14,000.[22] A rather large value of about 4 is obtained for the ratio of M_c/M_e, but this, of course, is no more than a tentative estimate. In order to locate M_c of bulk polymers, the shear creep study extending to a molecular weight of 2000 is now in progress in our laboratory.

Recently, Graessley and Segal have presented a semiempirical equation which expresses J_e in terms of the entanglement density E.[30] For highly entangled systems, the equation is simplified as

$$J_{eR}/J_e = (1/5)E \tag{3}$$

in which J_{eR} represents the steady-state compliance for a monodisperse collection of Rouse chains, *i.e.*

$$J_{eR} = (2/5)(M/\rho RT) \tag{4}$$

Here ρ is the density and RT has its usual meaning. Since E is given by M/M_e, the above equation (3) shows the independence of J_e on M, in agreement with the present result. However, the values of J_e and M_e given in Table II yield

$$J_{eR}/J_e = 0.052E \tag{5}$$

The numerical coefficient is smaller by a factor of about 4 than that in eq 3.

In conclusion, the present results seem to be favorable to the view that the independent nature of J_e on M first observed on polystyrene and poly(α-methylstyrene) is common to a wider class of narrow-distribution polymers, at least of nonpolar polymers.

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(30) W. W. Graessley and L. Segal, *Macromolecules*, **2**, 49 (1969).

Configurational Statistics of 1,4-Polybutadiene Chains

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ABSTRACT: 1,4-Polybutadiene chains are treated in terms of structural units CH—CH$_2$—CH$_2$-CH═ consisting of three single bonds bounded by double bonds. Although conformational interactions differ markedly depending on the steric configuration, cis or trans, of the adjoining double bonds, those within a given unit are essentially independent of the conformations of neighboring units in all cases. The units thus defined may be treated, therefore, as statistically independent. The present scheme as applied to the stereoregular polymers in which all double bonds are either cis or trans is virtually equivalent to that of Mark. It offers the advantage of being readily applicable to polymers comprising both cis and trans residues CH$_2$—CH═CH—CH$_2$ in any specified proportion and succession. Statistical weight parameters are chosen in the light of conformational energy calculations and newer results of spectroscopic investigations on low molecular analogs. Average chain dimensions and their temperature coefficients, strain-birefringence coefficients, average bond conformations, coefficients of rotational isomerization by stretching, and strain-induced dichroic effects are calculated as functions of the stereochemical composition. The properties of predominantly trans polymers are much more sensitive to stereoirregularity (*i.e.*, to cis residues) than are those of predominantly cis polymers.

Rotational isomeric state schemes for the statistical treatment of *cis*-1,4- and *trans*-1,4-polybutadiene chains and of the corresponding polyisoprenes were formulated by Mark.[1-3] He succeeded in giving a coherent account of the characteristic ratio $C_\infty = (\langle r^2\rangle_0/nl^2)_{n\to\infty}$ and of the temperature coefficient $\mathrm{d}\ln\langle r^2\rangle_0/\mathrm{d}T$ of the mean-square end-to-end distance $\langle r^2\rangle_0$ for each of these four polymers. His analysis is in satisfactory accord with results of experiments. Ishikawa and Nagai[4,5] applied the same scheme to the treatment of the strain birefringence of the polydienes.

In this paper we present a comprehensive treatment of the properties of poly-1,4-butadiene (PBD). In addition to revised calculations on the characteristic ratio, its temperature coefficient, and the strain birefringence,[3,6-8] we have investigated average bond conformations,[3,9] rotational isomerization with stretching,[10] and preferential orientations[11] of *cis*- and *trans*-C—CH═CH—C *residues* according to methods developed recently. Mark's[1,2] rotational isomeric scheme for PBD chains is reexamined and minor modifications are introduced. It is reformulated in terms of *structural units* CHCH$_2$CH$_2$CH═ embracing three single bonds and bounded by successive double bonds of the chain. Inasmuch as these may be either cis or trans, four kinds of structural units are distinguished. Through analysis of the interactions dependent upon rotations about the sequence of three single bonds comprising each kind of structural unit, a basis is established for treating chains containing both cis and trans double bonds (*i.e.*, both cis and trans residues) in any proportion and any order of succession. Calculations of the properties of PBD chains are carried out as a function of the fraction f_{cis} of cis residues throughout the range $0 \leq f_{\mathrm{cis}} \leq 1$. We thus explore the effects of stereoirregularity.

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(1) J. E. Mark, *J. Amer. Chem. Soc.*, **88**, 4354 (1966).
(2) J. E. Mark, *ibid.*, **89**, 6829 (1967).
(3) P. J. Flory, "Statistical Mechanics of Chain Molecules," Interscience, New York, N. Y., 1969.
(4) T. Ishikawa and K. Nagai, *J. Polym. Sci., Part A-2*, **7**, 1123 (1969).
(5) T. Ishikawa and K. Nagai, *Polym. J.*, **1**, 116 (1970).
(6) L. R. G. Treloar, "The Physics of Rubber Elasticity," Clarendon Press, Oxford, England, 1958.
(7) P. J. Flory, R. L. Jernigan, and A. E. Tonelli, *J. Chem. Phys.*, **48**, 3822 (1968).
(8) K. Nagai, *ibid.*, **51**, 1265 (1969).
(9) R. L. Jernigan and P. J. Flory, *ibid.*, **50**, 4165 (1969).
(10) Y. Abe and P. J. Flory, *ibid.*, **52**, 2814 (1970).
(11) P. J. Flory and Y. Abe, *Macromolecules*, **2**, 335 (1969).

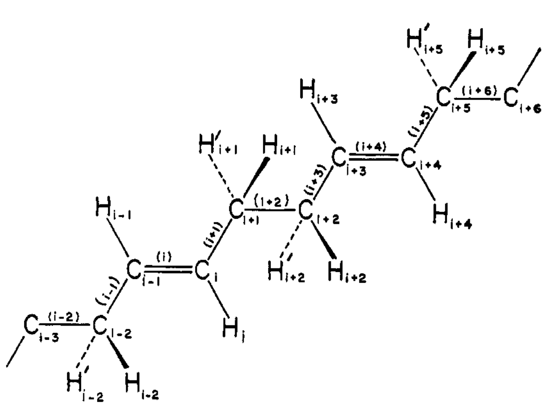


Figure 1. The 1,4-polybutadiene chain in the planar, all-trans conformation. This highly disfavored form is shown for convenience in enumerating atoms and bonds of the chain.

Theory

Conformational Energies and Rotational States. The serial numeration of atoms and bonds is indicated in Figure 1. Rotational angles φ about bonds of the chain skeleton are measured relative to the planar trans conformation for which $\varphi = 0°$.

X-Ray diffraction studies[12,13] on *cis-* and *trans*-PBD indicate that CH_2-CH_2 bonds such as bond $i + 2$ connecting C_{i+1} and C_{i+2} in Figure 1 assume the trans conformation in the crystalline state. The rotational states accessible to these bonds in the amorphous state or in solution are concluded to be trans and gauche ($\varphi \approx \pm 120°$) by analogy to CH_2-CH_2 bonds of normal alkanes and their derivatives, which generally assume both trans and gauche conformations in the gaseous or liquid state but choose the trans conformation in the crystalline state.

According to studies on the rotational isomerism of propylene and its homologs, the rotational energy minima for the C—C bond adjoining the double bond in the sequence C—C—C=C occurs at the skew ($\varphi \approx \pm 60°$) and cis ($\varphi = 180°$) conformations. Moreover, the barrier to internal rotation is considerably lower than that for C-C bonds of the saturated analogs.[14] For example, the height of the barrier to rotation of the methyl group about the C—C bond in propylene,[15] CH_3—CH=CH_2, is 1.98 kcal mol^{-1}, which is much smaller than 3.4 kcal mol^{-1} for the methyl groups in propane, CH_3—CH_2—CH_3.

These observations on lower homologs lead to the conclusion that the set of rotational states appropriate for the C—C bond adjoining a *trans*-C=C bond is cis (c), skew plus (s$^+$), and skew minus (s$^-$).[1–3,16,17] Further to be noted is the fact pointed out by Mark[1,2] that nonbonded interactions dependent upon one or more of the rotation angles for the three skeletal single bonds of the structural unit $CHCH_2CH_2CH$= following a trans double bond do not depend (to an appreciable degree) on rotations about single bonds of the preceding triplet. In other words, the incidence of a given conformation in such a structural unit is independent of the conformations adopted by neighboring units. Whereas the rotational states for individual bonds *within* a given unit are mutually interdependent[1–3] as discussed in the following section, the interdependence is interrupted by a trans double bond.

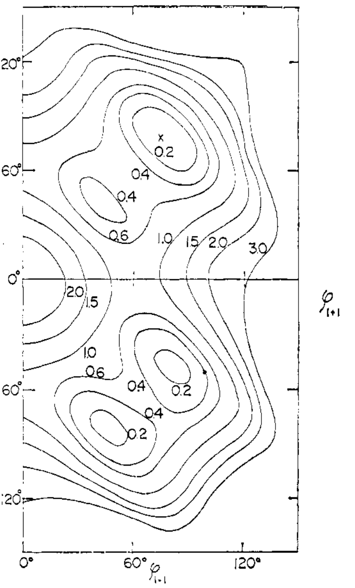
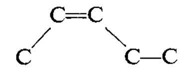


Figure 2. Conformational energy contours for the *cis*-C—CH_2—CH=CH—CH_2—C bond sequence as functions of the rotational angles φ_{i-1} and φ_{i+1} about two C—C bonds adjoining the C=C bond. The numbers on each contour indicate energies in kilocalories per mole. The location of the lowest minimum is shown by X.

