

CONFIGURATION-DEPENDENT PROPERTIES OF POLY(DIMETHYLSILOXANE) CHAIN*

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Abstract The intermolecular rotational potential energies for poly(dimethylsiloxane) (PDMS) chains are directly obtained from *a priori* probability $P_{\alpha\beta}$. Here the differing statistical weight matrices for the Si—O and O—Si bonds are considered in calculating the configuration partition function. In the Bahar's model, as the same statistical weight matrices for the Si—O and O—Si bonds are adopted, there exists a large deviation of *a priori* probability $P_{\alpha\beta}$ between the theory and the molecular dynamics (MD) simulation. Our model gives satisfactory agreement with experiment on the mean-square unperturbed end-to-end distance, the mean-square dipole moment and its temperature dependence, and the molar cyclization equilibrium constants for dimethylsiloxane oligomers. This new rotational isomeric state approach can be widely applied to other chains, such as $-\text{CH}_2-\text{C}[(\text{CH}_2)_m\text{H}]_2-$ and $-\text{O}-\text{Si}[(\text{CH}_2)_m\text{H}]_2$ for arbitrary m .

Keywords Poly(dimethylsiloxane), Configuration property, A priori probability

INTRODUCTION

Inorganic polymers are becoming an increasingly important area in polymer science and technology. Among the most important classes of these polymers are the polysiloxanes, made of alternating silicon and oxygen atoms. These polymers are noted for their stability at temperatures of 150°C or higher. Silicone polymers are used in a variety of commercial applications including lubricants, defoamers, grease, resins, and elastomers^[1]. Poly(dimethylsiloxane) (PDMS) is one of the most useful silicone elastomers used as gaskets, seals wire, cable insulation, surgical and prosthetic devices^[2]. Poly(dimethylsiloxane) has some unique configurational properties due to the difference in bond angles Si—O—Si and O—Si—O. The resulting configurational statistics of PDMS chains have been widely studied by many investigators for many years^[3-13]. The most widely used approach for the calculation of average statistical properties is based upon the rotational isomeric state (RIS) theory^[3-13]. The rotational isomeric state model of PDMS was first set up by Flory, Crescenzi, and Mark (FCM)^[4], and their model satisfactorily reproduces the experimentally observed unperturbed mean-square end-to-end distance $\langle R^2 \rangle$ and its temperature coefficient $\text{dln}\langle R^2 \rangle/\text{d}T$. The FCM model also gives a reasonable account of the experimentally measured mean-square dipole moments $\langle \mu^2 \rangle$. However, a serious disagreement is present between the experimentally observed^[14] cyclization equilibrium constants for oligomers of PDMS and the predictions of the FCM model^[15]. The cyclization equilibrium constants K_x measured for the oligomers with $x = 4-6$ repeat units turn out to be about 4 orders of magnitude higher than those

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computed based on the complete enumeration of the cyclic conformations of the FCM model. Recently, Bahar *et al.*^[12, 13] developed a new rotational state approach to study the configurational statistics of PDMS. The classical method for the formulation of matrix U of the configurational partition function Z for chains with pair-wise interdependent bonds is based on the analysis of conformational energy surface, computed as a function of ϕ_{i-1} and ϕ_i for the fragment of the chain composed of bonds $i-2$, $i-1$, i , and $i+1$ ^[16]. In the new approach we will instead formulate U using the detailed description of the P_η and $P_{\xi\eta}$ that is contained in a molecular dynamics trajectory^[12]. However, we noticed that the energy parameters calculated from the probability distribution for PDMS are *unreasonable*. Since the difference in the bond angles Si—O—Si (143°) and O—Si—O (110°) is large enough, their respective statistical weight matrices should be different. However, in Bahar's model^[12, 13], since the different statistical matrices for the Si—O and O—Si bonds are regarded as the same, their calculations are obviously wrong. This negligence leads to the result that the energy parameters calculated directly from probability distribution are wrong and cannot be used in the calculation of unperturbed chain dimensions, the mean-square dipole moment and its temperature dependence, and the molar cyclization equilibrium constants. Finally, in their model new energy parameters have to be adopted at random. However, we found that in Bahar's model some probabilities calculated by using their energy parameters are different from the probability distributions obtained from the molecular dynamics (MD) trajectory, and the maximum deviations are 106.4% and 70.4%, respectively. We think that the same statistical weight matrices for (Si—O, O—Si) and (O—Si, Si—O) bonds lead to a wrong result in their model. In this paper, the *differing* statistical weight matrices are considered in calculating the partition function of PDMS chain. The energy parameters are obtained through solving several equations. We find our model yields satisfactory results. Section 2 gives our model. Results are presented in sec. 3.

