Table IV. LCST's for n-Alkanes and Polymethylene

n-Alkane	LCST, °C Obsd	LCST, °C Calcd (eq 22)
n-C_6H_{14}	127,[a] 133,[b] 135[c]	70
n-C_7H_{16}	184[c]	120
n-C_8H_{18}	223[c]	150

[a] Reference 18. The molecular weight of the polymethylene was 10^6. [b] Reference 19. This value has been extrapolated to infinite molecular weight. [c] This work.

served. The calculations, however, are sensitive to the precise values of the parameters, and doubtless also to minor aberrations of the theory itself inasmuch as the LCST is located through a second derivative of the chemical potential. Moreover, the densities of the solvents are low in the range of the LCST's; they are in fact not very much greater than the critical densities for the pure liquids. At low liquid densities some of the assumptions underlying the treatment become questionable.[1,8] In view of these considerations, the measure of agreement between observed and calculated LCST's is gratifying. It is achieved without additional parameters beyond those assigned earlier on the basis of other measurements.

Inclusion of the term Γ_S improves the representation of lower critical miscibility. Calculations carried out without it predict limited miscibility for polymethylene (liquid) in n-C_6H_{14} and in n-C_7H_{16} at all temperatures above 20°; the LCST calculated on this basis for n-C_8H_{18} is about 80°.

Excess Coefficients of Expansion and Compressibility

Díaz Peña and Benítez de Soto[12] have measured the coefficients of expansion α and compressibility κ of solutions of n-C_6H_{14} and n-$C_{16}H_{34}$. Excess expansions

$$\alpha^E = (1/v)(\partial v^E/\partial T)_p = \alpha - (x_1v_1\alpha_1 + x_2v_2\alpha_2)/v \quad (23)$$

and excess compressibilities

$$\kappa^E = -(1/v)(\partial v^E/\partial p)_T = \kappa - (x_1v_1\kappa_1 + x_2v_2\kappa_2)/v \quad (24)$$

calculated from the results of their experiments are presented in Table V.

The values of α^E and κ^E given in the third and sixth columns of Table V have been computed from the thermal expansion coefficients, thermal pressure coefficients, and molar volumes of the components, and from α and $\kappa = \alpha/\gamma$ calculated for the mixture from T^* and p^* using eq 11*–13*. The agreement is excellent.

Table V. Excess Coefficients of Expansion and Compressibility for the Equimolar Mixture of n-Hexane and n-Hexadecane

Temp, °C	$10^3\alpha$, deg^{-1} Calcd	$10^3\alpha^E$, deg^{-1} Calcd	$10^3\alpha^E$, deg^{-1} Obsd[a]	$10^3\kappa$, cm^3 cal^{-1} Calcd	$10^3\kappa^E$, cm^3 cal^{-1} Calcd	$10^3\kappa^E$, cm^3 cal^{-1} Obsd[a]
30	1.024	−0.039	−0.049	4.56	−0.37	−0.37
40	1.038	−0.045	−0.057	4.90	−0.45	−0.47
50	1.054	−0.053	−0.064	5.27	−0.55	−0.57
60	1.072	−0.063	−0.071	5.67	−0.69	−0.66

[a] Reference 12.

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Interpretation of Random-Coil Configurations of *trans*-1,4-Polybutadiene and *trans*-1,4-Polyisoprene

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Contribution from the Department of Chemistry, Polytechnic Institute of Brooklyn, Brooklyn, New York 11201. *Received June 23, 1967*

Abstract: Results of calculations based on a rotational isomeric state model with neighbor dependence are used to interpret experimental values of the chain dimensions and their temperature coefficient for *trans*-1,4-polybutadiene and *trans*-1,4-polyisoprene. Similarities and differences in conformational and configurational properties between these polymers and *cis*-1,4-polybutadiene and *cis*-1,4-polyisoprene are elucidated. The interpretation of the properties of the *trans*-diene polymers is found to be consistent with that reported previously for the corresponding *cis*-diene chains.

In a recent investigation[2] a rotational isomeric state model treated by Ising lattice methods was successfully used to interpret the chain dimensions and their temperature coefficient for the *cis* forms of 1,4-polybutadiene (PBD), $\text{+}CH_2CH{=}CHCH_2\text{+}_x$, and 1,4-polyisoprene (PIP), $\text{+}CH_2C(CH_3){=}CHCH_2\text{+}_x$, in the limit of high degree of polymerization x. Such calculations can readily be extended to include the *trans* forms of these polymers, for which some experimental results are available.

In this approach, correlation of experimental and theoretical results yields estimates of the energies associated with various conformations of the chain backbone. Since some intramolecular interactions occurring in the *trans*-diene chains are very similar to

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[2] J. E. Mark, *J. Am. Chem. Soc.*, **88**, 4354 (1966).

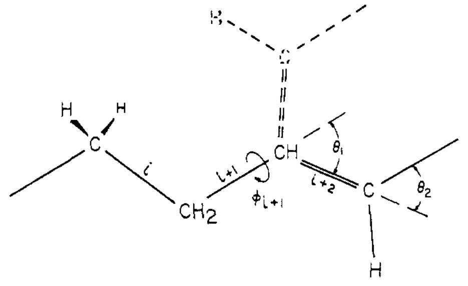

Figure 1. A section of the fully extended *trans*-1,4-polybutadiene chain; dotted lines show the 180° rotational state about CH_2–CH bond $i + 1$.

