

The radiation-induced polymerization of dimethylcyclosiloxanes in the liquid state: 3. Copolymerization of D₃ with D₄ and D₄ with D₅, reactivities and interpretation

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The radiation-induced copolymerization of octamethylcyclotetrasiloxane (D₄) with hexamethylcyclotrisiloxane (D₃) and octamethylcyclotetrasiloxane with decamethylcyclopentasiloxane (D₅) was used to examine the relative reactivities between the three cyclic monomers, under super-dry conditions. The copolymerization results have shown very similar reactivities of the three monomers. These results were in agreement with previously reported monomer reactivities and homopolymerization activation energies, as well as with the production of similar quantities of cyclic products. A single reaction mechanism for the polymerization of D₃, D₄ and D₅ is proposed for both the propagation and the backbiting reactions. This mechanism assumes that backbiting (giving D₆, D₅ and D₄ but not D₃) involves, as intermediates, silicenium ions solvated by nearby oxygens of their own chain, and propagation by a much more reactive unsolvated (unpaired) silicenium ion in lower concentration.

(Keywords: polymerization; dimethyl siloxanes; propagation)

INTRODUCTION

The radiation-initiated polymerization of dimethylcyclosiloxanes was first proposed to be cationic in nature by Chawla and St. Pierre¹⁻³. Further evidence of a cationic mechanism was presented previously, including the termination of the reaction of both decamethylcyclopentasiloxane (D₅) and octamethylcyclotetrasiloxane (D₄) by both trimethylamine and ammonia, and the square root dependence of the initial reaction rate of D₄ polymerization on the dose rate^{4,5}. To achieve a cationic polymerization it was necessary to exhaustively purify the monomers by 'super-drying' with long and repeated contact with numerous sodium mirrors. The reaction products from the radiation-induced polymerization of D₅, D₄ and D₃ (hexamethylcyclotrisiloxane) were shown to differ from the chemically induced reactions of the same monomers⁴⁻⁶. The by-products from the radiation-induced reactions were found to be primarily D₄ and D₅, with smaller amounts of D₆. This is in contrast to the chemically induced polymerization of the same

monomers, where D₃ was found to produce only D₆, D₉ and D₁₂ rings as by-products^{6,7}.

In the present paper the copolymerization of D₅ with D₄, and D₄ with D₃ will be used to examine the relative polymerization rates of D₃, D₄ and D₅. These rates will be compared to previously reported results for the three monomers: their initial polymerization rates, activation energies, and cyclic reaction by-products^{4,5}. A propagation mechanism will be presented to account for the reported observations for all three monomers.

EXPERIMENTAL

The D₃, D₄ and D₅ monomers were purified, dried and treated exactly as detailed in previous papers^{4,5,8}. For the copolymerization reactions, the two monomers were condensed into one 5 mm n.m.r. tube, using the same techniques as described previously. For the copolymerization of D₃ and D₄, the monomer solution was a liquid at room temperature and did not require the use of glass rods, which were necessary to prevent sublimation of pure D₃ to the top of the n.m.r. tubes. The sample composition and reaction products were determined by ¹³C n.m.r. spectroscopy both before and during the polymerization reaction. The samples were irradiated (0.1 Mrad h⁻¹), and the ¹³C n.m.r. spectra were recorded as previously reported⁴. Representative ¹³C n.m.r. spectra were reported in reference 4.

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RESULTS AND DISCUSSION

To achieve the radiation-induced cationic polymerization of these cyclic siloxane monomers (D_3 , D_4 and D_5), without termination by impurities, it is necessary to exhaustively purify the monomers using repeated contact with sodium mirrors^{4,5,8}. For the radiation-induced polymerization of each monomer, the resulting conversion curves showed that they have similar reactivities⁵. Another method used to examine the relative reactivities of pairs of monomers is to copolymerize the monomers. For the copolymerization reaction, any impurities present in one monomer would act in a similar fashion on both monomers, leaving the relative rates unchanged. *Figure 1* shows the products and reactants for the copolymerization of D_4 and D_5 at 90°C. The initial composition of monomers is 45 mol% D_5 and 55 mol% D_4 . After 1.4 Mrad the composition has changed to 58 mol% polymer (■), 15 mol% D_5 (▲) and 27 mol% D_4 (●). *Figure 1* also shows the amount of D_4 (○) and D_5 (△) that have reacted to form polymer. From the amount of D_4 and D_5 reacted, it is evident that neither D_4 nor D_5 is significantly more reactive than the other monomer.

