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Relation between Energy Contribution to Elastic Force and Strain Dependence of Modulus for Polybutadiene Vulcanizates

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SUMMARY

It is well known that the modulus $G = \tau/(\lambda - \lambda^{-2})$ varies with deformation, thus deviating from the predictions of statistical theories of rubber elasticity which require it to be constant. It has also been found that there is a nonnegligible energy contribution to the elastic force. It is postulated that these two phenomena are related because both arise from energetic interaction between chains.

Based on the lateral order of chains indicated by x-ray fiber diagrams of elongated noncrystallizable elastomers, it is suggested that energetic interaction of chains is induced by strain orientation. Proportionality between these two is assumed. The orientation distribution functions of end-to-end vectors and of statistical chain segments are considered. The proportionality constants are determined from the energy contribution to the strain dependence of the coefficient of thermal expansion. With the aid of these constants the modulus, corrected for energy contribution, is calculated. The observed and calculated elongation dependence of G agree reasonably well.

It is concluded that an energy interaction between aligned chains can account for the deviation of the observed stress elongation relation from the predictions of entropy elasticity theories.

INTRODUCTION

The resistance to deformation of elastomer vulcanizates arises mainly from the decrease in configurational entropy of flexible polymer chains interconnected to form a three-dimensional chain network. On deformation there are also changes in the energy of the network which lead to an energy contribution f_e, to the total elastic force f. For a variety of polymers the ratio $f_e/f = \varphi_e$ has been found to be a function of the degree of deformation.

Energy contributions may arise from two sources: intra- and interchain interaction energies. The latter vary with degree of deformation; the former are independent of strain as long as the end-to-end distances of the chains do not approach their contour lengths. It has recently been established for natural rubber that at small elongations ($< \sim 50\%$) φ_e does not depend on deformation nor on the presence of a diluent [1, 2]. These observations strongly support the assumption that φ_e is mainly attributable to intrachain energies. The data reported here confirm this postulate for cis-1,4-polybutadiene in the same region of strain.

The results on natural rubber referred to above were obtained from accurate measurements by a method of analysis that is much less sensitive to inevitable experimental errors than the conventional method used in earlier reports. In particular the sensitivity of values of φ_e to the rest-length (l_o) of the sample, a quantity difficult to measure accurately, was much reduced. For some polymer networks, however, an appreciable decrease of φ_e with increasing strain has been observed at high extensions where the influence of experimental errors in l_o is negligible [3, 4]. This dependence has not yet been explained satisfactorily.

This report considers the possibility that the energy contribution to the elastic stress at high elongations ($>100\%$) results from an energy interaction between sections of polymer chains. Such interaction becomes more and more likely when, on deformation, the fraction of chain sections oriented in near parallel directions increases with strain-induced anisotropy. It is worth considering this source of an energy contribution to the elastic force because strain induced crystallization is a well-known phenomenon. Furthermore, the halo in x-ray fiber diagrams of such noncrystallizable copolymers as those of isoprene/acrylonitrile [5], styrene/butadiene [6], and butadiene/acrylonitrile [6] contract to strong equatorial reflections on stretching. The two symmetrical dots in the x-ray photographs cannot be due to chain orientation alone. This strain-induced orientation must be accompanied by lateral ordering which results from interaction between chains.

Statistical theories of elasticity deal with the entropy component of elastic forces. They predict a constant value of the ratio $\tau/\lambda - \lambda^{-2}) = G$, for convenience called modulus. Here τ is the stress per undeformed cross section and λ is the ratio of deformed to undeformed dimensions in the direction of deformation. It has, however, been found that G varies with λ, particularly in extension and to a lesser extent in compression. This dependence of G on λ is often expressed by the value of C_2 in the Mooney-Rivlin equation [7, 8]:

$$G(\lambda) = \tau/(\lambda - \lambda^{-2}) = 2C_1 + 2C_2\, \lambda^{-1}; \qquad C_1, C_2 \text{ are constants} \tag{1}$$

which is based on continuum elasticity theory. It has been postulated that variation in $G(\lambda)$ and occurrence of an energy contribution are related [9]. This is also done here.

In this paper thermoelastic data and stress elongation relations will be reported on polybutadiene vulcanizates that exhibit a strong dependence of G on λ (large C_2 values). A correlation between these two sets of independent results is suggested. The energetic elastic force is attributed to an association between chain sections brought about by strain orientation. The fraction of polymer engaged in association depends on the degree of orientation. A simple relation between degree of association and orientation will be assumed. This relation contains a single parameter which is calculated from the thermoelastic data. Its value is then used to calculate stress-strain relations which are compared with the experimental stress-strain curves.