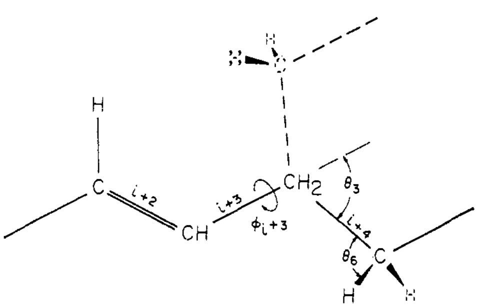

Figure 2. Subsequent section of the chain shown in Figure 1; dotted lines show the 180° rotational state about CH–CH_2 bond $i + 3$.

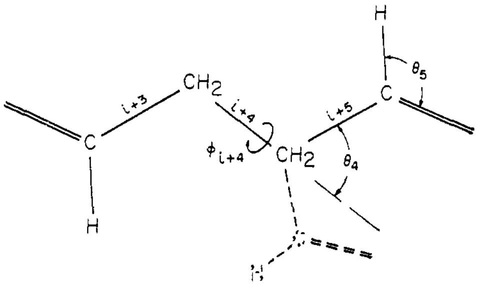

Figure 3. Subsequent section of the chain shown in Figure 1; dotted lines show the +120° rotational state about CH_2–CH_2 bond $i + 4$.

interactions in the *cis* forms of the same polymers, the energies of these interactions must be approximately the same for both forms. A single set of conformational energies should therefore be sufficient for interpreting configurational properties of both the *cis* and *trans* forms of PBD and PIP. The attempt to establish this consistent interpretation for the four diene polymers thus constitutes an important test of rotational isomeric state theory and is the purpose of the present study.

Theory

Structural Features of the Repeat Units. Values of bond lengths l_i and bond angles θ_i illustrated in Figures[3] 1 to 3 were adopted on the basis of results of studies of low molecular weight compounds;[4] they are listed in columns three and four of Table I, which pertains to both *trans*-PBD and *trans*-PIP. In the rotational isomeric state approximation,[5,6] each skeletal bond is assigned to one of a small number of discrete rotational states, these states generally being located at minima in the bond torsional potentials. On the basis of studies of propylene[7] and related compounds,[8,9] rotational states about CH_2–CH and CH–CH_2 bonds such as $i + 1$ and $i + 3$, respectively, of Figures 1 and 2 are assumed to occur at rotational angles $\phi = \pm 60$ and 180° (measured from a *trans* state of $\phi = 0°$). Double bonds such as $i + 2$ of Figure 1 are of course restricted to $\phi = 0°$ for the *trans*-diene polymers under consideration. The torsional potential found for *n*-alkyl compounds[8,9] suggests location of rotational states at 0 and ±120° for CH_2–CH_2 bonds such as $i+4$ of Figure 3. These conclusions are summarized in the last column of Table I.

Conformational Statistical Weights. Except for chain molecules in which steric interactions play a relatively minor role, as is the case for example in chains of sulfur and selenium,[10] the statistical weight for a rotational state depends on the rotational states of the immediately adjacent skeletal bonds. The paramount importance of this nearest neighbor dependence in a variety of chain molecules has been well documented.[11] In the case of interdependent rotational states,[12] generation of the configurational partition function for a chain may be accomplished using matrices the elements of which are the statistical weights appropriate for the various conformations adjacent bond pairs may adopt.[13,14] Following the analysis of *cis*-diene chains,[2] a six-by-six *rotational statistical weight matrix* $\mathbf{U}_i$ will be defined for each type of skeletal bond in the *trans*-diene chains. Rows of these matrices, associated with rotational states of bond $i - 1$, and columns, associated with states of bond i, will be indexed in the order $\phi = 0, 60, 120, 180, -120, -60°$. Thus, for example, element $\mathbf{U}_i$ (3, 4) will be the statistical weight assigned to the conformational sequence 120, 180° about bond pair $i - 1$, i. Finally, all statistical weights will be expressed relative to unity for the *trans*-diene chain having all repeat units -(C—C=C—C-)- in the conformation (60°, 0°, 60°, 0°).

We consider first the statistical weights for states of CH_2–CH bonds, such as $i + 1$ of Figure 1, in either *trans*-PBD or *trans*-PIP chains. Since the preceding bond is in either a 0 or ±120° state, only combinations of these states with ±60 and 180° states permitted

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(3) In these figures, the planar, all-*trans* form is shown only for purposes of illustration; in actuality, this is *not* a permitted conformation for these chain molecules.

(4) H. J. M. Bowen and L. E. Sutton, "Tables of Interatomic Distances and Configurations in Molecules and Ions," The Chemical Society, London, 1958; "Interatomic Distances Supplement," The Chemical Society, London, 1965.

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

(6) M. V. Volkenstein, "Configurational Statistics of Polymeric Chains," Interscience Publishers, Inc., New York, N. Y., 1963.

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

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

(9) D. R. Lide, Jr., *Ann. Rev. Phys. Chem.*, **15**, 225 (1964).

(10) J. A. Semlyen, *Trans. Faraday Soc.*, **63**, 743 (1967).

