TABLE II
RATE CONSTANTS FOR SCISSION OF CROSS-LINKAGES IN DEXSIL-201

T, °C	Weak links k_c, l./sec	%	Strong links k_c, l./sec	%
300	8.4×10^{-5}	45	7.5×10^{-6}	55
325	6.3×10^{-4}	30	4.3×10^{-5}	70
350		5	1.2×10^{-4}	95

Resolution of the curves into two exponentials using procedure X[8] gave the data in Table II for the weak and strong cross-linkages introduced by the peroxide cure of Dexsil-201. Thd weak cross-linkage has a rate constant surprisingly close to that of the cross-linkages in silicone rubber, and the variation of rate with temperature is also close (Table I). This result invites an identification of the weak cross-linkage with unprotected Si—C—C—Si (or perhaps Si—C—Si) bonds which could well be present in the Dexsil elastomers. The strong cross-linkage shows a lower activation energy but an extraordinarily low frequency factor of about 10^{11}. This indicates that cleavage requires an exceedingly complex arrangement of mass centers before a reaction can occur. In general, the overall activation energy of these ultrastable elastomers has been found to be very low (up to temperatures of 450°, where another reaction of higher energy dominates). The result for the strong cross-linkages found by this analysis was thus not entirely unexpected. The identity of the strong cross-linkage is not known, but it may involve the vinyl group which is attached to the pendent carborane groups incorporated in the Dexsil-201 elastomers.[3]

Conclusions

A technique, involving the comparison of two samples with different cross-link densities, was successfully used to determine the thermal stability of carbon–carbon cross-linkages in elastomers of various types. This technique subtracts out the inevitable reactions in the main chains of elastomers exposed to high temperatures.

Activation energies for carbon–carbon cross-link cleavage were about 55 kcal/mol, indicating a multistep cleavage reaction or bonds with activating neighboring groups. The presence of carbon–carbon bonds in thermally stable elastomers will, in most cases, limit their use temperature to less than 300°.

The highly stable Dexsil-201 (siloxane–carborane) elastomer proved to be an ideal matrix for the study of relatively weak cross-linkages. The peroxide cure was found to introduce two types of cross-linkages—one similar to that in conventional silicone rubber and the second much more stable, and possibly not containing a carbon–carbon bond.

(8) See ref 1, p 188.

The Equation of State for Rubber Elasticity. The Effect of Swelling on the Front Factor

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ABSTRACT: Force measurements at a fixed extension ratio were carried out for cross-linked silicone rubber swollen in a wide variety of solvents. From these measurements and using the theory of rubber elasticity, the value of α_N^2 was deduced. This is the ratio of the mean square end-to-end distance of the unconstrained network chains in the various swollen networks compared to the mean square end-to-end distance under roughly Θ conditions. A comparison was made between α_N^2 and α^2, the latter being measured in a dilute solution of the linear polymer in the same series of solvents. There was a qualitative similarity between these quantities, with α_N^2 smaller than α^2.

Recent developments[1] in the statistical theory of rubber elasticity yield the following equation for the stress–strain behavior of a swollen polymer network

$$f_s = \frac{NkT\langle r^2\rangle_0}{L_0\langle r_f^2\rangle}\left[\frac{L_s}{L_0} - \left(\frac{L_0}{L_s}\right)^2\frac{V_s}{V_0}\right] \qquad (1)$$

where f_s is the force required to maintain the swollen network at length L_s; L_0 and V_0 are the length and volume of the unstretched, unswollen network; V_s is its stretched, swollen volume; N is the number of network chains in the sample; $\langle r^2\rangle_0$ is the mean square end-to-end distance of the network chains in the unstretched, unswollen state; and $\langle r_f^2\rangle$ is the mean square end-to-end distance that the network chains would assume, in the stretched, swollen state at V_s, if the cross-links were removed. For an unswollen network eq 1 becomes

$$f_d = \frac{NkT\langle r^2\rangle_0}{L_0\langle r_f^2\rangle_d}\left[\frac{L_d}{L_0} - \left(\frac{L_0}{L_d}\right)^2\frac{V_d}{V_0}\right] \qquad (1a)$$

where the subscript d refers to the unswollen, stretched state. The quantity $\langle r_f^2\rangle/\langle r_f^2\rangle_d$ can be determined by combining results of force–length measurements on the

