

STUDY ON MEAN-SQUARE RADIUS OF GYRATION FOR POLYALKYLENEOXIDES*

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ABSTRACT

Taking account of the effect of heteroatoms in backbone, this article dealt with the mean-square radii of gyration of polyalkyleneoxides by the approach of matrix algebra in accordance with the rotational isomeric state model. Numerical calculation with the parameters available in the literatures indicated that the dependence of $\langle S^2 \rangle$ on the molecular weight can be expressed by the general formula:

$$\langle S^2 \rangle = aM^b$$

INTRODUCTION

Since 1960's, Flory and co-workers^[1-4] have calculated conformational energies for a number of model compounds and developed a systematic theory of conformational statistics for chain molecules. The quantitative estimate mainly focused on the characteristic ratio of the mean-square end-to-end distance and dipole moments of polymer chains. Another important conformation-dependent property of flexible chain molecules is the mean-square radius of gyration. With the development of technique, the mean-square radius of gyration has already readily been evaluated from light scattering or small-angle neutron scattering experiments. In addition, it is more precise to describe the unperturbed dimension of polymer chains by the mean-square radius of gyration rather than the end-to-end distance, especially for branched and star-shaped polymers due to the presence of more than two chain ends. Therefore, it is particularly important to estimate the mean-square radius of gyration.

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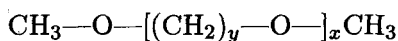
Previously, the following equation was utilized to describe the square radius of gyration of a polymer chain:

$$S^2 = \frac{1}{n+1} \sum_{i=0}^n s_i^2 \quad (1)$$

where S_i represents the distance from the i -th skeletal atom to the mass center of the macromolecules, and n is the total number of skeletal bonds in the polymer chain. In Eq. (1) the influences of both side groups and heteroatoms in the backbone are neglected. Recently, we have developed an expression of mean-square radius of gyration for polymers with side groups, which has been successfully applied to the calculation of $\langle S^2 \rangle$ for vinyl polymers^[5], poly-1, 1-disubstituted ethylenes^[6], and 1,4-polydienes^[7]. It is also interesting to investigate the effect of heteroatoms in backbone of a polymer chain on the mean-square radius of gyration. As an typical example, polymethylene oxide and other polyalkylene oxides are taken into account below. The dependence of $\langle S^2 \rangle$ on molecular weight M has been derived, which can be verified by means of light scattering or small angle scattering.

THEORETICAL TREATMENT

It is known that polyalkyleneoxides comprise oxygen atoms along the chain at regular interval:



where x is the number of repeated unit in the chain, and y is the methylene number within a repeated unit. In accordance with the structural feature of polyalkylene-oxide chains, the rigorous definition of square radius of gyration reads:

$$S^2 = M^{-1} \sum_{i=0}^{(y+1)x} m_i s_i^2 \quad (2)$$

Obviously, Eq. (2) is different from Eq. (1), and the former is more precise than the latter.

Fig. 1 shows parts of various polyalkyleneoxide chains in detail. From Fig. 1, it is evident that every bond in a repeated unit possesses different conformational characteristics, therefore the bonds under consideration can be distinguished from one another by assigning an alphabetical symbol to each of them. Following the scheme introduced by Flory^[1], statistical weight parameters σ and ω are defined respectively for each "first-order interaction" (i.e., the interaction between groups

separated by three bonds) and each "second-order interaction" (i.e., the interaction between groups separated by four bonds). Numerical subscripts are respectively affixed to statistical weight parameters to specify the polymer chains with which the parameters are associated.