(11) Reference 2 and references to previous studies given therein.

(12) Earlier treatments of *trans*-diene chains were restricted to either freely rotating or neighbor-independent chain models; see, for example, F. T. Wall, *J. Chem. Phys.*, **11**, 67 (1943); H. Benoit, *J. Polymer Sci.*, **3**, 376 (1948); A.-C. Tang and J.-C. Liu, *J. Chinese Chem. Soc.*, **18**, 110 (1951); H. Markovitz, *J. Chem. Phys.*, **20**, 868 (1952); A. A. Chistorazum, *Dokl. Akad. Nauk SSSR*, **89**, 999 (1953).

(13) H. A. Kramers and G. H. Wannier, *Phys. Rev.*, **60**, 252 (1941).

(14) G. F. Newell and E. W. Montroll, *Rev. Mod. Phys.*, **25**, 353 (1953).

Table I. Bond Lengths, Bond Angles, and Locations of Rotational States, *trans*-Diene Chains

	Example	Bond lengths, A	Bond angles, deg	Locations of rotational states, deg
l_{C-C}	l_{i+3}, l_{i+4}, and l_{i+5}[a]	1.53		
$l_{C=C}$	l_{i+2}[b]	1.34		
l_{C-H}		1.10		
$\angle CH_2{-}CH{=}CH$	$\pi - \theta_1$ and $\pi - \theta_2$[b]		125	
$\angle CH_2{-}C(CH_3){=}CH$			125	
$\angle CH{-}CH_2{-}CH_2$	$\pi - \theta_3$[c] and $\pi - \theta_4$[a]		112	
$\angle CH{=}C{-}H$	θ_5[a]		117.5	
$\angle CH{=}C{-}CH_3$			117.5	
$\angle CH_2{-}CH{-}H$	θ_6[c]		110	
$CH_2{-}\circlearrowleft{-}CH$	ϕ_{i+1}[b]			±60, 180
$CH{=}CH$				0
$CH{-}\circlearrowleft{-}CH_2$	ϕ_{i+3}[c]			±60, 180
$CH_2{-}\circlearrowleft{-}CH_2$	ϕ_{i+4}[a]			0, ±120

[a] Figure 3. [b] Figure 1. [c] Figure 2.

about bond *i* need be considered in constructing the matrix $\mathbf{U}_a$ associated with bond $i + 1$. It should be noted that in *cis*-diene polymers, 180° states about such bonds are excluded because of very strong repulsions between methylene groups[2] such as those separated by bonds *i* through $i + 3$ in Figure 1. In the 180° state of bond $i+1$ in *trans*-diene chains, however, the smallest distance between nonbonded hydrogen atoms is 2.22 A, between carbon atoms, 2.89 A, and between carbon and hydrogen atoms, 2.45 A. Since the intermolecular van der Waals radii of carbon and hydrogen atoms are approximately 1.7 and 1.2 A,[15] respectively, it may be concluded that strong steric repulsions are absent in this conformation. Additional qualitative consideration of interatomic distances suggests that when the preceding bond is in a 0° state, the energy of a 180° state about a CH_2–CH bond is not very different from that of a ±60° state. The statistical weight α assigned to a 180° state is therefore expected to be near that of the ±60° states, *viz.*, unity. If the preceding bond is ±120°, however, an additional interaction must be taken into account. In the conformation ±120°, 180° about bond pair i, $i + 1$, CH groups separated by bonds $i - 1$ through $i + 2$ are located 2.94 A from one another, with one trigonal hydrogen only 2.28 A from the other carbon atom. The possible suppressive effect of these interactions is taken into account by assigning a statistical weight of $\beta\alpha$ to ±120°, 180° conformations where it is anticipated that β will be less than unity. Since the above considerations apply to both *trans*-PBD and *trans*-PIP, the appropriate statistical weight matrix for CH_2–CH bonds in either polymer is

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

Double bonds such as $i + 2$ of Figure 1 are of course restricted to 0° in the polymers under consideration. The statistical weight matrix $\mathbf{U}_b$ for such bonds in any *trans*-diene chain is therefore simply

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

except for the second bond in the chain. Since it is not possible to define rotational states for its predecessor, the statistical weight matrix $\mathbf{U}_2$ for this double bond has only one nonzero element, $\mathbf{U}_2(1, 1) = 1$.

In *trans*-PBD, symmetry dictates that 180° rotational states about CH–CH_2 bonds such as $i + 3$ of Figure 2 receive the same statistical weight α appearing in $\mathbf{U}_a$ For such bonds, therefore, the statistical weight matrix $\mathbf{U}_c$ is

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

The 180° state about this bond is excluded, however, in the *trans*-PIP chain, which can be visualized by replacing the trigonal hydrogen atom on the left of Figure 2 by a methyl group. If $\phi_{i+3} = 180°$, the methyl group is only 2.41 A from the methylene group situated between bonds $i + 4$ and $i + 5$. Since the intermolecular van der Waals radius for the methyl group is approximately 2.0 A,[16] steric interactions would certainly be sufficient to exclude this conformation. Therefore, in the case of *trans*-PIP, the 1, 4 element of $\mathbf{U}_c$ must be set equal to zero; i.e., only ±60° states are permitted about CH–CH_2 bonds in this polymer.

