

고체 헥사메틸 사이크로트리실록산의 감마 방사화

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Gamma Radiolysis of Solid Hexamethylcyclotrisiloxane

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요 약 : 헥사메틸 사이크로 트리실록산을 고분자가 아닌 생성물을 확인하기 위하여 고체 상태 중합을 위하여 이용한 것보다 30-50배 큰 분량 (doses)에서 코발트 60 감마선을 조사하였다. 많은 환상과 선상의 올리고머의 실록산들을 발견 했으며 수소, 메탄과 에탄의 기체 수율은 폴리디메틸 실록산의 수율과 같았다.

Abstract : Hexamethylcyclotrisiloxane was irradiated by ^{60}Co gamma rays at doses 30 to 50 times higher than those used for the solid state polymerization in order to identify non-polymeric products. These were found to be a large number of oligomeric cyclic and linear siloxanes. Gas yields for hydrogen, methane and ethane were identical to yields from polydimethyl siloxanes.

INTRODUCTION

In the early 1950's Schmitz and Lawton¹ discovered the ability of high energy gamma irradiation to initiate polymerization of monomers in the crystalline state. Since that time a good deal of work has been done on "solid state polymerization", including some on crystalline monomers of siloxanes, that results when the monomers are irradiated with gamma rays.

Lawton et al.² first reported the solid state polymerization of hexamethylcyclotrisiloxane (D_3) by gamma irradiation in 1956 and subsequent studies involving irradiation initiation have been

reported by Burlant and Taylor.³ Since reactions involving siloxane rearrangement are usually produced by the action of ionic catalysts,⁴⁻⁶ rather than by free radical initiators, the irradiation induced polymerization probably also follows by an ionic mechanism. This assumption is reinforced by the observation that the initiation of the polymerization of D_3 cannot be effected by benzoyl peroxide or azobisisobutyronitrile despite the fact that it proceeds quite readily in the presence of acids⁷ or bases.⁸⁻¹¹

Chawla and St-Pierre⁹ have also studied the polymerization of this monomer by gamma irr-

adiation for the effect of ion scavengers, H_2O and NH_3 , and for crystal size etc. They used extraordinary precautions in drying the monomer and, as a consequence, were able to obtain very high yields.

The work that has been described previously has been done with low doses of γ -rays such that gas and low molecular weight product yields have been difficult to determine. The reason for this is, of course, the very high G value, 20~90, for the polymerization of this highly reactive cyclic compound. In the present work the doses were on occasion 30 to 50 times those used in polymerization studies since the objective was to elucidate irradiation induced events other than simple ring opening.

Previously, all workers have assumed that the "volatile" fraction obtained as products from the gamma-irradiated D_3 to be monomer. However, in the present work it is shown that this fraction is, in part, a series of cyclic or linear siloxane compounds. In addition, there are also still other products that may be crosslinked compounds.

EXPERIMENTAL

The experimental methods are essentially those described in previous papers^{10,11} on the gamma irradiation chemistry of various siloxanes.

Irradiation Source

The cobalt-60 Gamma cell 220 irradiation source (McGill University) operated at a dose rate 0.73 MR/hr as determined by a Fricke Dosimeter, assuming a G value^{12~14} of 15.6 for conversion Fe^{2+} ions to Fe^{3+} ions for a solution of 0.04 weight percent $FeSO_4$ in 0.8 N H_2SO_4 .

Monomer Preparation

The hexamethylcyclotrisiloxane (D_3) was supplied through the courtesy of the Silicon Products Department of the General Electric Co. It was dried by contacting it for 4hrs. at 70°C with finely dispersed sodium, previously melted and degassed under vacuum (10^{-5} torr) for 3 hrs. at 400°C. Analysis of the purified D_3

(m.p., 64.5°C) by v.p.c. indicated a purity of $\geq 99.9\%$. The purified D_3 was distilled, under vacuum, directly into the reaction tube.

Collection and Analysis of Products

Gaseous products were pumped from the irradiated samples, kept at a temperature of -82°C, by means of a Toepler pump and analyzed by gas chromatography, as described previously.¹⁰ After removal of the gases the remaining material was weighed into a tube and connected to a vacuum line. The products volatile at room temperature were distilled into a tube kept at liquid N_2 temperature and the remaining non-volatile products were weighed. After adding a known amount of toluene to this volatile matter it was also analyzed by gas chromatography.¹⁰ The final, nonvolatile portion was determined to be crosslinked polymer.

