred<sup>26</sup>; in the second the *trans* form is preferred for the C—O bonds and the *gauche* for the C—C bond<sup>27</sup>. Analysis of the polyphosphate chain<sup>28</sup> suggests the interesting situation in which *trans* and *gauche* states are about equally favoured, except that *gg* pairs, irrespective of signs ( $\pm$ ), are largely suppressed. The poly(dimethylsiloxane) chain<sup>29</sup>



prefers the *trans* conformation but, in contrast to the polymethylene chain, this preference does not bestow high extension owing to the large difference between bond angles at Si and O ( $\theta_{\text{Si}} = 70^\circ$ ,  $\theta_{\text{O}} \approx 37^\circ$ )<sup>30</sup>. Again,  $g^{\pm}g^{\mp}$  pairs are reduced to low incidence.

Interdependence is especially important in vinyl chains<sup>24</sup> owing to the proliferation of second order interactions produced by the presence of the substituent, to which attention was directed above.

Lest the impression be given that the threefold rotational potential is a universal norm, it is worth noting that the presence of *p*-phenylene rings in a chain generally introduces a segment having a twofold potential<sup>31</sup>. In the interesting case of a chain of sulphur atoms<sup>22</sup>, not only is the rotational potential twofold; in addition the *trans* (planar) form is energetically disfavoured to the extent of about 10 kcal mole<sup>-1</sup>. The preferred conformations occur at  $\varphi \approx \pm 90^\circ$ .

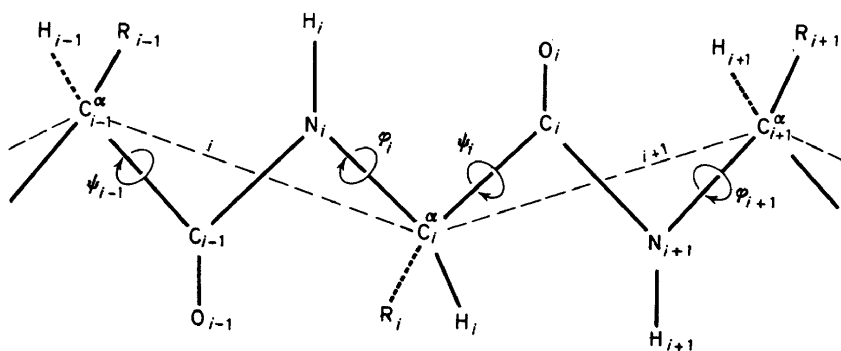
In vinyl chains the dependence of the rotational state of a bond on the state of its neighbour is so strong as to perpetuate the correlations from one bond to the next over many bonds<sup>15, 24</sup>. The 'long range' character of conformational interdependence is particularly marked for chains which are predominantly isotactic, i.e. which consist of a preponderance of *meso* dyads. If the substituent is branched in the manner of the last example of *Table 2*, then interdependence may be perpetuated over many units irrespective of the

stereochemical composition, as Abe<sup>13, 25</sup> has shown. The range of conformational interdependence in vinyl polymers has a profound effect on the properties of the chain<sup>24</sup> including not only its average dimensions but also its optical anisotropy<sup>9, 10</sup> and the breadths and magnitudes of the chemical shifts in its n.m.r. spectrum<sup>14, 15</sup>.

### CHAINS WITH LOCALIZED ROTATIONAL INTERDEPENDENCE

Whereas interdependence of the state of one bond on its predecessors continues without interruption throughout the chain in the examples discussed above, there are other kinds of chains in which interdependence is localized within individual repeat units. The conformations of the set of bonds comprising a given repeat unit are mutually interdependent in such chains, but the conformations of neighbouring units are independent. Interruption of the interdependence at the inter-unit junctions changes the complexion of the mathematical treatment. In the terminology of statistical mechanics, the macromolecule can then be treated as a collection of independent subsystems (i.e. units). It is a fact, however paradoxical it may appear, that the most complicated polymers (e.g. polysaccharides and polynucleotides) often fall into the category of more tractable chains in which interdependence is localized. The difficulties attending rational treatment of such chains may be ameliorated on this account.

