Effect of Terminal Bond on Configurational Statistics of Poly(dimethylsiloxane)

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ABSTRACT: A modified FCM (Flory, Crescenzi, and Mark) model is developed to study the configurational statistics of poly(dimethylsiloxane) (PDMS) chain. In the model, the theoretical molar cyclization equilibrium constants K_x for small dimethylsiloxane ring are in agreement with the experimental data, and the theoretical characteristic ratio $C_n = \langle R^2 \rangle / nl^2$ and its temperature coefficient for long ring are close to the experimental results.

KEY WORDS   Configurational Statistics / Poly(dimethylsiloxane) Chain / Rotational Isomeric State Model /

Silicone polymers are used in a variety of commercial applications including lubricants, defoamers, greases, resins, and elastomers.[1] Poly(dimethylsiloxane) (PDMS) is one of the most important silicone elastomers. PDMS has some unique configurational properties due to differing bond angles Si–O–Si and O–Si–O. The resulting configurational statistics of PDMS chains have been widely studied by many investigators. The most widely used approach for calculations of average statistical properties is based upon the rotational isomeric state (RIS) theory.[2-8] The rotational isomeric state model of PDMS was set up by Flory, Crescenzi, and Mark (FCM), and their model satisfactorily reproduces the experimentally observed unperturbed mean-square end-to-end distance $\langle R^2 \rangle$ and its temperature coefficient $d \ln \langle R^2 \rangle / dT$. The FCM model also gives a reasonable account of the experimentally measured mean-square dipole moments $\langle \mu^2 \rangle$. The molar cyclization equilibrium constants K_x of PDMS were first calculated by Flory and Semlyen.[9] However, a serious disagreement is present between experimentally observed[10] cyclization probabilities for oligomers of PDMS and predictions of the FCM model. The cyclization equilibrium constants K_x measured for the oligomers with $x = 4$—6 repeat unit turn out to be about 4 orders of magnitude higher than those computed based on the complete enumeration of the cyclic condormations of the FCM model. Recently, Bahar *et al.*[8] developed a new rotational isomeric state approach to study the configurational statistics of PDMS. This model yields satisfactory agreement with experiments on mean-square unperturbed end-to-end distance, mean-square dipole moment and molar cyclization equilibrium constants K_x ($x = 4$—11) for dimethylsiloxane oligomers. But it cannot account for the positive temperature coefficient of the unperturbed chain dimensions. We notice that this model is only used to calculate the mean-square unperturbed end-to-end distance and its temperature coefficient for infinite chains because eq 12—15 of ref 8 are obtained in the limit of $n \to \infty$. However, their approach yields a negative temperature coefficient of about $-2.34 \times 10^{-4} \deg^{-1}$ for the infinite chains. If the molar cyclization equilibrium constants K_x with $x = 4$—11 ($n = 2x$) are

calculated using the statistical weight factors $\sigma, \omega, \omega', \tau,$ and τ' defined by eq 12—15 of ref 8, this may be a wrong, because eq 12—15 are obtained from eq 6—11 in the limit of $n \to \infty$. In this paper, a modified FCM model is developed to investigated the configurational statistics of PDMS.

MODEL

In the modified FCM rotational isomeric state model of PDMS, each skeletal bond is assigned to either a trans ($\phi = 0$), gauche$^+$ ($\phi = 120°$) or gauche$^-$ ($\phi = 240°$) state and mutual interdependence of adjacent pairs of bond rotational states is taken into account by means of two statistical weight matrices U_{ia} and U_{ib}. The matrix U_{ia} applies to rotational about pairs of bonds centred on oxygen atoms and the matrix U_{ib} applies to rotational states about pairs of bonds centred on silicon atoms, thus,

$$U_{ia} = \begin{bmatrix} 1 & \sigma_i & \sigma_i \\ 1 & \sigma_i & \sigma_i \omega_i \\ 1 & \sigma_i \omega_i & \sigma_i \end{bmatrix}$$

$$U_{ib} = \begin{bmatrix} 1 & \sigma_i & \sigma_i \\ 1 & \sigma_i & \sigma_i \omega'_i \\ 1 & \sigma_i \omega'_i & \sigma_i \end{bmatrix} \quad (1)$$

The configuration partition function of PDMS is given by

$$Z = (1 \quad 0 \quad 0) \prod_{i=1}^{x-1} (U_{ia} U_{ib}) \begin{bmatrix} 1 \\ 1 \\ 1 \end{bmatrix} \quad (2)$$

and the mean-square end-to-end distance (or the mean-square dipole moment) may be calculated by serial multiplication of generator supermatrices as[10,11]

$$\langle f^2 \rangle = 2Z^{-1} g^* \prod_{i=1}^{x-1} (\mathscr{G}_{ia} \cdot \mathscr{G}_{ib}) g \quad (3)$$

where $\vec{f}$ is the bond vector $\vec{l}$ (or the bond dipole moment $\vec{m}$). For PDMS chain,

$$l = l_0 \begin{bmatrix} 1 \\ 0 \\ 0 \end{bmatrix}, \quad l_0 = 1.63 \text{ Å}$$

$$m = m_0 \begin{bmatrix} 1 \\ 0 \\ 0 \end{bmatrix}, \quad \begin{aligned} m_0(\text{Si–O}) &= -m_0(\text{O–Si}) \\ &= 0.60D = \mu_0 \end{aligned}$$

and

$$\theta_a = \angle \text{OSiO} = 70°, \quad \theta_b = \angle \text{SiOSi} = 37° \quad (4)$$

