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SHORT COMMUNICATION

INFLUENCE OF EXCLUDED VOLUME ON THE ENTROPY OF POLYMETHYLENE CHAINS

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Abstract—The influence of excluded volume on conformational entropy is studied for the polymethylene (PM) chain on a tetrahedral lattice. We find that the influence of excluded volume on entropy is temperature-dependent. The difference in entropy between PM chains with and without excluded volume becomes larger as the temperature increases. © 1998 Elsevier Science Ltd. All rights reserved

INTRODUCTION

The excluded volume, which changes many conformational properties of polymer chains, comes from the fact that segments of a real polymer chain occupy a position in space. This is a subject of great importance in polymer science [1].

The conformational entropy of polymer chains, also an important subject, has long been studied using many methods [2–6]. Flory's matrix multiplication method is the simplest one, but it can only deal with unperturbed polymer chains [2]. While the exact enumeration [6–8] of all the possible conformations of a polymer chain can provide the most precise results when the chain perturbed by long-range interactions, such as the excluded volume in this paper, it is only able to handle short chains.

In the present work we propose to find out to what degree does the excluded volume influence the conformational entropy of PM chains. The conformational entropy of unperturbed PM chains, S_0, is calculated using a matrix multiplication method, while that of PM chains perturbed by excluded volume, S_{EV}, is calculated using an exact enumeration method.

METHOD OF CALCULATION

The PM chains are generated on a tetrahedral lattice. The bond that binds two successive skeletal atoms can only occur in three ways, *trans*, *gauche*$^+$ and *gauche*$^-$. The primary statistical weight matrix is [9]:

$$\mathrm{U} = \begin{bmatrix} 1 & \sigma & \sigma \\ 1 & \sigma & \sigma\omega \\ 1 & \sigma\omega & \sigma \end{bmatrix} \tag{5}$$

where $\sigma = \exp(-E_\sigma/k_{\mathrm{B}}T)$, $\omega = \exp(-E_\omega/k_{\mathrm{B}}T)$ and $E_\sigma = 500$ cal/mol, $E_\omega = 2500$ cal/mol. k_{B} is the Boltzmann constant and T is absolute temperature. The entropy is in units of k_{B} hereafter.

The number of conformations, C_{N}, can be expressed as [7]:

$$C_N \cong u^N \cdot N^\alpha, \tag{2}$$

where N is chain length (defined as the number of bonds) and u and α are constants. Then the conformational entropy of a PM chain can be written as:

$$S_N \cong \alpha \cdot \ln N + \beta \cdot N, \tag{3}$$

where α and β are functions of the temperature, and can be derived from a series of β_N, where:

$$\beta_N = S_{N+1} - S_N \cong \beta + \alpha/N. \tag{4}$$

The conformational entropy of a PM chain is calculated by:

$$S = \ln Z + \langle E \rangle / T, \tag{5}$$

where Z and $\langle E \rangle$ are the partition function and the mean energy, respectively. Z and $\langle E \rangle$ are calculated with the matrix multiplication method for an unperturbed PM chain, and with the exact enumeration method for a perturbed one. The excluded volume is approximately considered as each skeleton atom occupying a sphere with a diameter 0.3 nm [10].

RESULTS AND DISCUSSION

The conformational entropies S_0 and S_{EV} are calculated for short PM chains of length from 7 to 17 bonds. The temperature T is varied, in increments of 10 K, from 60 to 400 K.

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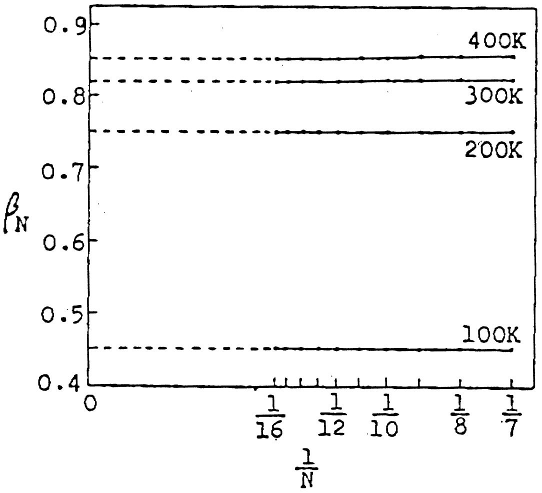

Fig. 1. Plots of β_N vs $1/N$ for a PM chain with excluded volume at various temperatures. The dashed line is a linear extrapolation based on the final pair of points in each case.

