Unperturbed Chain Dimensions of Stereoirregular 1, 4-Polybutadiene and 1, 4-Polyisoprene

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ABSTRACT: The characteristic ratios of stereoirregular 1,4-polybutadiene and 1,4-polyisoprene chains have been theoretically investigated by the Monte Carlo procedure in accordance with the model proposed by Mark. It was pointed out that the presence of discrete *cis* units in *trans*-rich chains significantly reduces the characteristic ratio while that of discrete *trans* units in *cis*-rich chains has little effect on the characteristic ratio.

KEY WORDS Characteristic Ratio / Chain Statistics / 1,4-Polybutadiene / 1,4-Polyisoprene / Stereoirregular Polymer / Monte Carlo Chain /

In recent years a great deal of attention has been paid to the effect of stereochemical configuration on the conformational statistical mechanical properties of polymer chains. The dependence of characteristic ratio $\langle R_0^2 \rangle / nl^2$, in which $\langle R_0^2 \rangle$ is the unperturbed end-to-end length, n the degree of polymerization, and l the bond length per structural unit, on the tacticity, *i.e.*, sequence distribution of stereoisomers, has been investigated by several authors. Such studies have been carried out for asymmetric vinyl chains,^{1,2} D, L-copolyptides,^{1,3} and D, L-polylactic acid.⁴

Many studies have already been published of random chain conformations of 1,4-polyisoprene in which the double bonds are either all in *trans* or *cis* form. Allegra, *et al.*,^{5,6} derived unperturbed end-to-end length of *cis*-1,4-polybutadiene. Mark investigated the unperturbed end-to-end length and its temperature coefficient for *cis*-1,4-polybutadiene and *cis*-1,4-polyisoprene.⁸ Further, Ishikawa and Nagai^{9,10} discussed the unperturbed end-to-end length and stress—optical coefficient for these four kinds of stereoregular diene-polymers.

Although stereoregular polymers are not classified as copolymer in usual sense, these can be treated as such by considering each stereoisomer as a molecular species which is experimentally

separable. In fact, some trials^{11–14} have been done to correlate the sequence distribution of stereoisomers with chain configuration of stereoirregular polymers.

An investigation concerned with sequence distribution of *trans* and *cis* units has been reported by Berger, *et al.*,¹⁵ with a polybutadiene chain whose *trans* content varied from 0 to 95 %. The relation between the characteristic ratio and *trans*—*cis* arrangement for rubber-like hydrocarbon polymers containing double bonds were also reported by Wall¹⁶ and Markovitz.¹⁷ With the use of a very simple model they simply assumed the distribution of *cis* and *trans* units to be random and moreover free rotation to be allowed only around the single bonds.

In this work, the characteristic ratio and its dependence on both the *trans* and *cis* contents and their sequence distribution will be calculated for stereoirregular 1,4-polybutadiene and 1,4-polyisoprene in accordance with interdependent rotational isomeric state model proposed by Mark,^{7,8} and Ishikawa and Nagai.^{9,10}

CALCULATION OF CHARACTERISTIC RATIO

Theory

In Figure 1, a portion of a 1,4-diene polymer chain is shown; 1,4-polybutadiene and 1,4-

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polyisoprene are represented by assigning, respectively, $R=H$ and $R=CH_3$. The angles φ 's of rotations are denoted as given in the Figure. In this figure, the i -th double bond is in *trans* ($\varphi_{i,2}=0$) and the $(i+1)$ -th double bond in *cis* ($\varphi_{i+1,2}=180^\circ$) conformation. Molecular parameters used in this work, i.e., bond angles and bond lengths, are those used by Mark^{7,8} and Nagai.^{9,10}

Figure 1. A portion of a 1,4-polydiene chain. $R=H$ and $R=CH_3$ correspond to polybutadiene and polyisoprene, respectively.

