A Thermodynamic Analysis of the Elastic Properties of Poly(dimethyl siloxane)

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Thermoelastic measurements have been made at constant volume on lightly crosslinked poly(dimethyl siloxane). The results show that 25 per cent of the retractive force is energetic in origin.

THE equilibrium retractive force required to hold an elastic body at constant elongation is given by the thermodynamic relation[1]

$$f=(\partial F/\partial L)_{T,V}=(\partial U/\partial L)_{T,V}-T(\partial S/\partial L)_{T,V} \tag{1}$$

The energetic and entropic components of the force can be obtained from thermoelastic measurements at constant volume, since

$$f_e\equiv(\partial U/\partial L)_{T,V}=f-T(\partial f/\partial T)_{L,V} \tag{2}$$

and

$$f_s\equiv -T(\partial S/\partial L)_{T,V}=T(\partial f/\partial T)_{L,V} \tag{3}$$

For normal solids $f_e > f_s$ but for rubbers $f_e < f_s$ and precise measurements of the relative magnitudes of these components give insight into the molecular processes associated with rubber elasticity.

Measurements at constant volume are much more complicated than at constant pressure, so much so that until 1963 all estimates of $(\partial f/\partial T)_{L,V}$ for rubbers were obtained indirectly from the corresponding constant pressure coefficients combined with relations based on the theory of infinitesimal strains or the kinetic theory of rubber elasticity. The earliest estimates were based on an approximation deduced from the theory of infinitesimal strains[1], viz.

$$(\partial f/\partial T)_{L,V}\simeq(\partial f/\partial T)_{\alpha,P} \tag{4}$$

Several chemically different rubbers were investigated, and the general conclusion was that the origin of the retractive force was overwhelmingly entropic.

In 1959, Flory, Hoeve and Ciferri[2] showed that equation (4) was an unsatisfactory approximation. Their arguments were formulated in terms of Flory's development[3] of the kinetic theory of rubber elasticity for networks composed of Gaussian polymer chains with temperature dependent chain dimensions for which the equation of state is

$$f=(NkT/L_i)(\overline{r_i^2}/\overline{r_0^2})(\alpha-\alpha^{-2}) \tag{5}$$

where α is the extension ratio (L/L_i) defined for fixed volume, $\overline{r_i^2}$ is the mean-square end-to-end distance for a network chain in the undeformed state and $\overline{r_0^2}$ is the corresponding value for a free chain unconstrained by network junction points. Taken in conjunction with equation (2) and a knowledge of $\mathrm{d}\ln \overline{r_0^2}/\mathrm{d}T$ obtained from the properties of dilute polymer solutions, equation (5) indicates that estimates of f_e/f based on equation (4) were considerably in error.

Later, Flory[4,5] also showed that the kinetic theory of rubber elasticity yields the relations

$$(\partial f/\partial T)_{L,V} = (\partial f/\partial T)_{L,P} + (f\beta_{L,P}/[\alpha^3 - 1]) \tag{6}$$

and

$$(\partial f/\partial T)_{L,V} = (\partial f/\partial T)_{\alpha,P} + (f\beta_{\alpha,P}/3) \tag{7}$$

where $\beta_{L,P}$ and $\beta_{\alpha,P}$ are the coefficients of thermal expansion at, respectively, constant L and α. Since the last term in equation (7) is not negligible, this analysis leads[6-8] to a different conclusion, namely that for many rubbers f_e makes a significant contribution to the retractive force.

Unfortunately both methods of estimating $(\partial f/\partial T)_{L,V}$ rely on theories of uncertain validity. For example, the theory of infinitesimal strains is extrapolated to large deformations and it is well known that in practice most rubbers show significant departures from equation (5). For these reasons we developed a rigorous method[9] for the direct determination of $(\partial f/\partial T)_{L,V}$ in which a hydrostatic pressure is applied to offset thermal expansion. Using the apparatus developed for the purpose, $(\partial f/\partial T)_{L,P}$ and $(\partial f/\partial P)_{T,L}$ can also be measured and thus a second rigorous estimate of the constant volume stress/temperature derivative can be obtained from the relation

$$(\partial f/\partial T)_{L,V} = (\partial f/\partial T)_{L,P} + (\partial f/\partial P)_{T,L}\,(\partial P/\partial T)_{L,V} \tag{8}$$

The thermal pressure coefficient can be evaluated in a subsidiary experiment. This direct approach has been applied to natural rubber and to butyl rubber. We now report an analysis of the elastic properties of poly(dimethyl siloxane) rubbers.

EXPERIMENTAL

Materials

Measurements were carried out on two samples designated A and B. Sample A was prepared by crosslinking poly(dimethyl siloxane) rubber of high molecular weight ($M_w \sim 500\,000$) with benzoyl peroxide for one hour at 140°C. Sample B was prepared in a similar way, but contained five per cent by weight of silicate powder (santocel 54). When the samples were extracted with carbon tetrachloride, the amount of soluble material in each case was found to be less than 0·5 per cent by weight of the sample. The densities of the samples, which were determined by flotation at 20°C, were found to be 1·048 and 1·076, respectively. Rubber pieces for use in the thermoelastic studies were bonded on to stainless-steel end-rods by means of 'Rhodorsil Caf 4', which is a self-vulcanizing elastomeric silicone adhesive manufactured by Rhône-Poulenc. The rubber–metal bond strengths governed the maximum extension ratio at which measurements could be made on the samples. Bearing in mind the time-consuming nature of our direct approach, $\alpha \simeq 1{\cdot}20$ was the upper limit at which it was possible to carry out a complete set of measurements.