STATISTICAL THEORY

Statistical Weight Matrices

In the rotational isomeric state model of PDMS, the conformation partition function is formulated as a serial product of statistical weight matrices. On the basis of the probability distribution curves resulting from molecular dynamics simulation, two statistical weight matrices of the form

$$U_a = \begin{bmatrix} \tau_a & \sigma & \sigma \\ 1 & \sigma\psi_a & \sigma\omega_a \\ 1 & \sigma\omega_a & \sigma\psi_a \end{bmatrix} \quad (1)$$

and

$$U_b = \begin{bmatrix} \tau_b & \sigma & \sigma \\ 1 & \sigma\psi_b & \sigma\omega_b \\ 1 & \sigma\omega_b & \sigma\psi_b \end{bmatrix} \quad (2)$$

are adopted for the pair of bonds (O—Si, Si—O) and (Si—O, O—Si), respectively^[12]. Where the statistical weights may be represented as Boltzmann factors in the energy E of the associated conformations:

$$\begin{aligned} \sigma &= \exp(-E_\sigma / RT), & \tau_a &= \exp(-E_{\tau,a} / RT), \\ \tau_b &= \exp(-E_{\tau,b} / RT), & \omega_a &= \exp(-E_{\omega,a} / RT) \\ \omega_b &= \exp(-E_{\omega,b} / RT), & \psi_a &= \exp(-E_{\psi,a} / RT), & \psi_b &= \exp(-E_{\psi,b} / RT) \end{aligned} \quad (3)$$

Here E_σ is the first-order interaction energy of gauche bonds relative to *trans* bonds. The energies for the second-order interactions for tt, g^+g^+ , and g^+g^- are denoted by E_τ (E_τ), E_ψ (E_ψ), and E_ω (E_ω), respectively. Here R is Boltzmann constant, and T is the absolute temperature. Serial

multiplication of statistical weight matrices yields the configurational partition function, $Z^{[16]}$,

$$Z = U_1 (U_a U_b)^{(x-1)} U_n \quad (4)$$

where

$$U_1 = (1 \ 0 \ 0), \quad U_n = (1 \ 1 \ 1)^T \quad (5)$$

and x is the number of monomer units ($x = n/2$, n is the number of bond). In the limit of $n \rightarrow \infty$, the partition function can be written as

$$Z = (\text{constant}) \lambda_1^{x-2} \quad (6)$$

where λ_1 is the largest eigenvalue of the matrix $(U_a \ U_b)$, and λ_1 is:

$$\lambda_1 = (1/2) \{ \tau_a \tau_b + \sigma [4 + \sigma (\psi_a + \omega_a) (\psi_b + \omega_b)] + [(\tau_a \tau_b - \sigma^2 (\psi_a + \omega_a) (\psi_b + \omega_b))^2 + 8\sigma (\tau_a + \sigma (\psi_b + \omega_b)) (\tau_b + \sigma (\psi_a + \omega_a))]^{1/2} \} \quad (7)$$

Application of the standard partial derivatives yields^[16]:

$$P_{g^+} = P_{g^-} = (1/2) P_g = (1/4) (\partial \ln \lambda_1 / \partial \ln \sigma) \quad (8)$$

$$P_{tt, a} = \partial \ln \lambda_1 / \partial \ln \tau_a \quad (9)$$

$$P_{tt, b} = \partial \ln \lambda_1 / \partial \ln \tau_b \quad (10)$$

$$P_{g^+g^+, a} = P_{g^+g^-, a} = (1/2) \partial \ln \lambda_1 / \partial \ln \psi_a \quad (11)$$