The *trans* and *cis* isomeric structures for double bonds in polybutadiene and polyisoprene chains are determined by the polymerization conditions (such as solvent, catalyst, temperature, etc.). The stereoirregularity of the polymers thus produced can also be changed by means of, for example, ultraviolet irradiation.¹⁵ However, the energy barrier around the double bond (π -bond) is estimated¹⁸ to be as high as 35–40 kcal/mol, so that it may be assumed that *trans*–*cis* isomerization does not occur under ordinary experimental conditions as used for the usual solution measurements. Accordingly, the sequence distribution of *trans* and *cis* units in the chain has to be directly related to copolymerization kinetics.

This work starts with the assumption that the sequence distribution of *trans* and *cis* units obeys a Markoffian process. Theory of copolymerization in accordance with the Markoffian process has been treated in detail by Peller.¹¹ Poly-peptide copolymers were investigated by the authors on this assumption previously.^{3,19}

As shown in Figure 1, the rotational angles for succeeding bonds in the i -th unit were designated as $\varphi_{i,1}$, $\varphi_{i,2}$, $\varphi_{i,3}$, and $\varphi_{i,4}$ (hereafter simply as φ_1 , φ_2 , φ_3 , and φ_4).

Firstly 1,4-polybutadiene will be examined. In accordance with Mark,⁷ the accessible states

for rotation around each bond are assumed to be as follows: φ_4 is 0° and $\pm 120^\circ$, both φ_1 and φ_3 are 180° and $\pm 60^\circ$ in the case of *trans* double bond ($\varphi_2=0^\circ$), and both φ_1 and φ_3 are 0° and $\pm 60^\circ$ in the case of *cis* double bond ($\varphi_2=180^\circ$). The same notations for statistical weights as that used by Mark^{7,8} and Nagai^{9,10} are employed. Rotational statistical weight matrices U_1 's associated with states of rotational angles $\varphi_{i,4}$ and $\varphi_{i+1,1}$ are given by eq 1 and 2 for $\varphi_{i+1,2}=trans$ and $\varphi_{i+1,2}=cis$, respectively.

For $\varphi_{i+1,2}$: *trans*

		φ_1		
		60°	180°	-60°
$U_1(t)=\varphi_4$	0°	1	α	1
	120°	1	$\beta\alpha$	1
	-120°	1	$\beta\alpha$	1

(1)

and for $\varphi_{i+1,2}$: *cis*

		φ_1		
		0°	60°	-60°
$U_1(c)=\varphi_4$	0°	1	1	1
	120°	1	1	1
	-120°	1	1	1

(2)

Statistical weight matrices U_3 's associated with states of rotational angles $\varphi_{i,1}$ and $\varphi_{i,3}$ are given by

for $\varphi_{i,2}$: *trans*

		φ_3		
		60°	180°	-60°
$U_3(t)=\varphi_1$	60°	1	α	1
	180°	1	α	1
	-60°	1	α	1

(3)

and for $\varphi_{i,2}$: *cis*

		φ_3		
		0°	60°	-60°
$U_3(c)=\varphi_1$	0°	δ	1	1
	60°	1	γ	γ
	-60°	1	γ	γ

(4)

Statistical weight matrices U_4 's associated with states of rotational angles $\varphi_{i,3}$ and $\varphi_{i,4}$ are given by

for $\varphi_{i,2}$: *trans*

		φ_4			
		0°	120°	-120°	
$U_4(t)=\varphi_3$	60°	1	σ	σ	(5)
	180°	1	$\beta\sigma$	$\beta\sigma$	
	-60°	1	σ	σ	

and for $\varphi_{i,2}$: *cis*

		φ_4			
		0°	120°	-120°	
$U_4(c)=\varphi_3$	0°	1	σ	σ	(6)
	60°	1	σ	σ	
	-60°	1	σ	σ	

It should be noted here that the statistical weight δ appearing in eq 4 is the same as that introduced by Nagai,⁹ and that eq 3, which was given in the form of product of two rotational statistical weight matrices associated with $(\varphi_{i,1}, \varphi_{i,2})$ and $(\varphi_{i,2}, \varphi_{i,3})$, appeared in the treatments of Mark⁸ and Nagai.¹⁰ It is written here in a form comparable with eq 4.

