propanol, and toluene, 2.2 g (73%) of 6-methyl-1-vinyluracil was obtained as white needles: mp 198.5–200.5; ir 3500 (m), 3030 (s), 2850 (s), 2480 (w), 1780 (s), 1470 (m), 1440 (m), 1380 (s), 1326 (m), 1225 (m), 1192 (m), 1685 (w), 1040 (m), 975 (m), 940 (m), 870 (m), 840 (m), 722 (w), 755 (m), 712 cm^{-1} (m); nmr (DMSO-d_6) (relative to TMS) δ 2.50 (s, 3 H, 6-Me), protons 5.92 (s, 1 H, 5 proton), 5.80 (d, J = 8 Hz, 2 H, β-methylene proton); 6.80 (q, J = 16 Hz, J = 8 Hz, 1 H, α-vinyl proton). *Anal.* Calcd for $C_7H_8N_2O_2$: C, 55.25; H, 5.29; N, 18.41. Found: C, 55.60; H, 5.40; N, 18.32.

Polymerization Initiated by γ Radiation. Monomers either in solution or in the solid state were degassed in glass polymerization tubes under 0.1-mm vacuum at −78° for at least 20 min. The tubes were sealed under vacuum and were then irradiated under the conditions given in Table I. The polymers were isolated by precipitation and washing with methanol, followed by dissolution in 0.1 *M* sodium hydroxide, filtration through Millipore Teflon filters, and precipitation by acidification with 0.1 *M* hydrochloric acid. After the polymers were washed with distilled water several times they were dried at 150° (0.1 mm) overnight. *Anal.* Calcd for poly(1-vinyluracil), $(C_6H_6N_2O_2)_n$: C, 52.16; H, 4.37; N, 20.28. Found: C, 52.13; H, 4.85; N, 20.26 (experiment 3); C, 52.08; H, 4.52; N, 20.10 (experiment 5); C, 52.13; H, 5.14; N, 20.28 (experiment 9). Calcd for poly(6-methyl-1-vinyluracil), $(C_7H_8N_2O_2)_n$: C, 55.25; H, 5.29; N, 18.41. Found: C, 55.09; H, 5.42; N, 18.26 (experiment 11).

Acknowledgment. Acknowledgment is given to Drs. Plass, McIntyre, and Imada of the Physics Department for allowing us to use the cobalt-60 source.

Radiation Cross-Linking of Polydimethylsiloxane. Cross-Linking and Fracture by Solubility Analysis

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ABSTRACT: Estimates of *G* values for cross-linking (X) and fracture (F) have been made from experimental determinations of the gel fraction formed by Co-60 γ-irradiation of polydimethysiloxane. Estimates were made for an oil ($M_w = 8.5 \times 10^4$) of $G(X) = 2.2 \pm 0.3$ and $G(F) = 0.7 \pm 0.2$. For a rubber ($M_w = 4.8 \times 10^6$), $G(X) \simeq 2.3$. When samples were cooled with liquid nitrogen during irradiation the yield of cross-links was depressed to one-half to two-thirds the value observed on irradiation at room temperature. Inclusion of 10%, by weight, of diethyl disulfide in the oil greatly decreased the yield of cross-links: $G(X) = 0.8$, $G(F) \backsimeq 0.4$. This observation provides evidence that at least two-thirds of the cross-links are formed from free radical precursors.

As part of an extensive study of the radiation chemistry of polydimethylsiloxane, Miller included yields of cross-links estimated on the simplifying assumption that concurrent fracture of the polymer molecules was negligible.[2] Kilb has shown that the dependence of limiting viscosity number on radiation dose can be analyzed to provide an estimate of the ratio of fractures to cross-links. However, the method was rather insensitive and only allowed the conclusion that the ratio was less than one for a polydimethylsiloxane exposed to electrons. A more precise upper limit of one-half was deduced from measurements of radiation-induced changes in molecular weight determined by both light scattering and by osmometry,[3] but this is still too high to justify the assumption that fracture may be neglected. Subsequently, in the course of a study concentrated mainly on electron spin resonance spectroscopy, Ormerod and Charlesby[4] mentioned that ratios of fractures to cross-links of 0.17 and 0.25, respectively, had been deduced from a sol–gel analysis of data previously reported by Charlesby[5] and by Miller.[2] The sol–gel analysis had been formulated by Charlesby and Pinner.[6]

