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# NMR study of the gamma radiolysis of poly(dimethyl siloxane) under vacuum at 303 K

David J.T. Hill[a,*], Christopher M.L. Preston[a], Andrew K. Whittaker[b]

[a]Polymer Materials and Radiation Group, Department of Chemistry, The University of Queensland, Brisbane, Qld 4072, Australia
[b]Centre for Magnetic Resonance, The University of Queensland, Brisbane, Qld 4072, Australia

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**Abstract**

The structural changes which occur on the $\gamma$-radiolysis of poly(dimethyl siloxane) (PDMS) under vacuum at 303 K have been investigated using $^{29}$Si and $^{13}$C NMR. New structural units consistent with main chain scission and crosslinking through both H-linking and Y-linking reactions have been identified. The results obtained at various absorbed doses have been used to calculate the *G*-values for scission and crosslinking. *G*-values for scission of $G(\mathrm{S}) = 1.3 \pm 0.2$, for H-linking of $G(\mathrm{D}^{\mathrm{CH_2}}\text{–R}) = 0.34 \pm 0.02$ and for Y-linking of $G(\mathrm{Y}) = 1.70 \pm 0.09$ were obtained for radiolysis under vacuum at 303 K. Thus crosslinking predominates over scission for radiolysis of PDMS under these conditions, and, by contrast with previous studies, Y-links have been shown to be the predominant form of crosslinks. © 2001 Elsevier Science Ltd. All rights reserved.

*Keywords*: Poly(dimethylsiloxane); $^{29}$Si & $^{13}$C solid-state NMR; $\gamma$-Radiolysis

## 1. Introduction

Poly(dimethyl siloxane) (PDMS), is the best known of the commercial polysiloxanes. PDMS and the other related polysiloxanes have low surface energies, low crystalline melting temperatures and high chain flexibilities at ambient temperatures. High molecular weight, linear PDMS polymers are extremely viscous liquids, whereas the crosslinked polymers are insoluble, colorless elastomers. These unique properties have led PDMS to find many commercial applications, ranging from medical goods to household products.

Structural crosslinks can be introduced into polysiloxanes by either chemical or radiolytic methods. The effects of high-energy radiation on the material properties of PDMS have been studied extensively over the past 50 years. For example, Warrick [1], Basfar [2] and other workers have reported on the improvements in the material properties of PDMS resulting from radiolysis, whereas yet other researchers, Charlesby [3], St. Pierre et al. [4], Miller [5] and Belova et al. [6], have reported that the major volatile products of radiolysis are hydrogen, methane and ethane. By way of example, Belova et al. found $G(\mathrm{H_2}) = 0.3$, $G(\mathrm{CH_4}) = 1.3$, $G(\mathrm{C_2H_5}) = 0.3$ and $G(\text{total gas}) = 1.9$ for $\gamma$-radiolysis of PDMS at 293 K.

Okamura et al. [7], Ormerod and Charlesby [8] and Menhofer and Heusinger [9] have identified the presence of $\mathrm{CH_3}\cdot$, $-\mathrm{CH_2}\cdot$ and $-\mathrm{Si}\cdot$ or $-\mathrm{O}\cdot$ radicals at 77 K, with *G*(R) 3.6 at 77 K. On subsequent annealing after radiolysis at 77 K, all radicals disappear below 195 K, but spin trapping studies [9] have revealed the presence of $-\mathrm{CH_2}\cdot$ and $-\mathrm{Si}\cdot$ radicals on radiolysis of PDMS at 298 K, with the $-\mathrm{Si}\cdot$ radicals being predominant. However, in the latter studies, oxygen centered radicals would not have been trapped.

Charlesby and Garratt [10] calculated the yield for crosslinking, $G(\mathrm{X}) = 2.32$, from a sol/gel analysis according to a H-linking mechanism, and they found that the gel dose approximately doubled in the presence of air. Charlesby [11] has also reported that in an inert atmosphere *G*(X) increases with increasing temperature, approximately doubling between 195 K and room temperature. St. Pierre [4] determined *G*(X) 2.5 for a PDMS short chain oligomer, by cryoscopic measurements in cyclohexane and Delides [12] found $G(\mathrm{X}) = 2.7$ by light scattering and a sol/gel analysis at 293 K.

Infrared studies of irradiated siloxanes have been reported by Bueche [13], Miller [5] and Belova [6]. Both Bueche and Miller reported the formation of Si–H structures and Belova suggested the formation of new types of Si–O bonds. The *G*-values for silmethylene and silethylene H-link formation were calculated by Miller from an infrared

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* Corresponding author. Tel.: +61-7-3365-4119; fax: +61-7-3365-4299.
*E-mail address:* hill@chemistry.uq.edu.au (D.J.T. Hill).

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analysis, and he measured the corresponding values for Si–Si H-type crosslinks by a bromination method. Miller reported *G*-values of 1.8, 0.5 and 1.1, respectively, for these three new structures. However, quantification of *G*-values from infrared studies requires a knowledge of group molar absorptivities, which are often not accurately known, and the majority of the new peaks in the FT-IR spectra are partially obscured by existing strong absorption bands, which limits the accuracy of the *G*-value measurements.