The conformational partition function Z of the chain was calculated using eq 1 to 6. Thus, the partition function Z of the chain of specified configuration is given by

$$Z = \mathbf{J}^* \mathbf{U}_3 \mathbf{U}_4 (\mathbf{U}_1 \mathbf{U}_3 \mathbf{U}_4)^{n-2} \mathbf{U}_1 \mathbf{U}_3 \mathbf{J} \quad (7)$$

where, $\mathbf{J}^* = (100)$, and $\mathbf{J} = \begin{bmatrix} 1 \\ 1 \\ 1 \end{bmatrix}$

and n is the degree of polymerization.

In particular, the partition for stereoregular 100-% *trans*-1,4-polybutadiene or 100-% *cis*-1,4-polybutadiene is obtained by using either eq 1, 3, and 5, or eq 2, 4, and 6 for $\mathbf{U}_1$, $\mathbf{U}_3$, and $\mathbf{U}_4$.

In the second place, 1,4-polyisoprene will be examined. For this, the statistical weight σ used for 1,4-polybutadiene was replaced by σ' as cited by Mark.^{7,8} Since *cis* conformation for $\varphi_3 (\varphi_3 = 180^\circ)$ in eq 3 and 5 is excluded on account of steric overlap of $R_i = (\text{CH}_3)_{i,4}$ with $(\text{CH}_2)_{i,4}$, eq 3 is reduced to

		φ_3			
		60°	180°	-60°	
$U_3(t)=\varphi_1$	60°	1	0	1	(8)
	180°	1	0	1	
	-60°	1	0	1	

and eq 5 is written as

		φ_4			
		0°	120°	-120°	
$U_4(t)=\varphi_3$	60°	1	σ'	σ'	(9)
	180°	0	0	0	
	-60°	1	σ'	σ'	

Other statistical weight matrices are the same as that for polybutadiene.

To calculate the characteristic ratio $\langle R_0^2 \rangle / n l^2$, the customary conventions for defining right-handed Cartesian coordinate systems about skeletal bonds and the bond transformation matrix¹ $\mathbf{T}(\theta_i, \varphi_i)$ with $i=1, 2, 3$ and 4, where θ_i is the bond angle supplement and φ_i the rotational angle, were used. Calculation of $\langle R_0^2 \rangle / n l^2$ was carried out by using the expression derived by Flory^{1,20} for chains of finite chain length.

The following $\mathbf{G}_i$ matrix was constructed using statistical weight matrix $\mathbf{U}_i$ and transformation matrix $\mathbf{T}_i$ for bond 3 and 4 ($i=3, 4$).

$$\mathbf{G}_i = \begin{bmatrix} \mathbf{U}_i & (\mathbf{I}_i^T \times \mathbf{U}_i) \parallel \mathbf{T}_i \parallel & \mathbf{O} \\ \mathbf{O} & (\mathbf{E}_3 \times \mathbf{U}_i) \parallel \mathbf{T}_i \parallel & \mathbf{I}_i \times \mathbf{U}_i \\ \mathbf{O} & \mathbf{O} & \mathbf{U}_i \end{bmatrix} \quad (10)$$

where $\parallel \mathbf{T}_i \parallel$ follows the definition given by Flory.^{1,20}

With respect to bonds 1 and 2, in order to obtain an expression given by a product of three $\mathbf{G}$ matrices regardless of whether bond 2 is *trans* or *cis* (though the expression^{7,8} is given by a product of four $\mathbf{G}$ matrices for *trans* chain, but of three $\mathbf{G}$ matrices for *cis* chain), $\mathbf{G}_{12}^*$ was defined as follows

