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Effects of the elastic deformation on the average conformations of polymethylene chains

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Abstract

The average conformation properties, such as the a priori probability $P_{\xi\eta}$ and the segmental orientation function $\langle P_2(\zeta)\rangle$ of polymethylene chains with chain length from $N = 13$ to $N = 21$ are investigated by enumeration calculation method based on the rotational-isomeric state (RIS) model. Here non-local interactions of L–J potential are also considered. In the process of tensile deformation, the a priori probability P_t increases with elongation ratio λ, meanwhile the a priori probability P_{g^+} (or P_{g^-}) decreases with elongation ratio λ, and it leads the average energy per bond to decrease. The segmental orientation distribution function $\langle P_2(\zeta)\rangle$ of short deformed polymethylene chains may be expressed in the form of

$$\langle P_2(\zeta)\rangle/(\lambda^2 - \lambda^{-1}) = a(\lambda^2 - \lambda^{-1}) + b$$

where a and b only depend on PM chain length. Many conformations will vanish in the process of deformation. We also investigate the probability density distribution function of gyration radius $P(S)$. For a given chain length, the maximum of $P(S)$ increase with λ, and the distributed region of $P(S)$ becomes smaller for large λ. Some comparisons with Flory–Fisk function of $P(S)$ are also made. Our calculations may provide some insights into the rubber-like elasticity.

Keywords: Rotational-isomeric state model; The a priori probability; Segmental orientation

1. Introduction

The problems of rubber-like elasticity are of considerable academic and applied interest. The elastic behavior exhibited by a polymer network upon moderate macroscopic deformation can be attributed to the deformation, and associated reduction in entropy, of the individual molecular chains connecting the network junction points. In the range of the statistics, most molecular theories of this 'rubber-like' elasticity employ the Gaussian distribution function for the required probabilities and end-to-end separation of a network chain [1,2]. But this theory does not adequately take into account the significant conformational differences known to exist among different types of polymeric chains [3]. Later, non-Gaussian theories have also been developed [2,4–6], but the ones currently available generally have the disadvantage of containing parameters which can be determined only by comparisons between theory and experiment. Flory and Abe put forward the rotational-isomeric state (RIS) theory based on the effects of elongation of a polymer chain on the apportionment of its bonds and bond sequences among various RIS [7]. The approach taken in the present investigation avoids the shortcoming of non-Gaussian theories by utilizing the wealth of information, which RIS theory provides on the spatial configurations of chain molecules [3], including most of those used in elastomeric networks. Curro and Mark improved a non-Gaussian theory of rubber-like elasticity based on RIS simulations of network chain configurations and investigated the rubber-like elasticity from the distribution functions for the end-to-end separation r of the chains using Monte Carlo (MC) method [8]. In some cases, non-Gaussian functions $W(r)$ are provided by analytical theories, in other cases can be deduced from the MC sampling of the chain configurations [2,9–15]. The MC network model of Stepto and Taylor is based on detailed molecular representations of network-chain structures [16,17], and also addresses the problem of chains in a rubbery network becoming fully extended. Chains are

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deformed individually and maximum chain extension is restricted, consistent with $W(r) = 0$, where $W(r)$ is the network-chain radial end-to-end distance distribution, generated using an RIS chain model. The other classical model is phantom network. This theory explains rubber elasticity in terms of the change of chain entropy when a polymer network is deformed [18,19]. But the theory ignores interactions between chains and assumes that the only influence on the configuration of a chain is the position of its end points. The theory also makes predictions regarding chain orientation [19,20]. Flory and Erman introduced the impede fluctuations of the junctions in the theory of elasticity of polymer networks. Effects of dilation by swelling on the stress–strain relationship are reproduced by the same set of parameters [21,22]. The other development of elasticity theory is tube model of de Gennes and Edwards who discussed possible motions for one polymer molecule performing wormlike displacements inside a strongly cross-linked polymeric gel G [23].

