undergoes a conformational transition during ionization in an isopropyl alcohol-water (4:1) mixture. Although the transition region is relatively broad compared with the range found for poly(methacrylic acid) in aqueous solution, the titration curve shows distinct characteristics of a polymer undergoing conformational change during ionization. This molecule probably assumes a compact globular coil structure at a low degree of ionization, possibly with some -COOH groups clustering together due to hydrogen bonding in the relatively nonpolar solvent. As the molecule dissociates, it transforms to a more extended state due to the breakdown of the hydrogen bonding and to the increasing repulsive forces of the charges along the chain. The free-energy change for this conformational transition has been estimated to range from 60 to 90 cal per mol; in view of the use of the Henderson-Hasselbalch equation to obtain the estimates they are regarded as tentative.

Three copolymers of the same chain length but different acid contents have been studied. A semiempirical treatment of the titration data indicated that although the start of titration region during ionization occurs at a lower degree of ionization for chains with higher acid content, the fraction of charge per residue at the onset of the titration seems to be the same for the three copolymers. This suggests that the distribution of charge may play little or no role in governing the onset of the transition.

Stress-Strain Isotherms and Stress-Temperature Coefficients of Poly(dimethylsiloxane) Networks in Compression

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ABSTRACT: Stress-strain isotherms at 30, 45, 60, 75, and 90° have been determined for compressed, unswollen poly(dimethylsiloxane) networks which had been prepared either in the undiluted state or in solution. For these networks in compression, deviations of the dependence of stress on strain from that predicted by the statistical theory of rubberlike elasticity are much less than is the case for polymer networks in elongation. The present data nonetheless give a value for the temperature coefficient of the unperturbed dimensions of the network chains which is in good agreement with published results on networks of poly(dimethylsiloxane) in elongation. This agreement thus seems to validate the intentional disregard of such deviations in analyses of stress-temperature measurements.

Most experimental studies of the elastic properties of rubberlike networks employ uniaxial elongation as deformation because of the relative ease with which such experiments may be carried out.[1-8] Comparatively little research has been done on networks in uniaxial compression because of difficulties due to the friction occurring between the compression plates and the sample surfaces in contact with them.[9,10] Since this friction interferes with the uniform expansion of the sample at these contact surfaces, a sample will frequently exhibit significantly nonuniform expansion ("barreling") in the direction perpendicular to that in which it is compressed. The corresponding uncertainty in the magnitude of the deformation of the sample obviously makes reliable interpretation of stress-strain data extremely difficult.

On the other hand, studies of networks in uniaxial compression have the very attractive characteristic of giving stress-strain relationships which exhibit much smaller deviations[3,10-20] ("Mooney-Rivlin C_2 terms"[21]) from the form predicted by the statistical theory[22,23] of rubberlike elasticity, than is the case for networks in uniaxial elongation. Such deviations from theory have in fact been held by some[24-29] to invalidate the interpretation of "thermoelastic" (stress-temperature) data carried out on elongated polymer networks at constant pressure, in particular the application of the statistical theory of rubberlike elasticity to such data in order to obtain the temperature coefficient of the unperturbed dimensions of the chains making up the network.[8,30-32] It is therefore obviously of very great

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(22) Reference 23 provides a list of references to papers in which the theory of rubberlike elasticity is developed.
(23) J. E. Mark, *J. Amer. Chem. Soc.*, **92**, 7252 (1970).
(24) For examples of studies concerned with the possible dependence of f_e/f on the Mooney-Rivlin constant $2C_2$, see ref 5 and 25-29.
(25) R.-J. Roe and W. R. Krigbaum, *J. Polym. Sci.*, **61**, 167 (1962).
(26) K. Yamamoto, S. Kusamizu, and H. Fujita, *Makromol. Chem.*, **99**, 212 (1966).
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interest to obtain thermoelastic data on networks in compression, where such deviations are minimized, frequently to the extent of being entirely negligible. Comparison of stress-temperature results obtained for the same polymer in uniaxial compression and elongation will then serve to determine whether error is committed by the intentional neglect of such deviations in analyses of thermoelastic data.