Measurement of $(\partial f/\partial T)_{L,P}$, $(\partial f/\partial T)_{L,V}$ and $(\partial f/\partial P)_{T,L}$

All three quantities were determined in the same apparatus; the latter together with its method of operation and calibration are described in detail elsewhere[9]. Changes in stress in the sample were determined from minute displacements of a steel strip, which were detected by a Phillips displacement pickup and direct-reading measuring bridge. In making force/temperature measurements at constant volume, the pressure is varied in step with the temperature so as to maintain the volume of the rubber constant. The pressure could be applied in increments of 0·01 atm up to 160 atm. The exact pressure required to offset each temperature variation was calculated from a knowledge of the thermal pressure coefficient. The coefficients of volume expansion and thermal pressure were determined in a set of subsidiary experiments by a method described elsewhere[9].

Plots obtained from all three sets of measurements were linear and repeated measurements were consistent to within ±1 per cent in each case. Hysteresis effects were completely absent. The latter was achieved by allowing the test-piece to relax overnight before each run at approximately 10 deg. C above the maximum temperature attained during the run. Whenever the extension ratio of the sample was changed the sample was allowed to relax for two days at this elevated temperature before recommencing measurements.

The time-scale adopted for measuring $(\partial f/\partial T)_{L,P}$ was as follows. With the system opened up to atmospheric pressure, the temperature was lowered in decrements of approximately 1 deg. C over the range 36° to 30°C. At each new temperature the system was given 50 minutes to equilibrate before readings were taken. Readings were then taken at increasing temperatures to ensure that the measurements were reversible. Measurements of $(\partial f/\partial T)_{L,V}$ were carried out in a similar way except that the pressure was varied during the course of the run. At the start of each run the system was thermostatically controlled at the maximum temperature and a pressure of 1 000 lb in^{-2} applied; as the temperature was reduced the applied pressure was then reduced a corresponding amount to maintain the rubber at constant volume.

Measurements of $(\partial f/\partial P)_{T,L}$ were carried out at 33°C. A pressure of 1 000 lb in^{-2} was applied to the system at the start of each experiment. When the system had come to equilibrium the applied pressure was decreased in decrements of 100 lb in^{-2} to atmospheric pressure, and then increased in similar increments back to a pressure of 1 000 lb in^{-2}. A period of five minutes was found to be sufficient for the system to come to equilibrium at each new pressure, although in practice 15 minutes was allowed before the bridge deflection was noted.

RESULTS AND DISCUSSION

Coefficients of volume expansion and thermal pressure for poly(dimethyl siloxane) in the undeformed state

In *Table 1*, we have listed thermal pressure coefficients determined on samples A and B over the temperature range 30° to 50°C. The experimental error in $\gamma_{L,V}$ is estimated to be ±1·5 per cent.

The coefficients of expansion $\beta_{L,P}$ of the samples A and B were also measured over the range 30° to 50°C. No curvature of the volume/temperature plots was detected, and the average values for $\beta_{L,P}$ at 40°C were found to be $(8{\cdot}3 \pm 0{\cdot}1) \times 10^{-4}$ and $(8{\cdot}0 \pm 0{\cdot}1) \times 10^{-4}$ deg^{-1}, respectively.

In the present study we have not explored the effect of extension on $\gamma_{L,V}$ and $\beta_{L,P}$. However, measurements carried out on other elastomers show[9,10] that over the range where it is possible to make equilibrium measurements these quantities are virtually independent of extension ratio.

Table 1. Thermal pressure coefficients for poly(dimethyl siloxane) rubber

Sample A

$(\partial P/\partial T)_{L,V}$ atm/deg. C	$7{\cdot}4_8$	$7{\cdot}3_2$	$7{\cdot}1_2$	$6{\cdot}9_9$	$6{\cdot}9_0$
T°C	31·00	35·60	41·10	45·70	49·00

Sample B

$(\partial P/\partial T)_{L,V}$ atm/deg. C	$7{\cdot}4_8$	$7{\cdot}3_3$	$7{\cdot}1_5$	$6{\cdot}9_4$	$6{\cdot}8_3$
T°C	33·20	36·20	40·60	45·90	48·50

Stress/strain behaviour

The stress/strain characteristics of the samples A and B over the range $1 < \alpha < 1{\cdot}3$ at $T = 33$°C were obtained by hanging weights from a balance pan suspended from the lower metal end-piece. The length between two fiducial reference marks was measured to within $\pm 0{\cdot}002$ cm with a cathetometer. Measurements were then taken under both loading and unloading conditions; hysteresis effects were undetectable when readings were taken at hourly intervals. Over the narrow range of α where measurements were taken, the data, somewhat surprisingly, fitted very well the behaviour predicted by equation (5); the elastic moduli, $f/(\alpha - \alpha^{-2})$ of samples A and B were found to be 4·96 and 7·92 kg cm^{-2}, respectively. The measurements were repeated six weeks after the first set had been taken, but were found to be completely reproducible.

