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## Energetic Stress in Rubbery Copolymers

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### SUMMARY

Thermoelastic measurements were performed for four rubbery copolymers: Viton A, ethylene-propylene rubber (EPR), Hycar, and styrene-butadiene rubber (SBR). The relative energy contribution,  $f_e/f$ , for these elastomers were calculated by means of a recently proposed equation which is based on the temperature coefficient of shear modulus. It was found that the relative energy contribution or the temperature coefficients of the unperturbed dimensions of EPR and SBR are not simply related to those of the parent homopolymers. In addition, the copolymers appear to bear an opposite sign compared with the homopolymers. The thermoelastic behavior of one elastomer, Viton A, was investigated over a 200°C range up to high loads. Linear relations were obeyed within experimental error. Calculations on the basis of statistical theory of rubber elasticity shows that this is to be expected for elastomers that are Gaussian in behavior.

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## INTRODUCTION

The fundamental understanding of the molecular dynamics underlying the physical behavior of bulk polymers in the rubbery state as well as polymers in solution is based on the recognition of the role of conformational entropy in these macromolecules. In the statistical theory of rubber elasticity, each chain between network junctures is assumed to be random. The total number of conformations available to the entire network is taken to be the product of those of the individual chains. Thus, entropy of the network is the sum of contributions of its individual chains. In order for this assumption to be valid, it is necessary that intermolecular interactions between neighboring chains be either negligible or unaltered by deformation. To establish the validity of the latter condition, thermoelastic measurements were carried out for a number of rubberlike materials. Some of the previous findings by these measurements showed that not only is the energy component of the elastic stress nonnegligible, but that it depends upon the extent of deformation as well [1-7]. That the elastic force is not purely entropic can be attributed to the existence of nonisoenergetic chains (intramolecular interaction). However, the observation that the relative energy contribution is in fact altered by deformation is in direct contradiction to the additivity principle, thus posing a serious challenge to one of the fundamental tenets of the theory.

In a recent series of papers, we have attempted to resolve this apparent inconsistency in the statistical theory of rubber elasticity [8-10]. It was shown that the relative energy contribution to the elastic stress,

$$f_e/f = 1 - \left( \frac{\partial \ln f}{\partial \ln T} \right)_{V,L} \quad (1)$$

is constant over the region of strain ( $\sim 30\%$ ) for which the statistical theory is valid. (In Eq. 1,  $f$  is the elastic force,  $f_e$  the energetic component of this force,  $T$  the absolute temperature, and  $V$  and  $L$  the volume and length of the stretched sample, respectively.) This was accomplished by the use of a new thermoelastic equation, which is based on the temperature coefficient of the shear modulus [8, 9]:

$$f_e/f = 1 - \frac{d \ln G}{d \ln T} - \beta_L^\circ T \quad (2)$$

where  $\beta_L^\circ$  is the linear thermal expansion coefficient of the unstretched sample, and  $G$  is the shear modulus.

In this paper we shall further scrutinize this problem by carrying out thermoelastic measurements on several synthetic elastomers, all of which are copolymeric in nature. Values of  $f_e/f$  thus obtained are discussed in the light of existing literature data. In addition, the linearity of the thermoelastic coefficient over a wide temperature range is studied.

## EXPERIMENTAL METHODS

Samples of Viton A were kindly supplied by the duPont Elastomers Department. It is a copolymer of perfluoropropylene (40%) and vinylidene fluoride (60%). Vulcanization was achieved by compounding 100 parts of Viton A with 8.5 parts magnesium oxide and 1.5 parts hexamethylene diamine carbamate. It was press-cured for 30 min at 150°C and then post-cured in the oven at 204°C for 24 hr. The ethylene-propylene rubber was obtained through the courtesy of the Goodyear Tire and Rubber Company. The EPR sample, containing 48 mole % propylene, was cured with 1.0 part dicumyl peroxide per hundred parts of rubber at 160°C for 20 min.

Samples of Hycar and styrene-butadiene rubber were cured in this laboratory. The Goodrich Hycar 1072, a 1-to-1 random copolymer of butadiene and acrylonitrile, was compounded with 2.5 parts of dicumyl peroxide per hundred parts of rubber, and cured at 150°C for 30 min. The SBR 1500, manufactured by Shell Chemical Company, was also cured at 150°C for 30 min with dicumyl peroxide. SBR 1500 contains 23.5% styrene and 76.5% butadiene.

