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## Gas production in the radiolysis of Poly(dimethylsiloxanes)

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## A B S T R A C T

A variety of small poly(dimethyl siloxanes) were irradiated with  $\gamma$ -rays followed by the determination of the production of methane and molecular hydrogen and characterization of spectroscopic changes in the medium. The yields of methane was found to be about twice that of molecular hydrogen indicating that breakage of the C-Si bond occurs at a frequency comparable to the breakage of the C-H bond. Both yields slowly decrease with increasing molecular weight of the medium. The presence of oxygen decreases the yield of both gases suggesting radical precursors to methane and molecular hydrogen, presumably the methyl radical and H atom, respectively. Temperature gravimetric analysis and UV-visible spectroscopy both suggest the formation of higher molecular weight compounds with radiolysis, which agrees with bond loss and formation observed in infrared spectroscopy.

## 1. Introduction

Polydimethylsiloxanes, PDMS, are very versatile compounds that are used in a wide variety of applications. These compounds have long been examined by radiolysis and much is known about their overall radiation chemistry (Miller, 1960). However, most of the studies on PDMS involve relatively high molecular weight compounds and the radiation effects examined are usually related to chain processes, such as cross linking or scission (Charlesby, 1955; Charlesby and Garratt, 1963; Delides, 1980; Dinh et al., 2011; Falcao et al., 1993; Gomes et al., 2006; Hill et al., 2001, 2000; Lancaster et al., 2012; Pankratova and Rudnev, 2006; Satti et al., 2010, 2008; Squire and Turner, 1972). In only a few instances has the production of gaseous compounds been examined in PDMS and in a simpler compound hexamethyldisiloxane, HMDS (Dewhurst and St Pierre, 1960; Miller, 1960; Tanny and St Pierre, 1971). Gas production is a valuable tool in understanding the overall radiolytic decomposition and it is especially important in practical applications involving the radiolysis of PDMS in enclosed environments. The large variety of commercially available PDMS compounds cover a range of viscosities and phases and thereby offers the opportunity to examine fundamental radiation processes as a function of physical characteristics that can affect reaction rates.

The siloxanes examined in this work all have the general chemical formula of  $(\text{CH}_3)_3\text{SiO}[\text{Si}(\text{CH}_3)_2\text{O}]_n\text{Si}(\text{CH}_3)_3$  where  $n=0,1,14$ , and 450 correspond to hexamethyldisiloxane, and poly(dimethylsiloxanes) with molecular weights of 237, 1200, and 14,000 Da, respectively. This work focuses on an examination of methane,  $\text{CH}_4$ , and molecular hydrogen,  $\text{H}_2$ , which are the two major gaseous compounds produced in the

radiolysis of PDMS. Low molecular weight PDMS compounds were used in order to facilitate extraction of the gases and for comparison with the results found with HMDS. Thermal gravimetric analysis was combined with UV-visible spectroscopy and infrared spectroscopy to give an indication of the overall response of these compounds in conjunction with gas production.

## 2. Experimental procedure

## 2.1. Materials and preparation

Hexamethyldisiloxane, poly(phenylmethylsiloxane) and poly(dimethylsiloxanes) with molecular weights of 237, 1200, and 14,000 Da were obtained from Alpha Aesar at the highest purity available and used as received. Aerated samples were flame sealed in Pyrex tubes 10 mm diameter and about 10 cm long. Deaerated samples were purged in same sized tubes with ultra-high purity (99.9999%) argon or evacuated three times at 77 K using a freeze, pump, thaw technique. Sample mass was typically about 0.5 g.