Thermoelastic studies

In *Table 2* we have listed values of f_e/f calculated from the direct determination of $(\partial f/\partial T)_{L,V}$ together with estimates of this ratio based on equation (8) and measurements of $(\partial f/\partial T)_{L,P}$ and $(\partial f/\partial P)_{T,L}$. That the two sets of data are in substantial agreement is a good indication that experimental readings were taken under equilibrium conditions.

In *Table 3* are given values of the dilation coefficent obtained using the thermodynamic relation

$$(\partial \ln V/\partial \alpha)_{P,T} = (L_i/V)\ (\partial f/\partial P)_{T,L}$$

These data are compared with the predictions of the kinetic theory of elasticity[2]

$$(\partial \ln V/\partial \alpha)_{P,T} = (L_i/V)\ (\beta_{L,T}/\gamma_{L,V})\ (f/[\alpha^3-1])$$

The theoretical and experimental results are seen to be in fairly close agreement; this behaviour is consistent with the stress/strain characteristics of the samples. Also included in *Table 3* are values of the dilation coefficient predicted by the infinitesimal theory of elasticity[1],

$$(\partial \ln V/\partial \alpha)_{P,T} = (L_i/3V)\ (\beta_{L,T}/\gamma_{L,V})\ (\partial f/\partial \ln L)_{P,T}$$

Even at the low extension ratios involved the experimental results are seen to depart significantly from those predicted by this approach.

Table 2. Results of thermoelastic measurements on poly(dimethyl siloxane)

Sample	α	f g	f_e/f *Direct*	f_e/f *Equation* (8)
A	1·101	1690	0·27 ± 0·02	0·26 ± 0·03
A	1·197	3058	0·25 ± 0·01	0·22 ± 0·02
B	1·102	2720	0·23 ± 0·02	0·27 ± 0·03

Table 3. Dilation coefficients of poly(dimethyl siloxane) at 33°C

Samples	α	← $(\partial \ln V/\partial \alpha)_{P,T} \times 10^5$ →		
		Experimental	*Kinetic theory*	*Inf. theory*
A	1·101	$4{\cdot}5_5$	$4{\cdot}4_7$	$4{\cdot}9_7$
A	1·197	$3{\cdot}9_4$	$3{\cdot}7_8$	$4{\cdot}6_8$
B	1·102	$7{\cdot}1_4$	$6{\cdot}8_5$	$8{\cdot}1_6$

Chain conformation

Equations (2) and (5) yield

$$(f_e/fT) = (\mathrm{d} \ln \overline{r_0^2}/\mathrm{d}T)$$

Used in conjunction with our experimental data, this relation leads to an average value for $\mathrm{d} \ln \overline{r_0^2}/\mathrm{d}T$ of $8{\cdot}2 \times 10^{-4}$ deg^{-1}. This result is in satisfactory agreement with the value of $7{\cdot}1 \times 10^{-4}$ deg^{-1} obtained by Crescenzi and Flory[11] from intrinsic viscosity measurements on athermal solutions of linear poly(dimethyl siloxane) in a low molecular weight siloxane. However, the agreement must be viewed with some caution, since using a similar method based upon the properties of athermal solutions, Ciferri[12] had earlier obtained a value between $2{\cdot}8 \times 10^{-4}$ and $3{\cdot}8 \times 10^{-4}$ deg^{-1} depending upon which theory he used to interpret his measurements.

Dilute solution measurements yield for the ratio $(\overline{r_0^2}/\overline{r_f^2})^{\frac{1}{2}}$, where $\overline{r_f^2}$ is the mean-square end-to-end distance for free rotation[13], a value of the order of 1·4. Taken in isolation this low value suggests that the molecules are highly flexible from a thermodynamic standpoint (i.e. the different rotational isomeric states have almost the same energy). In view of the high value we obtain for $\mathrm{d} \ln \overline{r_0^2}/\mathrm{d}T$ the latter interpretation cannot hold. The apparent discrepancy is the result of the alternating bond angles along the polymer chain for the two angles O—Si—O and Si—O—Si; the values are 109° 30′ and ~ 143°, respectively. It can easily be shown[13] that as the fraction of *trans* isomers along the chain increases the end-to-end dimensions do not continue to increase indefinitely, as they would with vinyl polymers, but reach a maximum after which they decrease to a very small value.

The same analysis allows the energy difference between rotational isomers to be calculated from f_e/f. Our results are consistent with the conclusions that *gauche* ± *gauche* ∓ sequences are largely suppressed, and that $\Delta U \sim 750$ cal mole^{-1} in favour of the *trans* isomer; in carrying out the analysis it is assumed that the stable isomers are the *gauche* and *trans* forms with energy minima at 120°, $-120°$ and 0°, respectively.

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