were obtained using a Co^{57} source in palladium, and the isomer shift values have been converted to shifts from a standard absorber of $Na_2Fe(CN)_5NO \cdot 2H_2O$ in order to facilitate comparisons with isomer shift values in the literature.[53]

To obtain the values for the isomer shifts, the centers of the resonance lines were found using the method of chords.[54] Quadrupole splittings were measured from center to center of the resolved doublets and the isomer shift of a compound exhibiting a QS was determined by averaging the two centers. For well-resolved lines the standard deviation for the IS and QS is ±0.08 mm/sec. Curve fitting was not attempted for asymmetric quadrupole splittings with poor resolution.

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Random-Coil Configurations of *cis*-1,4-Polybutadiene and *cis*-1,4-Polyisoprene. Theoretical Interpretation

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Abstract: The rotational isomeric state model with neighbor dependence is used to calculate random-coil dimensions of the *cis* forms of 1,4-polybutadiene, $[-CH_2-CH=CH-CH_2-]_x$, and 1,4-polyisoprene, $[-CH_2-C(CH_3)=CH-CH_2-]_x$, in the limit of large *x*. Comparison of calculated and experimental values of the *characteristic ratio* $\langle r^2 \rangle_0/nl^2$ and its temperature coefficient is used to determine intramolecular energies of various conformational sequences of the chain backbone. The form of lowest intramolecular energy closely corresponds to the conformation adopted by these two polymers in the crystalline state.

In a series of investigations over the last few years, the rotational isomeric state model has proved remarkably successful in the interpretation of configurational characteristics of chain molecules. An area of particular importance is the analysis of the chain extension, and frequently also its temperature coefficient, for polymer chains in the limit of high molecular weight. Such studies have been carried out for polyisobutylene,[1] polyethylene,[2,3] poly(dimethylsiloxane),[4] polyoxymethylene,[5] polyoxyethylene,[6] polypeptides,[7] and vinyl polymers of both tactic and atactic structure.[8] The fact that this model has also been shown to give a very satisfactory account of the dipole moments of α,ω-dibromo-*n*-alkanes[9] and oxyethylene molecules[10] in the region of short chain length strengthens confidence in its application.

The availability of experimental values of the chain extension and its temperature coefficient for *cis*-1,4-polybutadiene and *cis*-1,4-polyisoprene now permits similar analyses of these two polymers, which are of considerable importance because of their relatively simple chemical structure as well as their extensive commercial utilization. The correlation of experimental results with results calculated using a rotational isomeric state representation of these polymers should permit estimation of the energies associated with conformations accessible to the skeletal bonds.

Additionally, the conformation of these polymers in the crystalline state is known from detailed X-ray diffraction studies. It is therefore also of interest to compare this conformation with the conformation of lowest intramolecular energy, thereby gauging the effects, if any, of intermolecular interactions in the selection of a suitably regular chain conformation for adoption into a crystalline lattice.

Theory

Structure of the Repeat Units. On the basis of X-ray diffraction studies of crystalline *cis*-1,4-polybutadiene[11,12] and *cis*-1,4-polyisoprene[11,13,14] and extensive data on low molecular weight analogs,[15] the following structural parameters were adopted: $l_{C-C} = 1.53$ A, $l_{C=C} = 1.34$ A, $l_{C-H} = 1.10$ A, $\angle CH_2-CH=CH = \angle CH_2-C(CH_3)=CH = 125°$ (*e.g.*, $180° - \theta_1$, in Figure 1 and $180° - \theta_2$ in Figure 2), $\angle CH-CH_2-CH_2 = 112°$ (*e.g.*, $180° - \theta_3$ and $180° - \theta_4$ in Figure 1), $\angle CH_2-C-H = \angle CH_2-C-CH_3 = 117.5°$ (*e.g.*, θ_5 in Figure 1), and $\angle CH_2-CH-H = 110°$ (*e.g.*, θ_6 in Figure 2). The X-ray crystallographic studies of *cis*-1,4-polyisoprene by Bunn[13] suggest a somewhat smaller value of $\sim 118°$ for $\angle CH_2-C(CH_3)=CH$. This variation probably represents, at least in

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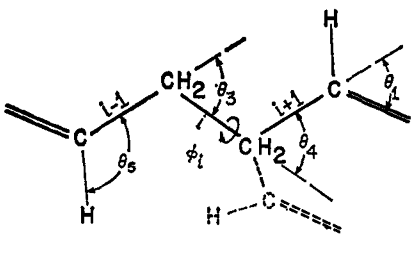

Figure 1.