Thermoelastic experiments were carried out by measuring the thermal expansion coefficients of the rubbers under a series of loads. Both strip and ring specimens were used for these measurements. Detailed experimental procedure has been previously described [9, 11] and will not be repeated here. For Viton A, measurements were performed over an extended temperature range (0-200°C). In this instance, fresh ring specimens were used for each load in order to minimize the possible effects of oxidative degradation at high temperatures. Strip samples were used for all other measurements.

## RESULTS AND DISCUSSION

### 1. Effect of Comonomers

Figure 1 shows the length-temperature data for Viton A for five different loads over a ~50°C interval. Excellent linearity is seen in the data for

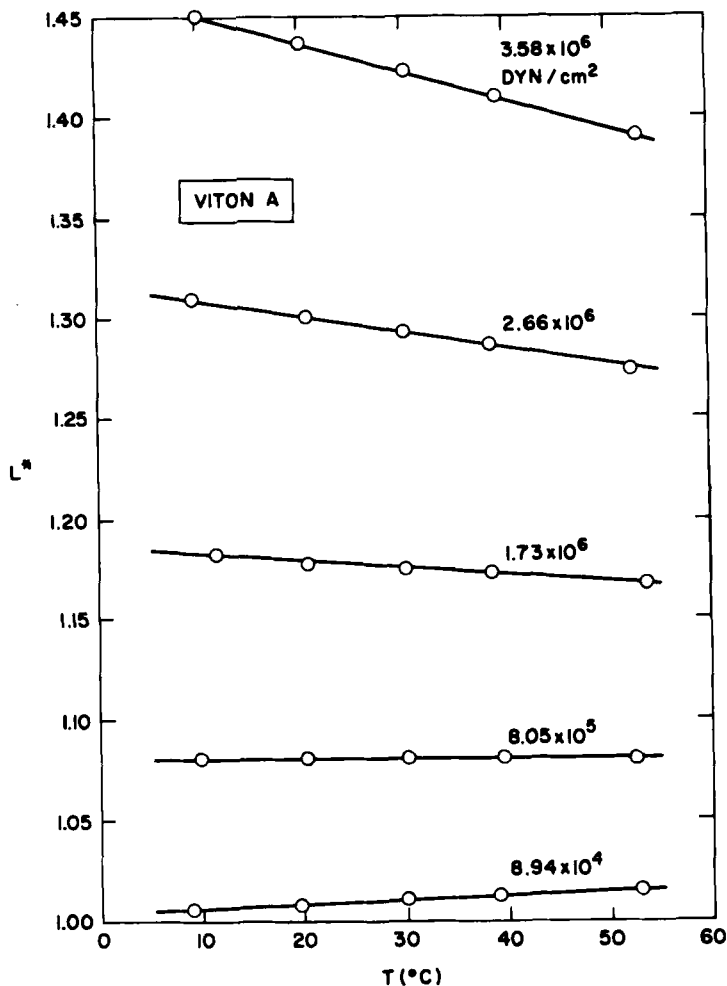


Fig. 1. Length-temperature curves of Viton A. Numbers on the right indicate the loads on the sample.  $L^*$  is the length of the sample reduced by the unstrained sample length at 30°C.

this and other elastomers in this range of temperatures. From the slopes of these data, the linear thermal expansion coefficients ( $\beta_L$ ) of the samples under stress can be readily obtained. To calculate the relative energy contribution ( $f_e/f$ ) by Eq. (2), we need to know the temperature coefficient of the shear modulus and the linear thermal expansion coefficient of the rubber at zero load ( $\beta_L^0$ ). These can be obtained by means of the following equation [9]:

$$\beta_L = \beta_L^\circ - \left( \frac{\lambda^3 - 1}{\lambda^3 + 2} \right) \left( \frac{d \ln G}{dT} + 2\beta_L^\circ \right) \quad (3)$$

where  $\lambda$  is the elongation ratio. In Figs. 2-5 are shown plots of  $\beta_L$  vs. the quantity  $(\lambda^3 - 1)/(\lambda^3 + 2)$  for the four elastomers. From the intercept and the slope of these plots,  $\beta_L^\circ$  and  $d \ln G/dT$  can be easily determined. Results of these thermoelastic data are given in Table 1.

