Radiation-induced polymerization of dimethylcyclosiloxanes in the liquid state: I. Influence of drying and nature of the propagation mechanism

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The radiation (cobalt 60 γ)-induced polymerization of octamethylcyclotetrasiloxane D_4 and decamethylcyclopentasiloxane D_5 has been studied in the liquid state. Progressive drying of the monomers over a succession of sodium mirrors led to increased rates and a levelling off at higher conversions. After 12 mirrors no further increases in rates were observed and the rates were reproducible. With the D_4 monomer a square-root dependence of the rate on the dose rate was found in agreement with the Hayashi–Williams equation for radiation-induced ionic polymerization under completely pure conditions. The conversions to polymer and cyclic byproducts were followed directly in nuclear magnetic resonance (n.m.r.) tubes with ^{13}C n.m.r. No post-radiation effects were observable. The complete inhibition of both the polymerization and the formation of cyclic byproducts by trimethylamine and ammonia clearly indicated a cationic mechanism. Triethylamine only partly inhibited the reactions, this is ascribed to steric interference with the growing chains or initiating species.

(Keywords: radiation-induced polymerization; dimethyl siloxanes; propagation mechanism)

INTRODUCTION

The radiation-induced ring-opening polymerization of cyclic dimethyl siloxane monomers was first reported in 1956 with hexamethyl-cyclotrisiloxane in the solid state[1]. Since then a number of other papers have been published[2–7]. In the early work, polymerizations of the hexamethyl, D_3, and the octamethyl, D_4, rings were only found in the solid state. The rates increased steadily up to the melting point and then dropped essentially to zero[1,2]. The effects of water, ammonia and nitrous oxide indicated a cationic mechanism[5,6]. Following the discovery that vinyl and other monomers could be polymerized in the liquid state by radiation via a cationic mechanism, if rigorously dried[8], Chawla and St. Pierre succeeded in polymerizing D_3 and D_4 in the liquid state[9]. More recently this work has been repeated in more detail[7], and extended to the D_5 monomer[10]. In this paper the D_4 and D_5 studies in the liquid state have been investigated in more detail. In particular, the effects of the degree of drying on the rates and the nature of the propagation mechanism have been studied.

EXPERIMENTAL

D_5 and D_4 were supplied by the Rhone-Poulenc Company. Their purity was checked by gas chromatography (>99.9%). The monomers were dried over sodium sulphate (24 h), freshly crushed calcium hydride (24 h, under vacuum), and transferred over a series of sodium mirrors, being allowed to contact each mirror for at least 24 h. Triethylamine (Aldrich Chemical Co.) was washed with an aqueous solution of 5% potassium hydroxide, distilled water, and dried over sodium sulphate (24 h). The second fraction from simple distillation was dried over calcium chloride (24 h), calcium hydride (24 h, under vacuum) and transferred over repeated sodium mirrors until dry. Trimethylamine (Aldrich Chemical Co.) was transferred directly from the lecture bottle through a column packed with silica gel (previously baked out under vacuum, 450°C, 2×10^{-5} torr) into a round bottom flask, under vacuum. It was then transferred over repeated sodium mirrors until dry. Ammonia was treated in the same manner as trimethylamine. The samples were condensed through an all glass vacuum system into nuclear magnetic resonance (n.m.r.) tubes. The elaborate procedures used will be described separately. The cobalt-60 source used was a Gamma Cell 220, from the Atomic Energy of Canada Ltd. Doses were calibrated using Fricke dosimetry, and corrected for the exponential decay. The average dose rate was about 0.1 Mrad s^{-1}. Two n.m.r. spectrometers were used for

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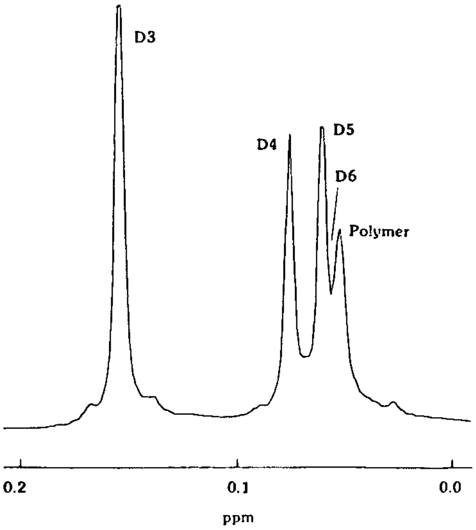