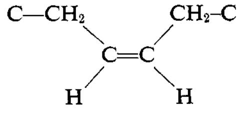
In the case of a *cis*-C=C bond, repulsions between hydrogen atoms of the adjoining groups (*e.g.*, methylene or methyl) diminish the barrier to rotation markedly. Thus, the barrier to rotation of the methyl groups of *cis*-2-butene is 0.73 kcal mol^{-1},[18] which is only about one-third of the value, 1.95 kcal mol^{-1}, for *trans*-2-butene.[19]

The cis conformation is precluded for the single bond following the cis double bond of the sequence



owing to severe steric repulsions involving the two terminal groups of this sequence. In addition to the remaining s$^+$ and s$^-$ states for such bonds of a cis-1,4 residue of butadiene, Mark[1] suggested that conformations in the vicinity of $\varphi = 0°$ (trans) make a significant, though minor, contribution. He concluded that both of the single bonds adjoining a cis double bond could not simultaneously occur in the trans conformation, however. To the extent that this rule applies, the two triplets of single bonds respectively preceding and following a cis double bond are not independent, in contrast to the case of two such triplets separated by a trans double bond.

In order to investigate in greater detail the degree of interdependence of rotations on either side of a *cis*-C=C bond, the approximate energy contour diagram shown in Figure 2 was calculated for the chain segment



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(12) G. Natta and P. Corradini, *Angew. Chem.*, **68**, 615 (1956).

(13) P. Corradini, *J. Polym. Sci., Part B*, **7**, 211 (1969).

(14) D. R. Hershbach, "Bibliography for Hindered Internal Rotation and Microwave Spectroscopy," Lawrence Radiation Laboratory, University of California, Berkeley, Calif., 1962.

(15) D. R. Lide, Jr., and D. E. Mann, *J. Chem. Phys.*, **27**, 868 (1957).

(16) G. Allegra, U. Flisi, and G. Crespi, *Makromol. Chem.*, **75**, 189 (1964).

(17) G. Allegra, *ibid.*, **110**, 58 (1967).

(18) T. N. Sarachman, *J. Chem. Phys.*, **49**, 3146 (1968).

(19) K. S. Pitzer, *Discuss. Faraday Soc.*, **10**, 66 (1951).

TABLE I
GEOMETRICAL PARAMETERS AND BOND POLARIZABILITIES FOR 1,4-POLYBUTADIENE

Bond lengths, Å	
C=C	1.34
=C—C- (such as bond $i + 1$)	1.51
-C—C- (such as bond $i + 2$)	1.53
C—H	1.10
Bond Angles, Deg	
$\pi - \angle$C=C—CH$_2$	55
$\pi - \angle$C=C—H	61
$\pi - \angle$C—C—C	68
$\angle$H—C—H	109
Bond Polarizabilities, 10^{-24} cm^3 [a,b]	
$\Delta\alpha_{C=C} = 3.04$	
$\Delta\alpha_{C-C} = 1.42$	
$\Delta\alpha_{C-H} = 0.22$	

[a] $\Delta\alpha = \alpha_{\parallel} - \alpha_{\perp}$. [b] C. Clément and P. Bothorel, *C. R. Acad. Sci.*, **258**, 4757 (1964).

TABLE II
PARAMETERS FOR THE INTRAMOLECULAR ENERGY FUNCTION

Atom pair	$10^{-3}a_{kl}$, kcal mol^{-1}	b_{kl}, Å	c_{kl}, Å^6 kcal mol^{-1}
C···C	909	4.6	360
C···H	86	4.6	130
H···H	9.1	4.5	45

with rotation angles φ_{i-1} and φ_{i+1} of the two CH$_2$—CH bonds flanking the *cis*-C=C bond treated as independent variables. The calculations were carried out according to the expression

$$E(\varphi_{i-1}, \varphi_{i+1}) = 0.99\,(\cos 3\varphi_{i-1} + \cos 3\varphi_{i+1}) + \sum_{k<l} [a_{kl} \exp(-b_{kl}/r_{kl}) - c_{kl}/r_{kl}{}^6] \text{ kcal mol}^{-1} \quad (1)$$

where r_{kl} is the distance between atoms k and l calculated using the geometrical parameters given in Table I; a_{kl}, b_{kl}, and c_{kl} are the constants whose values are given in Table II.[20,21] The balance of the diagram covering the range $\varphi_{i-1} < 0°$ is generated by inversion through the origin (φ_{i-1}, φ_{i+1}) = (0°, 0°). Energies indicated in kilocalories per mole with each curve are taken relative to the minimum marked by × near the point (φ_{i-1}, φ_{i+1}) = (60°, 60°). Energy maps similar to this one, but on a coarser scale showing less detail, were published by Allegra.[17]

Figure 2 indicates the presence of two minima in each quadrant. The two minima in the ++ (and the −−) quadrant have energies of 0 and 340 cal mol^{-1}. The calculated energies for the equivalent minima in the +− (and the −+) quadrant are 150 cal mol^{-1}. The two minima in each quadrant are separated by a very low saddle. They may be viewed as minor features in the broader basins occurring in the four quadrants of the contour energy surface. Hence, to a good approximation each such pair may be represented by a single state, in accordance with the similar device introduced by Abe, Jernigan, and Flory[20] in their analysis of the g$^\pm$g$^\mp$ states in *n*-alkane chains. The states here considered are appropriately located at (φ_{i-1}, φ_{i+1}) = (±60°, ± 60°) according to Figure 2.

The energy of the two minima in the s$^+$s$^-$ domain (and likewise in the s$^-$s$^+$ domain) falls between the energies of the two s$^+$s$^+$ (and s$^-$s$^-$) minima, according to the calculations yielding Figure 2. Comparing the s$^+$s$^-$ with the s$^+$s$^+$ domains, one observes that the respective areas below 0.2, 0.4, and 0.6 kcal mol^{-1} are similar in both of the quadrants shown in Figure 2. It follows that the statistical weights for the s$^\pm$s$^\pm$ and for the s$^\pm$s$^\mp$ should be about the same.

The saddle points near (0°, ±60°) and (±60°, 0°) are quite low, being less than 1 kcal mol^{-1} above the lowest minima; their energies are comparable to the barrier height, cited above, for rotation of the methyl groups of *cis*-2-butene. Hence, Mark's[1,2] conclusion that conformations near φ = 0° may contribute appreciably is supported by these calculations. Following him and other authors,[3,4,17] we introduce a fictitious rotational state at 0° for the C—C bonds adjoining a *cis*-C=C bond. Trans and skew rotational states are therefore assigned for CH$_2$—CH bonds such as bonds $i - 1$ and $i + 1$ adjoining a *cis*-C=C bond.

The energy of the conformation in which *both* of these bonds $i - 1$ and $i + 1$ are trans, *i.e.*, (φ_{i-1}, φ_{i+1}) = (0°, 0°) is sufficiently high to warrant a statistical weight of zero, in confirmation of Mark's[1] conclusion. On the other hand, its energy is only a little greater than twice the energy for each of the four "saddle" states ts$^\pm$ and s$^\pm$t. If, instead of suppressing the tt state altogether, we let $E_{tt} = 2E_{ts}$, then the energies for all states of the bond pair $i - 1$, $i + 1$ are additive in the energies of the individual bonds. This is the underlying condition for mutual independence of bond rotations. Its validity in this instance depends also on the approximate equivalence discussed above of the s$^\pm$s$^\pm$ and s$^\pm$s$^\mp$ states.

The mutual independence of the pair of bonds $i - 1$, $i + 1$ flanking the cis double bond assures that the triplets of single bonds of which each is a member are likewise independent (subject only to the trivial approximations discussed above). Thus, the triplet of single bonds comprising the structural unit as here defined, irrespective of whether it is bounded by cis or trans double bonds, may be regarded as independent of neighboring structural units. This circumstance greatly facilitates treatment of 1,4-polybutadiene chains comprising both cis and trans residues, as will be apparent below.

Statistical Weight Matrices. Rotational states appropriate for the several kinds of single bonds occurring in 1,4-polybutadiene chains have been delineated above. It remains to consider the higher order interactions[3] that depend upon two or more angles of rotation about single bonds of the chain skeleton. We have already pointed out that such interdependence between neighboring rotations is effectively terminated at the double bonds. Hence, it suffices to consider only the higher order interactions for a given triplet of single bonds, or, more accurately stated, interactions that depend on two or more of the rotations about single bonds of the *same* structural unit.

Listed in Table III are the triplet conformations which place nonbonded atoms of the relevant chain sequence CCH=CHCH$_2$CH$_2$CH=CHC at distances such that the encounter is appreciably repulsive. Interactions for the respective kinds of units bounded by two cis, by two trans, or by a cis and a trans double bond are listed separately as indicated. The necessary calculations were carried out using the structural data given in Table I. The criteria for steric overlap are specified by assigning radii of 1.08 Å to H and 1.60 Å to C atoms. These values were deliberately taken to be lower than the usual van der Waals radii of 1.2 and 1.7 Å,

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(20) A. Abe, R. L. Jernigan, and P. J. Flory, *J. Amer. Chem. Soc.*, **88**, 631 (1966).
(21) R. A. Scott and H. A. Scheraga, *J. Chem. Phys.*, **42**, 2209 (1965).

TABLE III
HIGHER ORDER INTERACTIONS[a] FOR THE BOND SEQUENCE
-CCH=CHCH$_2$CH$_2$CH=CHC-

Conformation	Significant atom–atom interactions and distances, Å	Statistical weight
	Cis,cis	
	None	
	Trans,trans	
cg±c	$H_{i-1}\cdots C_{i+3}$ (2.28), $H_{i-1}\cdots C_{i+4}$ (2.48), $C_{i-1}\cdots H_{i+4}$ (2.48), $C_i\cdots H_{i+4}$ (2.28)	β
cg±s± (or s±g±c)	$H_{i-1}\cdots C_{i+3}$ (2.28), $C_{i-1}\cdots H_{i+3}$ (2.26), $H_{i-1}\cdots H_{i+3}$ (1.60)	β
cg±s∓ (or s±g∓c)	$H_{i-1}\cdots C_{i+3}$ (2.28), $H_{i-1}\cdots C_{i+4}$ (2.12), $H_{i-1}\cdots H_{i+4}$ (1.94)	β
	Cis,trans	
tg±c	$C_i\cdots H_{i+4}$ (2.28)	$\beta^{1/2}$
s±g±c	$C_i\cdots H_{i+4}$ (2.28), $H_i\cdots C_{i+4}$ (2.26), $H_i\cdots H_{i+4}$ (1.60)	β
s±g∓c	$C_{i-2}\cdots H_{i+4}$ (2.10), $C_{i-1},\cdots H_{i+4}$ (2.12), $C_i\cdots H_{i+4}$ (2.28)	β

[a] Interactions depending on two or more rotations about single bonds.

respectively. According to eq 1, the interaction energy for the H$\cdots$H pair at $1.08 \times 2 = 2.16$ Å and that of the C$\cdots$H pair at $1.08 + 1.60 = 2.68$ Å are 130 and 150 cal mol^{-1}, respectively, above the values at the energy minima. Thus, the chosen radii set the approximate limits for appreciable steric repulsions.