Miller [14] also studied the radiolysis of PDMS at ambient temperature in the presence of mercaptan and he observed the formation of Si–H and Si–OH functionalities by infrared analysis. He proposed that the latter functional groups arose as a result of main-chain scission and hydrogen abstraction by Si–O· radicals. Quantification of these groups from infrared spectra led him to estimate a yield of chain scission of 0.26.

Thus, while the infrared studies have provided evidence for the formation of both scission and crosslink structures, the possible existence of other structures cannot be ruled out on the basis of the studies reported to date. In addition, the *G*-values for formation of the new polymer structures obtained from the infrared studies are subject to considerable uncertainty.

In the work reported herein, the structural changes in PDMS during γ-radiolysis at 303 K have been investigated using $^{29}$Si and $^{13}$C NMR spectroscopy. These studies allow the direct observation of several new structures formed on γ-radiolysis, and quantification of the peaks in the spectra allow *G*-values for the formation of these structures to be determined.

## 2. Experimental

PDMS (viscosity 1 Pa s) was obtained from Dow Corning Australia and, according to the manufacturer, the polymer chains were terminated by tri-methylated silicon atoms. $^{1}$H and $^{13}$C NMR were used to confirm the structure of the polymer and the purity of the PDMS. No evidence for the presence of any inhibitors or stabilizers was found in the samples. The PDMS samples were irradiated in glass ampoules under vacuum in a Nordian Gammacell to a range of doses at a dose rate of 6.5 kGy h$^{-1}$ at 303 K. For irradiations under vacuum, the samples were processed through a series of freeze thaw degassing cycles and then exhaustively evacuated at less than 10$^{-2}$ Pa for 24 h.

Solution-state NMR spectra were obtained using a Bruker AMX spectrometer equipped with a Bruker broad-band BSP 5 mm probe. The spectra were acquired at 79.49 MHz for $^{29}$Si and 100.62 MHz for $^{13}$C nuclei. The solution-state $^{29}$Si spectra of the polysiloxanes were obtained in $CDCl_3$ solutions (20% v/v) to which Cr(acac)$_3$ was added (0.03 M) as a paramagnetic relaxation agent [15]. Inverse gated decoupling was used to suppress the negative NOE of $^{29}$Si. A recycle delay of 10 s was found to be sufficient for full spin relaxation and the spectra were acquired for 16 h at room temperature using a π/2 pulse with a pulse time of 7 μs. Qualitative spectra were also obtained using the DEPT pulse sequence, in which case the spectra were acquired using a recycle delay of 3 s without addition of the relaxation agent. The DEPT sequence was optimized for a $^{2}J_{^{29}}\mathrm{Si}-{}^{1}\mathrm{H}$ coupling of 7 Hz, which was measured from the $^{1}$H spectrum.

The solid-state spectra were obtained using a Bruker MSL300 spectrometer operating at 59.601 MHz for $^{29}$Si and 75.435 MHz for $^{13}$C nuclei. Crosslinked PDMS powder was packed into a 7 mm zirconium oxide rotor and spun in a Bruker double air-bearing CP-MAS probe at the magic angle at a frequency of 2.5 kHz. The chemical shifts were measured relative to TMS via the external standards of adamantane for $^{13}$C and kaolinite for $^{29}$Si, and the spectra were all acquired at room temperature.

Solid-state $^{29}$Si spectra were collected using either a single pulse (SP) or the crosspolarization magic angle spinning (CP-MAS), technique. SP experiments were performed with a pulse time of 5.5 μs and a recycle delay of 100 s to allow complete spin relaxation, and hence yield quantitative peak intensities. Approximately, 1000 scans were acquired in each SP experiment. The CP-MAS experiments were conducted with a CP contact time of 15 ms and a recycle delay of 3 s.

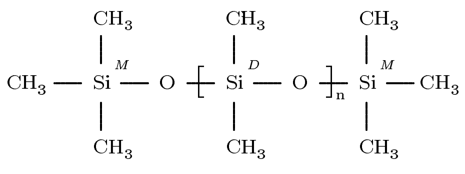
The *G*-values reported in the paper are based upon the number of events for 16 aJ of absorbed energy. The experimental errors in the calculated parameters are for approximately 95% confidence.

## 3. Results and discussion

The structure of linear PDMS is shown in Fig. 1. It contains two types of silicon units; one type at the chain ends and other type being characteristic of the silicon atoms within the chain. These two types of silicon atoms are labeled M and D, respectively according to the standard shorthand nomenclature for siloxane polymers [15]. This standard shorthand nomenclature will be used throughout this paper to identify the new molecular structures.

### 3.1. Characterization of unirradiated PDMS

The solution-state $^{29}$Si spectrum of unirradiated PDMS shown in Fig. 2 contains two major peaks, one due to the D siloxane units (−21.9 ppm) within the chain and one due to the M siloxane units (7.25 ppm) at the chain ends.



$$CH_3-\overset{CH_3}{\underset{CH_3}{\overset{M}{Si}}}-O\left[\overset{CH_3}{\underset{CH_3}{\overset{D}{Si}}}-O\right]_n\overset{CH_3}{\underset{CH_3}{\overset{M}{Si}}}-CH_3$$

Fig. 1. The structure of linear PDMS.