Figure 2 shows the copolymerization data for D_3 and D_4 at 90°C. The initial monomer concentrations were 50 mol% D_3 (▲) and 50 mol% D_4 (●). The total mole per cent of polymer produced (■), the mole per cent polymer produced from D_3 (△) and the mole per cent polymer produced from D_4 (○) are also shown in *Figure 2*. For the part of the reaction examined, it is evident that neither monomer is significantly more reactive than the other. The chemically induced polymer-

ization of D_3 was found to proceed much faster than the chemically induced polymerization of either D_4 or D_5 , which was attributed to ring strain in the D_3 monomer⁶. The copolymerization data shown in *Figure 2* demonstrate that for the radiation-induced polymerization of D_3 , ring strain does not appear to be a factor in determining the rate of polymerization.

The radiation-induced polymerization of D_3 , D_4 and D_5 was shown to be a cationic reaction. This was demonstrated by the square root dependence of the initial polymerization rate of D_4 on the dose rate, and by the termination of the reaction by small amounts of the cationic inhibitors, trimethylamine and ammonia. However, the more bulky triethylamine failed to completely terminate the reaction of D_4 ; this was interpreted as a steric effect⁴. This observation could prove important in determining a suitable reaction mechanism.

The reactivities of the three monomers examined were found to be remarkably close to each other. The evidence for this includes the initial reaction rates for D_3 , D_4 and D_5 , the activation energies of D_3 , D_4 and D_5 , and the copolymerization of D_4 with D_5 and D_3 with D_4 . The observations reported indicate that the size of the monomer ring does not affect the polymerization reaction. The postulated ring strain in D_3 gave a very specific set of products for the chemically induced polymerization, but it does not appear to be a major influence in the radiation-induced reaction. Ring strain in D_3 does appear to affect the by-products from the polymerization reactions. Measurable quantities of D_4 , D_5 and D_6 were all produced by backbiting, but no D_3 was detected from the reaction of D_4 or D_5 . Both D_4 and D_5 rings were

