Unperturbed Mean-Square Radius of Gyration of 1,2-Polybutadiene[†]

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ABSTRACT: Taking account of the geometric structure of side groups, the unperturbed mean-square radius of gyration $\langle S^2 \rangle$ of the typical polymer chains are derivated by using the rotational isomeric state theory. If the masses of the side groups are ignored, the expression of $\langle S^2 \rangle$ is in agreement with that reported by Flory. The root-mean-square radius of gyration of isotactic 1,2-polybutadiene is numerical calculated as $\langle S^2 \rangle^{1/2} = 0.298 M^{1/2}$ and the characteristic ratio of mean-square radius of gyration is greater 11% than that without considering the geometric structure of side groups.

KEY WORDS Rotational Isomeric State / Mean-Square Radius of Gyration / Side Groups / Geometric Structure / 1,2-Polybutadiene /

The rotational isomeric state approximation (RIS) has been used successfully to treat several properties of the polymer chains.[1,2] The theory is widely used to calculate the characteristic ratio $C_n = \langle R^2 \rangle / N l^2$ and the temperature coefficient $d(\ln\langle R^2 \rangle)/dT$ of the mean-square end-to-end distance $\langle R^2 \rangle$ of polymer chains. In general, $\langle R^2 \rangle$ is obtained from the mean-square radius of gyration $\langle S^2 \rangle$, measured by light-scattering or small-angle-neutron-scattering.[3-7] Therefore, it is particularly important to estimate the value of $\langle S^2 \rangle$. The mean-square radius of gyration of polymer chains without considering side groups, such as polyethylene (the effect of bond C–H is ignored), have been investigated by using the RIS theory. Recently, $\langle S^2 \rangle$ for the polymer with single side group has been studied.[8-10] The calculated values of $\langle S^2 \rangle$ for polyethylene (PE) and polypropylene (PP) with considering side groups (C–H) and (C–CH$_3$) are more

approched to the experimental data. In this paper, the mean-square radius of gyration of polymer chains with two side groups, which have the different geometric structures and the heavier group masses, are investigated by using the RIS theory, and the expression for $\langle S^2 \rangle$ may be apply to 1,2-polybutadiene (1,2-PBD), PP, polydimethylsiloxane (PDMS), and other monsubstituted polymers.

INVESTIGATION OF $\langle S^2 \rangle$ FOR POLYMERS WITH DIFFERENT SIDE GROUPS

A monosubstituted polymer chain with two side groups, shown in Figure 1(a), consists of x monomeric units. Each contains the atoms a, b, c, and f. The masses are m_a, m_b, m_c, and m_f, and the bond lengths l_a, l_b, l_c, and l_f, respectively. The skeletal atoms are numbered from 0 to $2x$, and the side groups b and c are

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from $(x+1)$ to $3x$, and $(3x+1)$ to $4x$, respectively. The square radius of gyration of the polymer is defined by

$$S^2 = M^{-1} \sum_{j=0}^{4x} m_j s_j^2 \qquad (1)$$

where M is the molecular weight, m_j is the mass of atom (or group) j, and s_j is the distance of atom j from the center of mass of the chain. Equation 1 may be also expressed as[1]

$$S^2 = M^{-2} \left(\sum_{0 \le i < j \le 2x} + \sum_{i=0}^{2x} \sum_{j=2x+1}^{4x} \right.$$
$$\left. + \sum_{i=2x+1}^{3x} \sum_{j=3x+1}^{4x} + \sum_{2x+1 \le i < j \le 4x} \right) m_i m_j r_{ij}^2$$
$$(2)$$

where r_{ij} is the distance from atom i to j, r_{ij} can be calculated by following way. The skeletal bond vector $\vec{l}_j$ is founded on the bond j with the direction from atom $j-1$ to j. Here, vector $\vec{l}_j$ is also expressed by matrix $\bar{l}_j$

$$\bar{l}_j = [l_j \ \ 0 \ \ 0]^T \qquad (3)$$

with 3×1 orders. A series of Cartesian reference frames $\{x_j, y_j, z_j\}$ affixed to consecutive skeletal bond vectors are connected by the axis transformation matrices T_j expressed by

$$T_j = \begin{bmatrix} \cos\theta & \sin\theta & 0 \\ \sin\theta\cos\Phi & -\cos\theta\cos\Phi & \sin\Phi \\ \sin\theta\sin\Phi & -\cos\theta\sin\Phi & -\cos\Phi \end{bmatrix}_j$$
$$= T(\theta_j, \Phi_j) \qquad (4)$$

where θ_j, the supplementary of bond angle, is the angle between bond vectors $\vec{l}_j$ and $\vec{l}_{j+1}$. That is, θ_a or θ_f is between vectors $\vec{l}_a$ and $\vec{l}_f$ or vectors $\vec{l}_f$ and $\vec{l}_a$ respectively. Φ_j is the angle of internal rotation for bond j. That is, Φ_a and Φ_f are the angle for bonds a and f respectively. Therefore the distance r_{ij} can be expressed by maxices T_j and $\bar{l}_j$. In accordance with the RIS theory,[1] the average value of S^2, which is expressed by $\langle S^2 \rangle$, may be calculated by the statistical weight matrix u_j depended on the conformation of the polymer. The conformation for some polymers, depend on the rotational angle Φ_j, is described by three-state model, one for the *trans* (t) and two for the *gauche* (g^+, g^-). The internal rotation of the side bonds may be ignored. Then, two statistical weight matrices u_a and u_f, depended on the states of Φ_a and Φ_f, are enough to describe the statistical characteristics of the chain in Figure 1(a). Therefore, $\langle S^2 \rangle$ is