Poly(dimethylsiloxane) (PDMS) is an ideal polymer for such an investigation. It is easily cross-linked into networks of great stability[33] and preliminary studies indicated that in the case of networks of this polymer, the cited frictional problems were quite minor. Furthermore, the thermoelastic properties of this polymer in elongation have been extensively investigated in a number of laboratories.[34-38]

In this study we have therefore undertaken to determine stress-strain isotherms, at a number of temperatures, for PDMS networks in compression. Such data will not only establish the magnitude of any deviations from the theoretically predicted stress-strain relationship, but will also suffice to give thermoelastic results which may be directly compared with those already reported for PDMS networks in elongation.

Theory

According to the statistical theory of rubberlike elasticity, the equation describing the uniaxial compression or elongation of an unswollen polymer network can be written in the alternative forms[31,32]

$$f^*/(\alpha - \alpha^{-2}) = (\nu kT / L_i A^*)(V/V_0)^{2/3} \qquad (1)$$

$$= (\nu kT / L_i A^*)[\langle r^2\rangle_i / \langle r^2\rangle_0] \qquad (2)$$

where f^* is the force divided by the cross-sectional area A^* of the undistorted sample at some convenient temperature, ν is the number of chains in the network, k is the Boltzmann constant, and α is the deformation (elongation or compression) defined by $\alpha = L/L_i$, L being the length of the distorted sample, and L_i the length of the undistorted sample at the volume V prevailing at the specified temperature T, pressure p, and force f.[31,32] The quantity $\langle r^2\rangle_i$ is the mean-square end-to-end distance for a network chain in the undistorted state of volume V; $\langle r^2\rangle_0$ and V_0 are the corresponding quantities for the free chain in the absence of the network cross-links. (Although the function $\alpha - \alpha^{-2}$ is negative in compression, so also is f^*, and the "modulus" $f^*/(\alpha - \alpha^{-2})$ is positive, as it is in elongation.) Stress-strain measurements on unswollen networks at constant temperature, at least in the case of elongation, usually show deviations from these simple equations in that $f^*/(\alpha - \alpha^{-2})$ is not independent of α.[39,40] For this reason, the semiempirical equation[21]

$$f^*/(\alpha - \alpha^{-2}) = 2C_1 + 2C_2\alpha^{-1} \qquad (3)$$

is frequently used to represent stress-strain isotherms. The constants C_1 and C_2 therein unfortunately have no sound basis in the current molecular theories of rubberlike elasticity, but the quantity $2C_2$ is customarily used as a measure of the departure of the dependence of stress on strain from that predicted in eq 1 and 2.

These equations are of importance in the analysis of force-temperature measurements on polymer networks, where one quantity of interest is the energetic contribution f_e to the elastic force f. This contribution is given by[2]

$$f_e = (\partial E/\partial L)_{V,T} \qquad (4)$$

and the fraction of the total force it represents by[2]

$$f_e/f = -T[\partial \ln |f/T|/\partial T]_{V,L} \qquad (5)$$

Since small, but significant, volume changes generally accompany the deformation of a rubberlike network at constant pressure,[41] determination of f_e/f from eq 5 requires the imposition of a hydrostatic pressure in order to meet the thermodynamic requirement of constant volume. Such experiments are notoriously difficult[38,42-44] and it has therefore become customary to transform the constant volume restriction to one of constant pressure, through recourse to an appropriate elastic equation of state.

Such modification carried out by use of eq 1 transforms[31,32,45,46] eq 5 into the experimentally more attractive forms

$$f_e/f = -T[\partial \ln |f/T|/\partial T]_{p,L} - \beta T/(\alpha^3 - 1) \qquad (6)$$

$$= -T[\partial \ln |f/T|/\partial T]_{p,\alpha} + \beta T/3 \qquad (7)$$

where $\beta = (\partial \ln V/\partial T)_p$ is the thermal expansion coefficient of the sample. Alternatively, use of eq 2 in conjunction with eq 5 yields[31,32,46]

$$d \ln \langle r^2\rangle_0/dT = -[\partial \ln |f/T|/\partial T]_{p,L} - \beta/(\alpha^3 - 1) \qquad (8)$$

$$= -[\partial \ln |f/T|/\partial T]_{p,\alpha} + \beta/3 \qquad (9)$$

where $\langle r^2\rangle_0$ is the already defined "unperturbed dimensions" of the chains in the network. Comparison of eq 8 and 9 with eq 6 and 7 then gives

$$d \ln \langle r^2\rangle_0/dT = f_e/fT \qquad (10)$$

an important equation establishing a direct connection between the thermodynamic quantity f_e/f and its molecular counterpart $d \ln \langle r^2\rangle_0/dT$.