The Cis,cis Unit. Interactions of higher order do not occur in any conformation accessible to the individual bonds of a cis,cis structural unit. It follows that the three single bonds situated between two cis double bonds are mutually independent. In the interests of developing a scheme universally applicable to all four kinds of sequences, however, we adopt a matrix formulation of the statistical weights. Letting $\mathbf{U}_a$, $\mathbf{U}_b$, $\mathbf{U}_c$, and $\mathbf{U}_d$ denote the statistical weight matrices for the four bonds of a structural unit commencing with the single bond ($i + 1$ in Figure 1) that follows the double bond at the beginning of a structural unit, we have for this case

$$\mathbf{U}_a = \begin{array}{ccc} t & s^+ & s^- \\ [\zeta & 1 & 1] \end{array} \tag{2}$$

$$\mathbf{U}_b = \left[\begin{array}{c|ccc} & t & g^+ & g^- \\ t & 1 & \sigma & \sigma \\ s^+ & 1 & \sigma & \sigma \\ s^- & 1 & \sigma & \sigma \end{array}\right] \tag{3}$$

$$\mathbf{U}_c = \left[\begin{array}{c|ccc} & t & s^+ & s^- \\ t & \zeta & 1 & 1 \\ g^+ & \zeta & 1 & 1 \\ g^- & \zeta & 1 & 1 \end{array}\right] \tag{4}$$

$$\mathbf{U}_d = \left[\begin{array}{c|c} t & 1 \\ s^+ & 1 \\ s^- & 1 \end{array}\right] \tag{5}$$

where ζ is the statistical weight[22] for the trans state of bond $i + 1$ and or of bond $i + 3$ relative to a value of unity for the s± states, and σ is the statistical weight for the g± states of CH$_2$–CH$_2$ bond $i + 2$ relative to a value of unity for the t state. Rotational states for single bonds are indexed on the margins of the matrices.

With statistical weight matrices defined in the manner of eq 2–5, the partition function for a structural unit spanning the portion of the chain from one double bond to the next is given by

$$z^{(4)} = \mathbf{U}_a\mathbf{U}_b\mathbf{U}_c\mathbf{U}_d \tag{6}$$

We so define the matrices $\mathbf{U}_a$–$\mathbf{U}_d$ as to preserve this relationship for each of the different kinds of structural unit. In the particular case of a cis,cis unit

$$z_{\text{cis,cis}}^{(4)} = (\zeta + 2)^2(1 + 2\sigma) \tag{7}$$

The foregoing formulation is equivalent to Mark's analysis apart from the implicit assignment of a statistical weight ζ^2 instead of zero to the tt state for the pair of bonds flanking a cis double bond. Since $\zeta \approx 0.10$ (see below; also see ref 1), the difference is trivial. The principal departure from Mark's formulation consists in the expression of the statistical weights in terms of the triplets of single bonds between the pair of cis double bonds, this formal alteration having been introduced for the specific purpose of developing a scheme readily applicable to a copolymer of cis and trans residues, as noted earlier.

The Trans,trans Unit. We let ρ denote the statistical weight[23] for the cis conformation of a single bond adjoining a *trans*-C=C bond relative to a value of unity for a skew conformation. Thus

$$\mathbf{U}_a = \begin{array}{ccc} c & s^+ & s^- \\ [\rho & 1 & 1] \end{array} \tag{8}$$

Statistical weight matrices for the remaining single bonds of the trans,trans unit depend on interactions of higher order. Those that are significant are listed in Table III. Of these, the C$\cdots$H interaction at a distance of 2.28 Å is peculiar to a cg±, or g±c, state for adjacent pairs of single bonds. Two such interactions occur in the cg±c conformation. Each of these H atoms is involved also in a weaker interaction with the remote C atom of the double bond at a distance of 2.48 Å in this conformation. Steric overlaps comparable in severity to those for the cg±c conformation occur in the others cited for a trans,trans unit in Table III. Assessment of the various interactions suggests adoption of the same weighting factor for the combination of *higher order* interactions in each of these distinguishable conformations. We therefore apply the factor β to each, as indicated in the last column of Table III.

Mark[2] applied the factor β^2 to the cgc conformation on the grounds that it possesses a cg and a gc pair. The present analysis suggests β as the more appropriate factor for interactions of higher order in this conformation. This implies a third-order dependence: the factor applicable to the second pair, and therefore to the third bond of the sequence, depends on the state of the first bond. Matrices of 3 × 9 and 9 × 3 order are therefore required as follows.

$$\mathbf{U}_b = \left[\begin{array}{c|ccccccccc} & ct & s^+t & s^-t & cg^+ & s^+g^+ & s^-g^+ & cg^- & s^+g^- & s^-g^- \\ c & 1 & 0 & 0 & \sigma & 0 & 0 & \sigma & 0 & 0 \\ s^+ & 0 & 1 & 0 & 0 & \sigma & 0 & 0 & \sigma & 0 \\ s^- & 0 & 0 & 1 & 0 & 0 & \sigma & 0 & 0 & \sigma \end{array}\right] \tag{9}$$

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(22) Our ζ corresponds to Mark's γ^{-1}.[1] See also ref 3, p 197.
(23) Our ρ corresponds to Mark's α.[2]

$$U_c = \begin{array}{c} \\ \text{ct} \\ \text{s}^+\text{t} \\ \text{s}^-\text{t} \\ \text{cg}^+ \\ \text{s}^+\text{g}^+ \\ \text{s}^-\text{g}^+ \\ \text{cg}^- \\ \text{s}^+\text{g}^- \\ \text{s}^-\text{g}^- \end{array} \begin{array}{c} \begin{array}{ccc} c & \text{s}^+ & \text{s}^- \end{array} \\ \begin{bmatrix} \rho & 1 & 1 \\ \rho & 1 & 1 \\ \rho & 1 & 1 \\ \rho\beta & \beta & \beta \\ \rho\beta & 1 & 1 \\ \rho\beta & 1 & 1 \\ \rho\beta & \beta & \beta \\ \rho\beta & 1 & 1 \\ \rho\beta & 1 & 1 \end{bmatrix} \end{array} \tag{10}$$

Finally

$$U_d = \begin{array}{c} \text{c} \\ \text{s}^+ \\ \text{s}^- \end{array} \begin{bmatrix} 1 \\ 1 \\ 1 \end{bmatrix} \tag{11}$$

The partition function $z_{\text{trans,trans}}^{(4)}$ is obtained by substitution of eq 8–11 in eq 6.

Cis,trans and Trans,cis Units. Higher order interactions for the s±g±c conformations are identical with those for the same conformations of the trans,trans unit (Table III). Interactions for s±g∓c approximate those of the same designation for the trans,trans. Hence, the same statistical weight factor β may be applied to both of these conformations as indicated in the last column of Table III. The conformation tg±c entails the single higher order interaction $C_i \cdots H_{i+4}$ at 2.28 Å. Although the energy associated therewith should be somewhat less than $^1/_2 E_\beta$, we assign the factor $\beta^{1/2}$ to this conformation, having in mind that owing to the low statistical weight (ζ) for the t state of the first bond of the sequence, the occurrence of this conformation must be rare.

On the foregoing basis, the statistical weight matrices for the cis,trans unit are as follows; U_a is given by eq 2.

$$U_b = \begin{array}{c} \\ \text{t} \\ \text{s}^+ \\ \text{s}^- \end{array} \begin{array}{c} \begin{array}{ccccccccc} \text{tt} & \text{s}^+\text{t} & \text{s}^-\text{t} & \text{tg}^+ & \text{s}^+\text{g}^+ & \text{s}^-\text{g}^+ & \text{tg}^- & \text{s}^+\text{g}^- & \text{s}^-\text{g}^- \end{array} \\ \begin{bmatrix} 1 & 0 & 0 & \sigma & 0 & 0 & \sigma & 0 & 0 \\ 0 & 1 & 0 & 0 & \sigma & 0 & 0 & \sigma & 0 \\ 0 & 0 & 1 & 0 & 0 & \sigma & 0 & 0 & \sigma \end{bmatrix} \end{array} \tag{12}$$

$$U_c = \begin{array}{c} \\ \text{tt} \\ \text{s}^+\text{t} \\ \text{s}^-\text{t} \\ \text{tg}^+ \\ \text{s}^+\text{g}^+ \\ \text{s}^-\text{g}^+ \\ \text{tg}^- \\ \text{s}^+\text{g}^- \\ \text{s}^-\text{g}^- \end{array} \begin{array}{c} \begin{array}{ccc} \text{c} & \text{s}^+ & \text{s}^- \end{array} \\ \begin{bmatrix} \rho & 1 & 1 \\ \rho & 1 & 1 \\ \rho & 1 & 1 \\ \rho\beta^{1/2} & 1 & 1 \\ \rho\beta & 1 & 1 \\ \rho\beta & 1 & 1 \\ \rho\beta^{1/2} & 1 & 1 \\ \rho\beta & 1 & 1 \\ \rho\beta & 1 & 1 \end{bmatrix} \end{array} \tag{13}$$

U_d is given by eq 11. Substitution of these matrices in eq 6 gives $z_{\text{cis,trans}}^{(4)}$.

