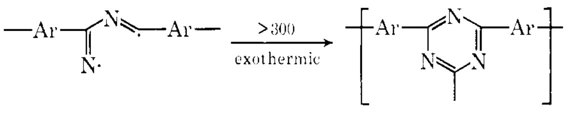
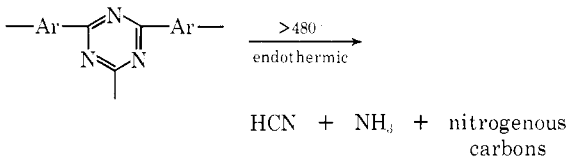
benzonitrile and pseudostable intermediates. The second step involves the recombination of nitrile radicals to form symmetrical triazine rings (eq 3).



(3)

Evidence for this reaction was obtained from mass spectral data of the decomposition products at high temperatures. A mass peak of 81 corresponding to the formation of symmetrical triazine was present in the spectra at 720° (Figure 6) but was absent in the spectra at 580° (Figure 4). Intermediate products such as the symmetrical triazine shown in eq 3 are thermally stable.[7] The formation of stable intermediate products is evident from the data in Figures 1 and 7.

Above 480° the intermediate residue decomposes endothermically with hydrogen cyanide and ammonia as the major nitrogeneous products formed. This reaction produces a maximum endotherm at 510° and maximum gas evolution at 580° (Figures 1 and 5).



A delay in mass loss from this endothermic reaction is surprising since the products formed are light gases and at these temperatures diffusion should not be rate determining. It is possible, however, that the endotherm involved fragmentation of the residue into larger species with subsequent cracking of fragments in the vapor phase. The resulting heat of vaporization could have been neutralized by the heat of decomposition of fragments thus explaining the lack of a DTA peak at the temperature of maximum gas evolution. The third major reaction takes place between 690 and 760° and reaches a maximum at 720° (Figure 1). Dehydrogenation was the major reaction in this temperature range as indicated by a 70.5% decrease in hydrogen in the elemental composition of the residue (Table I).

Degradation under oxidative conditions proceeds in two major steps (Figure 7). First the polymer decomposes thermally between 392 and 515° in a similar fashion to that under vacuum to form a stable intermediate which then oxidizes between 545 and 685° by a very strong exothermic process. The temperature of initial decomposition in air (Figure 7) was 392°, significantly higher than under vacuum (Figure 1), or in argon. Additional repetitive experiments were carried out to substantiate these findings and gave identical results. Apparently the polymer is stabilized in the presence of air by a mechanism presently not understood. This unusual stabilization phenomenon is presently under investigation.

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[7] G. F. Ehlers and J. D. Ray, *J. Polym. Sci., Part A*, **2**, 4989 (1964).

Thermal Stability of the Carbon–Carbon Cross-Linkage in Polymer Networks

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Received April 30, 1970

ABSTRACT: The thermal stability of carbon–carbon cross-linkages in elastomeric systems was studied by comparing the vacuum chemical stress relaxation of samples with different concentrations of these cross-linkages. The systems studied included silicone rubber, cross-linked polyethylenes, and Dexsil-201 rubber. Arrhenius activation energies of about 55 kcal/mol were found for the scission of these cross-linkages in the temperature range 300–350°. Cross-linkages added to a sample by additional curing were found to be, in general, more stable than those first formed. A more detailed analysis of the cleavage reaction was performed on peroxide-cured Dexsil-201 elastomer—made possible because the main chains of this material are stable at the temperatures used. Two species of cross-links were distinguishable: one having the same stability as the carbon–carbon cross-linkage in silicone rubber, another being ten times as stable and probably devoid of normal carbon–carbon bonds.

The exploration of the thermal stability of cross-linked elastomeric materials has almost necessarily paralleled the development of the techniques of chemical stress relaxation, because the more conventional methods of following chemical reactions do not lend themselves to these solid insoluble materials. Chemical stress relaxation is also one of the simplest, as well as one of the few, methods for direct, *in situ* measurement of the rate of reaction of the bonds in these intractable materials. It depends on the proportionality between the number of network chains in an elastomer and the elastic force generated by the sample on extension. The number of network chains in turn can be related to the number of scissions which occurred.[1]

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[1] A. V. Tobolsky, "Properties and Structure of Polymers," Wiley, New York, N. Y., 1960, Chapter V.