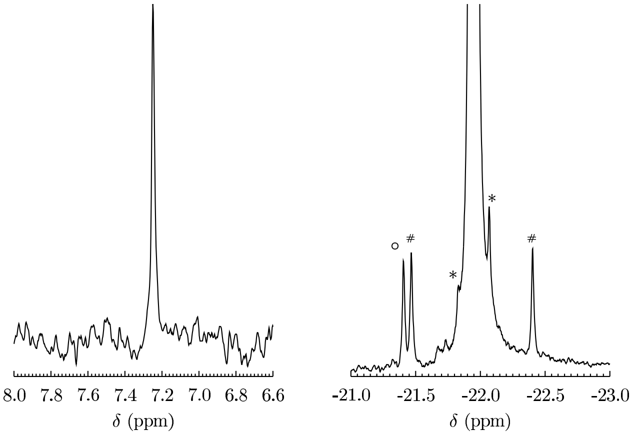


Fig. 2. Expansions of the solution-state $^{29}$Si NMR spectrum of PDMS showing the terminal siloxane region 6.6–8.0 ppm and the main chain siloxane region −21.0 to −23.0 ppm. ∗ Spinning side-bands, # $^{1}J_{^{29}Si-^{13}C}$ couplings, o $D_5$ impurity peak.

Expansions of the spectrum in the region of these peaks are shown in the figure. While there is no evidence for the presence of other peaks in the vicinity of the peak for the M siloxane units, other peaks are visible in the vicinity of the peak for the D siloxane units. Two of these peaks are spinning side bands at ±18.8 Hz, labelled ∗, and two other peaks, labeled #, arise from the $^{1}J_{^{29}Si-^{13}C}$ couplings of 75 Hz. The other peak, labeled o, at −21.41 ppm is due to the presence of a very small amount of a cyclic siloxane impurity $((CH_3)_2SiO)_5$, $D_5$, remaining from the polysiloxane synthesis [16].

The solution-state $^{13}$C carbon spectrum of the PDMS is shown in Fig. 3. It is characterized by two peaks arising from the chain end M siloxane units (1.8 ppm) and the D siloxane units (0.6 ppm). Also present are the spinning side bands, labeled ∗, and the satellite peaks arising from $^{1}J_{^{29}Si-^{13}C}$ coupling, labeled #.

The relative areas of the M and D peaks in the $^{29}$Si spectra can be used to calculate the molecular weight of the PDMS polymer, which was found to be $M_n \approx 10.0\ \mathrm{kg\ mol^{-1}}$.

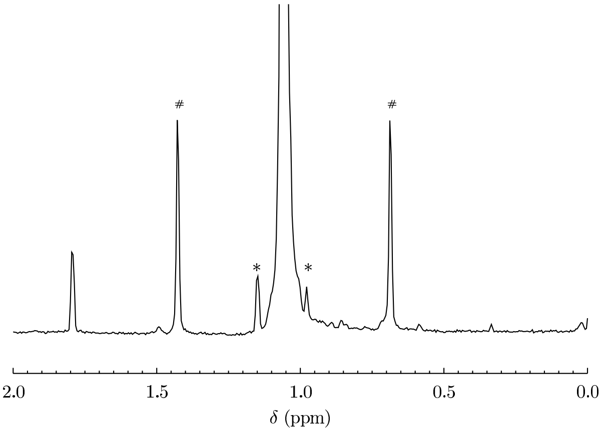


Fig. 3. The $^{13}$C NMR spectrum of PDMS. ∗ Spinning side-bands, # $^{1}J_{^{29}Si-^{13}C}$ couplings.

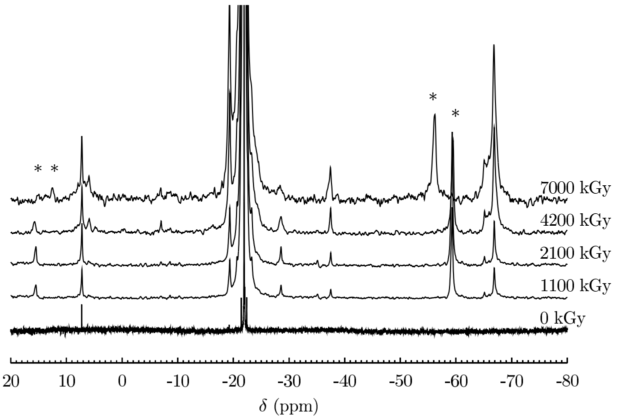


Fig. 4. Solid-state $^{29}$Si NMR spectra of PDMS following irradiation to a series of doses under vacuum at 300 K. The spectrum of the unirradiated polymer was obtained in solution. ∗ Spinning side bands.

### 3.2. Characterization of PDMS irradiated under vacuum

On irradiation, the polymer became crosslinked to form a colorless, elastic solid. The observed gel doses were: for 77 K and 184 K, 250 kGy; 303 K, 150 kGy and 373 K, 80 kGy. However, at the gel dose the concentrations of the crosslinks and of the other new structures formed are too low to produce visible peaks in the NMR spectra, and therefore, doses well in excess of the gel dose were used in the following analyses.

The solid-state SP $^{29}$Si NMR spectra for PDMS irradiated under vacuum to a series of absorbed doses are shown in Fig. 4, together with the solution-state spectrum of unirradiated PDMS for comparison. The spectra have been normalized to equal height for the peak for the D siloxane units at −21.9 ppm. A number of new peaks are clearly visible in the spectra of the irradiated samples and the intensities of these peaks are observed to increase with increasing dose. The intensity of the peak associated with the chain end M units also increases in intensity relative to the peak for the D units. The spinning side bands are indicated with asterisks.