THEORETICAL

The relative energetic elastic force is defined by the equation:

$$\varphi_e = 1 - \left(\frac{T\delta f}{f\delta T}\right)_{V,l} = 1 - \left(\frac{\delta \ln f}{\delta \ln T}\right)_{V,l} \tag{2}$$

where f is the elastic force and V and l are the volume and the length of the sample. For measurements of φ_e the condition of constant volume in Eq. (2) present severe experimental difficulties. Therefore, most investigators have preferred to obtain thermoelastic data under conditions of constant pressure and have relied on the following relation derived by Flory et al. [10] to obtain numerical values of φ_e:

$$\varphi_e = 1 - \left(\frac{\delta \ln f}{\delta \ln T}\right)_{p,l} - \frac{\beta T}{\lambda^3 - 1} \tag{3}$$

Here β is the thermal volume expansion coefficient, the value of which does not vary with elongation [11]. In the derivation of Eq. (3) it is assumed that G is independent of deformation. It is known that this is the case for small deformations only ($\lambda < \sim 1.3$). In this region values of φ_e are sensitive to λ and, therefore, to l_0 due to the form of the denominator of the last term in Eq. (3).

Shen et al. [1, 2] have pointed out that the following expression for φ_e is less sensitive to experimental errors:

$$\varphi_e = 1 - \frac{d \ln G(1)}{d \ln T} - \alpha(1)T \tag{4}$$

Here $\alpha(1)$ is the linear thermal expansion coefficient at constant stress in the direction of elongation at $\lambda = 1$.

The symbol G(1) refers to the shear modulus at $\lambda = 1$, i.e., $G(1) = \lim \lambda \to 1\ G(\lambda)$. By definition this quantity is independent of sample volume and deformation, which justifies the use of total differentials in Eq. (4). The differential term can be readily evaluated from experimental data with the aid of the following expression derived by Shen et al. [1, 2]:

$$\alpha(\lambda) = \alpha(1) - \left[\frac{d \ln G(1)}{dT} + 2\alpha(1)\right] \Big/ \left[\frac{\lambda^3 + 2}{\lambda^3 - 1}\right] \tag{5}$$

Equations (4) and (5) are subject to the same restrictions as Eq. (3); particularly, their validity is confined to the region of small deformations where G is constant. On the basis of the experimental observation that $G(\lambda)$ is smaller than G(1) for λ larger than about 1.3, we now introduce an as yet unspecified function $f(\lambda)$ with values between 0 and 1 such that

$$G(\lambda) = \{1 - f(\lambda)\}G(1) \tag{6}$$

With this additional strain dependent factor the relation between $\alpha(\lambda)$ and $\alpha(1)$ becomes:

$$\alpha(\lambda) = \alpha(1) - \left[\frac{d \ln G(1)}{dT} + 2\alpha(1)\right] \Big/ \left[\frac{\lambda^3 + 2}{\lambda^3 - 1} - \frac{\lambda\{df(\lambda)/d\lambda\}}{1 - f(\lambda)}\right] \tag{7}$$

Let $f(\lambda)$ contain an adjustable parameter. We now determine the value of this parameter that gives the "best" fit of the theoretical relation expressed in Eq. (7) to experimental values of $\alpha(\lambda)$. With the aid of this value the correctness of the choice of $f(\lambda)$ can now be judged by comparing values of $G(\lambda)/G(1)$ calculated from $f(\lambda)$ and Eq. (6) with experimental data.

The choice of $f(\lambda)$ is based on an assumed interaction of secondary forces between chain sections which are directionally ordered as a result of strain orientation. It must be assumed that this association between sections is dynamic in character since any permanent bonding between chains would severely restrict chain configurations and hence would require a strong increase in the entropic part of the elastic force contrary to observations. The interaction is envisaged to be a partial satisfaction of attractive forces between near parallel chain sections that thus lose some of their kinetic energy. Hence, the elastic forces relax.

The dimensions of the volume elements in which interactions occur must be smaller than the critical size of nuclei capable of spontaneous crystalline growth because no crystallites are observed by x-ray analysis except under extreme conditions of high estensions and low temperatures (see Experimental section). No measurements were conducted under these conditions. Furthermore, the fact that virtually no stress relaxation is observed is a strong indication of the absence of supercritical size nuclei (see next section).

The length of the chain sections that become directionally oriented on deformation must necessarily lie between two extremes, viz., the length of about a monomer unit and that of the end-to-end vectors of network chains. The strain dependence of the orientation distribution of the vectors is known, and also that of the statistical chain segments of the freely jointed equivalent chain model the length of which is only a few times that of a monomer unit. In the absence of a detailed picture on a molecular scale of the interactions considered, it is simply assumed that the relaxation of the elastic force is proportional to the degree of strain-induced orientation $F(\lambda)$. Mathematically: $f(\lambda) = cF(\lambda)$, where c is a constant.