$$\langle S^2 \rangle = M^{-2}(\langle S_1^2 \rangle + \langle S_2^2 \rangle + \langle S_3^2 \rangle) \qquad (5)$$

where

$$\langle S_1^2 \rangle = \sum_{0 \le i < j \le 2x} m_i m_j \langle r_{ij}^2 \rangle \qquad (6)$$

$$\langle S_2^2 \rangle = \left(\sum_{i=0}^{2x} \sum_{j=2x+1}^{4x} \right.$$
$$\left. + \sum_{i=2x+1}^{3x} \sum_{j=3x+1}^{4x} \right) m_i m_j \langle r_{ij}^2 \rangle \qquad (7)$$

$$\langle S_3^2 \rangle = \sum_{2x+1 \le i < j \le 4x} m_i m_j \langle r_{ij}^2 \rangle \qquad (8)$$

$\langle S_1^2 \rangle$ only relates to the skeletal atoms. Following Flory,[1,2] it has been given as

$$\langle S_1^2 \rangle = 2Z^{-1} F^* G_1^{(2x)} F = 2Z^{-1} F^* (G_a G_f)^x F \qquad (9)$$

where

$$F^* = [1 \ 0 \ \cdots \ 0] \quad F = [0 \ \cdots \ 0 \ 1 \ 1 \ 1]^T \quad (10)$$

$$G_j = \begin{bmatrix} u_j & m_{j-1} P g_j & m_{j-1} m_j (l_j^2/2) u_j \\ 0 & g_j & m_j g_j Q \\ 0 & 0 & u_j \end{bmatrix} \quad (11)$$

F^*, F, and G_j are matrices with 1×21, 21×1, and 21×21 orders respectively. j is taken $1, 3, 5 \cdots 2x-1$ for the atom a and $0, 2 \cdots 2x$ for the atom f. The partition function Z is

$$Z = J^* u_1^{(2x)} J = J^* (u_a u_f)^x J \qquad (12)$$

where

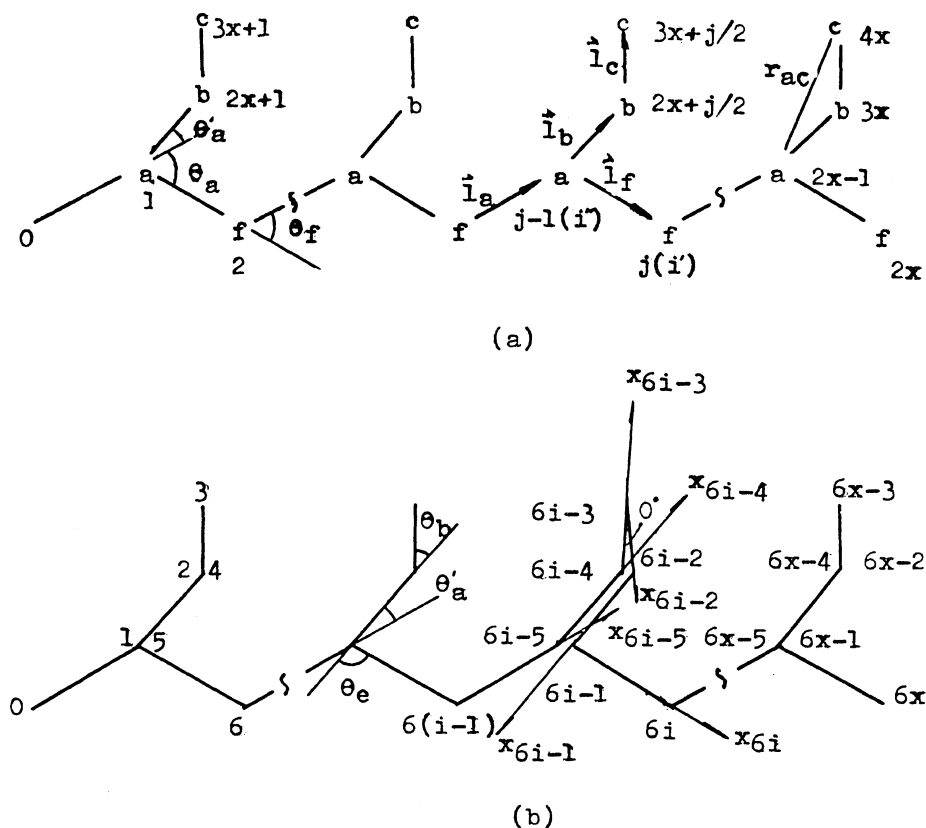$$J^* = [1 \ 0 \ 0] \quad J = [1 \ 1 \ 1]^T \qquad (13)$$

(a)

(b)

Figure 1. (a): Diagrammatic representation of the monosubstituted polymer with two side groups. (b): Diagrammatic representation of the consecutive Cartesian reference frames affixed to bonds.

$$g_j = \begin{bmatrix} u_j & (u_j \otimes \overline{l}_j^T) \| T \|_j & (l_j^2/2)u_j \\ 0 & (u_j \otimes E_3) \| T \|_j & u_j \otimes \overline{l}_j \\ 0 & 0 & u_j \end{bmatrix}$$

$$= g(u_j, l_j, T_j) \tag{14}$$

$$\| T \|_j = \begin{bmatrix} T(\Phi_t) & 0 & 0 \\ 0 & T(\Phi_{g^+}) & 0 \\ 0 & 0 & T(\Phi_{g^-}) \end{bmatrix}_j \tag{15}$$

J^*, J, g_j, and $\| T \|_j$ are matrices with 1×3, 3×1, 15×15, and 9×9 orders.

