

sence of chemisorption of carbon dioxide at  $-78^\circ$  on sample B of the Raney nickel since in preparing the catalyst a sodium hydroxide solution was used for leaching the aluminum from the nickel-aluminum alloy taken as starting material. No explanation for the absence of carbon dioxide chemisorption can be given until further work is done.

The adsorption isotherms for nitrogen in Fig. 1 enable one to estimate the average pore size to have a value of about 84 Å. in diameter. This is

based on the usual equation  $d = 4V/A$  where  $d$  is the diameter in centimeters,  $V$  is the pore volume and  $A$  is a surface area in square centimeters.

In summary, the data suggest that Raney nickel is a porous catalyst and that only about 20% of its surface is metallic. The remainder is non-metallic and probably consists largely of alumina formed during the leaching process by which the catalysts are prepared.

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## Radiation Chemistry of Polydimethylsiloxane.<sup>1</sup> II. Effects of Additives

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The electron-irradiation of polydimethylsiloxane oil  $[-Si(CH_3)_2O-]_n$  in the presence of several additives was studied. Oxygen decreases the crosslinking yield from the normal value of  $G = 3$  to a limiting minimum value of  $G = 1$ , and it is concluded that these "residual" crosslinks are not peroxide ( $-O-O-$ ) bonds. Reactive hydrogen transfer agents, such as mercaptans, are more effective than aromatic free-radical inhibitors (e.g., di-*t*-butyl-*p*-cresol, quinone) in retarding the crosslinking. The use of 10% mercaptan allows a direct measurement of primary  $>Si-CH_3$  scissions and the yield for these is  $G = 4$ , only slightly dependent on temperature between  $-40$  and  $+100^\circ$ . The yield of  $>SiOH$  end-groups formed by irradiation in the presence of 10% mercaptan indicates that, compared to crosslinking, radiation-induced free-radical scission of the siloxane backbone is negligible. The effects of  $H_2$ , diethyl disulfide, benzene and tetralin on the radiation-crosslinking of polydimethylsiloxane also are described.

### Introduction

The preceding paper<sup>2</sup> has described the electron-irradiation of polydimethylsiloxane  $[-Si(CH_3)_2O-]_n$  with emphasis on the gas and crosslinking yields as a function of temperature and radiation intensity. In the present paper, the effects of several additives:  $O_2$ ,  $H_2$ , aromatic free-radical inhibitors, mercaptans and a disulfide, and benzene and tetralin at solvent concentrations will be considered.

### Experimental

The silicone oil (30,000 c.s. viscosity), irradiation procedures and gel measurements were described in the previous paper.<sup>2</sup> A gel yield *vs.* irradiation dose curve was determined for this oil at  $25^\circ$  and an irradiation intensity of 14 Mr./min. For these conditions the radiation crosslinking yield is  $G(c.l.) = 3/100$  e.v. In the present work, the effect of additives on the crosslinking was determined by measuring the gel yield for a given irradiation dose,  $D$ , and converting this gel yield to the relative crosslinking yield by means of the standard gel *vs.* dose curve (ref. 2, Fig. 1). For example, a 10 Mr. dose in the pure silicone oil gave a gel yield of 80%. If, in the presence of additive, the same dose gave a gel yield of only 53%, this corresponds to an "equivalent dose,"  $D'$ , of 5 Mr., and it can be concluded that with the additive the relative crosslinking yield is 0.5 and, therefore,  $G(c.l.) = 1.5/100$  e.v.

For irradiations under elevated pressures of gas ( $O_2$ ,  $N_2$ ,  $H_2$ ) a special pressure cell was used. The cell window was of 2-mil stainless steel backed by a honeycomb grid of  $1/4$ " steel with  $1/4$ " diameter holes. The cell was sealed by flange and a neoprene O-ring gasket, which was shielded from the radiation. The gas pressures were measured by a Bourdon gage. Weighed samples of the silicone oil in an aluminum irradiation dish were equilibrated with the gas at the desired pressure for 30 minutes, although this was probably much longer than required for the attainment of gas solubility equilibrium in the 1 mm. thickness of oil. As usual, all irradiations were done in the same geometry with respect to the electron-beam. The dosimetry for the

cell was established from the gel yields for irradiations in the cell under 1 atmosphere of pure nitrogen.

The inhibitor-type additives (phenols and quinones) were purified by recrystallization from petroleum ether, followed by vacuum-drying. These were dissolved directly in the silicone oil, forming homogeneous solutions, before irradiation. The mercaptan additives were used without purification: *n*-butyl mercaptan and di-ethyl disulfide (Eastman) and dodecyl mercaptan (Delta Chemical Company).