$$\mathbf{G}_{12}^* = \begin{bmatrix} \mathbf{U}_1 & \mathbf{U}_1 (\mathbf{I}_2^T \times \mathbf{E}_3) \parallel \mathbf{T}_2 \parallel + (\mathbf{I}_1^T \times \mathbf{U}_1) \parallel \mathbf{T}_1 \parallel & (\mathbf{I}_1^T \times \mathbf{U}_1) \parallel \mathbf{T}_1 \parallel (\mathbf{I}_2 \times \mathbf{E}_3) \\ \mathbf{O} & (\mathbf{E}_3 \times \mathbf{U}_1) \parallel \mathbf{T}_1 \parallel \parallel \mathbf{T}_2 \parallel & (\mathbf{E}_3 \times \mathbf{U}_1) \parallel \mathbf{T}_1 \parallel (\mathbf{I}_2 \times \mathbf{E}_3) \\ \mathbf{O} & \mathbf{O} & \mathbf{U}_1 \end{bmatrix} \quad (11)$$

where $\times$ denotes the direct product of the matrices, and $\mathbf{E}_3$ the unit matrix of order 3. $\mathbf{G}_{12}^*(t)$, $\mathbf{G}_{12}^*(c)$, $\mathbf{G}_3(t)$, $\mathbf{G}_3(c)$, $\mathbf{G}_4(t)$ and $\mathbf{G}_4(c)$ were, respectively, defined for $\mathbf{U}_1(t)$, $\mathbf{U}_1(c)$, $\mathbf{U}_3(t)$, $\mathbf{U}_3(c)$, $\mathbf{U}_4(t)$ and $\mathbf{U}_4(c)$ in eq 1–6.

The characteristic ratio of a polymer chain of a specified configuration is given by the use of $\mathbf{G}$'s given by eq 10 and 11, and of Z given by

eq 7

$$\frac{\langle R_0^2 \rangle}{n\bar{l}^2} = 1 + \frac{2}{Zn\bar{l}^2} [1 \ 0 \dots 0] \times \mathbf{G}_{12;0}^* \mathbf{G}_3 \mathbf{G}_4 (\mathbf{G}_{12}^* \mathbf{G}_3 \mathbf{G}_4)^{n-2} \mathbf{G}_{12}^* \mathbf{G}_3 \begin{bmatrix} 0 \\ 0 \\ 0 \\ I_4 \times J \\ J \end{bmatrix} \quad (12)$$

where $n=3n'$, $\bar{l}^2=(I_1^2+I_2^2+I_3^2+I_4^2)/4$, and $\mathbf{G}_{12;0}^*$ denotes a matrix for the terminal bond and is obtained from eq 11 with $\mathbf{U}_1=\mathbf{E}_3$.

The characteristic ratio of 100-% *trans*-1,4-polybutadiene is obtained from eq 7 and 12 by using $\mathbf{U}_1(t)$, $\mathbf{U}_3(t)$ and $\mathbf{U}_4(t)$ in eq 1, 3, and 5 together with $\mathbf{G}_{12}^*$, $\mathbf{G}_3(t)$ and $\mathbf{G}_4(t)$.

The sequence distribution of *trans* and *cis* units in stereoirregular 1,4-butadiene and 1,4-polyisoprene chains can be treated in the same manner as that for polymers reported previously.³ Let the conditional probability that a *trans* unit is succeeded by a *trans* unit be p_{tt} , and further define p_{ct} , p_{tc} and p_{cc} likewise, and then the sequence probability matrix P is given by

$$P = \begin{bmatrix} p_{tt} & p_{tc} \\ p_{ct} & p_{cc} \end{bmatrix} \quad (13)$$

Relations, among these conditional probabilities p_{tt} , p_{tc} , p_{ct} , and p_{cc} , the *a priori* probabilities p_t , p_c , the monomer frequencies F_c and F_t , and the dimer frequencies F_{tt} , F_{tc} , F_{ct} , and F_{cc} , are the same as that mentioned in the authors' previous paper³ for polypeptide copolymers.

