Configurational Statistics of 1,4-Polyisoprene Chains

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ABSTRACT: The configurational characteristics of 1,4-polyisoprene (PIP) chains are treated in terms of the conformationally independent units $CH—CH_2—CH_2—C(CH_3)=$. Properties of PIP chains are calculated for the cis and trans stereoregular polymers and for those of intermediate composition measured by the fraction f_{cis} of cis residues. Conformational energy calculations confirm the choice of t (trans) and $s^{\pm}$ (skew) rotational states for the first single bond of the structural unit specified above, and c (cis) and $s^{\pm}$ states for the third, the second single bond being assigned the usual t and $g^{\pm}$ (gauche) states. In the case of the structural unit whose double bond is cis, the c state for the third single bond is precluded by a severe steric overlap. Energy calculations indicate $\varphi_{s\pm} \approx \pm 70°$ for the third single bond above, for both cis and trans units, instead of $\pm 60°$ (measured from the trans conformation). Properties of *cis*-PIP, unlike those of *trans*-PIP, are insensitive to the statistical weights; they depend strongly on certain of the geometrical parameters (*e.g.*, $\varphi_{s\pm}$), however. Calculations on *cis*-PIP and *trans*-PIP are compared with experimentally observed characteristic ratios C_n, temperature coefficients of C_n, stress-birefringence coefficients, and, in the case of *cis*-PIP, with strain dichroism observed for infrared bands. These quantities, together with coefficients of susceptibility to rotational isomerization by stretching, are calculated as functions of f_{cis}.

Unperturbed dimensions of *cis*-1,4-polyisoprene (*cis*-PIP) and *trans*-1,4-polyisoprene (*trans*-PIP) chains were treated by Mark[1,2] using a set of rotational isomeric states in close correspondence to those for *cis*- and *trans*-1,4-polybutadiene (PBD). The principal departure consisted in the suppression of the cis state for the $CH—CH_2$ single bond ($i + 1$; see Figure 1) adjoining the trans double bond; additionally, one of the statistical weight parameters (σ) was assigned a lower value. The strain birefringence of the PIP polymers has been interpreted by Ishikawa and Nagai[3,4] according to Mark's rotational isomeric state scheme.

In the course of reexamining the interactions in PIP chains with a view to formulation of a scheme applicable to "copolymers" comprising both *cis*-PIP and *trans*-PIP residues, the need for modifications of the previous analysis became apparent. A revised treatment of these polymers is set forth in the present paper, and it is applied to the calculation of configurational properties of the respective stereoirregular copolymers of cis and trans residues, $-CH_2—C(CH_3)=CH—CH_2-$, in various proportions as well as to the all-cis and all-trans stereoregular chains.

Theory

Steric Interactions of First Order and Selection of Rotational States. The trans form of the PIP chains, with serial numbering of atoms, groups and bonds, is shown in Figure 1. The substituent methyl groups produce interactions not present in the PBD chains, and these must be taken into account in adapting the previous treatment[1,2,5] to PIP chains.

An approximate energy contour diagram calculated for a *cis*-$CCH_2C(CH_3)=CHCH_2C$ sequence, consisting of bonds $i - 2$ to $i + 2$ in Figure 1, is shown in Figure 2 with rotational angles φ_{i-1} and φ_{i+1} for bonds $CH_2—C(CH_3)$ and $CH—CH_2$, respectively, as independent variables. The diagram was computed using eq 1 and the structural parameters given in Table I of the preceding paper,[5] the rotation of the CH_3 group about the C–C bond being fixed in such a way that one of the CH bonds lies in the plane of the double-bonded carbons and the atoms directly connected to them. The bond angle $\angle C=C—CH_3$ was assigned the value 124° obtained from the electron diffraction of 2-methyl-1-butene.[6] Energies indicated in kilocalories per mole with each contour are taken relative to the lowest minimum marked by × and occurring near $(\varphi_{i-1}, \varphi_{i+1}) = (75°, 75°)$. The balance of the diagram covering the range $\varphi_{i-1} < 0°$ is generated by inversion through the origin.

In addition to the minima shown in Figure 2, saddle points having energies slightly above 1 kcal mol^{-1} occur near $(\pm 70°, 0°)$. They correspond to those found for *cis*-PBD in skew,-trans conformations. The trans,skew saddles in the diagram for *cis*-PBD (see Figure 2 of ref 5) are eliminated in *cis*-PIP by the severe steric repulsion between $(CH_3)_{i-1}$ and $(CH_2)_{i-3}$ when $\varphi_{i-1} \approx 0°$. Thus, the energy for the trans conformation of bond $i - 1$ is rendered excessive by the interaction between these two groups which are then cis to one another.

In accordance with the foregoing features in the conformational energy as revealed in Figure 2, rotational states for bond $i + 1$ are taken to be trans (t), skew plus (s^+), and skew minus (s^-), with the statistical weight of the former (t) relative to the latter two ($s^{\pm}$) expressed by the parameter ζ, in accordance with the scheme applied to *cis*-PBD. The allowed states for bond $i - 1$, or for bond $i + 3$, the third member of the triplet of single bonds of the structural unit[5] $CHCH_2$-$CH_2C(CH)_3=$ demarcated by successive double bonds, are s^+ and s^-, each with a statistical weight of unity.

The centers of the domains surrounding the minima in Figure 2 and the location of the saddle region as well suggest $|\varphi_{i-1}| = |\varphi_{i+3}| \approx$ 70–75° and $\varphi_{i+1} \approx 0$ and $\pm 60°$ for the locations of the rotational states for these two bonds. The latter minima also depart from 60°; inasmuch as one of them occurs at $\varphi_{i+1} > 60°$ and the other at $\varphi_{i+1} < 60°$, retention of 60° for both should not involve appreciable error. The deviation of the former angles from $\pm 60°$ is caused by the repulsion between $(CH_2)_{i-3}$ and $(CH_3)_{i-1}$.[6]

Trial calculations indicate that changing the location of the rotational states for the CH_2-$C(CH_3)$ bond ($i - 1$ or $i + 3$) has a large effect on theoretical values of configurational properties of PIP chains, especially on those of *cis*-PIP. Some of the present calculations were carried out with φ_{i-1}

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(1) J. E. Mark, *J. Amer. Chem. Soc.*, **88**, 4354 (1966).

(2) J. E. Mark, *ibid.*, **89**, 6829 (1967).

(3) T. Ishikawa and K. Nagai, *J. Polym. Sci., Part A-2*, **7**, 1123 (1969).

(4) T. Ishikawa and K. Nagai, *Polym. J.*, **1**, 116 (1970).

(5) Y. Abe and P. J. Flory, *Macromolecules*, **4**, 219 (1971).