In some cases irradiated products were analyzed by differential infrared absorption. The calibration for  $>SiOH$  absorption at  $2.72\mu$  was made using known amounts of trimethylsilanol,  $(CH_3)_3SiOH$ , in a 10% solution of the silicone oil in  $CCl_4$  solvent. A linear correspondence between the  $2.72\mu$  differential absorbance and amount of added silanol was obtained. The resulting absorption coefficient for  $>SiOH$  was  $1.1 \times 10^6$  cm.<sup>2</sup>/mole. The infrared analysis for  $>SiH$  groups was described in the experimental part of the preceding paper.

### Results and Discussion

**Effect of Oxygen.**—Figure 1 shows the relative crosslinking yields, from gel measurements, normalized to the yield under nitrogen at 1 atmosphere, as a function of oxygen and nitrogen pressures. The slight decrease in the crosslinking with  $N_2$  pressure may be attributed to an increasing absorption of the radiation by the 1-cm. thickness of gas above the polymer sample. Under oxygen pressure, the crosslinking yield decreases rapidly and attains a limiting minimum value at about 35% of the nitrogen control, corresponding to  $G(\text{crosslink}) \approx 1.0$ . This limiting value above 150 p.s.i. oxygen, together with the observation that in this region, irradiations at 0.1 and 0.05-fold lower dose rates gave no further reduction in gel yield, show that this is a true limiting value and is not determined by the  $O_2$  concentration or the diffusion rate of  $O_2$  into the sample. It was established, also, that this "residual" crosslinking was not a post-irradiation effect since the same residual gel yield was obtained by irradiation under 200 p.s.i.  $O_2$  whether the samples were extracted immediately, stored at room

(1) Presented, in part, at a Symposium on Chemical Effects of High Energy Radiation, A.A.A.S. Meeting, Washington, D. C., Dec. 26-31, 1958.

(2) A. A. Miller, *THIS JOURNAL*, **82**, 3519 (1960).

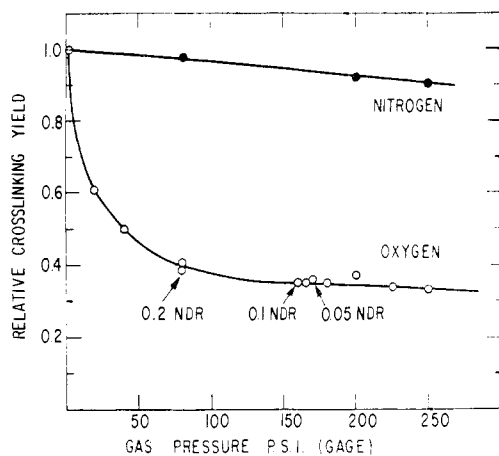


Fig. 1.—Effect of oxygen on the crosslinking yield; normal dose rate (NDR) = 13.8 Mr./minute.

temperature in air for one week prior to extraction or outgassed immediately after irradiation and then heated in a nitrogen atmosphere for 4 hr. at 150° prior to extraction.

The thermal stability of this "residual" gel was examined to determine whether these "residual" crosslinks might be peroxide (—OO—) crosslinks. Samples of the benzene-extracted "oxygen-gel" and "nitrogen-gel" as a control were swollen in a large excess of redistilled decalin solvent containing 1% di-*t*-butyl-*p*-cresol, under a nitrogen atmosphere for 10 hr. at 185°. The gels then were extracted in benzene, dried and weighed. The recoveries were 100% for the "nitrogen gel" and 70% for the "oxygen-gel." Hahn and Metzinger<sup>3</sup> synthesized and measured the thermal stabilities of peroxides of the type  $\text{>SiOOSi<}$  and  $\text{>SiOOC<}$ , and found for the former a half-life of 8 hr. at 135°, with an activation energy of about 40 kcal./mole. (This thermal stability is about the same as for di-*t*-butyl peroxide.<sup>4</sup>) Extrapolation to 185° gives a half-life of only about 2 minutes for the  $\text{>SiOOSi<}$  peroxide bond. The fact that the "oxygen-gel" could survive this temperature for as long as 10 hr. shows that at least the major portion of the residual crosslinks cannot be peroxide crosslinks.

It was also established that the residual crosslinks were not  $\text{>Si—Si<}$  bonds since swelling of the "oxygen-gel" in  $\text{Br}_2\text{—CCl}_4$  reagent, which should rapidly cleave the  $\text{>Si—Si<}$  bond (see  $\text{>Si—Si<}$  analysis in preceding paper<sup>2</sup>), did not dissolve the gel.

