

CALCULATION OF CONFORMATIONAL ENTROPY AND FREE ENERGY OF POLYSILANE CHAIN

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Abstract The conformational entropy S and free energy F were calculated by exact enumeration of polysilane chain up to 23 segments with excluded volume (EV) and long-range van der Waals (VW) interaction. A nonlinear relation between S_{EV+VW} and chain length n was found though S_{EV} was found to vary linearly with n . We found that the second-order transition temperature of polysilane chain with VW interaction increases with the increase of chain length, while that of polysilane chain without VW interaction is chain length independent. Moreover, the free energies F_{EV+VW} and F_{EV} are both linearly related with n , and $F_{EV+VW} < F_{EV}$ for all temperatures.

Keywords Polysilane, Exact enumeration, Conformational entropy, Conformational free energy

INTRODUCTION

Conformations of polymer chains depend largely on the conformational entropy, which is associated with the order of the system. In cases of polymer adsorption, chain conformations are much affected by their entropy and free energy^[1]. Calculation of the conformational entropy is important but is hard work. The entropy of a polymer chain in the θ -state in dilute solution (the chain is subjected only to short-range interactions) can be calculated using Flory's matrix multiplication method^[2]. Unfortunately, the method will no longer be valid when long-range (LR) interactions, such as excluded volume, van der Waals interaction, *etc.*, prevail among the chain segments.

Many methods have been developed for calculating the conformational entropy of polymer chain perturbed by LR interactions. Exact enumeration^[3-5] of all the possible conformations can calculate the entropy of such system, though it is only able to deal with short chains due to the tremendous number of conformations of long chains. Meirovitch's scanning method can treat relatively long chain and has been applied successfully to general chain models with excluded volume, to self-attractive random walks^[6, 7]. More recently, Collet and Premilat 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 to polyethylene chains^[8].

Among all these methods which are used to calculate the entropy of perturbed chains in dilute solution, including those which have not been mentioned here, the exact enumeration can provide the most precise results. Thus, the exact enumeration method has been widely used in polymer science, and its values are often treated as an important check of other methods. In our previous paper, we calculated the conformational entropy of short polysilane chain up to 17 segments with the exact enumeration method^[9]. In the present work, we have extended the chain length to 23 segments, and in addition, we calculated the conformational entropy and free energy of polysilane chains in a more general case. That is, the chain is submitted to van der Waals (VW) interaction in addition to the limit of excluded volume (EV). The calculation is performed on an off-lattice three rotational

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isomeric state (RIS) model (t, g^+, g^-) of polysilane. The effect of the VW interactions on the entropy and free energy was discussed.

METHOD OF CALCULATION

The skeleton of the polysilane molecule is wholly constituted of Si atoms. The bond length of Si—Si is 0.234 nm, while the bond angle of Si—Si—Si is 109.4° ^[10]. One skeletal Si atom and two H side atoms are designated as a segment here. Owing to the relatively small size and mass of the H atom the H of polysilane chain are neglected for simplicity. The primary statistical weight matrix of second-order interaction approximation is^[10]:

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

where

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

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

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

and $E_\sigma = -1.16 \text{ kJ mol}^{-1}$, $E_\psi = -1.00 \text{ kJ mol}^{-1}$, $E_\omega = -1.62 \text{ kJ mol}^{-1}$, T is the temperature, and R is the gas constant, $R = 8.31 \text{ J mol}^{-1} \text{ K}^{-1}$.

The second-order interaction is a type of short-range (SR) interaction which only considers these interactions among the nearest five segments along the chain including the excluded volume effect and the van der Waals interaction. Besides the SR interaction, we have also considered two types of LR interactions between any pair of non-neighboring segments. In this paper, therefore, the interaction between two segments is called the LR interaction if the spacing of these two segments along the chain is greater than four, i.e., $|j - i| > 4$, where i and j are the sequence number of segments. The first kind of LR interaction between non-neighboring segments i and j is represented by a hard sphere potential, which represents an excluded volume of each segment, as:

$$E_{ij} = \begin{cases} \infty, & r_{ij} < r_c \\ 0, & r_{ij} \geq r_c \end{cases} \quad (2.1)$$

where r_{ij} is the spatial distance. The second kind of LR interaction between these segments i and j is represented by a van der Waals potential and an excluded volume^[10],

$$E_{ij} = \begin{cases} \infty, & r_{ij} < r_c \\ 3.038 \times 10^{-2} / r^{12} - 12.80 / r^6, & r_{ij} \geq r_c \end{cases} \quad (2.2)$$

In calculating E_{ij} , the unit for distance r_{ij} is nm while that for E_{ij} is J mol^{-1} . The radius r_c of the excluded volume of chain segment is chosen as the van der Waals radius of the Si atom, i.e., $r_c = 0.410 \text{ nm}$ ^[10]. Because the statistical properties of an isolated chain are independent of the chain's external coordinate, the conformational entropy and free energy of a chain containing n segments can be determined by the internal rotations of $n - 2$ segments. In this paper, n is also called the chain length. Therefore, the first two segments are fixed in our calculation, while the next $n - 2$ segments are generated with an off-lattice model, each having three possible orientations (t, g^+, g^-).