The expressions of $\langle S_2^2 \rangle$ and $\langle S_3^2 \rangle$ must take account of the structure of the side groups in every repeat units. The mark from 0 to $4x$ in Figure 1(a) are renumered serially from 0 to $6x$ in Figure 1(b). Similarly, new Cartesian

reference frames $\{x_j, y_j, z_j\}$ affixed to the skeletal bonds and side group bonds are founded as shown Figure 1(b), where j is taken with $6i-5$, $6i-4$, $6i-3$, $6i-2$, $6i-1$, and $6i$ (or expressed as a, b, c, d, e, and f) respectively in the i-th repeat unit, and i is taken from 1 to x. Let the axis x_{6i-5}, x_{6i-4}, x_{6i-3}, and x_{6i} of the consecutive coordinate systems affixed to the bonds be in the direction of the bond vectors $\vec{l}_a$, $\vec{l}_b$, $\vec{l}_c$, and $\vec{l}_f$, respectively. The axis x_{6i-2} and x_{6i-1} affixed to the bonds b and c in opposite direction of the bond vectors $\vec{l}_b$ and $\vec{l}_c$, respectively. The axis y_j and z_j are defined by the similar way to the RIS theory. Then, θ'_a is the angle between axis x_{6i-5} and x_{6i-4}; θ_b is that between axis x_{6i-4} and x_{6i-3} or x_{6i-2} and x_{6i-1}; and θ_e is that between x_{6i-1} and x_{6i}. Φ_j may be separated into two parts, Φ_j and Φ'_j.

The former describes the states of internal rotation of bond j. The latter, depended on the geometric structure of the polymer, denotes the dihedral angle between plan $x_j y_j$ and plan $x_{j+1} y_{j+1}$ when Φ_j is in *trans*. Therefore, in each repeat unit, the axis transformation matrix T_j relating to consecutive coordinate systems is given by eq 4 as

$$\left.\begin{aligned}
T_{6i-5} &= T_a = T(\theta_a', \Phi_a + \Phi_a') \\
T_{6i-4} &= T_b = T(\theta_b, \Phi_b') \\
T_{6i-3} &= T_c = T(180°, 0°) \\
T_{6i-2} &= T_d = T(\theta_b, 180°) \\
T_{6i-1} &= T_e = T(\theta_e, \Phi_e') \\
T_{6i} &= T_f = T(\theta_f, \Phi_f + \Phi_f') \\
i &= 1, 2, 3 \cdots x
\end{aligned}\right\} \quad (16)$$

where Φ_a' and Φ_f' can be calculated by

$$\cos \Phi_a' = -(\cos \theta_e + \cos \theta_a' \cos \theta_a)/\sin \theta_a' \sin \theta_a \qquad (17)$$

$$\cos \Phi_f' = -(\cos \theta_a' + \cos \theta_f \cos \theta_e)/\sin \theta_f \sin \theta_e \qquad (18)$$

Φ_b' and Φ_e' are correlative to the dihedral angle between the plan of side groups and the plan of the skeletal bonds in all-*trans*, and Φ_b' and Φ_e' are connected by

$$\cos \theta_a' \cos \theta_e \cos^2 \theta_b + \sin \theta_a' \sin \theta_e \sin^2 \theta_b + \sin \theta_a' \sin \theta_e (\cos \Phi_b' \cos \Phi_e' + \sin \Phi_b' \sin \Phi_e') = -\cos \theta_a \quad (19)$$

Moreover, Φ_j' may be taken with the same angles in all repeat units for isotactic polymers, and with the different angles in the alternating units for syndiotactic polymers, even with the angles of probability in the different units for atactic polymers by using the computer simulation. Because of ignoring internal rotation of bonds b and c, *i.e.*,

$$\Phi_j = 0 \qquad (j = 6i-4, 6i-3, 6i-2, 6i-1 \text{ or } b, c, d, e) \qquad (20)$$

then, the statistical weight matrix u_j is

$$u_{6i-5} = u_a \qquad (i = 2, 3, \cdots x) \qquad (21)$$

$$u_j = E_3 \qquad (j = 6i-4, 6i-3, 6i-2, 6i-1, 1, 6x) \qquad (22)$$

$$u_{6i} = u_f \qquad (i = 1, 2, \cdots x-1) \qquad (23)$$

with E_3 being the identity matrix of orders 3. Using the method of matrix algebra, $\langle S_2^2 \rangle$ can be derivated by

$$\langle S_2^2 \rangle = \left(\sum_{i=0}^{2x} \sum_{j=2x+1}^{4x} + \sum_{i=2x+1}^{3x} \sum_{j=3x+1}^{4x} \right) m_i m_j \langle r_{ij}^2 \rangle = \left(m_f m_b \sum_{i'=0}^{x} \sum_{j=2x+1}^{3x} + m_f m_c \sum_{i'=0}^{x} \sum_{j=3x+1}^{4x} \right) \langle r_{ij}^2 \rangle$$

$$+ \left(m_a m_b \sum_{i''=1}^{x} \sum_{j=2x+1}^{3x} + m_a m_c \sum_{i''=1}^{x} \sum_{j=3x+1}^{4x} \right) \langle r_{ij}^2 \rangle + m_b m_c \sum_{i=2x+1}^{3x} \sum_{j=3x+1}^{4x} \langle r_{ij}^2 \rangle \qquad (24)$$

where

$$\left.\begin{aligned}
i' &= j/2 \qquad (j = 0, 2, 4 \cdots 2x) \\
i'' &= (j+1)/2 \qquad (j = 1, 3, 5 \cdots 2x-1)
\end{aligned}\right\} \qquad (25)$$

