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# THE RADIATION CHEMISTRY OF POLY(DIMETHYL-SILOXANE)

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**Abstract:** The radiation chemistry of poly(dimethyl siloxane) has been investigated with respect to identification of the nature of the small molecule chain scission products. Low molecular weight linear and cyclic products have been identified through the use of $^{29}$Si solution NMR, GPC and MALDI-TOF mass spectrometry. It has been suggested that the low molecular weight cyclic products are formed by back-biting depolymerization reactions.

## INTRODUCTION

Polysiloxanes, of which polydimethylsiloxane, PDMS, is the best known, are characterized by having low surface energies and high chain flexibility. Linear polysiloxanes are highly viscous liquids, whereas the crosslinked polymers are elastomers having low surface friction. These unusual properties have led the polysiloxanes to find a wide range of specialized industrial applications, either as siloxane homopolymers, copolymers or blends.

Crosslinked polysiloxanes can be prepared by a range of methods, including (i) the use of a tri or tetra functional siloxane comonomer, (ii) the incorporation of a thermal initiator, such as a peroxide, which will abstract hydrogen atoms from PDMS and so induce crosslinking or (iii) the exposure of PDMS to high energy irradiation.

The effect of high energy radiation on the material properties of PDMS was investigated by Bopp and Sisman (Ref. 1), who reported an improvement in the tensile properties on radiolysis. The change from a linear to a branched and then to a crosslinked elastomer was demonstrated, indicating that the PDMS was crosslinking. Ormerod and Charlesby (Ref. 2) also studied the changes in the tensile properties of PDMS following radiolysis, and more recently Basfar (Ref. 3) has reported a significant increase in the Shore-A in hardness with absorbed dose up to about 0.4 MGy.

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The radiation chemistry of PDMS was studied first by Charlesby (Ref. 4), who reported that the major volatile products of radiolysis were hydrogen, methane and ethane, and St. Pierre et al. (Ref. 5) found G(total gas) = 2. Okamura et al. studied radical formation (principally -$CH_2$•) and reported G(R) = 3.6. Charlesby (Ref. 4) also measured G(X) = 3, which was found to be independent of the molecular weight of the starting PDMS and he proposed the mechanism for crosslink formation shown in Figure 1, which is based on C - H and C - Si bond scission. Thus by the early 1960s the radiation chemistry of PDMS was beileved to be firmly established.

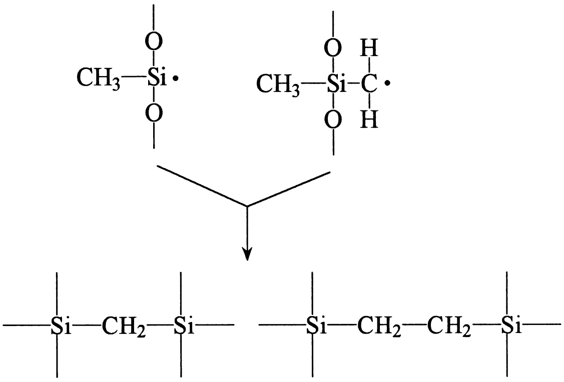

Figure 1. Mechanism for crosslinking proposed by Charlesby (Ref. 4).

The radiation sensitivity of PDMS can be modified by copolymerization with methyl phenyl or diphenyl siloxane, DPS. For example, Delides (Ref. 6) has studied the extent of protection afforded by the incorporation of the phenyl groups in PDMDPS through molecular weight and solubility studies. Crosslinking was assumed to proceed through an H-linking mechanism, and the nett G(X) was found to be non-linear in the weight fraction DPS, as shown in Figure 2, indicative of a near neighbour protective effect by DPS units. Delides estimated that a phenyl group could provide some protection for DMS neighbours up to about 6 units away.