(6) T. Shimanouchi, Y. Abe, and K. Kuchitsu, *J. Mol. Struct.*, **2**, 82 (1968).

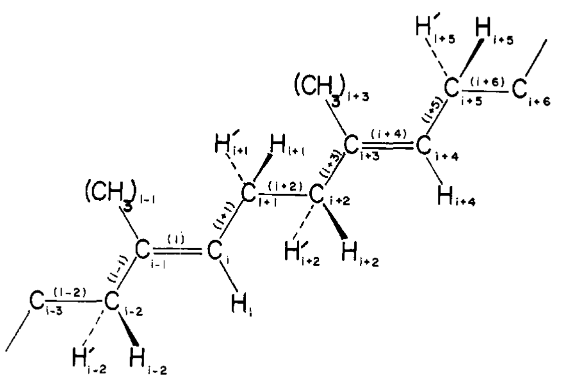

Figure 1. The 1,4-polyisoprene chain in the planar, all-trans form (strongly disfavored). Numerations of atoms and bonds are indicated.

$= \pm 70°$, although $\varphi_{i-1} = \pm 60°$ was retained for most of them in order to maintain correspondence with the treatment of the PBD chains.[5] (The choice of 70° rather than 75° was dictated by the shapes of the potential wells.)

For the intervening CH_2-CH_2 bond ($i + 2$), the states are trans, gauche plus (g^+), and gauche minus (g^-), with the statistical weight for each of the latter two ($g^\pm$) expressed by σ relative to unity for the former (t), exactly as for the corresponding bond in PBD chains. X-Ray diffraction studies reveal the trans conformation for this bond in the crystalline state for both *cis*-PIP[7,8] and *trans*-PIP.[8]

The statistical weights for first-order interactions in *cis*-PIP are compiled in the third column of Table I for each of the states of the *three* bonds, as specified in the second column.

In the case of a *trans*-PIP residue, the single bond $i - 1$, or $i + 3$, attached to the substituted carbon atom may assume c, s^+, and s^- states, the same as for the *trans*-PBD chain. The statistical weight parameter ρ employed for the corresponding bond in the *trans*-PBD chain is adopted for the cis state of bond $i + 3$ relative to $s^\pm$. As will be apparent, the skew states for this bond are subject to the same displacement from ±60° as those that obtain in the *cis*-PIP unit.

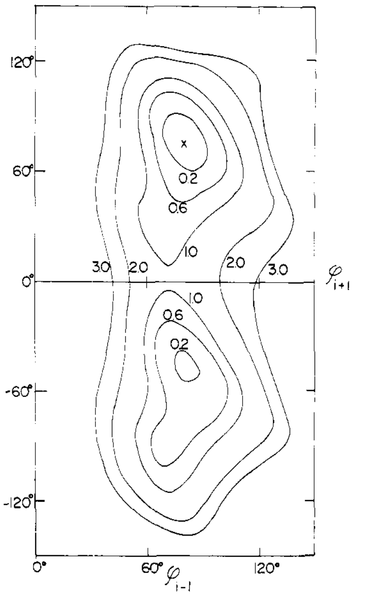

Figure 2. Conformational energy map with respect to rotations φ_{i-1} and φ_{i+1} about the bonds adjoining the double bond of the segment $CCH_2C(CH_3){=}CHCH_2C$ in which the double bond is cis. Contours at the energies indicated in kilocalories per mole above the energy at the lowest minimum × were calculated according to eq 1 of ref 5.

TABLE I

ROTATIONAL STATES AND STATISTICAL WEIGHTS FOR FIRST-ORDER INTERACTIONS IN PIP CHAINS

Bond	Rotational states	Statistical weights Cis	Statistical weights Trans
$i + 1$	t	ζ	ζ
	$s^\pm$	1	1
$i + 2$	t	1	1
	$g^\pm$	σ	σ
$i + 3$	c		ρ
	$s^\pm$	1	1

The single bond $i + 1$ attached to the unsubstituted carbon of the trans double bond cannot adopt the cis state owing to severe steric repulsions between $(CH_3)_{i-1}$ and $(CH_2)_{i-2}$ in this conformation. On the other hand, interactions between the $(CH_3)_{i-1}$ group and the two hydrogens H_{i+1} nearly obliterate the barrier between the two skew states. This is shown in Figure 3, where the approximate conformational energy associated with rotation about CH–CH_2 bond $i + 1$ in *trans*-PIP (solid curve) is compared with that for the corresponding bond in *trans*-PBD (dashed curve). The curves have been calculated in the same way as in Figure 2. The pendant CH_3 group was allowed to rotate so as to minimize the energy at each value of φ_{i+1}. The energies in the vicinity of $\varphi_{i+1} = 0$ being low for the *trans*-PIP chain, the introduction of a rotational state (t) at $\varphi_{i+1} = 0°$ is indicated. It is assigned the same statistical weight ζ as for the trans state of the corresponding bond in the structural units of *cis*-PBD and of *cis*-PIP.

Thus, the rotational states for the first single bond ($i + 1$) of the triplet in a structural unit of the *trans*-PIP chain are t and $s^\pm$ with statistical weights ζ and 1, respectively; those for the second bond ($i + 2$) are again t and $g^\pm$ with weights 1 and σ; and those for the third bond ($i + 3$ or $i - 1$) are c and $s^\pm$ with weights ρ and 1. These statistical weights for the bonds of a *trans*-PIP unit are given in the last column of Table I.

Mark[1] assigned a t state, in addition to $s^\pm$ states, to bond

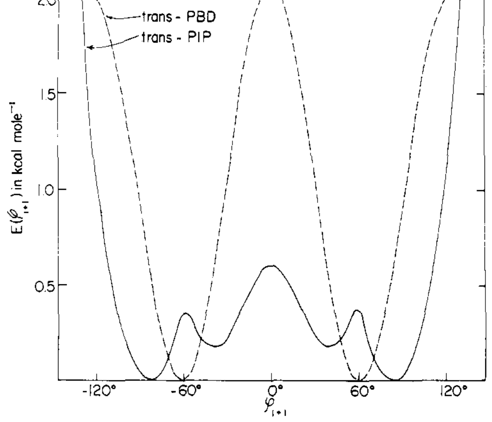

Figure 3. Conformational energy calculated as a function of the rotational angle φ_{i-1} of the CH—CH_2 bond of the segment $CCR{=}CHCH_2C$ ($R = H$ or CH_3) in which the double bond is trans.

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(7) S. C. Nyburg, *Acta Crystallogr.*, 7, 385 (1954).

(8) C. W. Bunn, *Proc. Roy. Soc.*, *Ser. A*, 180, 40 (1942).