Following Figure 1(b), $\langle S_2^2 \rangle$ is also expressed as

$$\langle S_2^2 \rangle = m_{\mathrm{f}} m_{\mathrm{b}} \sum_{h=0}^{x} \sum_{k=1}^{x} \langle r_{6h,6k-4}^2 \rangle + m_{\mathrm{f}} m_{\mathrm{c}} \sum_{h=0}^{x} \sum_{k=1}^{x} \langle r_{6h,6k-3}^2 \rangle$$

$$+ m_{\mathrm{a}} m_{\mathrm{b}} \sum_{h=1}^{x} \sum_{k=1}^{x} \langle r_{6h-5,6k-4}^2 \rangle + m_{\mathrm{a}} m_{\mathrm{c}} \sum_{h=1}^{x} \sum_{k=1}^{x} \langle r_{6h-5,6k-3}^2 \rangle$$

$$+ m_{\mathrm{b}} m_{\mathrm{c}} \sum_{h=1}^{x} \sum_{k=1}^{x} \langle r_{6h-4,6k-3}^2 \rangle$$

$$= 4 m_{\mathrm{f}} m_{\mathrm{b}} Z^{-1} J^{\divideontimes} \sum_{0 \leq h < k \leq x} u_1^{(6h)} P g_{6h+1}^{(6k-6h-4)} Q u_{6k-3}^{(6x-6k+4)} J$$

$$+ 4 m_{\mathrm{f}} m_{\mathrm{c}} Z^{-1} J^{\divideontimes} \sum_{0 \leq h < k \leq x} u_1^{(6h)} P g_{6h+1}^{(6k-6h-3)} Q u_{6k-2}^{(6x-6k+3)} J$$

$$+ m_{\mathrm{a}} m_{\mathrm{b}} \left[\sum_{h=1}^{x} r_{6h-5,6k-4}^2 + 4 Z^{-1} J^{\divideontimes} \sum_{1 \leq h < k \leq x} u_1^{(6h-5)} P g_{6h-4}^{(6k-6h+1)} Q u_{6k-3}^{(6x-6k+4)} J \right]$$

$$+ m_{\mathrm{a}} m_{\mathrm{c}} \left[\sum_{h=1}^{x} r_{6h-5,6k-3}^2 + 4 Z^{-1} J^{\divideontimes} \sum_{1 \leq h < k \leq x} u_1^{(6h-5)} P g_{6h-4}^{(6k-6h+2)} Q u_{6k-2}^{(6x-6k+3)} J \right]$$

$$+ m_{\mathrm{b}} m_{\mathrm{c}} \left[\sum_{h=1}^{x} r_{6h-4,6k-3}^2 + 4 Z^{-1} J^{\divideontimes} \sum_{1 \leq h < k \leq x} u_1^{(6h-4)} P g_{6h-3}^{(6k-6h+1)} Q u_{6k-2}^{(6x-6k+3)} J \right] \quad (26)$$

where

$$P = [E_3 \quad 0], \qquad Q = [0 \quad E_3]^T \quad (27)$$

P and Q are matrices of 3×15 and 15×3 orders, respectively. The first terms in eq 26 can be expressed by $4 m_{\mathrm{f}} m_{\mathrm{b}} Z^{-1} F^{\divideontimes} S(1)_1^{(x)} F$, where

$$S(1)_i = \begin{bmatrix} u_{6i-5}^{(6)} & P g_{6i-5}^{(6)} & P g_{6i-5}^{(2)} Q u_{6i-3}^{(4)} \\ 0 & g_{6i-5}^{(6)} & g_{6i-5}^{(2)} Q u_{6i-3}^{(4)} \\ 0 & 0 & u_{6i-5}^{(6)} \end{bmatrix} \quad (28)$$

and g_j from eq 14 may be expressed by

$$\left. \begin{aligned} g_{6i-5} &= g_{\mathrm{a}} = g(u_{\mathrm{a}}, l_{\mathrm{a}}, T_{\mathrm{a}}) \\ g_{6i-4} &= g_{\mathrm{b}} = g(E_3, l_{\mathrm{b}}, T_{\mathrm{b}}) \\ g_{6i-3} &= g_{\mathrm{c}} = g(E_3, l_{\mathrm{c}}, T_{\mathrm{c}}) \\ g_{6i-2} &= g_{\mathrm{d}} = g(E_3, l_{\mathrm{c}}, T_{\mathrm{d}}) \\ g_{6i-1} &= g_{\mathrm{e}} = g(E_3, l_{\mathrm{b}}, T_{\mathrm{e}}) \\ g_{6i} &= g_{\mathrm{f}} = g(u_f, l_{\mathrm{f}}, T_{\mathrm{f}}) \end{aligned} \right\} \quad (29)$$