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(1) A. V. Tobolsky and L. H. Sperling, *J. Phys. Chem.*, **72**, 345, (1968); A. V. Tobolsky and M. Shen, *J. Appl. Phys.*, **37**, 1952 (1966); K. Dusěk and W. Prins, *Advan. Polym. Sci.*, **6**, 1 (1969).

swollen with those on the unswollen network. Dividing eq 1a by eq 1 we obtain

$$\frac{\langle r_f^2\rangle}{\langle r_f^2\rangle_d} = \alpha_N^2 = \frac{f_d\left[\frac{L_s}{L_0} - \frac{V_s}{V_0}\left(\frac{L_0}{L_s}\right)^2\right]}{f_s\left[\frac{L_d}{L_0} - \left(\frac{L_0}{L_d}\right)^2\right]} \qquad (2)$$

since $V_d \approx V_0$. All the quantities on the right side of eq 2 can be easily measured with the exception of V_s/V_0. Bashaw and Smith,[2] however, have derived an expression for the increase in swelling which accompanies deformation of a swollen network

$$\frac{V_s}{V_s'} = \left(\frac{L_s}{L_s'}\right)^{1/2}\left[1 + \frac{1}{4}\left\{\left(\frac{L_s}{L_s'}\right)^{1/2} - 1\right\}\left(\frac{V_0}{V_s'}\right)^{2/3}\frac{\langle r_f^2\rangle_d}{\langle r^2\rangle_0}\right] \qquad (3)$$

where V_s' and L_s' are the volume and length of the swollen, unstretched sample. With the aid of the Bashaw–Smith expression, α_N^2 can be determined according to eq 2, assuming $\langle r^2\rangle_0/\langle r_f^2\rangle_d = 1$.

$\langle r_f^2\rangle$ is the end-to-end distance which would be attained by an equivalent linear chain in an environment comparable to that of the network chain. Hence the ratio $\langle r_f^2\rangle/\langle r_f^2\rangle_d = \alpha_N^2$ may be compared to that factor, usually denoted by α^2, which expresses the linear expansion of a polymer molecule in solution due to solvent polymer interaction.[3] $\alpha^2 = \overline{r^2}/\overline{r_0^2}$, where $\overline{r^2}$ is the mean square end-to-end distance of the polymer molecule in solution and $\overline{r_0^2}$ is that in the unperturbed state. The theory of polymer solutions[3] would then suggest that the factor $\langle r_f^2\rangle/\langle r_f^2\rangle_d$ in eq 2 could be varied through the introduction of different swelling agents to the polymer network; for each particular swelling agent the value of α_N^2 obtained from eq 2 can be compared with α^2. It must be realized, however, that even at the highest degree of swell swollen networks are not dilute solutions; therefore α_N^2 and α^2 will not necessarily be identical since the α^2 values, obtained from intrinsic viscosity measurements or calculated from solution theory expressions, refer to an infinitely dilute solution. The two quantities should be similar and a comparison of the two will demonstrate that the network reference dimensions, $\langle r_f^2\rangle$, vary in the same manner as the dimensions of an equivalent linear polymer in a comparable environment.

Experimental Section

Samples of cross-linked polydimethylsiloxane were obtained from Dr. A. C. Martellock of the General Electric Co., Waterford, N. Y. These elastomers were prepared from a polymer containing 0.05 mol % methylvinylsiloxane and end-blocked with dimethylvinylsiloxy groups; this polymer was press cured with 0.6% di-*t*-butyl peroxide followed by a 16-hr post cure at 150°. All samples were extracted with acetone in a Soxlet apparatus for 24 hr; they were then swollen in benzene containing 0.01% Ionox[4a] and dried in a vacuum oven until their weight became constant. The molecular weight between cross-links of this network was found to be 2.0×10^4 from force length measurements assuming $\langle r^2\rangle_0/\langle r_f^2\rangle_d = 1$.