$$P_{g^+g^+, b} = P_{g^+g^-, b} = (1/2) \partial \ln \lambda_1 / \partial \ln \psi_b \quad (12)$$

$$P_{g^+g^-, a} = P_{g^+g^+, a} = (1/2) \partial \ln \lambda_1 / \partial \ln \omega_a \quad (13)$$

$$P_{g^+g^-, b} = P_{g^+g^+, b} = (1/2) \partial \ln \lambda_1 / \partial \ln \omega_b \quad (14)$$

and leads ultimately to:

$$\begin{aligned} P_{g^+} = P_{g^-} = & (\sigma/8\lambda_1) \{ 4 + 2\sigma (\psi_a + \omega_a) (\psi_b + \omega_b) + [8\tau_a \tau_b + 16\sigma (\psi_b + \omega_b) \\ & (\tau_b + \sigma (\psi_a + \omega_a)) + 16\sigma (\psi_a + \omega_a) (\tau_a + \sigma (\psi_b + \omega_b)) \\ & + 24\sigma^2 (\psi_a + \omega_a) (\psi_b + \omega_b) - 4\sigma (\psi_a + \omega_a) (\psi_b + \omega_b) \\ & ((\tau_a \tau_b - \sigma^2 (\psi_a + \omega_a) (\psi_b + \omega_b))]/(2A^{1/2}) \} \end{aligned} \quad (15)$$

$$P_{tt, a} = (\tau_a/2\lambda_1) \{ \tau_b + [8\sigma (\tau_b + \sigma (\psi_a + \omega_a)) + 2\tau_b (\tau_a \tau_b - \sigma^2 (\psi_a + \omega_a) (\psi_b + \omega_b))]/(2A^{1/2}) \} \quad (16)$$

$$P_{tt, b} = (\tau_b/2\lambda_1) \{ \tau_a + [8\sigma (\tau_a + \sigma (\psi_b + \omega_b)) + 2\tau_a (\tau_a \tau_b - \sigma^2 (\psi_a + \omega_a) (\psi_b + \omega_b))]/(2A^{1/2}) \} \quad (17)$$

$$\begin{aligned} P_{g^+g^-, a} = & (\psi_a/4\lambda_1) \{ \sigma^2 (\psi_a + \omega_a) + [8\sigma^2 (\tau_a + \sigma (\psi_a + \omega_a)) - 2\sigma^2 (\psi_a + \omega_a) (\tau_a \tau_b - \sigma^2 (\psi_a + \omega_a) \\ & (\psi_b + \omega_b))]/(2A^{1/2}) \} \end{aligned} \quad (18)$$

$$\begin{aligned} P_{g^+g^-, b} = & (\psi_b/4\lambda_1) \{ \sigma^2 (\psi_a + \omega_a) + [8\sigma^2 (\tau_b + \sigma (\psi_a + \omega_a)) - 2\sigma^2 (\psi_a + \omega_a) (\tau_a \tau_b - \sigma^2 (\psi_a + \omega_a) \\ & (\psi_b + \omega_b))]/(2A^{1/2}) \} \end{aligned} \quad (19)$$

$$P_{g^+g^-, a} = (\omega_a/\psi_a) P_{g^+g^+, a} \quad (20)$$

$$P_{g^+g^-, b} = (\omega_b/\psi_b) P_{g^+g^+, b} \quad (21)$$

where

$$A = (\tau_a \tau_b - \sigma^2 (\psi_a + \omega_a) (\psi_b + \omega_b))^2 + 8\sigma (\tau_a + \sigma (\psi_b + \omega_b)) (\tau_b + \sigma (\psi_a + \omega_a)) \quad (22)$$

The probability distributions P_{τ} , $P_{\xi\eta, a}$ and $P_{\xi\eta, b}$ can be obtained by molecular dynamics simulation^[12]. Thus, in theory, the statistical weight factors σ , τ_a (or τ_b), ψ_a (or ψ_b), and ω_a (or ω_b) can be directly deduced from Eqs. (15)~(22) as the number of the coupled equations is the same as the number of the unknown parameters. However, as the coupled equations are more complicated, it is difficult to exactly solve the equations. Here the unknown statistical weight factors σ , τ_a (or τ_b), ψ_a (or ψ_b), and ω_a (or ω_b) can be solved by an iterative procedure.