Figure 1 250 MHz ^1H n.m.r. spectrum of cyclic siloxane monomers

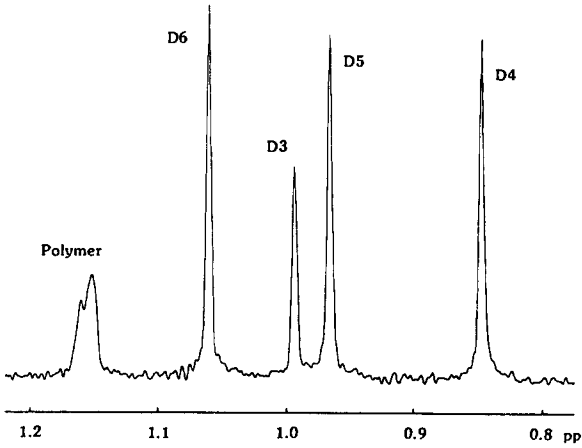

Figure 2 68.8 MHz ^{13}C n.m.r. spectrum of cyclic siloxane monomers

the determination of polymer and ring contents; a Bruker WM-250 spectrometer, and an IBM-NR100AF spectrometer, operating at proton frequencies of 250.13 and 100.13 MHz, respectively, and ^{13}C frequencies of 62.8 and 25.18 MHz.

Drying and analysis procedures

The first successful radiation polymerization of the D_3 and D_4 cyclic siloxane monomers in the liquid state was reported by Chawla and St. Pierre[9]. This was only achieved after the rigorous purification and super drying of the monomers[6,9]. All their manipulations were carried out under vacuum with only breakseals being used for the transfer steps. Conversions were determined by a combination of dilatometric and gravimetric measurements.

In the present work, more elaborate drying procedures were used and conversions to polymer and cyclics determined directly in n.m.r. tubes. This method was possible because separate experiments showed that the reaction terminated immediately following the removal from the radiation source. The monomers, D_4 and D_5, were dried by repeatedly treating them over a succession of sodium mirrors as described earlier. The high vacuum system used only grease-free stopcocks and breakseals. The final transfer to the 5 mm n.m.r. tubes was through tubing coated with metallic sodium. They were all parts of a vacuum rack which had been previously baked for 24 h at 450°C and 2×10^{-7} torr.

The n.m.r. analyses were carried out in sealed tubes without any n.m.r. solvent or deuterium lock. To obtain an n.m.r. spectrum, the deuterium lock sweep was disabled and the instrument was tuned on the proton free induction decay (f.i.d.). A typical proton n.m.r. spectrum of a siloxane mixture is shown in *Figure 1*. D_3 is cleanly separated from the other cyclic monomers, but D_4, D_5, D_6, and the polymer show similar chemical shifts, and are difficult to distinguish, and to obtain accurate integrations. *Figure 2* shows a ^{13}C n.m.r. spectrum of the monomers and polymer. All the peaks are clearly separated with reliable integrals being obtained. The ^{13}C Nuclear Overhauser Enhancement (NOE) was measured, and found to be 100% for both polymer and cyclic siloxanes in sealed n.m.r. tubes, so full proton decoupling (2 W) was used. The ^{13}C relaxation times (T_1) were measured for the siloxane monomers and polymer. Relaxation delays of five times the longest T_1 were used to ensure full relaxation and accurate integrals. Sixteen transients were usually acquired, with quadrature detection and phase cycling. Quadrature detection with phase cycling is a sequence designed to improve the signal-to-noise ratio. The sequence used involves alternately adding, subtracting, and rotating the phase of two received channels. Integration of the peaks was achieved by the Aspect 3000 DISB871 computer integration routine. ^{29}Si n.m.r. was not used because of long relaxation times (>30 s), poor sensitivity, and negative NOE, for the Si nucleus.