Polypeptides afford prime examples of chains with localized interdependence<sup>32</sup>. The structure of the L-polypeptide chain is illustrated in *Figure 1*. The partial double bonding of the amide linkage assures planarity of the



*Figure 1.* Two units of a polypeptide chain in the extended (planar) conformation. Virtual bonds connecting  $\alpha$ -carbon atoms are shown by dashed lines.

peptide unit, which is preponderantly *trans*. Hence, the atoms of a given 'peptide unit', defined as that portion of the molecule extending from one  $\alpha$ -carbon atom to the next (but exclusive of substituents H and R attached to the  $\alpha$ -carbons), are coplanar. It is convenient to introduce hypothetical 'virtual bonds', shown by dashed lines in *Figure 1*, between successive  $\alpha$ -carbon atoms. Their lengths are fixed at  $l_u = 3.80 \text{ \AA}$  by the geometry of the peptide unit.

The chain consisting of  $x + 1$  amino acid residues may be viewed as a succession of  $x$  virtual bonds, or virtual bond vectors, each spanning one peptide unit. Rotations are permitted about the two real bonds flanking the  $\alpha$ -carbon. The rotation about the N—C $^\alpha$  bond is designated by  $\varphi$  and the rotation about the C $^\alpha$ —C' bond by  $\psi$ , each being measured in the right-hand sense relative to the *trans* conformations where  $\varphi = 0$  and  $\psi = 0$ . Thus, the orientation of a peptide unit (and its virtual bond) relative to the preceding unit is determined by the angles  $\varphi$  and  $\psi$  for the pair of bonds at the intervening  $\alpha$ -carbon. The configuration of the chain as a whole is determined by the set  $\{\varphi, \psi\}$  of rotation angles at the internal C $^\alpha$  atoms. Representation of the chain in this manner by virtual bonds of fixed length and location within the respective structural units greatly simplifies analysis of the chain configuration.

As will be apparent from inspection of *Figure 1*, the rotations  $\varphi$  and  $\psi$  for a given bond pair are strongly interdependent; steric obstructions to rotation about one bond depend markedly on the value assigned to the rotation angle for the other. Careful inspection of models reveals, however, that the pair of rotations  $\varphi_i, \psi_i$  at C $^\alpha_i$  are quite independent of rotations of the adjoining pairs  $\varphi_{i-1}, \psi_{i-1}$  and  $\varphi_{i+1}, \psi_{i+1}$ . The conformational energy  $E_i(\varphi_i, \psi_i)$  for unit  $i$  therefore may be treated without regard for the assignments to other pairs. The total conformational energy for the chain as a whole can be expressed as the sum

$$E = \sum_{i=1}^x E_i(\varphi_i, \psi_i) \quad (7)$$

in which the independent variables  $\varphi_i, \psi_i$  are separated in pairwise fashion.

The conformational energy for the polymethylene chain and others considered above do not lend themselves to separation in like manner. Owing to the uninterrupted neighbour interdependence in those chains, the energy takes the form

$$E = \sum_{i=2}^{n-1} E_i(\varphi_{i-1}, \varphi_i) \quad (8)$$

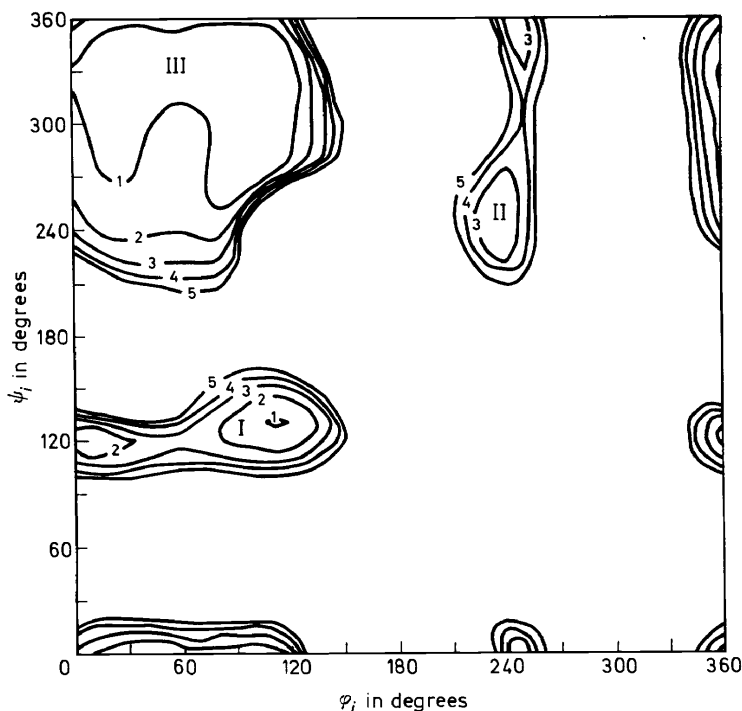
Resolution of the energy into a sum of terms such that each independent variable occurs in one and only one term of the sum is not possible for chains of this character.