Table II
Higher Order Interactions for Various Conformations of $-CH_2C(CH_3){=}CHCH_2CH_2C(CH_3){=}CHCH_2-$

Conformatioms	Atom pairs and interatomic distances, Å	Statistical weight factor
	Cis Unit (*i.e.*, Cis,cis or Trans,cis)	
$tg^{\pm}s^{\pm}$	$C_i\cdots(CH_3)_{i+3}$ (2.65), $H_i\cdots(CH_3)_{i+3}$ (1.94)	ω
$s^{\pm}g^{\pm}s^{\pm}$	$C_i\cdots(CH_3)_{i+3}$ (2.65), $H_i\cdots(CH_3)_{i+3}$ (1.94)	ω
$s^{\mp}g^{\pm}s^{\pm}$	$C_i\cdots(CH_3)_{i+3}$ (2.65), $C_{i-1}\cdots(CH_3)_{i+3}$ (3.03)	ω
	Trans Unit (*i.e.*, Trans,trans or Cis,trans)	
$tg^{\pm}c$	$C_i\cdots H_{i+4}$ (2.28)	$\beta^{1/2}$
$tg^{\pm}s^{\pm}$	$C_i\cdots(CH_3)_{i+3}$ (2.65), $H_i\cdots(CH_3)_{i+3}$ (1.94)	ω
$s^{\pm}g^{\pm}c$	$C_i\cdots H_{i+4}$ (2.28), $H_i\cdots C_{i+4}$ (2.26), $H_i\cdots H_{i+4}$ (1.60)	β
$s^{\pm}g^{\pm}s^{\pm}$	$C_i\cdots(CH_3)_{i+3}$ (2.65), $H_i\cdots(CH_3)_{i+3}$ (1.94)	ω
$s^{\pm}g^{\mp}c$	$C_i\cdots H_{i+4}$ (2.28), $C_{i-1}\cdots H_{i+4}$ (2.12), $(CH_3)_{i-1}\cdots H_{i+4}$ (2.08)	β
$s^{\mp}g^{\pm}s^{\pm}$	$C_i\cdots(CH_3)_{i+3}$ (2.65), $C_{i-1}\cdots(CH_3)_{i+3}$ (3.03)	ω

$i + 3$ for the *cis*-PIP unit, and he did not include a t state for the first bond ($i + 1$) of the *trans*-PIP unit.[2] In these two respects, the present assignment of rotational states departs from Mark's. Since both states—the one included by him and deleted here and the one disregarded by him but introduced here—are subject to the small statistical weight factor ζ, these differences are of minor importance.

Interdependence of Rotational States and Interactions of Higher Order. The vestiges of interdependence of rotations about the single bonds (*e.g.*, $i - 1$ and $i + 1$) flanking a double bond in *cis*-PBD discussed in the preceding paper[5] are suppressed in PIP chains (for both cis and trans residues) owing to preclusion of the trans state for bond $i - 1$, and hence for bond $i + 3$. Absence of conformational interdependence spanning the double bonds is thus assured in PIP chains for cis and trans units alike, and the conformations of triplets of single bonds in successive units are mutually independent.

Higher order interactions with a structural unit, *i.e.*, interactions dependent upon two or more rotational angles of a given triplet, were investigated through consideration of pairs of nonbonded atoms or groups occurring at distances smaller than the sums of their van der Waals radii. Following the criteria adopted in the previous paper,[5] we take 1.08 and 1.60 Å for the radii of H and C; the effective radius of CH_3, treated here as a spherical group, is taken as 1.80 Å. Pairs of atoms or groups occurring within the limits set by these radii are cited in Table II for the respective structural units in the conformations listed in the first column. Inasmuch as the steric interactions of the CH_3 group are equivalent to those of CH_2, the configurational character (cis or trans) of the first double bond of the segment cited in the heading of Table II is unimportant; only the second double bond affects the pattern of the interactions dependent upon rotations within the structural unit bounded by a pair of successive double bonds (see also Table I). Hence, only the two kinds of units distinguished by the character, cis or trans, of the second double bond need to be considered.

Higher order interactions occur in cis units only for those conformations in which the bond pair $i + 2$, $i + 3$ is $g^{\pm}s^{\pm}$ (and not for $g^{\pm}s^{\mp}$). The groups $(CH)_i$ and $(CH_3)_{i+3}$ are engaged in mutual repulsion in these conformations, and their spatial relation is very nearly the same as that of the two methylene groups separated by four skeletal bonds in an alkane chain when the central pair of bonds assumes a $g^{\pm}g^{\mp}$ conformation. Hence, the symbol ω previously identified[9] with the latter interaction is chosen to represent the corresponding one in the PIP chain, as specified in the last column of Table II. The fact that the severity of the steric overlaps is little dependent on the conformation of the first bond of the triplet justifies use of the same factor ω for each conformation of the cis structural unit in which the second and third bonds are $g^{\pm}s^{\pm}$.

Equivalent interactions occur for the same conformations ($g^{\pm}s^{\pm}$) within a trans unit; hence, the same factor ω is applicable to them as well (Table II). Additionally, the $g^{\pm}c$ conformations for bonds $i + 2$, $i + 3$ in trans units entail second-order interactions exactly like those occurring in *trans*-PBD; compare Table III of the preceding paper.[5] The factors β and $\beta^{1/2}$ introduced for the *trans*-PBD chain[5] are employed for PIP chains also.

The absence of the factor ω in Mark's analysis of PIP chains poses the major difference between the two treatments.

Statistical Weight Matrices. Let $\mathbf{U}_a$, $\mathbf{U}_b$, $\mathbf{U}_c$, and $\mathbf{U}_d$ be the statistical weight matrices for the four consecutive bonds of a structural unit, *e.g.*, for the bonds $i + 1$ to $i + 4$ in Figure 1. These matrices are defined so that their serial product yields the partition function $z^{(4)}$ for the unit; *i.e.*

$$z^{(4)} = \mathbf{U}_a\mathbf{U}_b\mathbf{U}_c\mathbf{U}_d \tag{1}$$

From the specification of rotational states and identification of statistical weights above, we have for a *cis*-PIP unit, *i.e.*, for a structural unit $CHCH_2CH_2C(CH_3){=}$ whose double bond is cis

$$\mathbf{U}_a = [\zeta \quad 1 \quad 1] \tag{2}$$

$$\mathbf{U}_b = \begin{bmatrix} 1 & \sigma & \sigma \\ 1 & \sigma & \sigma \\ 1 & \sigma & \sigma \end{bmatrix} \tag{3}$$

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

and

$$\mathbf{U}_d = \begin{bmatrix} 1 \\ 1 \end{bmatrix} \tag{5}$$

The states are indexed in the orders they are given in Table I.