Although the molecular origin of the elastic force in a rubber-like material has been acknowledged, the relationship between the macroscopic deformation and its molecular structure is not yet fully understood. The thermodynamics properties of rubber-like elasticity haven't been investigated in detail, and the energy changes in the deformation process haven't been considered, either. In fact, the energy contribution to elasticity is very important and cannot be ignored. Xiaozhen and Xiaofeng proposed a conformational elasticity theory based on the RIS model and discussed the elasticity behaviors of poly(*cis*-1,4-isoprene) and poly(*trans*-1,4-isoprene)chains in terms of the chemical structure [24]. We also investigated the elastic behaviors of short PM chains using enumeration calculation method [25], and the elastic behaviors of long PM chains using MC simulation method [26]. The results are close to the experimental data. In this paper, we will investigate the average conformation of short PM chains in the process of deformation using the RIS model and the enumeration calculation method.

2. Method of calculation

The RIS model used to parameterize the PM chain structures was that of Abe, Jernigan and Flory [27]. The geometric parameters are C–C bond length $l_{C\text{–}C} = 0.153$ nm and C–C–C bond angle is 112°. The rotational states are located at $\Phi_t = 0$, and $\Phi_{g^\pm} = \pm 112.5°$, respectively. The statistical weight matrix of PM chain is

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

where $\sigma = \exp(-E_\sigma/RT)$ and $\omega = \exp(-E_\omega/RT)$. The energy parameters for local interaction are $E_\sigma = 1674\ \mathrm{J\ mol^{-1}}$ and $E_\omega = 6276\ \mathrm{J\ mol^{-1}}$ [28]. We also consider the non-local interactions in our calculation, and the L–J potential is adopted [28],

$$E(r) = 4\varepsilon^*\left[\left(\frac{r^*}{r}\right)^{12} - \left(\frac{r^*}{r}\right)^{6}\right] \tag{2}$$

where the values of ε^* and r^* are $603.2\ \mathrm{J\ mol^{-1}}$ and 0.3264 nm, respectively [28].

When a force f acts on a PM chain, the atoms in a polymer chain move r distance along the force direction, at the same time, the atoms are compressed and drawn back r' in the vertical of the force direction. In the process of tensile deformation, many conformations would vanish. If the force $f = 0$, this is the isolated chain, and we assume that the minimum of end-to-end distance is r_{min}. If the force $f \neq 0$, the minimum of end-to-end distance of the elongated direction becomes $r_{min} + r$ (see Fig. 1). For simplicity, the minimum of end-to-end distance r_{min} equals to 0. If the force f acts on the chain in the direction of X-axis, the partition function of the system becomes

$$Z_X(r) = \sum_i \exp(-E_i/RT) \tag{3}$$

where $\sum_i$ is the sum of the conformations whose X-axis component of end-to-end distance is greater than r, meanwhile the Y-axis and Z-axis components of end-to-end distance are less than $r_{Y,max} - r'$ and $r_{Z,max} - r'$, respectively. The elongation ratio λ_e and the compress ratio λ_c are obtained from the root-mean-square of end-to-end

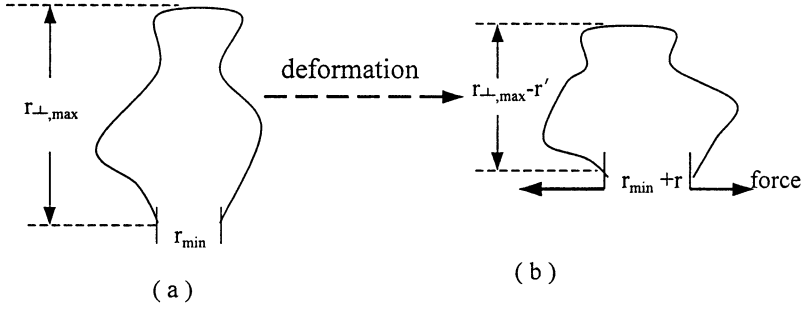

Fig. 1. Conformations of an isolated chain (a) and of a chain with a force acting on (b).