After all the possible conformations of the polysilane chain of length n are generated, the partition function can be calculated as:

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

where E_i is the energy of conformation i and the summation is over all the possible conformations. Similarly, the mean energy of the polymer chain is:

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

Then the conformational entropy and the free energy of the chain can be determined from:

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

and

$$F = -RT \ln Z = \langle E \rangle - TS \quad (6)$$

respectively.

In this paper, the conformational entropy S and free energy F of a single polysilane chain (or polysilane chain in dilute solution) are calculated for its various chain lengths at different temperature. The temperature ranges from 50 K to 440 K, while the chain length goes from 6 to 23.

RESULTS AND DISCUSSION

Figure 1 shows the dependence of the conformational entropy S of polysilane chain submitted to LR interactions on the chain length n . We can see that the entropy S_{EV} of a chain with EV is a linear function of n , which is in good agreement with our previous result obtained from relatively shorter chains (from 7 to 17)^[9]. But for chains with EV and VW interactions, the relation between S_{EV+VW} and chain length n is nonlinear and varies with temperature.

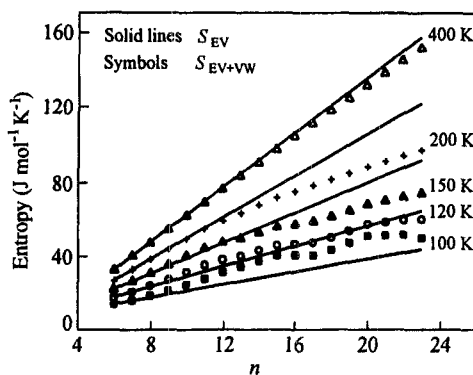


Fig. 1 Plots of the conformational entropies S_{EV} and S_{EV+VW} versus the chain length n at different temperatures

At high temperature, such as $T = 200$ K and $T = 400$ K in Fig. 1, one can find $S_{EV+VW} < S_{EV}$, indicating that VW attraction reduces the entropy of the chain, which is in agreement with Collet's calculation for polyethylene chain at 433 K^[8]. At a slightly lower temperature, for example $T = 150$ K, we find S_{EV+VW} of length $n = 9, 10, 11$ and 12 is greater than the corresponding S_{EV} of the same chain length. And at $T = 120$ K, and when $S_{EV+VW} > S_{EV}$, the chain length extends from 8 to 16. At $T = 100$ K, all the S_{EV+VW} for $n = 6$ to 23 are greater than the corresponding S_{EV} .

Therefore, a conclusion can be drawn about the influence of VW on the entropy of polysilane chain. At higher temperature or longer chain length, VW interaction among the chain's segments decreases the chain's entropy, i.e., $S_{EV+VW} < S_{EV}$. But at lower temperature or shorter chain length, the entropy becomes larger i.e., $S_{EV+VW} > S_{EV}$. With the decrease of temperature, the range of chain length with $S_{EV+VW} > S_{EV}$ extends.

At lower temperature, S_{EV+VW} is greater than S_{EV} for some chain length. But as the chain length reaches a

certain critical length n^* , the entropy S_{EV+VW} will drop again and the relation $S_{EV+VW} < S_{EV}$ will hold for all $n > n^*$. The value of n^* is dependent on the temperature T (see Fig. 2). The critical chain length n^* decreases with increasing temperature, and can be expressed approximately as:

$$n^* = 76.5 - 0.463T \quad (7)$$

where T is in Kelvin. Our previous work showed that the entropy S_{EV} is nearly equal to zero at $T_2 = 65 \text{ K}$ ^[9]. T_2 is defined as the second-order transition temperature where entropy S equals zero^[11], and T_2 is the chain length independence for a polysilane chain without VW interaction^[9]. For a polysilane chain with VW interaction, the entropy will be nearly zero for chain length $n \geq n^* = 46$ (at $T = 65 \text{ K}$). Since $S_{EV+VW} < S_{EV}$ for chain length $n > n^*$, then we conclude that, for a polysilane chain with VW interaction, the temperature at which $S_{EV+VW} = 0$ will increase with increasing chain length. That means the second-order transition temperature T_2 of the polysilane chain will increase with increasing chain length. Moreover, the chain length dependent transition temperature agrees with experimental findings^[11, 12].