Early studies using the chemical stress relaxation technique indicated that oxygen was influential in the relaxation of hydrocarbon rubbers such as natural rubber. It was further found that sulfur, commonly used as a vulcanizing agent, would form cross-linking bonds between the hydrocarbon chains which were also capable of undergoing scission reactions.[1] Conclusive demonstration of the latter point was obtained recently when sulfur-cured saturated hydrocarbon elastomers (*e.g.*, ethylene–propylene terpolymer, EPT) were found to show relaxation in the absence of oxygen whereas the corresponding peroxide-cured elastomers (carbon–carbon cross-linkages) did not.[2] These experiments were performed at temperatures around 130°.

The discovery of polymers with high thermal stability (for example, the silicones) has resulted in the exploitation of the species with proper molecular flexibility for cross-linked elastomers, often useful at temperatures approaching 300°. The traditional methods of curing these materials (peroxides, radiation) generally lead to abstraction of a hydrogen atom to form a carbon radical. Termination results in a carbon–carbon cross-linkage—quite stable under most conditions.

The invention of modified, stabilized siloxane chains[3] and their subsequent use in elastomers has generated the suspicion that the carbon–carbon cross-linkages, when used, were the weak points in the network, just as the sulfur–sulfur cross-linkage is the weak point in sulfur-cured EPT rubber.

A study was initiated to measure the apparent thermal stability of carbon–carbon cross-linkages in actual network environments to see what limitations these bonds place on the design of thermally stable elastomers. Using the technique of chemical stress relaxation under vacuum, the kinetic parameters, including activation energy, were to be measured. Activation energies, resulting from measurements of rates at various temperatures, have previously been determined for a number of weak network bonds such as sulfur–sulfur[1] and urethan.[4] They give, in some instances, an indication of the bond's inherent thermal stability. Unlike these weak bonds, the carbon–carbon cross-linkage in many elastomers will be comparable in stability to most main chain linkages, and the stress relaxation data for such elastomers will reflect a complicated summation of many types of reactions in the network. The separation of the reactions of the cross-linkages from all other interfering reactions may not be possible even theroetically, except in the simplest cases, because of the intractibility of sums of exponentials with an unknown number of terms; the function which results for multiple parallel reactions.

We feel that the most practical and direct way of separating the cross-link reactions from the main chain reactions is to make the assumption

$$\Delta n_e(t) = 2\Delta c(t) \qquad (1)$$

where $n_e(t)$ is the number of effective chains in a network as a function of time t, and $c(t)$ is the time dependent number of cross-linkages in the network. The quantity $n_e(t)$ is defined by the simple equation of state for a rubbery network, as

$$n_e(t) = F(t)/3RT(\alpha - \alpha^2) \qquad (2)$$

where α is the extension ratio, R is the gas constant, T is the absolute temperature, and F is the force per original cross-sectional area of the sample.

Equation 1 is used by measuring the time-dependent number of effective chains of two samples which differ only in cross-link density, and subtracting the two results. The difference should reflect only the reactions of the cross-links which were "added" to one sample to obtain the second, all other reactions cancelling out. In reality, this difference will be contaminated by main chain reactions for several reasons.

1. The contribution of the main chain linkage reactions to the force decay will not be totally independent of the cross-link density, although this problem should be at a minimum at the early stages of the degradation.

2. Mistakes in measuring $n_e(0)$ will introduce a contribution from main chain linkage reactions. It is generally difficult to measure the modulus (and thus $n_e(0)$) to better than 10%.

This problem can be minimized by using samples with substantial differences in cross-link density, and by selecting structures with relatively stable main chain linkages, which cross-link without degradation. Also, errors due to deviations from the stress–strain relationship given by eq 2 can be eliminated by using the same strain for both samples under consideration.

If all cross-linkages introduced are of the same type, eq 1 will give

$$\Delta n_e(t) = 2\Delta c(t) = 2\Delta c(0)e^{-k_c t} \qquad (3)$$

where k_c is the first-order rate constant for the disappearance of the cross-linkages. A variety of cross-linkages can be expected to give a sum of exponentials on the right-hand side of eq 3. Under certain conditions, it might be possible to resolve the exponentials, but it was decided (with one exception) that the initial slope of the log $\Delta n_e(t)$ *vs.* t curve would be used as the specific rate of cross-link cleavage. This number, for a sum of exponentials, will be a weighted average of all the time constants. It should be free of errors due to deviations from the two network theory,[1] which might appear at longer times in networks experiencing simultaneous degradation and cross-linking reactions. The initial section of the stress relaxation curve is also "independent" of network behavior theory,[5] the use of which is necessary at high degrees of degradation.