For the trans unit, $\mathbf{U}_a$ is again given by eq 2. The other matrices are

$$\mathbf{U}_b = \begin{bmatrix} 1 & 0 & 0 & \sigma & 0 & 0 & \sigma & 0 & 0 \\ 0 & 1 & 0 & 0 & \sigma & 0 & 0 & \sigma & 0 \\ 0 & 0 & 1 & 0 & 0 & \sigma & 0 & 0 & \sigma \end{bmatrix} \tag{6}$$

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[9] A. Abe, R. L. Jernigan and P. J. Flory, *J. Amer. Chem. Soc.*, **88**, 631 (1966); P. J. Flory, "Statistical Mechanics of Chain Molecules," Interscience, New York, N. Y., 1969.

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

			cis-PIP[b]		*trans*-PIP[b]	
Parameter	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[c]	1.00[c]	−0.123	−0.275	−0.699	−0.914
ζ	700	0.101	0.041	0.059	−0.010	−0.012
ρ	−300	1.60			0.240	0.334
β	2000	0.0446			−0.037	−0.040
ω	1200	0.154	0.023	0.049	−0.047	−0.079

[a] $X = \exp(-E_X/RT)$, except that $\zeta = 0.3\exp(-E_\zeta/RT)$. [b] All values calculated with $\varphi_{s\pm} = \pm 60°$ for bond $i + 3$ from the values of the parameters at 50° as given in the third column. [c] 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°.

$$\mathbf{U}_c = \begin{bmatrix} \rho & 1 & 1 \\ \rho & 1 & 1 \\ \rho & 1 & 1 \\ \rho\beta^{1/2} & \omega & 1 \\ \rho\beta & \omega & 1 \\ \rho\beta & \omega & 1 \\ \rho\beta^{1/2} & 1 & \omega \\ \rho\beta & 1 & \omega \\ \rho\beta & 1 & \omega \end{bmatrix} \qquad (7)$$

$$\mathbf{U}_d = \begin{bmatrix} 1 \\ 1 \\ 1 \end{bmatrix} \qquad (8)$$

The configurational partition function for a trans unit is given by the serial product of these four matrices, in accordance with eq 1.

Although the partition function $z^{(4)}$ depends only on the character of the second double bond demarcating the structural unit, and hence two such functions, $z_{\text{cis}}^{(4)}$ and $z_{\text{trans}}^{(4)}$, suffice for the treatment of a PIP chain irrespective of the disposition of cis and trans residues therein, the generator matrices for other quantities depend in general on the character of the preceding double bond as well. Hence, just as in the case of PBD chains, four matrices, cis,cis, cis,trans, trans,cis, and trans,trans, are required for $\mathcal{G}_k^{(4)}$, for $\mathcal{H}_k^{(4)}$, for $\mathcal{Q}_k^{(4)}$, and so on.

Results and Discussion

Statistical Weight Parameters. As the preceding analysis of nonbonded interactions clearly indicates, very nearly the same values of the parameters σ, ζ, and β should hold for PIP as those found[5] for PBD chains. In particular, the presence of the methyl substitutent in PIP should not affect (*i.e.*, should not diminish[1–4]) the value of σ. Hence, the same values of σ, ζ, and β given in Table IV of the preceding paper[5] are adopted here for PIP chains.

The principal hindering effect of the methyl substituent in PIP is manifested through the parameter ω, which, being much smaller than unity, represses $g^\pm s^\pm$ conformations for the bond pair $i + 2$, $i + 3$ for reasons given above. Additionally, repulsions in *trans*-PIP between one or the other of the hydrogens H_{i+1} and $(CH_3)_{i+3}$ when bond $i + 3$ is in either of the states $s^\pm$ cause the cis conformation for this bond to be preferred, whereas in *trans*-PBD the skew state is favored ($\rho = 0.627$ for PBD).

In support of this inference from the chain structure, the temperature coefficients of intensities of far-infrared bands of the compounds 2-methyl-1-butene[6,10] and 3-methyl-*trans*-2-pentene,[10] in the gaseous and liquid states, supplemented by the electron diffraction of the former compound in the gas, lead to values of −540 and −250 cal mol^{-1} for the respective differences E_ρ between the energies of the cis and skew conformations. With some bias in favor of optimizing the agreement of calculated with observed values of the characteristic ratio C_n and of the temperature coefficient $d\ln C_n/dT \equiv d\ln\langle r^2\rangle_0/dT$, we take $E_\rho = -300$ cal mol^{-1}, which is within the range indicated by the experiments cited above on small molecules. Thus, we let

$$\rho = \exp(300/RT) \qquad (9)$$

At 50°, $\rho = 1.60$.

No prior evidence exists on the energy E_ω for the second-order interaction between $(CH)_i$ and $(CH_3)_{i+3}$, apart from the expectation that it should be somewhat smaller than the value found for the corresponding second-order interaction between methylene groups in *n*-alkanes. For the latter,[9] $E_\omega \approx 2000$ cal mol^{-1}. Agreement with experiment is optimized by taking $E_\omega = 1200$ cal mol^{-1} for the relevant interactions in the PIP chains. Hence, we let

$$\omega = \exp(-1200/RT) \qquad (10)$$

At 50°, $\omega = 0.154$. Selected values for statistical weight parameters are listed in Table III together with their effects on the characteristic ratio and the stress-optical coefficient.

Comparison of Observed and Calculated Results for *cis* and *trans*-PIP. Quantities calculated from the stated set of parameters for PIP chains of $x = 300$ units ($n = 1199$ bonds) at a temperature of 50° are compared with experimental results in Table IV. All calculations were carried out according to the methods specified in the preceding paper.[5] The dependence of the characteristic ratio on each of the parameters σ, ζ, and β approximates that for the PBD chain, as given in the last column of Table IV of the preceding paper.[5] Change of E_ω from 1000 to 1500 cal mol^{-1} (a decrease of ω from 0.21 to 0.096) decreases C_n for *cis*-PIP by only about 1%; for *trans*-PIP, it is increased *ca.* 3%. The respective changes in d ln C_n/dT are −30 and −0.5%.

Calculations not reproduced here indicate that for the same value of ρ or E_ρ, the calculated characteristic ratios are always greater for *trans*-PBD than for *trans*-PIP. For example, the set of $\sigma = 1.0$, $\rho = 1.0$, $\zeta = 0.101$, $\beta = 0.0446$, and $\omega = 0.210$ gives $C_n = 6.71$ and 6.36 for *trans*-PBD and *trans*-PIP,

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(10) T. Shimanouchi and Y. Abe, *J. Polym. Sci., Part A-2*, **6**, 1419 (1968); see also T. Shimanouchi, Y. Abe, and M. Mikami, *Spectrochim. Acta, Part A*, **24**, 1037 (1968).