Retractive force measurements were made on a standard relaxation balance[4b] equipped with a liquid cell which enabled measurements to be made with the sample completely immersed in diluent. The experiments were performed in a thermostated room in which the temperature was 24 ± 1°. Runs during which the temperature varied by more than 2° were discarded.

The volume fraction of polymer in the swollen unstretched network was calculated from the weight of the dry and of the swollen network as described by Doty and Zable.[5] The density of the silicone network was determined by means of Archimedes' principle in dimethylformamide.

For intrinsic viscosity measurements 1000 cS Dow Corning 200 Fluid, a trimethyl end-blocked linear polydimethylsiloxane, was used. The number average molecular weight of this polymer was found to be 1.8×10^4 from the intrinsic viscosity–molecular weight relationship of PDMS in toluene.[6] Intrinsic viscosity measurements were made with Ubbelohde viscometers in a water bath maintained at a temperature of 25 ± 0.03°. Dilutions were made in the viscometers but checks for dilution errors were frequently made by also measuring directly solutions of known concentration. Furthermore, different viscometers were used for the determination of one η_{sp}/c *vs.* c plot; since the values obtained proved to be independent of the viscometer used, any shear rate effects can be ruled out.

Results and Discussion

The network expansion factor, α_N^2, was measured for a polydimethylsiloxane network swollen with a variety of swelling agents. These swelling agents fall into two categories; the first consists of a series of linear polydimethylsiloxane fluids of different molecular weight and the second consists of common low molecular weight organic solvents. The results are given in Table I and Table II. It can be seen that $\langle r_f^2\rangle$ in the swollen state depends on the nature of the swelling agent and is as much as 50% larger than in the dry state. Furthermore, the variation of α_N^2 with swelling agent follows very closely that which would be expected if the network reference dimensions are identical with the dimensions of a similar linear polymer.

The data in Table I show $\langle r_f^2\rangle$ decreasing with increasing molecular weight of the swelling agent. When the swelling agent is the silicone fluid whose molecular weight is approximately equal to the molecular weight

TABLE I
RESULTS FOR PDMS SWOLLEN IN SILICONE FLUIDS

Mol wt of swelling agent	V_1, cc	V'/V_0	α^2 (from eq 4)	α_N^2 (from eq 2)
200	245	6.15	1.81	1.51
350	400	5.05	1.58	1.42
750	800	3.27	1.37	1.23
3,200	3,300	2.72	1.12	1.16
4,000	4,200	1.89	1.10	1.06
7,300	7,530	1.85	1.06	1.05
18,000	18,500	1.67	1.02	1.01

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(2) J. Bashaw and K. J. Smith, Jr., *J. Polym. Sci., Part A-2*, 6, 1041 (1968).

(3) P. J. Flory, "Principles of Polymer Chemistry," Cornell University Press, Ithaca, N. Y., 1953.

(4) (a) A commercial antioxidant produced by the Shell Chemical Co.; it is 1,3,5-trimethyl-2,4,6-tris(3,5-di-*t*-butyl-4-hydroxybenzyl)benzene. (b) A. V. Tobolsky, "Structure and Properties of Polymers," Wiley, New York, N. Y., 1960.

(5) P. Doty and H. S. Zable, *J. Polym. Sci.*, **1**, 90 (1946).

(6) J. Brandrup and E. H. Immergut, Ed., "Polymer Handbook," Wiley, New York, N. Y., 1966.