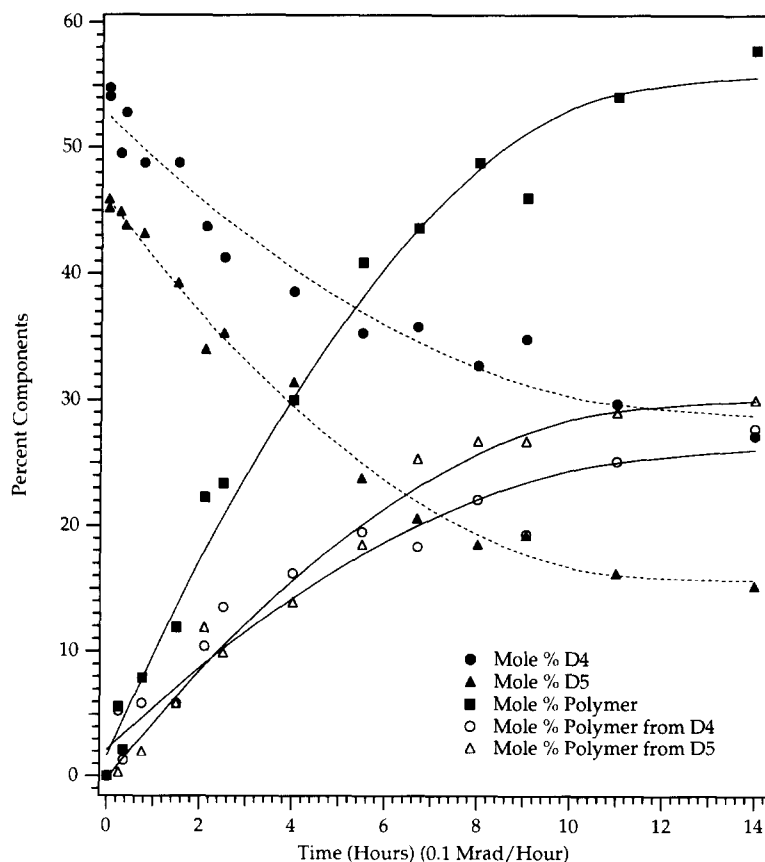


Figure 1 Copolymerization products from D_4 and D_5 at 90°C

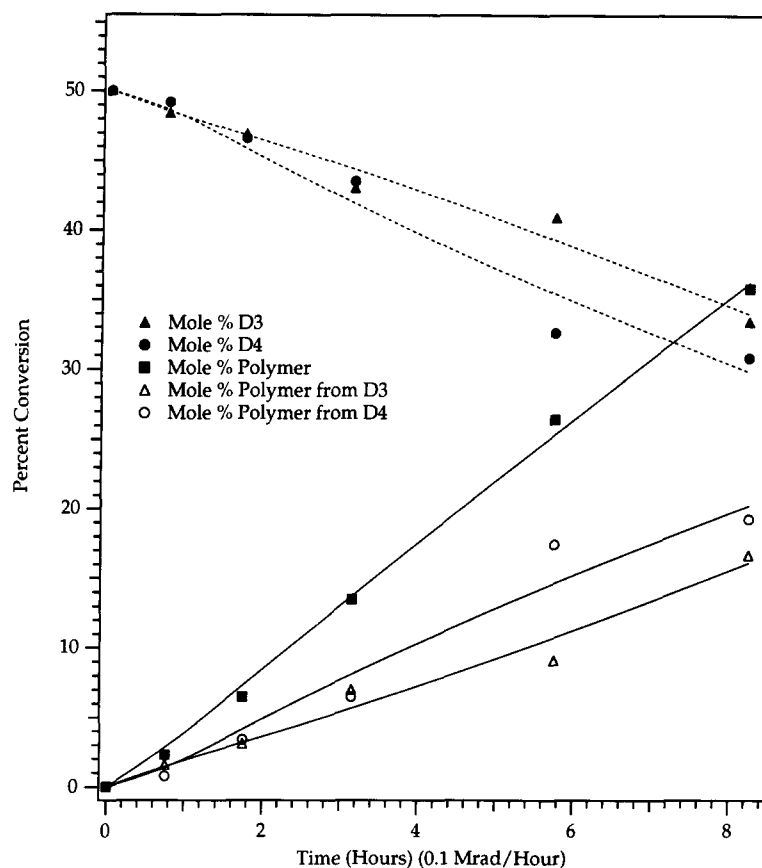


Figure 2 Copolymerization products from D₃ and D₄ at 90°C

the primary by-products, with a lesser amount of D₆ being formed.

It was reported that the amounts of D₄ and D₅ formed in the radiation polymerization of D₃ were equal. This was different from the reported polymerizations of D₄, D₅ and D₆ initiated by triflic acid, for which the concentration of D₄ at the end of the reaction was double that of D₅.

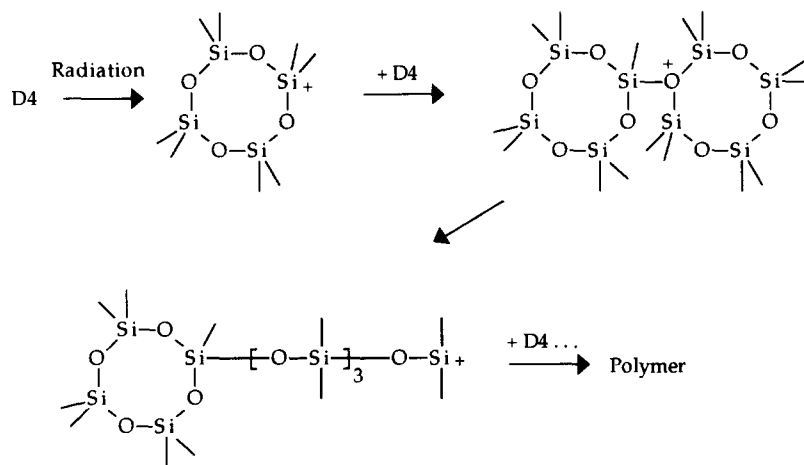
Two possible theories may be offered to explain the different reactivity of D₃ obtained for the radiation-induced polymerization and the chemically induced cationic polymerization (triflic acid⁷ or acetyl chloride/SbCl₅ complexes⁹). The first explanation might be the nearly exclusive formation, using chemical initiators, of all cyclic products (D_{3x}: D₆, D₉, D₁₂, ...) by end-to-end ring closure of the corresponding linear oligomers. However, using this explanation it is difficult to reconcile the simultaneous formation of high polymer ($M_n \approx 5 \times 10^5$), macrocycles ($M_n \approx 2 \times 10^4$) and a very large amount of D₆ (sometimes greater than 50%) that have been reported. Another possible explanation would be that D₆ (and perhaps D₉) might be formed by tertiary oxonium ions either by direct ring expansion⁷ or by a special type of backbiting involving the oxoniums⁹. Oxonium ions created by chemical initiators are more stable than the radiation-induced oxonium ions, owing to the proximity of a counter-ion of low nucleophilicity. This stabilization for chemically induced ions might exist for other cyclosiloxanes, but is larger with D₃ which is more basic than D₄.