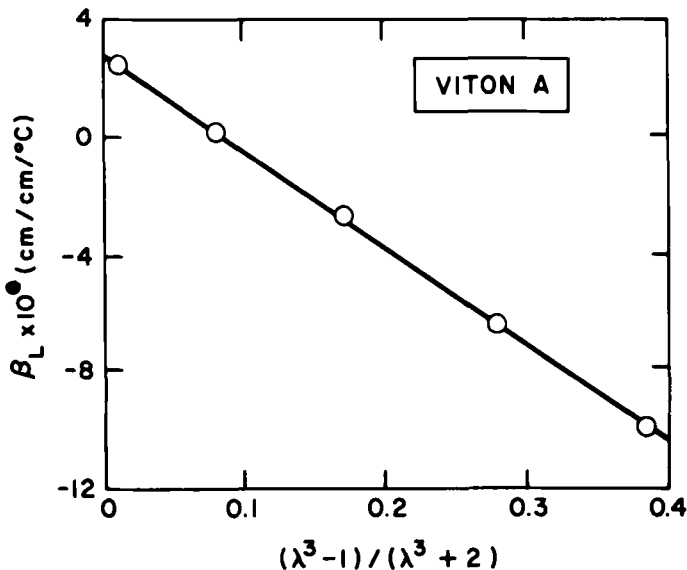


Fig. 2. Linear thermal expansion coefficients of Viton A under strain plotted against  $(\lambda^3 - 1)/(\lambda^3 + 2)$ .

Thermoelastic measurements have been carried out by previous workers for Viton [1], ethylene-propylene rubber, [6, 12] and styrene-butadiene rubber [13]. No data to our knowledge exists for Hycar. Figure 6 summarizes the known  $f_e/f$  data from the literature [1, 6, 12, 13] for the former elastomers. The relative energy contribution here were calculated by the following equation [14]:

$$f_e/f = 1 - (\partial \ln f / \partial \ln T)_{P,L} - 3\beta_L^\circ T / (\lambda^3 - 1) \quad (4)$$

It is apparent that values of  $f_e/f$  determined by Eq. (4) vary as a function

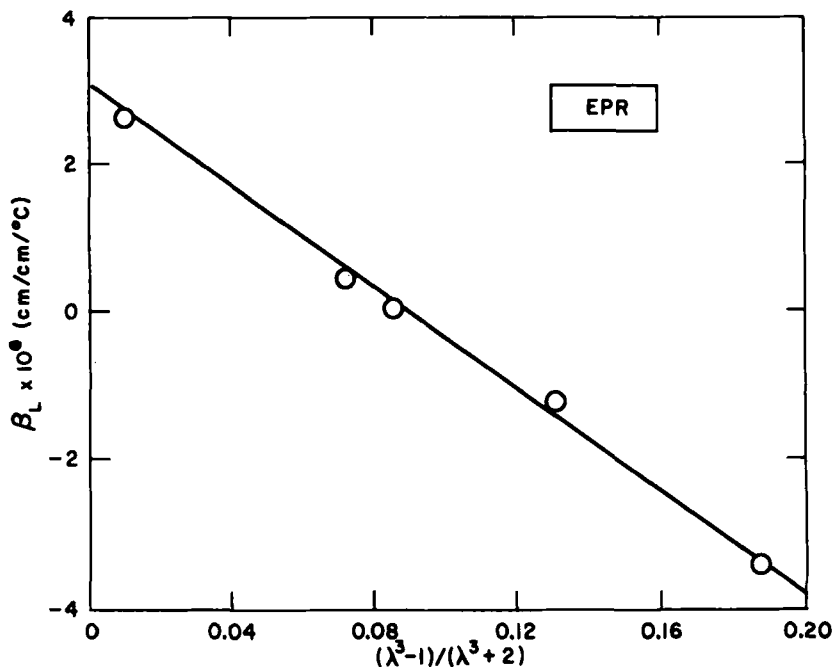


Fig. 3. Linear thermal expansion coefficient of ethylene-propylene rubber under strain plotted against  $(\lambda^3 - 1)/(\lambda^3 + 2)$ .

of elongation ratio. As we have mentioned previously, the strain dependence of the relative energy contribution is inconsistent with the principle of free energy additivity in the statistical theory of rubber elasticity. However, the source of this inconsistency turns out to be attributable to the sensitivity of the last term of Eq. (4) to errors in the determination of  $\lambda$ , especially in the region of low  $\lambda$ . This difficulty is circumvented by the use of Eq. (2), which is in fact equivalent to Eq. (4). The advantage of Eq. (2) is that it averages out the errors in the low strain region by using the temperature coefficient of shear modulus [8, 9]. Thus the internal consistency of the statistical theory is preserved.