The trans,cis unit is equivalent to the cis,trans; only the order of the bonds is reversed. Thus, for the trans,cis unit, U_a and U_b are given by eq 8 and 9.

$$U_c = \begin{array}{c} \\ \text{ct} \\ \text{s}^+\text{t} \\ \text{s}^-\text{t} \\ \text{cg}^+ \\ \text{s}^+\text{g}^+ \\ \text{s}^-\text{g}^+ \\ \text{cg}^- \\ \text{s}^+\text{g}^- \\ \text{s}^-\text{g}^- \end{array} \begin{array}{c} \begin{array}{ccc} \text{t} & \text{s}^+ & \text{s}^- \end{array} \\ \begin{bmatrix} \zeta & 1 & 1 \\ \zeta & 1 & 1 \\ \zeta & 1 & 1 \\ \zeta\beta^{1/2} & \beta & \beta \\ \zeta & 1 & 1 \\ \zeta & 1 & 1 \\ \zeta\beta^{1/2} & \beta & \beta \\ \zeta & 1 & 1 \\ \zeta & 1 & 1 \end{bmatrix} \end{array} \tag{14}$$

U_d is given by eq 5. Substitution in eq 6 yields $z_{\text{trans,cis}}^{(4)}$.

Configurational Properties. We consider chains having the constitution $CH_3CH{=}(CHCH_2CH_2CH{=})_{x-1}CHCH_3$, where x is the number of butadiene units. The number of structural units defined above is $x - 1$, and the total number of skeletal bonds is $n = 4x - 1$. Rotations about the terminal bonds, indexed 1 and n, respectively, are inconsequential inasmuch as the hindering potentials are threefold symmetric. Hence, they may be ignored insofar as the total partition function Z for the chain is concerned. On this basis we have

$$Z = \prod_{k=1}^{x-1} z_k^{(4)} = (z^{(4)})_1^{(x-1)} \tag{15}$$

The superscript $(x - 1)$ in parentheses in the latter expression denotes the serial product of $x - 1$ factors commencing with the factor having the index, 1, indicated by subscript. This notational device[3] finds further use below. Contributions of terminal bonds to various properties of the chains must of course be included.

The Characteristic Ratio. The characteristic ratio for a chain of n skeletal bonds is defined by

$$C_n = \langle r^2\rangle_0 \Big/ \sum_{i=1}^{n} l_i^2 = \langle r^2\rangle_0 / n\overline{l^2} \tag{16}$$

where $\langle r^2\rangle_0$ is the mean-square end-to-end length of the unperturbed chain and l_i is the length of the ith bond. For the polybutadiene chain we have

$$\sum_i l_i^2 = x(l_a^2 + l_b^2 + l_c^2 + l_d^2) - l_b^2 \tag{17}$$

where a–d identify bonds of the structural unit as defined above.

The square of the end-to-end distance for a specified conformation of the chain is given by [3,24]

$$r^2 = \mathbf{C^* G}_1^{(n)}\mathbf{C} \tag{18}$$

where $\mathbf{G}_1^{(n)}$ is the serial product $\prod_1^n \mathbf{G}_i$ of matrices

$$\mathbf{G}_i = \begin{bmatrix} 1 & 2\mathbf{l}^T\mathbf{T} & l^2 \\ 0 & \mathbf{T} & \mathbf{l} \\ 0 & 0 & 1 \end{bmatrix}_i \tag{19}$$

for each bond; $\mathbf{l}$ and $\mathbf{l}^T$ are representations of the bond vector in its column and row forms, $\mathbf{T}$ is the matrix of the transformation from the coordinate system of bond $i + 1$ to bond i in the specified rotational state, and

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(24) P. J. Flory and Y. Abe, *J. Chem. Phys.*, **54**, 1351 (1971).

$$\mathbf{C}^* = [1 \quad 0 \quad 0 \quad 0 \quad 0]$$

$$\mathbf{C} = \begin{bmatrix} 0 \\ 0 \\ 0 \\ 0 \\ 1 \end{bmatrix} \tag{20}$$

Inasmuch as only the last column of $\mathbf{G}_n$ is required, $\mathbf{T}$ for the nth bond need not be defined.

The average of r^2 over all configurations of the unperturbed chain is given generally by [3,24]

$$\langle r^2\rangle_0 = Z^{-1}(\mathbf{C}^* \otimes \mathbf{J}^*)\mathcal{G}_1{}^{(n)}(\mathbf{C} \otimes \mathbf{J}) \tag{21}$$

where

$$\mathcal{G}_i = \begin{bmatrix} \mathbf{U} & 2(\mathbf{U}\otimes \mathbf{l}^{\mathrm{T}})\|\mathbf{T}\| & l^2\mathbf{U} \\ \mathbf{0} & (\mathbf{U}\otimes \mathbf{E}_3)\|\mathbf{T}\| & \mathbf{U}\otimes \mathbf{l} \\ \mathbf{0} & \mathbf{0} & \mathbf{U} \end{bmatrix}_i \tag{22}$$

$\|\mathbf{T}\|$ is the diagonal array of matries $\mathbf{T}$ for the rotational states of bond i, $\mathbf{E}_3$ is the identity of order three, and

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

$$\mathbf{J} = \begin{bmatrix} 1 \\ \cdot \\ \cdot \\ \cdot \\ 1 \end{bmatrix} \tag{23}$$

The column and row orders of $\mathbf{J}^*$ and $\mathbf{J}$ conform to the row and column orders of $\mathbf{U}_1$ and $\mathbf{U}_n$, respectively. In the case of polybutadiene chains, with statistical weight matrices formulated as set forth above, $\mathbf{J}^* = \mathbf{J} = 1$; hence these factors vanish in eq 21.

Because of the independence of units in the polybutadiene chains, eq 21 may be simplified to

$$\langle r^2\rangle_0 = \mathbf{C}^*\mathbf{G}_1\mathbf{G}_2\langle \mathbf{G}^{(4)}\rangle_1{}^{(x-1)}\mathbf{G}_n\mathbf{C} \tag{24}$$

where $\langle \mathbf{G}^{(4)}\rangle_k$ is the averaged matrix for structural unit k defined by[25]

$$\langle \mathbf{G}^{(4)}\rangle_k = \mathcal{G}_a\mathcal{G}_b\mathcal{G}_c\mathcal{G}_d/z^{(4)}{}_k \tag{25}$$

and $\mathbf{G}_1$, $\mathbf{G}_2$, and $\mathbf{G}_n$ are the matrices given by eq 19 for bonds 1, 2, and n, with $\mathbf{T}$ (or those elements of it which are required) determined in each instance by the fixed geometry of terminal portions of the chain having the constitution specified above. Thus $\mathbf{G}_1$ and $\mathbf{G}_2$ refer to the CH_3—CH and CH═CH bonds at the beginning of the chain and $\mathbf{G}_n$ refers to the CH—CH_3 bond at the right-hand terminus.

Equation 24 is generally applicable to any 1,4-polybutadiene chain consisting of a specified sequence of cis and trans residues. For an all-cis chain, the serial product in eq 24 may be replaced by $\langle \mathbf{G}^{(4)}\rangle_{cc}$ raised to the power $x - 1$. For an all-trans chain, the matrix $\langle \mathbf{G}^{(4)}\rangle_{tt}$ is used. If the chain contains both cis and trans residues, it is necessary to evaluate also the matrices $\langle \mathbf{G}^{(4)}\rangle_{ct}$ and $\langle \mathbf{G}^{(4)}\rangle_{tc}$. The serial product in eq 24 is then generated by introducing the four matrices in the order dictated by the stereochemical structure of the chain.

If the succession of cis and trans residues is Markoffian, the mean-square end-to-end distance may be obtained by proceeding as follows. We consider specifically the case of first-order Markoff dependence of the succession of units. Let w_{cc} and w_{tt} be the respective conditional probabilities for succession of a cis by a cis and of a trans by a trans residue; then $w_{ct} = 1 - w_{cc}$ and $w_{tc} = 1 - w_{tt}$. Further, we define an averaged generator matrix as follows

$$\overline{\langle \mathbf{G}^{(4)}\rangle} = \begin{bmatrix} w_{cc}\langle \mathbf{G}^{(4)}\rangle_{cc} & w_{ct}\langle \mathbf{G}^{(4)}\rangle_{ct} \\ w_{tc}\langle \mathbf{G}^{(4)}\rangle_{tc} & w_{tt}\langle \mathbf{G}^{(4)}\rangle_{tt} \end{bmatrix} \tag{26}$$

Then

$$\langle r^2\rangle_0 = \mathbf{C}^*\mathbf{G}_1\overline{\mathbf{G}}_2(\overline{\langle \mathbf{G}^{(4)}\rangle})^{x-1}\begin{bmatrix} \mathbf{G}_n\mathbf{C} \\ \mathbf{G}_n\mathbf{C} \end{bmatrix} \tag{27}$$

where

$$\overline{\mathbf{G}_2} = [w_{c;2}\mathbf{G}_{c;2} \; w_{t;2}\mathbf{G}_{t;2}] \tag{28}$$

Here $\mathbf{G}_{c;2}$ and $\mathbf{G}_{t;2}$ represent the matrices $\mathbf{G}$ for bond 2 in the cis and trans configurations, respectively, and $w_{c;2}$ and $w_{t;2}$ are the *a priori* probabilities for cis and trans configurations of the first double bond, or the first residue, of the chain (*i.e.*, for bond 2). In this way, the succession of cis and trans residues is handled on a statistical basis and the necessary computations may be readily and efficiently carried out without explicit specification of the residue sequence as required, for example, by the more cumbersome route of Monte Carlo generation of sequences and use of eq 24.

For a random copolymer of cis and trans residues,

$$w_{cc} = w_{tc} = 1 - w_{tt} = 1 - w_{ct} = f_c \tag{29}$$

Average Bond Conformations. The *a priori* probability for a conformation η for one or more of the three single bonds of a structural unit of specified character is given by

$$p_\eta = z^{(4)\prime}{}_\eta/z^{(4)} \tag{30}$$

where $z^{(4)}$ is the partition function for the structural unit and $z^{(4)\prime}{}_\eta$ is the corresponding sum over those rotational states consistent with the conformation η. Thus, $z^{(4)\prime}{}_\eta$ may be obtained according to eq 6 through retention of only those elements that represent the state η in the statistical weight matrices for bonds included in the stipulation η, all other elements in these matrices being replaced by zeros. Values of p_η for the four kinds of structural units can be obtained in this way.