Experimental Section

Preparation of Networks. The sample[47] of poly(dimethylsiloxane)$(CH_3)_3Si-[OSi(CH_3)_2]_xOSi(CH_3)_3$ used in this study had a degree of polymerization x of approximately 7000 and, in order to facilitate cross-linking, contained approximately 0.5 mol % $Si(CH_3)(CH{=}CH_2)O$ units. It was degassed at room temperature in order to remove any absorbed oxygen which might complicate

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(47) We are indebted to Dr. John Saam of the Dow-Corning Corp. for providing us with this polymer.

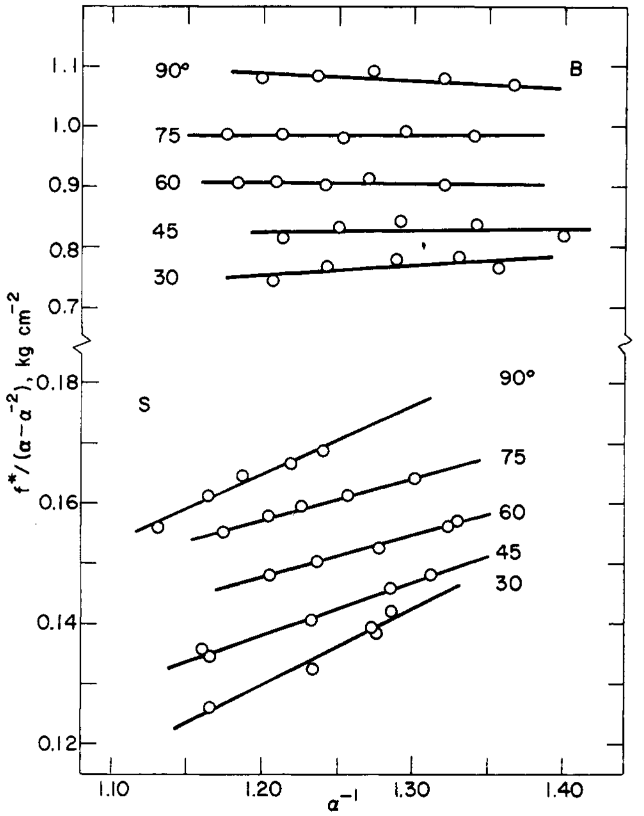

Figure 1. Stress-strain isotherms for PDMS networks prepared in the bulk, undiluted state (B) and solution (S), and studied in the unswollen state at temperatures ranging from 30 to 90°. For these results, the compression α is defined by $L(T)/L_i(30°)$, *i.e.*, the length of the sample at the specified temperature relative to the undeformed length at 30°.

subsequent cross-linking procedures. The first sample (B) was prepared by pouring the bulk (undiluted), liquid polymer into an aluminum-foil-lined, cylindrical brass mold having a well approximately 1.5 cm in diameter and 3 cm in length. The design of the mold was such that it could be sealed in an airtight manner, with the top and bottom surfaces of the cylindrical sample thus enclosed both accurately disposed perpendicular to its axis. The tightly sealed container was then irradiated with γ rays from a ^{60}Co source, at ambient temperature, to a total dose of 1.4 Mrad. The second sample (S) was prepared from a solution of the poly(dimethylsiloxane) in nitrogen-purged mesitylene; the concentration was 60 wt % polymer, which corresponds to a volume fraction of polymer of approximately 0.59. The solution was sealed into a mold identical with that already described but of sufficiently large interior dimensions to give a sample, when unswollen, approximately 2.3 cm in diameter and 4.5 cm in length. This sample was given a total γ-radiation dose of 3.3 Mrad.

The molds were not opened for at least 6 hr after irradiation in order to permit free radicals generated in the samples to decay. After the samples were removed from the molds, they were extracted with benzene, deswollen with methanol, and dried to constant weight, all at room temperature. Test sections for the elasticity measurements were demarcated by two tiny dye spots placed approximately 0.5 cm from the ends of each of the samples.