Chain Dimension

The mean-square end-to-end distance (or the mean-square dipole moment) may be calculated by serial multiplication of generator supermatrices as^[14, 16]:

$$\langle f^2 \rangle = 2 Z^{-1} g^* (G_A G_B)^{x-1} g \quad (23)$$

where

$$g^* = (1 \ 0 \ 0 \ \dots), \quad g = (1 \ 1 \ 1 \ 1 \ 1 \ 1 \ 1 \ 1 \ 1 \ 1 \ 1 \ 1 \ 1 \ 1 \ 1 \ 1)^T$$

and

$$G_i = \begin{bmatrix} U_i & (U_i \otimes f^T) \|T\| & (f^2/2)U_i \\ 0 & (U_i \otimes E_3) & U_i \otimes f \\ 0 & 0 & U_i \end{bmatrix} \quad i = a \text{ or } b \quad (24)$$

where f is the bond vector l (or the bond dipole moment m). For PDMS chain,

$$l = l_0 (1 \ 0 \ 0)^T, \quad l_0 = 0.163 \text{ nm} \quad (25)$$

and

$$m = m_0 (1 \ 0 \ 0)^T, \quad m_0 (\text{Si}-\text{O}) = -m_0 (\text{O}-\text{Si}) = 0.60\text{D} = \mu_0 \quad (26)$$

Cyclization Equilibrium

The Jacobson and Stockmayer^[17, 18] theory states that the molar cyclization equilibrium constant K_x for the ring-chain equilibrates is directly proportional to the concentration of cyclic compounds. In the limit of high extents of reaction, K_x is given by:

$$K_x = W_x / 2N_A x \quad (27)$$

where W_x represents the density of end-to-end vector r in the region $r \cong 0$ (in mol dm^{-3}) for an x -meric chain, and N_A is the Avogadro constant. W_x is given by

$$W_x = ((4/3) \pi r^3 Z_r / Z_c) \quad (28)$$

Z_r is the sum of statistical weights for all chain conformations with terminal atoms separated by less than or as much as r nm. For the particular case of cyclic dimethylsiloxanes of the form $[(\text{CH}_3)_2\text{SiO}]_x$, the partition function Z_c in Eq. (28) reads:

$$Z_c = U_1 (U_a U_b)^{x-2} U_a U_n \quad (29)$$

which differs from Eq. (4) due to the lack of the terminal (Si—O, O—Si) bond pair. The subscript c is appended to the partition function employed in the cyclization equilibrium to distinguish it from the one corresponding to the non-cyclic chain, Z .

RESULTS AND DISCUSSION

Statistical Matrices

In the FCM model^[4], molar cyclization equilibrium constants K_x for small cyclic dimethylsiloxane $[(\text{CH}_3)_2\text{SiO}]_x$ ($x = 4 \sim 6$) are calculated by the distances between the terminal silicon and oxygen atoms of the corresponding open chain molecules $[(\text{CH}_3)_2\text{SiO}]_x$ in all 3^{2x-3} conformations, and the results are that $\log K_x$ with $x = 4 \sim 6$ and $r = 0.3$ nm, are -4.04 , -3.73 , and -3.42 , respectively. However, the experimental results are -0.744 , -1.02 , and -1.49 , respectively, which are about 4 orders of magnitude higher than complete enumeration of the cyclic conformations of the FCM model. As the molar cyclization equilibrium constant is the important statistical property for PDMS chain, therefore, the FCM model should be improved. Recently, Bahar *et al.*^[12, 13] developed a new approach. In their model of PDMS chain, the statistical weight matrices are directly deduced from probability distribution obtained from molecular dynamics trajectories. However, their neglect of differing statistical weight matrices for the pair of bonds (O—Si, Si—O) and (Si—O, O—Si) leads to unsuccessful results, and they have to choose at random another set of seven statistical weight factors. Therefore, their energy parameters lead to the large deviations for *a priori* probability. A

modified method should be considered in the calculation of energy parameters.