The Jacobson and Stockmayer theory[12,13] provides the following expression for the molar cyclization equilibrium constants K_x (in mol 1^{-3}) for cyclics produced as eq 5

$$K_x = \bar{W}_x / 2N_A x \quad (5)$$

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

$$\bar{W}_x = ((4/3)\pi r^3)^{-1} \cdot Z_r / Z \quad (6)$$

Z_r is the sum of statistical weights for all chain conformations with terminal atoms separated by less than or as much as r Å.

Molar cyclization equilibrium constants K_x for small cyclic dimethylsiloxane $((\text{CH}_3)_2\text{SiO})_x$ with $x = 4$—6 calculated using the FCM model are far lower than those found experimentally. Therefore, for a small dimethylsiloxane ring, it is necessary to take account of the mutual interdependence of bond rotational states further down the chain in the FCM model. The statistical weight parameters ω_i and ω'_i in our model are different from the FCM model for the small dimethylsiloxane ring. For a long ring, they are the same as the FCM model. The difference between the FCM model and our model is that, in the FCM, statistical weight factors are the same for long and small rings, and in our model, are different.

RESULTS AND DISCUSSION

Molar cyclization equilibrium constants K_x

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for small cyclic dimethylsiloxane $((CH_3)_2SiO)_x$ $(x=4—6)$ are calculated by computing distances between the terminal silicon and oxygen atoms of the corresponding open chain molecules $((CH_3)_2SiO)_x$ in all 3^{2x-3} conformations, and using the FCM model. The results are that $\log K_x$ with $x=4—6$ and $r=3$ Å 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 those computed by the complete enumeration of the cyclic conformations of the FCM model. Small cyclic dimethylsiloxane $((CH_3)_2SiO)_4$ $(x=4)$ with the following sequences of rotational states $tg^+g^-g^+g^-g^+$ and $tg^-g^+g^+g^-g^+g^-$ are separated by less than $r=1.25$ Å. If statistical weight factors ω_i and ω_i' are increased, the theoretical molar cyclization equilibrium constants K_x may be close to the experiment constants. For $x=6—8$, the theoretical molar cyclization equilibrium constants K_x are in agreement with the experimental data, and the statistical weight factors ω_i and ω_i' in our model are the same as in the FCM model. Table I lists the statistical weight factors deduced from the above considerations. Nonbonded interaction depends on distances of the atoms. Because of the differing bond angle Si–O–Si and O–Si–O, the interaction energy of the group consisting of atoms may be different for long and small rings. This leads to different matrices U_{ia} and U_{ib} for small i.

Figure 1 displays the characteristic ratio of the mean-square end-to-end distance $C_n=$ $\langle R^2 \rangle/nl^2$ vs. n $(n=2x)$. The curve is drown on the basis of the modified model for PDMS chains $CH_3(Si(CH_3)_2O)_xSi(CH_3)_2$ at $T=$ 343 K. For small n, the characteristic ratio C_n is less than that calculated by the FCM model. For large n, the difference is insignificant. For example, the characteristic ratio C_n of $n=600$ is 6.43, which is less than that using the FCM model by 0.2%. We also calculated the temperature coefficient $d\ln\langle R^2 \rangle/dT$. The experimental values range from 0.28×10^{-3} deg^{-1} to 0.78×10^{-3} deg^{-1}.[2,14,15] Figure 2 shows a plot of $\ln\langle R^2 \rangle$ vs. T for temperature ranging from 323 K to 363 K. The slope of
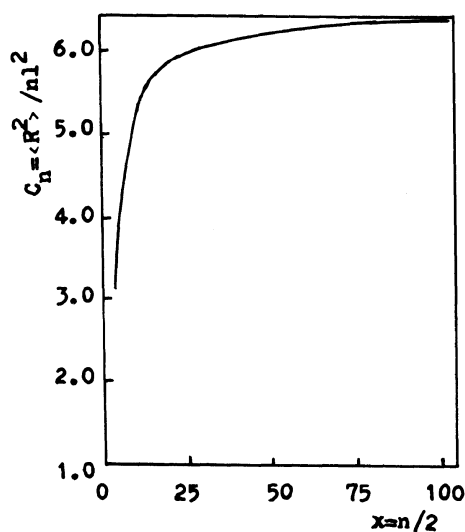

Figure 1. Dependence of $C_n=\langle R^2 \rangle/nl^2$ on $x=n/2$, at $T=343$ K.