Thus treatment with respect to chain configuration as denoted in terms of *trans* and *cis* sequence distribution is the same as that for D,L-copolypeptides whose chain configurations are defined by D and L sequence distribution. However, the correlation between chain configuration and chain conformation is not the same as between stereoirregular diene-polymers and D,L-copolypeptides. With respect to copolypeptides, the chains can be treated as semi-independent-rotation type and the chain conformations simply correlated^{1,3} with chain configuration in terms of tacticity. However, stereoirregular 1,4-polybutadiene and 1,4-polyisoprene chains should be treated as interdependent-rotation type, so that calculation of the characteristic ratio has to be performed by the

random number method. By the use of random numbers* generated in a computer for given values of P (obtained by assuming values for elements of sequence probability P in eq 13), *trans* or *cis* content was determined by the Monte Carlo procedure for chains composed of n double bonds. For thus specified molecular species, from the partition function and finally the characteristic ratio $\langle R_0^2 \rangle / n\bar{l}^2$ for every specified species, we obtain $\langle R_0^2 \rangle / n\bar{l}^2$, i.e., the mean value of $\langle R_0^2 \rangle / n\bar{l}^2$, by averaging $\langle R_0^2 \rangle / n\bar{l}^2$ over all species of Markoffian chain specified by the *a priori* probability and conditional probability.

RESULTS AND DISCUSSION

Input Numerical Values

To get numerical values of statistical weight to be used for the present calculations, let us refer to some experimental results⁷⁻¹⁰ obtained for stereoregular diene polymers. Mark⁸ suggested that $\sigma=1$, $\alpha=0.96$ and $\beta=0.25$ are applicable to *trans*-1,4-polybutadiene and, moreover, $\alpha=0.96$ and $\beta=0.25$ are also common to *trans*-1,4-polyisoprene. Ishikawa and Nagai¹⁰ pointed out that a set of numerical values, $\sigma=1$, $\alpha=1$ and $\beta=0.25$ reproduces the experimental results fairly well. Further, Mark⁷ and Ishikawa⁹ concluded that the value $\sigma=1$ is also valid for *cis*-1,4-polybutadiene. With respect to 1,4-polyisoprene, σ' (smaller than σ) should be used in place of σ . Mark⁸ assigned $\sigma'=0.54$; Ishikawa and Nagai¹⁰ assigned $\sigma'=0.536$ and $\sigma'=0.670$, on the basis of experimental values $\langle R_0^2 \rangle / n\bar{l}^2 = 7.35$ (Flory¹) and $\langle R_0^2 \rangle / n\bar{l}^2 = 6.55$ (Poddunyi²⁵), respectively. The value of $\sigma'=0.536$ was assigned for *trans*-1,4-polyisoprene. Since the numerical values of statistical weights suggested by Ishikawa and Nagai^{9,10} are based on the experimental values not only of the characteristic ratio but also of ΔT and its temperature dependence, they seem to be more reliable than the estimation by Mark.^{7,8} Ishikawa's values were there-

* The random number generated by KUNIRN using FACOM-230/60 electric computer of the Computational Center of Kyoto University was used. The subroutine KUNIRN was examined by this Center. Random numbers were generated by the mixed congruential method.

Table I. Statistical weight parameters and characteristic ratios

	Polybutadiene		Polysoprene		
	1,4- <i>trans</i>	1,4- <i>cis</i>	1,4- <i>trans</i>	1,4- <i>cis</i>	
Statistical weight parameters	$\alpha=1$ $\beta=0.25$ $\sigma=1$	$\delta=6$ $\gamma=30$ $\sigma=1$	$\alpha=1$ $\beta=0.25$ $\sigma=0.536$	$\alpha=1$ $\beta=0.25$ $\sigma'=0.670$	$\delta=0$ $\gamma=30$ $\sigma'=0.536$
$\langle R_0^2 \rangle / n\bar{l}^2$					
Calcd	5.77	4.85	7.30	6.50	4.92
Obsd	5.8 ^a	4.9 ^a	7.35 ^a	6.55 ^b	4.7 ^a

^a ref 1, 7, and 8. ^b ref 10.

fore used in most of this work for calculations.

