Radiation induced polymerization of dimethylcyclosiloxanes in the liquid state: 2. Polymerization kinetics of D3, D4 and D5 and the distribution of products

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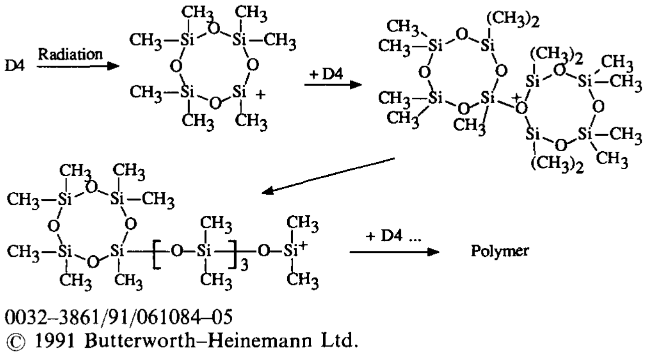
The rates of radiation induced polymerization in bulk of the cyclodimethylsiloxanes, D3, D4 and D5 have been determined under super-dried conditions. Drying was achieved by using repeated sodium mirrors. The initial rates, the final levelled-off conversions, the concentration of small cyclic products formed during the reaction by backbiting, and the activation energies, were found to be similar for all three monomers. These results are completely different from those observed with D3 in chemically initiated polymerizations in which the major cyclic product formed in large amounts from D3 was D6, compared with only small amounts of D6 with the radiation initiated reactions. It is concluded that with radiation initiation the propagation reaction and ring formation proceed through the same type of active centres with all three monomers.

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

INTRODUCTION

In a previous paper[1], a comparison was made between the radiation induced ring opening polymerization of D4 and D5. The monomers were purified, and then 'super-dried' by long and repeated contact with numerous sodium mirrors. It was found that the rates and final conversions became constant and reproducible after 12 or more mirrors. Furthermore, with D4 a plot of the rates of polymerization, R_p, *versus* the square root of the dose rates were linear and passed through the origin, as expected for an unpaired ionic polymerization free from terminating impurities[2]. Chawla and St Pierre[3–5] proposed that the radiation induced polymerization of the cyclic dimethyl siloxanes, both in the solid and liquid states, was cationic in nature. They suggested that the initiation involves the silicenium ion, e.g. D4$^+$. This would be formed by the loss of a CH_3^- ion by radiation, as had been identified in the mass spectra work of Orlov[6]. A possible reaction sequence would be:



Other earlier results[5,7] have pointed to a cationic mechanism but the data were somewhat ambiguous[7], particularly for D4 where some polymerization took place even with 4% of triethylamine (TEA) added. D3, however, was completely inhibited by the addition of 7.5% TEA. The situation was reexamined with D4 under very rigorous drying procedures, and the results were reported in our previous paper[1]. It was shown that TEA only partially slowed down the polymerization of D4 and D5, but that only 0.3% of trimethylamine (TMA) was sufficient to completely inhibit the reaction. Ammonia (0.3%) also inhibited the reaction. This is in full agreement with a cationic mechanism. Comparing the results described for D4 and D5 with those obtained for D3 in the earlier paper and in this work, both the rates and final conversions were quite similar for all three monomers. These results are in contrast with those observed in cationic and anionic chemically initiated systems in bulk and in solution close to room temperature. The reactivity of D3 for example, has been found to be between 10 to 100 times higher than that of D4 or larger cycles. This has been attributed to the existence of some ring strain in D3 which would be absent in larger rings. This interpretation is consistent with the enthalpy

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of polymerization for D3 of about 3 kcal per mole compared with close to zero for the larger rings.