The objective of the present work is to examine the applicability of the Charlesby–Pinner analysis to polydimethylsiloxanes and to extend its use to samples irradiated at low temperature and to samples including additives. These objectives were chosen to extend observations on the influence of these experimental variables made by Miller.[7]

Experimental Section

A sample of a polydimethylsiloxane oil (Vicasil 30,000) was donated by the General Electric Co. This is similar to the sample studied previously by Miller of weight-average molecular weight $M_w = 8.5 \times 10^4 \pm 10\%$. Measurements of solution viscosity were made and found to be consistent with a weight-average molecular weight within these limits. A sample of a polydimethylsiloxane rubber of $M_w = 4.8 \times 10^6$ was donated by the General Electric Co.

Samples of benzene and dodecanethiol were of laboratory reagent grade. A purified sample of diethyl disulfide was obtained from Mr. L. A. Miller.

Samples were thoroughly degassed by pumping *in vacuo;* the oil was repeatedly frozen until no more bubbles were formed on thawing. It was stripped of volatiles by heating for 24 hr in a vacuum oven at 100°. Measurements of solution viscosity showed that the molecular weight of the polymer remained within the limits mentioned above following this treatment. Each polymer sample was sealed in a glass ampoule at a pressure of $<10^{-4}$ mm.

The ampoules were exposed to Co-60 γ-rays at an ambient temperature of 35° and at a dose rate of 0.3–0.8 Mrad/hr. Ampoules irradiated in liquid nitrogen were taped to the inside sector of a Dewar flask which faced the Co-60 source. Immediately after

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(1) Address correspondence to D. R. Squire at North Carolina State University.

(2) A. A. Miller, *J. Amer. Chem. Soc.*, **82**, 3519 (1960).

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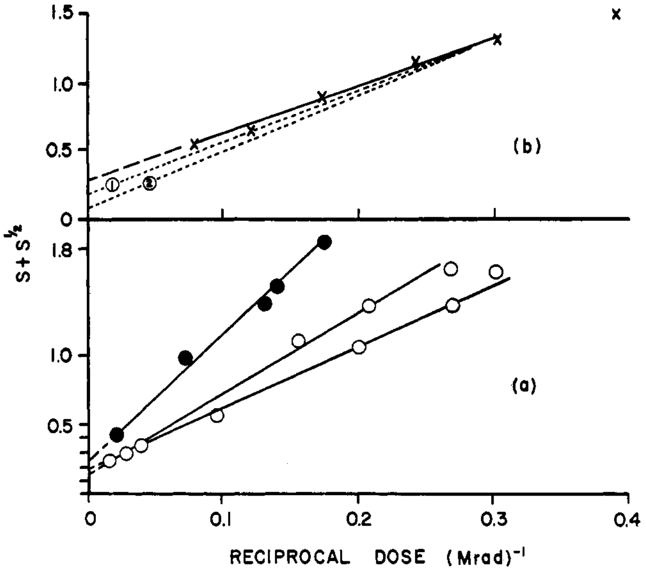


Figure 1. Solubility plots for silicone oil (M_w = 85,000). (a) ○, sample rigorously degassed and irradiated with γ-rays *in vacuo* at 35°, dose rate = 0.6 Mrad/hr; ●, as above but immersed in liquid nitrogen. (b) X, Miller's data for sample irradiated with electrons in nitrogen at 25°, dose rate = 692 Mrad/hr.[1]

irradiation samples were allowed to warm to room temperature while maintained *in vacuo*. The ampoules were opened to air in time periods ranging from several hours to several weeks. In preliminary experiments the amount of gel was found to be insensitive to this variable.