For end-to-end chain vectors the orientation distribution has been derived by Treloar [12]. It is described by the following relation:

$$dN_V/d\theta = \tfrac{1}{2}N_V(\lambda^{-2}\cos^2\theta + \lambda\sin^2\theta)^{-\frac{3}{2}}\sin\theta \qquad (8)$$

Here N_V is the number of vectors and θ is the angle between vector and extension direction. The shape of this distribution in the form $g_V(\lambda) = (dN_V/d\theta)_\lambda/(dN_V/d\theta)_1$ is shown in Fig. 1 for $\lambda = 1.5$. The area for $g_V > 1$

$$F_V(\lambda) = \int_0^{\omega_V} [g_V(\lambda) - 1]\,d\theta \qquad (\lambda > 1) \qquad (9)$$

is considered to be a measure of the strain-induced orientation of end-to-end vectors. It may also be argued that the integral in Eq. (9) should be taken

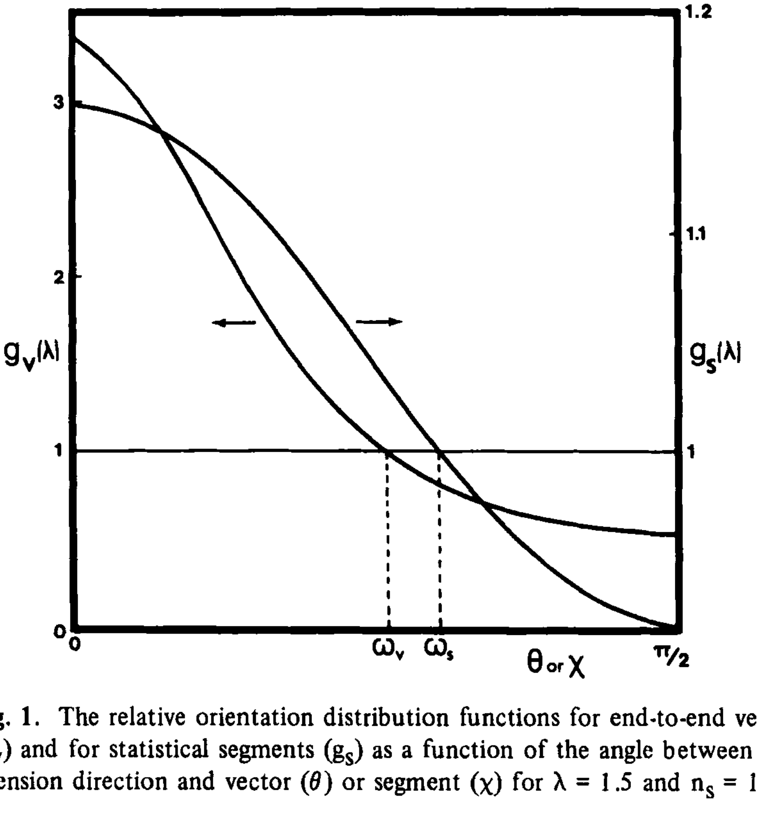

Fig. 1. The relative orientation distribution functions for end-to-end vectors (g_V) and for statistical segments (g_S) as a function of the angle between extension direction and vector (θ) or segment (χ) for $\lambda = 1.5$ and $n_S = 100$.

between the limits 0 and $\pi/2$ on the basis of a nonnegligible interaction energy of the type considered here in the undeformed state. Calculations show that it makes little difference which upper limit, ω or $\pi/2$, is assigned to the integrals in Eqs. (9) and (11) because the value of c is evaluated from data at high extensions where the negative area between ω and $\pi/2$ is much smaller than the positive area between 0 and ω.

The orientation distribution function of statistical segments has been derived by Roe and Krigbaum [13]. It is expressed by the following set of equations:

$$dN_S/d\cos\chi = N_S \sum_{l=0}^{\infty} w_l P_l(\cos\chi) \tag{10}$$

$$w_l = 2\pi\left(\frac{2}{2l+1}\right)^{1/2} \int_{-1}^{+1} c_l \frac{\lambda^3 P_l(\xi)d\xi}{2\{\lambda^3 - \xi^2(\lambda^3 - 1)\}^{3/2}}$$

$$C_l = \int_{-1}^{+1} f(\zeta)\, P_l(\zeta)\, d\zeta$$

$$f(\zeta) = \frac{\beta}{4\pi \sinh \beta} \exp(\beta\zeta)$$

$$\beta = \mathcal{L}^{-1}\left(\lambda/\{\lambda^3 - \xi^2(\lambda^3 - 1)\}n_s^{1/2}\right)$$