In Table I, numerical values of statistical weights used in this work and the characteristic ratios calculated from eq 7 and 12 are summarized together with experimental values for characteristic ratio. Calculations of characteristic ratios were performed for chains with a degree of polymerization of 120. Results obtained accord^{21,22} with those calculated for infinite chain length within 1-% deviation. With respect to discrepancies in experimental results for characteristic ratio of *trans*-1,4-polyisoprene, and those between experimental and calculated characteristic ratios of *cis*-1,4-polyisoprene, further studies are necessary. However, in this work, a set of parameters (see Table I) satisfying $\langle R_0^2 \rangle / n\bar{l}^2 = 7.3$ was chosen.

The change in physical properties of 1,4-polybutadiene and 1,4-polyisoprene as functions of stereoregularity is expected to be particularly noticeable in the vicinity of 100-% regularity, and small in the intermediate regularity region, as reported by Short, *et al.*,²³ for tensile strength as a function of stereoregularity. Progress in infrared and nuclear magnetic resonance (NMR) research has made it possible to determine in detail the microstructure of polybutadiene and polyisoprene. For example, NMR study can determine²⁴ the content of *trans* or *cis* units in 1,4-polyisoprene with an accuracy of $\pm 0.5\%$.

In this work, the characteristic ratio of stereoregular polymers having regularities near 100% will be discussed first.

When either *trans* or *cis* units are contained in polydiene chains in large excess compared with the other units, units of minor component

may appear randomly in the chain, so that the probability that a unit of a minor component is succeeded by the same kind of unit is very small and regarded as zero. By analogy with the authors' treatment¹⁹ for copolypeptides reported previously, if the *cis* unit is a minor component, then $p_{cc}=0$; and p_{tt} , p_{tc} and p_{ct} are obtained from $p_{tt}=(2p_t-1)/p_t$ and $p_{tc}=1-p_{tt}$. Accordingly, one can calculate, from eq 13, $\langle R_0^2 \rangle / n\bar{l}^2$ as a function of F_c by the method introduced above.

In Figures 2 and 3, the characteristic ratio was plotted against the monomer frequency of the minor component for 1,4-polybutadiene and 1,

Figure 2. Characteristic ratio $\langle R_0^2 \rangle / n\bar{l}^2$ of 1,4-polybutadiene ($n=140$) plotted against monomer frequency F_t or F_c , for *trans*-rich (○) (abscissa is *cis* content F_c), and *cis*-rich (●) (abscissa is *trans* content F_t) chains.

Figure 3. Characteristic ratio $\langle R_0^2 \rangle / n\bar{l}^2$ of 1,4-polyisoprene ($n=140$) plotted against monomer frequency F_t or F_c , for *trans*-rich (○) (abscissa is *cis* content F_c), and *cis*-rich (●) (abscissa is *trans* content F_t) chains.

4-polyisoprene, respectively. Each point in the Figures was obtained by averaging values calculated for 10 Monte Carlo chains with $n=140$. Error bars in the Figures represent the standard deviations. As is obvious from Figures 2 and 3, the characteristic ratios of *trans*-1,4-polybutadiene and *trans*-1,4-polyisoprene are significantly reduced by introducing small amount of *cis* units into the *trans*-chains. Conversely, the introduction of discrete *trans* units into *cis*-chains had little effect on the characteristic ratio even at 20-% *trans* content. Such results may be explained as follows. When *trans* units are introduced into *cis*-rich polybutadiene chains, the extended nature of the *trans* double bond is compensated for by bending conformation due to $\varphi_1, \varphi_3=180^\circ$ (see eq 3). As a result, the characteristic ratio is little changed. The same behavior is observed for a polyisoprene chain, because a conformation corresponding to $\varphi_1=180^\circ$ is possible as is obvious from eq 8. The fact that $\varphi_3=180^\circ$ is not possible for polyisoprene chains (*cf.*, $\varphi_1, \varphi_3=180^\circ$ is allowed for polybutadiene) is reflected in that the characteristic ratio of polyisoprene (Figure 3) tends to increase slightly with increasing *trans* content, but that of polybutadiene (Figure 2) decreases slightly with increasing *trans* content. It is also pointed out that the standard deviation becomes larger with increasing *cis* content for *trans*-rich chains, but it is very small for *cis*-rich chains, with respect to both polybutadiene and polyisoprene as shown in Figures 2 and 3.

