

CONFORMATIONAL PROPERTIES OF STRETCHED POLYETHYLENE CHAIN*

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Abstract When polyethylene chains are stretched, the chains are regarded as being confined in an infinite cylinder with decreasing diameter. The conformational properties of polyethylene chains confined in an infinite cylinder are investigated by using rotational isomeric state model. Using the average conformational energy and entropy and the average length, we can determine the elastic force f , or the fraction of the energy term to the total force f_e/f , where $f_e = \partial \langle U \rangle / \partial \langle r \rangle$ and $f = \partial \langle A \rangle / \partial \langle r \rangle$. Comparisons with experimental data are also made. The results of these microscopic calculations are discussed in terms of the macroscopic phenomena of rubber elasticity.

Keywords Rotational isomeric state model, Polyethylene chain, Elastic force, Rubber elasticity

INTRODUCTION

Rotational isomeric state (RIS) theory has been widely applied to investigate the statistical properties of polymer chains satisfactorily for interpreting the characteristic ratio and the temperature coefficient of this ratio^[1, 2]. Recently, Yang *et al.* proposed a conformational elasticity theory based on the rotational isomeric state model^[3, 4]. The macroscopic phenomena of rubber elasticity can be investigated in terms of the isolated polymer chains employing the rotational isomeric state model. The reason is that small angle neutron scattering (SANS) measurements of polymers in the bulk state prove that the configuration of chains in the elastic and glassy states of amorphous polymers is close to the chain configuration in solution under θ -condition^[5, 6]. When chains are stretched, the moving space perpendicular to the stretching direction becomes smaller and smaller, and a number of chain conformations would vanish. In this paper, we consider the effects of stretching a polymer chain containing a relatively small number of carbon-carbon bonds on the conformational properties. The processes of stretching polymer chains will be simulated through polymer chains confined in an infinite cylinder with a decreasing diameter. We can deduce the conformational properties (especially the elastic force) through calculating those conformations, which can fit in the cylinder. Comparisons with experiments are also made.

METHODS OF CALCULATION

In the rotational isomeric state model of polyethylene chains, each bond rotamer is assumed to be in one of the three conformations: *trans* conformation (t) which has the lowest energy and two *gauche* conformations (g^+) and (g^-) situated at rotations $\varphi_{\pm} = \pm 120^\circ$ from the *trans* conformation. Here the following statistical weight matrix of the polyethylene chain is adopted^[7]:

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

where:

$$\sigma = \exp(-E_\sigma/kT), \quad \omega = \exp(-E_\omega/kT) \quad (2)$$

In this paper, $E_\sigma = 2094$ J/mol, $E_\omega = 9374$ J/mol^[7]. The following bond lengths and valence angles are adopted: $l_{\text{CH}_2-\text{CH}_2} = 0.153$ nm, $l_{\text{C-H}} = 0.11$ nm, $\angle \text{CH}_2-\text{CH}_2-\text{CH}_2 = 112^\circ$, $\angle \text{H}-\text{CH}_2-\text{H} = 110^\circ$. The conformations confined in an infinite cylinder are defined as follows: a Cartesian coordinate system is affixed to the middle of the first C—C bond, and is used as a reference frame for expressing the x, y, z coordinates of each of the atoms in the chain fragments. The x, y, z coordinates of all atoms are calculated and then transformed to the Cartesian coordinate system x', y', z' whose x' -axis connects to the midpoints of the first and second bonds while all bonds are in *trans* states (see Fig. 1). When selecting cylinder conformations, we simply determine if $r = (x'^2 + y'^2)^{1/2} < r_c$, where r_c is the radius of the cylinder. If each atom in the polyethylene chain passes this test, then the conformation is considered. Because in the search for cylinder conformers each atom is considered as a volumeless point, a conformer found to fit in a cylinder of diameter $D' = 2r_c$ would actually fill a cylinder with diameter $D = D' + 1$ if van der Waals spheres of 0.05 nm are considered for each proton.

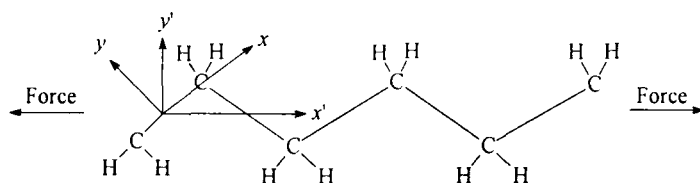


Fig. 1 A conformation confined in an infinite cylinder with all bonds in *trans* states

In the calculation of the conformation properties, matrix multiplication techniques are used. The averaging is made just for the sets of conformers found to fit in cylinders of diameter D . Let us suppose our polyethylene chain adopted the tg^+tg^-tt conformation. Its contribution to the partition function is $[U(1)U(1,1)U(1,3)U(3,1)U(1,2)U(2,1)U(1,1)]$, where $U(1)$ is the statistical weight matrix U with all elements in column 2 and 3 replaced by zero.