The energetic contribution to rubber elasticity, in the spirit of the statistical theory, is strictly intramolecular in origin. It can, in fact, be shown that  $f_e/f$  is related to the temperature coefficient of the unperturbed chain dimensions as follows [14-16]:

$$\frac{d \ln \langle r^2 \rangle_0}{dT} = \frac{f_e}{fT} \quad (5)$$

Table 1. Thermoelastic Data of Some Rubbery Copolymers<sup>a</sup>

Polymer	$\beta L$ ( $10^{-4}/^{\circ}\text{C}$ )	$d \ln G/dT$ ( $10^{-3}/^{\circ}\text{C}$ )	$f_e/f$	$\frac{d \ln (\zeta^2)_0}{dT}$ ( $10^{-4}/^{\circ}\text{C}$ )
Poly(vinylidene fluoride-co-perfluoropropylene), (Viton A)	3.0	2.8	0.05	1.6
Poly(ethylene-co-propylene), (EPR)	2.5	2.9	0.04	1.3
Poly(butadiene-co-acrylonitrile), (Hycar)	2.6	2.9	0.03	1.0
Poly(styrene-co-butadiene), (SBR)	2.9	3.4	-0.12	-3.9

<sup>a</sup> Reference temperature = 303°K.



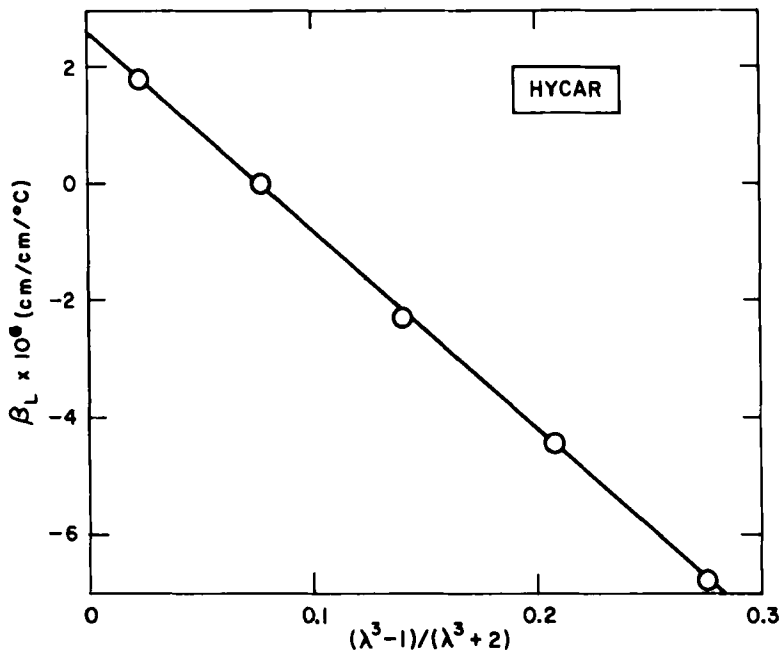


Fig. 4. Linear thermal expansion coefficient of Hycar under strain plotted against  $(\lambda^3 - 1)/(\lambda^3 + 2)$ .

These values for the elastomers studied in this work are given in the last column of Table 1.