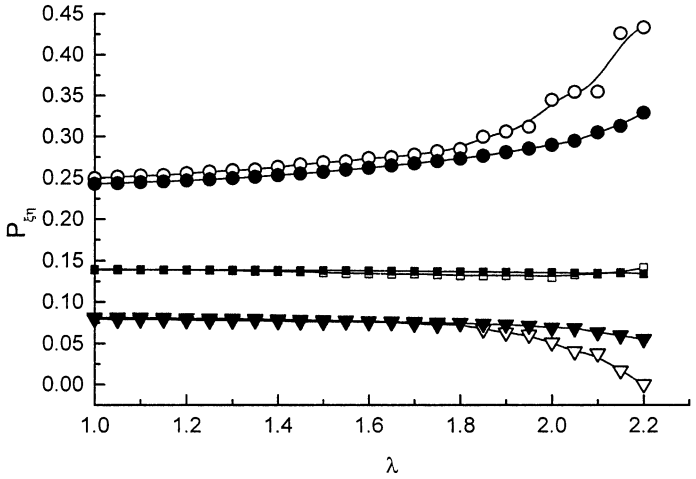

Fig. 2. The a priori probability $P_{\xi\eta}$ vs. elongation ratio λ of PM chains with 13 bonds and 21 bonds at $T = 423$ K. Here P_{tt} (●), $P_{g^{\pm}t}$ (■), and $P_{g^{\pm}g^{\pm}}$ (▼) are for 21-bond chain; and P_{tt}(○), $P_{g^{\pm}t}$ (□), $P_{g^{\pm}g^{\pm}}$ (▽) for 13-bond chain.

distance $\langle R^2\rangle_0^{1/2}$ of PM chain without deformation

$$\lambda_e = \frac{\langle R^2\rangle_0^{1/2} + r}{\langle R^2\rangle_0^{1/2}}, \qquad \lambda_c = \frac{\langle R^2\rangle_0^{1/2} - r'}{\langle R^2\rangle_0^{1/2}} \tag{4}$$

Thus, the partition function $Z(r)$ depends on λ_e and λ_c. Here we assume the case of simple elongation, i.e. $\lambda_X = \lambda_e$, $\lambda_Y = \lambda_Z = \lambda_e^{-1/2} = \lambda_c$; or $\lambda_Y = \lambda_e$, $\lambda_X = \lambda_Z = \lambda_e^{-1/2} = \lambda_c$; or $\lambda_Z = \lambda_e$, $\lambda_X = \lambda_Y = \lambda_e^{-1/2} = \lambda_c$. Therefore, the statistic properties of PM chains are taken as an average over three cases.

$$Z(r) = \frac{1}{3}\sum_{\alpha=X,Y,Z} Z_\alpha(r) \tag{5}$$

3. Results and discussion

3.1. Average conformation

In the process of tensile deformation, many conformational properties of polymers may be changed. For example, the conformations whose X-axis component of end-to-end distance is less than r and whose Y-axis and Z-axis components of end-to-end distance are greater than $r_{Y,\max} - r'$ and $r_{Z,\max} - r'$ will vanish, and the partition functions will decrease. For PM chains, the elastic force increases and so do the average dimensions during the process of deformation [25]. In fact, the average conformations are also changed. Here we discuss those properties.

We define the a priori probability $P_{\xi\eta}$ as

$$P_{\xi\eta} = \frac{\sum_i P_{\xi\eta,i}\, e^{-E_i/RT}}{\sum_i e^{-E_i/RT}} \tag{6}$$

where $P_{\xi\eta,i}$ is the probability when the i and $i+1$ bonds are in paired state ξ and η, and $\sum_i$ is the sum of the conformations without vanishing. The state ξ or η may be t, g^+, or g^-.

We calculate the a priori probability $P_{\xi\eta}$ of PM chains with chain length from 13 to 21 bonds at the various elongation ratios, and the results are shown in Fig. 2. P_{g^+t} (or P_{g^-t}) is almost constant during the tensile deformation, and the trends are the same for the different chain lengths. P_{tt} increases slowly in the region of small λ, and increases obviously when $\lambda > 1.9$, especially for short PM chain. At the same time, P_{tt} of 13-bond PM chain is greater than that of 21-bond PM chain. The value of $P_{g^+g^+}$ (or $P_{g^-g^-}$) is nearly unchanged in $\lambda < 1.9$, and decreases in the large scale of λ, especially for 13-bond PM chain.