RESULTS AND DISCUSSION

Chain Dimensions

The average length or end-to-end distance $\langle r \rangle$ for all conformers found to fit in a cylinder with diameter D is obtained by:

$$\langle r \rangle = \frac{\sum_i [(x_n - x_1)^2 + (y_n - y_1)^2 + (z_n - z_1)^2]^{1/2} \exp(-E_i/kT)}{\sum_i \exp(-E_i/kT)} \quad (3)$$

where E_i is the energy of polymer chain with all atoms in the cylinder. In Fig. 2, we plot the average length $\langle r \rangle$ against the diameter D of the infinite cylinder. The average lengths increase with decreasing diameter of the cylinder. For example, the maximum of the average length is 1.776 nm for chain length $N = 14$ and diameter $D = 0.5$ nm. The reason is that the direction of two midpoints of the terminal bonds is the x' direction when polymer bonds are in *trans* states, planar zigzag. The conformations of chains confined in an infinite cylinder with a very large diameter are the same as the conformations of the isolated chains. When a force acts on the chains, the chains are stretched slowly, and the average lengths increase. If all bonds assume the *trans* state, the average

length also becomes a maximum, while the diameter of infinite cylinder becomes a minimum. Here the stretching distances along the direction of the force acting on the chain are measured by the changes of the average length. If the forces acting on the chains are higher, the changes of the average length are also larger.

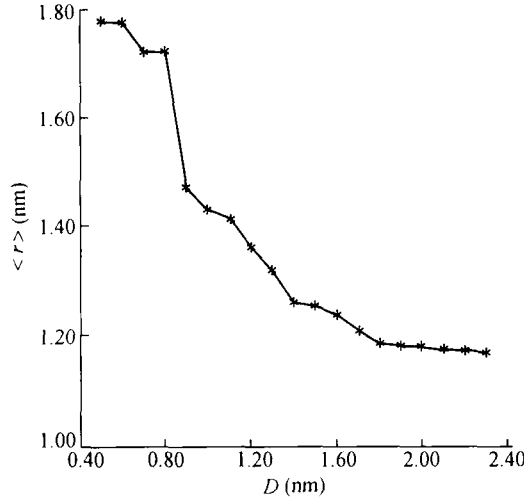


Fig. 2 The average length $\langle r \rangle$ against diameter D of cylinder with chain length $N = 12$ at $T = 373$ K

Elastic Forces

The average energy, entropy and Helmholtz free energy for the cylinder conformers of polyethylene chains are obtained by^[8]:

$$\langle U \rangle = \frac{RT^2}{Z} \frac{dZ}{dT} \quad (4)$$

$$\langle S \rangle = R \ln Z + \frac{RT}{Z} \frac{dZ}{dT} \quad (5)$$

$$\langle A \rangle = -RT \ln Z \quad (6)$$

where Z is the partition function of the cylinder conformers. The results are given in Figs. 3 and 4. In Fig. 3, we plot the average energy $\langle U \rangle$ and positive Helmholtz free energy $-\langle A \rangle$ against the average length $\langle r \rangle$ at different temperature with chain length $N = 16$ (here N is the number of carbon-carbon bonds). The curves signified by signs (*) and (Δ) are for $T = 323$ K, and the curves signified by signs (+) and ($\circ$) are for $T = 423$ K. We can know that $\langle U \rangle$ increases slowly with decreasing average length $\langle r \rangle$ at different temperatures, while $-\langle A \rangle$ also increase with decreasing average length $\langle r \rangle$, especially for small $\langle r \rangle$. In the meantime, we also calculate the conformational properties of polymer chains with different chain length at temperature $T = 373$ K, and the results are given in Fig. 4. The signs (*) and (Δ) are for $N = 14$, and the signs (+) and ($\circ$) are for $N = 18$. In our calculation, we find that the dependence of the average energy $\langle U \rangle$ and Helmholtz free energy $\langle A \rangle$ on the average length $\langle r \rangle$ is the same for various chain lengths.

The elastic force stored in the polymer chain fragments squeezed inside the cylinder is finally obtained from the dependence of $\langle U \rangle$ and $\langle A \rangle$ on the average length according to^[9]:

$$f_e = \partial \langle U \rangle / \partial \langle r \rangle \quad (7)$$

$$f = \partial \langle A \rangle / \partial \langle r \rangle \quad (8)$$

where f_e is the energy elastic contribution to the elastic force. In the rubber theory, the fraction of the energy term to the total force f_e/f is more important. Then, we calculate the ratio f_e/f of polymer chains with different chain lengths and the results of $N = 14$ and $N = 18$ at $T = 373$ K are given in Fig 5. In our calculation, the dependence

