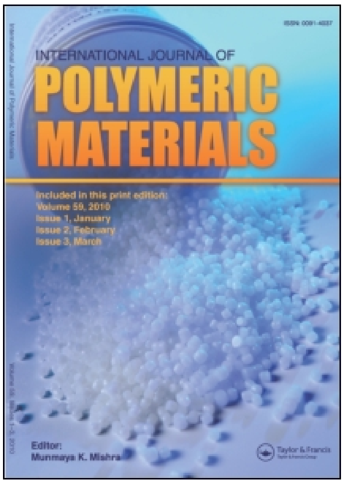

International Journal of Polymeric Materials
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713647664

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To cite this Article Tanny, G. B. and Pierre, L. E. St.(1972) 'Radiolytic Scissioning in Polydimethylsiloxane Networks', International Journal of Polymeric Materials, 1: 4, 279 — 293

To link to this Article: DOI: 10.1080/00914037208075290

URL: http://dx.doi.org/10.1080/00914037208075290

Intern. J. Polymeric Mater., 1972, Vol. 1, pp. 279–293

Radiolytic Scissioning in Polydimethylsiloxane Networks

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(*Received March* 21, 1972)

γ-radiation induced backbone cleavage in stressed polydimethylsiloxane networks displays the stress relaxation profile expected for random scission of a network possessing a Gaussian distribution of chain lengths. G (scission) as measured by stress relaxation, is found to be dose rate dependent below 0.4 Mr/hr, but does not reveal any atmospheric or temperature effects. The value of G (scission) $= 0.7$, obtained at a dose rate of 0.4 Mr/hr, is in good agreement with that determined from sol-dose measurements.

The postulated mechanism of scission is based upon a three step reaction scheme involving a siliconium ion produced initially by γ-ray cleavage of an SiO bond. The ion is capable of reacting with a neighbouring chain before it is terminated by an electron or some other neutralizing species. Mathematical analysis of this mechanism leads to the observed dose rate dependence.

INTRODUCTION

Due to the increasing use of nuclear energy, knowledge of the mechanical behaviour of materials subjected to ionizing radiation has assumed great importance. For this reason, the class of polymers designated as polysiloxanes have been the focus of particular attention as a result of their wide range of utility and apparent high stability.

In the earliest reports of the irradiation chemistry of silicones, investigators[1–6] could find evidence only for crosslinking processes. A careful study of the radiolysis products of a model silicone[7] showed, however, that scission

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of SiO bonds also occurred, and to a greater extent than believed previously.

Estimates of both *G* (scission) and *G* (crosslinks) have been obtained from a variety of experiments. However, all of the techniques used involve the inherent disadvantage of measuring either a ratio of scission to crosslinking or a net value of one or the other. Thus, if both crosslinking and scission take place simultaneously (as in this case), it is necessary to do at least two different types of experiments in order to separate the values of crosslinking and scission. Furthermore, there is reason to doubt that the values presently accepted for scissioning reactions in liquid, unstressed polymers can even be applied to "working" elastomers—that is, elastomers under stress. In the latter case, re-equilibration reactions cannot disguise scission events because a stressed chain, once ruptured, cannot reform in a load-bearing state.

A technique, which does make possible the direct estimation of scission without regard to concurrent crosslinking events, was devised by Tobolsky[8] and co-workers. It is based upon stress relaxation of a polymeric network maintained at constant elongation and temperature. Since the polymer is under stress during exposure to the radiation flux, the experiment yields information on the radiation events by measurement of the mechanical behaviour of the polymer.

This method of continuous stress relaxation was chosen for the present study. In order to check the results obtained, an estimate of *G* (scission) was also derived through the use of sol-dose experiments which yield the ratio of scission to crosslinking events.

THEORY OF STRESS RELAXATION

Since the theory of continuous stress relaxation has been presented at great length in several sources,[8-10] only a brief explanation of the terms used will be provided below. Let us assume that (i) the network is made up of chains possessing a gaussian distribution of chain lengths; (ii) the scission process is random and obeys first order kinetics; and (iii) the elastomer obeys the kinetic theory ideal equation of state for a rubber, in some range of extension. For such a system, Berry and Watson[9] derived the relation between stress relaxation and the average number of cuts per original network chain as

$$[f_o/f_t - 1] = at \tag{1}$$

where f_o is the force per unit original cross-section at time zero, f_t is the force per unit original cross-section at time t, a is the number of cuts per original network chain per unit time, and t is time.