Although statistical calculations of the conformational properties of homopolymer chains have reached a high degree of sophistication [17, 18], similar computations on the basis of the rotational isomeric model for random copolymers have not been performed. Thus it would be difficult for us to discuss the quantitative significance of our numerical data for the temperature coefficient of the unperturbed dimensions of copolymer chains. However, comparison of these data with those of the parent homopolymers might be illuminating. From Table 1, we note that  $d \ln \langle r^2 \rangle_0 / dt = 1.3 \times 10^{-4} / ^\circ\text{C}$  for our one-to-one random copolymer of ethylene and propylene. Theoretical calculations yielded  $-1.1 \times 10^{-3}$  and  $-4.0 \times 10^{-3}$ , respectively, for the values of  $d \ln \langle r^2 \rangle_0 / dT$  for polyethylene [19] and polypropylene [20]. Here we see that not only is there a lack of any evidence of the random copolymer's possessing an intermediate value of the parent homopolymers, but there is in fact a reversal of

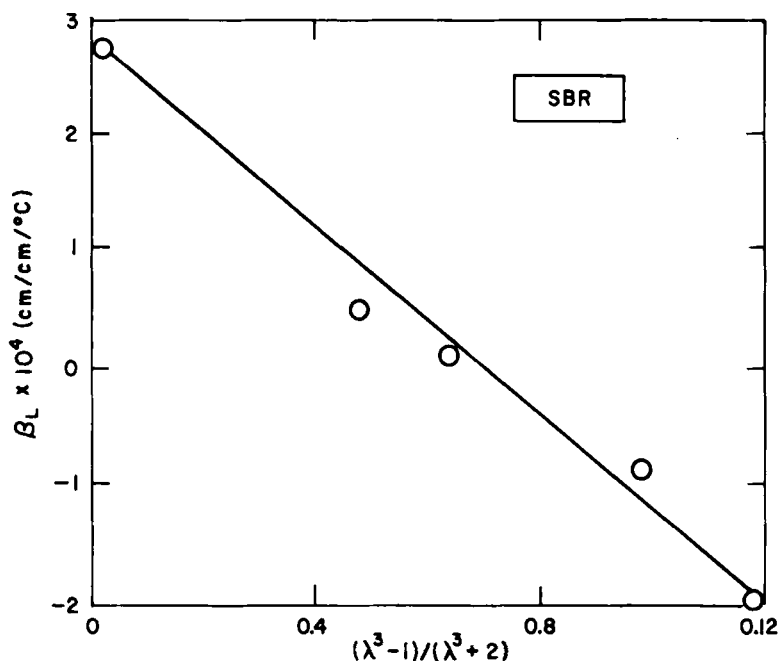


Fig. 5. Linear thermal expansion coefficient of styrene-butadiene rubber under strain plotted against  $(\lambda^3 - 1)/(\lambda^3 + 2)$ .

signs. In the case of SBR, we have obtained a value of  $-3.9 \times 10^{-4}/^\circ\text{C}$  for the temperature coefficient of the unperturbed dimension of the styrene-butadiene chain. Literature data, on the other hand, indicate that this coefficient is  $3.3 \times 10^{-4}/^\circ\text{C}$  for polybutadiene [21] and  $3.7 \times 10^{-4}/^\circ\text{C}$  for polystyrene [22]. Again, we observe the apparent lack of correlation with the copolymer. It is interesting to note that in both cases the homopolymers have the opposite temperature coefficients compared to the copolymers.

## 2. Effect of Temperature

In most thermoelastic experiments for rubbers, the range of temperature covered generally is in the neighborhood of  $\sim 50^\circ\text{C}$ . The lower temperature limit is generally imposed by the onset of glass transition or strain-induced crystallization. The latter is about  $0^\circ\text{C}$  for natural rubber, for example. Very high temperature must be avoided, on the other hand, due to the possibility of thermal degradation. Viton A, however, is a thermally

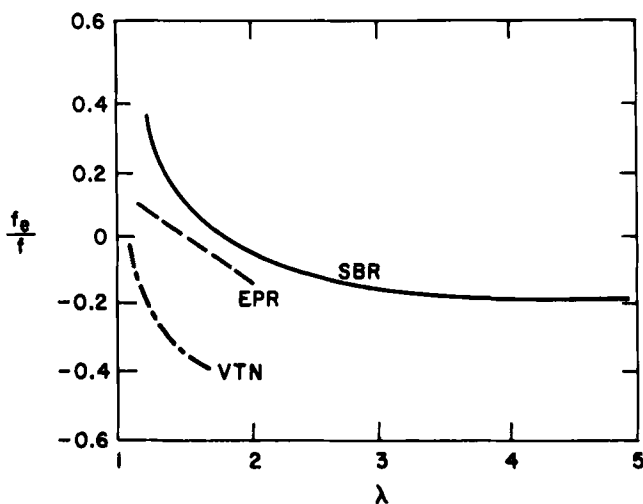


Fig. 6. Relative energy contribution of Viton [1], ethylene-propylene rubber and styrene-butadiene rubber [7, 13] as a function of elongation ratio. Values of  $f_e/f$  were calculated by Eq. (4).