The mechanism for the crosslinking of PDMS shown in Figure 1 was based upon inference drawn from indirect gas yield and molecular weight studies. However, recently Preston et al. (Ref 7) have studied the new structure formation in PDMS using solid state NMR. Solid state $^{29}Si$ NMR

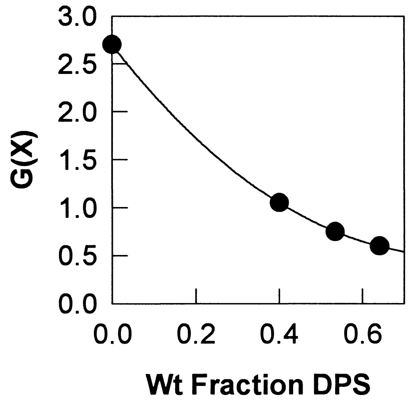

Figure 2.
Calculated from data for PDMDPS reported by Delides (Ref. 6)

showed the formation of several new structures following radiolysis and an increase in the concentration of methyl chain ends. Two of the new structures were assigned to crosslinks. One structure was assigned to Si - O - $CH_2$ - or D-type crosslinks, $G(X)_D = 0.23$, and the other structure was assigned to new - Si -O - Si - or T-type crosslinks, $G(X)_T = 1.46$. No evidence was found for new - Si -Si - crosslinks. Based upon quantitative NMR measurements, Preston et al. (Ref. 7) have estimated that G(X) lies in the range 1.58 - 1.69 for radiolysis of PDMS at 300 K.

Thus crosslinking occurs principally through a Y-linking process and not through H-linking. This observation has important consequences with respect to the determination of G(S) and G(X) from molecular weight measurements and may also offer an explanation for reported differences between radiation and chemically crosslinked PDMS (which would contain exclusively - Si - O - $CH_2$ - crosslinks), such as those reported by Basfar (Ref. 3).

The new peak which appeared in the solid state $^{29}Si$ spectrum at ≈ 19.4 ppm (see Figure 3) was assigned to a scission product (Ref. 7). To confirm this assignment and to further elucidate the presence of any other low molecular weight products, in the current work we have studied the extractable soluble fractions of polymer samples irradiated to doses above the gel dose ( ≈160 kGy).

## EXPERIMENTAL

PDMS samples were obtained from Dow Corning Australia and used as received. The molecular weight, $M_n$, of the virgin polymer was 10 kg mol$^{-1}$. The PDMS samples were irradiated in glass ampoules under vacuum at room temperature in a Nordian Gammacell to a dose of 2.2 MGy at a dose rate of 8.3 kGy hr$^{-1}$.

## RESULTS and DISCUSSION

### *NMR Studies*

The crosslinked PDMS gel was swollen in $CDCl_3$ for several weeks to allow extraction of small molecule scission products from the matrix. Quantitative $^{29}Si$ NMR spectra of the solution was obtained using a Bruker AMX400 NMR with inverse gated decoupling to suppress NOE effects. The NMR spectrum of the solution is shown in Figure 3, with a solid state spectrum of the irradiated polymer and the spectrum of unirradiated PDMS shown for comparison.

The spectra of the soluble extract has four major peaks at -22.15, -21.94, -21.54 and -19.08 ppm and several minor peaks. Of the major peaks, those at -19.08 -21.54 and -22.15 ppm are sharp while that at 21.94 ppm is broader and appears to be comprised of at least two components. The peak at 19.08 ppm in the extract spectrum corresponds to the peak at -19.4 ppm in the solid state spectrum, with the chemical shift difference arising through solvent effects, but the other extract peaks lie under the main $^{29}Si$ peak in the solid state spectrum. The peak at 21.94 in the extract spectrum corresponds with that of the $^{29}Si$ peak in the unirradiated polymer.

Using literature data (Ref. 8), the sharp peaks in the extract spectrum at -19.08, -21.54 and -22.15 ppm have been assigned to the cyclic siloxanes with 4, 5 and 6 membered rings, respectively. These siloxanes are believed to be formed by back biting of a chain scission radical, similar to that proposed for thermal degradation of PDMS (Ref. 9), and demonstrated in Figure 4. The collection of peaks observed at -21.94 ppm are believed to arise from linear or large cyclic siloxane chains resulting from main chain scission reactions.