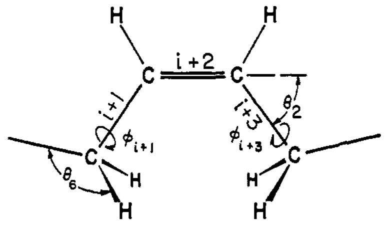

Figure 2.

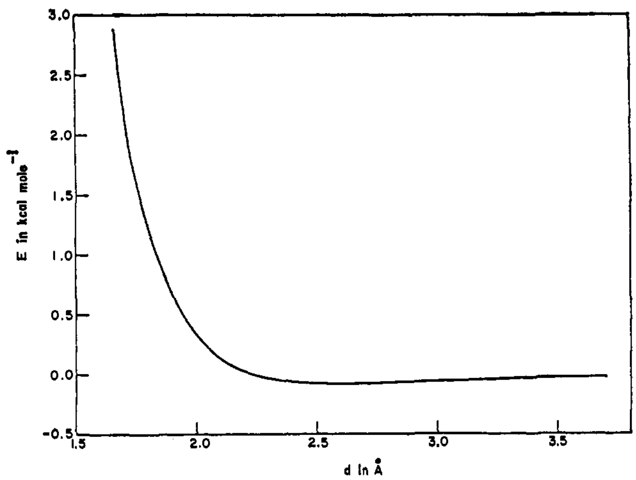

Figure 3. The H···H interaction energy E as a function of the distance d of separation.

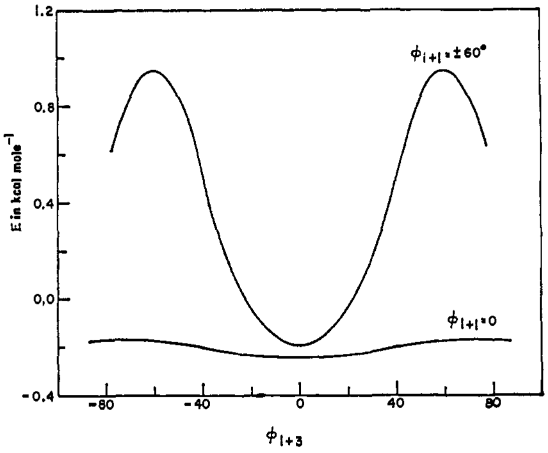

Figure 4. The interaction energy of methylene hydrogens as a function of the rotational angles about CH_2—C_2H_2—CH_2 bonds.

part, a skeletal adjustment to permit the most efficient packing of the chain into a crystalline lattice. In any case, uncertainties in such bond angles are of no great consequence in the present context.

Bond Rotational States. Rotational angles about bonds of the chain backbone will be defined relative to 0° for the planar *trans* conformation. In the case of rotations about CH_2—CH_2 bonds such as bond i in Figure 1, distinct minima in the torsional potential are known to exist at 0° and at ±120° (*gauche*± conformations);[16] in the rotational isomeric state approach, the location of these minima define discrete rotational "states" about each such bond. Similarly, studies of propylene[17] and related compounds[16,18] suggest the location of rotational states at ±60° and at 180° for CH—CH_2 bonds such as $i + 1$ and $i + 3$ of Figure 2. As shown below, however, intramolecular interactions between methylene hydrogens such as those shown in Figure 2 give rise to an additional minimum or state about some of these bonds.

The magnitude of these interactions may be estimated using a potential function of the form[19-21]

$$E = a\exp(-bd) - c/d^6 \qquad (1)$$

where d is the distance (A) of separation of the atoms, and, for hydrogen, b and c have the values 4.54 A^{-1} and 45.2 kcal $mole^{-1}$ (A^6), respectively.[21] The value $a = 9.17 \times 10^3$ kcal $mole^{-1}$ is obtained by minimizing the energy at the distance equal to the sum of the van der Waals radii of the two hydrogen atoms.[21] In Figure 3, this interaction energy is plotted against the distance of separation of the hydrogens. The H···H nonbonded energy summed over the pairwise interactions between the four methylene hydrogens shown in Figure 2 is plotted against the rotation angle ϕ_{i+3} in Figure 4 for $\phi_{i+1} = 0$ and ±60°. The absolute magnitude of these energies is open to question, however. Abe, Jernigan, and Flory[3] obtain a value of $a = 9.95 \times 10^3$ kcal $mole^{-1}$ by requiring eq 1 to yield the experimental energy difference between *trans* and *gauche* states in the n-alkanes. This illustrates a significant uncertainty in the interaction energies, particularly in the repulsive region of the curves; for example, the interaction energy for two hydrogens at a separation of 1.8 A is estimated by these two sets of parameters to be 1.26[21] and 1.48[3] kcal $mole^{-1}$, respectively. For this reason it was not considered reliable to add these nonbonded energies to the well-established torsional energy[16] $0.99\,[1 - \cos 3(\phi + 60°)]$ kcal $mole^{-1}$ for rotations about bonds $i + 1$ and $i + 3$. Nonetheless, comparison of the two curves in Figure 4 strongly suggests that the occurrence of one bond in the bond pair CH_2—C_2H_2-CH_2 in a rotational state of ±60° can give rise to an effective minimum at $\phi = 0°$ for the other bond. Thus, the rotational pairs 0°,±60° and ±60°,0° but not 0°,0° would be accessible to the bond pair.