In order to calculate G (scission), one utilizes the equation

$$G\ (\text{scission}) = aN_o/(\phi/100) \tag{2}$$

where N_o is the original number of elastically active chains/gm, and ϕ is the dose rate in e.v./gm/unit time.

EXPERIMENTAL

Apparatus

A miniature relaxometer for use in the confined space of a Gammacell 220 ^{60}Co source has already been described.[11] This apparatus, which was utilized to obtain all the stress relaxation data reported herein, was placed in a stainless steel cannister equipped to provide control of the atmosphere and temperature.

Procedure

When a sample had been elongated to the desired extension, the relaxometer was placed in a chamber which was then evacuated and refilled with the gas for the experiment desired. To eliminate moisture, environmental gases were passed through a calcium sulphate or silica gel column immersed in a low temperature dewar flask. After the cell reached the desired temperature, the signal from the relaxometer was monitored until it maintained a constant value for a length of time equal to that of the anticipated experiment. The entire apparatus was then lowered into the γ-flux.

Experiments at different temperatures were performed on the sample by observing scission for a period of time, removing the apparatus from the γ-field and changing the temperature. When thermal equilibrium was restored, the apparatus was reintroduced to the radiation flux and the process repeated.

Source and Dosimetry

The source of ^{60}Co radiation was a Gammacell 220 (Atomic Energy of Canada Limited). The cavity is cylindrical (16 cm in diameter and 20 cm high), and the flux homogeneity in the sample vicinity was $\pm 5\%$ of that determined by Fricke[12] dosimetry. Since the electron densities of the silicone gum and the dosimeter solution are very nearly equal, no correction of the dose rate was necessary.

Materials

Polydimethylsiloxane gum, GE SE076, density 0.98 gm/cc, was treated under vacuum at 150°C for 24 hours to remove a volatile fraction. The ratio of

$\overline{M}_w/\overline{M}_n$ of the treated gum, determined on a Waters gel permeation chromatograph, was 1.7 and the number average molecular weight,[13] $\overline{M}_n$, was 5.0×10^5 gm/mole.

All chemical reagents were reagent grade and were used directly.

Sample Preparation

Samples vulcanized by γ-rays were obtained by pressing the gum in a mold between aluminium foil sheets, and giving the samples the desired 'vulcanization' dose.

Chemically cured samples were prepared by dissolving PDMS and benzoyl peroxide (1.6 gm/100 gm PDMS) in hexane. The viscous solutions were stirred until homogeneity was achieved and the solvent was then removed by pumping under vacuum for 24 hours at 25°C.

The gum was subsequently pressed in a mold between aluminium foil sheets and cured at 130°C for 2.5 hours.

By means of a die, samples were cut from the sheets, weighed, treated with toluene in a soxhlet extractor for 120 hours, and placed in fresh solvent at 25°C for 48 hours.

Swelling measurements were made according to the procedure of Holly.[14] Weighed duplicate strips of sample were swollen in toluene at 25°C for 120 hours, wiped free of excess solvent and weighed in the swollen state. The samples were then completely freed of solvent by pumping in a vacuum oven at 100°C for 24 hours, and reweighed.

The Flory-Rehner equation[15] was used to calculate the network density.

Procedure for Sol-Dose Experiments

Samples of PDMS were placed in glass ampoules and degassed *in vacuo* at about 1 μ for 24 hours, after which they were sealed and irradiated. For experiments in air, gum was placed in aluminium dishes and exposed to the radiation. Extraction of weighed amounts of irradiated gum was performed in a soxhlet extractor using Whatman seamless thimbles of known weight and toluene as solvent. All extractions were carried out for at least 120 hours. After extraction, the thimbles and gel were dried in a vacuum oven at 100°C for 24 hours and reweighed.