RESULTS AND DISCUSSION

In earlier papers[7,10] only three or less sodium mirrors were used for the drying procedure. The dramatic effect of drying further with more sodium mirrors is shown in *Figure 3* with D_5 monomer at 90°C. The rates increased with each additional mirror up to 12, no further changes occurred up to 15 mirrors. It can be assumed that the increased rates and final conversions are due to the

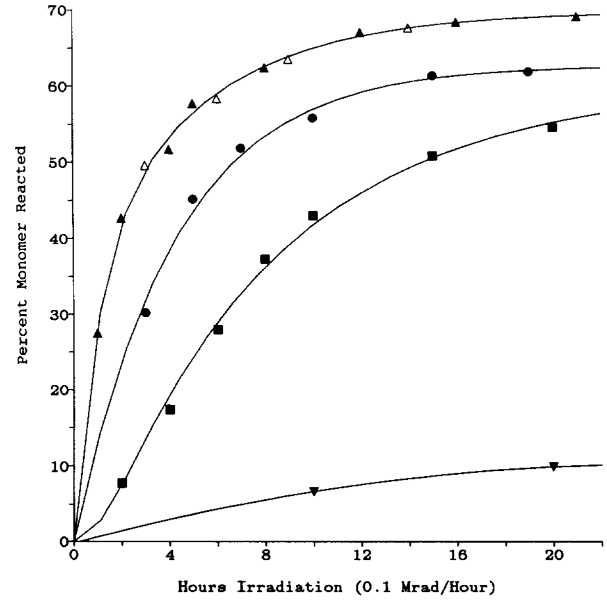

Figure 3 Polymerization of D_5 from successive sodium mirrors (90°C): no. 8, ▼; no. 10, ■; no. 11, ●; no. 12, ▲; no. 13, △

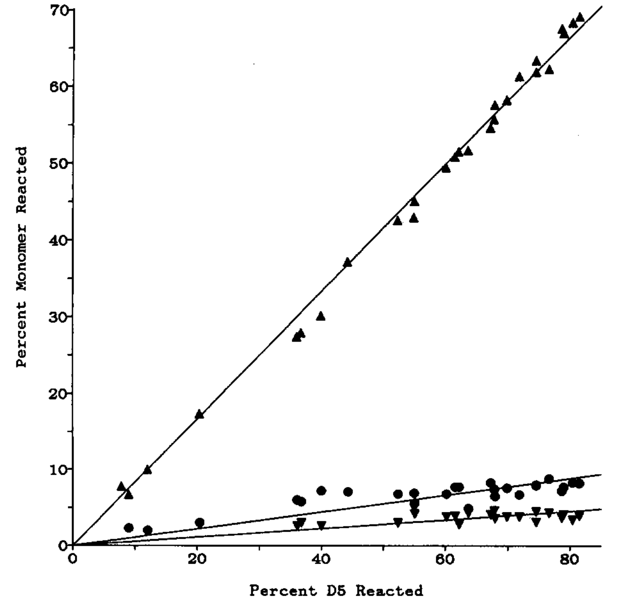

Figure 4 Polymerization of D_5, per cent products *versus* per cent monomer reacted (same data as *Figure 3*). From sodium mirrors 8–14: polymer, ▲, D4, ●; D6, ▼

progressive removal of terminating species, presumably water. During the reaction small amounts of cyclic compounds were also formed. *Figure 4* shows the same data as *Figure 3* but plotted as per cent products formed *versus* per cent D_5 reacted and including the rings. The relative proportion of cyclic products to polymer was found to be the same for reactions with different rates and final conversions. It was also found that the production of rings tended to level off in the same way. The results indicated that no significant depolymerization of the final polymer took place. The levelling off phenomenon is understandable since the samples are solid and crosslinked after about 40% polymerization. It is probable that residual protonic impurities with the less purified monomers, believed to be mainly water, were still terminating the growing chains leading to lower plateau yields. The levelling off phenomenon even in the absence of terminating impurities is also understandable. The terminating species, presumably the methyl anion, is small and would rapidly diffuse into the gel and terminate the growing chains. The competing chain growth is slowed at this point due to the lower monomer concentration and possibly lowered diffusion for the bulky monomer molecules to the active sites. *Figure 4* also indicates that the termination equally affects both the polymerization and ring formation.