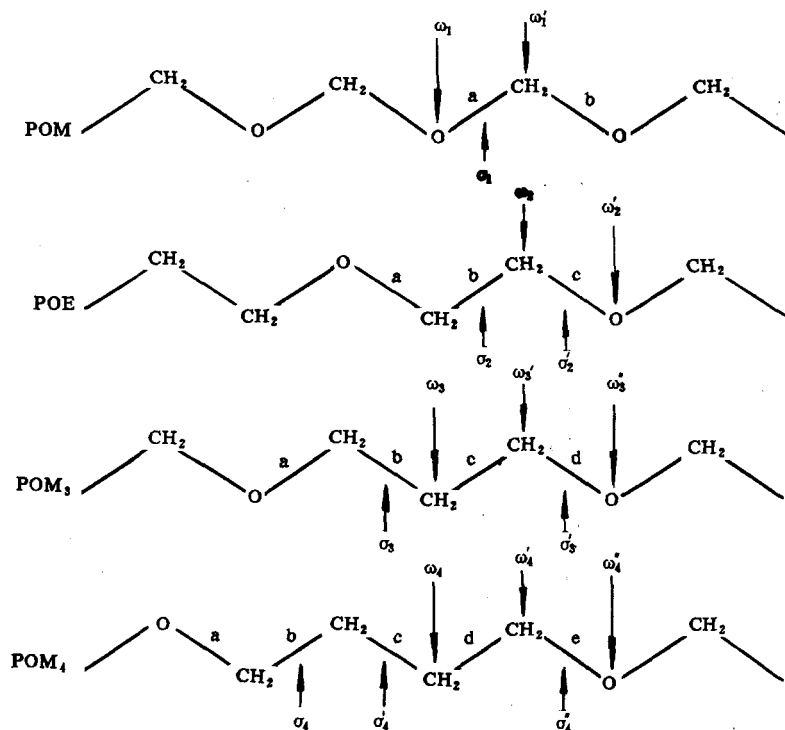


Fig. 1. Schematic drawing of polyalkyleneoxide chains

The calculation of conformational energies, the random coil dimensions and dipole moments of the polyalkyleneoxides has been implemented by several authors^[8-14]. The most important characteristic of these polymer chains is the decisive preference of the gauche conformation over the *trans* one. However, theoretical calculation based on semi-empirical conformational energy function^[8-14] fails to reproduce the experimental values. Abe and Mark^[15] implicated the intramolecular interactions involving oxygen atom as origin of the disagreement between theoretical and experimental data, and gave a quantitative estimation of the magnitude of discrepancy for each of the interaction thus involved. In addition, they took account of the possible effect of displacements ($\Delta\varphi$) of any rotational states from their perfectly symmetrical location at 0°, 120° and -120°, and gave the theoretical values of conformational energies by using the most reliable semi-empirical potential energy functions, which were compared with the experimental data to find the optimal

values of conformational energies.

The statistical weight matrix of every bond in each of the polyalkyleneoxide chains shown in Fig. 1 can be expressed by a general formula^[1,15].

$$U = \begin{bmatrix} 1 & \sigma & \sigma \\ 1 & \sigma & \sigma\omega \\ 1 & \sigma\omega & \sigma \end{bmatrix} \quad (3)$$

The row and columns are indexed in the order of t, g⁺ and g⁻ following the conventional procedure, and the statistical weight parameters σ and ω are Boltzmann factors of corresponding conformational energies, respectively. Referring to tt state, the conformational energies E_σ and E_ω thus required are associated with respective rotational minima defined by two consecutive bond rotations. The conformational parameters and rotational angles reported by Abe and Mark^[15] are listed in Table 1. The energy minimum of t state was always found at 0°. In terms of Eq. (2), the mean-square radii of gyration of various polyalkyleneoxides are further calculated in the following sections of this work by using the conformational parameters given in Table 1.

Table 1 Parameters of conformational energy and rotational angle
for various polyalkyleneoxides

Polymer	Conformational energy* (J/mol)	Rotational angle (deg.)
POM	$E_{\sigma 1} = -5852$	$\varphi_{g\pm} = \pm 115$
	$E_{\omega 1} = 6285$	
POE	$E_{\sigma 2} = -2095$	$\varphi_{g\pm} (\text{C—O}) = \varphi_{g\pm} (\text{C—C}) = \pm 110$
	$E_{\sigma'_2} = 3771$	
	$E_{\omega 2} = 1676$	
POM ₃	$E_{\sigma 3} = -1676$	$\varphi_{g\pm} (\text{C—O}) = \pm 110$ $\varphi_{g\pm} (\text{C—C}) = \pm 120$
	$E_{\sigma'_3} = 3771$	
	$E_{\omega 3} = 2514$	
POM ₄	$E_{\sigma 4} = -838$	$\varphi_{g\pm} (\text{C—O}) = \pm 110$ $\varphi_{g\pm} (\text{C—C} \rightarrow \text{C—O}) = \pm 120$ $\varphi_{g\pm} (\text{C—C} \rightarrow \text{C—C}) = \pm 112.5$
	$E_{\sigma'_4} = 2095$	
	$E_{\sigma''_4} = 3771$	
	$E_{\omega 4} = 2514$	