When the end-to-end distance of the chain is fixed at the value r, the mean *a priori* probability p_η that a unit selected at random occurs in a conformational state specified by η is given by[10]

$$p_{\eta;r} = p_\eta\{1 + \delta_{\eta;2}[(r^2/\langle r^2\rangle_0) - 1] + O(x^{-2})\} \tag{31}$$

The coefficient $\delta_{2;\eta}$ depends on the chain structure through the relation[10]

$$\delta_{\eta;2} =$$

$$(3/2)\left\{2(Z_\eta\langle r^2\rangle_0)^{-1}\mathcal{J}^*\mathcal{H}_{\eta;1}\mathcal{H}_{\eta;2}\left(\prod_{k=1}^{x-1} \mathcal{H}_{\eta;k}{}^{(4)}\right)\mathcal{H}_{\eta;\mathrm{n}}\mathcal{J} - 1\right\} \tag{32}$$

with

$$\mathcal{H}_{\eta;k}{}^{(4)} = \mathcal{H}_{\eta;\mathrm{a}}\mathcal{H}_{\eta;\mathrm{b}}\mathcal{H}_{\eta;\mathrm{c}}\mathcal{H}_{\eta;\mathrm{d}} \tag{33}$$

where the $\mathcal{H}_\eta$'s are constructed according to

$$\mathcal{H}(\mathcal{G},\eta) = \begin{bmatrix} \mathcal{G} & \mathcal{G}_\eta{}' \\ \mathbf{0} & \mathcal{G} \end{bmatrix} \tag{34}$$

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(25) The matrix $\langle \mathbf{G}^{(4)}\rangle_k$ corresponds to the matrix previously denoted[3] by $\mathfrak{G}_k{}^{(4)}$.

The matrix $\mathcal{G}$ is given by eq 22, and $\mathcal{G}_\eta'$ is obtained from it through replacement of $\mathbf{U}$ in eq 22 by the matrix $\mathbf{U}_\eta'$ obtained from $\mathbf{U}$ by setting all elements equal to zero except those for the state η.

Strain Birefringence[3,7,8] **and Strain Dichroism.**[11] The stress optical coefficient B is given by

$$B = (2\pi\Gamma_2/27kT)(\tilde{n}^2 + 2)^2/\tilde{n} \tag{35}$$

where $\tilde{n}$ is the mean refractive index of the sample and Γ_2 is a parameter defined by

$$\Gamma_2 = (9/10)\sum_i \langle \mathbf{r}^{\mathrm{T}} \cdot \hat{\alpha}_i \cdot \mathbf{r} \rangle_0 / \langle r^2 \rangle_0 \tag{36}$$

It depends on the configurational characteristics of a polymer chain. In eq 36, $\hat{\alpha}_i$ is the traceless tensor

$$\hat{\alpha}_i = \boldsymbol{\alpha}_i - (1/3)\mathrm{trace}(\boldsymbol{\alpha}_i)\cdot\mathbf{E}_3 \tag{37}$$

where $\boldsymbol{\alpha}_i$ is the group polarizability tensor for the bond i and the bonds associated with it. Expressions for $\hat{\alpha}_i$ in the coordinate systems of bond i are given in the Appendix. The sum in the numerator in eq 36 may be calculated according to

$$\sum_i \langle \mathbf{r}^{\mathrm{T}} \cdot \hat{\alpha}_i \cdot \mathbf{r} \rangle_0 = 2Z^{-1}\cdot \mathcal{J}^* \mathcal{Q}_1 \mathcal{Q}_2 (\Pi \mathcal{Q}_k{}^{(4)}) \mathcal{Q}_n \mathcal{J} \tag{38}$$

with

$$\mathcal{Q}_k{}^{(4)} = \mathcal{Q}_a \mathcal{Q}_b \mathcal{Q}_c \mathcal{Q}_d \tag{39}$$

where $\mathcal{Q}_a$, etc. are obtained by substitution of the corresponding $\mathbf{U}_a$, etc., $\hat{\alpha}_a$, etc., given in Appendix, and other geometrical quantities into the expression

$$\mathcal{Q} = \begin{bmatrix} \mathbf{A} & \mathbf{B} \\ \mathbf{0} & \mathbf{C} \end{bmatrix} \tag{40}$$

$$\mathbf{A} = \begin{bmatrix} \mathbf{U} & (\mathbf{U}\otimes\mathbf{l}^{\mathrm{T}})\|\mathbf{T}\| & {}^1\!/_2(\mathbf{U}\otimes\mathbf{l}^{\mathrm{T}}\otimes\mathbf{l}^{\mathrm{T}})\|\mathbf{T}\otimes\mathbf{T}\| \\ \mathbf{0} & (\mathbf{U}\otimes\mathbf{E}_3)\|\mathbf{T}\| & (\mathbf{U}\otimes\mathbf{E}_3\otimes\mathbf{l}^{\mathrm{T}})\|\mathbf{T}\otimes\mathbf{T}\| \\ \mathbf{0} & \mathbf{0} & (\mathbf{U}\otimes\mathbf{E}_9)\|\mathbf{T}\otimes\mathbf{T}\| \end{bmatrix} \tag{41}$$

$$\mathbf{B} = \begin{bmatrix} (\mathbf{U}\otimes\hat{\alpha}^{\mathrm{R}})\|\mathbf{T}\otimes\mathbf{T}\| & \mathbf{U}\otimes[\hat{\alpha}^{\mathrm{R}}(\mathbf{l}\otimes\mathbf{E}_3)]\|\mathbf{T}\| & {}^1\!/_2\mathbf{U}[\hat{\alpha}^{\mathrm{R}}(\mathbf{l}\otimes\mathbf{l})] \\ \mathbf{0} & (\mathbf{U}\otimes\hat{\alpha})\|\mathbf{T}\| & \mathbf{U}\otimes[(\mathbf{E}_3\otimes\mathbf{l}^{\mathrm{T}})\hat{\alpha}^{\mathrm{C}}] \\ \mathbf{0} & \mathbf{0} & \mathbf{U}\otimes\hat{\alpha}^{\mathrm{C}} \end{bmatrix} \tag{42}$$

$$\mathbf{C} = \begin{bmatrix} (\mathbf{U}\otimes\mathbf{E}_9)\|\mathbf{T}\otimes\mathbf{T}\| & (\mathbf{U}\otimes\mathbf{l}\otimes\mathbf{E}_3)\|\mathbf{T}\| & {}^1\!/_2(\mathbf{U}\otimes\mathbf{l}\otimes\mathbf{l}) \\ \mathbf{0} & (\mathbf{U}\otimes\mathbf{E}_3)\|\mathbf{T}\| & \mathbf{U}\otimes\mathbf{l} \\ \mathbf{0} & \mathbf{0} & \mathbf{U} \end{bmatrix} \tag{43}$$

$\mathcal{Q}_1$, $\mathcal{Q}_2$, and $\mathcal{Q}_n$ in eq 38 represent the first, second, and final bonds of the chain (see analogous definitions of $\mathbf{G}_1$, $\mathbf{G}_2$, and $\mathbf{G}_n$ in eq 24). The symbols $\hat{\alpha}^{\mathrm{R}}$ and $\hat{\alpha}^{\mathrm{C}}$ occurring in these equations denote the row and column forms respectively of $\hat{\alpha}$.[3,7]

The dichoric ratio D of a band having a transition dipole moment $\mathbf{d}_i$ associated with bond i, or residue i, is given by

$$D = 1 + (3G_2^*/2n')(\lambda^2 - V/V_0\lambda) \tag{44}$$

for a network subjected to simple elongation in the amorphous (rubbery) state. In this equation n' is the number of bonds or residues possessing the given transition moment (*e.g.*, n' may be the number of cis residues if the absorption is associated with the cis double bond), λ is the extension ratio along the axis of elongation measured relative to the length of the undistorted specimen in the isotropic reference state of volume V_0 such that $\langle r^2 \rangle = \langle r^2 \rangle_0$, V is the volume of the deformed network, and G_2^* represents the average preferential orientation of the moments $\mathbf{d}_i$ for all bonds i. This latter quantity is defined by

$$G_2^* = \sum_i{}' \beta_{2;i} \tag{45}$$

where $\beta_{2;i}$ is the orientation coefficient for the moment $\mathbf{d}_i$ associated with bond i, or residue i; it is defined as the coefficient of $r^2/\langle r^2 \rangle_0$ in the series

$$\langle \cos^2 \Phi_i \rangle_r = (1/3) + \beta_{2;i}\frac{r^2}{\langle r^2 \rangle_0} + \ldots \tag{46}$$

$\langle \cos^2 \Phi_i \rangle_r$ being the average squared cosine of the angle Φ_i between the moment $\mathbf{d}_i$ and the end-to-end chain vector $\mathbf{r}$. The prime appended to the summation sign in eq 45 denotes that only those bonds, or residues, having a nonzero moment $\mathbf{d}_i$ are included.

The coefficient G_2^* of preferential orientation is related to the chain structure by

$$G_2^* = (6/5)(p_\eta Z \langle r^2 \rangle_0)^{-1} \mathcal{J}^* \mathcal{R}_1 \mathcal{R}_2 (\Pi \mathcal{R}_k{}^{(4)}) \mathcal{R}_n \mathcal{J} \tag{47}$$

where

$$\mathcal{R}_k{}^{(4)} = \mathcal{R}_a \mathcal{R}_b \mathcal{R}_c \mathcal{R}_d \tag{48}$$

and $\mathcal{R}_a$–$\mathcal{R}_d$ are constructed according to

$$\mathcal{R} = \begin{bmatrix} \mathbf{A} & \mathbf{B}' \\ \mathbf{0} & \mathbf{C} \end{bmatrix} \tag{49}$$

with $\mathbf{A}$ and $\mathbf{C}$ given by eq 41 and 43, and with $\mathbf{B}'$ defined by eq 42 for bonds carrying a transition moment, $\hat{\alpha}$ in eq 42 being replaced by the traceless tensor formed from $\mathbf{dd}^{\mathrm{T}}/d^2$; for all other bonds $\mathbf{B}'$ is null.