After opening an ampoule, gelled samples of polymer could be removed by scooping out with a spatula. Portions were cut and weighed (W_1 = 0.2-0.4 g) into lens tissue paper and immersed in benzene (50 ml). The liquid was decanted after 2 days and replaced by fresh benzene. The insoluble gel fraction was removed after a further 2 days and pumped *in vacuo* to constant weight (W_2). The sol fraction was determined as $S = 1 - W_2/W_1$. In preliminary experiments it was found that the value of S was not significantly changed by more lengthy extraction nor by more frequent replacement of the solvent. Experimental points, to be displayed subsequently, were the mean determined from two or three samples obtained from a single ampoule. The individual results generally agreed within 2%.

Dodecanethiol or diethyl disulfide was added to the degassed oil to constitute 10%, by weight. The mixture was thoroughly stirred and portions removed for degassing and sealing in vacuum, as required. After irradiation the weight of polymer was assumed to correspond to $0.9W_1$, where W_1 is the weight of the mixture. On the assumption that the additive is completely extracted by the benzene, the sol fraction was estimated as $S = 1 - W_2/0.9W_1$, where W_2 is the weight of insoluble matter pumped *in vacuo* to constant weight. In the case of diethyl disulfide the other extreme assumption that could be made is that the additive combines with the polymer with a value of $G(C_2H_5S \text{ combined}) = 6$. This was found to make only a negligible difference to the value of S estimated as described above.

General Considerations

Charlesby and Pinner applied probability theory to calculate gel formation in an initially linear polymer with a random molecular weight distribution for the case in which fractures and tetrafunctional cross-links are introduced at random and in proportion to the radiation dose.[6] Equation 1 relates the soluble fraction S after dose R with fracture and cross-link densities per unit dose, p and q, respectively, and includes as a parameter the average number of repeat units per molecule before irradiation, U. According to eq 1, a plot of $S + S^{1/2}$ *vs.* R^{-1} is linear; q and hence G(cross-linked units) can be obtained from the slope (eq 2). In explanation of the numerical factor in eq 2, it is to be noted that 1 Mrad $\equiv 6.23 \times 10^{19}$ eV/g. The G value for cross-links, G(X), is half G(cross-linked units) because each cross-link connects two units (eq 3). The intercept, pq^{-1}, provides a G value for fractures, G(F), according to eq 4.

$$S + S^{1/2} = pq^{-1} + (qUR)^{-1} \tag{1}$$

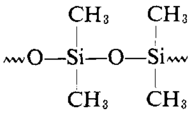
$$G(\text{cross-linked units}) = \frac{0.96 \times 10^6}{M_n(\text{slope})} \tag{2}$$

$$G(\text{X}) = \frac{1}{2}\, G(\text{cross-linked units}) \tag{3}$$

$$G(\text{F}) = G(\text{cross-linked units})\text{intercept} \tag{4}$$

In practice, most polymer samples have a molecular weight distribution which differs so much from a random distribution that experimental data do not conform to eq 1. This lack of conformity has been documented in most detail for a variety of polyethylenes which, typically, have a ratio of weight-to-number-average molecular weights (M_w/M_n) of about 15, in contrast to the value of 2 characteristic of a random distribution.[8] On the other hand, good conformity has been reported for a polyisoprene sample which was randomized by oxidative chain scission of purified natural rubber. The values of G(X) and G(F) calculated from eq 3 and 4 were in agreement with values calculated from other methods of polymer characterization.[9] A further observation made for a sample of purified rubber which was not randomized was that a value of G(X) calculated from the slope of a plot of experimental data according to eq 1 gave an approximately correct value. By contrast, incorrect values of G(F) were obtained by use of eq 4.