Thin (0.025 cm.) films of the silicone polymer were irradiated under 200 p.s.i. oxygen and nitrogen and examined by infrared absorption. The most pronounced change in the former was the appearance of a carbonyl absorption at  $5.8\mu$  and this was absent in the nitrogen control. The  $5.8\mu$  absorbance was approximately linear with dose, giving values of 0.44 at 16.6 Mr. and 0.80 at 33.2 for the 0.025 cm. films. Vacuum-pumping on these samples at room temperature for 8 hr. and remeasurement of the absorbances gave only a small decrease, showing that the carbonyl was bound to the polymer rather

than being in volatile products (e.g. formaldehyde). The type of carbonyl could not be resolved from these infrared spectra, but dimethylsiloxane structure precludes the formation of ketone so that aldehyde or its oxidation product, carboxyl, are the more likely possibilities. Using average extinction coefficients obtained by Cross and Rolfe<sup>5</sup> for aliphatic aldehydes:  $K = 1.3 \times 10^5 \text{ cm.}^2/\text{mole}$  and for aliphatic acids:  $K = 5.3 \times 10^5 \text{ cm.}^2/\text{mole}$ , we obtain for an absorbance of 0.44 at 16.6 Mr., the yields  $G = 10$ , if aldehyde, and  $G = 2.4$ , if carboxyl. In an independent study on hexamethyl-disiloxane,  $(\text{CH}_3)_3\text{SiOSi}(\text{CH}_3)_3$ , using vapor-phase chromatography for analysis, Dewhurst and St. Pierre<sup>6</sup> found that irradiation in the presence of oxygen

produced  $\text{>SiC}\begin{matrix} \text{O} \\ // \\ \text{OH} \end{matrix}$  groups, with no measurable

amount of  $\text{>SiCHO}$ . This evidence strongly suggests that in the present experiments, although aldehyde may be an intermediate, it is rapidly oxidized further to carboxyl.

One of the explanations for the residual crosslinking which was considered was that some of the

$\text{>SiC}\begin{matrix} \text{O} \\ // \\ \text{OH} \end{matrix}$  formed in the oxidation decomposes to

$\text{>SiOH} + \text{CO}$  and condensation of the silanol groups in different polymer molecules produces a crosslink:  $2 \text{ >SiOH} \rightarrow \text{>SiOSi<} + \text{H}_2\text{O}$ .<sup>6</sup> To test this possibility, a low molecular weight monofunctional silanol,  $(\text{CH}_3)_3\text{SiOH}$ , was added to the polymer before irradiation. The relative crosslinking yields for irradiations in the presence and absence of oxygen are listed in Table I.

TABLE I  
EFFECT OF  $(\text{CH}_3)_3\text{SiOH}$  ON THE RADIATION CROSSLINKING OF POLYDIMETHYLSILOXANE

$(\text{CH}_3)_3\text{SiOH}$ , %	Atmosphere	Relative crosslinking yield
0	$\text{N}_2^a$	1
0	$\text{O}_2^a$	0.33
5	$\text{N}_2$	.8
10	$\text{N}_2$	.6
5	$\text{O}_2^a$	.20
10	$\text{O}_2^a$	.16

<sup>a</sup> Gas pressures = 200 p.s.i.

These data show that 5 and 10%  $(\text{CH}_3)_3\text{SiOH}$  suppress crosslinking to some extent in the absence of  $\text{O}_2$ . With both  $\text{O}_2$  and the silanol present, although the crosslinking is retarded further, it is not eliminated completely. It can be estimated the number of added  $\text{>SiOH}$  groups is 50 to 100 times the maximum which could be produced in the poly-

mer by irradiation via the  $\text{>SiC}\begin{matrix} \text{O} \\ // \\ \text{OH} \end{matrix}$  intermediate.

Therefore, if the residual crosslinks were due to condensation of  $\text{>SiOH}$  groups in the polymer, they should be suppressed completely by the very large excess of the added, low molecular-weight silanol and this is not observed. In fact, the results sug-

(5) L. H. Cross and A. C. Rolfe, *Trans. Faraday Soc.*, **47**, 354 (1951).

(3) W. Hahn and L. Metzinger, *Makromol. Chem.*, **21**, 113 (1956).  
(4) A. V. Tobolsky and R. B. Mesrobian, "Organic Peroxides," Interscience Publishers, Inc., New York, N. Y., 1954.

(6) L. E. St. Pierre and H. A. Dewhurst, *J. Phys. Chem.*, **64**, 1060 (1960).

gest that the effects of O<sub>2</sub> and silanol in suppressing the crosslinking are approximately additive.

The possibility of non-radical crosslinking processes which might not be inhibited by O<sub>2</sub> (e.g., "molecular" or "ion-molecule" reactions) was considered but dismissed on the basis of evidence provided by other radical scavengers to be presented later in this paper. Tentatively, it is proposed that both the  $\text{>SiCH}_2\cdot$  and the  $\text{>Si}\cdot$  polymer radicals produced by irradiation are rapidly scavenged by oxygen to form the corresponding peroxy radicals.

The  $\text{>SiCH}_2\text{OO}\cdot$  is ultimately oxidized to  $\text{>SiC}\begin{matrix} \text{O} \\ \diagup \\ \text{OH} \end{matrix}$  while the  $\text{>SiOO}\cdot$  is an intermediate in a reaction forming the residual crosslinks.