Statistical Weight Matrices. In the case of neighbor-dependent rotational states, generation of statistical weights for various configurations of the chain requires construction of arrays of statistical weights for pairs of

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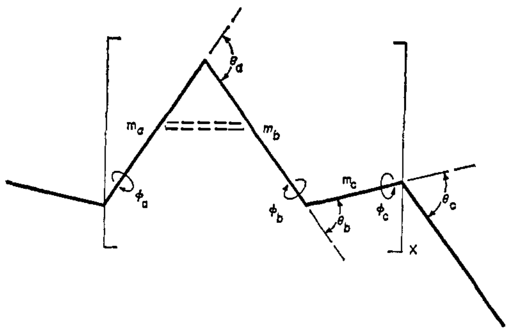

Figure 5. Geometric simplification of the *cis* $\left[\mathrm{C{-}C{=}C{-}C}\right]_x$ chain.

bond sequences.[22] In the case of *cis*-1,4-polybutadiene and *cis*-1,4-polyisoprene, it is convenient to define for each skeletal bond a 6 × 6 *rotational statistical weight matrice* $\mathbf{U}_i$ having rows associated with states of bond $i - 1$ and columns with states of bond i, both row and column indices referring to $\phi = 0, 60, 120, 180, -120$, and $-60°$ in this specified order. The obvious interdependence of rotational states about bonds such as $i + 1$ and $i + 3$ of Figure 2 can best be taken into account by adoption of a geometric simplification first used by Benoit[23] in an early treatment of the dimensions of *cis*-1,4-polybutadiene chains in the approximation of neighbor-*independent* rotational states. Since bonds $i + 1$, $i + 2$, and $i + 3$ in the *cis* forms of both chains are constrained to lie in a plane, bonds $i + 1$ and $i + 3$ can be extended so as to replace the three bonds by two effective or virtual bonds. This simplification, shown diagramatically in Figure 5, results in two bonds of length $m_a = m_b = 2.70$ A, joined at a bond angle supplement of $\phi_a = 110°$.

Rotational pairs $\pm 60°, \pm 60°$ and $\pm 60°, \mp 60°$ about such bonds are essentially equivalent and are assigned a statistical weight γ relative to a statistical weight of unity for the pairs $0°, \pm 60°$ and $\pm 60°, 0°$. The magnitude of γ may be estimated by examination of the H···H interactions involved. The "transition" $0°, \pm 60° \rightarrow \pm 60°, \pm 60°$ or $\mp 60°, \pm 60°$ involves two important effects: (i) a change in torsional energy of -1.98 kcal mole^{-1},[16] and (ii) hydrogens which had a closest approach of 2.45 A are now both located within the plane of bonds $i + 1$, $i + 2$, and $i + 3$ at a distance of separation of 1.83 A, the change in interaction energy[21] for the four hydrogens amounting to approximately $+1.2$ kcal mole^{-1}. The predicted energy for the transition, -0.8 kcal mole^{-1}, should be taken as only a crude approximation in view of the uncertainties in the magnitude of the interaction energy (see above). In any case, the parameter γ should be considerably greater than unity, and since substitution of a methyl group for one of the trigonal hydrogens shown in Figure 2 has no effect on these interactions, γ should have the same value for *cis*-1,4-polybutadiene and *cis*-1,4-polyisoprene. Rotational states at 180°, however, are unquestionably excluded since two pairs of hydrogen atoms on methylene groups separated by bonds i through $i + 3$ by the conformational sequence 0, 180, 180, $\pm 60°$ are separated by only 1.40 A, whereas the sum of the van der Waals radii of these atoms is approximately 2.4 A.[24] The extremely high energy of such a state is readily seen by reference to Figure 3. The sequence statistical weights may be generated in the usual manner[22] by multiplication of the following two statistical weight matrices.