Table I. Energy parameters (kcal mol^{-1})[a]

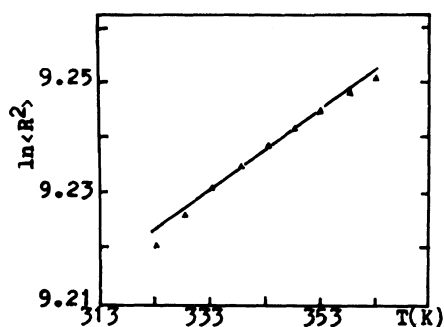| i	E_{ω_i}	$E_{\omega_i'}$
1	0.0	0.0
2	0.0	0.0
3	0.1	0.1
4	0.3	0.5
5	0.6	1.0
$\geqslant 6$	1.05	∞

[a] $E_{\sigma_i}=0.85$ (kcal mol^{-1}).

Figure 2. Plot of $\ln\langle R^2 \rangle$ vs. temperature for a PDMS chain 600 bonds in length.
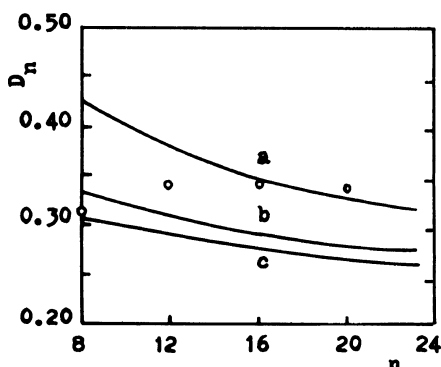
Figure 3. Dependence of D_n ($D_n = \langle\mu^2\rangle/n\mu_0^2$) on n at $T = 303$ K. The dots are the experimental results from Sutton and Mark.[16] a, Bahar et al.; b, this work; c, FCM model.
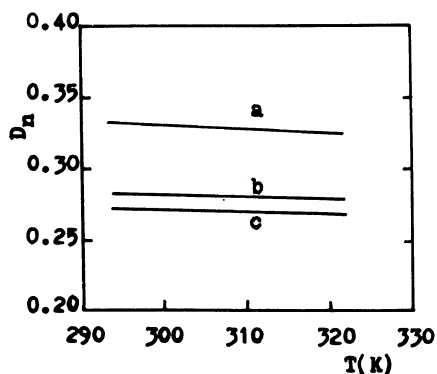

Figure 4. Plot of D_n vs. temperature for $n = 20$. a, Bahar et al.; b, this work; c, FCM model.

this line is the temperature coefficient and we obtain 0.71×10^{-3} deg^{-1} for a chain of length 600 bonds. It should be emphasized that we calculated a positive temperature coefficient, a very necessary condition for this molecule, since all experiments showed a positive number the because a positive temperature coefficient explains so many of the elastic and flexible properties of PDMS.

The dependence of D_n, $D_n = \langle\mu^2\rangle/n\mu_0^2$, (where $\langle\mu^2\rangle$ is the mean-square dipole moment, and μ is the dipole of a Si–O bond,) on the number n of skeletal bonds is shown in Figure 3. The dots represent experimental measurements by Sutton and Mark.[16] The line
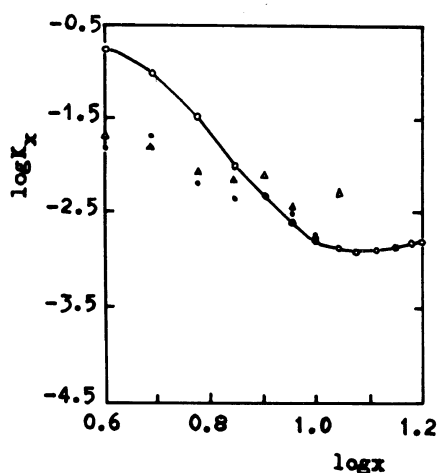

Figure 5. Theoretical molar cyclization equilibrium constants K_x for cyclic dimethylsiloxane at $T = 383$ K ($\bullet$) calculated by the direct computational method. The corresponding experimental values[11] are denoted as ($\bigcirc$), and the results from Bahar et al. are denoted as ($\triangle$).[8]

b was theoretically obtained using our model. The present theoretical yields a larger than that using the FCM model, and less than that of Bahar et al.[8] In Figure 4, temperature dependence of D_n for $n = 20$ is also given. Our values are greater than those using the FCM model, and less that the theoretical results reported by Bahar et al.[8]

Figure 5 displays the results of the molar cyclization equilibrium constants K_x from experiments (empty circles) by Brown and Slusarczuk[11] in an equilibrate in toluene solution at 383 K. The dashed circles follow from our model ($x = 4$—10), in agreement with experiments, and the results are calculated for $r = 1.25$ Å.

The differing bond angles O–Si–O and Si–O–Si may lead to difference in conformation between a long dimethylsiloxane ring and a small one. In the rotational isomeric state (RIS) model, statistical weight factors σ and ω are often obtained by comparing theoretical plots of C_n against σ (or ω) with experimental data.[10,17] In this paper, the energy parameters are determined by comparing theoretical K_x against ω and ω' with experimental data for

small x. Although the statistical weight matrices are obtained approximately, the configurational statistics of PDMS in our model agree with the experimental data.

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