Polydimethylsiloxanes are expected, from their method of synthesis, to be linear polymers which approximate to a random molecular weight distribution. Kilb showed this to be the case for a sample with M_w/M_n = 2.2, by fractionation. They are also expected to meet another desideratum for conformity with eq 1, which is that the yields of cross-links and fractures should be proportional to radiation dose. Many polymers might be expected to fail to meet this desideratum because of progressive changes in the unsaturation pattern resulting from irradiation. As has been emphasized by Miller,[2] there is no obvious way in which unsaturation could be produced by irradiation of polydimethylsiloxane.



$$\sim\!\!\sim O-\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{Si}}-O-\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{Si}}\sim\!\!\sim$$

I

Results and Discussion

Cross-Links and Fractures. Data obtained after irradiation at room temperature are plotted according to eq 1 in Figures 1a and 2. For comparison, data reported by Miller in the form of a plot of per cent gel *vs.* dose have been replotted in Figure 1b. In the definition of a linear plot less emphasis is placed on data obtained after low doses, on the grounds that insufficient fracture would have occurred to help randomize the distribution initially present. A quantitative discussion of the way in which the incidence of random fracture leads to a random molecular weight distribution has been given by

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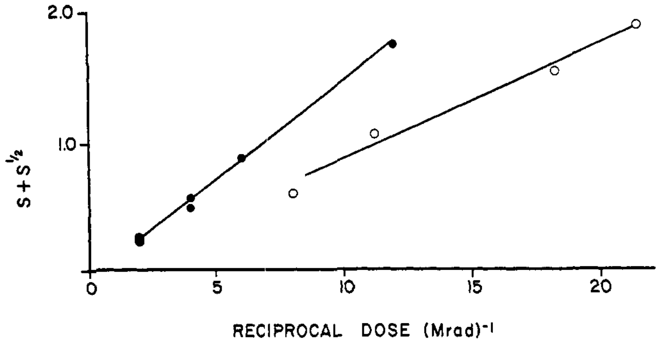

Figure 2. Solubility plots for silocone rubber (M_w = 4.8 × 10^6): ○, sample irradiated at 35°; ●, sample irradiated in liquid nitrogen.

Bovey.[10] In the case of the low molecular weight polymer, following the above precept leads to neglect of only one datum; for R^{-1} = 0.39 Mrad^{-1} in Figure 1b. In the case of the high molecular weight polymer the gel fraction was formed after such low doses (<0.13 Mrad) that this distinction was not made (Figure 2).

Estimates of G values for cross-links and fractures for samples irradiated at room temperature are given in Table I. The data obtained for the low molecular weight polymer are scattered, but when bounds are selected as shown in Figure 1a a value may be estimated of G(X) = 2.2 ± 0.3. This range is lower than the mean value of G(X) = 2.6 deduced from a compilation of data, obtained by various other methods, from eight laboratories by Ormerod and Charlesby. More disturbingly, it is smaller than the value of G(X) = 3.3 calculated from a similar analysis (Figure 1b) of data reported for a nominally equivalent sample by Miller. Actually, this latter work was done with a sample exposed under nitrogen to 800 keV electrons at a much higher dose rate of 692 Mrad/hr. However, in general, changes in dose rate are not expected to have such a marked influence on values of G(X). More specifically, Miller provided evidence for a negligible dose rate effect by showing that the gel content was little changed by decreasing the dose rate by two orders of magnitude. A possible explanation for the lowness of the present value is that the molecular weight of the polymer may have been reduced below its initial value as a consequence of the heat treatment given to flush out volatiles. However, this possibility was investigated experimentally and rejected. Another possibility, that the low value was due to incorrect dosimetry, was rejected on the grounds that the source used had been continuously monitored over a period of years during which it provided acceptable G values for a variety of known reactions. Therefore, in the absence of any obvious reason for the present low value, it is concluded that further more extensive studies are necessary to establish an absolute value of G(X).

Although the data for the high molecular weight polymer are limited, an approximate value may be obtained from Figure 2 of $G(X) \simeq 2.3$, which is in agreement with the value obtained for the low molecular weight sample.

For the low molecular weight polymer, G(F) = 0.7 ± 0.2 from the bounds in Figure 1a. No corresponding estimate was made for the high molecular weight sample because the data are too sparse and scattered (Figure 2).