Results and Discussion

Statistical Weight Parameters. Values were chosen for the various statistical weight parameters by considering, first, the conformational energies of model compounds insofar as such information is available; secondly, by inference from the severity of the steric overlaps involved, these being compared with similar interactions in other polymeric chains for which the corresponding parameters have been evaluated; and, finally, by adjustment to achieve agreement with experimental results on the dimensions of PBD polymers.

The change in the infrared spectral intensities of 1,5-hexadiene with temperature observed by Tosi and Ciampelli[26] indicates a value of $E_\sigma \approx 200$ cal mol^{-1}. They deduced similar values (0–200 cal mol^{-1}) from the infrared spectra of *cis*-PBD and *trans*-PBD. A pair of methine (CH) groups are apposed in the gauche conformation. In polymethylene, CH$_2$ groups are similarly situated in the gauche conformation, for which $E_\sigma \approx 500$ cal mol^{-1}. In view of the smaller size of the former group, a lower energy is to be expected. Following Mark,[1,2] we take $E_\sigma = 0$, with

$$\sigma = \exp(-E_\sigma/RT) \tag{50}$$

assigned a value of unity for the principal calculations. We have performed additional calculations with $E_\sigma = 100$ and -100 cal mol^{-1}.

The threefold barrier to internal rotation of the methyl groups of *cis*-2-butene was determined to be 730 cal mol^{-1}

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[26] C. Tosi and F. Ciampelli, *Eur. Polym. J.*, **5**, 759 (1969).

TABLE IV
SELECTED VALUES OF PARAMETERS AND THEIR EFFECTS ON THE CHARACTERISTIC RATIO AND THE STRESS-OPTICAL COEFFICIENT

			cis-PBD (50°)		*trans*-PBD (50°)	
Parameter X	E_X, cal mol^{-1}	X^a at 50°	d ln C_n/d ln X	d ln Γ_2/d ln X	d ln C_n/d ln X	d ln Γ_2/d ln X
σ	0^b	1.0^b	−0.074	−0.133	−0.437	−0.549
ζ	700	0.101	0.040	0.053		
ρ	300	0.627			0.124	0.140
β	2000	0.0446			−0.030	−0.031

[a] $X = \exp(-E_X/RT)$ except for ζ, which is given by $\zeta = 0.3 \exp(-E_\zeta/RT)$; *cf.* eq 51. [b] Calculations also carried out, as reported below, for $E_\sigma = +100$ and -100 cal mol^{-1}, giving $\sigma = 0.86$ and 1.17 at 50°.

by microwave spectroscopy.[18] E_ζ can be identified approximately with this value. It is apparent from the energy map in Figure 2 that we cannot neglect the difference in entropy between the postulated trans and the skew states for single bonds adjoining a cis double bond. Following Ishikawa and Nagai,[4] we let

$$\zeta = g_\zeta \exp(-E_\zeta/RT) \qquad (51)$$

with $E_\zeta = 700$ cal mol^{-1} and g_ζ subject to adjustment. Agreement with experimental values of the characteristic ratio C_n and of the temperature coefficient d ln C_n/dT of *cis*-PBD is optimized by taking $g_\zeta = 0.3$. Accordingly, we let $\zeta = 0.3 \exp(-700/RT) = 0.101$ at 50°. The quantities ζ and g_ζ elude precise physical interpretation. They serve rather to take account of minor contributions from conformations in *the range from* -60 *to* $+60°$, which otherwise would be ignored.

The energy difference between the cis and skew forms of 1-butene was found to be 150 ± 150 cal mol^{-1} from the microwave study carried out by Kondo, Hirota, and Morino.[27] The infrared spectroscopic investigation on *trans*-2-pentene, carried out by Alaki, Abe, and Shimanouchi[28] likewise showed the skew form to be more stable than the cis, the energy difference being *ca.* 250 cal mol^{-1}. We conclude that $0 < E_\rho < 400$ cal mol^{-1} for *trans*-PBD. Interactions cited in Table III suggest that β should be comparable in magnitude to the factor $\omega = \exp(-2000/RT)$ for the $g^\pm g^\mp$ state of *n*-alkanes.[3,20] Agreement with experiments on the characteristic ratio and its temperature coefficient for *trans*-PBD is optimized by taking

$$\rho = \exp(-E_\rho/RT) \qquad (52)$$

$$\beta = \exp(-E_\beta/RT) \qquad (53)$$

with $E_\rho = 300$ and $E_\beta = 2000$ cal mol^{-1}.

Selected values of statistical weight parameters are listed in Table IV together with the dependence of C_n and Γ_2 on each of the parameters.

The parameters ζ and ρ correspond to Mark's γ^{-1} and α, respectively.[1,2] The value $\zeta = 0.101$ is in virtual agreement with Mark's $\gamma = 10$.[1] Mark[2] chose $\rho = 0.96$ ($E_\rho = 30$ cal mol^{-1}) and $\beta = 0.24$ ($E_\beta = 1100$ cal mol^{-1}), which differ somewhat from the values in the present work. The differences are of little importance, however, since the dependence of configurational properties of *trans*-PBD on the parameters ρ and β is small, as shown in Table IV, and, on the other hand, experimental values of the properties are not very accurate. As shown in the following paper,[29] smaller values ($\beta < 0.1$) are indicated for 1,4-polyisoprene chains.

TABLE V
CONFIGURATIONAL PROPERTIES OF
PBD CHAINS AT 50°

	cis-PBD		*trans*-PBD	
	Obsd	Calcd^a	Obsd	Calcd^a
C_n	4.9 (±0.2)^{b,c}	5.08	5.8 (±0.2)^d	6.20
$10^3 \times$ d ln C_n/dT, deg^{-1}	0.4^{e,f}	0.16	−0.65^d	−0.11
$10^{24} \times \Gamma_2$, cm^3	3.0,^{g} 4.5^h	3.53	3.5,^{i} 5.1^h	4.00

[a] Calculated from the preferred set of parameters: $\sigma = 1.0$, $\rho = 0.627$, $\zeta = 0.101$, $\beta = 0.0446$, and from the bond polarizabilities of C. Clément and P. Bothorel, *C. R. Acad. Sci.*, **258,** 4757 (1964). [b] G. Moraglio, *Eur. Polym. J.*, **1,** 103 (1965). [c] M. Abe and H. Fujita, *J. Phys. Chem.*, **69,** 3263 (1965). [d] Reference 2. [e] Reference 4. [f] R. H. Becker and J. E. Mark, unpublished results. [g] Samples swollen in decalin (ref 4 and 5). [h] Unswollen samples (ref 4 and 5). [i] Samples swollen in CCl$_4$ (ref 4 and 5).

The dependence of C_n on each of the statistical weight parameters, as calculated by Mark,[2] is very nearly the same as that given in Table IV.

Comparison of Theoretical Calculations with Experimental Results for Stereoregular Polymers. Quantities calculated for PBD chains with $x = 300$ units, or $n = 1199$ bonds, at a temperature of 50°, are compared with experimental results in Table V. The preferred set of statistical weight parameters given in Table IV was used for these calculations in conjunction with the structural data and bond polarizabilities given in Table I.

Expressions obtained for the stress-optical parameter Γ_2 at 50° follow (see eq 36–43). For *cis*-PBD

$$\Gamma_2 = 1.031\Delta\alpha_{\mathrm{C=C}} + 0.611\Delta\alpha_{\mathrm{C-C}} - 2.123\Delta\alpha_{\mathrm{C-H}} \qquad (54)$$

For *trans*-PBD

$$\Gamma_2 = 0.550\Delta\alpha_{\mathrm{C=C}} + 2.099\Delta\alpha_{\mathrm{C-C}} - 2.973\Delta\alpha_{\mathrm{C-H}} \qquad (55)$$

For the random copolymer of cis and trans units in equal proportions (see the following section)

$$\Gamma_2 = 0.738\Delta\alpha_{\mathrm{C=C}} + 1.217\Delta\alpha_{\mathrm{C-C}} - 2.314\Delta\alpha_{\mathrm{C-H}} \qquad (56)$$

The coefficients in these expressions have been obtained by computation of the contributions of the several kinds of bonds to $\hat{\alpha}_i$ in eq 42. The calculated values of Γ_2 quoted in Table V are obtained from eq 54 and 55 by substituting therein the bond polarizabilities of Clément and Botherel[30] (see Table I), which were deduced from the Rayleigh scattering of *cis*- and of *trans*-2-butene and of tetramethylethylene, each in the pure liquid state. The bond polarizabilities given by Denbigh[31] yield values of Γ_2 which are *ca.* 30% smaller for

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(27) S. Kondo, E. Hirota, and Y. Morino, *J. Mol. Spectrosc.*, **28,** 471 (1968).

(28) Y. Alaki, Y. Abe, and T. Shimanouchi, paper presented at 16th Annual Meeting of the Society of Polymer Science of Japan, Tokyo, Japan, May 1967.

(29) Y. Abe and P. J. Flory, *Macromolecules*, **4,** 230 (1971).

(30) C. Clément and P. Bothorel, *C. R. Acad. Sci.*, **258,** 4757 (1964).

(31) K. G. Denbigh, *Trans. Faraday Soc.*, **36,** 936 (1940).

cis-PBD and *ca.* 10% larger for *trans*-PBD than those given in Table V.

The properties of the *cis*-PBD chain are insensitive to the statistical weight parameters, as shown by the calculations in Table IV. The change of E_σ from 0 to 100 cal mol^{-1} causes an increase of only 1% in the characteristic ratio C_n of *cis*-PBD. The same change of E_σ causes an increase of about 6% in C_n for *trans*-PBD and a large decrease in d ln C_n/dT. Calculations not reproduced here show that C_n for *trans*-PBD is increased *ca.* 2% by changing E_β from 2000 to 2500 cal mol^{-1}; a corresponding change in C_n is produced by decreasing E_ρ from 300 to 200 cal mol^{-1}. Configurational properties of the *trans*-PBD chain depend more strongly on E_σ than on E_ρ and E_β.