Here N_s is the number of statistical segments, n_s is the number of statistical segments per chain, χ is the angle between segment and extension direction, P_l are normalized Legendre polynomials, and $\mathcal{L}^{-1}$ is the inverse Langevin function. The other symbols are auxiliary mathematical variables. Most of the data given below result from measurements on networks for which $\sim 50 < n_s < \sim 150$. These values of n_s were determined from the position of the upswing in Mooney-Rivlin plots. In this report n_s is taken to be 100. As long as n_s is relatively large the results are very insensitive to the value of n_s adopted. The shape of the distribution function $g_s(\lambda) = (dN_s/d\cos\chi)_\lambda/(dN_s/d\cos\chi)_1$ for $\lambda = 1.5$ and $n_s = 100$ is also shown in Fig. 1. The area

$$F_s(\lambda) = \int_0^{\omega_s} [g_s(\lambda) - 1]\, d\chi \qquad (\lambda > 1) \tag{11}$$

is taken to measure the strain-induced orientation of chain segments. In the discussion both $f_v = c_v F_v(\lambda)$ and $f_s = c_s F_s(\lambda)$ will be used in conjunction with Eqs. (6) and (7) to assess the validity of the assumption of an energy interaction proportional to the degree of orientation.

It is appropriate here to remind the reader than chain orientation also influences the entropic part of the elastic force, but this effect is taken into account in the statistical theories of elasticity. Second, orientation affects the competition of chain segments for space (packing entropy). DiMarzio [14] has discussed the deformation dependent part of the configurational energy arising from this competition. From his quantitative treatment of this effect it can be concluded that for $n_s = 100$, $G(2)/G(1) = 0.99 - 0.98$. The experimental values for this ratio are, however, much smaller.

EXPERIMENTAL

Polymer and Vulcanizates

The polybutadiene used is characterized by the following data: cis-1,4 content 92.8%; intrinsic viscosity (toluene, 30°C) 3.57 dl/g; M_n 3.0 X 10^5. The vulcanization with dismethylazodicarboxylate of sheets obtained by evaporation of solvent from solutions cast onto a mercury surface has been described [15]. The chain concentrations were calculated from the concentrations of the cross-linking agent [15].

Thermoelastic Measurements

Samples in the shape of common commercial rubber bands were suspended by means of Teflon rings with U-shaped cross sections in the center tube of a condenser. The upper ring was attached to the pan of an automatic analytical balance and the lower ring was connected to a small laboratory jack. A stream of dry nitrogen was maintained through the condenser center tube. Constant temperature water was pumped through the outer tube of the condenser. Further details of the procedure can be found in Ref. 15.

The samples were allowed to relax at the desired elongation ϵ for at least 16 hr. Then the stress was measured at 4 to 7 elongations in the range $(1 \pm 0.02)\epsilon$. These sets of measurements were repeated at seven different temperatures in the range -20 to 40°C. Stress and temperature equilibrium is reached in time periods less than ¼ hr. Measurements at any one temperature were always concluded in less than 1½ hr. Experiments could be conducted at temperatures lower than the crystallization temperature of the polymer because the rate of crystallization at the temperatures applied here is negligibly small. This can be verified by calculations based on the data published by Mitchell [16].

It is easy to detect strain-induced crystallization because it results in relatively fast stress relaxation. This is shown in Fig. 2 for $\lambda = 3.5$. Crystallization was confirmed by x-ray analysis for the stretched samples exposed for ¼ hr at -18.6°C and for 1 hr at -10.2°C. No crystallinity could be detected by this method in the sample elongated for 24 hr at 3.4°C. Measurements at temperatures equal to or higher than 3.4°C only were made for $\lambda = 3.5$. No stress relaxation was observed for samples extended to 250% at the lowest temperature (– 16°C) imposed.

The results are not affected by the sequence of variations in elongation (see Fig. 3) nor by the order in which the temperature was varied. This is shown in Fig. 4. Note that time lapse between measurements varied from

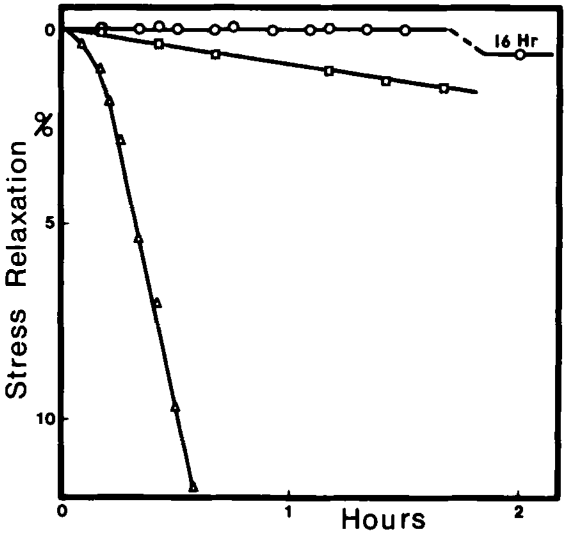

Fig. 2. Stress relaxation as a function of time. Extension ratio 3.5. Chain concentration 0.070 mole/1. Temperature: (○) -18.6, (□) -10.2, and (△) +3.4°C.