stable elastomer which also has a relatively low glass transition temperature ( $-25^{\circ}\text{C}$ ). Thus we are able to perform thermoelastic measurements for this material over a much wider temperature range (0 to  $200^{\circ}\text{C}$ ). Since excellent linearity is usually observed for the limited temperature range ( $\sim 50^{\circ}\text{C}$ ) for all the elastomers in their stress-temperature (constant load) measurements, it is of interest to determine if any deviation from linearity occurs in a more extended temperature range. In Fig. 7 the thermoelastic data for Viton A are shown. It is seen that the length-temperature changes under constant load are linear within experimental error. Only in the very high temperatures are curvatures observed. In this temperature region the possibility of degradation must not be discounted.

We now examine this phenomenon in the light of the statistical theory of rubber elasticity. We wish to compute the second derivative of stress with respect to temperature. Since it is well known from thermodynamic identity that

$$\left(\frac{\partial f}{\partial T}\right)_{P,L} = -\left(\frac{\partial \Delta S}{\partial L}\right)_{P,T} \quad (6)$$

where  $\Delta S$  is the entropy change due to the applied strain, it then follows that

$$\left(\frac{\partial^2 f}{\partial T^2}\right)_{P,L} = -\frac{1}{TL_0} \left(\frac{\partial \Delta C_L}{\partial \lambda}\right)_{P,T} \quad (7)$$

where  $C_L = C_{P,L} - C_{P,L_0}$ , and  $C_{P,L}$  and  $C_{P,L_0}$  are the constant pressure heat capacities for the strained and unstrained rubber, respectively. We have already shown in a previous publication that [23]

$$\begin{aligned} \Delta C_L = \frac{GV_0}{2} \left( \frac{1}{T} - \frac{d \ln G}{dT} - 3\beta_L^\circ \right) \left( \lambda^2 + \frac{2}{\lambda} - 3 \right) \\ + GV_0 \beta_L^\circ \left( \lambda - \frac{1}{\lambda^2} \right) \end{aligned} \quad (8)$$

where  $V_0$  is the unstrained volume of the rubber. Combining Eqs. (7) and (8), we obtain

$$\begin{aligned} \left(\frac{\partial^2 f}{\partial T^2}\right)_{P,L} = -\frac{GA_0}{T} \left( \frac{1}{T} - \frac{d \ln G}{dT} - 3\beta_L^\circ \right) \left( \lambda - \frac{1}{\lambda^2} \right) \\ - \frac{GA_0 \beta_L^\circ}{T} \left( 1 + \frac{2}{\lambda^3} \right) \end{aligned} \quad (9)$$

Equation (9) can be further simplified by Eq. (2) and the equation of state for rubber elasticity [14, 16] to

$$f = GA_0(\lambda - 1/\lambda^2) \quad (10)$$

In Eq. (10),

$$G = \frac{\nu k T}{V_0} \langle r^2 \rangle / \langle r_0^2 \rangle_0 \quad (11)$$

$A_0$  and  $V_0$  are the cross-sectional area and volume of the rubber at zero force, zero pressure, and temperature  $T$ ;  $V$  is the volume at force  $f$ , pressure  $P$  and temperature  $T$ ;  $\lambda$  is the relative extension ratio;  $\nu$  is the number of network chains in the sample;  $k$  is Boltzmann constant; and  $\langle r_0^2 \rangle_0$  and  $\langle r^2 \rangle_0$  are the mean square end-to-end distances of the chain