Bond type *a*

$$\mathbf{U}_a = \begin{bmatrix} 1 & 1 & 0 & 0 & 0 & 1 \\ 0 & 0 & 0 & 0 & 0 & 0 \\ 1 & 1 & 0 & 0 & 0 & 1 \\ 0 & 0 & 0 & 0 & 0 & 0 \\ 1 & 1 & 0 & 0 & 0 & 1 \\ 0 & 0 & 0 & 0 & 0 & 0 \end{bmatrix} \qquad (2)$$

Bond type *b*

$$\mathbf{U}_b = \begin{bmatrix} 0 & 1 & 0 & 0 & 0 & 1 \\ 1 & \gamma & 0 & 0 & 0 & \gamma \\ 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 \\ 1 & \gamma & 0 & 0 & 0 & \gamma \end{bmatrix} \qquad (3)$$

In *cis*-1,4-polybutadiene, a *gauche* rotation of $+120°$ about a CH_2—CH_2 bond such as bond i of Figure 1 markedly decreases the distance between trigonal hydrogens. These distances, calculated as a function of the rotational states of the intervening bonds $i - 1$ and $i + 1$, are given in the third column of Table I. On the basis of results given in Figure 3, none of these distances would give rise to significant steric repulsions. Therefore, in contrast to the corresponding situation in polyethylene,[2,3] where interactions between hydrogens separated by 2.0 A in *gauche* states give rise to a repulsive energy of ~0.5 kcal mole^{-1}, it is apparent that a rotation of 120° about such a bond in *cis*-1,4-polybutadiene is accompanied by an energy change which is either small and negative, or zero.

Table I. Important H···H Distances for *Gauche* Rotational States in *cis*-1,4-Polybutadiene and *cis*-1,4-Polyisoprene

ϕ_{i-1}, deg	ϕ_{i+1}, deg	Distance (A) in polybutadiene	Distances (A) in polyisoprene
0	0	2.577	3.451, 3.193, 1.789
0	60	2.238	3.143, 1.603, 2.092
0	−60	3.407	4.253, 4.574, 3.482
60	0	2.238	2.978, 2.518, 1.194
60	60	2.237	2.977, 1.193, 2.513
60	−60	3.105	3.825, 4.236, 2.853
−60	0	3.407	4.385, 3.907, 2.707
−60	60	3.105	4.096, 2.561, 2.870
−60	−60	4.139	5.109, 5.199, 4.173

Analysis of this transition in *cis*-1,4-polyisoprene requires examination of distances between a trigonal hydrogen and hydrogens on the methyl substituent. The fourth column of Table I lists these distances which have been calculated assuming that one of the methyl hydrogens eclipses the neighboring double bond, as suggested by microwave spectroscopy measurements on propylene.[17] An attempt to estimate the energy involved in this transition about bond i must take into

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(22) H. A. Kramers and G. H. Wannier, *Phys. Rev.*, **60**, 252 (1941); G. F. Newell and E. W. Montroll, *Rev. Mod. Phys.*, **25**, 353 (1953).

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(24) L. Pauling, "The Nature of the Chemical Bond," 3rd ed, Cornell University Press, Ithaca, N. Y., 1960; A. Bondi, *J. Phys. Chem.*, **68**, 441 (1964).

account the fact that ±60° states are the most frequently occurring states about bonds $i - 1$ and $i + 1$; the corresponding H···H distances, in general, would not give rise to steric repulsions. An energy change comparable to that occurring in the *cis*-1,4-polybutadiene chain would therefore be expected. It is important to note that *gauche* rotational states are always separated by two virtual bonds; rotational pairs ±120°, ∓120° which cause "pentane-type" interferences[2,3] are therefore absent *a priori*. In addition, examination of H···H distances indicates that accessible rotational pair such as ±60°,∓120° about CH—CH$_2$—CH$_2$ bonds do not in general bring about interactions not already accounted for in the present scheme. Therefore a statistical weight of σ relative to unity for *trans* is appropriate for +120° states irrespective of the rotational state of the preceding bond. Using symmetry arguments for transitions to −120° permits construction of the matrix

Bond type c

$$\mathbf{U}_c = \begin{bmatrix} 1 & 0 & \sigma & 0 & \sigma & 0 \\ 1 & 0 & \sigma & 0 & \sigma & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 \\ 1 & 0 & \sigma & 0 & \sigma & 0 \end{bmatrix} \tag{4}$$

(As is now obvious, $\mathbf{U}_a$, $\mathbf{U}_b$, and $\mathbf{U}_c$ may be reduced to 3×3 matrices. They are retained in their present form to facilitate future comparisons with the corresponding statistical weight matrices appropriate to the *trans* forms of polybutadiene and polyisoprene.) Although the energy E_σ for such *gauche* states assuredly will not be positive in *cis*-1,4-polybutadiene,[25] this possibility cannot be completely ruled out in the case of *cis*-1,4-polyisoprene.