moreover, $S(1)_i$ may be identified with

$$S(1) = \begin{bmatrix} u_{\mathrm{a}} u_{\mathrm{f}} & P g_{\mathrm{a}} g_{\mathrm{b}} g_{\mathrm{c}} g_{\mathrm{d}} g_{\mathrm{e}} g_{\mathrm{f}} & P g_{\mathrm{a}} g_{\mathrm{b}} Q u_{\mathrm{f}} \\ 0 & g_{\mathrm{a}} g_{\mathrm{b}} g_{\mathrm{c}} g_{\mathrm{d}} g_{\mathrm{e}} g_{\mathrm{f}} & g_{\mathrm{a}} g_{\mathrm{b}} Q u_{\mathrm{f}} \\ 0 & 0 & u_{\mathrm{a}} u_{\mathrm{f}} \end{bmatrix} \quad (30)$$

Similar to the other terms in eq 26, then, $\langle S_2^2 \rangle$ can be given

$$\langle S_2^2 \rangle = 4Z^{-1}[m_f m_b F^* S(1)^x F + m_f m_c F^* S(2)^x F$$
$$+ m_a m_b F^* S(3)^x F + m_a m_c F^* S(4)^x F + m_b m_c F^* S(5)^x F] \tag{31}$$

where

$$S(2) = \begin{bmatrix} u_a u_f & P g_a g_b g_c g_d g_e g_f & P g_a g_b g_c Q u_f \\ 0 & g_a g_b g_d g_c g_e g_f & g_a g_b g_c Q u_f \\ 0 & 0 & u_a u_f \end{bmatrix} \tag{32}$$

$$S(3) = \begin{bmatrix} u_a u_f & u_a P g_b g_c g_d g_e g_f & (l_b^2/4) u_a u_f \\ 0 & g_a g_b g_c g_d g_e g_f & g_a g_b Q u_f \\ 0 & 0 & u_a u_f \end{bmatrix} \tag{33}$$

$$S(4) = \begin{bmatrix} u_a u_f & u_a P g_b g_c g_d g_e g_f & (r_{ac}^2/4) u_a u_f \\ 0 & g_a g_b g_c g_d g_e g_f & g_a g_b g_c Q u_f \\ 0 & 0 & u_a u_f \end{bmatrix} \tag{34}$$

$$S(5) = \begin{bmatrix} u_a u_f & u_a P g_c g_d g_e g_f & (l_c^2/4) u_a u_f \\ 0 & g_a g_b g_c g_d g_e g_f & g_a g_b g_c Q u_f \\ 0 & 0 & u_a u_f \end{bmatrix} \tag{35}$$

$$r_{ac}^2 = l_b^2 + l_c^2 + 2 l_b l_c \cos \theta_b \tag{36}$$

they are matrices of orders 21×21. Similarly, $\langle S_3^2 \rangle$ can be derivated by

$$\langle S_3^2 \rangle = \left(\sum_{2x+1 \le i < j \le 3x} + \sum_{3x+1 \le i < j \le 4x} \right) m_i m_j \langle r_{ij}^2 \rangle$$

$$= m_b^2 \sum_{1 \le h < k \le x} \langle r_{6h-4,6k-4}^2 \rangle + m_c^2 \sum_{1 \le h < k \le x} \langle r_{6h-3,6k-3}^2 \rangle$$

$$= 2Z^{-1} \Bigg[m_b^2 J^* \sum_{1 \le h < k \le x} u_1^{(6h-4)} P g_{6h-3}^{(6k-6h)} Q u_{6k-3}^{(6x-6k+4)} J$$

$$+ m_c^2 J^* \sum_{1 \le h < k \le x} u_1^{(6h-3)} P g_{6h-2}^{(6k-6h)} Q u_{6k-2}^{(6x-6k+3)} J \Bigg]$$

$$= 2Z^{-1}[m_b^2 F^* S(6)^x F + m_c^2 F^* S(7)^x F] \tag{37}$$

where

$$S(6) = \begin{bmatrix} u_a u_f & u_a P g_c g_d g_e g_f & 0 \\ 0 & g_a g_b g_c g_d g_e g_f & g_a g_b Q u_f \\ 0 & 0 & u_a u_f \end{bmatrix} \tag{38}$$

$$S(7) = \begin{bmatrix} u_a u_f & u_a P g_d g_e g_f & 0 \\ 0 & g_a g_b g_c g_d g_e g_f & g_a g_b g_c Q u_f \\ 0 & 0 & u_a u_f \end{bmatrix} \tag{39}$$

Therefore, the unperturbed mean-square ra-

dius of gyration of the polymer chains, such as isotactic and syndiotactic 1,2-PBD, can be calculated by eq 5—39 or by the following equation

$$\langle S^2 \rangle = 2Z^{-1}M^{-2}F^*(G_aG_f)^xF$$
$$+ 2Z^{-1}M^{-2}\sum_{q=1}^{7} m(q)F^*S(q)^xF \quad (40)$$

where $m(1)$—$m(7)$ replace $2m_fm_b$, $2m_fm_c$, $2m_am_c$, $2m_am_c$, $2m_bm_c$, m_b^2, and m_c^2, respectively. The first term in eq 40, only related to the skeletal atoms of the polymer, is derivated without considering the side groups. The second term may be regarded as the revision with considering the geometric structure of side groups. The expression 40 is easy to be executed numerical calculation.