RESULTS AND DISCUSSION

Effects of Temperature and Atmosphere on Stress Relaxation

Figure 1 shows three typical examples of stress relaxation data derived from experiments in nitrogen at 34°C and 0.4 Mrads/hr. Calculations (Table I)

TABLE I

Stress relaxation and network density variation (N_2 Atm)

Sample no	Method of crosslinking	$No \times 10^{-19}$ (chains/gm)	$\alpha \times 10^5$ cuts/chain/min	G (scission)
1	γ	0.9_5	29.0	0.7_1
2	γ	1.8_3	16.5	0.7_7
3	γ	4.3_4	6.3	0.6_8
4	chemical	0.9_3	29.0	0.7_0

Dose rate = 4.0×10^5 rads/hr; Temp = 34°C.

reveal that the number of scissions per chain per minute, α, decreases proportionately with the increase in network density, but the value of G (scission) remains constant within experimental error. All of the data are for scission within the γ-flux; no postirradiation scission was observed.

The linearity of the data in Figure 1 supports the assumption of first order kinetics. Since α (the number of scissions/chain/min), displays an inverse

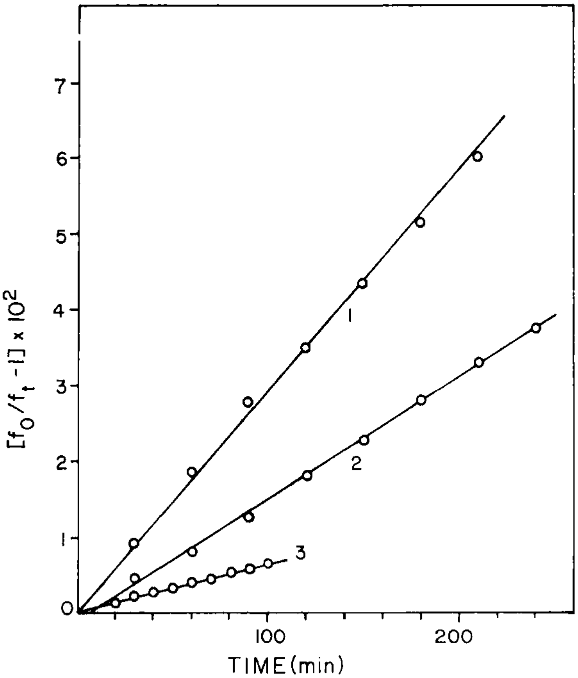

FIGURE 1 γ-ray induced stress relaxation of crosslinked PDMS in N_2, 0.4 Mrads/hr
1 $N_o = 0.95 \times 10^{19}$ chains/gm
2 $N_o = 1.83 \times 10^{19}$ chains/gm
3 $N_o = 4.3 \times 10^{19}$ chains/gm

dependence on the network density, N, it is concluded that cleavage is occurring randomly between crosslinks, rather than specifically at a crosslink site.[8] This conclusion is reinforced by the fact that samples crosslinked to the same network density by either γ-rays or benzoyl peroxide yielded identical values of α (Table I). Crosslinks from γ-rays have been shown[7] to be mostly of the form $\equiv\text{Si—CH}_2\text{—Si}\equiv$, with a few $\equiv\text{Si—CH}_2\text{—CH}_2\text{—Si}\equiv$ and $\equiv\text{Si—Si}\equiv$, while those of chemical curing are nearly all $\equiv\text{Si—CH}_2\text{—CH}_2\text{—Si}\equiv$.[8] If extensive scission at crosslink sites was occurring, one would expect the rate of scission to be influenced by the nature of the crosslinks.

Stress relaxation experiments were performed under a variety of experimental conditions. In all cases, the data remained linear, so that a change in the variables, atmosphere, dose rate or temperature does not require alteration of the form of the mathematical function used to plot the data. A summary of all the data obtained from stress relaxation at 25°C and 34°C is shown in Table II.