The CH_2–CH_2 bonds in *trans*-diene polymers can adopt 0 or ±120° states. When the preceding bond in the *trans*-PBD chain is in a ±60° state, interactions involved in the "transition" 0 to ±120° about bonds such as $i + 4$ in Figure 3 are very similar to those

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(15) A. Bondi, *J. Phys. Chem.*, **68**, 441 (1964).

(16) L. Pauling, "The Nature of the Chemical Bond," 3rd ed, Cornell University Press, Ithaca, N. Y., 1960.

occurring in *cis*-PBD. Consideration of the appropriate interatomic distances[2] lead to the conclusion that 0 and ±120° states are of approximately equal energy. In addition, correlation of calculated and experimental values of the chain dimensions of *cis*-PBD[2] indicate that the energy difference is only approximately 0.2 kcal mole^{-1}. Since, unfortunately, the dimensions of the *cis*-PBD chain are relatively insensitive to this energy difference,[2] one is limited to the statement that the statistical weight σ for a ±120° state should be approximately the same as that of a 0° state, *viz.*, unity. If the preceding bond is in a 180° state, however, interactions between CH groups require inclusion of the same factor β appearing in $\mathbf{U}_a$. Thus, the statistical weight matrix $\mathbf{U}_d$ for rotations about CH_2–CH_2 bonds in *trans*-PBD is

$$\mathbf{U}_d = \begin{bmatrix} 0 & 0 & 0 & 0 & 0 & 0 \\ 1 & 0 & \sigma & 0 & \sigma & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 \\ 1 & 0 & \beta\sigma & 0 & \beta\sigma & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 \\ 1 & 0 & \sigma & 0 & \sigma & 0 \end{bmatrix} \qquad (4)$$

The replacement of the trigonal hydrogen on the right of Figure 3 with a methyl group can be expected to change the statistical weight for ±120° states about CH_2–CH_2 bonds in *trans*-PIP. In any case, the energy difference between 0 and ±120° states should be very nearly the same for *trans*-PIP and *cis*-PIP, as can readily be seen in Figure 3. The distances separating methyl hydrogens from the trigonal hydrogen, reported in the analysis of *cis*-PIP,[2] suggest that the statistical weight σ' for such ±120° states is less than or equal to unity. For *trans*-PIP chains, therefore

$$\mathbf{U}_d = \begin{bmatrix} 0 & 0 & 0 & 0 & 0 & 0 \\ 1 & 0 & \sigma' & 0 & \sigma' & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 \\ 1 & 0 & \sigma' & 0 & \sigma' & 0 \end{bmatrix} \qquad (5)$$

The form of matrix $\mathbf{U}_b$ immediately shows that interdependence of bond rotational states is confined within short sequences of the chain, as is the case in *cis*-diene polymers[2] and in *trans* polypeptides.[17] It should also be mentioned that each **U** can be reduced to a matrix of lower order; they are retained in their six-by-six form to facilitate comparison with the corresponding statistical weight matrices of the *cis*-diene chains.[2]

The Partition Function and Characteristic Ratio. Application of one-dimensional Ising lattice methods[13,14] to the rotational isomeric state model of the *trans*-diene chain gives for the configuration partition function

$$Z = J^*\mathbf{U}_2\mathbf{U}_c\mathbf{U}_d(\mathbf{U}_a\mathbf{U}_b\mathbf{U}_c\mathbf{U}_d)^{x-2}\mathbf{U}_a\mathbf{U}_b\mathbf{U}_c J \qquad (6)$$

where subscripts a through d refer to consecutive bonds in the repeat unit $-\!\!\left(\mathrm{C{-}C{=}C{-}C}\right)\!\!-$, $J^* = [1\ 0\ 0\ 0\ 0\ 0]$, and

$$J = \begin{bmatrix} 1 \\ 1 \\ 1 \\ 1 \\ 1 \\ 1 \end{bmatrix}$$

The mean square end-to-end distance $\langle r^2\rangle_0$ of the *trans*-diene chain in the unperturbed state[18] will be expressed relative to nl^2, where $n = 4x$ is the number of skeletal bonds, and $l^2 = (^1/_4)(l_a{}^2 + l_b{}^2 + l_c{}^2 + l_d{}^2)$ is their mean square length. Since nl^2 would be the value of $\langle r^2\rangle_0$ if the chain were freely jointed, the *characteristic ratio* $\langle r^2\rangle_0/nl^2$ represents the factor by which the actual, unperturbed dimensions depart from those of this simple model. Calculation of this ratio[19,20] proceeds by construction of right-handed Cartesian coordinate systems about each bond of the chain backbone. Convenience suggests that the x axis be taken along each skeletal bond i, with the positive y axis lying in the plane determined by bonds i and $i - 1$ and making an acute angle with bond $i - 1$. For these conventions, the transformation matrix

$$\mathbf{T}_i = \begin{bmatrix} \cos\theta_i & \sin\theta_i & 0 \\ \sin\theta_i\cos\varphi_i & -\cos\theta_i\cos\varphi_i & \sin\varphi_i \\ \sin\theta_i\sin\varphi_i & -\cos\theta_i\sin\varphi_i & -\cos\varphi_i \end{bmatrix} \qquad (7)$$