If the geometric structure of the second side groups for the polymer chain is ignored, eq 40 can be reduced to that of the polymer chains with single side group as follows: The first, the mass m_b is assumed to be zero, eq 40 may be simplified to

$$\langle S^2 \rangle = 2Z^{-1}M^{-2}F^*[(G_aG_f)^x + 2m_fm_cS(2)^x$$
$$+ 2m_am_cS(4)^x + m_c^2S(7)^x]F \quad (41)$$

The second, the structure of side groups is changed into one side group instead of two side groups. Let vector $\vec{l}_c$ be taken in the direction of vector $\vec{l}_b$, i.e., θ_b and Φ_b are regarded as 0° and 180° respectively, or the axis transformation matrices T_b and T_d become the identity matrix. Then, Φ_e' given by eq 19 as

$$\cos\Phi_e' = (\cos\theta_a + \cos\theta_e\cos\theta_a')/\sin\theta_e\sin\theta_a' \quad (42)$$

The third, the bond length l_b is regarded as zero. Substituting eq 16—18 and 42 into eq 29, g_j can be expressed by

$$\left.\begin{array}{l} g_a = g(u_a, l_a, T_a) \equiv g_\alpha \\ g_b = g(E_3, 0, E_3) = E_{15} \\ g_c = g(E_3, l_c, T_c) \equiv g_\beta \\ g_d = g(E_3, l_c, E_3) \\ g_e = g(E_3, 0, T_e) \\ g_f = g(u_f, l_f, T_f) = g_\delta \end{array}\right\} \quad (43)$$

where E_{15} is the identity matrix of orders 15. Moreover, we have

$$g_dg_e = g(E_3, l_c, T_c) \equiv g_\gamma \quad (44)$$

Then, $S(2)$, $S(4)$, and $S(7)$ can be simplified to

$$S(2) = \begin{bmatrix} u_au_f & Pg_\alpha g_\beta g_\gamma g_\delta & Pg_\alpha g_\beta Qu_f \\ 0 & g_\alpha g_\beta g_\gamma g_\delta & g_\alpha g_\beta Qu_f \\ 0 & 0 & u_au_f \end{bmatrix} \quad (45)$$

$$S(4) = \begin{bmatrix} u_au_f & u_aPg_\beta g_\gamma g_\delta & (l_c^2/4)u_au_f \\ 0 & g_\alpha g_\beta g_\gamma g_\delta & g_\alpha g_\beta Qu_f \\ 0 & 0 & u_au_f \end{bmatrix} \quad (46)$$
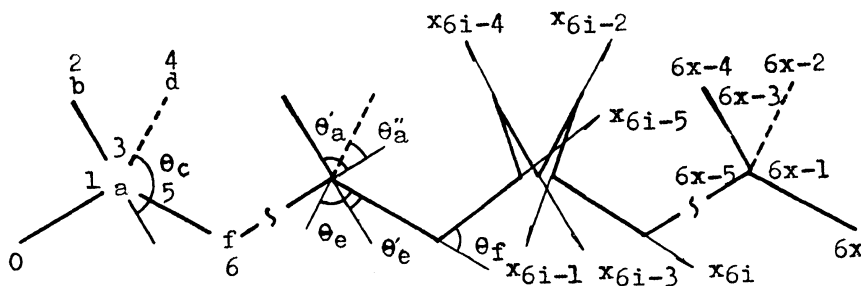

Figure 2. Diagrammatic representation of the consecutive Cartesian reference frames affixed to the bonds for the polymer, such as PDMS.
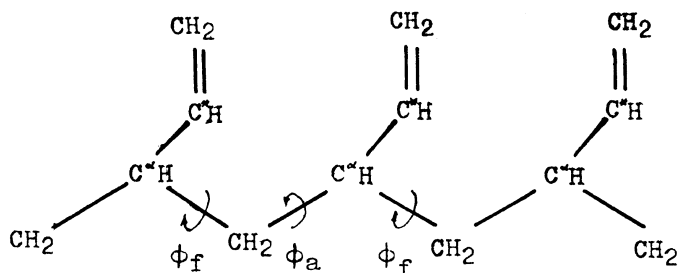
Figure 3. Schematic representation of the isotactic 1,2-polybutadiene chain in the all-*trans*.

$$S(7) = \begin{bmatrix} u_a u_f & u_a P g_\gamma g_\delta & 0 \\ 0 & g_\alpha g_\beta g_\gamma g_\delta & g_\alpha g_\beta Q u_f \\ 0 & 0 & u_a u_f \end{bmatrix} \quad (47)$$

Therefore, eq 41 can be investigated the mean-square radius of gyration of the polymers with single side group, such as isotactic and syndiotactic PP.

