Calculation of the Conformational Entropy of Polysilane[†]

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ABSTRACT: Exact enumeration method is used to calculate the conformational entropy of polysilane chain, submitted to short-range interaction and long-range interaction, with an off-lattice RIS model. The conformational entropy is in proportion to chain length at any temperature (from 50 K to 400 K). It varies with temperature, can be expressed as the function of temperature. And we find the second-order transition temperature (T_2) of polysilane is about 65 K.

KEY WORDS Exact Enumeration Method / Conformational Entropy / Polysilane /

Conformations of polymer chains depend largely on conformational entropy which is associated with the order of the system. Calculation of the conformational entropy is an important and hard work. The entropy of a polymer chain at θ -state in a dilute solution (the chain submitted only to short-range interaction) can be calculated with the method of Flory's matrix multiplication.¹ But this method will be ineffective when long-range interaction prevails among the chain segments.²

There are several methods for calculating the conformational entropy of polymer chain perturbed by long-range interaction. Exact enumeration^{2–4} of all the possible conformations can calculate the entropy of such system, but it is only able to deal with short chain (10–20 segments) due to the tremendous number of conformations for long chain. Meirovitch's scanning method can treat relatively long chain.^{5,6} More recently, Collet and Premilat⁷ proposed a method for calculating the conformational entropy of much longer polymer chains based on the mean probabilities obtained from Monte Carlo simulation and applied it successfully on polyethylene chain.

Among all these methods which are used to calculate the entropy of perturbed chain, including those not mentioned here, the exact enumeration can provide most precise results, others can only provide approximate results. So, it is widely used in polymer science,^{2–4,8–10} which results are often treated as an important check of other methods.⁵ In the present work, we propose to calculate the conformational entropy of the polysilane chain with the exact enumeration method. The calculation is performed on an off-lattice three rotational isomeric state (RIS) model of polysilane. The polymer chain was submitted not only to short-range interaction (RIS), but also to long-range interaction (excluded volume in the work) in a manner similar to that proposed by Jianmin *et al.*²

METHOD OF CALCULATION

The skeleton atoms of the polysilane chain are all the

silicon, the bond length of the Si–Si is fixed as 2.34 Å, the bond angle of the Si–Si–Si is 109.4°. The primary statistical weight matrix is¹¹

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

where

$$\sigma = \exp(-E_\sigma/kT)$$

$$\psi = \exp(-E_\psi/kT)$$

$$\omega = \exp(-E_\omega/kT)$$

and $E_\sigma = -0.278 \text{ kcal mol}^{-1}$, $E_\psi = -0.240 \text{ kcal mol}^{-1}$, $E_\omega = 0.387 \text{ kcal mol}^{-1}$, k is the Boltzmann constant.

The long-range interaction between non-neighbor atoms i and j is represented by a hard sphere potential which represents an excluded volume^{2,7}

$$E_{ij} = \begin{cases} \infty, & r_{ij} < r_c \\ 0, & r_{ij} \geq r_c \end{cases} \quad (2)$$

r_{ij} is the distance between two atoms, and $|i-j|$ must be greater than 4. Simply, we only consider the skeleton atoms Si, chain side atoms H are neglected,¹² r_c is chosen as the Van der Waals radii of Si–Si in this paper, so r_c is 4.10 Å.¹¹ Since the statistical properties of an isolated chain (chain in a dilute solution) are independent of its external coordinates, they only depend on the internal rotation of bonds of the chain, so conformations of a chain with N bonds are determined by the internal rotation of $N-2$ bonds, thus the conformational entropy of the chain depends on the rotation of $N-2$ bonds.¹ Therefore, the first two bonds are fixed in our calculation, the next $N-2$ bonds are generated with an off-lattice model, each has three possible orientation (t , g^+ , g^-). The successive two rotational angles are determined by¹¹

	tt	tg	gt	g^+g^+
ϕ_i, ϕ_{i+1}	$(0^\circ, 0^\circ)$	$(0^\circ, \pm 125^\circ)$	$(\pm 125^\circ, 0^\circ)$	$(\pm 125^\circ, \pm 125^\circ)$
	$g^\pm g^\mp$			
ϕ_i, ϕ_{i+1}	$(\pm 120^\circ, \mp 120^\circ)$			

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All the possible conformations of the polysilane chain of N bonds are generated. Then the partition function

can be calculated as^{2,13}

$$Z = \sum_i \exp(-E_i/kT) \quad (3)$$

where E_i is the energy of conformation i and the summation is over all the possible conformations. T is the temperature, k is the Boltzmann constant as in eq 1.

The mean energy of the polymer chain is:

$$\langle E \rangle = Z^{-1} \cdot \sum_i E_i \cdot \exp(-E_i/kT) \quad (4)$$

Then the conformational entropy per mol of the chain is:

$$S = R \cdot \ln Z + \langle E \rangle / T \quad (5)$$

here $R = N_0 k$, N_0 is Avogadro constant, $R = 1.987 \text{ cal K}^{-1} \text{ mol}^{-1}$.

In this paper, the conformation entropies S at different temperature are calculated, the temperatures range from 50 K to 400 K. Since it takes a great deal of CPU time of a computer, the chain length is limited to 17 bonds.