TABLE II

	Using eq 2 for V_s/V_s'		Assuming $V_s/V_s' = 1$		
Swelling agent	α_N^2	α_N^2/α_N^2(ref)	α_N^2	α_N^2/α_N^2(ref)	$[\eta]$
Methyl ethyl ketone	1.30	1.00	1.54	1.00	0.095
Ethyl iodide	1.31	1.00	1.53	1.02	0.090
Cumene	1.37	1.05	1.59	1.06	0.105
Benzene	1.39	1.07	1.63	1.09	0.114
Toluene	1.44	1.11	1.71	1.14	0.123
Chloroform	1.44	1.11	1.66	1.11	0.137
Methylene chloride	1.47	1.13	1.70	1.13	0.120
Methylchlohexane	1.50	1.15	1.74	1.16	0.132
Cyclohexane	1.53	1.16	1.79	1.17	0.134
Heptane	1.55	1.19	1.82	1.21	0.137
Carbon tetrachloride	1.59	1.22	1.87	1.24	0.148
Acetone	0.96		1.16		

between cross-links of the network ($M_{\text{fluid}} = 1.8 \times 10^4$; $M_c = 2.0 \times 10^4$), α_N^2 is essentially unity indicating no change in the reference dimensions between the dry and swollen states. This result, which certainly lends credence to the contention that $\langle r_f^2 \rangle$ is the same as $\overline{r^2}$ for a linear polymer in a comparable environment, cannot be considered trivial in view of the relatively high degree (167%) to which the silicone network is swollen in this particular fluid.

The values of α_N^2 can be compared in Table I to α^2 values calculated from Flory's[7] expression

$$\alpha^5 - \alpha^3 = \frac{2CM^{1/2}}{V_1}(1 - 2\mu) \tag{4}$$

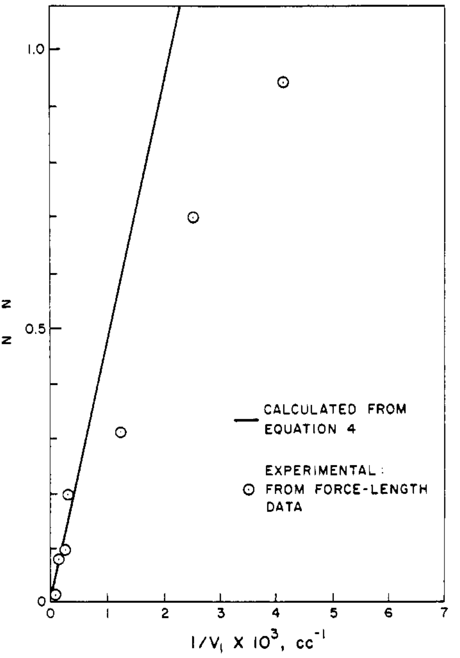

Figure 1. $\alpha_N^5 - \alpha_N^3$ and $\alpha^5 - \alpha^3$ calculated from eq 4 *vs.* $1/V_1$ for the silicone swelling agents.

where M is the polymer molecular weight, V_1 is the molar volume of the solvent, μ is the specific solvent–polymer interaction parameter. For this case it is assumed that μ is equal to zero. In Figure 1, $\alpha_N^5 - \alpha_N^3$ and $\alpha^5 - \alpha^3$ are plotted against $1/V_1$. Equation 4 predicts fairly well the values of α_N^2 for the higher molecular weight swelling agents; however, as the molecular weight of the swelling agent decreases the values of α_N^2 predicted by eq 4 become significantly larger than the experimentally determined α_N^2 values. Assuming that eq 4 gives reasonably good values of α^2, there are two factors which may contribute to this deviation. First, there is the concentration effect; eq 4 gives the expansion of a polymer molecule in solution at infinite dilution whereas α_N^2 is obtained from measurements on swollen polymer networks in which the polymer concentration is not negligible. The size of a polymer molecule in a good solvent decreases with increasing concentration, and this dependence of $\overline{r^2}$ on concentration should increase as the molecular weight of the solvent decreases.[8,9] Second, there may be a significant effect of the cross-links on the statistics of the network chains, as has been suggested by Mijnlieff and Jaspers,[10] which would cause slight differences between $\langle r_f^2 \rangle$ and $\overline{r^2}$; this effect is expected to increase as the degree of swell of the network increases.