### *GPC Studies*

The soluble fractions of an irradiated PDMS were extracted into chloroform for analysis by GPC. A Waters Alliance GPC fitted with two Waters linear Ultrastyragel columns and one Waters 100Å column and a refractive index detector was used to study the molecular weight profile of the

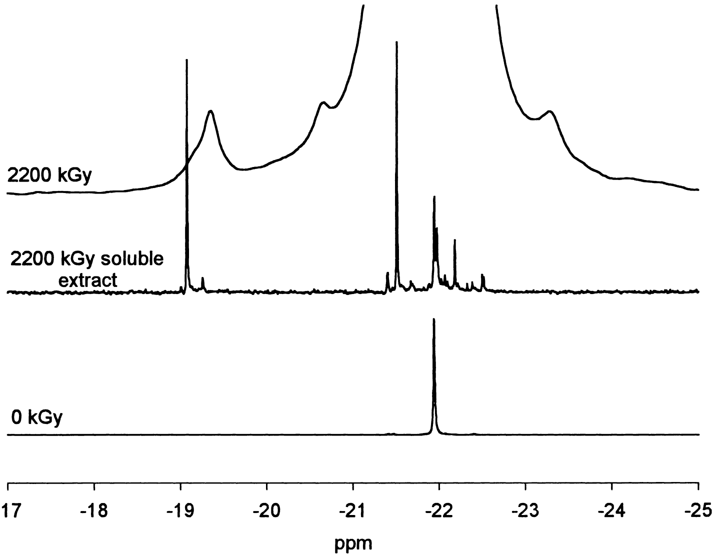

Figure 3. NMR spectra of irradiated polymer, extract solution and unirradiated PDMS.

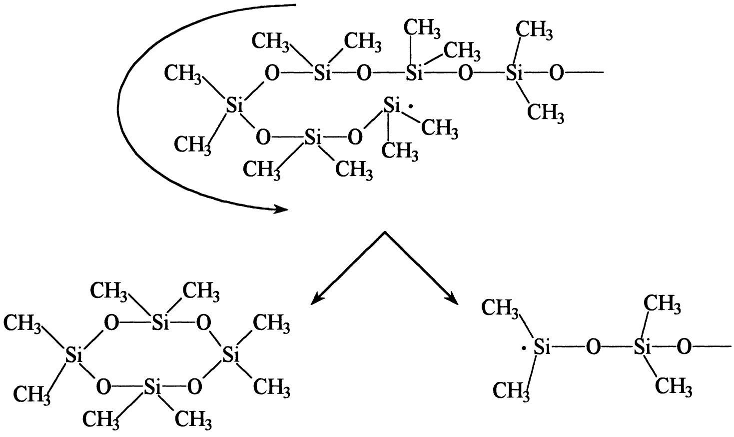

Figure 4. Mechanism for formation of cyclic PDMS scission products.

scission products. The GPC chromatogram of the extract is shown in Figure 5, together with that for the unirradiated polymer.

The chromatogram of the extract shows two peaks, both at higher elution volumes than that for the unirradiated polymer, which indicates that the extracted components correspond to scission products. There is no evidence for the presence of any remaining virgin polymer. The extract peak at an elution volume of 24.5 mL is broad and corresponds to a polystyrene peak molecular weight of ≈ 1600 g $mol^{-1}$, while the peak at an elution volume of 27.3 mL has a shoulder and thus appears to be comprised of at least two components. The latter peak corresponds to a polystyrene molecular weight of ≈200 g $mol^{-1}$.

*MALDI-TOF Studies*

To confirm the observations from the NMR and GPC studies MALDI-TOF mass spectra were obtained of the extracted scission products using a Micromass TOF-Spec E mass spectrometer. The matrix used in the analysis was 4-hydroxybenzilidine malononitrile (0.1 M in acetone) mixed 1:10 with sodium iodide (0.005 M in 90 % acetone / water). 1 μL of this mixture was applied to the target plate and allowed to dry before application of 1 μL of the extract sample in chloroform. After the sample preparation was allowed to dry, the mass spectrum was obtained in the reflection mode.

A mass spectrum of the range m/z = 850-4500 is shown in Figure 6. This shows a peak with a broad molecular weight distribution with the peak at an m/z = 1113 ( after subtraction of the mass of $Na^+$), which corresponds to ≈ 15 DMS units in a cyclized molecule. The separation of the successive peaks in the mass spectrum is m/z = 74, which corresponds to the mass of a DMS unit. The number average molecular weight of the extract component revealed in the mass spectrum in Figure 6 is 1862 g $mol^{-1}$, corresponding to about 25 DMS repeat units in the average chain.