Experimental Section

The stress relaxation experiments were all done under vacuum (0.5 μ) in a spring balance of recent design.[6] The samples were conditioned under vacuum at 250° for 16 hr before each run to eliminate hydroperoxides and weak linkages. The temperature was raised rapidly to the test temperature (300, 325, or 350°) and held for 1 hr. The sample was then extended (usually between 5 and 10%) and force *vs.* time measurements were started. In general,

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(2) P. F. Lyons, T. C. P. Lee, and A. V. Tobolsky, *Rubber Chem. Technol.*, **39**, 1634 (1966).

(3) H. Schroeder, *Inorg. Macromol. Rev.*, **1**, 45 (1970).

(4) A. Singh and L. Weissbein, *J. Polym. Sci., Part A-1*, **4**, 2551 (1966).

(5) J. Scanlan, *ibid.*, **43**, 501 (1960).

(6) M. T. Shaw and A. V. Tobolsky, Office of Naval Research Technical Report, RLT 111, Contract No. N00014-67-A-0151-0011, Task No. NR 056-377, Dec 1968.

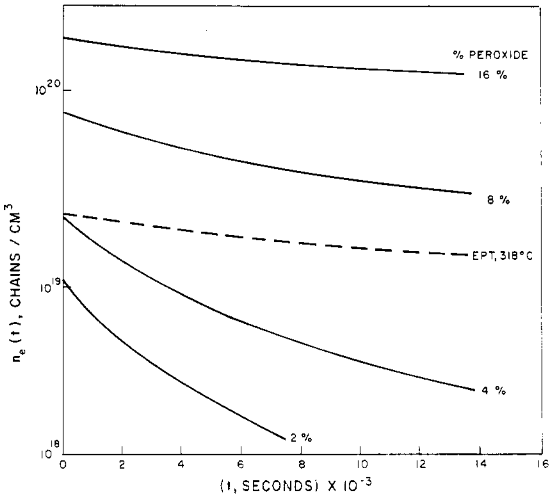

Figure 1. Typical chemical stress relaxation curves for various cross-link densities, using low-density polyethylene at 325° as an example. A comparison of this material with ethylene-propylene terpolymer (EPT) at 318° is included.

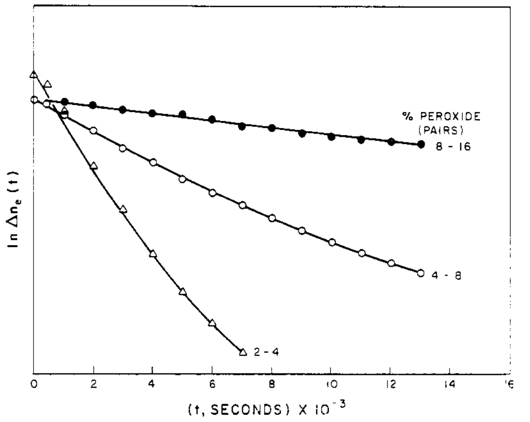

Figure 2. Typical difference curves, the initial slopes of which are used to get k_c. Note dependence on absolute cross-link density.

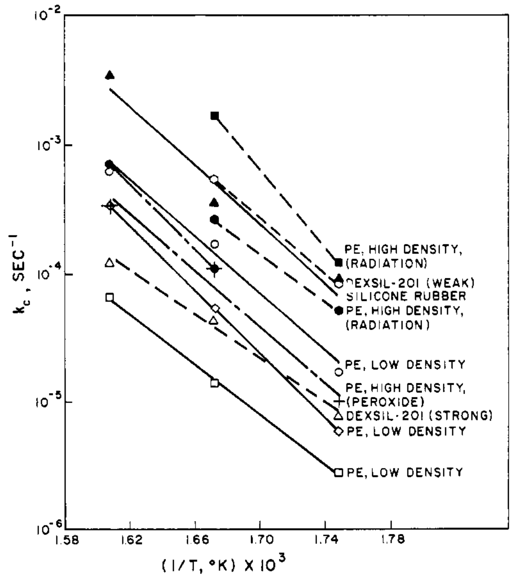

Figure 3. Arrhenius correlation of k_c with temperature for the elastomers studied.

every effort was made to treat samples to be compared according to eq 1 in exactly the same way.