In addition, some other rather peculiar differences have been observed between the chemically initiated cationic polymerization of D3 and other cycles. Chemically initiated cationic polymerizations for all the cyclosiloxanes, e.g. by triflic acid, generally takes place with the simultaneous formation of high polymer (molecular weights of 10^5 or higher), lower molecular weight polymer, (10^3 to 2×10^4), and small cyclics (D3 to D12). D5 and D6 behave similarly to D4, these results have been documented in more detail[8]. D4 and D5 gave cyclics in concentrations which decreased with increasing ring size ($D4 > D5 > D6$). The larger rings have been attributed to be formed by end-to-end ring closures of linear oligomers, or by backbiting. The smaller cyclic products were considered to be formed by backbiting reactions. D3 polymerizations have given quite different results. The cyclic products formed were mainly of the $D3_x$ type with concentrations decreasing with increasing ring size ($D6 > D9 > D12$)[10,11]. The reactions were under kinetic control leading to the rapid simultaneous formation of D6, D9, D12, higher cyclics, and high polymer. The concentration of all these species *versus* percent monomer reacted, increased linearly from the origin up to high conversions. This linear relationship was also observed for the molecular weights of the high polymers indicating the presence of a constant concentration of macromolecules[11]. These results have been interpreted as resulting from the presence of two populations of growing chains, one being a living polymer and the other having reactive end groups permitting the formation of cyclics by end-biting[10,11]. The more recent cationic polymerizations initiated by complexes of $SbCl_5$ and acid chlorides have given similar results, with D6 being formed in even higher amounts than with triflic acid[13].

In the present paper the rates of radiation initiated polymerizations of D3, D4 and D5 and the various types of products formed will be compared with chemically initiated polymerizations of the same monomers. An attempt will be made to draw some conclusions regarding the nature of the active species.

EXPERIMENTAL

The D4 and D5 monomers were purified, dried, and treated exactly as detailed in the previous paper[1]. D3, however, is a solid at room temperature with a melting point of 64°C. This made the various vacuum transfer steps and the bulk n.m.r. measurements particularly difficult. The monomer could only be contacted with the sodium mirrors for 2 h at 75°C because of the ability of the sodium to initiate anionic polymerization, up to 12 sodium mirrors were used to obtain dry D3 monomer. There were usually traces of polymer residue left in the flasks after transfer of the monomer. The D3 monomer purity was checked using proton n.m.r. spectroscopy, and found both before and after drying, to contain about 4% (mol%) of D4 monomer. For the polymerizations of D3 a modified n.m.r. tube apparatus was also needed. To prevent D3 from subliming to the top of the n.m.r. tube when heated, vacuum racks were prepared with glass rods (4 mm) suspended by glass hooks over the n.m.r. tubes, inside the apparatus. After condensing D3 into the n.m.r. tube, under vacuum, the top of the glass rods were broken with a small magnet, allowing the glass rods to fall into the n.m.r. tubes. The tubes were sealed off under vacuum just above the top of the glass rods. The samples were then irradiated (0.1 Mrad h^{-1}), and the ^{13}C n.m.r. spectra were recorded as previously reported[1]. To obtain quantitative ^{13}C n.m.r. spectra of the siloxane rings and polymer, the Nuclear Overhauser Effect, T_1 relaxation times and digital resolution were all accounted for.

RESULTS AND DISCUSSION

In our previous paper[1] the polymerization of D4 and D5 was shown to proceed at a rate that corresponds to a pure system, that is, a system with no impurities to terminate the reaction. This was demonstrated, after 12 sodium mirrors, with reproducible rate curves for each monomer, and a square root dependence of the polymerization rate on the dose rate, for D4. The mole percent of each monomer (D5, D4 and D3) converted to polymer ($DP > D6$) at 90°C, is shown in *Figure 1*, together with our reported values for D3, at a higher dose rate[7]. The initial rates for conversion of these monomers to polymer, for a dose rate of 0.1 Mrad h^{-1} are D5, $R_p = 2.1 \times 10^{-4}$ m s^{-1} l^{-1}; D4, $R_p = 4.2 \times 10^{-4}$ m s^{-1} l^{-1}; D3, $R_p = 2.4 \times 10^{-4}$ m s^{-1} l^{-1}.