will effect the transformation of bond $i + 1$ into the coordinate system of bond i. Also required in the calculation of $\langle r^2\rangle_0/nl^2$ are the pseudo-diagonal matrix $\|\mathbf{T}_i\|$ containing as pseudo-elements the transformation matrices $\mathbf{T}_i$

$$\|\mathbf{T}\|_i = \begin{bmatrix} \mathbf{T}_i(\varphi_i = 0°) & & & & & \\ & \mathbf{T}_i(\varphi_i = 60°) & & & & \\ & & \mathbf{T}_i(\varphi_i = 120°) & & & \\ & & & \mathbf{T}_i(\varphi_i = 180°) & & \\ & & & & \mathbf{T}_i(\varphi_i = -120°) & \\ & & & & & \mathbf{T}_i(\varphi_i = -60°) \end{bmatrix} \qquad (8)$$

and the matrix

$$\mathbf{G}_i = \begin{bmatrix} \mathbf{U}_i & (\mathbf{E} \times \mathrm{l}_i{}^T)(\mathbf{U}_i \times \mathbf{E}_3)\,\|\mathbf{T}\|_i & \mathbf{0} \times \\ \mathbf{0} & (\mathbf{U}_i \times \mathbf{E}_3)\,\|\mathbf{T}\|_i & (\mathbf{E}_3 \times \mathrm{l}_i)\mathbf{U}_i \\ \mathbf{0} & \mathbf{0} & \mathbf{U}_i \end{bmatrix} \qquad (9)$$

where $\mathbf{E}_3$ is the three-by-three unit matrix, l_i is the column vector having elements l_i, 0, 0 and transpose $\mathrm{l}_i{}^T$, and × denotes the matrix direct product.[19,20] The characteristic ratio may now be written[19,20] as shown in eq 10, where the matrix $\mathbf{U}_1$ required in $\mathbf{G}_1$ is simply the six-by-six unit matrix.

$$\langle r^2\rangle_0/nl^2 = 1 + (2/Znl^2)[1\ 0\ \ldots\ 0] \times \mathbf{G}_1\mathbf{G}_2\mathbf{G}_c\mathbf{G}_d(\mathbf{G}_a\mathbf{G}_b\mathbf{G}_c\mathbf{G}_d)^{x-2}\mathbf{G}_a\mathbf{G}_b\mathbf{G}_c \begin{bmatrix} 0 \\ \cdot \\ \cdot \\ \cdot \\ \cdot \\ 0 \\ \mathbf{J} \times \mathrm{l}_d \\ \mathbf{J} \end{bmatrix} \qquad (10)$$

Experimental Results

Molecular weights M, intrinsic visosities $[\eta]$, and osmotic second virial coefficients in decalin at 55° have been determined[21] for two fractions of polybutadiene having essentially 100% *trans*-1,4 content

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[17] D. A. Brant and P. J. Flory, *J. Am. Chem. Soc.*, **87**, 2791 (1965).

[18] P. J. Flory, "Principles of Polymer Chemistry," Cornell University Press, Ithaca, N. Y., 1953.

[19] P. J. Flory, *Proc. Natl. Acad. Sci. U. S.*, **51**, 1060 (1964).

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

[21] G. B. Thomas and J. E. Mark, unpublished results; G. B. Thomas, M.S. Thesis, The Polytechnic Institute of Brooklyn, 1966.

on the basis of their infrared spectra. These results were interpreted using the equation[22]

$$[\eta] = \Phi[\langle r^2\rangle_0/M]^{3/2}M^{1/2}\alpha_\eta{}^3 \qquad (11)$$

where Φ is a universal constant equal to 2.1×10^{21} for gaussian coils in thermodynamically good solvents,[18] and α_η is a correction factor for long-range interactions. The required values of α_η were obtained from the second virial coefficients using the method of Orofino and Flory.[23] Use of these quantities in eq 11 gives $\langle r^2\rangle_0/nl^2 = 5.8 \pm 0.2$ for *trans*-PBD.

The value of the characteristic ratio for *trans*-PIP was calculated from the molecular parameter $K_\Theta = [\eta]_\Theta M^{-1/2}$ obtained from intrinsic viscosities $[\eta]_\Theta$ in *n*-propyl acetate at the Θ temperature, 60°, and molecular weights reported[24] for a sample of *trans*-PIP having no detectable *cis* content on the basis of infrared analysis. Use of the relationship[22]

$$K_\Theta = \Phi[\langle r^2\rangle_0/M]^{3/2} \qquad (12)$$

where $\Phi = 2.5 \times 10^{21}$ for gaussian coils at the Θ temperature[25] gives 7.35 for the characteristic ratio of this polymer.

The corresponding values for *cis*-PBD and *cis*-PIP will be recorded here for purposes of comparison. Interpretation[2] of molecular weights and intrinsic viscosities[26–28] obtained under Θ conditions on samples of polybutadiene having a *cis*-1,4 content of at least 95% gives $\langle r^2\rangle_0/nl^2 = 4.9$. Using similar results[24] obtained on a sample of polyisoprene of presumably high *cis*-1,4 content gives 4.7 for the characteristic ratio of *cis*-PIP.