It has been found in polyethylene[3] and in vinyl polymers[8] that interactions between nonbonded atoms can shift the location of the rotational minima from their normal values. Such distortions are not expected for the two types of bonds occurring in the *cis* polymer chains under consideration for the following reasons: (i) although interactions occurring upon rotations about CH—CH$_2$ are certainly considerable, they are very nearly symmetrical with respect to the rotation angles involved, and (ii) the interactions associated with CH$_2$—CH$_2$ bonds are expected to be too weak to cause any significant shift in the rotational minima.

The Partition Function and Characteristic Ratio. The partition function Z of the *cis*-1,4-polybutadiene and *cis*-1,4-polyisoprene chains, using the structural simplification shown in Figure 5, is[22,26]

$$Z = \mathbf{J}^*\mathbf{U}_b\mathbf{U}_c(\mathbf{U}_a\mathbf{U}_b\mathbf{U}_c)^{x-2}\,\mathbf{U}_a\mathbf{U}_b\mathbf{J} \tag{5}$$

where

$$\mathbf{J}^* = [100000],\ \mathbf{J} = \begin{bmatrix} 1 \\ 1 \\ 1 \\ 1 \\ 1 \\ 1 \end{bmatrix}$$

and x is the degree of polymerization.

Calculation of the characteristic rato $\langle r^2\rangle_0/n'm^2$ of the mean-square end-to-end distance $\langle r^2\rangle_0$ of a chain (Figure 5) having $n' = 3x$ bonds of average square length $m^2 = {}^1/_3(m_a^2 + m_b^2 + m_c^2)$ and unperturbed by long-range interactions, to the corresponding quantity $n'm^2$ of the same chain in the idealization that all skeletal bonds are freely jointed, requires transformation matrices for each type of skeletal bond. Using the now customary conventions[26,27] for defining right-handed cartesian coordinate systems about such bonds gives the transformation matrix

$$\mathbf{T}_i = \begin{bmatrix} \cos\theta_i & \sin\theta_i & 0 \\ \sin\theta_i\cos\phi_i & -\cos\theta_i\cos\phi_i & \sin\phi_i \\ \sin\theta_i\sin\phi_i & -\cos\theta_i\sin\phi_i & -\cos\phi_i \end{bmatrix} \tag{6}$$

where θ_i, the bond angle supplement, and ϕ_i, the rotation angle, are shown for $i = a$, b, and c in Figure 5. The characteristic ratio may be written[26]

$$\langle r^2\rangle_0/n'm^2 = 1 + (2/Zn'm^2)[1\,0\cdots 0]\mathbf{G}_1\mathbf{G}_b\mathbf{G}_c(\mathbf{G}_a\mathbf{G}_b\mathbf{G}_c)^{x-2} \times \mathbf{G}_a\mathbf{G}_b \begin{bmatrix} 0 \\ \cdot \\ \cdot \\ \cdot \\ \cdot \\ 0 \\ \mathbf{J} \times \mathbf{m}_c \\ \mathbf{J} \end{bmatrix} \tag{7}$$

where

$$\mathbf{G}_i = \begin{bmatrix} \mathbf{U}_i & (\mathbf{E} \times \mathbf{m}_i^{\mathrm{T}})(\mathbf{U}_i \times \mathbf{E}_3)\|\mathbf{T}\|_i & \mathbf{0} \\ \mathbf{0} & (\mathbf{U}_i \times \mathbf{E}_3)\|\mathbf{T}\|_i & (\mathbf{E}_3 \times \mathbf{m}_i)\mathbf{U}_i \\ \mathbf{0} & \mathbf{0} & \mathbf{U}_i \end{bmatrix} \tag{8}$$

the symbol × being used to denote the matrix direct product.[26] The matrix $\mathbf{U}_1$ required in $\mathbf{G}_1$ is simply the 3×3 unit matrix $\mathbf{E}_3$. The super matrix $\|\mathbf{T}\|_i$ contains the transformation matrixes $\mathbf{T}_i$ evaluated at the indicated values of ϕ_i

$$\|\mathbf{T}\|_i \begin{bmatrix} \mathbf{T}_i\ (\phi_i = 0°) & & & & & \\ & \mathbf{T}_i\ (\phi_i = 60°) & & & & \\ & & \mathbf{T}_i\ (\phi_i = 120°) & & & \\ & & & \mathbf{T}_i\ (\phi_i = 180°) & & \\ & & & & \mathbf{T}_i\ (\phi_i = -120°) & \\ & & & & & \mathbf{T}_i\ (\phi_i = -60°) \end{bmatrix} \tag{9}$$