Stress-Compression Measurements. The cylindrical polymer sample was placed vertically between two smoothly machined Teflon platforms, one directly above the other. The relatively small friction between the sample and the Teflon surfaces was further reduced by coating these surfaces with a slurry of graphite and oligomeric, liquid trimethylene glycol, a mixture which is not absorbed by the poly(dimethylsiloxane) network. The lower platform was attached to a strain gauge and this lower assembly could be moved along a vertical support. The upper platform was permanently fixed to this support and thus the length of the compressed sample could be adjusted by movement of the strain gauge assembly. The entire unit was located in a Pyrex glass cell partially submerged in an oil bath thermostatted to ±0.1°. Finer control of the temperature of the sample was achieved by use of an additional pair of small thermostatting heaters placed within the cell. The temperature of the sample itself was obtained from a thermocouple almost in contact with it. A slow stream of prepurified nitrogen passing through the cell protected the sample from oxidative degradation.

Table I
Values of $2C_2$[a] for Poly(dimethylsiloxane) Networks in Compression

	Sample B		Sample S	
Temp (°C)	Const L	Const α	Const L	Const α
30	0.16	0.16	0.13	0.13
45	0.01	0.08	0.09	0.09
60	−0.02	0.18	0.07	0.08
75	0.01	0.29	0.07	0.09
90	−0.13	0.21	0.12	0.15

[a] kg cm^{-2}.

The strain gauge employed, a Statham UC3 transducer-UL4 load cell, had a capacity of either 2 or 10 lb and was run by a constant voltage dc power supply (Hewlett-Packard Model 6217A). Its output was displayed on a recorder (Leeds and Northrup, Model Speedomax W Azar) and was calibrated at each temperature of interest, at frequent time intervals, by means of a set of standard balance weights.

At the start of each isothermal experiment, the rest length L_i of the sample was measured to ±0.001 cm using a micrometer slide cathetometer (Gaertner Model M940-303P). The sample was then compressed to the largest deformation desired, typically a value of the compression α of approximately 0.7. Stress relaxation at this maximum deformation was then permitted to occur overnight; after such relaxation, the network invariably met the condition arbitrarily chosen to signify elastic equilibrium, *viz.*, constant force for a period of at least 15 min. This value of the force and the corresponding length of the sample were recorded and the length was permitted to increase by a convenient amount. Equilibrium forces and lengths were thus obtained for a series of five deformations in the approximate range α = 0.7–0.9. The stress-strain isotherm obtained from these data was then checked for reversibility using a series of decreasing values of α. No significant irreversibility was found by this technique and no significant barreling of the samples was evident upon visual inspection through the cathetometer. After each run, the sample was permitted to recover under null force for at least 12 hr. The undistorted length L_i was then remeasured and used to calculate precise values of the compression α. Such isotherms were obtained for both the B and S samples at temperatures of 30, 45, 60, 75, and 90°.

The cross-sectional (circular) area A^* of both undistorted samples at 30° was calculated from their diameters, which were obtained by means of a micrometer. The thermal expansion coefficient was determined from values of the length L_i of an undistorted sample at a number of temperatures, measured by means of the cathetometer, and use of the equation $\beta/3 = (\partial \ln L_i/\partial T)_p$.[46]

Results and Discussion

Figure 1 shows a plot of $f^*/(\alpha - \alpha^{-2})$ *vs.* α^{-1}, as suggested by eq 3, at each of the temperatures employed in this study. As is frequently done in stress-temperature studies,[8] the values of the deformation α in these results were calculated using a value of the rest length of the sample at some convenient, constant temperature; in this case the definition $\alpha = L(T)/L_i(30°)$ was employed. All lines show in this figure were located by the method of least squares. Values of $f^*/(\alpha - \alpha^{-2})$ read from these curves at selected values of α^{-1} would give force–temperature results equivalent to those obtained in a thermoelastic experiment carried out at constant length. Similar plots, not shown here, were obtained using the alternative definition $\alpha = L(T)/L_i(T)$, which utilizes the rest length of the sample at the actual temperature of the isotherm being determined. Values of $f^*/(\alpha - \alpha^{-2})$ obtained from