Properties in Relation to Stereochemical Composition. Characteristic ratios and their temperature coefficients calcuted according to eq 16 and 27 are plotted in Figures 3 and 4, respectively, as functions of the fraction of *cis*-C═C residues in the chain for the three values of E_σ indicated on the respective curves. As Figures 3 and 4 show, the dependence of C_n and of (d ln C_n/dT) on f_{cis} departs markedly from linearity. The curves for C_n in Figure 3 exhibit steep descents as f_{cis} increases in the range 0.0–0.6, then become comparatively insensitive to composition. They display minima with f_{cis} in the range of 0.7–0.9. Figure 4 shows also that (d ln C_n/dT) passes through zero near this range of f_{cis} if $E_\sigma \geq 0$. Experimental data suitable for comparison with these predictions on the effects of stereoirregularity are not available.

The stress-birefringence parameter Γ_2 is plotted in Figure 5 against f_{cis} for the three values of E_σ indicated. Each point for stereoirregular chains (*i.e.*, for $0.0 < f_{\text{cis}} < 1.0$) represents the average over 15 Monte Carlo chains, and the standard deviation is indicated by a vertical bar. Minima with f_{cis} are displayed also for the stress-birefringence coefficient. The minima are more pronounced and located in lower ranges of f_{cis} than those for the characteristic ratio shown in Figure 3.

Figures 3–5 show that configurational properties of PBD chains with $f_{\text{cis}} \approx 0$ are very sensitive to the stereochemical composition. The importance of using highly stereoregular samples in experiments designed to reveal the properties of the *trans*-PBD chain is apparent.

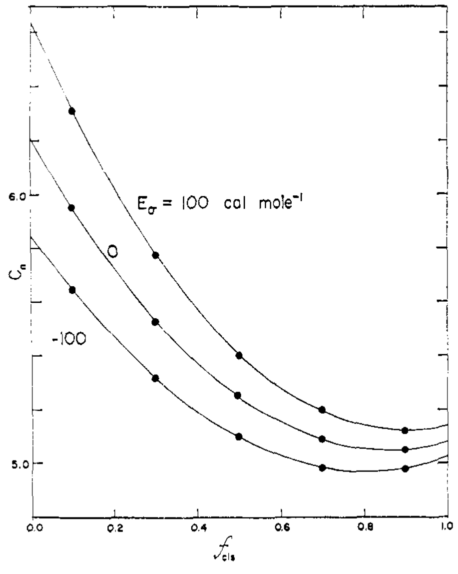

Figure 3. Characteristic ratios plotted against the fraction f_{cis} of *cis*-C═C bonds for the three values of E_σ indicated on the respective curves. Preferred values of other parameters (see Table IV) have been used.

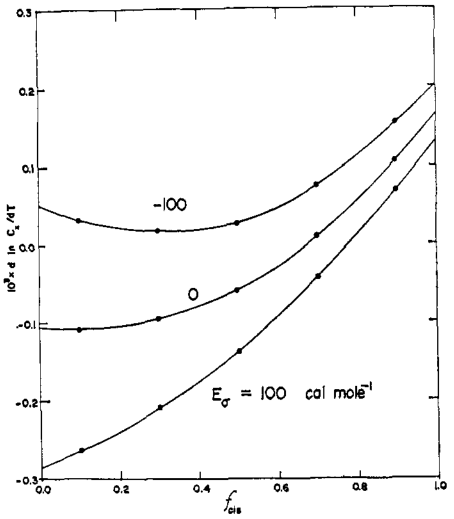

Figure 4. Temperature coefficients of the characteristic ratio plotted against f_{cis}. See legend for Figure 3.

Preferential Orientation and Strain Dichroism. Preferential orientations $G_2{}^*$ of the three coordinate axes for a C═C bond—the x axis being parallel to C═C, the y axis in the plane CC═CC and making an acute angle with the preceding C—C bond, and the z axis chosen to form a right-handed rectangular coordinate system—were calculated as a function of f_{cis} using the selected values of the statistical weight parameters (Table IV). The parameter $G_2{}^*$ was calculated for the *trans*-C═C bonds in chains with f_{cis} = 0.0–0.5 and for the *cis*-C═C bonds in chains with f_{cis} = 0.5–1.0. The ratios $G_2{}^*/f_{\text{cis}}$ or $G_2{}^*/f_{\text{trans}}$ are plotted against f_{cis} in Figure 6. Monte Carlo calculations were employed for chains with $0.0 < f_{\text{cis}} < 1.0$. Standard deviations, being very small, are not shown in Figure 6. The values of $G_2{}^*$ for the three coordinate axes are not independent; they must meet the condition[11]

$$G_2{}^*(x) + G_2{}^*(y) + G_2{}^*(z) \equiv 0 \qquad (57)$$

required by

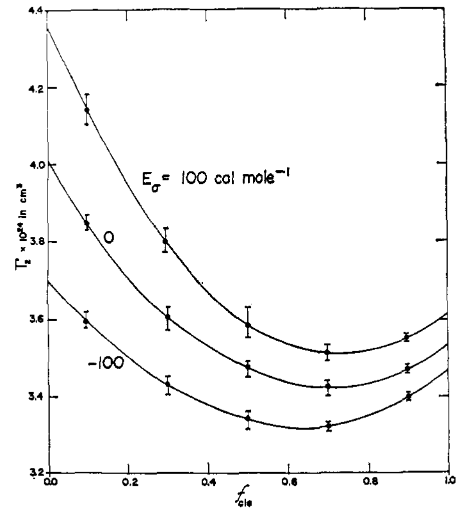

Figure 5. The stress-birefringence parameter plotted against f_{cis}. See legend for Figure 3.

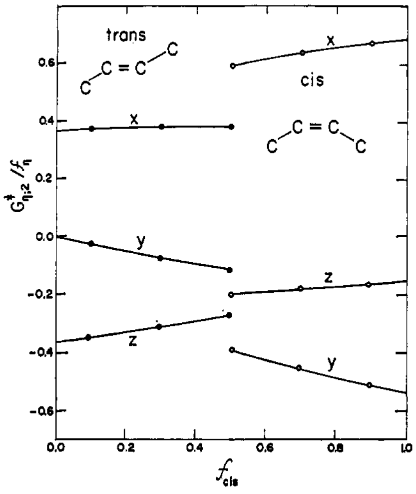

Figure 6. Preferential orientations of the principal coordinate axes of (○) *cis*- and (●) *trans*-C—CH=CH—C units plotted against f_{cis}. The preferred set of parameters given in Table IV was used for calculations.

$$\cos^2 \Phi_t^x + \cos^2 \Phi_t^y + \cos^2 \Phi_t^z \equiv 1 \qquad (58)$$

(see eq 45 and 46).

Calculations with $E_\sigma = \pm 100$ cal mol^{-1}, which are not reproduced here, indicate that the calculated orientation of C=C bonds depends very little on E_σ. A change of E_σ from 0 to 100 cal mol^{-1} increases $G_2^*(x)$ from 0.69 to 0.70 for *cis*-PBD ($f_{\mathrm{cis}} = 1.0$) and decreases $G_2^*(x)$ from 0.37 to 0.36 for *trans*-PBD ($f_{\mathrm{cis}} = 0$).

The ratios G_2^*/f_{cis} and G_2^*/f_{trans} are more appropriate measures of preferential orientation of a residue than G_2^*. The latter quantity, defined by eq 45, is the sum of n' terms, $\beta_{2;i}$, where n' is the number of *cis*-C=C bonds for η = cis and the number of *trans*-C=C bonds for η = trans. Thus, for chains of the same length n, it is linearly related to f_{cis}. Inasmuch as $\beta_{2;i}$ decreases as $1/n$ for long chains,[10,11] both G_2^* and G_2^*/f_η rapidly approach constant values with increase in n at fixed composition f_{cis}. The fact that the changes in G_2^*/f_{cis} and G_2^*/f_{trans} as f_{cis} increases are very small indicates that the orientation of a C=C bond (sufficiently separated from the ends of the chain) is only slightly dependent on the stereochemical composition (f_{cis}) over the range for which calculations were carried out.

The G_2^*'s shown in Figure 6 represent the preferential orientation of a CCH=CHC residue induced by elongation of a chain in the amorphous state. For a cis residue, orientation of the CCH=CHC plane takes place mainly as a rotation of this plane about the axis perpendicular to it, as indicated by the relatively small absolute value of $G_2^*(z)$. For a trans residue the absolute value of $G_2^*(y)$ is very small. This means that, as the chain is stretched, the CCH=CHC plane is rotated predominantly about the axis which lies in this plane and is perpendicular to the C=C bond, but this axis itself remains essentially unoriented. The *cis*-C=C bond is more susceptible than a *trans*-C=C bond to orientation along the direction of elongation.

As represented by eq 44, the dichroism of an infrared band associated with the CCH=CHC residue is related to the parameter G_2^* for a unit vector in the direction of the transition moment for the given absorption band. The direction of the transition dipole moment for the C=C stretching vibration at 1665 cm^{-1} for the cis double bond is strictly along the y axis owing to the C_{2v} symmetry of this residue.[32] The transition moment for the band of medium strength at 1415 cm^{-1}, which is assigned to the C-H in-plane bending, is parallel to the x axis. For *trans*-CCH=CHC residues, the very strong band at 978 cm^{-1} assigned to the C—H out-of-plane wagging is associated with a transition moment directed along the z axis. Experimental observations on infrared dichroism in amorphous PBD networks have not been reported.