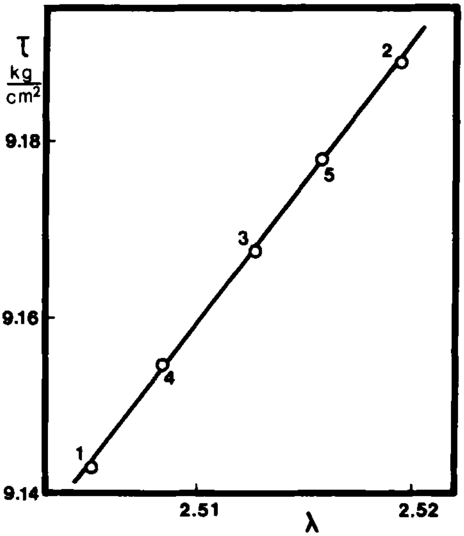

Fig. 3. Stress vs. strain. Chain concentration 0.074 mole/l. Temperature -0.7°C. The numbers indicate the sequence of the measurements.

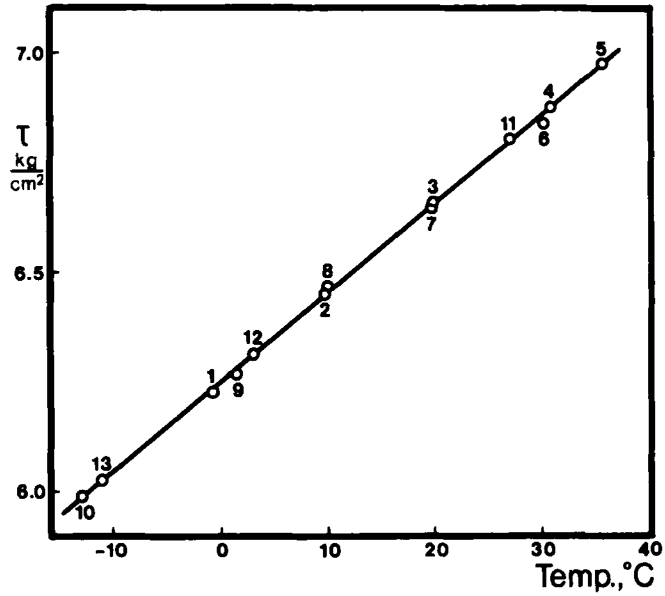

Fig. 4. Stress vs. temperature. Extension ratio 1.94. The numbers indicate the sequence of the measurements. Time interval between consecutive measurements 10-60 min except between Points 9 and 10 where the time interval is 16 hr.

10 min to 1 hr; that between measurements 9 and 10 was 16 hr. Immediately after an experiment the samples exhibited some set but after a few days even the weakest cross-linked samples, which had been extended to high elongations, regained their original lengths to within a few tenths of 1%. No differences were found in swelling ratios of the samples determined before and after the mechanical measurements.

Typical results are shown in Fig. 5. Pairs of λ values were determined at a selected stress value from least squares lines through each two sets of data at consecutive temperatures. The thermal expansion coefficient was calculated from the slope of the least square line through the points in a plot of $\Delta\lambda$ vs. ΔT. The expansion coefficient of unstretched samples was determined from the variation of length with temperature of samples floating on mercury with the aid of a traveling microscope.

The results are tabulated in Table 1. The calculations were performed with an IBM 360 Model 75 computer.

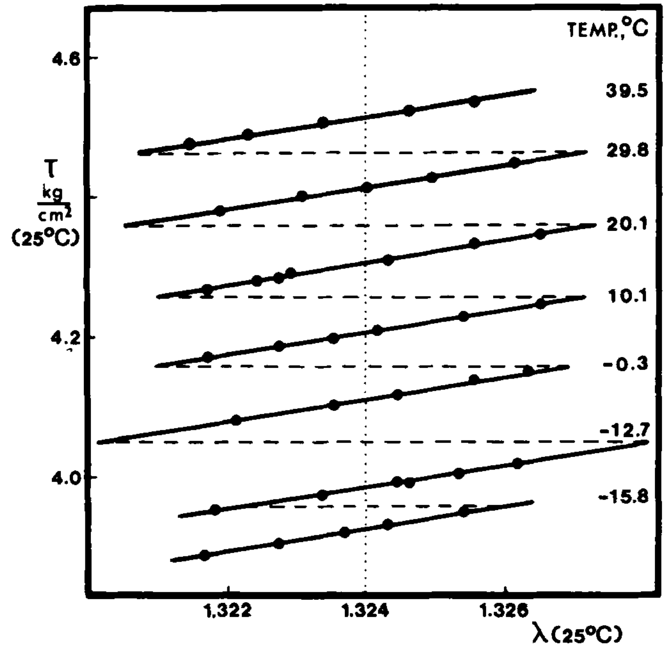

Fig. 5. Stress vs. strain (both calculated on the basis of sample dimensions at 25°C). Time interval between measurements 10 min. Chain concentration 0.070 mole/l.