It is to be noted further that the energy function  $E_i(\varphi_i, \psi_i)$  for the peptide residue depends only on the substituent R $_i$  of residue  $i$ ; it does not depend, in general, on the substituents R of adjoining residues (the proline residue excepted<sup>33</sup>). The stereochemical configuration of the residue is important of course. Here we take for granted that it is of the L-configuration.

In view of the localized dependence of the energy associated with residue  $i$  on the angles of rotation for the single bonds attached to its  $\alpha$ -carbon and the exclusive dependence of the energy function for the  $i$ th unit on the substituent R $_i$ , it is expedient to formulate an energy function for each kind of residue. The energy  $E(\varphi, \psi)$  estimated for the L-alanyl residue by semi-empirical calculations is shown in the form of a contour diagram in *Figure 2*. Contours are drawn at intervals of 1 kcal mole $^{-1}$ . Two principal minima

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appear: one occupying a large domain in the upper left-hand quadrant, and the other a very restricted region near  $120^\circ, 120^\circ$ . The former accounts for more than 93 per cent of the partition function  $z^{(2)}$  associated with the two angles; the latter contributes about 5.5 per cent. The former represents comparatively extended conformations not far removed from the *trans, trans* conformation. The latter (approximately  $g^+g^+$ ) represents a more compact conformation. The partition function  $z^{(2)}$  estimated by integration over the surface in *Figure 2* is *ca.* 1.25 squared radians at  $300^\circ\text{K}$ , which corresponds



*Figure 2.* Conformational energy contours at intervals of 1 kcal mole<sup>-1</sup> for the L-alanyl residue. From Brant, Miller and Flory, ref. 32.

to 3.2 per cent of the configuration space. The partition function per bond,  $\{z^{(2)}\}^\ddagger \approx 1.12$  radian, is somewhat greater than for polymethylene (see *Table 1*).

Average properties for the chain as a whole may be determined by first taking the average of the appropriate quantity over the configuration space of one residue, each configuration being weighted according to the energy as represented in *Figure 2*. For the evaluation of  $\langle r^2 \rangle$ , the required quantity is the orthogonal matrix  $T_i$  for transformation of a vector from the coordinate system affixed to peptide units  $i + 1$  to that of unit  $i$ . For other quantities the

appropriate generator matrix (corresponding to  $\mathcal{P}_i$  in equation 6) must be averaged. In general, if  $\mathbf{M}$  is the matrix to be averaged, we may take

$$\langle \mathbf{M} \rangle = \sum_{\varphi, \psi} \omega_{\varphi, \psi} \mathbf{M}(\varphi, \psi) / \sum_{\varphi, \psi} \omega_{\varphi, \psi} \quad (9)$$

where  $\omega_{\varphi, \psi}$  is the statistical weight given by the Boltzmann factor for the energy  $E(\varphi, \psi)$  at  $\varphi, \psi$  on the energy surface, and the summation is taken over terms at uniform intervals of  $\varphi$  and of  $\psi$ , e.g. at intervals of  $10^\circ$ . The desired average property for the chain as a whole is readily calculated from  $\langle \mathbf{M} \rangle$ . For example, in the limit of a very long chain of identical residues

$$\lim_{x \rightarrow \infty} (\langle r^2 \rangle / x l_u^2) = (\mathbf{E} + \langle \mathbf{T} \rangle) (\mathbf{E} - \langle \mathbf{T} \rangle)^{-1}$$

where  $\mathbf{E}$  is the identity matrix of order three and  $l_u$  is the length of the virtual bond. If the chain consists of a variety of residues as in the case of a protein, then it is necessary to proceed according to equation 6, factors for the various residues being introduced in the order of their occurrence in the chain.