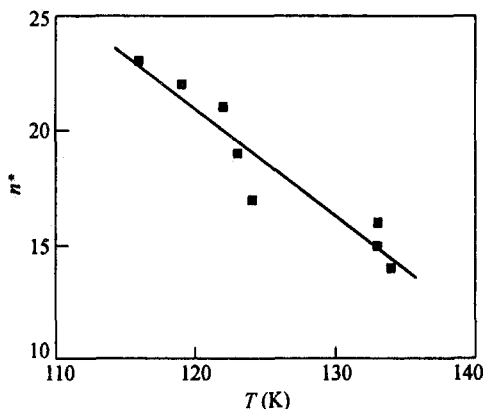


Fig. 2 Plot of the critical chain length n^* versus the temperature T . The solid line is the linear fit.

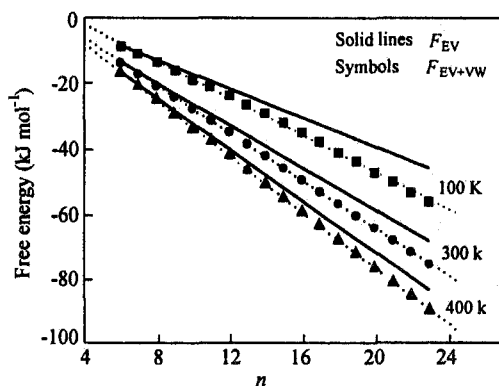


Fig. 3 Plots of the conformational free energies F_{EV} and F_{EV+VW} versus the chain length n at different temperatures. The dotted lines are the linear fits of F_{EV+VW} .

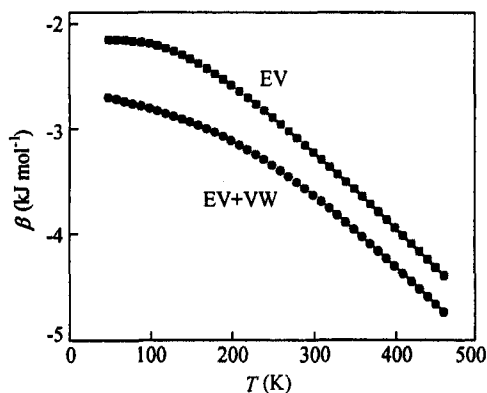


Fig. 4 Dependence of β , the free energy per segment, on the temperature T

However, the free energies F_{EV+VW} and F_{EV} of polysilane chain with and without VW interaction always show a linear relation with the chain length at any temperature (see Fig. 3). Both F_{EV+VW} and F_{EV} can be expressed approximately as:

$$F = \alpha + \beta n \quad (8)$$

Parameters α and β are functions of temperature T . When n is large, α can be neglected in Eq. (8), therefore, the slope β can be treated as the free energy per segment, that is $\beta = \frac{F}{n}$. The dependence of β_{EV} and β_{EV+VW} on the temperature T is shown in Fig. 4. One can see that β_{EV+VW} is always less than β_{EV} and they both decrease with T . When T is higher than 300 K, both β_{EV+VW} and β_{EV} decrease linearly with temperature with nearly the same slope. The rate of decrease of β_{EV} is about $7.07 \text{ J mol}^{-1} \text{ K}^{-1}$, while that of β_{EV+VW} is about $6.95 \text{ J mol}^{-1} \text{ K}^{-1}$.

CONCLUSIONS

The conformational entropy S and free energy F of polysilane chains are calculated by using an exact enumeration method. The influence of long-range van der Waals (VW) interaction on the conformational entropy S and free energy F is studied. A nonlinear relation between S_{EV+VW} and chain length n is found though S_{EV} varies linearly with n . At higher temperature or longer chain length, VW interaction decreases the entropy of the chain, but at lower temperature or shorter chain length, it increases the entropy. If we define the critical chain length n^* at which S_{EV+VW} crosses over from $S_{EV+VW} > S_{EV}$ at small n to $S_{EV+VW} < S_{EV}$ at large n , we find that n^* decreases almost linearly with temperature. The second-order transition temperature T_2 of the polysilane chain increases with increasing chain length, which agrees with the experimental findings. On the other hand, the free energies F_{EV+VW} and F_{EV} both show linear relation with n , and $F_{EV+VW} < F_{EV}$ for all temperatures.

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