The purity of the reaction system can also be checked in another way by comparing the experimental dependence of the rate on the dose rate (intensity). The Hayashi–Williams equation for the rates for a system completely free of impurities is[8]

$$R_p = k_p[M](R_i/k_t)^{1/2}$$

where R_p is the rate of polymerization, $[M]$ the monomer concentration, R_i the rate of initiation and k_p and k_t the rate constants for propagation and termination, respectively. The polymerization rates R_p, using 12 sodium mirrors, are shown plotted against the square root of the dose rate in *Figure 5* for D_4 monomer at 25°C in bulk. A straight line fitted the data with a correlation coefficient of 0.997. This indicates the Hayashi–Williams equation is, indeed, obeyed which would not be the case if terminating impurities were present.

Thus two pieces of evidence have been presented, showing that the monomers are free of protonic impurities, which would slow or terminate the reaction. The first, with D_5, is the reproducible conversion curve reached after drying the monomers over 12 and more sodium mirrors. The second with D_4 is the square-root dependence of the polymerization rate on the dose rate.

The powerful inhibiting effects of even traces of water clearly indicate that the polymerization is ionic in nature.

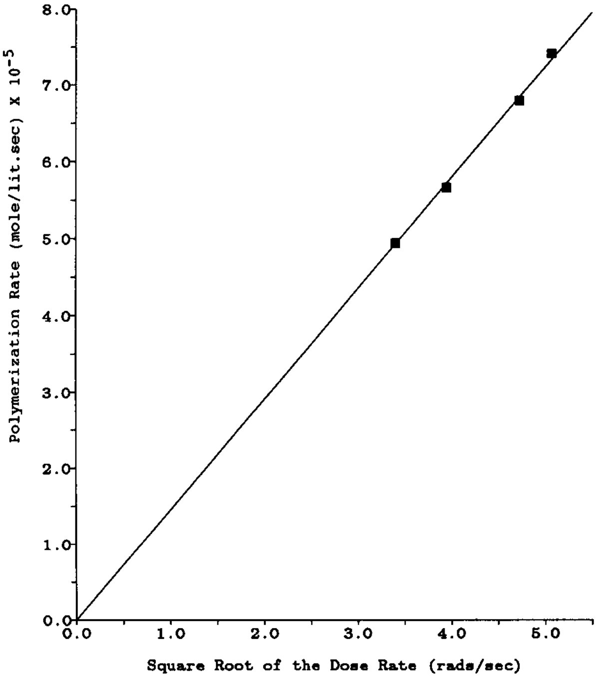

Figure 5 Polymerization rate of D_4 (25°C) *versus* square root of the dose rate

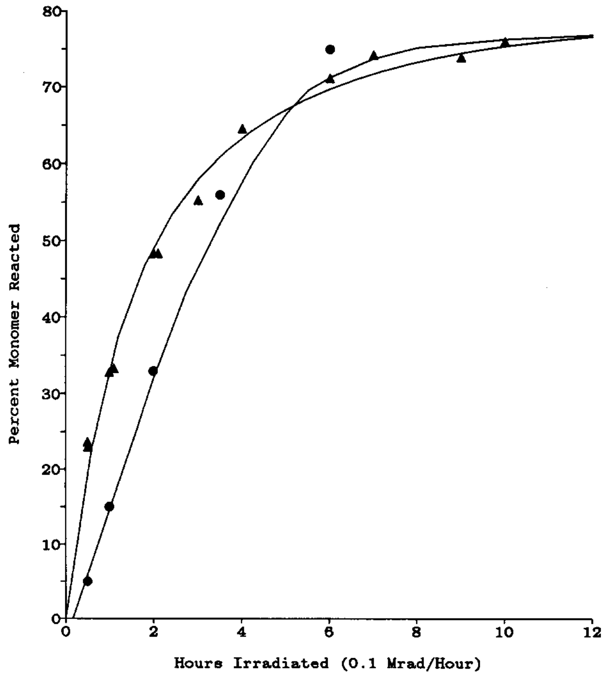

Figure 6 Polymerization of D_4 with (●) and without (▲) triethylamine (90°C)