In Fig. 5, the solid-state $^{29}$Si CP-MAS spectrum of a sample irradiated under vacuum to 7 MGy is shown in a comparison with the spectrum of the same sample obtained in a single pulse experiment. The solid-state spectra shown in Fig. 5 have been normalized to equal intensity for the peaks for the main-chain silicon nuclei. Because of the reduced mobility of the polymer chains after irradiation, the transfer of magnetization from protons to silicon atoms will be enhanced for silicon atoms involved in crosslinks, and therefore, the peaks associated with these silicon atoms will have enhanced intensities in the CP spectrum. On the other hand, silicon atoms in mobile groups, such as those at chain ends, will have relatively lower intensity in the CP spectrum.

Several features of the two spectra in Fig. 5 are therefore of interest. Four of the peaks in the CP spectrum are

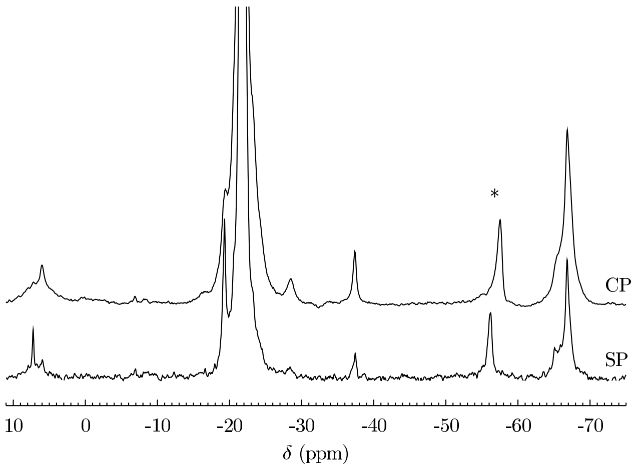


Fig. 5. Single pulse (SP) and CP-MAS (CP) $^{29}$Si NMR spectra of PDMS irradiated to 7 MGy under vacuum at 300 K. * Spinning side band.

relatively more intense than they are in the SP spectrum. These are the peaks at −66.9, −37.4, −28.6, and 6.0 ppm. The peaks which are lower in intensity in the CP spectrum are the peaks at −19.3 and 7.26 ppm. Thus, from this analysis of the 'CP-effect' described earlier, the former four peaks can be assigned to crosslink structures and the latter two peaks to chain end structures. The new peaks which appear in the $^{29}$Si spectra of the irradiated samples are summarized in Tables 1–3.

The solution-state $^{13}$C spectrum of unirradiated PDMS and the solid-state SP and CP $^{13}$C spectra of radiation crosslinked PDMS are shown in Fig. 6. No peaks were observed outside the chemical shift range shown in the figure. Several new peaks are observed in the 4 to 10 and 0 to −4 ppm ranges of the spectra after radiolysis. The peaks at −1 and −2.5 ppm are relatively strong peaks in both the SP and CP spectra, while the intensity of the peak at 6.5 ppm in the CP spectrum is reduced over that in the SP spectrum and the broad peak envelope at 7–10 ppm is enhanced in the CP spectrum. The significant new peaks which are observed in the carbon spectra are summarized in Tables 1–3.

### 3.3. Assignments of NMR spectra

The assignments of the new peaks in the $^{29}$Si and $^{13}$C NMR are presented in Tables 1–3, where Table 1 contains the peaks assigned to new side-chain structures, Table 2 contains the peaks assigned to new chain end structures and Table 3 contains the peaks assigned to new crosslink structures. The peak assignments have been made by comparison of their resonance positions with those for reported peak assignments of model compounds.

The reactions of the radicals which have been reported as being formed in PDMS on irradiation can lead to formation of a variety of new D and T type structures (see Tables 1–3 and Fig. 7). For example, the methylene radicals could form $D^{CH_2}$–R (silmethylene crosslinks), $D^{CH_2}$–$CH_2$–R (silethylene crosslinks), $D^{CH_2}$–$CH_3$ (side-chain structures),

Table 1
New side-chain structures formed during radiolysis of PDMS in vacuum (O = obscured peak; N = unchanged)

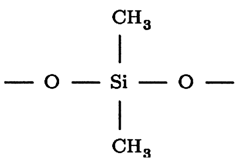
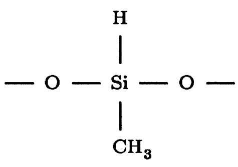
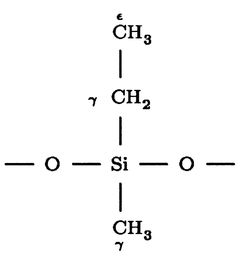
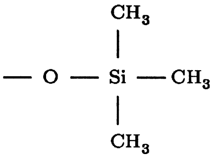
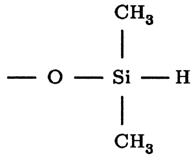
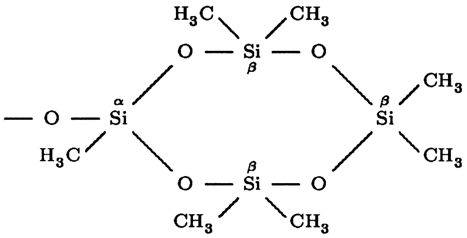
| Unit | Structure | Chemical shift (ppm) | | CP effect | |
|---|---|---|---|---|---|
| | | $^{29}$Si | $^{13}$C | $^{29}$Si | $^{13}$C |
| D |  $-O-\overset{CH_3}{\underset{CH_3}{Si}}-O-$ | − 21.9 | 1.1 | – | – |
| $D^H$ |  $-O-\overset{H}{\underset{CH_3}{Si}}-O-$ | − 37.4 | 6.6 | O | * |
| $D^{CH_2}CH_3$ |  $-O-\underset{\underset{\gamma}{CH_3}}{\overset{\overset{\overset{\epsilon}{CH_3}}{\gamma\,CH_2}}{Si}}-O-$ | − 21.7 (O) | −1.2 (γ)<br>6.6 (δ)<br>9.3 (ϵ) | O | N (γ)<br>N (δ)<br>N (ϵ) |