In the curves presented here, no one monomer was polymerized significantly faster than the other monomers. This is quite different from chemically initiated cationic polymerizations in which the rates for D3 are much higher than those for D4, by a factor of about 100, for both protonic and nonprotonic initiations. The increased rates for chemically initiated anionic D3 polymerizations have been attributed to ring strain in the D3 monomer. The results presented here indicate that ring strain in D3 is not a significant factor for radiation induced bulk polymerizations. The results shown in *Figure 1*, also show that similar limiting conversions are reached with the

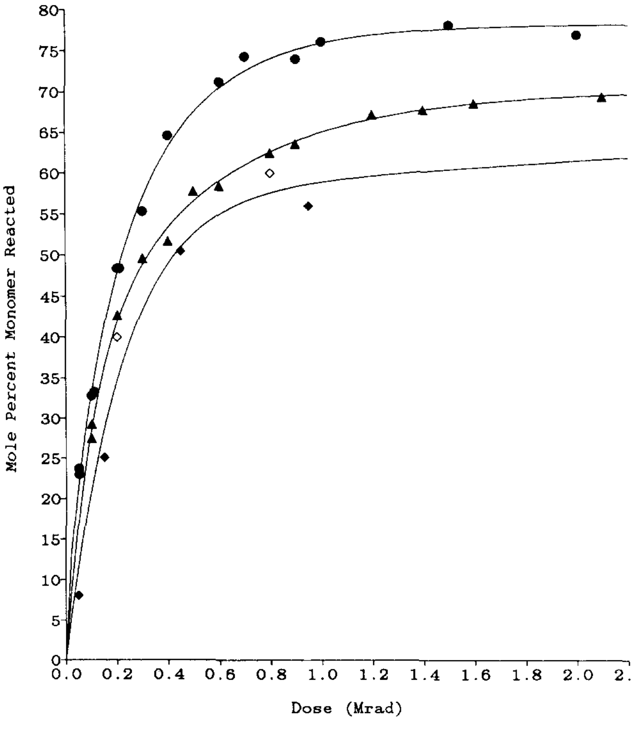


Figure 1 Mole percent of monomer reacted: ▲, D5; ●, D4; ◆, D3; ◇, D3 (ref. 7) to form polymer ($DP > 6$), *versus* dose

three monomers. However, it must be acknowledged that D3 is less easily purified and handled in our system than D4 and D5 as described earlier. This could be responsible for some slowing down of the reaction, but the possible presence of impurities does not seem to be sufficient to explain the rate of D3 being similar to D4 and D5 because we shall show later that copolymerization experiments between D3 and D4 lead also to the conclusion that they have similar reactivities.

Figures 2, *3* and *4* show the polymer produced from D5, D4 and D3, together with the amount and type of rings formed during the reaction. For each monomer the cyclic products are formed in the same relative amounts.

Table 1 lists the final product distribution for all three monomers, including polymer, unreacted monomer, and cyclic products, which are formed during the reaction by backbiting of the polymer chain. For the polymerization of D4 and D5, no detectable amount of D3 was found, within the limits of the n.m.r. technique used ($\approx 0.2\%$). For all three monomers the major cyclic products were D4 and D5. This is quite different from the chemically initiated cationic reaction where D6 was the major cyclic formed from D3, and both D4 and D5 were only found in small amounts. In chemically induced cationic polymerizations, D5 has been found to be slightly more reactive than D4. This is in agreement with the activation energies derived from the Arrhenius plots for the radiation induced polymerization of D4 (5.6 kcal mol^{-1}) and D5 (3.8 kcal mol^{-1}) shown in *Figure 5*.

The activation energy for D3 can be estimated from the literature as 3 kcal mol^{-1} (ref. 5). These three activation energies do not show the large difference that would be expected if one of the monomers was significantly more reactive.