A possible initiation sequence for the radiation-initiated polymerization reaction, presented previously, involved the loss of a CH₃⁻ ion to form a silicenium ion,

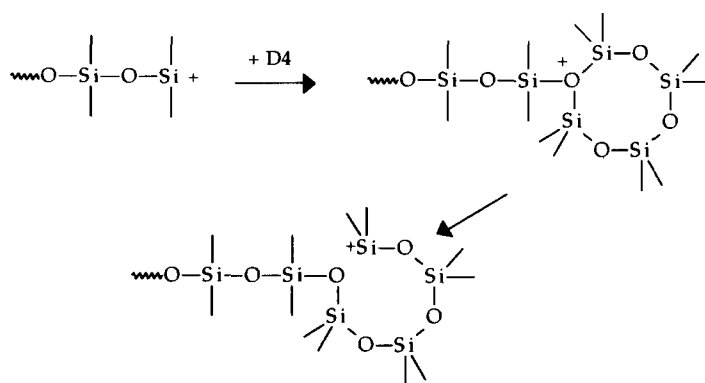
as shown in *Scheme 1*. This initiation mechanism agrees with the mass spectra work of Orlov¹⁰, which reported the loss of a CH₃⁻ ion. The initial monomer that loses a methyl ion does not undergo ring opening, indicating that ring size would not influence the initiation step. To support the reported experimental observations, the subsequent propagation steps would also have to be independent of ring size. There are two possible theories that could explain these observations.

The first explanation is that any ring strain in the monomers, particularly D₃, does not significantly affect the reactivity of the monomer. For the radiation-induced polymerizations, this would result in the same products being formed from D₃, D₄, D₅ and D₆ at similar rates. This is consistent with the reported observations, but would not explain the higher activation energies, and ineffectiveness of triethylamine as a cationic inhibitor. For the chemically initiated polymerizations, this explanation would suggest a different mechanism for the polymerization of D₃ relative to D₄, D₅ and D₆.

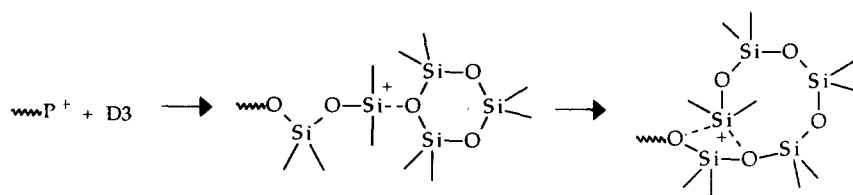
A second theory is for a single active centre to be the rate-determining step for the propagation reaction. When a new monomer unit adds onto the growing chain, the whole ring adds to the active end (*Scheme 2*). The newly formed silicenium ion will still be in close proximity to the backbone oxygens. This could lead to stabilization of the silicenium ion through a preferential bicoordination (or solvation) with the oxygens of the same chain in the fourth or fifth position, as shown in *Scheme 3* (for the example of D₃). If the oxonium ion in the solvation ring is more stable, relative to a non-solvated oxonium ion, then reaction of the solvation ring to form polymer and cyclic by-products will be the rate-limiting step. Such



Scheme 1



Scheme 2



Scheme 3

a solvation ring may also explain the equal distribution of cyclic by-products formed by backbiting (D_4 , D_5 and D_6). Some solvation rings of larger size might also be present, but at lower concentrations, leading to the formation of larger cyclic by-products (e.g. D_6). The formation of D_3 would be much less probable because of increased repulsion between the methyl groups, and greater steric strain when forming the six-member ring. No evidence of D_3 formation was found in these experiments, but the sensitivity of the n.m.r. analysis would probably not detect amounts less than 1%.