Table 2
New chain-end structures formed during radiolysis of PDMS in vacuum (O = obscured peak; D = decreased)

| Unit | Structure | Chemical shift (ppm) | | CP effect | |
|---|---|---|---|---|---|
| | | $^{29}Si$ | $^{13}C$ | $^{29}Si$ | $^{13}C$ |
| M |  | 7.3 | 0.6 (O) | D | O |
| $M^H$ |  | − 6.9 | 0.4 (O) | D | O |
| $D_{el}$ |  | − 19.3 (β)<br>− 65.1 (α) | 1.1 (O) | D (β)<br>O (α) | O |

as well as $D^{CH_2}OR$ and $D^{CH_2}SiR$, which are branching structures.

The silmethylene crosslink is a H-type crosslink (see Fig. 8) formed by the combination of a side-chain methylene radical and an in-chain silicon radical. The silethylene is also a H-type crosslink, and is formed by the combination of two side-chain methylene radicals. The chemical shifts of the silicon nuclei in both structures would be expected to be in the spectral region near the main chain D units [17]. In the $^{29}Si$ spectra, the new peak at −28.6 ppm is observed to increase in intensity in the CP spectrum compared to the SP spectrum. Beshah [18] has suggested that silicon nuclei involved in a silethylene crosslink would have a chemical shift approximately 1 ppm up-field from the main-chain D peak. This peak would be obscured by the broad line of the main-chain peak in the solid-state spectra, and consequently, the peak at −28.6 ppm has been assigned to the silicon nuclei in a silmethylene crosslinks.

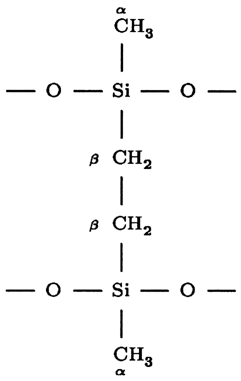
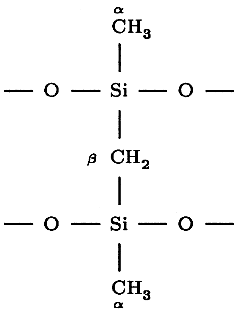
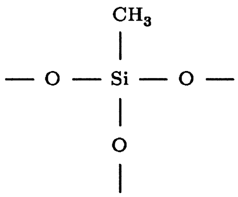
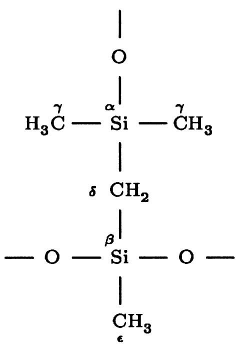
The carbon nuclei involved in the silmethylene structures (see Fig. 8) can also be identified in the $^{13}C$ NMR spectra. It has been shown that replacing the methyl group bonded to a silicon atom by a first row electron donor atom causes the remaining methyl groups attached to the same silicon to shift up-field [18], in contrast to the analogous carbon based polymers, where a downfield shift is observed. The largest new peak in the $^{13}C$ spectra appears at −2.3 ppm and has been attributed to the methyl groups directly attached to silicon nuclei in the silmethylene crosslink. This chemical shift region is also characteristic of methyl groups attached to a silicon atom, which is also attached to a methoxy group, but the lack of a peak around 50 ppm due to the alkoxy carbon, rules out this assignment.

The methylene carbons within the silmethylene crosslinks are observed as a broad resonance centered at 8.5 ppm. The ratio of the intensities of the two peaks at −2.3 and 8.5 ppm, is very close to 2:1, which is in good agreement with the proposed structure. These peaks at −2.3 and 8.5 ppm are enhanced in the CP spectrum, as would be expected for a crosslink structure with decreased mobility.

Silicon nuclei in new ethyl-substituted $D^{CH_2}–CH_3$ units cannot be observed in the $^{29}Si$ spectra as the peak would lie at −21.7 ppm, which would be obscured. However, in the $^{13}C$ NMR spectra, three new peaks at −1.2 ppm ($Si–{}^{*}CH_3$), 6.6 ppm ($Si–{}^{*}CH_2–CH_3$) and 9.3 ppm ($Si–CH_2–{}^{*}CH_3$) are observed, all of which are not significantly affected by crosspolarization, indicating that they are parts of mobile groups. This suggests that some ethyl side-groups are indeed formed [19]. The presence of ethyl side-chains has not been considered earlier, but may actually account for some of the $D^{CH_2}–R$ units previously observed by infrared spectroscopy by Miller [5].