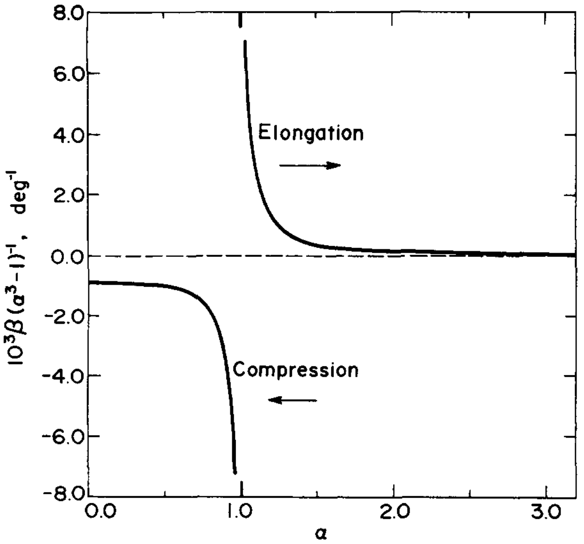

Figure 2. Values of the term $\beta(\alpha^3 - 1)^{-1}$, which corrects thermoelastic data at constant pressure and length to constant volume and length, shown as a function of the relative length or deformation α of the sample. Results have been calculated for PDMS at 60°, for which the thermal expansion coefficient β has the value 0.916×10^{-3} deg^{-1}.[50]

these curves at various values of α^{-1} would represent thermoelastic results pertaining to constant compression α, *i.e.*, to results obtained on a sample whose length L is adjusted in the manner which will maintain a constant ratio α between L and the undistorted length L_i at each temperature of measurement.

Values of $2C_2$ obtained from the slopes of the lines in both types of plots, for both samples, are given in Table I. As is immediately evident from these entries, $2C_2$ is very small in compression, having an average magnitude of only 0.11 (±0.05) kg cm^{-2}. De Candia and Amelino[18] have reported the somewhat larger value $2C_2 = 0.20$ kg cm^{-2} for an unswollen PDMS network in compression. This latter result, however, is probably not reliable because the sample employed contained filler and was of such short length (1.5 cm) that uncertainties arising from inhomogeneous deformation would be expected to be particularly serious. Of primary importance here, however, is the fact that values of $2C_2$ for unswollen PDMS networks in elongation[18,33,37,48,49] are generally three to ten times the magnitude of the average value of $2C_2$ found in the present study for PDMS networks in compression. (The ratio $2C_2/2C_1$ is also frequently used to characterize stress-strain isotherms; the physical meaning of the extrapolation required to obtain $2C_1$, however, is not understood at present, thus making evaluation of this ratio extremely difficult. In any event, this ratio is small in the case of sample B, but not in the case of sample S, which is much less highly cross-linked.)

The value of the thermal expansion coefficient β at 60°, the average temperature employed in this study, is 1.0×10^{-3} deg^{-1} according to the length-temperature measurements described earlier. This result is in satisfactory agreement with the range 0.83-0.99×10^{-3} deg^{-1} reported for this coefficient in the literature.[34-38,50,51] Because of the importance of this quantity in the present analysis, it was decided to use the most reliable value, $\beta = 0.916 \times 10^{-3}$ deg^{-1} at 60°, determined by Shih and Flory[50] with particular care, as required by its subsequent use in the analysis of the thermodynamic properties of PDMS solutions. When thermoelastic measurements in elongation are carried out, for example to obtain values of d ln $\langle r^2\rangle_0$/dT, conditions of constant length are usually preferred over conditions of constant deformation α, for two reasons. The measurements at constant length are considerably easier to perform and the term $\beta/(\alpha^3 - 1)$ correcting constant volume to constant pressure conditions in eq 8 can be reduced to a very small value by performing the measurements at relatively large values of the elongation α. This is demonstrated in Figure 2, where $\beta/(\alpha^3 - 1)$ is shown as a function of α for PDMS at 60°. As is also shown in the figure, it is impossible in compression measurements to decrease this correction term to the point where it can be expected to be small relative to the desired quantity d ln $\langle r^2\rangle_0$/dT, which is typically the order of 1×10^{-3} deg^{-1}. The stress-strain isotherms in the present study were therefore analyzed to give force-temperature data which correspond to conditions of constant α, where the correction term, as shown in eq 9, is simply $\beta/3$.