TABLE II

Summary of stress relaxation results

Atm	Temp °C	Dose rate rads/hr	$N_0 \times 10^{-19}$	$\alpha \times 10^5$	G (scission)	G (scission) average
Air	25	2.5×10^4	3.0_7	2.4_0	3.0	3.1 ± 0.1
			0.8_3	8.6_2	3.2	
N_2	25	2.4×10^4*	3.3_0	2.0_8	2.8	2.8 ± 0.1
			3.3_7	2.0_8	2.9	
O_2	25	2.4×10^4*	3.2_7	2.2_2	3.0	2.8 ± 0.3
			2.3_8	2.5_2	2.5	
N_2	34	2.1×10^5	0.8_7	24.0	1.0	1.0
Air	34	4.0×10^5	0.8_9	29.0	0.68	0.68 ± 0.03
			0.9_3	29.0	0.71	
			0.8_8	32.1	0.74	
			4.4_0	5.6_5	0.65	
			4.3_0	5.5_0	0.62	
N_2	34	3.9×10^5*	0.9_5	29.0	0.71	0.66 ± 0.06
			1.8_3	16.5	0.77	
			4.4_0	4.8_0	0.54	
			4.4_6	5.8_5	0.65	
			4.3_4	6.2_7	0.68	
O_2	34	3.9×10^5*	4.5_0	4.8_0	0.55	0.54 ± 0.02
			4.2_0	4.8_0	0.52	

*Change in dose rate due to natural decay of source intensity with time. Note that, due to the non-homogeneity of the γ field, and the error in the measurement, there is a minimum uncertainty of ±7% in the value of the dose rate.

From inspection of the results, the following preliminary conclusions regarding the scission process may be drawn:

a) Since differences in G (scission) values obtained for all atmospheres at a given dose rate are well within the estimated range of uncertainty ($\Delta\ G/G = \pm 0.13$), one may conclude that there is no atmospheric effect. Thus, it is unlikely that the mechanism by which chains are scissioned includes a free radical species in any step *prior* to the cutting of an $\equiv$Si—O bond.

b) The measurement of chain scission by stress relaxation is independent of the presence of simultaneous crosslinking events occurring in the polymer. It has been pointed out[6,16] that oxygen has an inhibiting effect on crosslinking. According to the "two network theory",[17] network chains created by crosslinks introduced after the network is stretched, do not support the initially imposed stress. Since G (scission) remains constant under both conditions of crosslinking (N_2 atmosphere) and inhibited crosslinking (O_2 atmosphere), the validity of the "two network" theory is confirmed under the conditions of the present work.

Measurements of G (scission) as a function of temperature from 34–65°C, and in all atmospheres did not reveal a significant change in the rate of cleavage. Although the temperature dependence was only studied at the highest dose rate (4.0×10^5 rads/hr), one would not expect the existence of a scission activation energy to be dose rate dependent since the γ-energy is many orders of magnitude greater than kT and any chemical intermediates in the scission process would be highly excited.

Sol-Dose Experiments

As commented upon in the introduction, another estimate of G (scission) may be obtained from the ratio of scission to crosslinking and the value of G (crosslink). Sol-dose experiments give this ratio and therefore may be used with G (crosslink) values obtained from the literature to yield G (scission). This value can then be compared to the results obtained from stress relaxation. (All of the data will then be utilized to propose a mechanism of scission and to examine the mathematical implications of this mechanism.)

In order to relate the parameters of crosslinking, scission and dose for polymers which possess an initially random distribution of molecular weights, Charlesby and Pinner[18] derived the relation

$$S + S^{1/2} = X_0/Y_0 + 1/Y_0\mu D \tag{4}$$

where S is the soluble fraction (as opposed to the nonsoluble gel fraction), X_0 is the number of chain scissions per gram per unit dose, Y_0 is the number of crosslinks per gram per unit dose, μ is the initial number average molecular weight, and D is the absorbed dose.

It is important to note that X_0 is the equivalent of G (scission), and that this type of experiment measures G (scission) as the number of "permanent" chemical scissions which have occurred. The latter point will be seen to have definite importance with regard to the mechanism of scission.

Results of Sol-Dose Experiments

The data from sol-dose experiments in both air and vacuo are shown in Figure 2, plotted as $S + S^{1/2}$ versus $1/D$. As predicted by Eq. (4), linear plots are obtained, whose intercepts, X_0/Y_0, represent the ratio of scission to crosslinking. Since the value of G (crosslinks) is larger in vacuo than in air due to the presence of oxygen, the slope of the plots, $1/\mu Y_0$, inversely reflects the respective values† of G (crosslinks).