Table IV

Configurational Properties of PIP Chains at 50°

	cis-PIP		*trans*-PIP	
	Obsd	Calcd[a]	Obsd	Calcd[a]
C_n	4.7,[b,c]	4.55	6.6,[d] 7.4[c,e]	6.95
		3.84		6.60
10^3d ln C_n/dT, deg^{-1}	0.41,[f] 0.56[g]	0.18		−0.96
		0.16		−1.04
$10^{24}\Gamma_2$, cm^3	2.4,[h] 2.9[i]	2.84	3.5,[h] 5.5[i]	4.59
		2.25		4.60

[a] Calculated from the preferred set of parameters given in the third column of Table III and the bond polarizabilities of C. Clément and P. Bothorel, *C. R. Acad. Sci.*, **258,** 4757 (1964) (see Table I of the preceding paper[5]). The upper figure is for $\varphi_{s\pm} = \pm 60°$ and the lower one for $\varphi_{s\pm} = \pm 70°$ for bond $i + 3$. [b] Reference 1. [c] H. Wagner and P. J. Flory, *J. Amer. Chem. Soc.*, **74,** 195 (1952). [d] Ya. Poddubnyi, E. G. Erenburg, and M. A. Eryomina, *Vysokomol. Soedin., Ser. A*, **10,** 1381 (1968). [e] Reference 2. [f] A. Ciferri, C. A. J. Hoeve, and P. J. Flory, *J. Amer. Chem. Soc.*, **83,** 1015 (1961). [g] A. Ciferri, *Makromol. Chem.*, **43,** 152 (1961). [h] For specimens swollen with isotropic solvents [see ref 4 and A. N. Gent, *Macromolecules*, **2,** 262 (1969)]. [i] For unswollen specimens [see ref *h* above, ref 4, and D. W. Saunders, *Trans. Faraday Soc.*, **52,** 1414 (1956)].

respectively. Changing ω (which represents an interaction that does not occur in PBD chains) has little effect on the characteristic ratio of PIP, as stated above. Consequently, the surprising fact that the experimental values for C_n are actually greater for *trans*-PIP than for *trans*-PBD is almost entirely attributable to the difference in sign of E_ρ for the two polymers.[4]

The stress-optical coefficients were calculated using the tensor expressions for group polarizability anisotropies given for PBD chains in the preceding paper,[5] with only the obvious modifications required by the presence of the methyl substituent (see Appendix of the present paper). Bond polarizabilities obtained by Clément and Bothorel[11] (see Table I of the preceding paper[5]) have been used for all calculations presented here. General expressions for Γ_2 calculated as a function of bond polarizabilities from the preferred set of statistical weight parameters, with $\varphi_{i+3} = \pm 60°$, are, for *cis*-PIP

$$\Gamma_2 = 0.825\Delta\alpha_{\mathrm{C=C}} + 0.605\Delta\alpha_{\mathrm{C-C}} - 1.666\Delta\alpha_{\mathrm{C-H}} - 0.133\Delta\alpha_{\mathrm{C-CH_3}} \quad (11)$$

for *trans*-PIP

$$\Gamma_2 = 0.192\Delta\alpha_{\mathrm{C=C}} + 3.539\Delta\alpha_{\mathrm{C-C}} - 4.022\Delta\alpha_{\mathrm{C-H}} - 0.111\Delta\alpha_{\mathrm{C-CH_3}} \quad (12)$$

and

$$\Gamma_2 = 0.527\Delta\alpha_{\mathrm{C=C}} + 1.328\Delta\alpha_{\mathrm{C-C}} - 2.071\Delta\alpha_{\mathrm{C-H}} - 0.066\Delta\alpha_{\mathrm{C-CH_3}} \quad (13)$$

for the random stereoirregular chain with $f_{\mathrm{cis}} = 0.5$

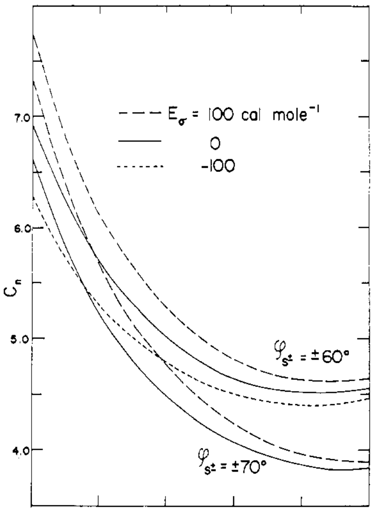

Figure 4. Characteristic ratio C_n plotted against the fraction f_{cis} of *cis*-C=C bonds. Calculations carried out for a temperature of 50° with E_σ = 100 (- - -), E_σ = 0 (———), and E_σ = −100 (------) cal mol^{-1} and ζ = 0.101, ρ = 1.60, β = 0.0446, and ω = 0.154. Values of $\varphi_{s\pm}$ for CH—C(CH$_3$) bonds are indicated with each curve.

The location of the skew states for CH$_2$–C(CH$_3$) bonds such as bond $i + 3$ has a large effect on the characteristic ratio and the stress-optical coefficient of *cis*-PIP (see Table IV). Changing $\varphi_{s\pm}$ for these bonds from ±60 to ±70° decreases C_n by *ca.* 15% and Γ_2 by *ca.* 20%. The theoretical value of C_n calculated for the more realistic location of the skew states at $\varphi_{s\pm} = \pm 70°$ is in poor agreement with the quoted experimental results. Owing to the insensitivity of $C_{n,\mathrm{calcd}}$ for *cis*-PIP to the statistical weight parameters, the discrepancy cannot be improved appreciably through any reasonable choice of values for these parameters. According to calculations not included here, alteration of the skeletal valence angle at the methyl-substituted ethylene carbon atom likewise does not resolve the discrepancy. On the other hand, the observed value of C_n for this polymer is subject to an error which is abnormally large because of experimental difficulties imposed by its vulnerability to oxidative degradation.[12] Errors in the determination of the Θ point and of the molecular weight may together admit of an uncertainty of ±15% in the value of C_n. Thus, the large discrepancy between the observed value and that calculated with $\varphi_{s\pm} = \pm 70°$ for

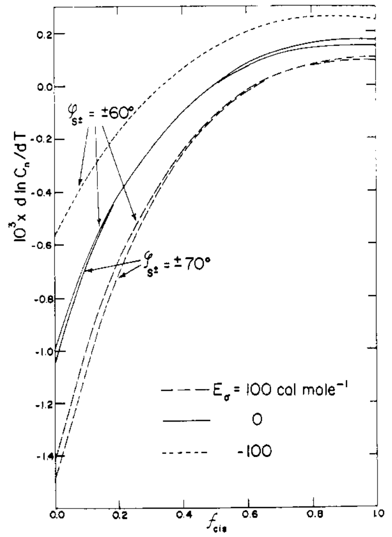

Figure 5. Temperature coefficients of characteristic ratios, d ln C_n/dT, plotted against the stereochemical composition f_{cis}. Parameters used are given in the legend for Figure 4.