*The energy minima of tt state were always found at (0°, 0°)

1. POM chains

The first member of polyalkyleneoxides is polyoxymethylenes (POM), or more commonly, polyformaldehyde. Its repeat unit embraces two bonds which are specified as bond a and bond b, respectively, as shown in Fig. 1. POM chain has the

following constitution:



where x is the number of monomeric units in the chain molecule. Therefore the total number of skeletal bonds is $n = 2x + 2$. The skeletal atoms are numerated from 0 to n , and the skeletal bonds from 1 to n . By means of the conventional approach^[5-7], the improved mean-square radius of gyration of a polyformaldehyde chain can be derived:

$$\langle S^2 \rangle = Z^{-1} M^{-2} (J^* \otimes J_{p'}) \tilde{G}_1^{(n)} (J \otimes J_{Q'}) \quad (4)$$

where

$$\tilde{G}_i = (U_i \otimes E_7) \| G_i \| \quad (5)$$

and

$$G_i = \begin{bmatrix} 1 & m_{i-1} J_p g_i & m_{i-1} m_i J_p g_i J_Q \\ 0 & g_i & m_i g_i J_Q \\ 0 & 0 & 1 \end{bmatrix} \quad (6)$$

In Eq. (6), m_i is the mass of the i -th skeletal atom or atom group, and M indicates the molecular weight of the polymer chain. Furthermore, we define the structural unit matrix by:

$$\tilde{G}^{(2)} = \tilde{G}_a \tilde{G}_b \quad (7)$$

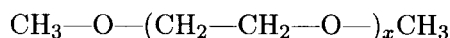
where $\tilde{G}_a$ and $\tilde{G}_b$ are obtained by substituting the relevant parameters of bonds a and b into Eq. (5), respectively. Accordingly, we finally have the following equation

$$\langle S^2 \rangle = Z^{-1} M^{-2} (J^* \otimes J_{p'}) \| G_1 \| [\tilde{G}^{(2)}]^x \| G_n \| (J \otimes J_{Q'}) \quad (8)$$

Now we are able to calculate the mean-square radius of gyration of POM chains by way of Eq. (8).

2. POE chains

Every structural unit of polyoxyethylene (POE) embraces three bonds which are specified as bonds a, b and c, respectively. The constitution of POE is as follows:



which consists of x monomeric unit or $n = 3x + 2$ skeletal bonds. Let

$$\tilde{G}^{(3)} = \tilde{G}_a \tilde{G}_b \tilde{G}_c \quad (9)$$

where $\tilde{G}_a$, $\tilde{G}_b$ and $\tilde{G}_c$ are defined in the same manner as in Eq. (5), and obtained by substituting the pertinent parameters of bonds a, b and c of the structural unit of POE into Eq. (5), respectively, then we get:

$$\langle S^2 \rangle = Z^{-1} M^{-2} (J^* \otimes J_{P'}) \|G_1\| [\tilde{G}^{(3)}]^x \|G_n\| (J \otimes J_{Q'}) \quad (10)$$

This is the improved expression of mean-square radius of gyration of polyethylene oxide.

3. POM_3 chains

The constitution of poly(trimethylene oxide) (POM_3) reads:



which consists of $n = 4x + 2$ skeletal bonds. Every monomeric unit of POM_3 embraces four bonds which are symbolized by a, b, c and d, respectively. Putting

$$\tilde{G}^{(4)} = \tilde{G}_a \tilde{G}_b \tilde{G}_c \tilde{G}_d \quad (11)$$

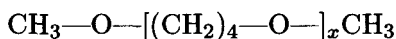
then the mean-square radius of gyration of POM_3 can be deduced as follows

$$\langle S^2 \rangle = Z^{-1} M^{-2} (J^* \otimes J_{P'}) \|G_1\| [\tilde{G}^{(4)}]^x \|G_n\| (J \otimes J_{Q'}) \quad (12)$$

It is easy to calculate the value of $\langle S^2 \rangle$ for poly(trimethylene oxide) chains in terms of Eq. (12).

4. POM_4 chains

The repeated unit of poly(tetramethylene oxide) (POM_4 , polytetrahydrofuran) consists of five skeletal bonds, which are specified as bonds a, b, c, d and e, respectively. The constitution of a polytetrahydrofuran chain can be illustrated by:



There are $n = 5x + 2$ skeletal bonds in the POM_4 chain.