Figure 6 shows the data from *Figures 2*, *3* and *4*, plotted as the mol% of monomer converted to each product *versus* the total mol% of the monomer consumed, which represents the molar composition of the reaction mixture during the course of the reaction. The data for D5 and D4 polymerizations were corrected for the amount of each starting monomer formed by backbiting during the reaction. These values were obtained from the amount of D4 and D5 formed during the polymerization of D3, D4 and D5 (*Figures 2*, *3* and *4*). For each product the data can be fitted to one curve, indicating that the product compositions are equivalent, even from different starting

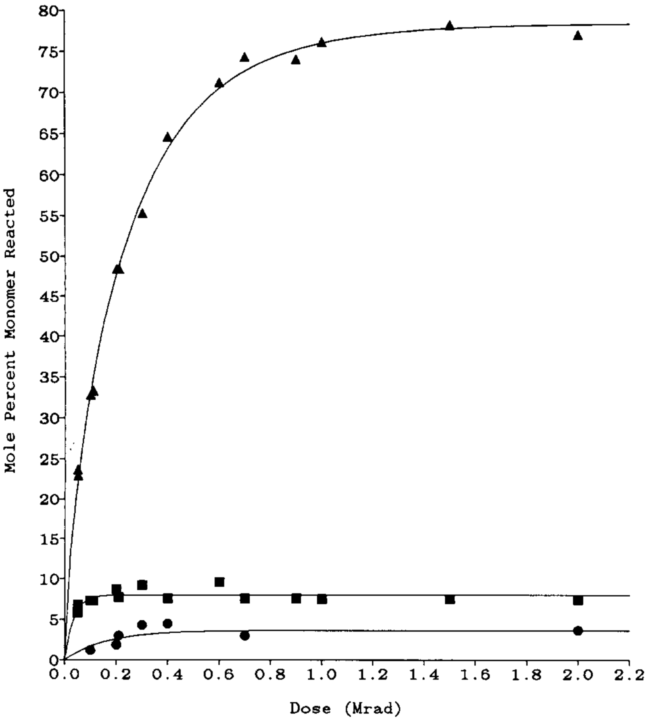


Figure 2 Mole percent D4 converted to polymer (DP > 6) (▲), D5 (■) and D6 (●) (at 90°C) *versus* dose

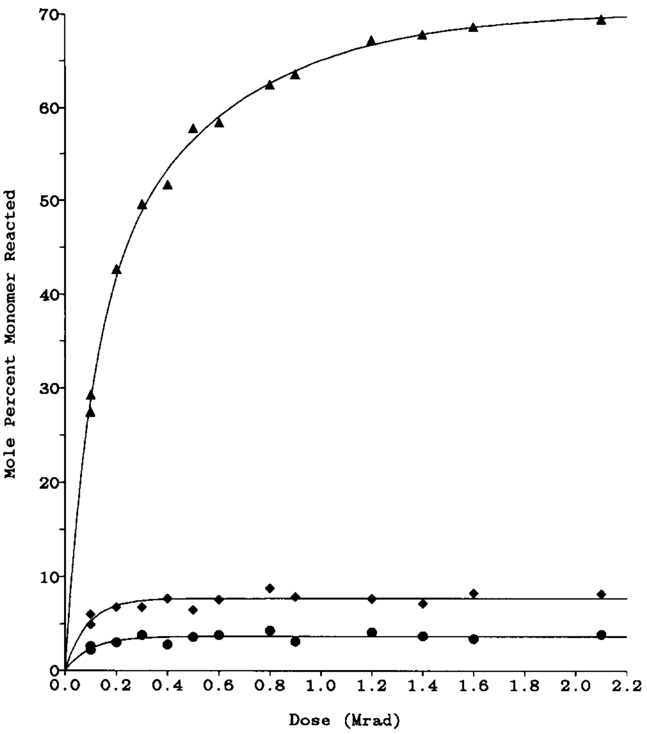


Figure 3 Mole percent D5 converted to polymer (DP > 6) (▲), D4 (◆) and D6 (●) (at 90°C) *versus* dose