So far, no experimental results are known concerning the relationship between the characteristic ratio, and the *trans* (or *cis*) content or sequence distribution. Though not sufficient to estimate characteristic ratio, Berger and Buckley¹⁵ have investigated the intrinsic viscosity $[\eta]$ of stereoirregular 1,4-polybutadiene as a function of stereoregularity. According to their results, $[\eta]$ was almost unchanged in the *cis*-rich region up to 30-% *trans* content, but decreased rather markedly in the *trans*-rich region by the addition of small amounts of *cis* units. These results are qualitatively in accord with the authors' theoretical results.

Recently, Durand and Teyssie²⁶ have succeeded in synthesizing the "equibinary polybutadiene, an equimolar *trans*—*cis* stereoisomer,

Figure 4. Characteristic ratio $\langle R_0^2 \rangle / n l^2$ of equibinary polydiene ($n=140$) plotted against the conditional probability f that a unit is succeeded by the same kind of unit, for 1,4-polybutadiene (●) and 1,4-polyisoprene (○) chains.

though the sequence distribution of *trans* and *cis* in the chains may not be still obvious. The characteristic ratio of equibinary polydiene was calculated as a function of sequence distribution in terms of the conditional probability f . Results obtained were plotted in Figure 4. $f=0$ corresponds to an alternating polymer; $f=0.5$ denotes randomly distributed *trans*—*cis*-equimolar polymer. The characteristic ratios for alternative polymers are 4.67 for 1,4-polybutadiene and 5.36 for 1,4-polyisoprene. The standard deviation becomes larger as f approaches 1.

Though it is possible to calculate the characteristic ratio for other cases than equimolar polymer, calculations have not been carried out in this work.

The present calculations were performed in accordance with the model proposed by Mark.^{7,8} This model is valid as a first-order approximation to explain the characteristic ratio and the stress—optical coefficient $\Delta I'$, but may be oversimplified as mentioned by Flory¹ and Nagai.¹⁰ Especially for *trans* chains, third-order interactions have to be taken into account together with the second-order interaction as used here. The third-order interaction is such an interaction as produced simultaneously by $\varphi_{i;3}$, $\varphi_{i;4}$ and $\varphi_{i+1;1}$ in Figure 1. Therefore, such interaction may also depend on the conformation (*trans* or *cis*) for $\varphi_{i;2}$ and $\varphi_{i+1;2}$. So, if

the third-order interaction is taken into account one should construct statistical weight matrices (such as $U_1(tt)$, etc.) corresponding to conformations with respect to two successive double bonds, and then calculate the characteristic ratio. However, to this end, further studies are necessary to rotational isomerism of model compounds for estimation of statistical weights and refinement of the model.

Note. This work was reported at the 20th Annual Meeting of the Society of Polymer Science, Japan (Tokyo), May 27, 1971. The preprint was presented before the meeting (March 10, 1971). Therefore, papers^{27,28} of Drs. Abe and Flory which appeared in March–April issue, 1971 of “Macromolecules” dealing with item similar to this paper were not known to the authors. Their paper takes into account higher orders of interaction and uses an averaged generator matrix for calculation of the characteristic ratio, but did not specify explicitly the arrangement of monomer units. This present paper deals with only second-order interactions, but the characteristic ratio was calculated for Monte Carlo chains by taking into account explicitly *trans* and *cis* sequence.

In spite of the differences in model and calculation, both results equally suggest that the characteristic ratio is more sensitive to stereo-irregularity for *trans*-rich chains than for *cis*-rich chains.

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