There was no evidence in the NMR spectra for structures resulting from the reaction between methylene radicals and silicon-oxy radicals formed via main chain scission. This would result in the formation of alkoxy type carbons in $D^{CH_2}–OR$ units, which would be clearly visible in the carbon

Table 3
New chain-crosslinked structures formed during radiolysis of PDMS in vacuum (O = obscured peak; I = increased)

| Unit | Structure | Chemical shift (ppm) | | CP effect | |
|---|---|---|---|---|---|
| | | $^{29}$Si | $^{13}$C | $^{29}$Si | $^{13}$C |
| $D^{CH_2}CH_2R$ |  | − 23 (O) | − 2.3 (α)<br>8.5 (β) | O | I (α)<br>I (β) |
| $D^{CH_2}R$ |  | − 28.6 | − 2.3 (α)<br>8.5 (β) | I | I (α)<br>I (β) |
| T |  | − 66.9 | 2.1 (O) | I | I |
| $M^{CH_2}R$ |  | 6.0 (α)<br>− 28.6 (β) | 0.6 (O) (γ)<br>8.5 (O) (δ)<br>− 2.3 (O) (ϵ) | I (α)<br>O (β) | I (γ)<br>O (δ)<br>O (ϵ) |

spectra. However, there is evidence for a small amount of reaction between methylene radicals and silicon radicals formed by main-chain scission. This would form a crosslink consisting of $D^{CH_2}$–R and $M^{CH_2}$–R units (see Fig. 9). The peak due to the silicon nuclei in a $D^{CH_2}$–R unit in the $^{29}$Si spectra would coincide with the silmethylene crosslink mentioned above, but the $M^{CH_2}$–R unit can be identified from the small new peak at 6.0 ppm. This peak is observed to increase in intensity in the CP spectrum, confirming its assignment to a crosslink structure of this type.

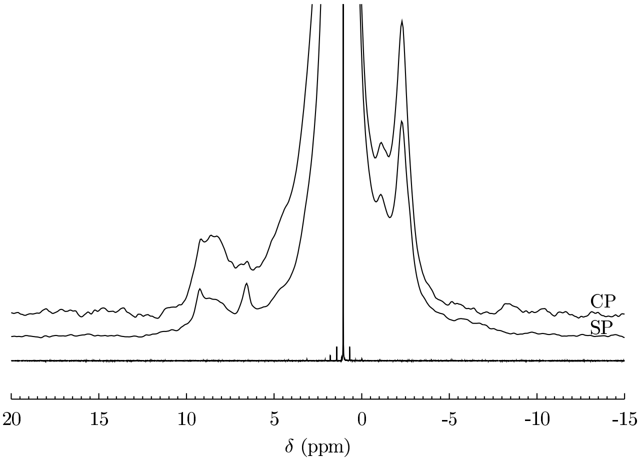


Fig. 6. Single pulse (SP) and CP-MAS (CP) $^{13}$C NMR spectra of PDMS irradiated to 7 MGy under vacuum at 300 K. The solution spectrum of unirradiated PDMS is also shown for reference.

The formation of $D^H$ units is confirmed by the new peak at −37.4 ppm in the $^{29}$Si spectrum. These units are formed on replacement of a methyl group by a proton along the backbone of the polymer. The chemical shift for the $D^H$ has been reported earlier [17,18,20,21]. The enhancement due to crosspolarization that is observed for this peak is not due to restricted mobility, but rather that the directly bonded hydrogen atom can more efficiently transfer magnetization to the silicon nuclei than can more remote protons on a methyl groups.

Reaction of the main-chain silicon radical formed by scission of a methyl group with a silicon-oxy radical formed by main-chain scission (see Fig. 10) would result in formation of a tri-oxygenated silicon crosslink (a T unit). The large peak at −66.9 ppm is characterized by excellent CP efficiency, and is hence assigned to the formation of crosslinks based on these T units. This assignment has been based upon previously reported chemical shifts for this structure [21–24], where the T unit was formed in siloxane networks prepared by hydrolysis condensation polymerization. Importantly, it should be noted that this is a Y-type crosslink.

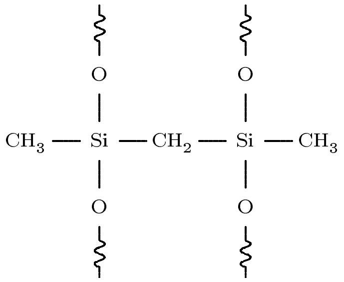


Fig. 7. The extended structure of a T unit illustrating the structure of the neighboring D units.

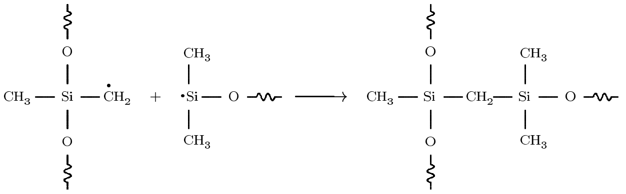


Fig. 8. The structure of silmethylene crosslinks.

Earlier, Bueche [13] and Belova [6] have speculated that new siloxane bonds may be formed during the γ-irradiation of PDMS, but this is the first direct evidence of such reactions. In fact, it appears that the formation of these new T units is the primary mechanism for crosslinking during γ-radiolysis. The Y-crosslinks are formed in addition to the silmethylene and silethylene H-crosslinks. The presence of both H- and Y-crosslinks in irradiated PDMS has not been considered earlier.