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

(12) H. Wagner and P. J. Flory, *J. Amer. Chem. Soc.*, **74,** 195 (1952).

bond $i + 3$ may be due in large part to experimental errors.

The increase of $|\varphi_s|$ from 60 to 70° renders $\Gamma_{2,\mathrm{calcd}}$ smaller than $\Gamma_{2,\mathrm{obsd}}$ for the unswollen polymer, but improves the agreement with the $\Gamma_{2,\mathrm{obsd}}$ for the network swollen in isotropic solvents (see Table IV). The former, like $C_{n,\mathrm{calcd}}$, is insensitive to the statistical weight parameters.

Properties in Relation to Stereochemical Composition. Characteristic ratios and their temperature coefficients calculated according to eq 16 and 27 of the preceding paper[5] are plotted in Figures 4 and 5, respectively, as functions of the fraction of cis residues for the indicated values of E_σ and of $\varphi_{s\pm}$ for C–C(CH$_3$) bonds. The dependence of C_n on f_{cis} shown in Figure 4 is similar to that for PBD chains.[5] The curves exhibit steep descents as f_{cis} increases from 0.0 to *ca.* 0.6 and then become comparatively insensitive to f_{cis}. They display minima with f_{cis} in the range 0.8–0.9.

The curves for d ln C_n/dT of Figure 5 are convex upward, whereas those for PBD chains shown in Figure 4 of the preceding paper[5] are concave. They rise rapidly with f_{cis} from 0.0 to *ca.* 0.6, then show little further change as f_{cis} is increased to 1.0. For PBD chains the increase of d ln C_n/dT with f_{cis} is more rapid for $f_{\mathrm{cis}} > 0.5$ than in the lower range. All of the curves for $-100 \leqq E_\sigma \leqq 100$ cal mol^{-1} in Figure 5 cross the ordinate d ln $C_n/\mathrm{d}T = 0$. The intersection for $E_\sigma = 0$ occurs at $f_{\mathrm{cis}} = 0.5$. For PBD chains the value of d ln C_n/dT calculated for $E_\sigma = 0$ changes sign at $f_{\mathrm{cis}} = 0.7$.

Stress-birefringence coefficients Γ_2 are plotted in Figure 6 against f_{cis} for the three values of E_σ and for two values of $\varphi_{s\pm}$ for C–C(CH$_3$) bonds. Each point in the range $0.0 < f_{\mathrm{cis}} < 1.0$ represents the average over 15 Monte Carlo chains. The standard deviations are indicated by vertical bars. Minima with f_{cis} are also displayed in this case. These features are common to the characteristic ratios and the stress-birefringence coefficients of both PBD and PIP chains.

Preferential Orientation and Strain Dichroism. Susceptibilities G_2^* of the three coordinate axes (defined in the preceding paper[5]) for a C=C bond to orientation by elongation were calculated using the parameters given in Table III together with $\varphi_{s\pm} = \pm 60°$ for bond $i + 3$. The calculations were carried out for *trans*-C=C bonds in the range $f_{\mathrm{cis}} =$ 0.0–0.5 and for *cis*-C=C bonds in the range $f_{\mathrm{cis}} =$ 0.5–1.0. The ratios G_2^*/f_{cis} or G_2^*/f_{trans} are plotted in Figure 7 against f_{cis}. Also plotted in this figure are the preferential orientation coefficients G_2^* for two other axes lying in the CC=CC plane, one, indicated by a, along the C–CH$_3$ bond, and the other, indicated by b, perpendicular to the C–CH$_3$ bond. Monte Carlo calculations were performed for 15 chains for each point in the range $0.0 < f_{\mathrm{cis}} < 1.0$. Standard deviations, being very small, are not shown in Figure 7. The values of G_2^* for the several directions meet the following conditions (see eq 57 of the preceding paper[5])

$$G_2^*(x) + G_2^*(y) + G_2^*(z) = 0 \qquad (14)$$

$$G_2^*(a) + G_2^*(b) + G_2^*(z) = 0 \qquad (15)$$

As in the case of PBD chains,[5] the calculated orientations of C=C bonds were found to depend very little on σ. The curves in Figure 7 for *cis*-C=C bonds are very similar to those shown for PBD chains in Figure 6 of the preceding paper.[5] The remarks offered there on the preferential orientation of *cis*-C=C bonds of PBD chains apply also here.

The effects of elongation on the orientation of *trans*-C=C bonds of PIP chains differ in several respects from the behavior of *trans*-C=C bonds in PBD chains. First, the ratios G_2^*/f_{trans} change considerably as f_{cis} increases from 0.0 to 0.5. Second, the dependences on f_{cis} (see Figure 7) are nonlinear. It follows that orientation of *trans*-C=C bonds is affected considerably by the arrangement of trans and cis residues in the chain.

Dichroism of infrared bands associated with the CC(CH$_3$)=CHC residue is related to G_2^* calculated above; see eq 44 of the preceding paper.[5] According to theory,[5,13] the departure

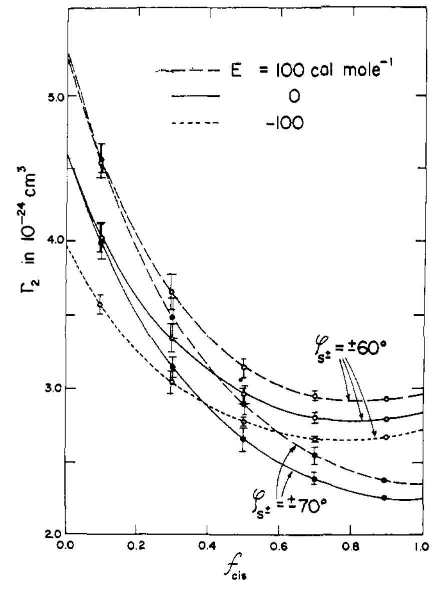

Figure 6. Stress-birefringence parameters Γ_2 plotted against stereochemical composition f_{cis}. Each point within the range of $0 < f_{\mathrm{cis}} < 1$ represents the average for 15 Monte Carlo chains of $n = 1199$ bonds. Vertical bars denote standard deviations.