An unbelievably high value of G(F) = 2.0 is obtained from the plot of Miller's data in Figure 1b, resulting in a ratio of fractures to cross-links of 0.75. As mentioned earlier, Ormerod and Charlesby stated that they made a similar analysis of Miller's data and obtained a ratio of 0.25. The reason for this discrepancy is not clear, although there is the difficulty of reading values accurately from a curve of per cent gel *vs.* dose. The difficulty is compounded because of some uncertainty in the choice of a straight-line plot. In order to give an impression of the sensitivity of the estimates to this choice, two arbitrary lines have been drawn in Figure 1b. The corresponding values are: line 1, G(X) = 3.1, G(F) = 1.2; line 2 G(X) = 2.7, G(F) = 0.6. Another factor which would markedly affect the value of the intercept, and hence of G(F), would be the presence of small amounts of low molecular weight "impurities," such as water, which would be registered in the sol fraction by most methods of gravimetric analysis. The extent of spurious contributions from this source may be judged from the following figures: for 1% "impurity," S = 0.01 and $S + S^{1/2}$ = 0.11; for 2% impurity, S = 0.02 and $S + S^{1/2}$ = 0.16. Evidently estimates of fractures should be restricted to samples which have been thoroughly stripped of impurities.

TABLE I
VALUES OF G(X) AND G(F) AT ROOM TEMPERATURE

Source	Slope	Intercept	G(X)	G(F)	G(F)/ G(X)
Figure 1 upper bound	5.93	0.14	1.9	0.5	0.25
Figure 1 lower bound	4.46	0.18	2.5	0.9	0.35
Figure 1b (Miller)	3.46	0.30	3.3	2.0	0.75
Figure 2 (higher mol wt)	0.086	Not definitive	2.3		

TABLE II
VALUES OF G(X) AND G(F) NEAR −196°C

Source	Slope	Intercept	G(X)	G(F)	G(F)/ G(X)
Figure 1a (oil)	8.95	0.24	1.3	0.6	0.5
Figure 2 (rubber)	0.15		1.3		

Temperature of Irradiation. Miller found that the gelation of polydimethylsiloxane was dependent on the temperature or irradiation. As the temperature was raised above 100° a progressively smaller gel fraction was obtained up to the maximum temperature investigated near 300°. Values of G(X) calculated on the assumption of zero fracture followed a similar trend. In order to account for this it was suggested that "the decrease in apparent cross-linking yield at elevated temperatures is due to an ionic rearrangement of the siloxane backbone catalyzed by traces of ionic impurities or by radiation." The gel fraction was also found to decrease on lowering the temperature of irradiation by liquid nitrogen refrigeration. In this case the assumption of zero fracture was retained and calculations made on this basis indicated that G(X) was decreased to about two-thirds of the value obtained at room temperature. In independent support of this contention, infrared analytical data were interpreted to show that the G value for silicon–silicon cross-links was suppressed to zero; at 25°, $G(>\text{Si–Si}<) = 1.1$.[7]

The results in Figures 1a and 2 provide the G values for samples irradiated near −196° shown in Table II. Comparison of Tables I and II shows that irradiation at the low

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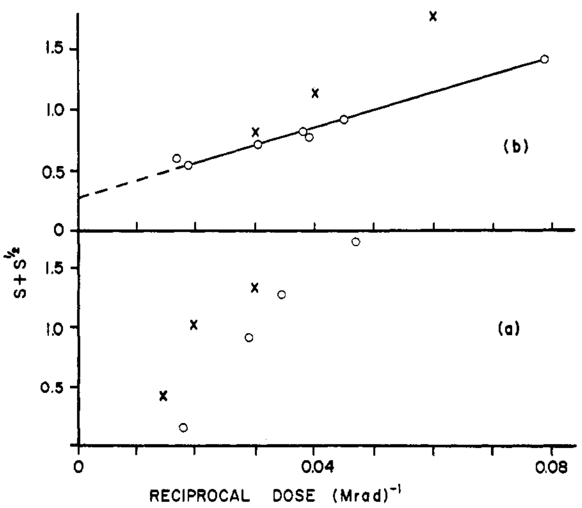