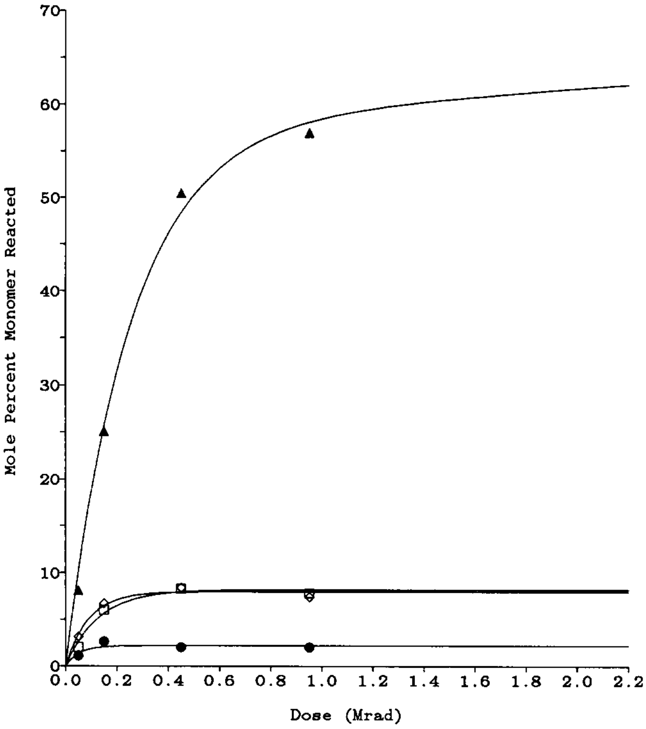


Figure 4 Mole percent D3 converted to polymer (DP > 6) (▲), D6 (●), D5 (□) and D4 (◇) (at 90°C) *versus* dose

Table 1 Final product composition for cyclic siloxane monomers polymerized by radiation in bulk (90°C)

Reaction products	Mole percent monomer reacted		
	D5	D4	D3
Polymer	69.4	76.0	57.0
D6	3.9	3.7	2.0
D5	18.5	7.3	7.8
D4	8.2	13.0	7.4
D3	0.0	0.0	25.8
	100.0	100.0	100.0

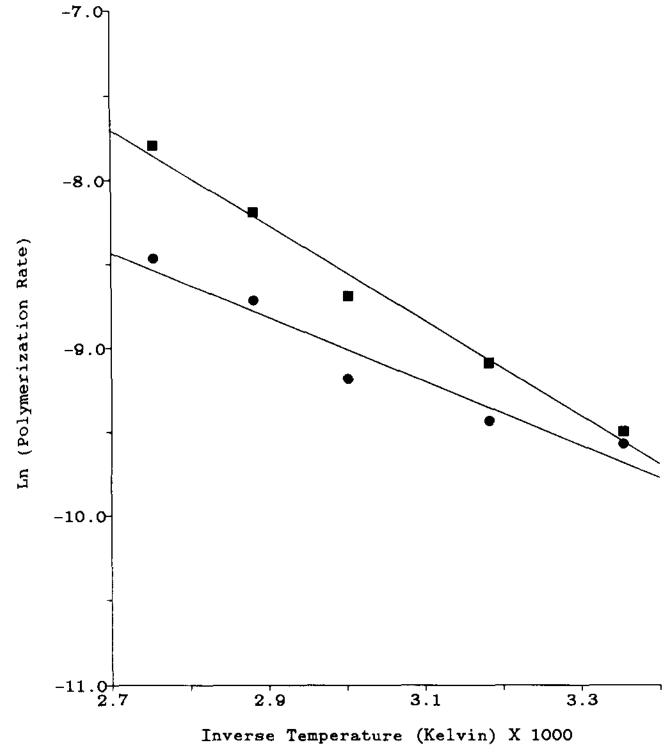


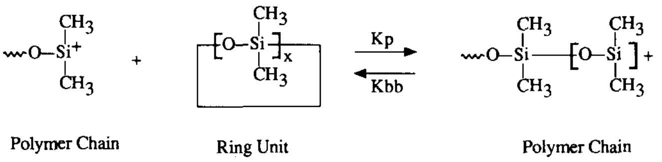
Figure 5 Arrhenius plot for the polymerization of D4 (■) and D5 (●)

monomers. This would not be the case if any of the monomers produced markedly different ratios of products, as D3 has been shown to do for chemically initiated reactions.