The concentration of dissolved oxygen in these experiments was determined from solubility measurements as a function of O<sub>2</sub> pressure up to 300 p.s.i. The value obtained for a 26,000 c.s. oil was  $6 \times 10^{-6}$  mole O<sub>2</sub>/g./atm. at 30°. Thus, at 200 p.s.i. (gage) or about 15 atmospheres the solubility is  $9 \times 10^{-5}$  mole/g. The calculated solubility for equilibrium with 1 atmosphere of air (0.2 atm. O<sub>2</sub>) is  $1.2 \times 10^{-6}$  mole O<sub>2</sub>/g.

**Effect of Hydrogen.**—The irradiation of polydimethylsiloxane in the presence of dissolved hydrogen was examined briefly to explore the possibility of a "back-reaction" of molecular hydrogen with the polymer radicals, as evidenced by a decrease in the crosslinking yield. The silicone oil was equilibrated with 200 p.s.i. of H<sub>2</sub> in the pressure cell for 30 minutes and irradiated at 4.2 and 8.4 Mr. The gel yields corresponded to "equivalent doses" of 4.2 and 8.0 Mr., respectively, showing negligible suppression of crosslinking. (A control irradiated under 200 p.s.i. of N<sub>2</sub> at a dose of 8.4 Mr. gave a gel yield corresponding to the expected "equivalent dose" of 8.4 Mr.) These experiments show that back reactions of polymer radicals with H<sub>2</sub>, i.e.,  $\text{>SiCH}_2\cdot + \text{H}_2 \rightarrow \text{>SiCH}_3 + \text{H}\cdot$  and  $\text{>Si}\cdot + \text{H}_2 \rightarrow \text{>SiH} + \text{H}\cdot$ , were not occurring to a noticeable extent under the conditions of the experiment. (A rapid subsequent abstraction reaction by the H· atoms, which could nullify the above processes by reforming polymer radicals:  $\text{H}\cdot + \text{>SiCH}_3 \rightarrow \text{H}_2 + \text{>SiCH}_2\cdot$ , is not likely for thermal H· atoms at room temperature.)

**Effect of Free-Radical Inhibitors.**—Samples of the silicone oil containing increasing amounts of dissolved di-*t*-butyl-*p*-cresol were irradiated at room temperature at a dose of 10 Mr. and the relative crosslinking yields were determined from gel measurements. The results are shown in Fig. 2. In the range 0.01 to 0.1 mole/l. inhibitor the crosslinking is suppressed by only 10 to 20%. Since  $G(\text{c.l.}) = 3$  for the pure polymer,<sup>2</sup> a 10 Mr. dose would produce a crosslink concentration of 0.026 mole/l. Thus, a 0.1 mole/l. inhibitor concentration is more than sufficient to react with the polymer radicals which are formed. At the highest concentrations, 11 and 22%, the weight fraction of inhibitor is sufficiently high so that direct absorption of radiation energy by the additive cannot be neglected.

(7) P. Cannon, L. E. St. Pierre and A. A. Miller, *J. Chem. Eng. Data*, **5**, 236 (1960).

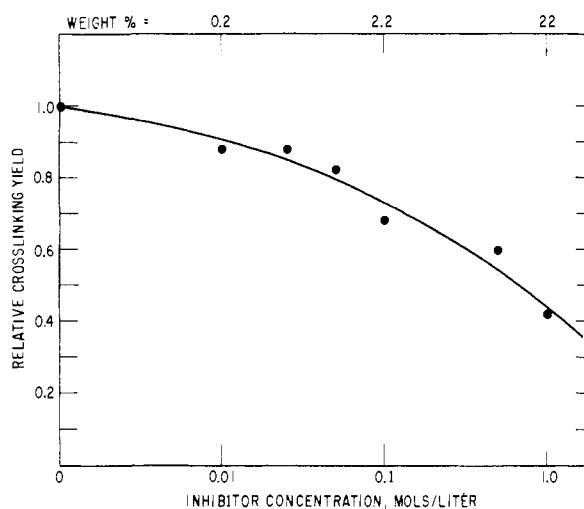
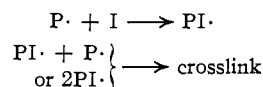


Fig. 2. —Effect of di-*t*-butyl-*p*-cresol on crosslinking yield.

It is likely that although the additive, I, may react efficiently with the polymer radicals, P·, it can also contribute to the crosslinking



Evidence for this is the known addition of radicals to aromatic inhibitor molecules<sup>8</sup> and the fact the irradiations of polyethylene<sup>9</sup> or natural rubber<sup>10</sup> in the presence of such inhibitors result in a chemical binding to the polymer structure. Furthermore, it was observed in the present work with di-*t*-butyl-*p*-cresol, quinone and 4-*t*-butyl-anthraquinone that in all cases the crosslinked gels possessed a yellow color which could not be extracted by benzene. This would be due to inhibitor molecules, or fragments, chemically bound to the silicone gel. Irradiations of the silicone itself with no additive always gave colorless gels.