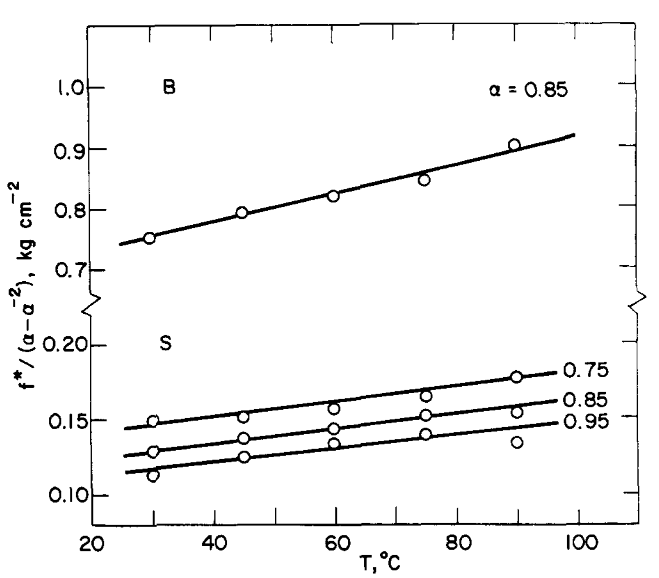

Figure 3. Values of $f^*/(\alpha - \alpha^{-2})$ shown as a function of temperature for unswollen PDMS networks for illustrative values of α. These results were obtained from plots of $f^*/(\alpha - \alpha^{-2})$ *vs.* α^{-1}, where $\alpha = L(T)/L_i(T)$ and thus pertain to constant deformation or compression, rather than to constant length.

Table II
Thermoelastic Results on Poly(dimethylsiloxane) in Compression

Sample	α	$-10^3(\partial \ln\lvert f/T\rvert/\partial T)_{p,\alpha}$	f_e/f	$10^3(\mathrm{d}\ln\langle r^2\rangle_0/\mathrm{d}T)$
B	0.95	0.396	0.21	0.70
	0.90	0.272	0.17	0.58
	0.85	0.137	0.13	0.44
	0.80	−0.009	0.09	0.30
	0.75	−0.171	0.04	0.13
			$\overline{0.13}$ (±0.05)	$\overline{0.43}$ (±0.17)
S	0.95	0.115	0.13	0.42
	0.90	0.135	0.13	0.44
	0.85	0.155	0.14	0.46
	0.80	0.175	0.14	0.48
	0.75	0.197	0.15	0.50
			$\overline{0.14}$ (±0.01)	$\overline{0.46}$ (±0.02)

Values of the force f were calculated from the stress-strain isotherms at intervals of 0.05 in $\alpha = L(T)/L_i(T)$,

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Table III
Survey of Thermoelastic Results on Poly(dimethylsiloxane)

Method	Range of α	Range of T (°C)	f_e/f	$10^3(\mathrm{d}\ln\langle r^2\rangle_0/\mathrm{d}T)$	Source
Const p,L	1.25–2.51	17–100	0.15 (±0.03)	0.46 (±0.10)	Ciferri[34]
p,L	1.34–2.10	40–100	0.27 (±0.02)	0.78 (±0.06)	Mark and Flory[35]
p,L	1.10–1.52	−40–125	0.15	0.48	Sperling and Tobolsky[36]
p,f	1.20–1.80	25–70	0.18 (±0.06)	0.57 (±0.18)	Barrie and Standen[37]
V,L	1.10–1.20	30–36	0.25 (±0.02)	0.82 (±0.07)	Allen *et al.*[38]
p,α	0.75–0.95	30–90	0.13 (±0.03)	0.45 (±0.10)	Chen, Yu, and Mark

over what is probably the experimentally most reliable range, 0.95–0.75. Typical results are presented in Figure 3, where the lines shown have been located by least-squares analysis. Other results have been omitted for reasons of clarity. Values of the coefficient $(\partial \ln |f/T|/\partial T)_{p,\alpha}$ for all values of α cited are shown in the third column of Table II. Values of f_e/f and d ln $\langle r^2\rangle_0/\mathrm{d}T$ at 60° calculated therefrom by means of eq 7 and 9 are given in the last two columns of the table. Since these two quantities contain equivalent information[8,30-32] and the latter is directly interpretable in terms of rotational isomeric state theory,[52-54] the remaining discussion will be presented in terms of d ln $\langle r^2\rangle_0/\mathrm{d}T$ alone.