The solvation ring may also explain why the activation energies in the radiation-induced polymerization of D_3 , D_4 and D_5 are greater than might be expected ($4.5 \pm 1.5 \text{ kcal mol}^{-1}$). These values are higher than those reported for the radiation-initiated polymerizations of styrene, α -methyl styrene, isobutylene ($\approx 0 \text{ kcal mol}^{-1}$) and cyclopentadiene ($< 2 \text{ kcal mol}^{-1}$)¹¹, but lower than those reported for vinyl ethers ($5\text{--}10 \text{ kcal mol}^{-1}$). The relatively high activation energies for vinyl ethers have

been explained by a complexation of ether groups on the polymer chain, the global apparent activation energy (E_{app}) being given by¹²:

$$E_{app} \approx E(+) - \Delta H_p$$

where ΔH_p (negative) is the solvation enthalpy. A similar case of intrachain solvation, the proposed solvation ring, may also explain the higher activation energies observed for radiation-induced polymerizations of D_3 , D_4 and D_5 .

CONCLUSIONS

The radiation-induced polymerization of dimethylcyclosiloxane monomers has been shown to be cationic in nature. This was demonstrated by plotting the initial polymerization rate (R_p) versus the square root of the dose rate for D_4 , which gave a linear plot. This would be expected for a cationic unpaired-ion polymerization in which terminating impurities are absent. The cationic inhibitors, trimethylamine and ammonia, were shown

to terminate the reaction, also indicating a cationic mechanism. The reported polymerization rates and activation energies for D₅, D₄ and D₃ did not show significant reactivity differences between the three monomers. Copolymerization data for D₅ with D₄ and for D₄ with D₃ supported these data. These observations were different from the chemically induced reactions, where large differences in the reactivities of the three monomers have been reported. The composition of cyclic products from the radiation-induced reactions was found to be equivalent for the polymerization of all three monomers (3 mol% D₆, 8 mol% D₅, 8 mol% D₄ and 0 mol% D₃). In the polymerization of D₃ particularly, the amount of D₆ formed is the same as for the other monomers, contrary to chemically initiated reactions for which the amount of D₆ depends on the initial monomer. The lack of formation of D₃ can be attributed to strain in the six-member ring; however, the same ring strain in D₃ was not observed to produce a faster polymerization reaction compared to D₄ and D₅.

One possible explanation could be that any ring strain in the monomers does not significantly affect their reactivities. This explanation would suggest a different mechanism for the chemically initiated polymerization of D₃ relative to D₄, D₅ and D₆. This would explain the results from radiation-induced reactions, but fails to explain the inability of triethylamine to terminate the polymerization of D₄, and the larger activation energies reported.

A second explanation is of a single reaction mechanism for all three monomers that incorporates one solvation-ring active centre, accounting for both the polymerization reaction and the ring formation reaction. This type of mechanism could occur if the silicinium ion on the growing chain remains in the proximity of the oxygens on the polymer backbone. This solvation-ring complex would serve to delocalize the cationic charge, stabilize the intermediate, and put the silicinium ion in position to react with several oxygens on the backbone, to form D₄, D₅ and a lesser amount of D₆. Reaction of the

solvation-ring complex with a new monomer would propagate the polymer chain. Ring strain in the six-member ring would make backbiting to form D₃ unlikely. With the same solvation-ring complex for all three monomers, any differences in reactivities between the monomers would be lost. This mechanism could account for the similar reactivities, by-products and activation energies observed for the three monomers. The cationic inhibitor, triethylamine, failed to completely terminate the polymerization reaction. The mechanism proposed involves a bulky active centre, and might explain why the larger triethylamine molecule could not terminate the reaction, while the smaller trimethylamine and ammonia did terminate the reaction.

ACKNOWLEDGEMENT

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