The samples used in this study included networks based on high-density and low-density polyethylene, silicone rubber and a dimethylsiloxane-carborane copolymer, commonly known as Sib-2 or Dexsil-201. All samples (except the radiation-cured polyethylene) were Soxhlet extracted and vacuum dried before use.

The low-density polyethylene samples supplied by I. L. Hopkins of Bell Telephone Laboratories, Murray Hill, N. J., were cured in the melt with 2, 4, 8, and 16% dicumyl peroxide. Peroxide-cured high-density samples were prepared by Dr. D. Schaffhauser of Allied Chemical Corp., Morristown, N. J., using 2.5 and 5% dicumyl peroxide. The radiation-cured high-density polyethylene samples were obtained through the courtesy of Dr. R. Brand of Mobil Chemical Co., Metuchen, N. J. They were cross-linked with 5.8, 11.6, and 17.4 mrads of high-energy electrons. The silicone rubber samples, cross-linked with 0.6% di-*t*-butyl peroxide *via* 0.05 and 0.2 mol % vinyl groups, were donated by Dr. A. C. Martellock of the General Electric Co., Waterford, N. Y.

The Sib samples, based on Dexsil-201 gum,[3] were cured with 0 and 5% dichlorobenzoyl peroxide for 5 min at 110° and air post cured (16 hr at 100°, 8 hr at 150°, and 4 hr at 200°). In this gum, cross-linkages form in the absence of peroxide, probably due to the action of residual polymerization catalyst and water. These cross-linkages proved to be very inert. The SiB samples were supplied through the courtesy of Dr. J. F. Sieckhaus of the Olin Chemical Corp., New Haven, Conn.

Results and Discussion

Typical log $n_e(t)$ *vs.* t and log $\Delta n_e(t)$ *vs.* t curves are illustrated in Figures 1 and 2, using low-density polyethylene as an example. As expected, the force decay is complex, involving many contributing reactions. The log $n_e(t)$ *vs.* t plots in some cases, such as Figure 2, appeared to be quite linear over most of the time scale while in other cases there was a definite curvature, suggesting the presence of two or more types of cross-links of different reactivities. In these cases, the initial slope was used as the rate constant for cross-link cleavage.

The rate constants for the various test temperatures are plotted according to the Arrhenius equation in Figure 3, giving the activation energies and frequency factors listed in Table I. The activation energies are

Table I
Arrhenius Activation Energies for Carbon-Carbon Cross-Link Cleavage Reaction

Material	E^*, kcal/mol	A, sec^{-1}
Polyethylene, high density, radiation cure	57 ± 15^a	$10^{16.3}$
Polyethylene, high density, peroxide cure	$55 + 3$	$10^{15.6}$
Polyethylene, low density, peroxide cure	52 ± 8	$10^{14.4}$
Polydimethylsiloxane, peroxide through vinyl cure	$[52]^b$	$[10^{15.7}]$
Dexsil-201, dichlorobenzoyl peroxide cure		
Weak bonds	[52]	$[10^{15.7}]$
Strong bonds	42	$10^{1.09}$

[a] The ± value represents the range of available data about the mean. [b] Figures in brackets are based on two rate constants only.

all surprisingly close at about 55 kcal/mol, independent of the structure of the network main chains. The frequency factors show a somewhat greater range of $10^{14.4}$ to $10^{16.3}$. It should be noted that these data, while representative, are tentative and subject to further refinement.

It is not possible to assign the activation energy to any particular step in the reaction of the cross-linkages, since it represents an overall value. A cleavage step is expected to be rate controlling (and thus contribute most to the over-all activation energy), but the scission need not proceed by a "unimolecular" dissociation into two radicals. The dissociation may involve a radical intermediate (for example, one from a previous scission that has migrated along the chain to the cross-link) or a nonradical multicenter process.[7] The range of carbon bond strengths is from about 10 kcal/mol (hexaphenylethane) to around 85 kcal/mol (diamond). Combinations which lead to two allyl radicals or an allyl and a tertiary carbon radical are in the range of 55–60 kcal/mol. Structures which could generate these radicals are possible in the hydrocarbon elastomer studied. Radiation and peroxide curves are known to introduce unsaturation into the polyethylene, for example.

The activation energies listed will be minimums, because the rate constant measured at the high temperatures will be determined by cross-linkages of greater stability than that measured at low temperatures. This results from the necessity of equilibrating the sample at the test temperature before the measurements are started, which, at the higher temperatures, will remove many of the weak cross-linkages.