At first, we calculate *a priori* probability $P_{\alpha\beta}$ by using molecular dynamics simulation, which is similar to Bahar's model^[12] The conjugate gradient energy minimization scheme and the Sybyl force field from Tripos were used. Additional parameters for the silicon atom are adapted from the work of Frierson^[13]. The results are:

$$\begin{aligned} P_{g^+}^{MD} &= 0.294, & P_{tt,a}^{MD} &= 0.115, & P_{tt,b}^{MD} &= 0.115, & P_{g^+g^+,a}^{MD} &= 0.090, \\ P_{g^+g^+,b}^{MD} &= 0.086, & P_{g^+g^-,a}^{MD} &= 0.051; & P_{g^+g^-,b}^{MD} &= 0.078 \end{aligned} \quad (30)$$

which is the same as Bahar's model^[12].

In order to find the statistical weight factors σ , τ_a (or τ_b), ψ_a (or ψ_b), and ω_a , (or ω_b) which fit Eqs. (15)~(22), we adapt an iterative procedure here. The procedure is as follows. We first introduce a new function:

$$\begin{aligned} F(X) &= (P_{g^+} - 0.294)^2 + (P_{tt,a} - 0.115)^2 + (P_{tt,b} - 0.167)^2 + (P_{g^+g^+,a} - 0.090)^2 + (P_{g^+g^+,b} - 0.086)^2 + \\ & (P_{g^+g^-,a} - 0.051)^2 + (P_{g^+g^-,b} - 0.078)^2 \equiv \sum_{i=1}^7 f_i^2(X) \end{aligned} \quad (31)$$

where the vector:

$$\begin{aligned} X &\equiv (x_1 \ x_2 \ x_3 \ x_4 \ x_5 \ x_6 \ x_7)^T \equiv (\sigma \ \tau_a \ \tau_b \ \psi_a \ \psi_b \ \omega_a \ \omega_b)^T \\ f_1(X) &= P_{g^+} - 0.294, \quad f_2(X) = P_{tt,a} - 0.115, \quad f_3(X) = P_{tt,b} - 0.167, \\ f_4(X) &= P_{g^+g^+,a} - 0.090, \quad f_5(X) = P_{g^+g^+,b} - 0.086, \\ f_6(X) &= P_{g^+g^-,a} - 0.051, \quad f_7(X) = P_{g^+g^-,b} - 0.078 \end{aligned} \quad (32)$$

and P_{g^+} , $P_{tt,a}$, $P_{tt,b}$, $P_{g^+g^+,a}$, $P_{g^+g^+,b}$, $P_{g^+g^-,a}$, $P_{g^+g^-,b}$ are defined by Eqs. (15)~(22). Therefore, to solve Eqs. (15)~(22) we need to find a vector X , which fits $F(X) = \min$. Here Newton's method is used^[19]. The calculation is as follows. We indicate the initial estimate by $X^{(1)}$ and the k th solution by $X^{(k)}$. The $(k+1)$ th solution follows from:

$$X^{(k+1)} = X^{(k)} - [G^{(k)T} G^{(k)}]^{-1} G^{(k)T} f^{(k)} \quad (33)$$

where $X^{(k)}$ is a vector, $f^{(k)}$ is a vector whose i th component is f_i , and the matrix $G^{(k)}$ is the Hessian^[19], with elements $G_{ij}^{(k)} = \partial f_i / \partial x_j$. In order to avoid the complex differentiation, which is necessary to find $G_{ij}^{(k)}$, differences were used for the derivatives: $G_{ij}^{(k)} \cong \Delta f_i / \Delta x_j$. After a long time, a reasonable vector X can be found. Our results are given in Table 1, in which the energy parameters of column 2 are given by Bahar *et al.*^[12] using the *same* statistical weight matrices for U_a and U_b in their calculation. Those of column 4 are also given by Bahar *et al.*^[13], which are determined only by comparing the theoretical results of $\langle R^2 \rangle$, $\langle \mu^2 \rangle$, and K_x against statistical weight factors. The energy parameters of the FCM model are also shown in Table 1. Our results

Table 1 Energy parameters (kcal/mol)