Stress-Strain Measurements

The apparatus and the procedure used to obtain stress-strain data have been described [15].

RESULTS AND DISCUSSION

Two vulcanizates of cis-1,4-polybutadiene were used. Samples A and B had chain concentration $[\nu]$ of 0.070 and 0.130 mole/l, respectively. The experimental values of $\alpha(\lambda)$ at low extensions are plotted in Fig. 6 in the form suggested by Eq. (5), viz., $\alpha(\lambda)$ vs. $(\lambda^3 - 1)/(\lambda^3 + 2)$. From the intercepts and the slopes of the least squares lines through the data points in Fig. 6 the following values of φ_e were calculated with the aid of Eqs. (4) and (5): A, $\varphi_e = 0.25 \pm 0.04$ (standard deviation); B, $\varphi_e = -0.03 \pm 0.06$.

Table 1. Linear Expansion Coefficient $\alpha(\lambda)$ of cis-1,4 Polybutadiene as a Function of Extension Ratio

$[\nu]$[a]	λ[b]	$\alpha(\lambda) \times 10^4$	$[\nu]$	λ	$\alpha(\lambda) \times 10^4$
0.070	1	1.99	0.116	1	2.04
	1.025	1.15			
	1.063	0.23			
	1.119	-1.38	0.130	1	2.06
	1.324	-6.53		1.013	1.78
	1.551	-12.3		1.034	0.78
	1.767	-15.8		1.106	-2.02
	2.101	-22.6		1.311	-8.99
	2.512	-32.4		1.502	-14.2
	2.514	-33.6		1.890	-26.0
	3.554	-66.8			

[a] $[\nu]$, Chain concentration, mole/l, 25°C.
[b] λ, Extension ratio, 25°C.

Other values for a cis-1,4-polybutadiene network were calculated from the data shown in Fig. 2 of Ref. 2 (temperature, 30°C). The values of φ_e found were 0.32 and 0.16 for vulcanizates obtained by cross-linking with 0.5% and 1-4% dicumylperoxide, respectively. These values differ somewhat from those reported here. These differences may well be due to the type of curing agents used which are known to affect the mechanical properties of vulcanizates [15].

In Fig. 7 the results for higher extensions have been included. For Vulcanizate B no results could be obtained at $\lambda > 1.9$ because samples broke repeatedly during the 16-hr period of relaxation preceding the measurements. Large deviations from the initially linear relation between $\alpha(\lambda)$ and $(\lambda^3 - 1)/(\lambda^3 + 2)$ are observed. These deviations correspond to a large decrease in φ_e to negative values at high elongations. Values of φ_e less than zero have been reported for natural rubber [17]. For this polymer these values clearly result from strain-induced crystallization. This is not the case here (see Experimental section).

The constants c_v and c_s in $f(\lambda) = cF(\lambda)$ with F given by Eqs. (9) and (11) were calculated with the aid of a computer to give curves representing the relation expressed in Eq. (7), which "best" fit the experimental data in Fig. 7. The methods used to evaluate the function $F(\lambda)$ and $dF(\lambda)/d\lambda$ are

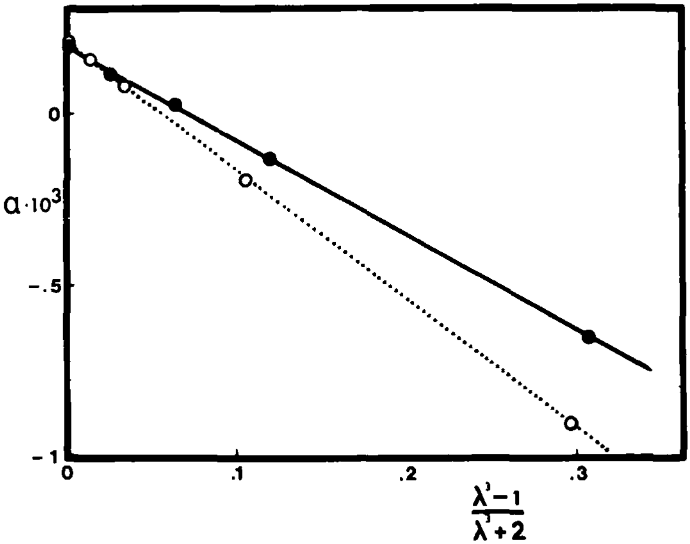

Fig. 6. Linear thermal expansion coefficient versus $(\lambda^3 - 1)/(\lambda^3 + 2)$. Chain concentration (●) 0.070, and (○) 0.130 mole/l.

given in the Appendix. Thus values of $c_V = 0.0944$ and $c_S = 9.11$ were found. The corresponding curves of $\alpha(\lambda)$ are drawn in Fig. 7. These similarly shaped curves are indistinguishable from the straight lines through the data points up to extension ratios of about 1.4. The lines then curve to large negative values of α following the data points, to which they have been fitted with a single adjustable parameter, closely.