It is interesting to contrast inhibitor action in *non-chain* crosslinking reactions and in *free-radical chain* reactions. In the former, even if the polymer radicals are efficiently scavenged by the inhibitor, a crosslink may still occur through the inhibitor molecule, as suggested above. In the case of chain reactions, on the other hand, the necessary and sufficient condition for inhibition is that a radical inactive in propagation be formed:  $\text{R}\cdot + \text{I} \rightarrow \text{RI}\cdot$  and whether or not these inactive RI· radicals subsequently dimerize is not critical for the inhibition.

Experiments with 1% quinone (0.09 mole/l.) and 1% 4-*t*-butyl-anthraquinone (0.04 mole/l.) also gave only 10 to 20% inhibition of crosslinking for radiation doses up to 10 Mr.

**Effect of Mercaptans.**—In view of the preceding discussion regarding inhibition of crosslinking, it appeared that reactive hydrogen transfer agents, such as mercaptans, should be more effective in the suppression of crosslinks. This is indeed the case and, furthermore, irradiation in the presence of

(8) See C. Walling, "Free Radicals in Solution," John Wiley and Sons, Inc., New York, N. Y., 1957, p. 165.

(9) M. Prober, Abstract, Paper No. 94, Div. of Polymer Chem., 134th A. C. S. Meeting, Chicago, 1958.

(10) D. T. Turner, *J. Polymer Sci.*, **27**, 503 (1958).

small amounts of this type of additive provides useful information regarding (1) radiation-induced scissions of the siloxane backbone and (2) the primary radiation yield for  $\text{>Si-CH}_3$  scissions.

The majority of these experiments were done with 10 weight % of *n*-butyl mercaptan,  $\text{C}_4\text{H}_9\text{SH}$  dissolved in the 30,000 c.s. silicone oil. In some cases, where a lower volatility was required, *n*-dodecyl mercaptan,  $\text{C}_{12}\text{H}_{25}\text{SH}$ , was employed in the same per cent. concentration, and the results were essentially the same for the two additives.

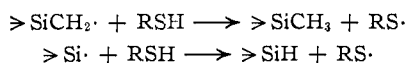
The gel data for samples irradiated at room temperature and at the normal dose rate of 13.8 Mr./minute are given in Table II.

TABLE II  
GEL YIELDS FOR 30,000 C.S. SILICONE OIL CONTAINING 10%  $\text{C}_4\text{H}_9\text{SH}$

Dose, Mr.	Gel yield, %	$D'$ , Mr. <sup>a</sup>
20	0	..
30	(Trace)	2.5
40	43.3	4.1
60	60.6	6.0
80	89.5	20

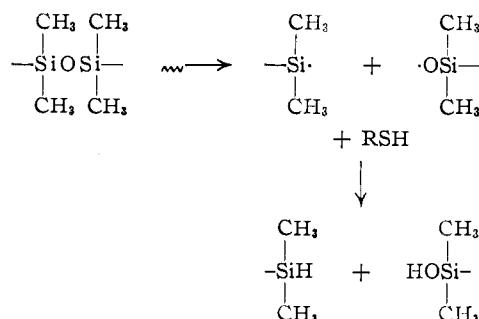
<sup>a</sup>  $D'$  = "Equivalent dose" derived from gel yield *via* Fig. 1, ref. 2.

The dose for incipient gelation was about 30 Mr. compared to the 2.5 Mr. for the pure polymer. The ratio of the "equivalent dose,"  $D'$ , to the actual dose,  $D$ , shows that in the range 30 to 60 Mr. the crosslinking yield has been reduced by a constant factor of 10, that is, from  $G = 3$  for the pure polymer to  $G = 0.3$ , in the presence of the mercaptan. The increase in the  $D/D'$  ratio at 80 Mr. may be attributed to the fact that the major part of the mercaptan has been consumed at this stage of the irradiation. The retardation of crosslinking by added mercaptan can be explained readily by simple hydrogen transfer with the polymer radicals formed by irradiation



This hydrogen transfer reaction saturates the polymer radical making it no longer available for crosslinking. Thus, the inhibition of crosslinking by mercaptans is in contrast to their action in free-radical *chain* reactions, such as polymerizations, where the  $\text{RS}\cdot$  radical can initiate new chains and the over-all effect is chain transfer with no inhibition.