Parameter, α	Energy $E_{\alpha}^{a)}$	$E_{\alpha}^{b)}$	$E_{\alpha}^{c)}$	$E_{\alpha}^{d)}$
σ	0.20	0.85	0.30	1.32
τ_a	0.37	0.00	0.35	1.02
τ_b	0.02	0.00	-0.10	0.93
ω_a	0.45	∞	0.60	0.31
ω_b	0.04	1.05	0.35	-0.14
ψ_a	0.12	0.00	0.25	-0.03
ψ_b	0.06	0.00	0.20	-0.20

a) from molecular dynamics analysis of ref 12; b) from the FCM model;

c) from the Bahar's model of Ref. [13]; d) present work

are those in column 5. In order to investigate the rationality of our energy parameters, we calculate *a priori* probabilities, and the results are given in Table 2. In Table 2, *a priori* probabilities calculated by using Bahar’s model have large deviation from the probabilities obtained from molecular dynamics simulations. For example, the largest deviations for Bahar’s model are 106.4% ($P_{g^+g^+,b}$) and 70.4% ($P_{tt,a}$) respectively. Most of the deviations are greater than 10%. From Table 2, we know that our results are reasonable, and the deviations are less than 6%.

Table 2 *A priori* probability $P_{\alpha\beta a}$ or $P_{\alpha\beta b}$

$\alpha\beta$, a or b	$P_{\alpha\beta}^{a)}$	$P_{\alpha\beta}^{b)}$		$P_{\alpha\beta}^{c)}$		$P_{\alpha\beta}^{d)}$	
		Calculation	Deviation	Calculation	Deviation	Calculation	Deviation
g^+ or g^-	0.294	0.284	-3.4%	0.239	-18.7%	0.277	-5.8%
tt, a	0.115	0.124	7.8%	0.196	70.4%	0.121	5.2%
tt, b	0.167	0.175	4.8%	0.258	54.5%	0.160	-4.2%
g^+g^+ , a	0.090	0.131	45.6%	0.077	-14.4%	0.086	-4.4%
g^+g^+ , b	0.086	0.156	81.4%	0.108	25.6%	0.090	4.7%
g^+g^- , a	0.051	0.075	45.1%	0.043	-15.6%	0.049	-3.9%
g^+g^- , b	0.078	0.161	106.4%	0.085	9.0%	0.081	3.8%

a) from molecular dynamics simulation; b) calculated by using statistical weight factors of column 2 of Ref [13]; c) calculated by using statistical weight factors of column 4 of ref 13; d) our results.

Unperturbed Chain Dimension and Mean-Square Dipole Moments

Figure 1 displays the characteristic ratio of the mean-square end-to-end distance $C_n = \langle R^2 \rangle / nl^2$ versus n ($n = 2x$) at $T = 343K$. For small n , the characteristic ratio C_n is less insignificant than that calculated by the FCM model. For large n , the curve is almost indistinguishable from those reported by Flory and Semlyen^[15], using the FCM model. The asymptotic limit $C_\infty = 6.45$. We also calculate the temperature coefficient $d\ln\langle R^2 \rangle / dT$ of mean-square of end-to-end distance, and yield a negative temperature coefficient. The value is about $-8.5 \times 10^{-4} \text{ deg}^{-1}$. Neglect of the higher order interactions may be important for $d\ln\langle R^2 \rangle / dT$ if they are strongly dependent on temperature^[12, 13].

We also calculate the mean-square dipole moments and its temperature dependence. The dipole ratio is

$$D_n = \langle \mu^2 \rangle / n\mu_0^2 \tag{34}$$

where μ_0 is the dipole of a Si—O bond (or O—Si bond) . The results are given in Figs. 2 and 3. In Fig. 2, the dots (●) represent experimental results measured by Sutton and Mark^[20] at $T = 303 \text{ K}$.