We also conclude the a priori possibility P_ξ of state ξ, defined by

$$P_\xi = \sum_{\eta=t,g^+,g^-} P_{\xi\eta} \tag{7}$$

Fig. 3(a) and (b) shows the relationship between P_ξ and the elongation ratio λ. We find the probability P_t increases immensely and P_{g^+} (or P_{g^-}) decreases with the elongation ratio λ. Compared to P_t, the change of P_{g^+} is more inconspicuous, especially for small elongation ratio λ. For example, P_t without elongation ($\lambda = 1.0$) is 0.53 and becomes 0.72 at $\lambda = 2.4$. For P_{g^+}, the value ranges from 0.24 to 0.14. The microstructures will influence the macroscopical properties. For example, if the first-order interaction approximation is considered only, the average energy per bond can be obtained by

$$\langle E\rangle = E_t P_t + E_{g^+} P_{g^+} + E_{g^-} P_{g^-} \tag{8}$$

where $E_t = 0$, $E_{g^\pm} = 1674$ J/mol^{-1}, and $P_{g^+} = P_{g^-}$. This leads the average energy per bond to decrease, and the energy contribution to force is negative, which is in agreement with the experimental results [25]. The average conformation properties of polymer molecules play

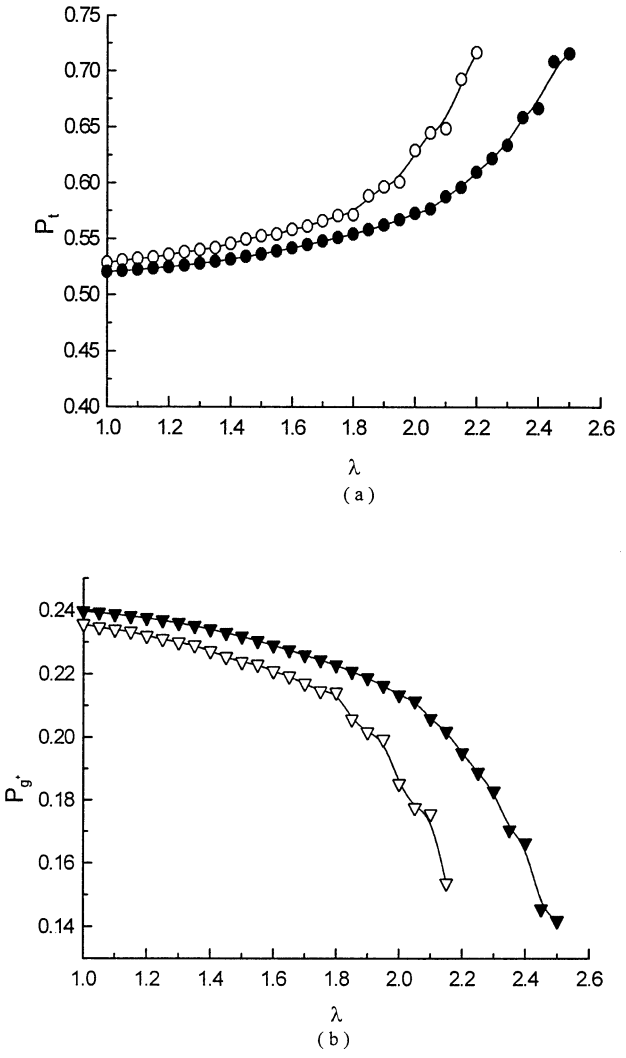

Fig. 3. The a priori probability P_ξ vs. elongation ratio λ of PM chains with 13 bonds and 21 bonds at $T = 423$ K. (a) (●) is P_t for 21-bond chain, and (○) for 13-bond chain; (b) (▼) is P_{g^+} for 21-bond chain, and (▽) for 13-bond chain.

important roles in the interpretation of many aspects of polymer behavior.