The reaction with mercaptan was employed to measure possible radiation-induced scissions of the main-chain occurring simultaneously with crosslinking, a fundamental problem in all polymer irradiation work. Two independent types of analyses were made: viscosity and infrared analysis for end-groups. Samples containing 10% *n*-butyl mercaptan were irradiated at 10 and 20 Mr., below the gel point, and intrinsic viscosities were measured in toluene at 25°. These were converted to  $M_v$  using the relation given in the preceding paper.<sup>2</sup> The second method was based on the premise that if radiation-induced, free-radical scissions of the main chain occurred, the cleaved polymer radicals should react rapidly with the mercaptan to form  $\text{>SiH}$  and  $\text{<SiOH}$  end-groups



Of these two end-groups, only  $\text{>SiOH}$  can be used to count the scissions since  $\text{>SiH}$  is produced in much greater abundance by another reaction which does not involve main-chain scission (see below). These analyses were made in 1.0 mm. cells with 10% solutions in  $\text{CCl}_4$  using a high-resolution, differential method and the  $\text{>SiOH}$  absorbance calibration described earlier in this paper.

TABLE III  
VISCOSITY AND  $\text{>SiOH}$  ANALYSIS FOR IRRADIATIONS OF 10%  $\text{C}_4\text{H}_9\text{SH}$  IN SILICONE OIL

Dose, Mr.	$[\eta]$ , cc./g.	$M_v$	$A_{2.72\mu^2}$	$G(\text{>SiOH})$
0	35.0	75,000	0	..
10	36.5	79,400	0.0025	0.26
20	46.0	112,000	0.0050	0.26

<sup>a</sup> For 10%  $\text{CCl}_4$  solution in 1 mm. cell.

The viscosity data show that even when the crosslinking has been suppressed to one-tenth of its normal value, the intrinsic viscosity and apparent molecular weight,  $M_v$ , increase with irradiation. Any quantitative conclusion regarding scissions from these viscosity data requires a detailed analysis of the effects of branching, due to any residual crosslinking, on the intrinsic viscosity-molecular weight relationships in the pre-gel region.<sup>11</sup> Furthermore, an analysis by Kilb of this Laboratory indicates that this method is not very sensitive for detecting scissions at low scission/crosslink ratios.<sup>12</sup>

The infrared analysis shows a linear increase in  $\text{>SiOH}$  concentration with irradiation and leads to a value of  $G(\text{>SiOH}) = 0.3$ , which must correspond to the free-radical scission yield. Thus, the scission/crosslink ratio obtained for the polydimethylsiloxane polymer is 0.1 and is consistent with the earlier conclusions, based on the linearity of the log sol *vs.* log dose plot,<sup>2,13</sup> that relatively little main-chain scission is observed in the irradiation of this polymer.

Irradiation in the presence of mercaptan followed by differential infrared analysis for  $\text{>SiH}$  at  $4.63\mu$  was used to measure the radiation yield for the primary scissions of the methyl group. Samples containing 10 weight % butyl or dodecyl mercaptan were irradiated at 10 Mr. over a temperature range from  $-180^\circ$  (glass) to  $100^\circ$ . The  $\text{>SiH}$  absorbances were measured in 10%  $\text{CCl}_4$  solution. To ensure that all of the radiation-produced  $\text{>Si}$ -polymer radicals were being scavenged by the ex-

(11) See F. A. Bovey, "Effects of Ionizing Radiation on Natural and Synthetic High Polymers," Interscience Publishers, Inc., New York, N. Y., 1958, p. 85.

(12) R. W. Kilb, *J. Phys. Chem.*, **63**, 1838 (1959).

(13) A. Charlesby, *Proc. Royal Soc. (London)*, **230A**, 120 (1955).

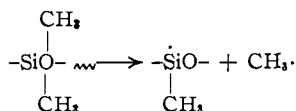
cess mercaptan, two additional experiments were done at 25°, one at the normal dose rate of 13.8 Mr./minute and the second at only one-tenth this intensity, 1.38 Mr./minute. The resulting  $\geq$ SiH absorbances were identical.

TABLE IV  
EFFECT OF TEMPERATURE ON THE  $\geq$ SiH YIELD IN SILICONE WITH 10% RSH (10 Mr.)

Temp., °C.	$A_{4.65\mu}^a$	$G(\geq \text{SiH})$
-180	0	0
-40	0.044	4.2
25	.042	4.0
100	.038	3.6

<sup>a</sup> 10% solutions in 1.0 mm. cells.

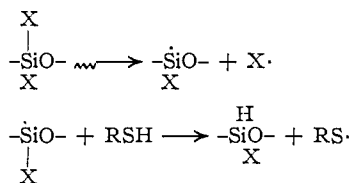
Since the  $\geq$ SiH yield does not increase with a 10-fold decrease in radiation intensity, which should favor the radical-mercaptan reaction over radical-radical recombination, it is concluded that the scavenging of the polymer radicals by the mercaptan is complete. The  $\geq$ SiH yields in Table IV must, therefore, correspond to the yield of primary reaction



It is significant that at -40 and 25° these yields are considerably higher than the *net* methyl radical yields as observed by gas measurements<sup>2</sup>:  $G'(\text{CH}_3\cdot) = G(\text{CH}_4) + 2G(\text{C}_2\text{H}_6)$  at the same temperatures. Thus, a significant fraction of the  $\text{CH}_3$  produced in the primary radiation process undergoes recombination with polymer radicals and does not appear in the evolved gas.