Let

$$\tilde{G}^{(5)} = \tilde{G}_a \tilde{G}_b \tilde{G}_c \tilde{G}_d \tilde{G}_e \quad (13)$$

the mean-square radius of gyration of polytetrahydrofuran can be expressed by:

$$\langle S^2 \rangle = Z^{-1} M^{-2} (J^* \otimes J_{P'}) \|G_1\| [\tilde{G}^{(5)}]^x \|G_n\| (J \otimes J_{Q'}) \quad (14)$$

Comparing Eqs. (8), (10), (12) and (14) with one another, we can find the general expression of mean-square radius of gyration for polyalkyleneoxides:

$$\langle S^2 \rangle = Z^{-1} M^{-2} (J^* \otimes J_{P'}) \|G_1\| [\tilde{G}^{(y+1)}]^x \|G_n\| (J \otimes J_{Q'}) \quad (15)$$

where y is the number of methylene groups within a repeated unit in the chain.

NUMERICAL CALCULATION

Using the parameters given in Table 1, we have numerically calculated the mean-square radius of gyration in terms of Eqs. (8), (10), (12) and (14) for the polyalkyleneoxides aforementioned with $x = 1000$ at specified temperature as printed in the Table 2. The characteristic ratios of the mean-square end-to-end distance ($\langle r^2 \rangle / nl^2$) and the mean-square radius of gyration ($\langle S^2 \rangle / nl^2$) are listed in Table 2, respectively. Furthermore, it can be obtained that:

$$\langle r^2 \rangle / \langle S^2 \rangle \approx 6 \quad (16)$$

This result is in fair agreement with the relationship obtained from freely jointed chain model^[1].

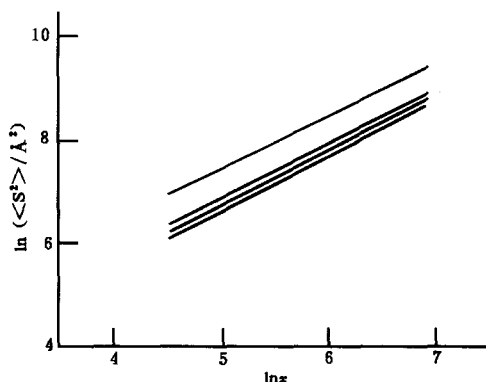


Fig. 2 Logarithmic relation between mean-square radius of gyration and the degree of polymerization, from the upper line to the lower one: POM₄, POM₃, POM and POE

By analogy to the previous conclusion for monosubstituted vinyl polymers^[5], poly-1, 1-disubstituted ethylenes^[6] and poly-1, 4-dienes^[7], the logarithmic relation between $\langle S^2 \rangle$ and chain length becomes linear when $x > 100$ (refer to Fig. 2). Therefore the dependence of $\langle S^2 \rangle$ on molecular weight can still be expressed by the general formula:

$$\langle S^2 \rangle = aM^b \quad (17)$$

The values of constants a and b are given in Table 3. That the values of b approach 1 indicates that, analogous to vinyl polymers^[5,6] and 1, 4-polydienes^[7], the mean-square radius of gyration is approximately proportional to the molecular weight. This relationship has been experimentally verified for polypropylene^[16], polystyrene^[17,18] etc. However, the experimental report for $\langle S^2 \rangle$ of polyalkyleneoxides is less available in the literatures.

Table 2 Characteristic ratios $\langle r^2 \rangle / nl^2$ and $\langle S^2 \rangle / nl^2$ of various polyalkyleneoxides with 1000 units

Polymer	$\langle r^2 \rangle / nl^2$	$\langle S^2 \rangle / nl^2$	T (K)	$\langle r^2 \rangle / \langle S^2 \rangle$
POM	9.28	1.53	298	6.07
POE	5.04	0.84	303	6.00
POM ₃	4.34	0.72	303	6.03
POM ₄	6.09	1.01	303	6.03

Table 3 Values of constants a and b in Eq. (17)

Polymer	a	b	T (K)
POM	0.1450	1.0344	298
POE	0.1148	1.0062	303
POM ₃	0.1031	1.0054	303
POM ₄	0.1468	1.0058	303

Keywords:

Radius of gyration; Polyalkyleneoxide; Matrix algebra; Unperturbed dimension

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