3.2. Density distribution function P(S) of the PM chains

Many properties of polymers rely heavily on some knowledge of the average and the distribution of molecular dimensions of polymers. Here we discuss the density distribution function of gyration radius $P(S)$. If $Z(r)$ is the partition function defined by Eq. (5), $f_n(S)$ is

$$f_n(S) = \sum_{i'} e^{-E_{i'}/RT} \tag{9}$$

where $\sum_{i'}$ is the sum of the Boltzman factor whose gyration radius lies between S and $S + \Delta S$, we have

$$\int_S^{S+\Delta S} P(S)\,dS = \frac{f_n(S)}{Z(r)} \tag{10}$$

If $Z(r)$ is large enough, ΔS small enough, and $P(S)$ decreases or increases monotonously, the left of Eq. (10) may also be written [29]

$$\int_S^{S+\Delta S} P(S)\,dS = P\left(S + \frac{\Delta S}{2}\right)\Delta S \tag{11}$$

thus

$$P\left(S + \frac{\Delta S}{2}\right) = \frac{f_n(S)}{Z(r)\,\Delta S} \tag{12}$$

Simulations are carried out for PM chains with chain length from $N = 13$ to $N = 21$ and $\lambda = 1.0$, 1.5, and 2.0. We calculate the probability density distribution function $P(S)$ using Eq. (12). Here ΔS is equal to $0.05\langle S^2\rangle^{1/2}$ in our calculation. The results are shown in Fig. 4(a) and (b). Fig. 4(a) is the case of 13-bond PM chain and Fig. 4(b) is of 21-bond PM chain. The values of $S/\langle S^2\rangle^{1/2}$ with the maximum probability density of $P(S)$ become small during the process of deformation. We also conclude that the shape of curves becomes higher and narrower with the elongation ratio increasing and the trend is much more notable in long chains relative to short ones. On the other hand, in the large scale of the abscissa ($S/\langle S^2\rangle^{1/2}$) (for example $S/\langle S^2\rangle^{1/2} > 1.15$), $P(S)$ decreases with the elongation ratio λ. For example, in Fig. 4(a), $P(S)$ decreases from 0.42 for $\lambda = 1.0$ to 0.05 for $\lambda = 2.0$ at the $S/\langle S^2\rangle^{1/2} = 1.20$. It makes clear that the conformations at the large scale of S vanish faster than that at the small ones in the process of elongation. The reason may be that the root-mean-square of radius of gyration $\langle S^2\rangle^{1/2}$ increases in the process of deformation and the value of S is completely different at the same abscissa for different λ. At the same time, the changes of the gyration radius and the end-to-end distance do not synchronize. It is important that the conformations with large end-to-end distance may have small gyration radius, and small contribution to the sum of the Boltzman factor, defined by Eq. (9). For the case of 21-bond PM chain without elongation ($\lambda = 1.0$), we find that the values of $P(S)$ is almost the same in the range of $S/\langle S^2\rangle^{1/2} = 0.80$ to $S/\langle S^2\rangle^{1/2} = 1.15$ [29]. For the Gaussian chains, Flory and Fisk used the empirical relationship given by Eq. (13) to represent the probability function $P(S)$ [30]

$$P(S) = AS^6 \exp(-3.5S^2/\langle S^2\rangle) \tag{13}$$

where A represents a constant. In Fig. 4(b), we also plot $P(S)$ according to Eq. (13) as a function of $S/\langle S^2\rangle^{1/2}$ for the cases of $\lambda = 1.0$ and $\lambda = 2.0$, and there exists deviations between our simulation results and Flory and Fisk's function. Contrary to our calculations, the maximum value of $P(S)$ of Flory and Fisk's function decreases with elongation. The reason is that the mean-square of radius gyration decreases with λ. Those calculations may provide some insights into the microscopic of rubber-like elasticity.