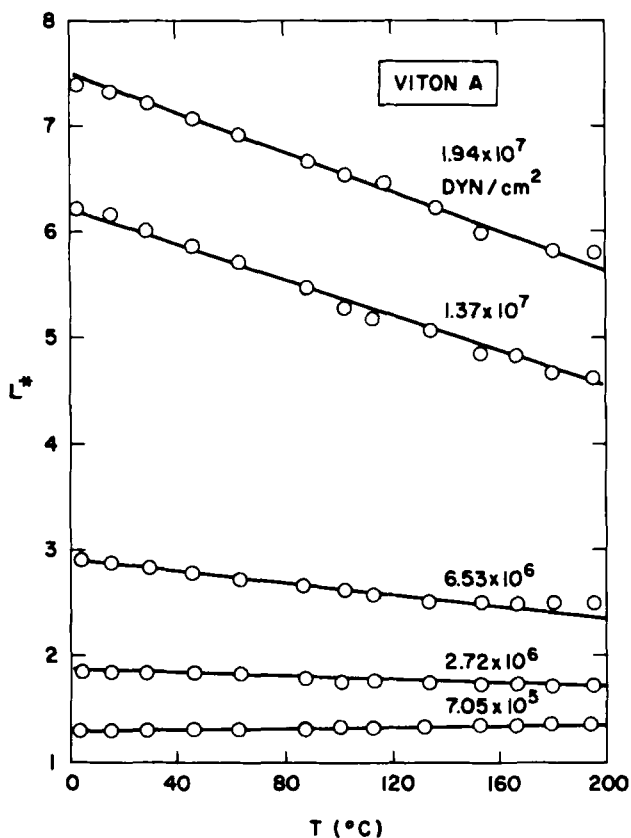


Fig. 7. Length-temperature curves of rings of Viton A over an extended temperature and load range. Values and symbol have the same meaning as in Figure 1.

in volume  $V_0$  and in free space, respectively. The ratio  $\langle r_0^2 \rangle / \langle r^2 \rangle_0$  is commonly known as the front factor. Thus,

$$\left( \frac{\partial^2 f}{\partial T^2} \right)_{P,L} = \frac{f}{T} \left\{ \beta_L^\circ \left[ 2 + \frac{1}{\lambda} \left( \frac{\lambda^3 + 2}{\lambda^3 - 1} \right) \right] - \frac{f_e}{fT} \right\} \quad (12)$$

If the thermoelastic coefficient is linear, then one would expect the second derivatives of stress with respect to temperature to be zero. For our Viton A sample,  $f$  is about  $3 \times 10^6$  dynes/cm<sup>2</sup> at  $\lambda = 2$  (100% extension), and  $\beta_L^\circ$  and  $f_e/fT$  are both of the order of  $10^{-4}/^\circ\text{C}$  (see Table 1). Thus

$(\partial^2 f/\partial T^2)$  is of the order of 10 dynes/cm<sup>2</sup>/°C<sup>2</sup>. This is a very small change, and certainly is beyond the sensitivity of our method of determination. Of course, Eq. (12) shows that the second temperature derivative of stress is a function of elongation. At higher elongations, one would expect a greater  $(\partial^2 f/\partial T^2)_{p,L}$ . However, since this expression is based on the statistical theory, its validity is strictly limited only to the low strain region. Even the use of higher order strain energy functions, such as the Mooney-Rivlin function, is not expected to produce dramatically different results.

To examine the curvature of the length-temperature plot given by Fig. 7, we only need to make the following transformations:

$$\left(\frac{\partial L}{\partial T}\right)_{p,f} = -\left(\frac{\partial f}{\partial T}\right)_{p,L} / \left(\frac{\partial f}{\partial L}\right)_{p,T} \quad (13)$$

or

$$\left(\frac{\partial^2 L}{\partial T^2}\right)_{p,f} = -\left(\frac{\partial^2 f}{\partial T^2}\right)_{p,L} / \left(\frac{\partial f}{\partial T}\right)_{p,T} \quad (14)$$

Based on Eq. (10), Eq. (14) becomes

$$\left(\frac{\partial \beta_L}{\partial T}\right)_{p,f} = -\left(\frac{\partial \ln f}{\partial T}\right)_{p,L} / \left(\frac{\lambda^3 - 1}{\lambda^3 + 2}\right) \quad (15)$$

In Eq. (15), the quantity  $(\lambda^3 - 1)/(\lambda^3 + 2)$  is nearly zero at small values of  $\lambda$  and approaches unity at high strains. This term tends to make any deviation from linearity of the length-temperature plot even less than that of the stress-temperature plot. Thus we feel that our experimental results are consistent with theoretical predictions. Previous calorimetric measurements of stretched natural rubber also led to similar conclusions [23].

#### ACKNOWLEDGMENTS

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