

Rapid Communication

CHEMICAL STRUCTURE DEPENDENCE OF THE INTERNAL ENERGY
CONTRIBUTION IN RUBBER ELASTICITY*

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Abstract Conformational elasticity theory recently developed has been used to explore the internal energy contribution to the elastic force f_e/f as a function of strain for poly(*cis*-1,4-isoprene) and poly(*trans*-1,4-isoprene). Calculated f_e/f values are in good agreement with those obtained experimentally. Results show that behavior of f_e/f is mainly contributed by chemical structure, or intramolecular interaction, supporting the experimental observations, and that the internal energy contribution is strain dependent.

Keywords Conformational elasticity theory, Internal energy contribution, Poly(*cis*-1,4-isoprene), Poly(*trans*-1,4-isoprene)

For a long time, it was assumed that rubber elasticity originated only from the change in entropy, and the contribution of internal energy to the elasticity f_e/f was zero. However, experimental results show that f_e/f is not zero^[1] and f_e/f is different for different elastomers^[2]. Such facts suggest that this value is chemical structure dependent. However, whether the ratio f_e/f is strain dependent remains in dispute. Flory^[3], Shen^[4] and Allen^[5] thought that the ratio f_e/f is independent of the degree of deformation in small and moderate deformation, while Roe^[6] and Gent^[7] thought that f_e/f is dependent on the degree of deformation. Unfortunately, both Gaussian statistical theory^[8, 9] and non-Gaussian statistical theory^[10] are athermal and chemical structure independent, and both theories cannot provide in principle the possible dependence of f_e/f on the chemical structure and the amount of strain.

“Conformational elasticity theory”^[11, 12] has recently been proposed by our group. It is based on the rotational isometric state (RIS) model and affine deformation. It is assumed that the total internal energy consists of local conformation interaction only and the intermolecular interaction is omitted. The chain conformational distribution function obtained from this theory is a function of both the conformational energy and the end-to-end distance. This theory is thermodynamic and chemical structure dependent, thus providing the opportunity to clarify the classical argument about the internal energy contribution. In the preceding work, we used the theory to obtain the stress-strain curves^[11, 12] and the averaged f_e/f for poly(*cis*-1,4-isoprene) and poly(*trans*-1,4-isoprene) successfully. In the present work, we concentrated on exploring the nature of f_e/f and its strain dependent behavior in the case of the two polymers mentioned above.

The polymer models studied here consist of six repeating units with 24 bonds. The structural parameters, energy information, calculated contour maps and calculated stress-strain curves for poly(*cis*-1,4-isoprene) and poly(*trans*-1,4-isoprene) are the same as those used or obtained in the preceding paper^[12]. The temperature for the ensemble average is 300 K.

Figure 1 shows the obtained change of energy elastic force with normalized strain for poly(*cis*-1,4-isoprene)

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and poly(*trans*-1,4-isoprene), respectively. The calculated f_e curve for poly(*cis*-1,4-isoprene) is the same as the early one^[12] and quite close to that reported in Anthony's experiment^[1]. However, differences appear in the last stage, where the experimental curve does not rise like the predicted one. This is due to the fact that the chain is experimentally not stretched as long as the calculated one. Therefore, before 85% of normalized extension ratio the behavior of the internal energy elastic force is close to experimental data, which proves that the theory we used is rational. The energy elastic force curve for the *trans*-polymer appears different and is firstly provided. In the range of 50%–80%, f_e assumes negative values. This indicates that for large deformation, the *trans*-polymer releases much energy while the *cis*-polymer absorbs much energy. Difference between the two polymers in their energy elastic force profile is obviously due to their different chemical structures.