In Fig. 8 experimental results of $G(\lambda)/G(1)$ are shown in a Mooney-Rivlin type plot for 10 vulcanizates with chain concerntrations ranging from 0.04 to 0.13 mole/l. For G(1) the average value of G was taken from 4 to 6 measurements in the range of 2 to 7% elongation. The curves have been drawn according to Eq. (6) with both $f(\lambda)$ functions relating to vector or chain segment orientation. It is to be noted that most results fall between the curves G_V and G_S. The data points are in reasonable agreement with the Mooney-Rivlin relation (Eq. 1). This relation holds in the region of λ^{-1} between about 0.3 to 0.7. For extension ratios larger than about 3 to 4 the finite extensibility of the network chains comes into play, giving rise to values of G larger than corresponds to the Mooney-Rivlin equation. Accurate measurements at elongations smaller than about 30 to 40% lead to the conclusion that G is constant at low extensions. These experiments were done

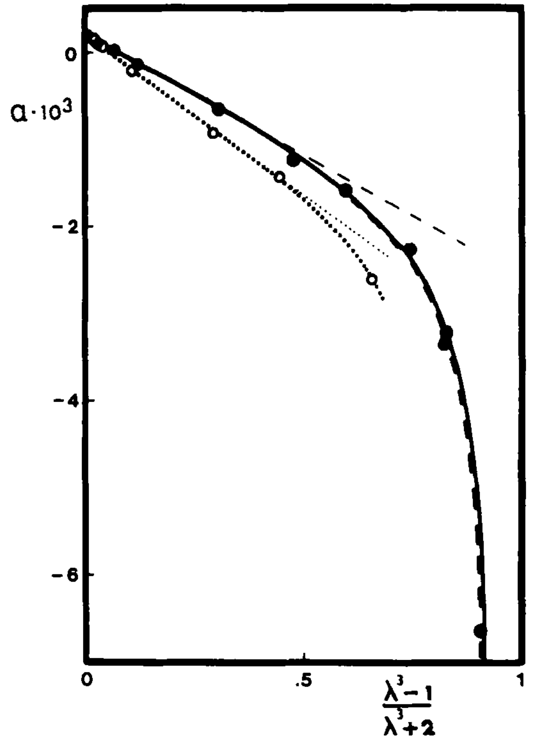

Fig. 7. Linear thermal expansion coefficient versus $(\lambda^3 - 1)/\lambda^3 + 2)$. Chain concentration: (●) 0.070 and (○) 0.130 mole/l. (——) Calculated from Eq. (7) and the end-to-end vector distribution function, $c_V = 0.0944$. (- -) calculated from Eq. (7) and the chain segment distribution function, $c_S = 9.11$.

with five different types of vulcanizates; some of the results have been published [15, 18].

In comparing the experimental points with the calculated lines for $G(\lambda)/G(1)$ it is to be noted that the curves predict a deviation from constant G which agrees approximately with the observed behavior. This is significant in view of the fact that the empirical parameters c_V and c_S, which determine the magnitude of this deviation, are obtained from thermoelastic data and are used here to compare calculated isothermal stress-strain relations with experimental data.

It may, furthermore, be pointed out that the deviation from ideal entropic-elastic behavior in compression is much less than in extension. On elongation orientation is toward the stretching direction. In a compressed material, however, the tendency of chains to become parallel is much less because orientation is toward planes perpendicular to the force direction, not toward a single direction. Therefore the functions F which express degree of orientation are smaller in compression than on elongation. This is depicted in Fig. 9, which shows the values of the orientation functions $F_V(\lambda)$ and $F_S(\lambda)$.*

The only direct evidence for the existence of an enhanced intramolecular attractive potential on orientation assumed here is the concentration on stretching of the amorphous halo in x-ray fiber diagrams into equatorial spots. This is considered too weak a basis for assigning a specific form of the energy potential of chain interaction.

That the shapes of the curves in Fig. 8 differ somewhat from the experimental relation is not surprising in view of the simple linear relation