of f_e/f on the diameter D of an infinite cylinder is the same for various chain lengths at the same temperature or at different temperatures for the same chain length. In Fig. 5, the ratio f_e/f is close to zero for large diameter, and the ratio f_e/f decreases quickly for $D = 1.15\sim 1.35$ nm. However, the ratio f_e/f is close to $-0.43\sim -0.47$ for $D = 1.05\sim 1.15$ nm, which agrees well with the experimental data^[10]. The value of f_e/f was determined for a cross-linked network of polyethylene chain in the amorphous state, and the result is -0.42 ± 0.05 ^[10]. We know polyethylene chains in the amorphous state are multi-chain systems, and the thermodynamic functions of multi-chain systems can not be obtained theoretically. Through our calculations, we find that the approximate model of this system is the polymer chain confined in an infinite cylinder with diameter $D = 1.05\sim 1.15$ nm. The conformational properties of the multi-systems, especially thermodynamics properties, may be obtained approximately by using our model.

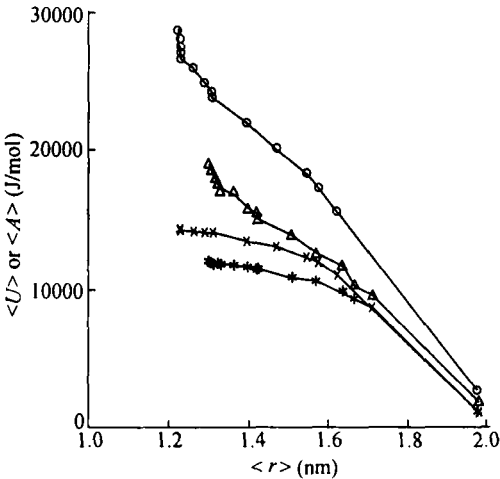


Fig. 3 The conformational energies $\langle U \rangle$ and positive Helmholtz free energies $-\langle A \rangle$ are plotted against the average length $\langle r \rangle$ at different temperature for chain length $N = 16$
Here (*) is $T = 323$ K and $\langle U \rangle$, (Δ) is $T = 323$ K and $-\langle A \rangle$; and (+) is $T = 423$ K and $\langle U \rangle$, ($\circ$) is $T = 423$ K and $-\langle A \rangle$

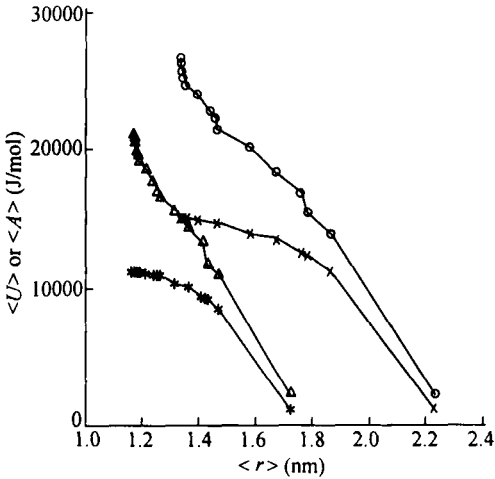


Fig. 4 The conformational energies $\langle U \rangle$ and positive Helmholtz free energies $-\langle A \rangle$ are plotted against the average length $\langle r \rangle$ with various chain length at temperature $T = 373$ K
Here (*) is $N = 14$ and $\langle U \rangle$, (Δ) $N = 14$ and $-\langle A \rangle$; and (+) is $N = 18$ and $\langle U \rangle$, ($\circ$) is $N = 18$ and $-\langle A \rangle$

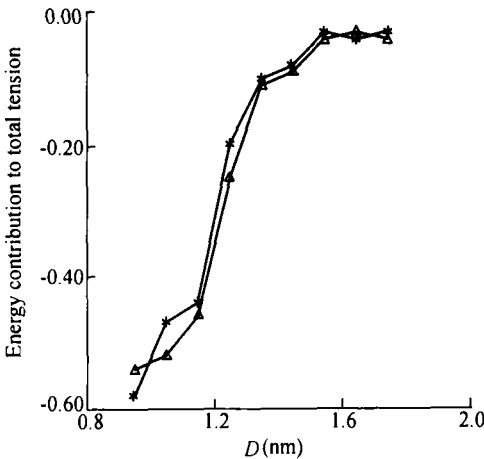


Fig. 5 Plot of the ratio of the energy contribution to the total tension f_e/f versus diameter D for different chain length at $T = 373$ K
(*) $N = 14$, (Δ) $N = 18$

Abe and Flory^[11] have discussed quantitatively the rotational isomerism of polymer chains produced during stretching. Except for very short chains or at high degrees of extension, they found that moderate extensions produce very small conformational changes. Only at very high extension ratios ($\langle r \rangle / \langle r \rangle_{\text{free}}$), will the intramolecular, conformational entropic, and possibly energetic contributions to the elastic force be expected to be significant. As it will take a very long computer time to calculate the statistical properties of a long polymer chain, in this paper we only consider short polymer chains. This method may be useful to study statistical properties, and especially to study thermodynamic properties of multi-chain systems.

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