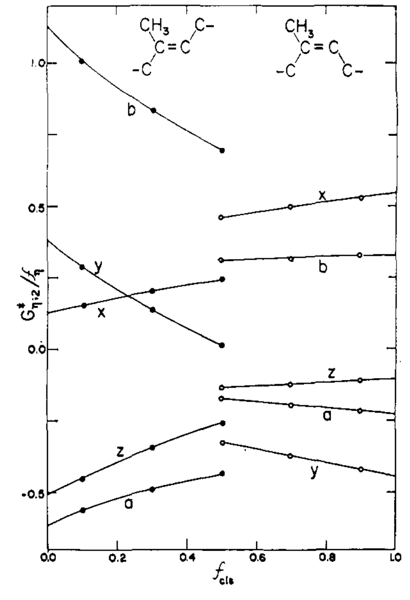

Figure 7. Ratios $G_{\eta;2}^*/f_\eta$ for η = cis (○) and for η = trans (●) plotted against f_{cis}. x, y, and z represent the respective coordinate axes along the C=C bond, in the plane of this bond, and perpendicular to this plane; a represents the axis along the C—CH$_3$ bond, and b is perpendicular to the C—CH$_3$ bond and to the z axis. Calculations were carried out for chains of $x = 300$ units with $\varphi_{s\pm} = \pm 60°$ for bonds such as $i + 3$, the preferred set of statistical weight parameters being used (Table III). Each point within the range $0 < f_{\mathrm{cis}} < 1$ represents the average for 15 Monte Carlo chains.

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[13] P. J. Flory and Y. Abe, *Macromolecules*, **2**, 335 (1969).

Table V

Dichroism of Infrared Bands Associated with the *cis*-CC(CH$_3$)=CHC Residue

Band, cm^{-1}	Axis of transition moment	$D - 1$, obsd[a] at $\lambda = 3$	G_2^*, calcd	$D - 1$ at $\lambda = 3$, calcd; eq 16
835	z	−0.08	−0.10	−0.013
1129	x?	0.2	0.55	0.070
1380	Approximately a	−0.04	−0.23	−0.030
1664	Between x and y	0.07	0.55 (for x)	0.071
			−0.45 (for y)	−0.058

[a] Reference 14.

of the dichroic ratio from unity is given for simple elongation by

$$D - 1 = (3G_2^*/2n')(\lambda^2 - 1/\lambda) \qquad (16)$$

λ being the extension ratio along the axis of elongation and n' the number of absorbing units (either cis or trans) in a chain of the network. Orientation functions, $F = (D - 1)/(D + 2)$, of several infrared bands were measured as functions of extension ratio λ of amorphous networks of *cis*-PIP (vulcanized natural rubber) by Gotoh, Takenaka and Hayama.[14] Approximate values of $D - 1$ estimated from their graphs showing F for four bands as functions of λ are given in the third column of Table V. The stress at $\lambda = 5$ reported by Gotoh, *et al.*,[14] suggests that $x \approx 100$. Calculated values of G_2^* and of $D - 1$ are presented in the last two columns of Table V.

The transition moment for the =C—H out-of-plane wagging vibration at 835 cm^{-1} is parallel to the z axis. However, this band is affected by crystallization, as indicated both by a shift in frequency and an increase in intensity. The observed value of $D - 1$ may be presumed to have been much enhanced on this account.

The mixed mode at 1129 cm^{-1} comprises =C—H in-plane bending, C=C stretching, and other vibrations. The transition moment is not established for this bond; its large positive dichroism suggests that it may be approximately parallel to the double bond, *i.e.*, to the x axis. This uncertainty precludes quantitative comparison with theory.

The 1380-cm^{-1} band is assigned to the CH$_3$ symmetric deformation mixed with C-CH$_3$ stretching. The transition moment should therefore be approximately parallel to the a axis specified above. Although experimental difficulties[14] cast doubt on the accuracy of the experimental result in this instance, the agreement with theory is quite satisfactory.

The 1664-cm^{-1} band is assigned to a complex mode consisting of C=C stretching and =C—C stretching. The transition moment is directed between the x and y axes. The observed dichroism agrees well with calculation from $G_2^*(x)$ but not with $G_2^*(y)$.

Little more than qualitative agreement can be claimed for the comparisons between observed and calculated dichroic ratios in Table V. It is noteworthy that the correct sign is predicted for the three examples free of experimental ambiguity in this regard. The 835-cm^{-1} band aside, trends in the magnitude of $D - 1$ are satisfactorily predicted. With experimental refinements, quantitative tests of theory may be possible.

Corresponding experiments have not been reported for *trans*-PIP networks. The calculated value of G_2^* for the a axis is negative and large while that for the b axis is positive and large. Thus, the CH$_3$ symmetric deformation vibration should display strong perpendicular dichroism while the CH$_3$ asymmetric deformation should exhibit strong parallel dichroism.

Table VI

A Priori Probabilities and Rotational Isomerization by Stretching Calculated for PIP Chains[a]

Rotational conformation η	p_η	$n'\delta_{\eta;2}$	$\Delta_{\eta;2}$
cis-PIP			
C—C(CH$_3$)=CH—C bond sequence			
s$^{\pm}$cs$^{\pm}$	0.238	1.34	0.32
s$^{\pm}$cs$^{\mp}$	0.238	−1.41	−0.34
CH$_2$—CH$_2$ bond			
t, $\sigma = 1.17$	0.426	0.46	0.20
t, $\sigma = 1.00$	0.464	0.41	0.19
t, $\sigma = 0.86$	0.503	0.37	0.19
g$^{\pm}$, $\sigma = 1.17$	0.287	−0.34	−0.10
g$^{\pm}$, $\sigma = 1.00$	0.268	−0.35	−0.09
g$^{\pm}$, $\sigma = 0.86$	0.249	−0.37	−0.09
trans-PIP			
C—C(CH$_3$)=CH—C bond sequence			
ct	0.290	1.12	0.32
s$^{\pm}$t	0.355	−0.43	−0.15
cts$^{\pm}$	0.138	1.12	0.15
s$^{\pm}$ts$^{\pm}$	0.168	−1.10	−0.18
s$^{\pm}$ts$_{\mp}$	0.168	0.24	0.04
CH$_2$—CH$_2$ bond			
t, $\sigma = 1.17$	0.554	1.76	0.98
t, $\sigma = 1.00$	0.592	1.74	1.03
t, $\sigma = 0.86$	0.629	1.73	1.09
g$^{\pm}$, $\sigma = 1.17$	0.223	−2.17	−0.48
g$^{\pm}$, $\sigma = 1.00$	0.204	−2.52	−0.51
g$^{\pm}$, $\sigma = 0.86$	0.186	−2.93	−0.54

[a] Calculations carried out using the statistical weight parameters given in Table III, except as indicated for σ, together with $\varphi_{s\pm} = \pm 60°$ for CH$_2$—C(CH$_3$) bonds.