In the liquid state between -40 and +100° there is only a small temperature dependence of the  $\geq$ SiH yield. It is somewhat surprising that in the glass-state at -180° the  $\geq$ SiH yield is zero. Although the reaction of  $\geq$ Si· and RSH might be prevented by the immobilities of the reactants in the glass matrix, it was expected that reaction should still occur when the sample was subsequently thawed to the liquid state in the absence of oxygen.

Irradiation in the presence of mercaptan may be a novel, general method for introducing  $\geq$ SiH groups at random in any polysiloxane where radiation-induced scissions of a substituent on a silicon atom occur



These reactive  $\geq$ SiH groups may be used for subsequent crosslinking (curing) of, or grafting to, the polysiloxane. For a 20 Mr. irradiation at 25° with 10% RSH,  $G(\geq \text{SiH}) = 4$ , and it can be estimated that the resulting soluble polymer will contain  $7 \times 10^{-5}$  mole/g.  $\geq$ SiH units or 1  $\geq$ SiH for every 400  $\geq$ SiCH<sub>3</sub>. For the 30,000 c.s. polymer, with  $\bar{M}_w = 85,000$ , this corresponds to about 6  $\geq$ SiH

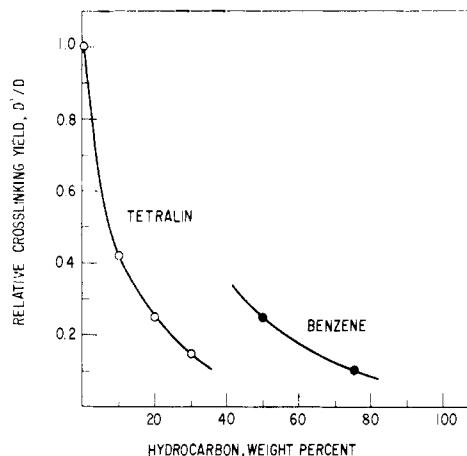


Fig. 3.—Effects of hydrocarbons on crosslinking yield.

groups per initial "weight-average" polymer molecule.

The effect of 10% diethyl disulfide,  $(\text{C}_2\text{H}_5\text{S})_2$ , was examined briefly, and it was found that it also reduced the crosslinking yield, although to a lesser extent than the mercaptans.

TABLE V  
GEL YIELDS FOR 30,000 c.s. SILICONE OIL CONTAINING 10%  $(\text{C}_2\text{H}_5\text{S})_2$

Dose, Mr.	Gel yield, %	$D'$ , Mr.
10	0	..
20	15.1	2.6
30	54.5	5.3
40	72	7.6

The suppression of crosslinking as given by the ratio of "equivalent dose" to actual dose,  $D'/D$ , is 0.13 to 0.19 for the 20 to 40 Mr. dose range, compared to 0.1 for *n*-butyl mercaptan up to 60 Mr. (Table II). The initial molar concentration of the disulfide was about 25% less than that of the mercaptan owing to the difference in molecular weights of these two additives.

The suppression of crosslinking by the disulfide, which obviously cannot be attributed to the hydrogen transfer mechanism proposed for the mercaptan, may be due to removal of polymer radicals by the reaction:  $\text{P}\cdot + \text{RSSR} \rightarrow \text{PSR} + \text{RS}\cdot$ . Such a displacement reaction on the S-S bond has been demonstrated in polymerization chain-transfer.<sup>14</sup> It is also possible that a preferred, direct radiolysis of the relatively labile S-S bond may produce sufficient radicals to contribute to the inhibition of crosslinking:  $\text{RSSR} \xrightarrow{\text{radiation}} 2 \text{RS}\cdot$ ;  $\text{P}\cdot + \text{RS}\cdot \rightarrow \text{PSR}$ . Further studies on the kinetics of the disulfide effect are required to establish the relative importance of these two mechanisms of crosslinking inhibition. It is perhaps significant that while butyl mercaptan is more than 1000-fold as effective as dibutyl disulfide for chain transfer in styrene polymerization,<sup>14</sup> it is only about two-fold as effective as the disulfide for the inhibition of crosslinking in the present system.

**Hydrocarbon Additives and Solvents.**—In some miscellaneous experiments the effects of two hydrocarbons in the concentration range 10 to 75 weight

(14) See ref. 8, pp. 153, 156.