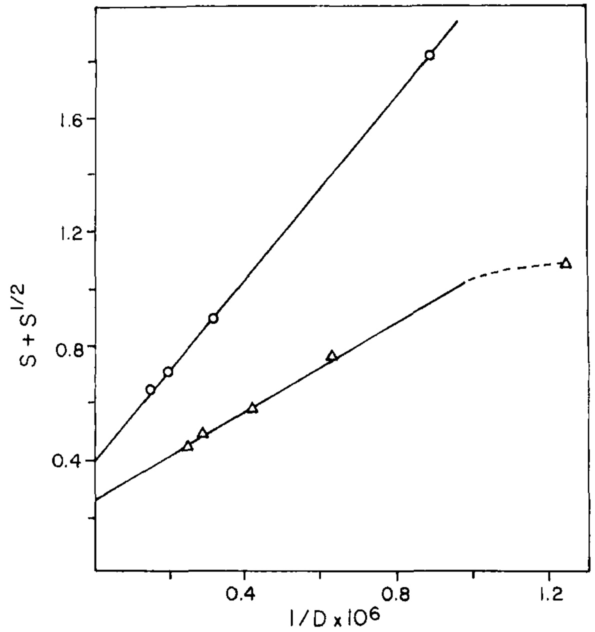

FIGURE 2 Sol-dose experiments for PDMS irradiated in air and vacuo

○ - air
△ - vacuo

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†In order to calculate G (scission, air) at 7.0×10^5 rads/hr, G (crosslinks, air) is required. The latter may be obtained from the slopes of the lines in Figure 2 ($1/\mu Y_0$), and the value of G (crosslinks, vacuo), as follows:

Since the initial degree of polymerization, μ, is constant,

$$\text{slope (air)} = \frac{(1/\mu Y_0)\ \text{air}}{(1/\mu Y_0)\ \text{vacuo}} = \frac{(Y_0)\ \text{vacuo}}{(Y_0)\ \text{air}} = \frac{G\ (\text{crosslink, vacuo})}{G\ (\text{crosslink, air})} \tag{5}$$

From the value of G (crosslink, vacuo) $= 2.8$,[21] one calculates G (crosslink, air $= 1.7$.

TABLE III

G (scission) results calculated from sol-dose experiments

Dose rate rads/hr	Atmosphere	*G* (scission)/ *G* (crosslink)	*G* (crosslink)	*G* (scission)
4.0×10^5	vacuo	0.27 ± 0.01	2.8 ± 0.1 §	$0.7_8 \pm 0.0_6$
7.0×10^5	air	0.39 ± 0.01 (0.40)‡	1.7¶ ± 0.1	$0.6_8 \pm 0.0_6$
8.4×10^6	N_2	0.25†	$2.8 - 0.1$ §	0.7

† Ref. 19; ‡ Ref. 20; § Ref. 21; ¶ see footnote on previous page.

The values of X_0/Y_0 from Figure 2 have been combined with literature values of X_0/Y_0,[19,20] and *G* (crosslink)[21] in order to calculate the *G* (scission) values shown in Table III.

One can see that *G* (scission) does not change significantly in the range of dose rate studied, and that it is independent of atmospheric effects. The latter point is in complete agreement with results from stress relaxation. Furthermore, the value of 0.78 in Table III for *G* (scission) in vacuo at a dose rate of 4.0×10^5 rads/hr agrees quite well with that found at the same dose rate in nitrogen from stress relaxation (0.7) (Table II).

An estimate of *G* (scission) = 0.3 was made by Miller.[22] It was based on the increase in Si—OH groups observed when PDMS is irradiated in the presence of a mercaptan. Charlesby[19] replotted the results of Miller's sol-dose experiments (PDMS irradiated in N_2), according to Eq. (4), and found *G* (scission)/*G* (crosslinks) = 0.25. This yields a value for *G* (scission) = 0.7, which is in agreement with the present results. Based on his own value of 0.167 for *G* (scission)/*G* (crosslink), Charlesby[19] calculated *G* (scission) = 0.4. This value, however, was obtained from experiments using a mixed neutron-γ flux radiation, rather than pure γ-rays, and thus may not be strictly comparable with the present results. During the course of the present study, other data were reported from the γ-irradiation of PDMS in air, by Baker, Charlesby and Morris[20] which yielded *G* (scission)/*G* (crosslink) =0.40. As may be seen from Table III, this ratio leads to a value for *G* (scission) = 0.7 in air, which is again in agreement with the present data.