TABLE VI

A Priori PROBABILITIES AND ROTATIONAL ISOMERIZATION WITH STRETCHING CALCULATED FOR PBD CHAINS[a]

Rotational conformation η	p_η	$n'\delta_{\eta;2}$	$\Delta_{\eta;2}$
cis-PBD			
C—CH=CH—C bond sequence			
$s^\pm$ c $s^\pm$	0.227	1.21	0.27
$s^\pm$ c $s^\mp$	0.227	−3.37	−0.31
CH$_2$—CH$_2$ bond			
t, σ = 1.169	0.330	0.39	0.12
t, σ = 1.0	0.333	0.35	0.12
t, σ = 0.856	0.369	0.31	0.11
$g^\pm$, σ = 1.169	0.350	−0.17	−0.06
$g^\pm$, σ = 1.0	0.333	−0.18	−0.06
$g^\pm$, σ = 0.856	0.315	−0.18	−0.06
trans-PBD			
C—CH=CH bond sequence			
c t	0.118	0.76	0.09
$s^\pm$t	0.441	−0.09	−0.04
C—CH=CH—C bond sequence			
c t c	0.014	3.02	0.04
c t $s^\pm$	0.052	0.47	0.02
$s^\pm$ t $s^\pm$	0.194	−0.95	−0.18
$s^\pm$ t $s^\mp$	0.194	0.61	0.12
CH$_2$—CH$_2$ bond			
t, σ = 1.169	0.417	1.32	0.55
t, σ = 1.0	0.455	1.38	0.63
t, σ = 0.856	0.494	1.42	0.70
$g^\pm$, σ = 1.169	0.291	−0.94	−0.28
$g^\pm$, σ = 1.0	0.272	−1.15	−0.31
$g^\pm$, σ = 0.856	0.253	−1.39	−0.35

[a] Calculated with ζ = 0.101, ρ = 0.267, β = 0.0446, and with σ = 1.00 except as noted. Values of σ = 1.169 and 0.856 correspond to E_σ = −100 and +100 cal mol^{-1}, respectively, for a temperature of 50°.

Average Bond Conformations and Rotational Isomerization by Stretching. The *a priori* probabilities p_η for several conformations (η) of the structural segments C—CH=CH—C and CH$_2$—CH$_2$ in PBD chains, and their changes with elongation as represented by $\delta_{\eta;2}$, were calculated using the preferred set of parameters given in the third column of Table IV. The results are given in Table VI. The coefficient $\delta_{\eta;2}$ defined by eq 31 is inversely proportional to n' for sufficiently long chains. Thus, the values for $\delta_{\eta;2}$ multiplied by n' listed in the third column of Table VI are indicative of the intrinsic susceptibility to isomerization by extension of the chain.

The absolute change in number of bonds or bond sequences in the rotational state η caused by unit increase in $r^2/\langle r^2\rangle_0$ is

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[32] Actually the C=C stretching vibration is mixed with the C—C stretching and C—H bending vibrations. The vibrational mode is symmetric with respect to the twofold symmetry axis which is perpendicular to the C=C bond. Thus the transition moment is also perpendicular to the C=C bond. For discussions on infrared spectra of *cis*- and *trans*-PBD, see M. A. Golub and J. J. Shipman, *Spectrochim. Acta*, **16**, 1165 (1960); **20**, 701 (1964).

convergent as $n' \rightarrow \infty$. It is given by

$$\Delta_{\eta;2} = n'\delta_{\eta;2}p_\eta \tag{59}$$

Values for $\Delta_{\eta;2}$ calculated from p_η and $n'\delta_{\eta;2}$ listed in the second and third columns of Table VI are given in the last column.

For the *cis*-PBD chain, the number of s±cs± conformations for the C—CH═CH—C bond sequence increases, while that of s±cs∓ decreases. Rotational isomerization favoring the former is consistent with the fact that it is a more extended conformation than the latter. Changes in the trans and gauche populations of CH_2–CH_2 bonds are very small.

The number of s±ts± conformations for the C—CH═CH—C bond sequence in the *trans*-PBD chain is decreased by stretching; all other conformations are increased. These changes are smaller than those for the same bond sequence of *cis*-PBD. The increase in incidence of the trans state for CH_2–CH_2 bonds is much greater in the case of *trans*-PBD.

In summary, rotational isomerization with stretching is more marked among C—CH═CH—C bond sequences in *cis*-PBD than among CH_2—CH_2 bonds; the reverse is true for *trans*-PBD. The degrees of rotational isomerization are very small in an absolute sense (compare ref 10). For chains of 100 units, less than one bond sequence, or bond, is affected per chain when $r^2/\langle r^2\rangle_0$ is altered by one unit, *e.g.*, increased from 1 to 2.

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Appendix

Anisotropies of Group Polarizability Tensors. The group polarizability $\boldsymbol{\alpha}_i$ associated with bond i comprises the sum of polarizabilities of those bonds which are fixed in the coordinate system for skeletal bond i, as illustrated below. We let $\Delta\alpha_{C-C}$, $\Delta\alpha_{C=C}$, and $\Delta\alpha_{C-H}$ represent the difference $\alpha_\parallel - \alpha_\perp$ between polarizabilities along the indicated bond and perpendicular to it. Further, $\xi = (\pi - \angle CCC)/2$, $\theta' = \pi - \angle C{=}C{-}C$, $\chi = \pi - \angle C{=}C{-}H$, and $\psi = {}^1/_2\angle HCH$.

$\hat{\alpha}_a$. The bonds fixed in the coordinate system for $CHCH_2$ bond $i + 1$ in Figure 1 are C_i–C_{i+1} and C_i–H_i. Transforming the traceless bond polarizability tensor for bond C_i–H_i in its own coordinate system, ${}^1/_3\mathrm{diag}(2\Delta\alpha_{C-H}, -\Delta\alpha_{C-H}, -\Delta\alpha_{C-H})$, to that in the coordinate system of bond C_i–C_{i+1} and adding ${}^1/_3\mathrm{diag}(2\Delta\alpha_{C-C}, -\Delta\alpha_{C-C}, -\Delta\alpha_{C-C})$ for bond C_i–C_{i+1} to it, we have eq 60.

$\hat{\alpha}_b$ and $\hat{\alpha}_c$. These two tensors for the groups $(CH_2$–$C)_{i+2}$ and $(CH_2$–$C)_{i+3}$ correspond to the tensors for CH_2 groups given previously;[8,33] that is, eq 61 holds.

$\hat{\alpha}_d$. This tensor comprising polarizabilities for C═C and C—H bonds is given in the coordinate system of the C═C bond by eq 62.

$\hat{\alpha}_1$, $\hat{\alpha}_2$, and $\hat{\alpha}_n$. $\hat{\alpha}_1$ required for $\mathfrak{Q}_1$ is identified with the traceless polarizability tensor for the CH_3 group. Thus

$$\hat{\alpha}_1 = ({}^1/_3)(\Delta\alpha_{C-C} - \Delta\alpha_{C-H})\mathrm{diag}(2, -1, -1) \tag{63}$$

Obviously, $\hat{\alpha}_2 = \hat{\alpha}_d$ given by eq 62. Finally, $\hat{\alpha}_n$ is obtained by replacement of $\Delta\alpha_{C-C}$ by $\Delta\alpha_{CH_3} = \Delta\alpha_{C-C} - \Delta\alpha_{C-H}$ in eq 60. Thus $\hat{\alpha}_n$ is given by eq 64.

$$\hat{\alpha}_a = \begin{bmatrix} ({}^2/_3)\Delta\alpha_{C-C} + ({}^1/_2)[\cos 2(\theta' + \chi) + {}^1/_3]\Delta\alpha_{C-H} & ({}^1/_2)\sin 2(\theta' + \chi)\Delta\alpha_{C-H} & 0 \\ ({}^1/_2)\sin 2(\theta' + \chi)\Delta\alpha_{C-H} & -({}^1/_3)\Delta\alpha_{C-C} - ({}^1/_2)[\cos 2(\theta' + \chi) - {}^1/_3]\Delta\alpha_{C-H} & 0 \\ 0 & 0 & -({}^1/_3)\Delta\alpha_{C-C} - ({}^1/_3)\Delta\alpha_{C-H} \end{bmatrix} \tag{60}$$

$$\hat{\alpha}_b = \hat{\alpha}_c = \begin{bmatrix} ({}^2/_3)\Delta\alpha_{C-C} + 2(\cos^2\xi\cos^2\psi - {}^1/_3)\Delta\alpha_{C-H} & -2(\sin\xi\cos\xi\cos^2\psi)\Delta\alpha_{C-H} & 0 \\ -2(\sin\xi\cos\xi\cos^2\psi)\Delta\alpha_{C-H} & -({}^1/_3)\Delta\alpha_{C-C} + 2(\sin^2\xi\cos^2\psi - {}^1/_3)\Delta\alpha_{C-H} & 0 \\ 0 & 0 & -({}^1/_3)\Delta\alpha_{C-C} + 2(\sin^2\psi - {}^1/_3)\Delta\alpha_{C-H} \end{bmatrix} \tag{61}$$

$$\hat{\alpha}_d = \begin{bmatrix} ({}^2/_3)\Delta\alpha_{C=C} + ({}^1/_2)(\cos 2\chi + {}^1/_3)\Delta\alpha_{C-H} & -({}^1/_2)(\sin 2\chi)\Delta\alpha_{C-H} & 0 \\ -({}^1/_2)(\sin 2\chi)\Delta\alpha_{C-H} & -({}^1/_3)\Delta\alpha_{C=C} - ({}^1/_2)(\cos 2\chi - {}^1/_3)\Delta\alpha_{C-H} & 0 \\ 0 & 0 & -({}^1/_3)\Delta\alpha_{C=C} - ({}^1/_3)\Delta\alpha_{C-H} \end{bmatrix} \tag{62}$$

$$\hat{\alpha}_n = \begin{bmatrix} ({}^2/_3)\Delta\alpha_{C-C} + ({}^1/_2)[\cos 2(\theta' + \chi) - 1]\Delta\alpha_{C-H} & ({}^1/_2)\sin 2(\theta' + \chi)\Delta\alpha_{C-H} & 0 \\ ({}^1/_2)\sin 2(\theta' + \chi)\Delta\alpha_{C-H} & -({}^1/_3)\Delta\alpha_{C-C} - ({}^1/_2)[\cos 2(\theta' + \chi) - 1]\Delta\alpha_{C-H} & 0 \\ 0 & 0 & -({}^1/_3)\Delta\alpha_{C-C} \end{bmatrix} \tag{64}$$

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(33) R. L. Jernigan and P. J. Flory, *J. Chem. Phys.*, 47, 1999 (1967).