Although the values of d ln $\langle r^2\rangle_0/\mathrm{d}T$ are found to be independent of α in the case of the solution cross-linked sample (S), there is a significant decrease in this coefficient with decreasing α in the case of the sample (B) prepared in the undiluted state. This dependence on α obviously complicates comparison of the present results with those obtained from other thermoelastic studies on PDMS networks. The reason for this variation is not known but, in any case, the average values obtained for the two samples are in good agreement with each other, yielding the overall result 10^3 d ln $\langle r^2\rangle_0/\mathrm{d}T$ = 0.45 (+0.10) deg^{-1}. Most importantly, these results for PDMS networks in compression are in satisfactory agreement with published results[34-38] on PDMS networks in elongation. In general, these results were obtained from networks prepared in the undiluted, unoriented state and studied unswollen, in elongation at constant length; exceptions include the preparation of networks in solution,[34] and the study of networks at constant force,[37] or at constant volume.[38] These studies, which are described in the first five rows of Table III, yield an average value of 10^3 (d ln $\langle r^2\rangle_0/\mathrm{d}T$) of 0.62 (±0.10) deg^{-1}. If particular emphasis is placed on the result obtained by direct evaluation of the derivative $(\partial \ln |f/T|/\partial T)_{V,L}$ in eq 5, then the entire collection of results in Table III seems to indicate the best value of 10^3 (d ln $\langle r^2\rangle_0/\mathrm{d}T$) to be 0.70 (±0.10) deg^{-1}, in good agreement with the value[35] 0.78 (±0.06) used in the rotational isomeric state analysis of PDMS chains.[55] In any case, since values of $2C_2$ are so different under conditions of compression and elongation, the agreement between the values of d ln $\langle r^2\rangle_0/\mathrm{d}T$ obtained using these different types of deformation lends strong support to the intentional disregard[8,30-32] of the $2C_2$ correction term in analyses of thermoelastic data. As pointed out elsewhere,[8] there is a variety of additional experimental evidence also in support of this conclusion.

Agreement between values of d ln $\langle r^2\rangle_0/\mathrm{d}T$ obtained from thermoelastic measurements in compression and in elongation has also been reported for polystyrene[8,56] and for natural rubber.[8,57] These studies are probably not as definitive, however, as the present study in this regard. The first[56] of these studies involved measurements on polystyrene networks in swelling equilibrium with solvent, and such data are considerably more difficult[58] to interpret than are measurements on thermodynamically closed systems. In the second study,[57] on natural rubber, only a very small range of compression, α = 0.88–1.00, was investigated, and the permanent bonding of the sample to the compression plates would seem to have made it impossible to entirely avoid inhomogeneity in the deformation.

It is perhaps appropriate to conclude by reiterating here the origin of the positive value observed for d ln $\langle r^2\rangle_0/\mathrm{d}T$ for PDMS. We first point out that the recent interpretation of the positive value of this coefficient for another member of the siloxane series, poly(phenylmethylsiloxane), by de Candia and Turturro[59] is entirely incorrect. In the case of siloxane chains, an increase in the unperturbed dimensions is associated with a *decrease* in the number of trans states about skeletal bonds and *not* an increase, as was concluded by de Candia and Turturro.[59] As has now been abundantly pointed out in the literature,[53,55,60] a decrease in the number of trans states in such chains increases the unperturbed dimensions since the inequality of skeletal bond angles in Si–O– chains make the all-trans conformation in these molecules one of very small end-to-end distance. In PDMS, trans states are of relatively low energy and since they also represent very compact conformations, an increase in temperature increases $\langle r^2\rangle_0$, in agreement with experiment.

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(52) See, for example, ref 53 and 54.

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