Since the present sol-dose data appear to satisfactorily confirm both the stress relaxation experiments and the literature results, consideration can now be given to the topics of dose rate dependence and the scission mechanism.

Mechanism and Kinetic Analysis of Scission

A. *Dose Rate Dependence of* G (*Scission*) In Figure 3, the values of *G* (scission) found from stress relaxation and sol-dose experiments, compiled

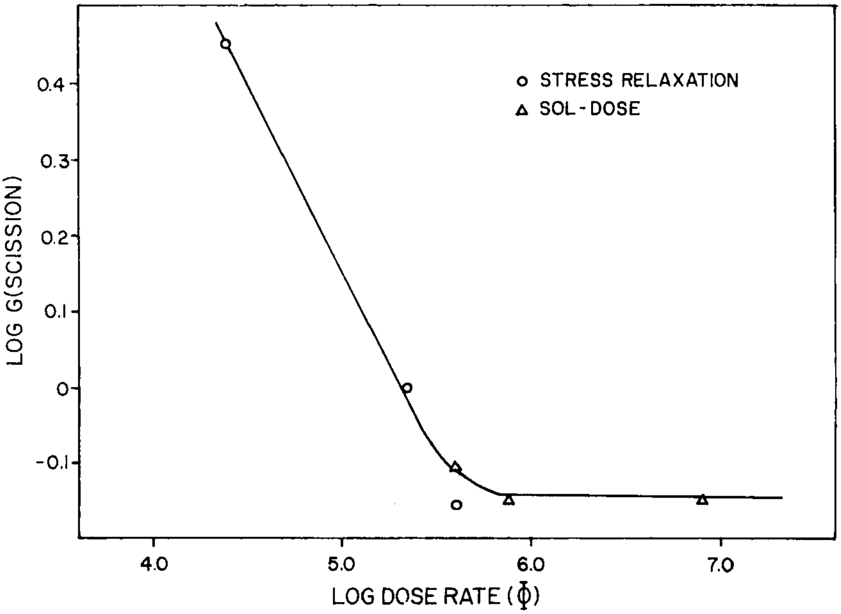

FIGURE 3 Log *G* (scission) versus log Dose Rate for irradiated PDMS

in Tables II and III, respectively, have been plotted on a log *G* (scission) versus log Dose Rate basis. Up to a dose rate of approximately 4.0×10^5 rads/hr, *G* (scission) has a negative dose rate dependence; above this dose rate, *G* (scission) is dose rate independent.

The kinetic order of the dose rate dependent region (Region I), may be obtained as follows:

The number of cuts per chain per unit time is a.

Let $$a = B\phi^n \tag{6}$$

where B, n are constants and ϕ remains the dose rate. Now from Eq. (2),

$$G\,(\text{scission}) = aN_0/(\phi/100)$$

Substituting Eq. (6) into Eq. (2) we obtain

$$G\,(\text{scission}) = 100\, B\phi^{n-1}N_0 \tag{7}$$

Thus, the slope of Region I in Figure 3 is

$$n - 1 = 0.48 \tag{8}$$

i.e., $$n = 0.52 \text{ or } \approx 0.5 \tag{9}$$

For the plateau region, the slope is zero and

$$n = 1 \tag{10}$$

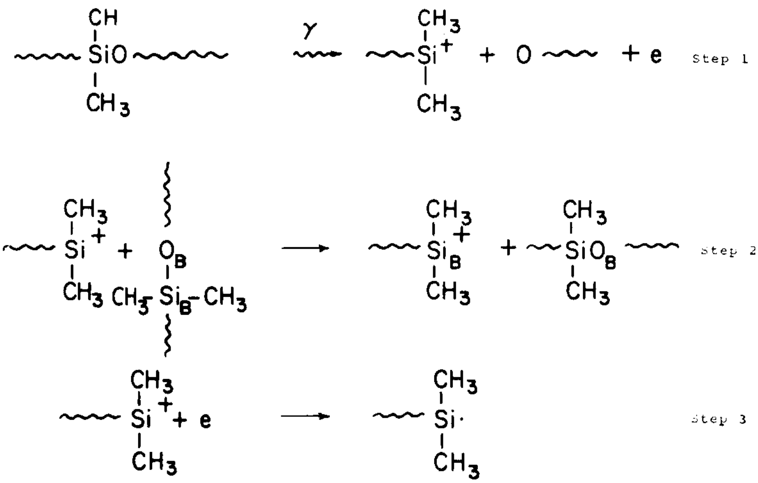

FIGURE 4 The mechanism of γ-ray induced scission in PDMS networks

These coefficients of the dose rate dependence, ($n = 0.5$, $n = 1$), will be used in establishing the kinetics and in elucidating the mechanism of scission (*vide infra*).