RESULTS AND DISCUSSION

The conformational entropies of short polysilane chain submitted to short-range interaction (RIS) and long-range interaction (hard sphere) at temperature from 50 K to 400 K are calculated, while the chain length N is from 7 up to 17. The number of all possible conformations of such chain is listed in Table I.

The conformational entropy per mol S versus $N-2$ is shown in Figure 1 for the temperature from 50 K to 400 K. Results show that the conformational entropy is a linear function of $N-2$ at any temperature, give a relationship similar to that obtained for much longer chain using Monte Carlo method by Collet⁷:

$$S = a(N-2) + b \quad (6)$$

The reason we use $N-2$ instead of chain length N here is that the internal rotations of $N-2$ bonds contribute to the conformational entropy.

a and b in eq 6 are dependent on the temperature, the values of a and b at different temperature are listed in Table II. a and b can be expressed as the function of temperature. Using the least square method, we get a and b which are good for the temperature from 50 K to 400 K,

$$\begin{aligned} a &= 2.380 \times 10^{-2} - 0.6745\tau + 7.229\tau^2 - 4.448\tau^3 \\ &\quad - 7.602\tau^4 + 6.748\tau^5 \\ b &= 0.6980 + 0.5737\tau + 4.624\tau^2 - 29.20\tau^3 \\ &\quad + 42.53\tau^4 - 19.21\tau^5 \end{aligned} \quad (7)$$

where τ has a relationship to temperature T , $\tau = \exp(\varepsilon/kT)$. ε is minus, the magnitude of ε is arbitrary, we choose $\varepsilon = E_\sigma = -0.278 \text{ kcal mol}^{-1}$ here. One merit of choosing τ instead of T in eq 7 is that a and b will converge when temperature tends infinity. Also, the mean square deviation of a and b are largely decreased when we use τ , especially at high temperature. The value of a and b under 50 K or above 400 K can be estimated from the tendency of them near 50 K or 400 K.

The linear relations of S versus $N-2$ are so good that

Table I. The number of all possible configurations of the polysilane chain submitted to short-range interaction and long-range interaction^a

N	7	8	9	10	11	12
Ω	143	363	937	2405	6137	15701
N	13	14	15	16	17	
Ω	40115	102401	261297	666125	1697653	

^a N is the chain length (defined as the number of bonds of the chain), Ω is the number of all the possible configurations.

Figure 1. The plots of the configuration entropy per mol S versus $N-2$ at different temperature, $R = 1.987 \text{ cal K}^{-1} \text{ mol}^{-1}$.

Table II. Values of a and b at different temperature

T	a	b
50 K	8.432×10^{-3}	0.7441
100 K	0.2088	0.8225
150 K	0.4880	0.6989
200 K	0.6689	0.5535
250 K	0.7694	0.4509
300 K	0.8257	0.3889
350 K	0.8590	0.3518
400 K	0.8799	0.3290

it seems reasonable to consider that the relations are still valid for long chain. Let S_m stand for the entropy per bond per mol of an infinity chain, then

$$S_m = \lim_{N \rightarrow \infty} S/(N-2) = a \quad (8)$$

In Figure 2, we show $S/(N-2)$ versus temperature T for chain length $N=7, 12$, and 17 , S_m versus T is also shown. It indicates that $S/(N-2)$ decreases as N increases, and converges rapidly when N increases. Since the internal rotation of bonds contributes the conformational entropy, when the chain length increases, the space near the bond is gradually occupied by other bonds, the

Figure 2. The plots of the configuration entropy per internal rotation angle $S/(N-2)$ versus the temperature, for chain length $N=7$, 12, 17, and $N=\infty$, $R=1.987 \text{ cal K}^{-1} \text{ mol}^{-1}$.

rotation of the bond is obstructed by degrees, so the entropy $S/(N-2)$ decreases steadily.

Figure 2 also shows that the conformational entropy decreases as the temperature decreases. This agrees with Gibbs-DiMarzio's explanation about the relation between conformation and temperature.¹⁴ They thought that the conformations of polymer chains rearranged when the temperature decreased. At high temperature, the chains didn't prefer to any special conformations, but at low temperature, the chains began to prefer some low energy conformations. When the temperature reached T_2 (second-order transition temperature), the chains preferred to the lowest energy conformations, therefore the conformational entropy became zero. Because of the limitation of the computer's precision, the error of calculation will be gradually large when one reduces the temperature, for some of the factors $\exp(-E_i/kT)$ in eq 3 and 4 become very small or very

large at very low temperature. Therefore the calculation of the entropy of very low temperature becomes difficult and even impossible. Thus, T_2 must be determined by extrapolating from high temperature.

The curve of S_m versus T is almost straight in the region between 80 K and 140 K where the entropy S_m varies rapidliest. Extrapolating to the lower temperature from this linear region, one will find that the crossover temperature between $S_m=0$ and S_m for high temperature range is about 65 K. S_0 , the T_2 of polysilane chain which submitted to short-range interaction and an excluded volume is about 65 K.

Exact enumeration method has been used in attempt to calculate the conformational entropy of polysilane chain submitted to short-range interaction and an excluded volume. The conformational entropy appears proportional to chain length at any temperature. It varies with temperature, and show that the second-order transition temperature of polysilane in dilute solution is about 65 K, but we can't check it for lack of experimental value.

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