However, a closer inspection of the mass spectrum reveals the presence of a collection of peaks associated with each m/z ratio, as demonstrated in the insert in Figure 6. The collection of peaks at m/z =1210, for example, arises from polymer chains containing atoms of various isotopic abundance. In addition, the insert shows that there are 5 sets of peaks which are repeated across the whole m/z range. This grouping of peaks, which also show the isotopic distribution profile, can be accounted for by the presence of a variety of end-groups associated with ends of linear

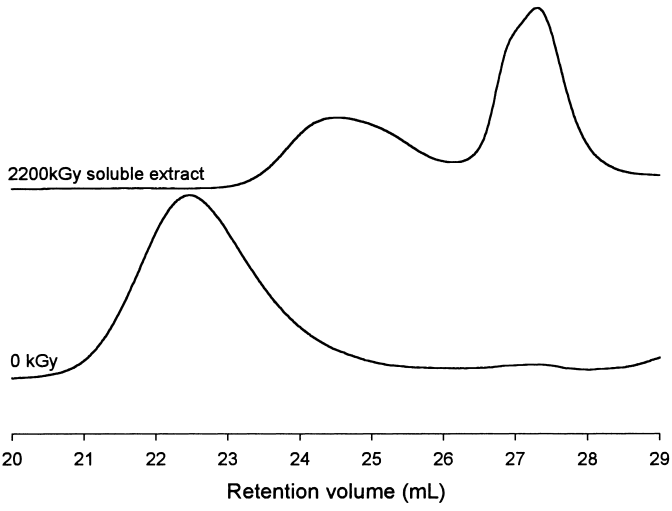

Figure 5. GPC chromatograms of irradiated polymer extract and virgin PDMS.

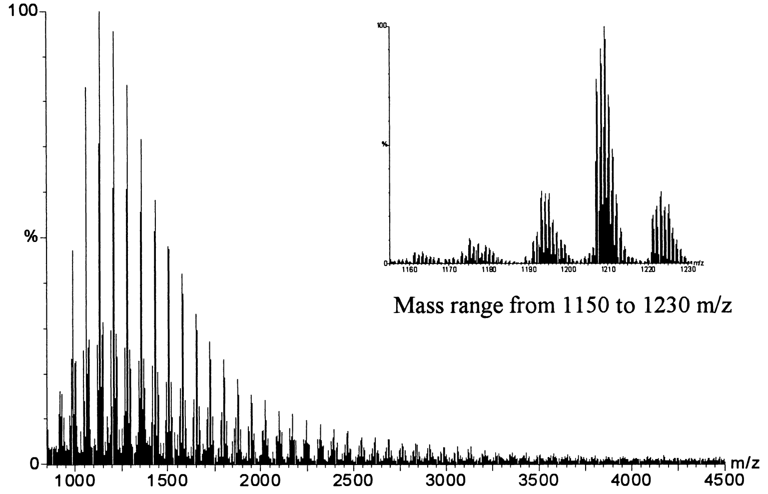

Figure 6. MALDI-TOF mass spectrum of irradiated polymer extract for PDMS.

PDMS chains. The proportions of the cyclic to linear PDMS chains in this mass range appear to be roughly equal.

The component of the extract which gives rise to the MALDI-TOF spectrum shown in Figure 6 corresponds to the higher molecular weight component of the GPC chromatogram (Figure 5). The component which contains the lower molecular weight cyclic products ( e.g. those containing less than 10 repeat units) cannot be identified by MALDI-TOF because of matrix interference effects.

## CONCLUSIONS

On radiolysis of PDMS at ambient temperature main chain scission and crosslinking reactions occur with the yield of crosslinking exceeding that of scission. Crosslinking occurs principally through a Y-linking mechanism, while scission results in the formation of low molecular weight cyclized products, probably formed by back-biting reactions. In addition, somewhat higher molecular weight cyclic and linear chain scission products are also formed.

### ACKNOWLEDGEMENTS

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