Average Bond Conformations and Rotational Isomerization by Stretching. The *a priori* probabilities p_η and their changes with stretching of the chain were calculated for several conformations η of the C—C(CH$_3$)=CH—C bond sequence and of the CH$_2$—CH$_2$ bond in PIP chains. The parameters given in Table III were used together with $\varphi_{s\pm} = \pm 60°$ for bonds such as $i + 3$. The results are shown in Table VI. The quantity $\delta_{\eta;2}$ appearing in this table is defined by eq 31 of the preceding paper.[5] It represents the relative change of p_η per unit increase in $r^2/\langle r^2\rangle_0$. The quantity $\Delta_{\eta;2}$ tabulated in the last column and defined by eq 59 of the preceding paper[5] represents the change in the number of bonds or bond sequences having the conformation η caused by unit increase in $r^2/\langle r^2\rangle_0$.

Most of the discussion on rotational isomerization of PBD chains in the preceding paper[5] applies also to PIP chains.

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(14) R. Gotoh, T. Takenaka, and N. Hayama, *Kolloid-Z. Z. Polym.*, **205**, 18 (1965).

Rotational isomerization by stretching takes place predominantly in C—C(CH_3)═CH—C bond sequences for *cis*-PIP and in CH_2—CH_2 bonds for *trans*-PIP chains.

The *a priori* probability for the trans state for CH_2–CH_2 bonds is considerably greater for PIP chains than for PBD chains owing to the second-order interdependence of rotations imposed by $\omega \ll 1$. Rotational isomerization about these bonds takes place to a greater degree for PIP chains than for PBD chains. For example, with $\sigma = 1.0$ we obtain $p_t = 0.455$, $n'\delta_{t;2} = 1.38$, and $\Delta_{t;2} = 0.63$ for *trans*-PBD chains, whereas for *trans*-PIP, $p_t = 0.592$, $n'\delta_{t;2} = 1.74$, and $\Delta_{t;2} = 1.03$.

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Appendix

Anisotropies of Group Polarizability Tensors. The only modifications required for the adaptation of expressions for PBD chains given in the Appendix of the previous paper are the replacement of $\chi = \pi - \angle C{=}CH$ by $\chi' = \pi - \angle C{=}C{-}CH_3$ and of $\Delta\alpha_{C-H}$ by $\Delta\alpha_{C-CH_3}$ in the previous eq 62 for $\hat{\alpha}_d$.[5] Thus $\hat{\alpha}_d$ is given by eq 17. The tensor $\hat{\alpha}_2$ for the second bond is identical with $\hat{\alpha}_d$ given by this equation.

$$\hat{\alpha}_d = \begin{bmatrix} (2/3)\Delta\alpha_{C=C} + (1/2)[\cos 2\chi' + 1/3]\Delta\alpha_{C-CH_3} & -(1/2)(\sin 2\chi')\Delta\alpha_{C-CH_3} & 0 \\ -(1/2)(\sin 2\chi')\Delta\alpha_{C-CH_3} & -(1/3)\Delta\alpha_{C=C} - (1/2)[\cos 2\chi' - 1/3]\Delta\alpha_{C-CH_3} & 0 \\ 0 & 0 & -(1/3)\Delta\alpha_{C=C} - (1/3)\Delta\alpha_{C-CH_3} \end{bmatrix} \tag{17}$$

Modified Free-Volume Theory of Penetrant Diffusion in Polymers

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Murray Hill, New Jersey 07974. *Received December 21, 1970*

ABSTRACT: Fujita's formulation of the free-volume theory of penetrant diffusion is modified by introducing a reference temperature and reference free volume which need not coincide with those for the viscosity. The modified theory, unlike its predecessor, can accommodate data for small as well as large penetrant molecules and also accounts for some earlier empirical correlations.

The application of free-volume theory to the interpretation of diffusion of large organic molecules in polymers has met with notable success.[2] Specifically, it has been shown that the dependence of the diffusion coefficient on temperature and concentration can be described by the same type of equation which represents the dependence of viscosity on these two variables. However, the predicted interrelations between the diffusion and the viscosity data did not hold for penetrant molecules of small size, *e.g.*, poly(vinyl acetate)–water and poly(methyl acrylate)–water.[3] The reason for this discrepancy can be rationalized by the consideration that the diffusion of small molecules requires a portion of the free-volume distribution different from that involved in the diffusion of large molecules comparable in size to the chain segment. In this paper, we would like to formulate this concept in an expression which contains a reference point for the free volume of diffusion not necessarily identical with that of viscous flow.

Let us first summarize Fujita's[2] derivations (Fujita's notation is used in the text with the exception that φ represents the volume fraction of diluent)

$$D(\varphi, T) = A_d \exp[-B_d/f_d(\varphi, T)] \tag{1}$$

$$f_d(\varphi, T) = f_d(0, T) + \beta_d(T)\varphi \tag{2}$$

and

$$D_0(T) = D(0, T) = A_d \exp[-B_d/f_d(0, T)] \tag{3}$$

In these equations, the subscript d refers to the diffusion process, A is a frequency factor, B corresponds to the minimum hole size for the jump process, f is the average fractional free volume of the system, and β describes the effectiveness of the diffusant molecules for increasing the free volume of the give polymer. The viscosity of the system is expressed in a similar manner with the use of subscript v

$$\eta_0(T) = A_v \exp[B_v/f_v(0, T)] \tag{4}$$

Combination of eq 1 and 4 yields

$$\ln D_0(T) = C - \frac{B_d f_v(0, T)}{B_v f_d(0, T)} \ln \eta_0(T) \tag{5}$$

If the condition given by eq 6 is met

$$f_v(0, T) = f_d(0, T) \tag{6}$$

then

$$\begin{aligned} \ln D_0(T) &= C - (B_d/B_v) \ln \eta_0(T) \\ &= C' - (B_d/B_v) \ln a_T \end{aligned} \tag{7}$$

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[1] (a) State University of New York; (b) University of Massachusetts; (c) Bell Telephone Laboratories.

[2] H. Fujita, *Fortschr. Hochpolym-Forsch.*, **3**, 1 (1961).

[3] (a) A. Kishimoto, E. Maekawa, and H. Fujita, *Bull. Chem. Soc. Jap.*, **33**, 988 (1960); (b) H. Fujita and A. Kishimoto, *J. Polym. Sci.*, **28**, 547 (1958).