Owing to the preference for the extended conformation noted above, the characteristic ratio for the L-polypeptide in which  $\text{R} = -\text{CH}_2-\text{CH}_2-\text{R}'$  is quite large, being about nine<sup>34</sup>.

The structures of polysaccharides permit their representation according to the same scheme as the polypeptides. Two repeat units of the cellulose chain are shown in Figure 3, the anhydroglucose rings being in the stable chair ( $C_1$ ) form. The vectors connecting successive ether oxygen atoms are fixed by this ring conformation. They serve as the virtual bonds spanning successive units of the chain. The orientation of one unit with respect to its predecessor depends on the two angles which specify rotations about the ether oxygen bonds. These oxygen atoms which join successive units are well separated, the length of the virtual bond being 5.45 Å. Hence, rotations about the pair of single bonds flanking an ether oxygen are independent of neighbouring rotational pairs. The same conditions hold for the amylose chain in which the glycosidic linkage is of the  $\alpha$  configuration instead of  $\beta$ . Hence, both of these chains can be treated according to the scheme outlined above for polypeptides.

Yathindra and Rao<sup>35</sup> and Brant and co-workers<sup>36</sup> have calculated conformational energies for these polymers as functions of the rotational

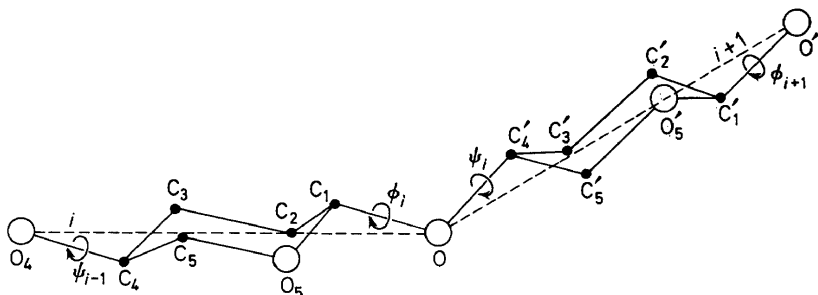


Figure 3. Two units of the cellulose chain with  $\varphi = \psi = 0$ . Virtual bonds are shown by dashed lines. From Yathindra and Rao, ref. 35.

angles, designated  $\varphi$  and  $\psi$  by analogy to the polypeptides. In each case  $E(\varphi, \psi)$  is characterized by one major minimum. The significance of comparisons of the conformation energy surfaces must be qualified by recognition of drastic differences in the geometries of these isomeric polysaccharides. It is noteworthy nevertheless that the minimum for the cellulose chain<sup>35</sup> centres near  $\varphi = 60^\circ$ ,  $\psi = 0^\circ$ , i.e. fairly close to the fully extended (coplanar) form at  $\varphi = 0^\circ$ ,  $\psi = 0^\circ$  shown in *Figure 3*. Chains of typical cellulose derivatives have characteristic ratios

$$\langle r^2 \rangle / x_l^2 \approx 40 \text{ to } 60$$

clearly indicating an unusually high degree of extension.

The minimum calculated for amylose is even more confined than that for cellulose<sup>35, 36</sup>. This finding indicates the amylose chain to be 'stiffer' than cellulose in the sense of the usage above of this ill-defined term. Its characteristic ratio, about six, is much smaller than for cellulose, and this fact has generally been accepted as supporting the opposite assertion, namely, that the amylose chain is much more flexible than that of cellulose. The conformational energy calculations (and indeed, even qualitative examination of models) refute this view.

The domain of the minimum for the amylose chain<sup>36</sup> occurs near  $\varphi = -25^\circ$ ,  $\psi = 180^\circ$ . In contrast to the cellulose chain<sup>35</sup>, it is well removed from the locus of extended conformations. For this reason the characteristic ratio for the amylose chain<sup>35</sup> is much less than that of cellulose. The comparison of these two polysaccharide chains underscores the importance of distinguishing chain extension from stiffness.