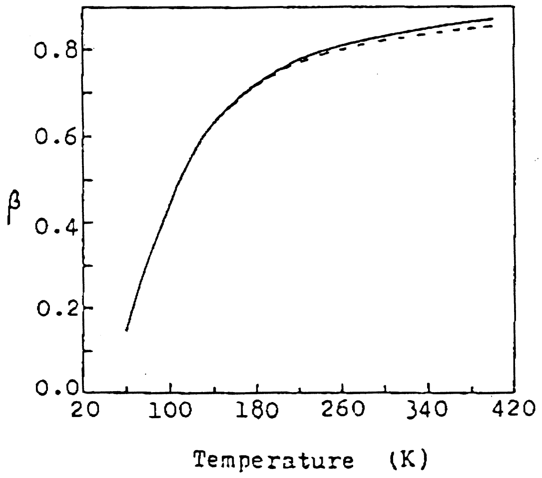

Fig. 2. The β value of unperturbed PM chains (——) and perturbed PM chains (–––) as a function of temperature.

The behaviour of β_N as a function of $1/N$ is shown in Fig. 1 for a perturbed PM chain at various temperatures. One can estimate

$$\alpha \cong 0 \tag{6}$$

at these temperatures. It means that all the values of α in the temperature region from 60 to 400 K approximate to zero. The value of β is strongly dependent on temperature and increases steadily with temperature. Similar behaviour is found for unperturbed PM chains.

Since $\alpha \cong 0$, then the difference in entropy between an unperturbed chain and a perturbed one is:

$$\Delta S = S_0 - S_{\mathrm{EV}} \cong (\beta_0 - \beta_{\mathrm{EV}})N, \tag{7}$$

where β_0 and β_{EV} represent the values of β for an unperturbed chain and a perturbed one, respectively.

Figure 2 shows the dependence of β_0 and β_{EV} on temperature. β_0 and β_{EV} decrease as the temperature decreases and β_0 is always greater than β_{EV}. One can find that the difference between β_0 and β_{EV} is very small at low temperatures, but it becomes steadily larger as the temperature increases. This indicates that the influence of excluded volume on the conformational entropy is very small at low temperatures, and is dependent on the temperature.

Careful investigation shows that ΔS in the region from 60 to 400 K can be fitted according to:

$$\Delta S/N \cong 0.0015\sigma + 0.05\sigma^2. \tag{8}$$

Our results show that the conformational entropy of PM chains decrease after introducing the excluded volume. The influence of excluded volume on the entropy is dependent on temperature and becomes larger as the temperature increases.

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REFERENCES

1. Yamakawa, H., *Modern Theory of Polymer Solutions*. Interscience, New York, 1971.
2. Flory, P.J., *Statistical Mechanics of Chain Molecules*. Wiley, New York, 1969.
3. Go, N. and Scheraga, H. A., *Macromolecules*, 1976, **9,** 533.
4. Meirovitch, H., *Macromolecules*, 1983, **16,** 249.
5. Collet, O. and Premilat, S., *Macromolecules*, 1993, **26,** 6076.
6. Sykes, M. F., Guttman, A. J., Watts, M. G. and Roberts, P. D., *J. Phys*., 1972, **A5,** 653.
7. Rapaport, D. C., *J. Phys*., 1976, **A9,** 1521.
8. Jianmin, X., Xubing, S. and Zhiping, Z., *Eur. Polym. J*., 1989, **25,** 601.
9. Abe, A., Jernigan, R. L. and Flory, P. J., *J. Am. Chem. Soc*., 1966, **88,** 631.
10. Winnik, M. A., Rigby, D., Stepto, R. F. T. and Lemaire, B., *Macromolecules*, 1980, **13,** 699.