The results of the measurements of α_N^2 for the polydimethylsiloxane network swollen in several low molecular weight liquids are given in Table II along with the intrinsic viscosity of a linear polydimethylsiloxane polymer (of molecular weight equal to the molecular weight between cross-links of the network) in each of the solvents. It can be seen that both α_N^2 and $[\eta]$ vary from solvent to solvent in the same manner, which is to be expected if $\langle r_f^2 \rangle$ and $\overline{r^2}$ are identical.

α^2 can be obtained from the ratio of the intrinsic viscosity in the particular solvent to the intrinsic viscosity in a Θ solvent, as suggested by the Flory–Fox[11] equation

$$[\eta] = KM^{1/2}\alpha^3 = \frac{\Phi(\overline{r^2})^{3/2}}{M} \tag{5}$$

since $\alpha^2 = 1$ in a Θ solvent by definition. To avoid any error arising from specific solvent effects on the unperturbed dimensions it is necessary to reduce both the α_N^2 and the α^2 data by their values in the same reference solvent. From eq 2 we obtain

$$\alpha_N^2/\alpha_N^2(\text{ref}) = \langle r_f^2 \rangle / \langle r_f^2 \rangle \text{ref} \tag{6}$$

and from the Flory–Fox[11] relation (5) we obtain

$$([\eta]/[\eta]_{\text{ref}})^{2/3} = \frac{\overline{r^2}}{\overline{r^2}_{\text{ref}}} \tag{7}$$

$\alpha_N^2/\alpha_N^2(\text{ref})$ and $([\eta]/[\eta]_{\text{ref}})^{2/3}$ for ten solvents calculated from Table II are plotted against each other in Figure 2. If the two quantities were identical, all the points

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[7] P. J. Flory, *J. Chem. Phys.*, **17**, 303 (1949).

[8] M. Fixman, *Ann. N. Y. Acad. Sci.*, **89**, 657 (1961).

[9] T. B. Grimley, *Trans. Faraday Soc.*, **57**, 1974 (1961).

[10] P. F. Mijnlieff and W. J. M. Jaspers, *J. Polym. Sci., Part A-2*, **7**, 357 (1969).

[11] P. J. Flory and T. G Fox, *J. Amer. Chem. Soc.*, **73**, 1904 (1951).

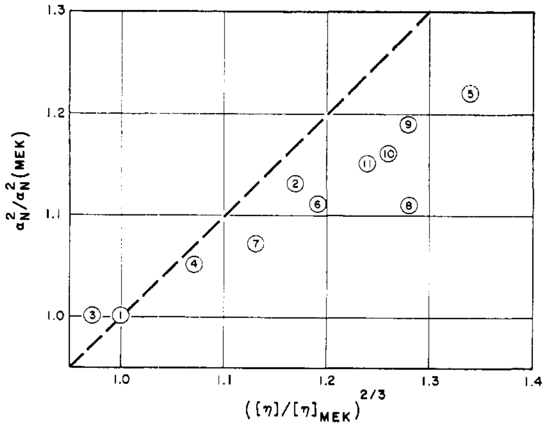

Figure 2. $\alpha_N^2/\alpha_N^2(\text{ref})$ *vs.* $([\eta]/[\eta]_{\text{ref}})^{2/3}$ for the organic swelling agents listed in Table II. The numbers refer to the swelling agents as follows: 1, methyl ethyl ketone; 2, methylene chloride; 3, ethyl iodide; 4, cumene; 5, carbon tetrachloride; 6, toluene; 7, benzene; 8, chloroform; 9, *n*-heptane; 10, cyclohexane; 11, methylcyclohexane.

in Figure 2 would fall on the dashed line which passes through the origin and has a slope of unity; however, the straight line which best fits the data has a slope of 0.7. This may be attributed to the two factors mentioned above: concentration differences and possible influence of the cross-links on α_N^2.