(The fact that rotations about CH$_2$—CH$_2$ bonds are independent of the rotational states of the neighboring bonds confines the interdependence within the repeat unit. An analogous situation of mutually independent sequences of bonds occurs in the *trans* polypeptide

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[25] G. Allegra, U. Flisi, and G. Crespi [*Makromol. Chem.*, **75**, 189 (1964)] have treated the *cis*-1,4-polybutadiene chain using a model containing the following serious errors: (i) the interdependence of bond rotational states is completely ignored, (ii) pairs of *trans* states about CH$_2$–C$_2$H$_2$–CH$_2$ bonds are permitted, and (iii) the energy E_σ is assumed *a priori* to be positive, without investigation of the H···H interactions involved.

[26] P. J. Flory, *Proc. Natl. Acad. Sci. U. S.*, **51**, 1060 (1964); P. J. Flory and R. L. Jernigan, *J. Chem. Phys.*, **42**, 3509 (1965).

[27] x axis along the bond, y axis in the plane determined by the bond and the preceding bond, the positive y direction making an acute angle with the preceding bond.

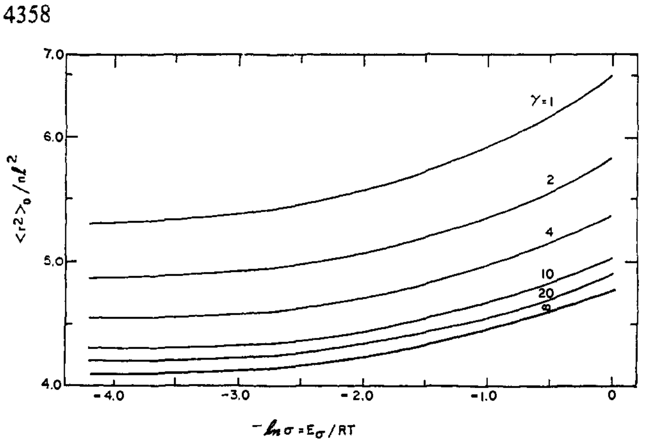

Figure 6. The characteristic ratio plotted against $-\ln\sigma$ for several values of γ.

chain;[7] the computational simplifications realized therein could also be employed in a scheme alternative to the above methodology without loss of rigor.)

In order to facilitate comparison of the dimensions of *cis*-1,4-polybutadiene and *cis*-1,4-polyisoprene with those of other polymers, particularly *trans*-1,4-polybutadiene and *trans*-1,4-polyisoprene, the characteristic ratio will be multiplied by $n'm^2/nl^2$ where $n = 4x$ explicitly includes the double bonds and $l^2 = {}^1/_4(3l_{\mathrm{C-C}}^2 + l_{\mathrm{C=C}}^2)$ is the mean square of all the skeletal bonds. Thus, henceforth, the characteristic ratio will be taken to mean $\langle r^2\rangle_0/nl^2$.

Experimental Results

Values of the molecular parameter $K_\Theta = [\eta]_\Theta M^{-1/2}$ for *cis*-1,4-polybutadiene have been obtained from molecular weights M and intrinsic viscosities $[\eta]_\Theta$ in Θ systems by a number of workers: (i) Danusso and co-workers[28] report a value of 1.85×10^{-3} dl g^{-1} (g mole)$^{-1/2}$ in isobutyl acetate at 20.5°, (ii) Moraglio[29] finds values of 1.89 and 1.82×10^{-3} from measurements in *n*-heptane at -1° and in *n*-propyl acetate at 35.5°, respectively, and (iii) Abe and Fujita,[30] values of 1.81, 1.79, and 1.57×10^{-3} in diethyl ketone at 10.3°, in methyl isoamyl ketone at 12.6°, and in methyl *n*-propyl ketone at 59.7°, respectively. Calculation of the characteristic ratio from the average of these values using the relationship[31]

$$K_\Theta = \Phi[\langle r^2\rangle_0/M]^{3/2} \tag{10}$$

where $\Phi = 2.5 \times 10^{21}$ for Gaussian chains at the Θ temperature,[32] gives $\langle r^2\rangle_0/nl^2 = 4.9 \pm 0.2$, variations due to changes in the temperature of determination being unimportant in the present context.