The 1,4-polyisoprenes are further examples of natural polymers in which interdependence is localized<sup>17, 37</sup>. Virtual bonds are unsuitable here. However, neighbour dependence of rotations about skeletal single bonds is interrupted by the double bond. It is convenient therefore to define a repeat unit to consist of the three single bonds succeeding a double bond and to include therewith the following double bond<sup>17</sup>. Rotational interdependence occurs within the set of three single bonds but these three bonds can be considered to be unaffected by the rotational states of the single bonds of preceding and following units. The chain can therefore be treated in terms of independent repeat units, the conformational energy of the unit being fully determined by the rotational states of its three single bonds. The isomeric polymer *cis*-1,4-polyisoprene (natural rubber), can be treated analogously<sup>17</sup>, the conformations of repeat units defined in the same manner being mutually independent. The corresponding synthetic 1,4-polybutadienes, in which the methyl substituent is replaced by a hydrogen atom, are susceptible also to treatment as chains of independent units consisting of four bonds inclusive of the double bond<sup>37, 38</sup>. Polymers in which both *trans* and *cis* units occur are readily amenable to treatment as well.

Other polymers which may be treated as sequences of independent units include polyesters<sup>39</sup>, polyamides<sup>40</sup> and polycarbonates<sup>31</sup>. In each case rotational interdependence obtains within the structural unit, but is interrupted by the functional linkage. A recent study of polynucleotide chains<sup>41</sup> brings them also within the scope of analysis as chains of configurationally

independent repeat units, despite their complicated chemical structure. Each unit can be represented approximately by two virtual bonds, one spanning four skeletal bonds and the other two.

## CONCLUSIONS

The examples selected for brief discussion above illustrate the variety of chemical structures to be found even amongst the more familiar macromolecular substances. Not only do the impedances to rotation differ greatly from one example to another; the geometrical characteristics of the skeletal frameworks are widely diverse as well.

With these facts in mind, it becomes clear that no simple mathematical model can adequately represent all polymer chains. The two models that have been most widely used in attempts to this end are the Kuhn freely jointed chain and the Porod-Kratky wormlike chain. Through arbitrary adjustment of the bond length, certain properties, like  $\langle r^2 \rangle$  or the mean-square radius of gyration, can of course be matched by either model in the long-chain limit. The former model is quite unsatisfactory for chains of shorter length. In some cases the wormlike chain reproduces the spatial dimensions down to fairly short chains; in other cases it fails to represent the dependence of these properties on chain length in the lower range with sufficient accuracy. In any event, the parameters chosen to optimize the agreement between calculations according to the model and experimental data do not lend themselves to physical interpretation in terms of the actual structure. The arbitrary parameters of the model on the one hand and the geometrical and conformational characteristics of the chain on the other are fundamentally incongruous.

Properties such as dipole moments, optical anisotropies, strain dichroism and rotational isomerization by deformation are quite beyond the scope of the artificial models owing to the fact that they depend on vector or tensor contributions of individual units. The spatial orientations of these contributions within the unit are all important. Only if the contributions can be construed to be cylindrically symmetrical with respect to the axis of the hypothetical unit can one of the aforementioned models be applied. This condition seldom is fulfilled.

Artificial models have, to be sure, served an important purpose in establishing the forms of various mathematical relationships by means of which to represent and correlate experimental results. Now that methods are available for treating properties of polymer chains realistically, in terms of their structures, artificial models have been rendered largely superfluous. However, the importance of these newer methods lies not so much in the facility with which they can be applied to the analysis of chemical and physical properties, but rather in the insights they afford to the understanding of the spatial configurations of polymeric chains. Through their use, conformational schemes may be put to test; and their validation or rejection can be expected eventually to lead to a realistic comprehension of the spatial-configurational characteristics which underlie the special properties of polymeric chains of various kinds.

The foregoing commentary must be qualified by the acknowledgement that



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the methods discussed apply only to equilibrium properties of polymer chains. This present limitation notwithstanding, one may safely assert that the dynamic properties of polymers cannot be rationally interpreted without a thorough comprehension of structure–configuration relationships.

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