In the carbon spectra, the peak due to the methyl groups directly attached to the T units falls at 2.1 ppm [25], and so is obscured by the broad peak arising from the other α-methyl carbons in the spectrum. However, the broadening of the main peak near 3 ppm in the CP spectrum may indicate a contribution due to the T units, which would be expected to undergo crosspolarization efficiently.

The formation of T type network structures by reaction of a silicon-oxy radical with a silicon radical within the main chain may not be the only mechanism for the formation of crosslinks of this type. The formation of T units has been discussed earlier in the literature in the preparation of silicon oxycarbide ceramics [26]. Fig. 10 shows the concerted mechanism proposed for the formation of T units in this process, which also liberates a methyl radical. A similar mechanism may be responsible for the formation of T units on irradiation of PDMS.

Evidence for scission of main-chain silicon–oxygen bonds on radiolysis is also found through the appearance of new chain end $M^H$ and $M^{CH_3}$ structures, which are characterized by the new peaks in the $^{29}$Si spectra at −6.9 and 7.3 ppm, respectively.

The reactions of two silicon-centered radicals formed either by the loss of a methyl group or by main-chain scission could result in the production of crosslinks based on Si–Si bonds. The formation of such crosslinks in γ-irradiated PDMS has been suggested earlier. For example, Miller [5] reported a *G*-value of 1.1 for the formation of these structures. The presence of such structures should be revealed in the $^{29}$Si spectra through the appearance of a peak at −55 ppm [27]. However, no peak was found in the $^{29}$Si

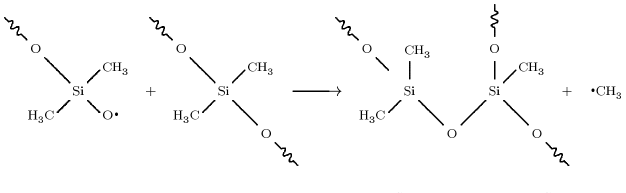


Fig. 9. The mechanism for formation of $D^{CH_2}R$ (α) and $M^{CH_2}$–R (β) structures.

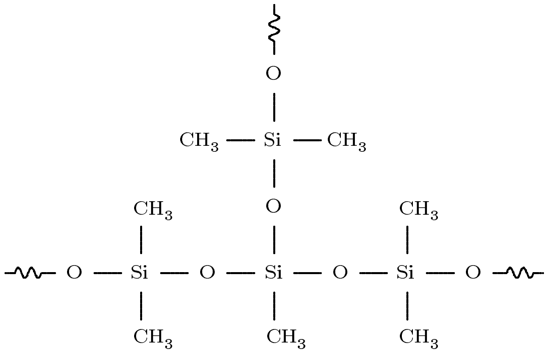


Fig. 10. Reaction of a silicon-oxy radical with a neighboring dimethylsiloxane unit.

spectra of any of the PDMS samples, including those irradiated up to 7 MGy, suggesting that these structures do not contribute significantly to the crosslinking process.

The relatively large new peak at $-19.3$ ppm in the $^{29}$Si NMR spectra is also considered to be due to reactions of the silicon-oxy radical. The peak demonstrates very poor CP efficiency, suggesting that the structure responsible is very mobile, or in a proton deficient environment. Given that the structure responsible for the peak must be based on a di-oxygenated silicon atom to appear in this region of the spectrum, there are few possibilities for its assignment. A chain end structure appears the most likely origin of the peak. The tetravalent silanone chain end (=Si=O) would appear to be unlikely due to its highly reactive nature [28,29]. In fact, silanones are extremely hard to isolate and it seems improbable that they would remain stable at room temperature in a crosslinked PDMS sample. The presence of a divalent silicon structure also appears to be unlikely, as the elements at the top of group IV have a very strong tendency to be tetravalent [30].

As the peak at $-19.3$ ppm appears to be of similar intensity to the peak assigned to the new T crosslinks, it may be speculated that the two peaks are due to different silicon nuclei in these structures. An extended T based structure is shown in Fig. 7. It can be seen that, for each silicon involved in a T link, there are three neighboring D type silicon nuclei. It would therefore be expected that a peak resulting from these neighboring D units would be three times the size of that due to the T unit, and therefore, this could not explain the appearance of this peak in the spectra. In addition, a structure of this type would be expected to show good CP efficiency due to the restricted mobility near the crosslink, which this peak clearly does not display.

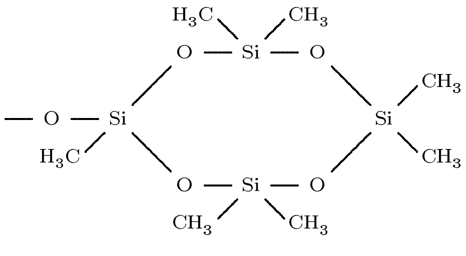


Fig. 11. Typical structure of an end-loop $D_{el}$ unit demonstrating the two types of silicon atoms present.