The monosubstituted polymer chain shown in Figure 3 is also investigated by eq 40. The mass m_j, the bond length l_j and the angle θ_j are defined as above or shown in Figure 2. The axis transformation matrix T_j is given by

$$\left. \begin{aligned} T_{6i-5} &= T_a = T(\theta_a', \Phi_a + \Phi_a') \\ T_{6i-4} &= T_b = T(180°, 0°) \\ T_{6i-3} &= T_c = T(\theta_c, \Phi_c') \\ T_{6i-2} &= T_d = T(180°, 0°) \\ T_{6i-1} &= T_e = T(\theta_e, \Phi_e') \\ T_{6i} &= T_f = T(\theta_f, \Phi_f + \Phi_f') \end{aligned} \right\} \quad (48)$$

where Φ_a', Φ_c', Φ_e', and Φ_f' can be calculated by

$$\cos \Phi_a' = -(\cos \theta_c + \cos \theta_a' \cos \theta_a'')/\sin \theta_a' \sin_a'' \quad (49)$$

$$\cos \Phi_c' = (\cos \theta_a'' + \cos \theta_a' \cos \theta_a)/\sin \theta_a' \sin \theta_c \quad (50)$$

$$\cos \Phi_e' = (\cos \theta_e' + \cos \theta_c \cos \theta_e)/\sin \theta_c \sin \theta_e \quad (51)$$

$$\cos \Phi_f' = -(\cos \theta_f'' + \cos \theta_f \cos \theta_e)/\sin \theta_e \sin \theta_f \quad (52)$$

where θ_a'' is angle between axis x_{6i-5} and x_{6i-2}, θ_e' is angle between x_{6i-3} and x_{6i}. Then, g_j may be expressed by

$$\left. \begin{aligned} g_{6i-5} &= g_a = g(u_a, l_a, T_a) \\ g_{6i-4} &= g_b = g(E_3, l_b, T_b) \\ g_{6i-3} &= g_c = g(E_3, l_b, T_c) \\ g_{6i-2} &= g_d = g(E_3, l_d, T_d) \\ g_{6i-1} &= g_e = g(E_3, l_d, T_e) \\ g_{6i} &= g_f = g(u_f, l_f, T_f) \end{aligned} \right\} \quad (53)$$

where the statistical weight matrix u_j is also given by eq 21—23. The expression of $S(1)$, $S(3)$, and $S(6)$ are similar expressions to eq 30, 33, and 38, respectively. Others of $S(q)$ are given

$$S(2) = \begin{bmatrix} u_a u_f & P g_a g_b g_c g_d g_e g_f & P g_a g_b g_c g_d Q u_f \\ 0 & g_a g_b g_c g_d g_e g_f & g_a g_b g_c g_d Q u_f \\ 0 & 0 & u_a u_f \end{bmatrix} \quad (54)$$

$$S(4) = \begin{bmatrix} u_a u_f & u_a P g_b g_c g_d g_e g_f & (l_d^2/4) u_a u_f \\ 0 & g_a g_b g_c g_d g_e g_f & g_a g_b g_c g_d Q u_f \\ 0 & 0 & u_a u_f \end{bmatrix} \quad (55)$$

$$S(5) = \begin{bmatrix} u_a u_f & u_a P g_c g_d g_e g_f & (r_{bd}^2/4) u_a u_f \\ 0 & g_a g_b g_c g_d g_e g_f & g_a g_b g_c g_d Q u_f \\ 0 & 0 & u_a u_f \end{bmatrix} \quad (56)$$

$$S(7) = \begin{bmatrix} u_a u_f & u_a P g_e g_f & 0 \\ 0 & g_a g_b g_c g_d g_e g_f & g_a g_b g_c g_d Q u_f \\ 0 & 0 & u_a u_f \end{bmatrix}$$

$$\text{(57)}$$

where

$$r_{bd}^2 = l_d^2 + l_b^2 + 2 l_b l_d \cos \theta_c \qquad \text{(58)}$$

$m(1)$—$m(7)$ in eq 40 replaces $2m_f m_b$, $2m_f m_d$, $2m_a m_b$, $2m_a m_d$, $2m_b m_d$, m_b^2, and m_d^2, respectively. Therefore the mean-square radius of gyration of the polymer with considering two side groups, such as PDMS, may be investigated by eq 40, too.

If the structures of two side groups are ignored, or the masses of side groups b and c in Figure 1 (or b and d in Figure 2) are assumed to be zero, the second term of eq 40 becomes zero. Then, the expression is in agreement with that by Flory.[1,2]

CALCULATION OF $\langle S^2 \rangle$ FOR ISOTATIC 1,2-POLYBUTADIERE

The unperturbed mean-square radius of gyration for one polymer depends on the conformational characteristics, the geomatric structure and the distribution of atom masses in a monomer. Such as isotactic 1,2-PBD shown in Figure 3, the conformation can be described by three-state model, the *trans* ($0°$) and the *gauche* ($120°$ and $-120°$). The statistical weight matrices u_a and u_f are[11-15]

$$u_a = \begin{bmatrix} \eta \omega'' & 1 & \tau \omega' \\ \eta & \omega & \tau \omega' \\ \eta \omega' & \omega' & \tau \omega \omega'' \end{bmatrix} \qquad \text{(59)}$$

$$u_f = \begin{bmatrix} \eta & 1 & \tau \\ \eta & 1 & 0 \\ \eta & 0 & \tau \end{bmatrix} \qquad \text{(60)}$$

where the statistical weight η is the first-order interaction between $C^\alpha H$ and $C^* H$, τ is that between $C^\alpha H$ and $C^* H$, CH_2; ω, ω' and ω''

are the second-order interaction between CH_2 and CH_2, $C_2 H_3$ and CH_2, $C_2 H_3$ and $C_2 H_3$, respectively. The statistical weight ξ corresponding to the temperature T may be defined by the relationship

$$\xi = \xi_0 \exp(-E_\xi / RT)$$
$$(\xi = \eta, \tau, \omega, \omega', \omega'') \qquad \text{(61)}$$

where

$$E_\xi = (E_0/2)(1 - \cos 3\Phi_j) + \sum_{\alpha < \beta} (a_{\alpha\beta}/r_{\alpha\beta}^{12} - b_{\alpha\beta}/r_{\alpha\beta}^6) \qquad \text{(62)}$$

the barrier height E_0 is $11.70 \, \text{kcal mol}^{-1}$. The interaction parameters $a_{\alpha\beta}$ and $b_{\alpha\beta}$ are listed in Table I(a). The conformational energy E_ξ and the conformational parameter ξ_0 are given by Table I(b).[15] The geometric parameters for isotactic 1,2-PBD are listed Table I(c), and the dihedral angle between the plan of side groups and the plan of skeletal bonds in all-*trans* is $90°$. Thus, Φ_b' can be calculated by

