

A CONFORMATIONAL ELASTICITY THEORY*

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Abstract A new statistical theory based on the rotational isomeric state model describing the chain conformational free energy has been proposed. This theory can be used to predict different tensions of rubber elongation for chemically different polymers, and the energy term during the elongation of natural rubber coincides with the experimental one.

Keywords Polymer; Conformation; Entropy; Elasticity

Most of the studies on rubber elasticity over the past seventy years or so are concentrated on how the conformation of polymer chains changes during rubber deformation. This has been realized to some extent but more remain unknown. To our knowledge, Gaussian chain model^[1,2] and some non-Gaussian chain models^[3,4] for athermal system were proposed in the 1930's~1940's, and scientists have continually made a lot of efforts on the network theories^[1,2,5~9] based on the above models. Therefore, these theories are athermal and independent of the chemical structure of polymer chains.

In the present study, we proposed a new theory — conformational elasticity theory, which describes conformational free energy of polymer chains at atomistic level. It is thus thermal and chemical structure dependent.

The frame of the theory is (1) the molecular model is the rotational isomeric state (RIS) model^[10]; (2) the conformational distribution function of a chain molecule, $P(R, E)$, is described as a function of two variables, namely the end-to-end distance of a chain conformation and the energy of the conformation; (3) the rule of changes in the conformational distribution function during deformation is that a number of chain conformations would vanish.

From the conformational distribution function, the partition function of the system can be expressed as

$$Z = \int_0^{R_{\max}} \int_{E_{\min}}^{E_{\max}} P(R, E) e^{-E/kT} dR dE \quad (1)$$

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and Helmholtz free energy can be simply obtained:

$$A(r) = -kT \ln[Z(r)] \quad (2)$$

Under a constant temperature and a constant volume, the work, which is resulted from a change of distance r , is equal to the derivative of Helmholtz free energy. Stress of the system during deformation will be calculated from derivatives of the conformational free energy to the strain.

We use the frame under the ideal deformation, which obeys (1) a network consists of chains with the same length and every chain end must be located at a junction of the network; (2) the end-to-end distances of the chains in the network distribute as well as polymer chains in bulk; (3) the vectors of the end-to-end distances of all chains in the system align themselves along X , Y , Z axes respectively; and (4) a deformation along one of the axes must independently decrease the number of chain conformations. The molecular deformation mechanism proposed here is the affine condition.

The elongation ratio λ_s and the compression ratio λ_c are obtained from the root-mean-square of the end-to-end distance $\langle R^2 \rangle^{1/2}$, and the longest end-to-end distance $R_{\max}$ based on the conformational distribution function of the polymer system. Therefore we have

$$\lambda_s = \frac{r + \langle R^2 \rangle^{1/2}}{\langle R^2 \rangle^{1/2}} \quad \text{and} \quad \lambda_c = \frac{R_{\max} - r}{R_{\max}} \quad (3)$$

Considering the volume of the system is incompressible, assuming the total stress is contributed from an average value of the modulus and the strain along X , Y , Z axes respectively. Now, we have the stress of the system as

$$\sigma = \frac{1}{3} \sum_{\alpha} G_{\alpha} \lambda_{\alpha}, \quad (\alpha = X, Y, Z) \quad (4)$$

In the case of simple elongation, $\lambda_X = \lambda$; $\lambda_Y = \lambda_Z = (\lambda)^{-1/2}$, the stress-strain curve of poly(*cis*-1, 4-isoprene) with 20 backbone bounds was obtained, as shown in Fig. 1. It shows a very different feature from that obtained by Gaussian chain theory. The stress for the elongation ratio above 50% of the whole range still ascends quickly.

In Fig. 1, the calculated value for the small-scale deformation is about 20 ~ 30 N/mm², and for the strain state of 60% of the whole stretching range is about 60 N/mm². As compared with the experimental data^[11], ~ 14 N/mm², which is obtained from a more efficient network cross-linked by the vulcanization and the

mastication with carbon black, one may find that the value is about four times larger. The calculated tension appears relatively so large and this is due to the interaction between chain segments in the real system, which is not as efficient as that in the affine condition to hold the chain ends in moving.

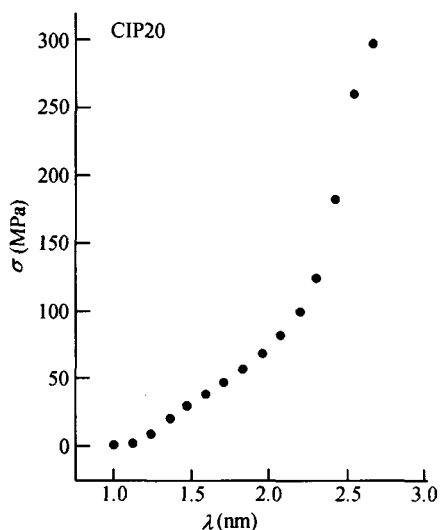


Fig. 1 The stress-strain curve of poly(*cis*-1, 4-isoprene) predicted by the present theory

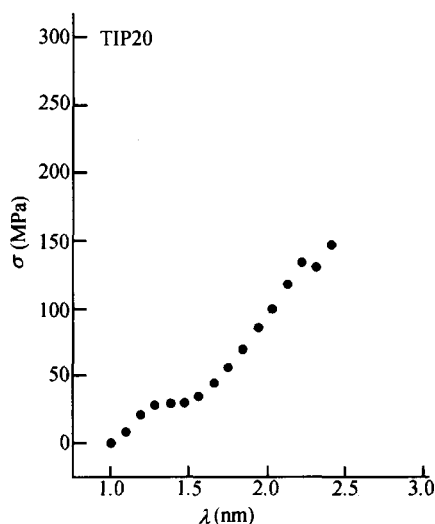


Fig. 2 The stress-strain curve of poly(*trans*-1, 4-isoprene) predicted by the present theory

The stress-strain curve of poly(*trans*-1, 4-isoprene) with 20 backbone bonds appears quite different. Even though non-Gaussian theories can describe the large-scale deformation, they yet have no such ability, like the present theory, to predict the difference of deformation behaviors for different polymers. As data indicate, when $\lambda = 2$, it is about 75 N/mm^2 for the *cis*-polymer and $\sim 100 \text{ N/mm}^2$ for the *trans*-polymer. The tension of *trans*-polymer, therefore, is almost 1.3 times of the *cis*-polymer. This feature even appears at the beginning stage $\lambda < 1.2$ (Fig. 2), where the tension for *trans*-polymer is remarkably larger than that for the *cis*-polymer. Experimentally, this feature was possibly observed in a study of the rubbery state of the guttapercha by Qian et al.^[12]

Since the conformational distribution function includes the conformational energy, the energy term of the elastic force can be calculated by using the present theory. Historically, the contribution of conformational energy to the rubber deformation is calculated theoretically for the first time. For poly(*cis*-1, 4-isoprene), the energy elastic contribution, or the fraction of the energy term to the total force f_e/f , can be obtained of ~ 0.13 . It is coincided with the experimental data ~ 0.13 ^[13], and in between the observations ~ 0.20 ^[14] and 0.11 ^[15] for natural rubber. It is

obviously a reasonable value predicted by the present theory. This result proves that the process of rubber elastic deformation is predominated by the mechanism in terms of the conformational elasticity theory.

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