B. *The Mechanism of Scission* On the basis of the foregoing data, one may suggest a scission mechanism of the type shown in Figure 4. This proposes the following mode of scission:

In step (1) an SiO bond is broken due to interaction with a γ-ray. The resulting siliconium ion attacks a neighbouring chain and undergoes SiO bond rearrangement in step (2). This step causes an additional network scission and regenerates a siliconium ion. Termination, insofar as scission is concerned, occurs when the ion captures an electron or other neutralizing fragment to become either a free radical or a neutral species.

In establishing the nature of the active species as a siliconium ion in this reaction, two factors were important. First, the presence of oxygen did not affect the reaction and secondly, N_2O markedly affected the rate of scission. It has been shown[23] that N_2O behaves as an electron scavenger in the following manner:

$$N_2O + e \rightarrow [N_2O^-] \rightarrow N_2, O_2, NO_2 \qquad (11)$$

Blank experiments showed that N_2O did not by itself cause any stress relaxation but its presence during irradiation doubled the usual value of G (scission) (Table IV). Jenkins[24] has reported a similar observation. These results support the presence of a siliconium ion in the cleavage reaction and a termination by electrons.

TABLE IV

Effect of N_2O on G (scission)

Trial	P_{N_2O} cm	Rate constant $\times 10^4$ min^{-1}	Network density $\times 10^{-19}$ chains/gm	G (scission)
1	—	2.9	0.9_0	0.65
2	4.3	5.7	0.9_7	1.54
3	7.0	5.3	0.9_7	1.40

Dose rate = 4 × 10^5 rads/hr.

The mechanism can now be analyzed mathematically on this basis in order to (i) determine if it is consistent with the observed dose rate dependence and (ii) calculate the kinetic chain length of the cationic rearrangement reaction (step 2).

Let us first consider the dose rate dependence. The first step in Figure 4 represents the radiation cross-section for the interaction of an SiO bond with a γ-ray. In a well formed network, almost all (about 98% or more) of the SiO bonds are part of elastically active chains. Thus, to a first approximation, every initial scission of an SiO bond will be registered as a decrease in the stress. Therefore, the number of active centres produced per gram per unit time, R_i, as measured by stress relaxation, is equal to an efficiency factor, K_1 times the concentration of SiO bonds per gram [SiO], times the flux dose rate, ϕ.

i.e. $$R_i = k_1[\mathrm{SiO}]\phi \qquad (12)$$

The second step involves attack by an active centre on a neighbouring SiO bond. This attack can take place on an SiO bond several units removed from the active centre, but on the same chain segment as the active centre (intramolecular attack), or it can take place on an SiO bond of a neighbouring chain (intermolecular attack).

Since this analysis is for results obtained from stress relaxation, we must use in our rate equation only those events which are measured by a change in stress. Now, intramolecular attack will not be seen by the stress relaxation experiment, since such a rearrangement occurs on a chain segment which has already been cut.[25] Intermolecular scission, on the other hand, will be observed because it cuts a chain which, at the time of the cut, was still bearing a load. Thus, the number of intermolecular cuts per gram per unit time, R_{inter}, will be equal to a rate constant, $k_2 x$ the concentration of active centres, $[\equiv \mathrm{Si}+]$, x the concentration of SiO bonds in the immediate vicinity of the active centre *which are still load bearing.* For simplicity we may take the latter quantity to be just the concentration of SiO bonds per gram multiplied by some factor ϵ, where ϵ represents the fraction of SiO bonds in the vicinity of the active centre, which are still load bearing.