Similar analysis of results obtained by Wagner and Flory[33] for *cis*-1,4-polyisoprene in *n*-propyl ketone at 14.5° suggests a value of $\langle r^2\rangle_0/nl^2 = 4.7$ for this polymer.[34]

The temperature coefficient of $\langle r^2\rangle_0$ for *cis*-1,4-polybutadiene has been determined by force–temperature measurements on elongated networks of the cross-linked polymer in the amorphous state;[35] the value obtained is $\mathrm{d}\ln\langle r^2\rangle_0/\mathrm{d}T = 0.40 \times 10^{-3}$ deg^{-1} for the temperature range 50 to 90°.

Interpretation[36] of results of a similar study of *cis*-1,4-polyisoprene from -10 to 70° by Wood and Roth[37] gives $\mathrm{d}\ln\langle r^2\rangle_0/\mathrm{d}T = 0.41 \times 10^{-3}$ deg^{-1}. More recent work by Ciferri,[38] over the range 30 to 70°, suggests the somewhat higher value 0.56×10^{-3} deg^{-1}.

Correlation of Theoretical and Experimental Results

Values of the characteristic ratio have been calculated from eq 7 for $x = 120$, a degree of polymerization sufficiently large to ensure close approach to the asymptotic limit $[\langle r^2\rangle_0/nl^2]_{n\to\infty}$.[7,10] Figure 6 shows these values plotted against $-\ln\sigma$ for a series of values of γ. The two parameters will be considered expressible as Boltzmann factors in the energies of the associated conformations

$$\sigma = \exp(-E_\sigma/RT) \tag{11}$$

$$\gamma = \exp(-E_\gamma/RT) \tag{12}$$

where R is the gas constant. The temperature coefficient of $\langle r^2\rangle_0$ may then be calculated from the expression

$$\mathrm{d}\ln\langle r^2\rangle_0/\mathrm{d}T = -(1/T)[\ln\sigma(\partial\ln\langle r^2\rangle_0/\partial\ln\sigma) + \ln\gamma(\partial\ln\langle r^2\rangle_0/\partial\ln\gamma)] \tag{13}$$

The limiting curve for $\gamma \to \infty$ corresponds to permitting only ±60° states about CH—CH$_2$ bonds. Attempts to interpret the experimental results for *cis*-1,4-polybutadiene using this simple model were unsuccessful: (i) values of the characteristic ratio calculated for the range $\sigma \geqslant 1$ indicated by analysis of interactions between nonbonded atoms do not reach the experimental value, 4.9, and (ii) calculations in which this stipulation is relaxed in order to reproduce the observed characteristic ratio predict a negative temperature coefficient of $\langle r^2\rangle_0$, in disagreement with the experimental value.

Values of γ in the range 2 to 20 do give the required value of the characteristic ratio for *cis*-1,4-polybutadiene for $\sigma \geqslant 1$. The temperature coefficient $10^3\,\mathrm{d}\ln\langle r^2\rangle_0/\mathrm{d}T$ increases from 0.35 deg^{-1} at $\gamma = 2$ to 0.60 deg^{-1} at $\gamma = 4$ and then decreases to 0.30 deg^{-1} with further increase of γ to 20. Exact coincidence with the experimental values of the characteristic ratio and its temperature coefficient is obtained for $\gamma = 10$ and $\sigma = 1.4$, the corresponding energies at 70° being $E_\gamma = -1.6$ kcal mole^{-1} and $E_\sigma = -0.2$ kcal mole^{-1}. (Agreement could also be obtained by choice of $E_\gamma = -0.5$ kcal mole^{-1} and $E_\sigma = -2.2$ kcal mole^{-1}. This latter energy, however, is totally unrealistic for the attraction between two nonbonded hydrogen atoms at any distance of separation, and this set of parameters may, therefore, safely be discarded.) Unfortunately, the

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(34) A word of caution should perhaps be given at this point. Polymers with reactive double bonds in the chain backbone are susceptible to branching and intra- and intermolecular cross linking even in the presence of inhibitors. The occurrence of such structural deviations would significantly lower the observed characteristic ratio. Since *cis*-1,4-polyisoprene displays this susceptibility to a marked degree, the cited difference between its characteristic ratio and that of *cis*-1,4-polybutadiene must be accepted with some reservations.

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characteristic ratio is very insensitive to γ and σ in the vicinity of $\gamma = 10$ and $\sigma = 1.4$: $\partial \ln \langle r^2 \rangle_0 / \partial \ln \gamma = -0.0449$ and $\partial \ln \langle r^2 \rangle_0 / \partial \ln \sigma = -0.0786$. The particularly low value of the former quantity is undoubtedly due at least in part to structural features inherent in the chain under consideration. Transitions from states of 0 to ±60° about CH—CH$_2$ bonds are not nearly as effective in changing the dimensions of a polymer chain as are the transitions from 0 to ±120° occurring in polyethylene,[2,3] poly ethers,[5,6,10] vinyl polymers,[8] and other molecules of similar skeletal structure. In any case, the energies determined for both *cis*-1,4-polybutadiene and *cis*-1,4-polyisoprene should be regarded as only rough estimates.