CONCLUSIONS

The differences in reactivity between D3, D4 and D5 described in the present work are too small to be considered significant. The conversion curves were all similar. The maximum final yields of polymer ranged from 68 to 75% at 90°C, using the highest conversion for D3 from ref. 7 (68% at 3.5 Mrad)[7]. When the yields of the various products were plotted as a function of the amount of monomer converted, after correction for monomers formed by backbiting, the same product distribution was reached regardless of the starting monomer. D4 and D5 were formed in equal amounts by backbiting, with D6 only being formed in small amounts. This is very different from chemically initiated cationic polymerizations of D3, for which D6 is the main cyclic product. The activation energies were also measured for D4 and D5 and compared to the literature values for D3. Again the differences were far less than might be expected if D3 was much more reactive.

The similarities observed for both the rates and the product distributions, particularly for the cyclic products, lead to the conclusion that the propagation reaction and the ring formation proceed through the same type of active centre for all three monomers. A suitable scheme was suggested earlier by the present authors[14] and appears to be valid for all the monomers including D3:



This is completely different from chemically initiated reactions, which show a wide variation in both reaction rates and types of products, according to the starting monomer. Different reactivities have been observed not only for D3, for which the mechanism might be different, but also for D4, D5 and D6 both in homopolymerization and copolymerization reaction systems.

The similar results observed in this work for the three monomers may come from the very high reactivity of the silicenium ion, and its small size, leading to much lower conformational requirements in the propagation step. These considerations will be discussed in more detail in Part 3 of this series which will deal also with the copolymerization data.

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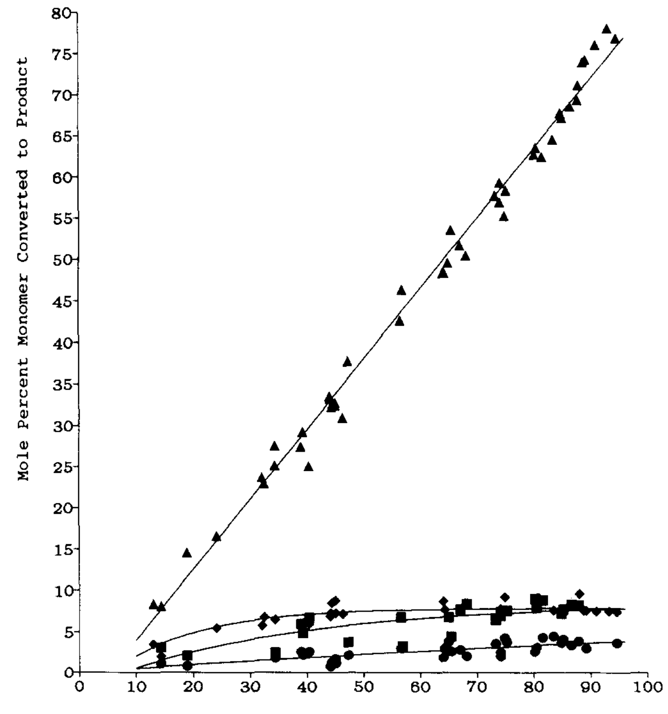

Figure 6 Mole percent of products formed from the polymerization of D3, D4 and D5 (90°C) *versus* the mole percent of monomer reacted. Polymer (▲), D4 (■), D5 (◆), D6 (●)

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