2.2. Gamma ray irradiation and  $\text{H}_2$  determination

Irradiations with  $\gamma$ -rays were performed in self-contained Shepard  $^{60}\text{Co}$  sources at the University of Notre Dame Radiation Laboratory. Two sources with dose rates of 30 Gy/min and 157 kGy/min as determined using the Fricke dosimeter were used. No difference in outcome between the sources was observed. Irradiated sample cells were inserted into Tygon tubing, connected to a SRI 8610 gas

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chromatograph using a four-way valve, flushed with the carrier gas, and cracked open to allow for the measurement of the gases produced during irradiation. The GC has a thermal conductivity detector (TCD) and was used with a carrier gas of ultra-high-purity (99.9999%) argon. A 3 m column filled with molecular sieves was used for hydrogen measurement and a 1 m Porapak R column was used for methane, both maintained at 40 °C. In this configuration, the system had a sensitivity limit of 1  $\mu\text{L}$  of  $\text{H}_2$  and the error in measurement of this gas is estimated to be within 5%. Separation of methane and air was difficult in aerated samples so the GC was coupled to a Balzers quadrupole QMI 422 mass spectrometer. Calibration was performed by the injection of pure methane. The error in methane measurement under these conditions was about 10%. Radiation chemical yields, G values, are given in the traditional units of molecules/100 eV (1 molecule/100 eV=1.04 mol/J).

### 2.3. Characterization of solid media

Thermal gravimetric analysis (TGA) was performed with a Mettler-Toledo TGA/DSC 1 to measure weight loss of the samples on heating. A constant heating rate of 10 or 5  $^\circ\text{C min}^{-1}$  was used for the higher mass 1250 and 14,000 Da samples, respectively, up to temperatures of 600  $^\circ\text{C}$ . The lower molecular weight 237 Da and hexamethyldisiloxane were heated at a rate of 1  $^\circ\text{C min}^{-1}$  due to their rapid evaporation. The samples were purged with nitrogen gas at 50 mL/min, and weighed approximately 10 mg. The samples were given a dose of 100 kGy before analysis.

Two spectroscopic methods, UV–visible spectroscopy and Fourier transform infrared spectroscopy (FTIR), were used to analyze the media following irradiation. UV–visible spectroscopy was performed with a Thermo Fisher Scientific Evolution 220. A 2 mm path length cuvette was filled with the polymer dissolved in carbon tetrachloride. A Bruker Vortex 70 instrument was used for the FTIR measurements. Samples were contained between two KBr salt plates. The spectra were normalized using a concentration factor calculated from a comparison of the 2960  $\text{cm}^{-1}$  peak to that of a fixed concentration of polymer dissolved in carbon tetrachloride in a 2 mm cuvette. This peak corresponds to the C-H stretch and it is the major peak observed at the upper IR region examined here. The samples received a dose of 100 kGy for spectroscopic analysis.

## 3. Results and discussion

### 3.1. Gas Production with $\gamma$ -ray radiolysis

Samples for gas analysis were typically irradiated at several doses up to 150 kGy of total dose. Linearity was observed for the production of both  $\text{CH}_4$  and  $\text{H}_2$  in all cases. Fig. 1 shows a dose response for the production of  $\text{H}_2$  in aerated and in deaerated 237 Da PDMS. The linear fit of these response curves was then used to generate radiation chemical yields, which are expressed here in the conventional units of molecules/100 eV (1 molecule/100 eV=1.04 mol/J).

Yields of  $\text{CH}_4$  and  $\text{H}_2$  in the gamma radiolysis of aerated and deaerated HMDS and the three PDMS compounds are shown in Fig. 2 as a function of the molecular weight of the medium. The abundance of methyl groups on these compounds leads to a rather large yield of  $\text{CH}_4$ . Most hydrocarbons have a yield of  $\text{H}_2$  that is much greater than any gaseous product containing carbon. The yield of  $\text{CH}_4$  is surprisingly high compared to that for  $\text{H}_2$  and indicates that breakage of the C-Si bond is comparable in frequency to breakage of the C-H bond. Of course, this conclusion assumes that the methyl radical and H atom precursors predominately undergo H atom abstraction reactions with the medium. Both of the radical precursors could recombine with polymer radicals, but one would expect such reactions to be comparable in magnitude. Similarly, both of the radical precursors could undergo combination reactions, but little of that is expected at low dose rates