The temperature coefficient of $\langle r^2\rangle_0$ has been estimated for *cis*- and *trans*-PBD and -PIP from force–temperature measurements on elongated networks of the polymers in the amorphous state. In a study[29] of butadiene and isoprene polymers of essentially 100% *trans*-1,4 content, it was not possible, however, to obtain networks stable over the temperature ranges employed: 90 to 110° for *trans*-PBD and 40 to 90° for *trans*-PIP. This instability was manifested as a small difference between temperature-increasing and temperature-decreasing portions of a force–temperature cycle. The results of this study, $\mathrm{d}\ln\langle r^2\rangle_0/\mathrm{d}T = -0.65 \times 10^{-3}$ deg^{-1} for *trans*-PBD and -0.27×10^{-3} deg^{-1} for *trans*-PIP, must therefore be considered only qualitative estimates. The negative temperature coefficients of $\langle r^2\rangle_0$ obtained for these *trans*-diene polymers is of considerable interest, however, since this coefficient is positive for both *cis*-PBD and *cis*-PIP. For *cis*-PBD the value $\mathrm{d}\ln\langle r^2\rangle_0/\mathrm{d}T = 0.40 \times 10^{-3}$ deg^{-1} was obtained[29] over the range 50 to 90°, in reasonable agreement with the values 0.13 to 0.43×10^{-3} deg^{-1} found by other workers[30] for the interval 0 to 70°. Interpretation[31] of results obtained on *cis*-PIP networks from −10 to 70° by Wood and Roth[32] yields $\mathrm{d}\ln\langle r^2\rangle_0/\mathrm{d}T = 0.41 \times 10^{-3}$ deg^{-1}, in reasonable agreement with the value 0.56×10^{-3} deg^{-1} reported by Ciferri[33] for the range 30 to 70°

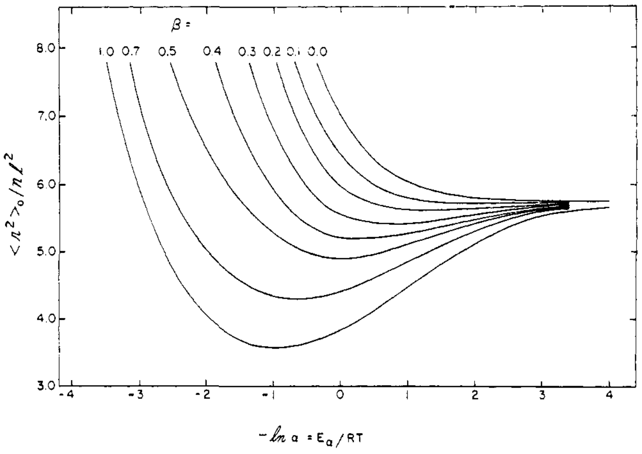

Figure 4. The characteristic ratio $\langle r^2\rangle_0/nl^2$ for *trans*-1,4-polybutadiene plotted as a function of $-\ln\alpha$ for $\sigma = 1$ and values of β as indicated.

As has already been pointed out,[2] measurements of configurational properties of chain molecules containing reactive double bonds are fraught with difficulty because of the possibility of chain branching or cross-linking. On the basis of comparison of gelation times of uninhibited solutions of these diene polymers, *cis*-PIP seems to be the most susceptible to these types of structural deviations. The low value of the characteristic ratio obtained for this polymer[24] could be due in part to this difficulty. In addition, these diene chains undoubtedly have some steric imperfections. The configurational properties of highly isotactic vinyl polymers were found to be dramatically affected by the presence of only a few per cent of steric inversions, since such irregularities cause disruption of the preferred, highly extended helical conformations.[34] Since the interdependence of bond rotational states is restricted within short chain sequences in both *cis*- and *trans*-diene chains, long helical segments are not favored in these polymers. The effect of these irregularities is therefore undoubtedly much less important in diene chains, but it is well to recognize this additional possible source of experimental difficulty.

Correlation of Theory and Experiment.

Values of $\langle r^2\rangle_0/nl^2$ were calculated from eq 10 using $x = 120$ and bond lengths, bond angles, and rotational angles given in Table I. At a degree of polymerization of 120, the characteristic ratio is assuredly within 1% of its value in the limit of infinite chain length.[20,35,36] In Figure 4 the characteristic ratio for *trans*-PBD is plotted against $-\ln\alpha$ for $\sigma = 1$ and values of β ranging from 0 to 1. Temperature coefficients of $\langle r^2\rangle_0$ may be calculated from the temperature dependence of the statistical weights. For this purpose, each statistical weight will be ex-

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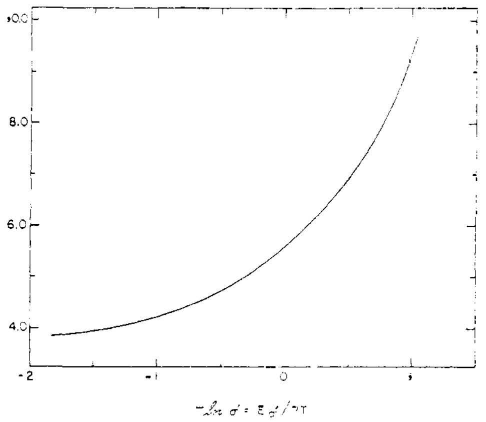