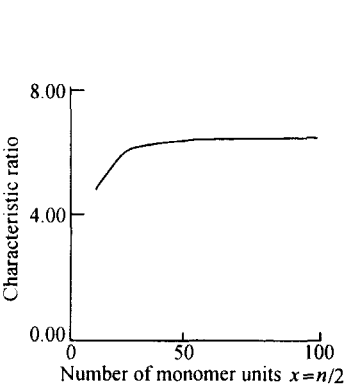


Fig. 1 Dependence of characteristic ratio C_n on $x = n/2$ at $T = 343 \text{ K}$

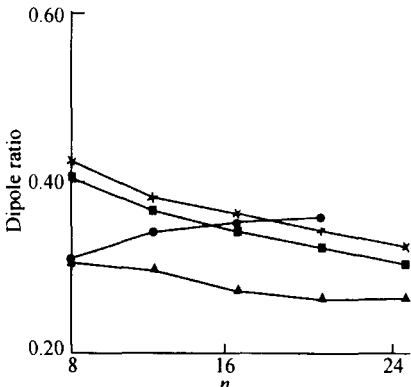


Fig. 2 Dependence of the dipole ratio D_n on n at $T = 303 \text{ K}$
(+) Bahar *et al.*^[13], (▲) FCM model^[4], (●) the experimental data and (■) the present model

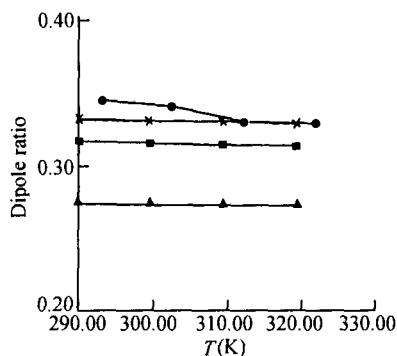


Fig. 3 Temperature dependence of D_n for $n = 20$ (+) Bahar *et al.*^[13]; ($\blacktriangle$) FCM model^[4]; ($\bullet$) the experimental data and ($\blacksquare$) the present model

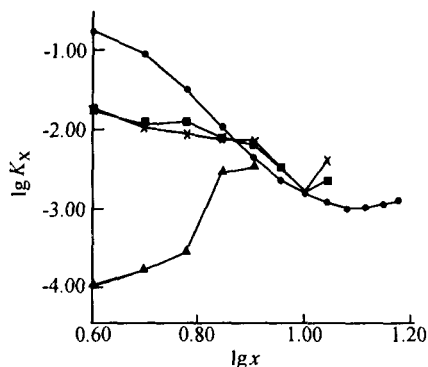


Fig. 4 Molar cyclization equilibrium constants K_x for cyclic dimethylsiloxane $((\text{CH}_3)_2\text{SiO})_x$ at $T = 383\text{ K}$ (+) Bahar *et al.*^[13]; ($\blacktriangle$) FCM model^[4]; ($\bullet$) the experimental data and ($\blacksquare$) the present model

The dots (+) and ($\blacktriangle$) are theoretically obtained by using Bahar's model^[12, 13] and the FCM model^[4], respectively. The present theoretical ($\blacksquare$) yields a reasonable result. Temperature dependence of D_n for $n = 20$ is also given in Fig. 3. Our values are greater than those using the FCM model, and less than the theoretical results reported by Bahar *et al.*^[12, 13].

Cyclization equilibrium

Cyclization equilibrium constant K_x is an important statistical parameter for PDMS chain. The experimental data was first obtained by Brown and Slusarczuk^[14] in an equilibrium condition in toluene solution at $T = 383\text{ K}$, see Fig. 4. Theoretical results are given by Eq. (27) using a rigorous procedure based on the complete enumeration and weighting of all cyclic conformers contributing to Z_c . However, previous studies indicate that a larger deviation exists for shorter oligomers. Fig. 4 shows dependence K_x with x under different model. The dots ($\blacktriangle$) are found from the complete enumeration of cyclic oligomers weighted according to the FCM model. Those results are obtained by adopting $r = 0.3\text{ nm}$ as the critical separation between chain ends to form a cyclic structure. The dots ($\blacksquare$) and (+) represent results according to our model and the Bahar model. In general, our results agree well with the experimental data. In particular, our data is more closer to experimental data than the Bahar model for $x = 11$. Here $r = 0.125\text{ nm}$.

Our model could be widely applied to investigate the statistical properties of chains with alternating chain atoms, such as polyoxymethylene, polysilane, polydimethylsilane, and polyphosphate, or those polymers in the form of $(\text{ABC})_x$. This model could also be applied to three-order interaction, or higher-order interaction. This investigation is in progress.

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