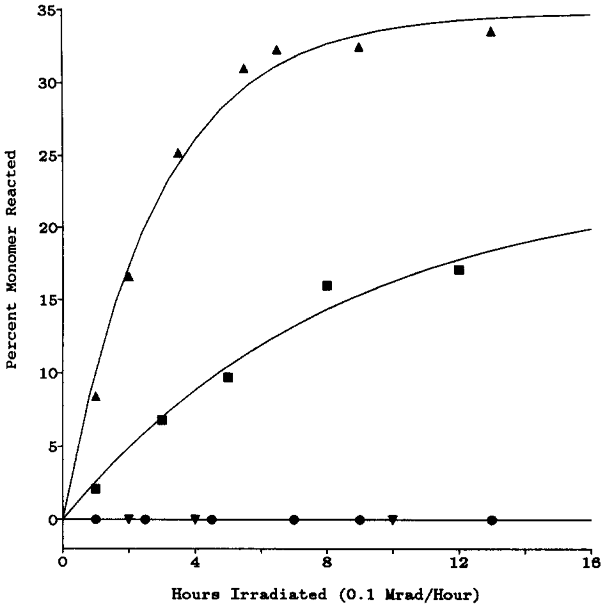

Figure 7 Polymerization of D_4 with trimethylamine, compared with no inhibitor and triethylamine (25°C). Polymer from: D4, ▲; D4 and 3.0% TEA, ■; D4 and 3.0% TMA, ●; D4 and 0.3% TMA, ▼

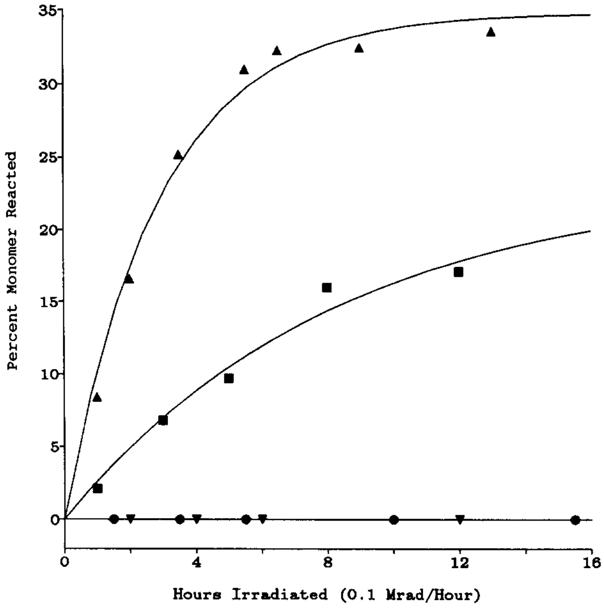

Figure 8 Polymerization of D_4 with ammonia, compared with no inhibitor, and triethylamine (25°C). Polymer from: D4, ▲; D4 and 3% TEA, ■; D4 and 3.0% NH_3, ●; D4 and 0.3% NH_3, ▼

It could be cationic or anionic, however the solid-state experiments of Chawla and St. Pierre indicated a cationic process[5,6]. Earlier work[7], with D_3 and D_4 in the presence of triethylamine (TEA), a cationic inhibitor, gave somewhat ambiguous results. The solubility of the TEA in the monomers was verified by ^1H n.m.r. The results were repeated with the present, more rigorously dried, D_4 monomer and 3% TEA. The results are presented in *Figure 6* for 90°C and *Figure 7* at 25°C. Only a small, about 15% reduction in the rate was found at 90°C but a 36% reduction at 25°C. The results supported, but did not prove, a cationic mechanism, possibly with some steric hindrance, being involved. Two less bulky cationic inhibitors trimethylamine (TMA) and ammonia were therefore tried each at 3 and 0.3% concentrations. These results at 25°C are presented in *Figures 7* and *8*. Both TMA and ammonia completely terminated any polymerization. No cyclic products were formed. It seems clear that the polymerization and ring formation are both dependent on a cationic process.

CONCLUSIONS

The radiation polymerization of cyclic siloxane monomers has been shown to be ionic in nature. Trace amounts of water, which terminate ionic but not free radical reactions, were shown to inhibit the polymerization reactions. A series of sodium mirrors were successfully used to dry the monomers to give reproducible rates and yields. In addition D_4 was shown to obey the Hayashi–Williams equation for completely pure systems. A series of inhibitors was used to establish the cationic mechanism. The more bulky TEA only retarded the reaction but TMA and ammonia caused total inhibition. The lower effectiveness of TEA is interpreted as being due to steric effects.

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