Table I(a). Exclusionary parameter $a_{\alpha,\beta}$ and London astigmatic parameter $b_{\alpha\beta}$

Atom and atoms pair	$a_{\alpha\beta} \times 10^{-5}/$ $\text{Å}^{12} \cdot \text{kJ} \cdot \text{mol}^{-1}$	$b_{\alpha\beta} \times 10^{-2}/$ $\text{Å}^6 \cdot \text{kJ} \cdot \text{mol}^{-1}$
$C \cdots C$	16.5	15.2
$C \cdots H$	2.3	5.3
$H \cdots H$	0.3	2.0
$C^* \cdots C^*$	46.7	22.8
$C^* \cdots C$	27.9	18.6
$C^* \cdots H$	4.3	6.5
$C_2 H_3 \cdots C^*$	697.2	192.2
$C_2 H_3 \cdots C$	110.0	53.7
$C_2 H_3 \cdots H$	17.7	19.3

Table I(b). The conformational energies E_ξ and the conformational parameter ξ_0 for isotactic 1,2-PBD

ξ	ξ_0	$E_\xi / \text{J} \cdot \text{mol}^{-1}$
η	1.0	1670
τ	0.4	4180
ω	0.7	2930
ω'	1.2	5850
ω''	1.0	10450

Table I(c). The geometric parameter for isotactic 1,2-PBD

Bond	Bond length/Å	Bond angle	Angle/°
$C-C^a$	1.53	$\angle CC^aC^* \angle CC^aC$	112
C^a-C^*	1.51	$\angle C^aCC^a$	112
$C^*=C$	1.35	$\angle C^aC^*C$	120
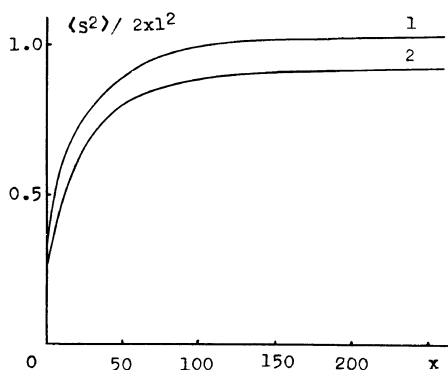
Figure 4. The characteristic ratios $\langle S^2\rangle/2xl^2$ vs. the degree of polymerization x at 340 K for isotactic 1,2-polybutadiene considering side groups 1 and without considering side groups 2.

$$\sin \Phi_b' = -(\cos(\theta_a/2))/\sin \theta_a' \qquad (63)$$

Substituting the geometric parameters into eq 17—19 and eq 63, we have

$$\left.\begin{array}{ll} \Phi_a' = 126.8°, & \Phi_f' = 233.2° \\ \Phi_b' = -63.4°, & \Phi_e' = 73.2° \end{array}\right\} \qquad (64)$$

The characteristic ratios of mean-square radius of gyration $\langle S^2\rangle/2xl^2$ vs. the degree of polymerization x at 340 K for isotactic 1,2-PBD with considering side groups and without considering side groups may be numerical calculated shown in Figure 4, where l is the length of bond C^a-C. The ratio of mean-square radius of gyration for isotactic 1,2-PBD with considering side groups is greater 11% than that without considering side groups when x exceeds 200. The root-mean-square radius of gyration, depended on the molecular weight M, is

$$\langle S^2\rangle^{1/2} = 0.298 M^{1/2} \qquad (65)$$

The mean-square radius of gyration for isotactic PP with considering side groups, which has been reduced as eq 14—47, is given the identical result with the experimental data, i.e., the molecular weight dependence of root-mean-square radius of gyration is obtained as

$$\langle S^2\rangle^{1/2} = 0.34 M^{1/2} \qquad (66)$$

Besides, the relation for PE without considering side groups is given[1]

$$\langle S^2\rangle^{1/2} = 0.423 M^{1/2} \qquad (67)$$

and with considering side groups given[10]

$$\langle S^2\rangle^{1/2} = 0.44 M^{1/2} \qquad (68)$$

the latter is more approached to the experimental data[9]

$$\langle S^2\rangle^{1/2} = 0.45 M^{1/2} \qquad (69)$$

The ratio for PE with considering the side group is greater 8% than that without considering the side group. Obviously, if the geometric structure of side groups is considered, the centers of mass of monomers will be changed. Then, the distances of the center of mass of chain from the centers of mass of each monomer are changed. That is, the dimension of the polymer chain is also changed. Therefore, it is possible that the ratio of mean-square radius of gyration of polymer chains with considering the geometric structure of side groups is different form that without considering the geometric structure of side groups.

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