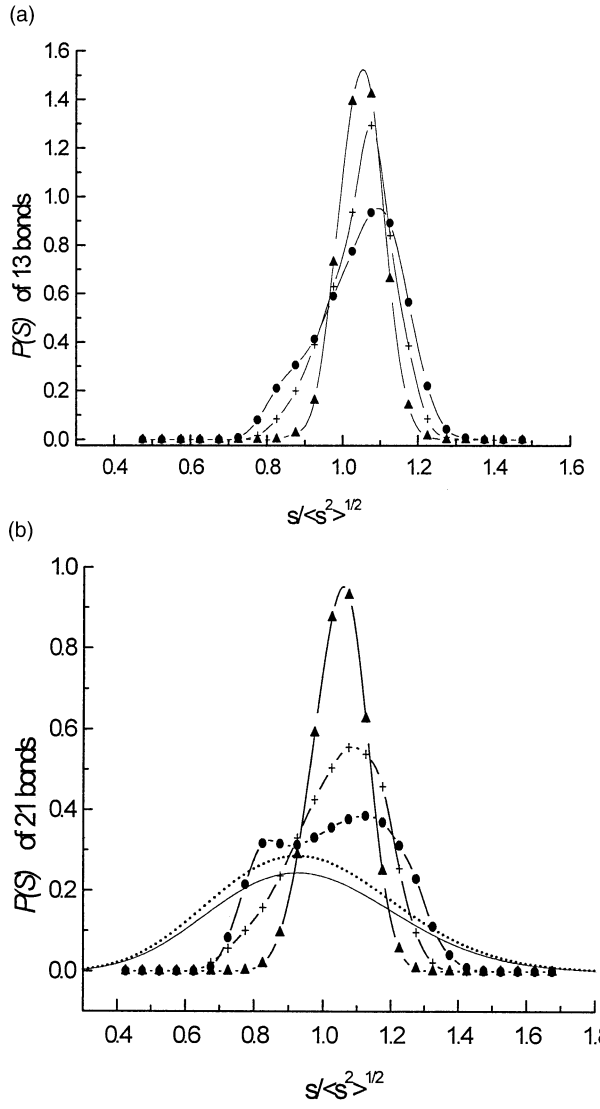

Fig. 4. Probability density distribution function $P(S)$ vs. $S/\langle S^2\rangle^{1/2}$ under various elongation ratio of PM chain with 13-bond (a) and 21-bond (b) at $T = 423$ K. Here (●), (+), and (▲) represent $\lambda = 1.0$, 1.5, and 2.0, respectively. The dot and solid lines are Flory–Fisk functions for 21-bond PM chain with $\lambda = 1.0$ and 2.0, respectively.

3.3. Orientation distribution function $P_2(\zeta)$ of deformed PM chain

More recent investigations show the segmental orientation is very important. Segmental orientation is relative to the statistical properties of polymer chains and it can be measured directly by using techniques such as NMR and infrared dichroism [31–33]. Recently, Taylor and Stepto used the MC method to interpret the orientation of PM networks in uniaxial deformation [34,35]. But they haven't considered the effects of chain length and the non-local interactions on segmental orientation. Here we deal with the orientation of short PM chains using the RIS model.

The segmental orientation is defined by Legendre

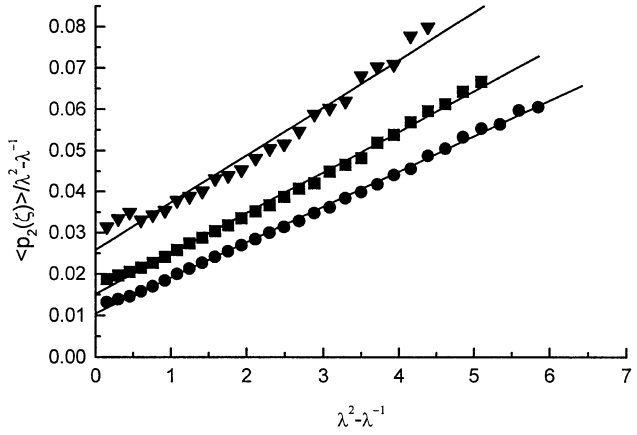

Fig. 5. The values of $\langle P_2(\zeta)\rangle/(\lambda^2 - \lambda^{-1})$ vs. $(\lambda^2 - \lambda^{-1})$ of PM chain at $T = 423$ K. Here (●), (■), and (▼) represent chains of 21, 17, and 13 bonds, respectively.