Figure 5. The characteristic ratio for *trans*-1,4-polyisoprene *vs.* $-\ln\sigma'$ for $\alpha = 0.96$ and $\beta = 0.217$.

pressed as a Boltzmann factor in the energy of the conformation with which it is associated; for example

$$\alpha = \exp(-E_\alpha/RT) \qquad (13)$$

where R is the gas constant. It then follows that

$$d\ln\langle r^2\rangle_0/dT = -(1/T)[\ln\alpha(\partial\ln\langle r^2\rangle_0/\partial\ln\alpha) + \ln\beta(\partial\ln\langle r^2\rangle_0/\partial\ln\beta) + \ln\sigma\,(\partial\ln\langle r^2\rangle_0/\partial\ln\sigma)] \qquad (14)$$

Temperature coefficients of $\langle r^2\rangle_0$ calculated at the experimental value[21] $\langle r^2\rangle_0/nl^2 = 5.8$ for *trans*-PBD decrease monotonically as β increases from 0 to 1; at $\beta = 0$, $d\ln\langle r^2\rangle_0/dT = 0.1 \times 10^{-3}$ deg^{-1}, and at $\beta = 0.5$, -2.2×10^{-3} deg^{-1}. The experimental values, $\langle r^2\rangle_0/nl^2 = 5.8$[21] and $d\ln\langle r^2\rangle_0/dT = -0.65 \times 10^{-3}$ deg^{-1},[29] are reproduced uniquely at $\alpha = 0.96$ and $\beta = 0.24$. At 100°, the average temperature of the force–temperature measurements on *trans*-PBD, the corresponding energies are $E_\alpha = 0.03$ kcal mole^{-1} and $E_\beta = 1.1$ kcal mole^{-1}, in satisfactory agreement with conjectures based on qualitative consideration of the interactions involved. Coefficients expressing the dependence of $\langle r^2\rangle_0$ on α, β, and σ are given in the second column of Table II. The value of $\partial\ln\langle r^2\rangle_0/\partial\ln\sigma$ is included only for purposes of comparison; it does not contribute to $d\ln\langle r^2\rangle_0/dT$ since in eq 14 it is multiplied by $\ln\sigma$, which is zero for the assumption that $\sigma = 1$.

Table II. Dependence of the Characteristic Ratio on Statistical Weights: *trans*- and *cis*-Diene Chains

	trans-1,4-Polybutadiene	*trans*-1,4-Polyisoprene	*cis*-1,4-Polybutadiene	*cis*-1,4-Polyisoprene
$\partial\ln\langle r^2\rangle_0/\partial\ln\alpha$	0.118	0.0497		
$\partial\ln\langle r^2\rangle_0/\partial\ln\beta$	−0.184	−0.0823		
$\partial\ln\langle r^2\rangle_0/\partial\ln\sigma$	−0.493		−0.0786	
$\partial\ln\langle r^2\rangle_0/\partial\ln\sigma'$		−0.562		−0.0649
$\partial\ln\langle r^2\rangle_0/\partial\ln\gamma$			−0.0449	−0.0487

To a good approximation, the same values of α and β should apply to the *trans*-PIP chain; σ', however, may be considerably smaller than σ, as has already been pointed out Figure 5 shows a plot of $\langle r^2\rangle_0/nl^2$ *vs.* $-\ln\sigma'$ for *trans*-PIP, using $\alpha = 0.96$ and $\beta = 0.217$, the values of these parameters appropriate for 65°, the average temperature used in the determination[29] of $d\ln\langle r^2\rangle_0/dT$. The experimental value[24] of $\langle r^2\rangle_0/nl^2 = 7.35$ is obtained at $\sigma' = 0.543$ ($E_{\sigma'} = 0.4$ kcal mole^{-1} at 65°), a plausible result. Values of the partial derivatives of $\langle r^2\rangle_0$ with respect to α, β, and σ' are given in the third column of Table II; their use in the appropriate form of eq 14 predicts a moderately large, negative temperature coefficient of the dimensions, $d\ln\langle r^2\rangle_0/dT = -1.4 \times 10^{-3}$ deg^{-1}. This value is in only qualitative agreement with the small, negative value, -0.27×10^{-3} deg^{-1}, obtained from preliminary force–temperature measurements.[29]

The value $\sigma' = 0.543$ should also represent the statistical weight of ±120° states about CH_2–CH_2 bonds in *cis*-PIP. Its use in the appropriate calculation[2] gives $\langle r^2\rangle_0/nl^2 = 5.24$ and $d\ln\langle r^2\rangle_0/dT = 0.21 \times 10^{-3}$ deg^{-1}, in reasonable agreement with the experimental values, 4.7[24] and 0.41 to 0.56×10^{-3} deg^{-1},[31-33] respectively. The values of the derivatives of $\langle r^2\rangle_0$ with respect to the statistical weights used for *cis*-PIP[2] are given in column five of Table II; included for purposes of comparison are the corresponding quantities for *cis*-PBD.[2]

Discussion

Because of difficulties encountered in obtaining experimental results for diene polymers, the energies given above must be considered only rough estimates; this is particularly true in those cases (see Table II) where the chain dimensions are not very sensitive to the statistical weight parameters. Nonetheless, these calculations provide much insight into the configurational properties of diene chains.