From consideration of the accuracy to which the quantities on the right-hand side of eq 2 can be measured, one would expect that the maximum error in the values of α_N^2 thus obtained should be less than 10%. In order to determine the probable error involved, α_N^2 was measured several times with different samples swollen in the same solvent. This procedure was carried out with both cyclohexane and acetone. Ten measurements of α_N^2 in cyclohexane varied from 1.49 to 1.62 which gives a maximum deviation of 9%; α_N^2 in acetone varied from 0.92 to 1.01 which gives a maximum deviation of 10%. It can be concluded that the α_N^2 values reported here are accurate to well within 10%.

We have shown that the network reference dimensions do indeed depend on the actual state of the network. In the case of swollen polydimethylsiloxane the variation in $\langle r_f^2 \rangle$, to a very good approximation, has been shown to be the same as $\overline{r^2}$ for a corresponding linear polymer in a comparable environment. At higher degrees of swell differences between α_N^2 and α^2, which may not be due solely to concentration effects, suggest the possibility that the presence of the cross-links may cause slight differences between $\langle r_f^2 \rangle$ and $\overline{r^2}$.

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TABLE III
SILICONE SWELLING AGENTS

Mol wt of swelling agent	V_s/V_s' from eq 3	V_s/V_s' exptl
200	1.05	1.07
350	1.04	1.08
750	1.04	1.04
3,200	1.05	1.04
4,000	1.06	1.02
7,300	1.04	1.10
18,000	1.05	1.06

Appendix

Since the Smith–Bashaw equation is used to calculate α_N^2, it is necessary to determine to what extent the results reported here depend on the assumptions used to derive this equation. Starting with the Flory theory of swelling Smith and Bashaw obtain the following expression

$$\frac{\left(\frac{1}{2}-\mu\right)v_s^2+\sum_{n=3}^{\infty}\frac{v_s^n}{n}}{\left(\frac{1}{2}-\mu\right)v^2+\sum_{n=3}^{\infty}\frac{v^n}{n}}=\frac{\left[v_s^{1/3}-\frac{v_s}{2}\right]}{\left[\frac{v_s^{1/3}}{\alpha}-\frac{v}{2}\right]} \tag{8}$$

where v_s is the volume fraction of polymer in the swollen, unstretched network ($v_s = V_0/V_s'$) and v is the volume fraction of polymer in the swollen, stretched network ($v = V_0/V_s$). $\langle r^2_0 \rangle/\langle r_f^2 \rangle_d$ is assumed to be unity and is thus omitted in eq 8. When $v_s \ll 1$, the sums can be neglected and eq 8 reduces to eq 3. When v_s is not $\ll 1$, as is the case in the experiments reported here, the value of V_s/V_s', according to eq 8, will be slightly smaller than that predicted by eq 3. If the increased swelling with elongation is ignored, *i.e.*, if it is assumed that $V_s = V_s'$, α_N^2 calculated from eq 2 would be significantly larger, as shown in Table II for the low molecular weight organic swelling agents. $\alpha_N^2/\alpha_N^2(\text{ref})$ would be virtually unchanged, however, and the comparison of α_N^2 with $[\eta]^{2/3}$ demonstrated in Figure 2 would still hold. The conclusions about the variation in $\langle r_f^2 \rangle$ are valid independent of any assumptions concerning V_s/V_s'.

V_s/V_s' was determined for the network swollen in the silicone fluids by measuring the dimensions of the swollen samples with a cathetometer before and after stretching. The results are given in Table III. Since this method involves taking the difference of two large numbers it is not expected to be very accurate; however, the data indicate that there is a distinct increase in swelling with elongation and that this increase is reasonably well predicted by eq 2. Therefore, we feel that the α_N^2 values given in Tables I and II, calculated using the Smith–Bashaw expression equation (3), should be reasonably correct.