polynomial, and there is

$$\langle P_2(\zeta)\rangle = \left\langle \frac{1}{2}(3\cos^2\zeta - 1)\right\rangle \equiv \frac{\sum_i \frac{1}{2}(3\cos^2\zeta - 1)\exp(-E_i/RT)}{\sum_i \exp(-E_i/RT)} \quad (14)$$

where $\sum_i$ is the sum of the conformations without vanishing. ζ is the effective angle between a segment vector and the strain direction. We calculated the value of $\langle P_2(\zeta)\rangle$ of short PM chains with chain length from $N = 13$ to $N = 21$ using Eq. (14) at various elongation ratio λ (λ from 1.00 to 2.45), and the results are given in Fig. 5. In Fig. 5, we find that $\langle P_2(\zeta)\rangle/(\lambda^2 - \lambda^{-1})$ may be expressed in the form of

$$\langle P_2(\zeta)\rangle/(\lambda^2 - \lambda^{-1}) = a(\lambda^2 - \lambda^{-1}) + b \quad (15)$$

and the coefficients a and b only depend on PM chain length N. With increasing N, a and b decreases slowly (see Fig. 6). Roe and Krigbaum made the assumption that the chains of N bonds can be replaced by freely jointed (Gaussian) chains consisting of m links and $\langle P_2(\zeta)\rangle$ can be determined analytically as a function of deformation [20]. The Roe and Krigbaum's expression is

$$\langle P_2(\zeta)\rangle = \left(\frac{1}{5m}\right)(\lambda^2 - \lambda^{-1}) + \left(\frac{1}{25m^2}\right) \times (\lambda^4 + \lambda/3 - 4\lambda^{-2}/3) + \cdots \quad (16)$$

In Eq. (16), if m is large enough, $1/25m^2 \to 0$, this means that $1/25m^2(\lambda^4 + \lambda/3 - 4\lambda^{-2}/3)$ may be ignored. Therefore, the segmental orientation $\langle P_2(\zeta)\rangle$ becomes linear with $(\lambda^2 - \lambda^{-1})$ [34,35]. Here we only discuss the case of short PM chain considering excluded volume, $(1/25m^2)(\lambda^4 + \lambda/3 - 4\lambda^{-2}/3)$ can not be ignored, and have a complex relationship with elongation ratio λ. Our calculations show that the Kuhn and Grün model for the elasticity behaviors of rubbery network is not realistic and is very misleading in terms of

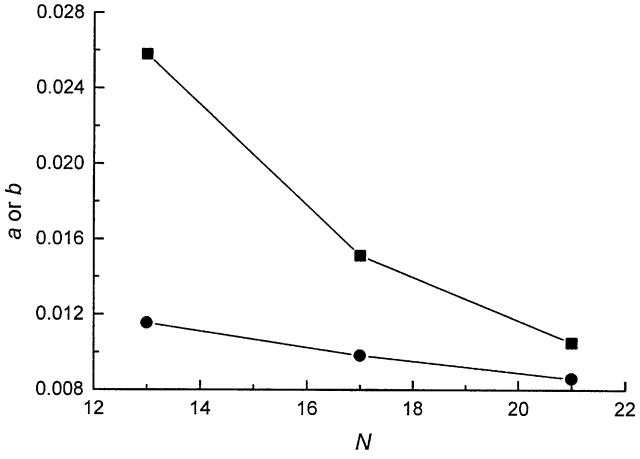

Fig. 6. The values of a (●) and b (■) vs. N for PM chain at $T = 423$ K.

physical understanding [36], and the segmental orientation of short PM chains are different from the Gaussian chains. The molecular orientation of long PM chains with considering non-local interactions and excluded volume will be discussed using MC method in the future.

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