The characteristic ratio of *trans*-PBD, 5.8, is only about 18% larger than that of *cis*-PBD, 4.9. There are two reasons why this difference is relatively small: (i) essentially free rotation occurs about CH_2–CH_2 bonds in both molecules, and (ii) the increase in $\langle r^2\rangle_0$ due to the *structural* change of fixing double bonds at 0° in *trans*-PBD is largely offset by the accompanying accessibility of compact 180° states about neighboring CH_2–CH and CH–CH_2 bonds.

trans-PIP, in turn, has a characteristic ratio, 7.35, considerably larger than that of *trans*-PBD; this is due primarily to the suppression of compact ±120° states about CH_2–CH_2 bonds caused by the methyl group in the *trans*-PIP chain. There would also be an expected increase in $\langle r^2\rangle_0$ because of the suppression, by the methyl group, of 180° states about CH–CH_2 bonds. The accompanying mitigation of the suppressive effect of these 180° states on ±120° states about neighboring CH_2–CH_2 bonds, however, decreases the importance of this change.

According to the above calculations, the characteristic ratio of *cis*-PIP should be approximately 7% larger than that of *cis*-PBD, the increase resulting from the higher energy of ±120° states about CH_2–CH_2 bonds in the former polymer.

The characteristic ratio of *trans*-PIP is approximately 40% larger than that predicted for *cis*-PIP, 5.24. The effect of *structural* restriction of double bonds to 0° is thus seen to be much greater in the isoprene chains than in the butadiene chains, where the corresponding increase is only 18%. This is a direct result of the fact that a higher fraction of CH_2–CH_2 bonds are in 0° states in the isoprene chains. Chemically "transforming" double bonds from *cis* to *trans* causes a much greater change in the dimensions of a diene chain already having a considerable fraction of 0° states about other bonds, since for the all-*trans* diene chain $\lim_{n\rightarrow\infty} \langle r^2\rangle_0/nl^2 = \infty$. Similarly, the presence of *trans* double bonds enhances the effect of the suppression of ±120° states about CH_2–CH_2 bonds. Thus, whereas the characteristic ratio of *cis*-PIP should be only 7% greater than that of *cis*-PBD, the value for *trans*-PIP exceeds that for *trans*-PBD by 27%.

The moderately large negative temperature coefficient $d \ln \langle r^2\rangle_0/dT = -0.65 \times 10^{-3}$ deg^{-1} for *trans*-PBD results primarily from transitions 180°, 0° → 180°, ±120° about CH–CH_2–CH_2 bond pairs as the temperature is increased. In *trans*-PIP, an additional contribution arises from the increase in the number of ±120° states about CH_2–CH_2 bonds with increasing temperature, and a large, negative coefficient $d \ln \langle r^2\rangle_0/dT = -1.4 \times 10^{-3}$ deg^{-1} is predicted. In contrast, the positive temperature coefficients of $\langle r^2\rangle_0$ found for *cis*-PBD and *cis*-PIP are due primarily to transitions to more extended conformations about CH_2–C_2H_2–CH_2 bond pairs (*e.g.*, ±60°, ±60° → 0°, ±60°) as the temperature is increased.

Thus, on the basis of presently available experimental results, a reasonably consistent interpretation of the configurational properties of both the *trans* and *cis* forms of PBD and PIP has been obtained.

Both *trans*-PBD and *trans*-PIP crystallize in a number of forms, but the configurations of the chains in these modifications have not yet been unambiguously determined.[37–41] Comparison of the configurations of these chains in a crystalline lattice with the configuration of lowest intramolecular energy, in an attempt to determine the effect of intermolecular interactions,[2] is therefore not possible at the present time.

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Valence-Shell Calculations on Polyatomic Molecules. I. CNDO SCF Calculations on Nitrogen and Oxygen Heterocyclics[1a]

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Abstract: Valence-shell SCF MO calculations using the complete neglect of differential overlap approximation (CNDO/2) are described for the azines and for five-membered heterocyclic compounds containing carbon, nitrogen, and oxygen. The calculated dipole moments, unlike those of similar calculations using the extended Hückel method, are in excellent agreement with experiment. The total charge densities, but not the π-electron densities, are shown to be linearly related to C^{13} chemical shifts. The Karplus–Pople theory of chemical shifts is found to lead to a less satisfactory agreement between theory and experiment, especially for carbon atoms without hydrogens.

There have been many attempts to explain the ground-state properties of molecules, *e.g.*, dipole moments and nmr chemical shifts, in terms of molecular orbital (MO) theory. Most of these attempts have been confined to the behavior of the π electrons, or the effect of the σ electrons has been included in a very empirical fashion.[2,3] Originally this was necessary because of limitations of computation, but this is no longer so, and *ab initio* calculations of the Roothaan LCAO type, including all the electrons and using large basis sets of atomic orbitals, are now possible for quite large molecules.[4] However, such calculations are very expensive to carry out and, although pilot calculations on a few reference molecules of different types will be of enormous value,[5] it seems likely that there will always be room for semiempirical methods in the interpretation and prediction of relationships between structure and properties.

There are at present two categories of methods: (1) numerous versions of the extended Hückel theory (EHT), which includes overlap but neglects electron-repulsion integrals completely have been suggested,[6–9]

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