Therefore $$R_{inter} = k_2 [\equiv\text{Si}+] [\text{SiO}]\epsilon \qquad (13)$$

The overall rate of scission, R_{sciss}, is thus the sum of R_i and R_{inter}, i.e.

$$R_{sciss} = R_i + k_2 [\equiv\text{Si}+] [\text{SiO}]\epsilon \qquad (14)$$

Expressing this in terms of G values, Eq. (14) becomes

$$G\ (\text{sciss}) = G(i) + \frac{k_2 [\text{Si}+] [\text{SiO}]\epsilon}{(\phi/100)} \qquad (15)$$

Now, the rate of generation of siliconium ions, $\frac{d[\equiv\text{Si}+]}{dt}$, is given by

$$\frac{d[\equiv\text{Si}+]}{dt} = \underset{(\text{step 1})}{R_i} \quad \underset{(\text{step 3})}{- k_3 [\equiv\text{Si}+] [\text{e}]} \qquad (16)$$

If we assume a steady state in which charge conservation is obeyed, then

$$\frac{d[\equiv\text{Si}+]}{dt} = 0, \text{ and}$$

$$[\equiv\text{Si}+] = (R_i/k_3)^{1/2} \qquad (17)$$

and substituting Eq. (12)

$$= (k_1[\text{SiO}]\phi/k_3)^{1/2} \qquad (18)$$

Substituting Eq. (18) into Eq. (15) we obtain

$$G\ (\text{sciss}) = G(i) + 10^2 k_2 (k_1/k_3)^{1/2} [\text{SiO}]^{3/2} \epsilon \phi^{-1/2} \qquad (19)$$

Inspection of the above equation reveals that it contains a term which has a negative half power dependence on dose rate as well as a term independent of dose rate. Such an equation describes the behaviour observed in Figure 3, i.e. the value of G (scission) decreases as the dose rate, ϕ, increases, until a constant value of G (scission) is reached.

Thus, the first objective of the analysis, the rationalization of the dose rate dependence of G (scission) has been achieved. This, of course, does not constitute a proof that the mechanism in Figure 4 is correct; it is only a necessary condition for the mechanism to be given consideration.

Now, if the agreements found in Figure 3, at 0.4 Mrads/hr, between G (scission) measured† and G (scission) calculated‡ remains constant over the

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†Table II – 4 – from stress relaxation.
‡Table II – 6 – from sol-dose and G (crosslinks).

entire plateau region of dose rate, it implies that the number of cuts measured equals the number of "initial" scissions caused by the γ-ray. Thus,

$$G\,(\text{sciss}) = G(i) = 0.7 \tag{20}$$

The kinetic chain length of step (2), ν, can now be obtained from the equation

$$\nu = [G\,(\text{sciss}) - G(i)]/G(i) \tag{21}$$

Thus, in the dose rate dependent region, at 2.5×10^4 rads/hr, where G (scission) = 2.8, each scission due to a γ-ray is followed by three scissions due to cationic rearrangement reactions as in step (2) of Figure 4. Examination of the radiation chemistry of other siloxane systems provided supporting evidence for the scheme which has just been outlined.[21,25]

It is of interest to note that the mechanism suggested in Figure 4, and the kinetics associated with it, are quite analagous to those for γ-induced polymerization of cyclic siloxane molecules. Certain similarities in the effects observed should therefore exist.

Chawla and St. Pierre[26] studied the solid state polymerization of hexamethylcyclotrisiloxane, D_3, and concluded that the mechanism was cationic. This conclusion was based upon the fact that inhibitors such as H_2O or NH_3 could effectively inhibit the polymerization.

Furthermore, the polymerization took place only in the γ-flux, exhibited a negative half-power (0.59) dependence of G (polymer) on dose rate and showed an increase in G (polymer) in the presence of N_2O. All of these phenomena are in close accord with the stress relaxation data. Most interesting is the fact that calculation of G (initiation) from the polymerization data yields a value between 0.5–0.8, which is in agreement with the value of 0.7 determined for $G(i)$ in Eq. (20).

From the foregoing data, it is clear that a substantial part of the radiation chemistry of siloxane rubber involves main chain scission and subsequent rearrangement processes.

Acknowledgements

The authors wish to acknowledge the assistance and support of the Defence Research Board of Canada and Atomic Energy of Canada, Ltd., in the performance of this work. One of us (G.B.T.) is also indebted to the National Research Council of Canada for a Research Fellowship.

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