Figure 2 shows that, for branched polyethylene, the rate constant for cross-link cleavage decreases as the cross-link density increases. The possibility that this result is a pecularity of the method of arriving at k_c was considered, but most models for network behavior do not allow as much dependence as was observed. Another possibility is that the cross-links introduced at high peroxide concentration could be, on the average, more stable than those formed at lower concentrations. This is reasonable for branched polyethyelenes, where the branch points could increase the probability of forming weak cross-linkages, while at greater extents of cross-linking only secondary sites would be available.

Qualitatively, the same dependence of k_c on cross-link density was observed for radiation-cured "linear" polyethylene. The same argument used for branched polyethylene can apply, because linear polyethylene probably features some branch points, but with less force.

The SiB polymers present a situation which is reminiscent of ethylene–propylene terpolymers cured with sulfur (strong main chains and weak cross-links) except that the thermal energies involved are 50% greater. The stable backbone of the SiB formulations presents an ideal background for the study of the carbon–carbon cross-linkage, reducing interference from main chain scissions to a minimum. Unfortunately, it is difficult to introduce carbon–carbon cross-linkages into the already cross-linked Dexsil-201 gum. Dichlorobenzoyl peroxide should, in analogy to silicone rubber technology, give carbon–carbon cross-linkages *via* methyl groups. Dichlorobenzoyl peroxide (5%), heated at 110° for 5 min with Dexsil-201, yields about 3 × 10^{-5} mol/cm^3 of cross-linkages, enough to measure by chemical stress relaxation.

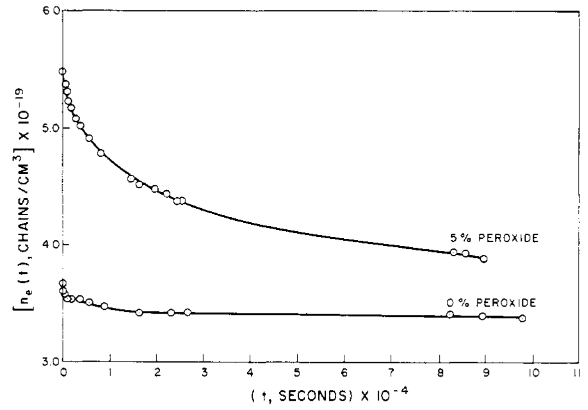

Figure 4. Stress relaxation of Dexsil-201 elastomer with and without peroxide illustrating ideal behavior (little main chain scission).

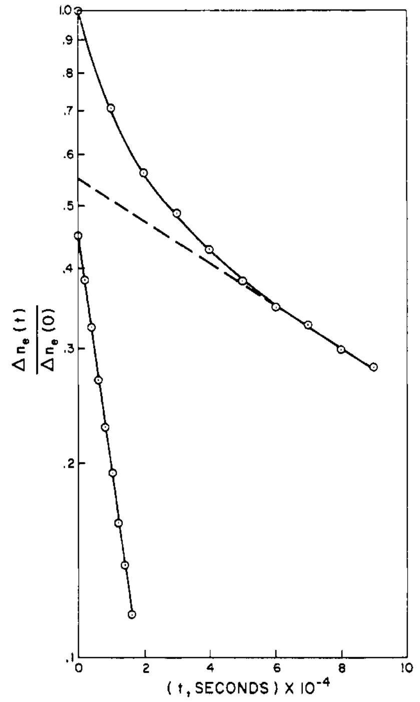

Figure 5. Illustration of the resolution of the difference curve for Dexsil-201 into two exponentials.

The Dexsil-201 elastomer prepared without peroxide proved to be nearly absolutely stable in the temperature range 300–350°. The force after a small initial decay remained constant for the duration of the run. The effective number of chains for the peroxide-cured samples showed a steady rate of decay, and the value of $n_e(t)$ tended to approach that of the corresponding sample cured without peroxide (Figure 4). This nearly ideal behavior prompted a more detailed analysis of the $\Delta n_e(t)$ *vs.* t curves, which indicated the presence of two types of cross-linkages (Figure 5).

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(7) W. J. Bailey, *Soc. Plast. Eng. Trans.*, 59 (1965).

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

	Weak links		Strong links	
T, °C	k_c, l./sec	%	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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Received April 30, 1970

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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* To whom correspondence should be addressed.

(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. Dušek and W. Prins, *Advan. Polym. Sci.*, **6**, 1 (1969).