% were examined. Redistilled tetralin and reagent-grade benzene were added to the 30,000 c.s. silicone polymer and gel determinations made on samples of the irradiated solutions. In all cases, the gel yields are based on the polymer content of the original solution. From the corrected gel yields for doses in the range 10 to 40 Mr., the equivalent dose,  $D'$ , was determined from Fig. 1 of the preceding paper. In Fig. 3 the suppression of crosslinking,  $D'/D$ , is shown as a function of the amount of diluent.

Compared to the mercaptans, described in the previous section, tetralin is much less effective in retarding crosslinking. Thus, at 10 weight % (tetralin  $\approx$  0.75 mole/l., butyl mercaptan  $\approx$  1.1 mole/l.), the  $D'/D$  ratios are 0.4 and 0.1, respectively, for tetralin and *n*-butyl mercaptan. Benzene is even less effective than tetralin. From

Fig. 3 it can be seen that it requires 50% benzene (6.4 mole/l.) to produce the same suppression of crosslinking,  $D'/D = 0.25$ , as only 20% tetralin (1.5 mole/l.). The fact that, on either a weight or a molar basis, considerably more benzene than tetralin is required to suppress crosslinking suggests that such factors as hydrogen transfer and radiation yield of radicals, both of which should be higher for tetralin than for benzene, are more important than "protection" by energy transfer to aromatic solvent molecules in this polymer system.

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## Electronegativity, Non-bonded Interactions and Polarizability in the Hydrogen Halides and the Interhalogen Compounds

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The dissociation energies of the compounds in the title have been corrected for non-bonded interactions by an empirical scheme. The corrected values were used to calculate the electronegativities for the five elements. A new scale of electronegativity is proposed based upon the ionization energy of hydrogen. Using the charges predicted by the electronegativity values and the charges calculated from dipole moments of the hydrogen halides, inductive charge transmission coefficients were obtained and shown to be related to the molecular geometry and to the longitudinal polarizabilities of the bonds.

Despite wide usage and acceptance, the concept of electronegativity and the relationship to ionic character have remained obscure. We propose to introduce two factors, inductive charge transfer and non-bonded interactions, in considering the problem. By correction of the experimental dissociation energies for a series of diatomic molecules for non-bonded interactions it looked to be possible to use Pauling's<sup>1</sup> method to calculate a set of electronegativity differences from which a revised set of electronegativities could be obtained. In order to be of value, such a set should show very little, if any, inconsistency between differences in electronegativity taken from the set as compared with those calculated from the corrected dissociation energies.<sup>2</sup> With such electronegativity values, a comparison with the charges as calculated from dipole moments could be made and a transmission coefficient for charge transfer (or partial neutralization of charge across a given bond) calculated. Such transmission coefficients should bear a relationship to the geometry of the molecule as should the longitudinal polarizability of the bond. This program has been carried through, and considering the simplicity of the model the results have been surprisingly satisfactory.

(1) L. Pauling, "The Nature of the Chemical Bond," 3rd ed., Cornell University Press, Ithaca, N. Y., 1960, p. 80, 82, 88.

(2) See Table III in M. L. Huggins, *THIS JOURNAL*, **75**, 4123 (1953), for an example of the lack of concordance even in the revised electronegativities proposed by Huggins, but using experimental dissociation energies.

It seems to be commonly agreed that non-bonded interactions exist in those molecules in which filled orbitals lie in proximity to each other. Such interactions have been used successfully in estimating the enthalpy and entropy of hydrocarbons,<sup>3</sup> and Mulliken<sup>4</sup> has considered the halogen molecules from the viewpoint that negative bond order is the counterpart in l.c.a.o. m.o. theory of nonbonded repulsions in v.b. theory. Such a repulsion in a halogen-halogen bond (absent or weak in a hydrogen-halogen bond) should weaken the bond.<sup>4</sup> According to v.b. theory non-bonded interactions exist not only between lone pairs on adjacent atoms but also between every electron on one atom and every electron of like spin on the other. Of these non-bonded interactions, those between electrons in orbitals of like symmetry (both  $\sigma$ , or both  $\pi^+$  or both  $\pi^-$ ) are repulsions, and these are often strong, just as between two lone pairs one on each atom. Non-bonded attractions occur between electrons of unlike symmetry and on different atoms ( $\sigma_A$ ,  $\pi_B$  attractions,  $\pi_A^+$ ,  $\pi_B^-$  attractions). The net effect of the non-bonded interactions not involving lone pairs on each atom may be and is fairly large. Magnitudes of terms of this sort have been discussed by Mulliken<sup>5</sup> who gives earlier references. Since the approach used here has been empirical,

(3) K. S. Pitzer, *ibid.*, **70**, 2140 (1948); **72**, 4493 (1950).

(4) R. S. Mulliken, *ibid.*, **77**, 884 (1955); *J. Chem. Phys.*, **23**, 2343 (1955).

(5) R. S. Mulliken, *J. Phys. Chem.*, **56**, 295 (1952).