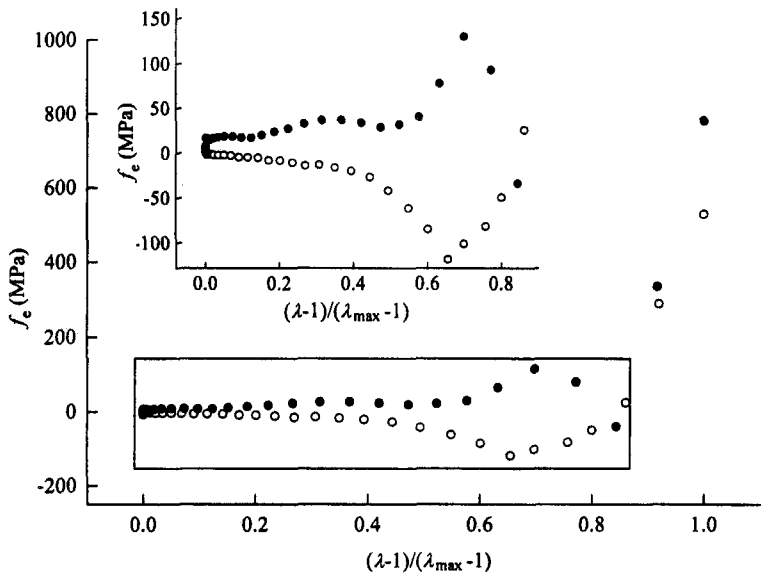


Fig. 1 The energy elastic force for poly(*cis*-1,4-isoprene) ● and poly(*trans*-1,4-isoprene) ○
Top: Experimental; Bottom: calculated

Figure 2 shows the energy contribution to the elastic force f_e/f as a function of strain for these two polymers. The value of f_e/f is mostly positive for the *cis*-polymer but mainly negative for the *trans*-polymer. Conventionally, the value of f_e/f is an average of several measurements, and the averaged value is somewhat a rough one, since it depends on the range used in averaging. Even though Flory did not presume that f_e/f depends on the strain^[3], there are still exist different opinions from Flory's viewpoint^[6, 7]. Usually the value obtained experimentally was at small or moderate deformation. For the *trans*-polymer, when the calculated f_e/f is averaged at small and

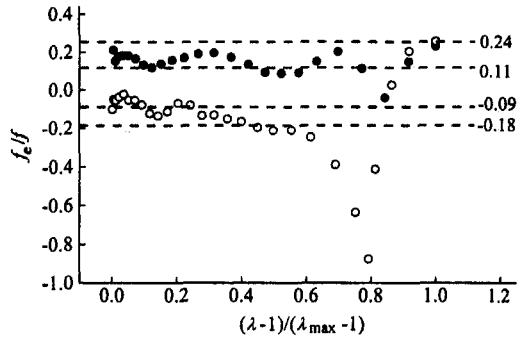


Fig. 2 The internal energy contribution to the elastic force for poly(*cis*-1,4-isoprene) ● and poly(*trans*-1,4-isoprene) ○

moderate deformation, the value is ca. -0.1 . If the strain range averaged is extended to 85%, the value becomes ca. -0.17 and the value averaged over the whole strain range is ca. -0.15 . The values reported by others are from -0.18 to -0.09 ^{2, 7} for poly(*trans*-1,4-isoprene). These relatively consistent results indicate that the curves behavior predicted are f_e/f is reasonable.

The same situation occurs with the *cis*-polymer. As predicted in Fig. 2, one may obtain an averaged f_e/f value of either ca. 0.2 or ca. 0.1 at small or moderate deformation. If the average is over the whole strain range, the value will be ca. 0.15 . These calculated data lies within the range of 0.11 to 0.24 obtained experimentally³⁻⁷. Due to the complexity of chemical cross-links and the entanglements, it is very difficult to stretch samples of different origins to the same elongation on a molecular level. In other words, the draw ratio obtained macroscopically for a sample may not be the right measure microscopically. Different samples may disobey the affine condition to different extents. Such departure from affine condition will lead to considerable error on the location along the elongation axis. However, these observed values f_e/f provide important evidence of the reasonable range of f_e/f , for example, 0.11 – 0.24 for the *cis*-polymer and -0.18 to -0.09 for the *trans*-polymer. The range of the data is positively valid to explain the curvy behavior of predicted f_e/f for both polymers.

The present study shows that conformational elasticity theory supports the idea that the value of f_e/f is dependent on the strain, and could well interpret those experimental data. Therefore, the internal energy contribution surely depends on chemical nature of the polymers.

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