A possible explanation for the peak is the formation of a $D_{el}$-type structure shown in Fig. 11. Computer simulations have shown that these so-called "bowtie" structures may be produced in relatively high concentrations during the polymerization of siloxane polymers [31]. Such structures have also been identified earlier by $^{29}$Si NMR in PDMS networks [24]. The chemical shifts of the di-oxygenated silicon atoms in these cyclic structures are slightly different to those of the main-chain silicons. $^{29}$Si chemical shifts have been shown to be very sensitive to bond strain and angle in silicates [32,33] and silsesquioxane molecules [31], so the chemical shifts of the small cyclic oligomers, *Dn*, where $n < 5$, are found to differ from the *D* repeat unit in a linear polymer. Thus the observed chemical shift of $-19.3$ ppm suggests that the silicon atoms responsible for this peak are probably associated with a cyclic structure [34,35], see Fig. 11, formed by a backbiting reaction, with the concomitant release of a methyl radical.

The tri-oxygenated silicon shown in Fig. 11 is also in a slightly different environment to the T unit involved in a crosslink. Consequently, the small peak at $-65.1$ ppm, which is partially overlapped by the larger T crosslink peak, has been assigned to the T type units of these cyclic chain end structures.

### 3.4. G-values for formation of new structures

The yields of the principal new structures formed on radiolysis were determined by integration of the peaks in the $^{29}$Si NMR spectra over a range of doses. These data are presented in Fig. 12. The *G*-values for the formation of the structures were then calculated from the slopes of the data in the figure and are shown in Table 4.

The principal new scission products of the radiolysis are $M^H$, $D_{el}$ and $M^{CH_3}$ units. The overall *G*-value for formation

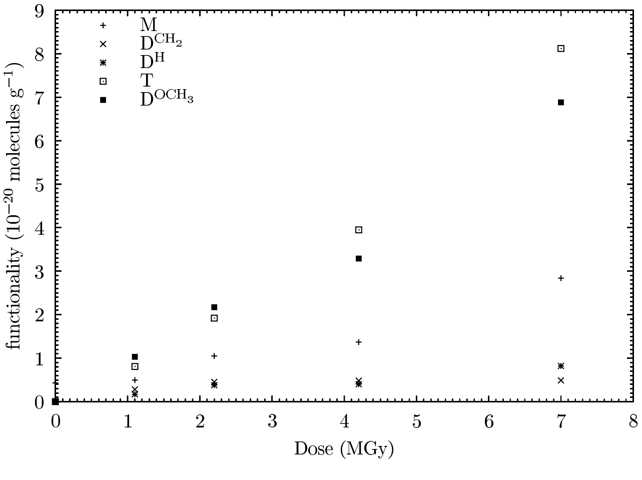


Fig. 12. Yields of new structures versus absorbed dose for γ-irradiation of PDMS under vacuum at 300 K.

Table 4
*G*-values for new structures formed on radiolysis of PDMS in vacuum calculated from the peaks indicated in the solid-state $^{29}$Si NMR spectra (E = chain end; S = side-chain; X = crosslink)

| Structural unit | $\delta_{29}$Si (ppm) | *G*-value | Classification |
|---|---|---|---|
| $M^H$ | −6.9 | 0.06 ± 0.03 | E |
| $D_{el}$ | −19.3 | 0.5 ± 0.07 | E |
| M | 7.3 | 0.69 ± 0.07 | E |
| $D^H$ | −37.4 | 0.19 ± 0.02 | S |
| $M^{CH_2}R$ | 6.0 | 0.10 ± 0.05 | X |
| $D^{CH_2}R$ | −28.6 | 0.34 ± 0.02 | X |
| T | −66.9 | 1.7 ± 0.09 | X |

of these products is 1.3. Of the new structures, the latter two are formed in the highest yields. There has been no report of the formation of cyclic end-group structures on radiolysis earlier, but the presence of $M^{CH_3}$ has been recorded. The $M^H$ units in irradiated PDMS have also been reported earlier, but the *G*-value found here is approximately half the values reported by Miller [14] and Bueche [13].

The dominant crosslinking reaction on radiolysis was found to be leading to the formation of T-type crosslinks, with a *G*-value of 1.7. The presence of these crosslinks has been proposed before, but no *G*-values have been reported earlier. The *G*-value of 0.34 obtained for the formation of silmethylene H-crosslink structures is much less than the value of 1.8 reported by Miller [5], but the uncertainty in the infrared spectroscopy measurements was admitted by Miller to be large. The corresponding *G*-value for the silethylene crosslink structures could not be obtained from the $^{29}$Si spectra, because these peaks are overlapped by the intense peak from the main-chain silicon atoms.

Apart from the formation of Y-type crosslinks, the other major side-chain substitution reaction observed was the formation of new $D^H$ units with a *G*-value of 0.19. The formation of $D^H$ units has been reported before, but reliable estimates of the yields have not been made previously.

## 4. Conclusions

On radiolysis of PDMS at ambient temperature under vacuum, new main-chain scission and crosslinking structures are formed, with the total yield of crosslinking exceeding that of scission. The solid-state $^{29}$Si NMR spectra of PDMS, irradiated under vacuum at 300 K revealed that crosslinking occurs principally through a Y-linking mechanism. Solid-state $^{13}$C NMR spectra of the irradiated PDMS were less revealing of the nature of new structure formation than the $^{29}$Si spectra. The overall *G*-values obtained from the $^{29}$Si NMR spectra for scission was approximately 1.3 ± 0.3 and for silmethylene H-links and siloxane Y-links were approximately 0.34 ± 0.02 and 1.7 ± 0.1, respectively.

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