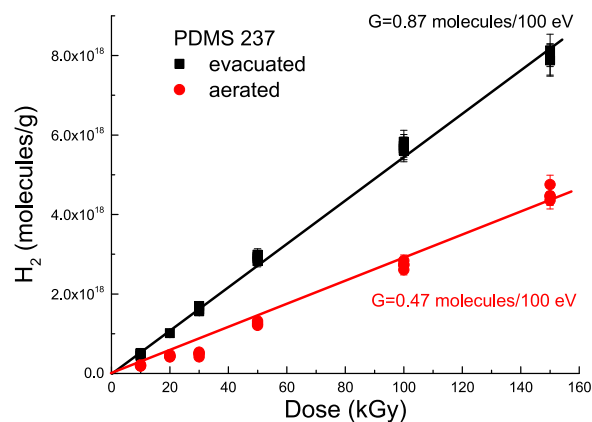


Fig. 1. Production of  $\text{H}_2$  as a function of dose in the  $\gamma$ -radiolysis of 237 Da poly (dimethylsiloxane).

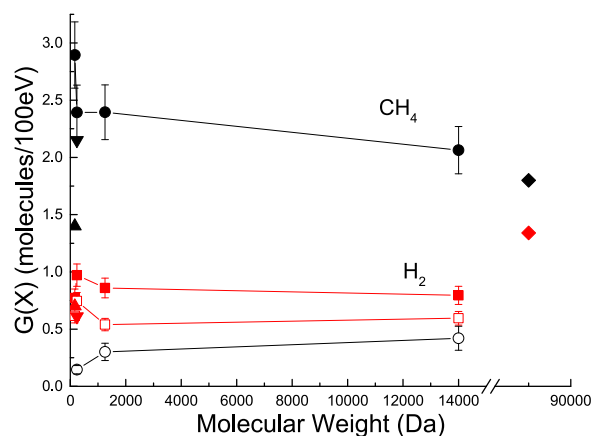


Fig. 2. Yields of  $\text{CH}_4$  (●) and  $\text{H}_2$  (■) in deaerated (closed symbols) and aerated (open symbols) from  $\gamma$ -irradiated hexamethyldisiloxane and various poly (dimethyl siloxanes) as a function of molecular weight. Literature values of  $\text{CH}_4$  and  $\text{H}_2$  are given for deaerated hexadimethyldisiloxane (▲), and poly (dimethylsiloxane) at 235 Da (▼) and at 85,000 Da (◆) (Dewhurst and St Pierre, 1960; Miller, 1960; Tanny and St Pierre, 1971).

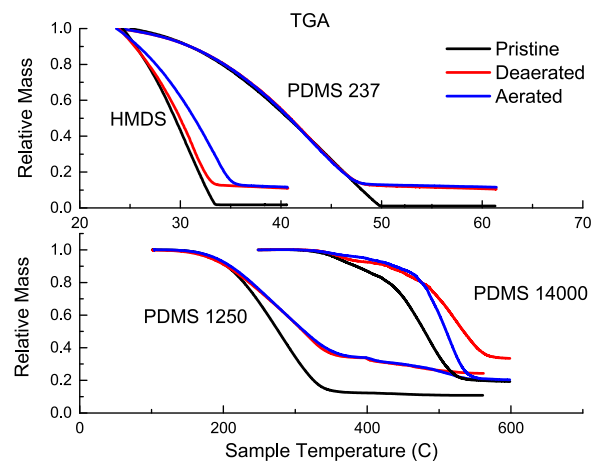


Fig. 3. Thermal gravimetric analysis of hexamethyldisiloxane and several poly (dimethyl siloxanes)  $\gamma$ - irradiated to 100 kGy.

and the lack of significant yields of ethane as discussed below.

With a few exceptions there is a small decrease in gas yields with increasing molecular weight. Increasing viscosity with increasing molecular weight may be leading to a slight cage effect in which recombination of the radical with the corresponding carbon or silicon centered radical is competing with H atom abstraction reactions to give

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