The value $\gamma = 10$ should also be appropriate for *cis*-1,4-polyisoprene; if the value $\langle r^2 \rangle_0 / nl^2 = 4.7$ is accepted for this polymer (see footnote 34), a value of $\sigma = 2.46$ ($E_\sigma = -0.6$ kcal mole^{-1}) is required. For these values of the parameters, eq 13 predicts $\mathrm{d} \ln \langle r^2 \rangle_0 / \mathrm{d}T = 0.56 \times 10^{-3}$ deg^{-1}, in excellent agreement with experiment. It is anticipated, however, that a more reliable estimate of E_σ for 1,4-polyisoprene chains may be obtained from interpretation of $\langle r^2 \rangle_0 / nl^2$ and $\mathrm{d} \ln \langle r^2 \rangle_0 / \mathrm{d}T$ for the *trans* form of this polymer.

Discussion

Comparison of experimental and calculated values of the characteristic ratio and its temperature coefficient for *cis*-1,4-polybutadiene and *cis*-1,4-polyisoprene provides the following information: (i) the energy of a pair of 60° states about bond pairs CH—C$_2$H$_2$—CH relative to conformations ±60°,0° and 0°,±60° is of the order of -1 kcal mole^{-1}, and (ii) the energy of a *gauche* state about a CH$_2$—CH$_2$ bond is either the same as that of a *trans* state or is possibly a few hundred cal mole^{-1} lower.

The basis for the positive temperature coefficient of $\langle r^2 \rangle_0$ for these polymers can be seen by examination of the two terms in brackets in eq 13. The increase in dimensions due to transitions to more extended conformations about CH—C$_2$H$_2$—CH bond pairs (*e.g.*, ±60°,±60° $\rightarrow$ 0°,±60°) as the temperature is increased accounts for approximately 70% of the magnitude of the observed temperature coefficient, the remainder being due to *gauche* to *trans* transitions about CH$_2$—CH$_2$ bonds.

According to the present study, repeat unit +C—C=C—C+ conformations (±60°,180°,±60°,0°) and (±60°,180°,∓60°,0°) should be of approximately the same intramolecular energy as (±60°,180°,±60°, ±120°) and (±60°,180°,∓60°,±120°). X-Ray diffraction studies of the crystal structures of *cis*-1,4-polybutadiene[11,12] and *cis*-1,4-polyisoprene[11,13,14] indicate a conformational sequence $[(\pm 60°,180°,\pm 60°,0°); (\mp 60°,180°,\mp 60°,0°)]_{x/2}$ for the chains in the crystalline state. This final choice is apparently made on the basis of the relative efficiencies with which these conformations may be incorporated into a crystalline lattice.

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A Kerr-Effect Study of the Low pH Configuration Changes of Bovine Plasma Albumin in Aqueous Solutions

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Abstract: Electric birefringence measurements have been made on dilute aqueous solutions of bovine plasma albumin (BPA) in order to observe its acid configuration transitions. As the pH was reduced from the isoelectric value of 5.1, the relaxation times of both samples studied fell abruptly at pH 4.1 and at pH 3.6. These decreases were accompanied by increased contributions from the induced dipolar effects and are considered as confirmation of the two-stage expansion of the quadruple-unit molecule proposed by Foster. When studied near the isoelectric point, the two samples displayed different relaxation times, each of which could be substantiated by results recorded in the literature. The difference probably arose from the presence of larger particles in the solutions. Both samples demonstrated the ready formation of nonreproducible quantities of associates of BPA when the pH was lowered below 3.2. The method appears to display molecular configuration changes admirably.

It is now well known that if a solution of randomly arrayed optically anisotropic macromolecules, which are either dipolar or electrically anisotropic, is placed in an electric field, the molecules orientate to a position of minimum potential energy. The ordering of the particles so obtained renders the solution birefringent. This Kerr electrooptical effect is completely reversible in that Brownian motion disorientates the molecules upon removal of the applied field. However, as the molecules require a finite time to respond to changes of the applied field, a relaxation of the birefringence, characterized by a relaxation time of τ sec is observed. τ is a function of the size and shape of the molecules and of the viscosity of the particular solvent. Thus, for applied pulsed fields, observations on both the steady maximum and the transient values of the bire-