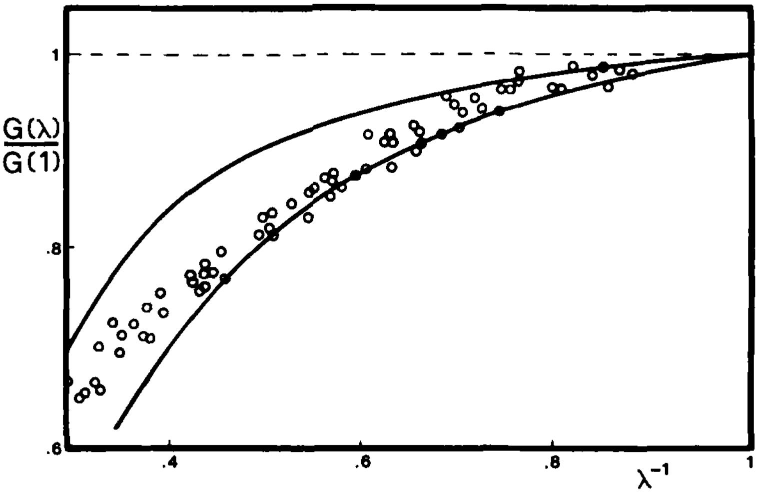

Fig. 8. Relative modulus vs. 1/λ. (○) Chain concentrations 0.04-0.13 mole/l. Lower solid line calculated from Eqs. (6) and (9) with $c_V = 0.0944$. Upper solid line calculated from Eqs. (6) and (11) with $c_S = 9.11$.

between energetic interaction of chains and degree of orientation assumed. From the presentation in Fig. 8 one may conclude that the assumption of an energetic interaction between aligned chains can account for the deviation of experimental stress-elongation data from the entropic elasticity theories.

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*For $\lambda < 1$ the limits of the integrals in Eqs. (9) and (11) are ω and $\pi/2$.

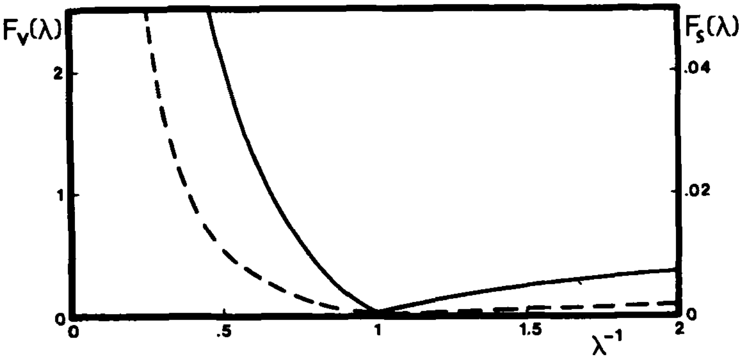

Fig. 9. Orientation distribution functions for end-to-end vectors (F_V) (—) and for chain segments (F_S) (- -) as a function of $1/\lambda$ in extension and compression.

APPENDIX

Evaluation of $F_V(\lambda)$ and $F_V'(\lambda)$

By combining Eqs. (8) and (9) and rearranging we obtain:

$$F_V(\lambda) = \lambda^{-3/2} \int_0^{\omega_V} (1 - k^2 \cos^2 \theta)^{-3/2}\, d\theta - \omega_V \qquad \text{with } k^2 = 1 - \lambda^{-3}$$

and

$$\omega_V = \cos^{-1} [\lambda/(1 + \lambda + \lambda^2)^{1/2}]$$

For $\lambda \geqslant 1$, a new variable, $\varphi = \tan^{-1} (\lambda^{3/2} \tan \theta)$, is introduced. The above integral can then be written as

$$\int_0^{\omega_V'} (1 - k^2 \sin^2 \varphi)^{1/2}\, d\varphi \qquad \text{with } \omega_V' = \tan^{-1} (\lambda^{3/2} \tan \omega)$$

This is the elliptic integral of the second kind, values of which have been tabulated. For $\lambda \leqslant 1$, $F_V(\lambda)$ is written in a different form

$$F_V(\lambda) = \lambda^3 \int_{\omega_V}^{\pi/2} (1 - l^2 \sin^2 \theta)^{-3/2}\, d\theta - (\pi/2 - \omega_V) \qquad \text{with } l^2 = 1 - \lambda^3$$

The integral can be rearranged with $\psi = \pi/2 - \theta$ to:

$$\int_0^{\pi/2 - \omega_V} (1 - l^2 \cos^2 \psi)^{-3/2}\, d\psi$$

Introducing $\varphi = \tan^{-1}(\lambda^{3/2} \tan \psi)$ again leads to the elliptic integral of the second kind:

$$\int_0^{\pi/2 - \omega_V'} (1 - 1^2 \sin^2 \varphi)^{1/2}\, d\varphi \qquad \text{with } \omega_V' = \cot^{-1}(\lambda^{-3/2} \cot \omega)$$

The derivative $F_V'(\lambda) = dF_V(\lambda)/d\lambda$ can be obtained by differentiation of F_V with respect to k and the relation $dE(k)/dk = [E(k) - K(k)]/k$, where E(k) and K(k) are the elliptic integrals of the second and first kind, respectively.

Evaluation of $F_S(\lambda)$ and $F_S'(\lambda)$.

The function F_S was calculated on the computer. The summation in Eq. (10) converges fast. Four terms were taken into account. The derivative of F_S was obtained by numerical differentiation.

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