Figure 3. Influence of additives on solubility plot for silicone oil (M_w = 85,000). (a) O, *n*-dodecyl mercaptan (10%, by weight), γ-rays; X, *n*-butyl mercaptan (10%, by weight); electrons (Miller's data).[7] (b) 10% by weight diethyl disulfide, O, present data, X, Miller's data.[7]

temperature results in $G(X)$ being decreased by one-half to two-thirds of the value observed at room temperature. These results are, therefore, consistent with Miller's findings. They serve to emphasize the need for further work on the stoichiometry of the cross-linking reactions in relation to gas formation. As pointed out by Miller, the ratio of $G(H_2 + CH_4 + C_2H_6)/G(X) \approx 1$ observed at room temperature is consistent with the simple hypothesis that each cross-link is accompanied by the formation of one molecule of gas. Inexplicably, near −196° $G(H_2 + CH_4 + C_2H_6)/G(X) \approx 1.5$, according to Miller's data.[2]

Influence of Additives. Miller investigated the influence of a number of additives on the radiation chemistry of polydimethylsiloxane and found that mercaptans (RSH), equivalently *n*-butyl mercaptan and *tert*-dodecyl mercaptan, were most efficient in retarding gel formation, followed by diethyl disulfide (R–S–S–R).[7] He suggested that their role was to intercept polymer free radicals which otherwise combine to form cross-links, and hence gel. The reactions suggested may be exemplified in reactions I and II by reference to one of the two possible polymer radicals involved (the other is $>$Si·)

$$>\text{Si–CH}_2\cdot + \text{RSH} \longrightarrow\ >\text{Si–CH}_3 + \text{RS}\cdot \qquad \text{(I)}$$

$$>\text{Si–CH}_2\cdot + \text{RSSR} \longrightarrow\ >\text{SiCH}_2\text{SR} + \text{RS}\cdot \qquad \text{(II)}$$

The efficiency of *n*-butyl mercaptan was found to decrease markedly with increasing dose, and this was attributed to its consumption. It was found by infrared analysis that hydroxyl groups were formed, and this allowed an estimate of fractures on the assumption that $G(F) \equiv G(>\text{SiOH}) = 0.26$.

Results of the present work with 10%, by weight, of *n*-dodecyl mercaptan are plotted in Figure 3 along with calculations made from results tabulated by Miller for a similar sample of polymer containing 10% *n*-butyl mercaptan. Neither set of data conforms to eq 1. Presumably, because of consumption of the additive, the rate of cross-linking does not remain constant, as is required for application of eq 1, but instead increases with increasing dose.

The results obtained in the present work in the presence of 10% diethyl disulfide (10^{-3} mol/g) do conform to eq 1 and provide the following values: $G(X) = 0.8$, $G(F) = 0.4$. The only other definitive study of the influence of a scavenger on both cross-linking and fracture was made for rubber containing nitrobenzene (2.5×10^{-4} mol/g).[11] The studies are in agreement that a large concentration of a free-radical scavenger can prevent about two-thirds of the cross-links from forming. In the rubber system the presence of scavenger increased the yield of fractures by 90%. In the silicone oil it is doubtful whether the estimates of fractures are sufficiently accurate to sustain such detailed comparisons.

It is not clear why a mercaptan should lose its efficiency as a scavenger more rapidly than does a disulfide. One possible clue is the observation that thiophenol undergoes sensitized decomposition when irradiated in admixture with polyisobutylene.[12] By contrast, disulfides seem to behave in the simple manner suggested in reaction II. For example, a radioactively tagged disulfide was found to give a plausible value for G(polyisobutylene radicals).[13]

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(13) G. Ayrey and D. T. Turner, *ibid., Part B*, **1**, 185 (1963).