RESULTS AND DISCUSSION

Gamma irradiation of pure solid hexamethylcyclotrisiloxane yielded H_2 , methane and ethane as gaseous products with $G(H_2)=0.49$, $G(CH_4)=1.91$, $G(C_2H_6)=0.35$ for a total gas yield of $G=2.75$. A chromatogram of the liquid products, shown in Fig. 1, indicates that the major portion of the liquid products, as defined by coincident retention times by v.p.c., are cyclic siloxanes ranging from D_4 to D_{22} , with small amounts of linear siloxanes of the type

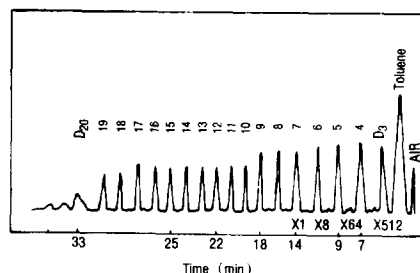


Fig. 1. Vapour phase chromatogram of liquid products obtained from the radiolysis of D_3 at a dose of 43.8 MR. (column conditions: initial temperature 50°C, temperature programmed at 10°C/min to 300°C).

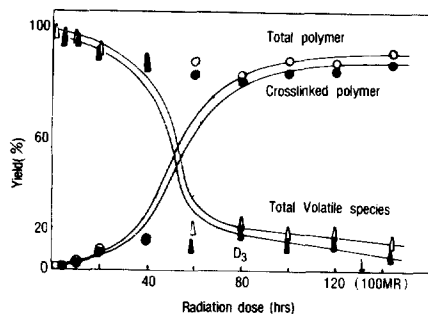


Fig. 2. Polymer yields from the irradiated D_3 as a function of dose. (dose rate=0.73 MR/hr). (\circ : total polymer, \blacktriangle : D_3)

$(CH_3)_3Si-O-Si(CH_3)_2-O-Si(CH_3)_3$ (MDM), $(CH_3)_3Si-O-Si(CH_3)_2-O-Si(CH_3)_2-O-Si(CH_3)_3$ (MD_2M), etc.

Fig. 2 shows the yield of the material left after the removal of the gases from the gamma irradiation of D_3 . The yield of crosslinked polymer, i.e., insoluble product, increases slowly until a dose of about 55MR (40 hrs of irradiation) but rises sharply between 40 and 60 hours after which it becomes constant. Other soluble products, although much less in actual amount, seem to follow a similar pattern. The amount of unreacted D_3 , of course, shows decreases in a trend that is exactly opposite to that for the formation of product.

The dramatic rise in reaction rate may be ascribed to a pseudo-liquid diffusibility at this particular stage of polymerization. As the time of irradiation increases the amount of liquid product increases thus lowering the melting point of the D_3 with resulting increase in mobility. Furthermore, since the polymer being formed is non-crystalline at the temperature of irradiation the overall behaviour might be expected to be similar to a solid state polymerization at temperatures just below the melting temperature. The rates of such polymerizations have also been observed to be very high.

The bell-shaped curve for the G values of the polymerization behaviour, Fig. 3, is as expected for the data in Fig.2. Again, the rise is due

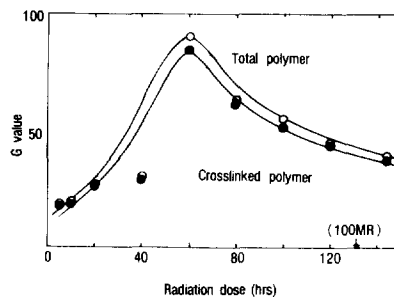


Fig. 3. G(polymer) for irradiation of D_3 as a function of dose. (dose rate=0.73 MR/hr). (\circ : total polymer)

to a loosening of the crystal structure due to formation of liquid products as the irradiation proceeds. This makes easier the small diffusions necessary to effect polymerization. A maximum is reached as this process continues. The post-maximum part of the curve is a reflection of simple first order, in $[D_3]$, polymerization kinetics associated with the diminishing D_3 concentration.

The G values for the formation of those cyclic and linear siloxanes, produced in relatively high yield, as a function of irradiation time are shown in more detail in Figs. 4 and 5, respectively. As can be seen, except in the cases of D_4 and D_5 , the yields are low, of the order of one to 10% of the gas yields. The results, of course, exhibit a higher relative error than do those for the high yield species but nevertheless a number of interesting trends are obvious. In the case of the cyclic products it appears that during the early stages of irradiation low molecular weight cyclic species are present in fairly large quantities and as the reaction proceeds these species are either fragmented themselves or, more likely, are incorporated into the larger molecules. The linear species (Fig.5), also present in low quantities, exhibit a similar behaviour with the exception of MDM. This species is obviously a reaction product of monomer with CH_3^+ and its higher yield would be explained on the basis of the large amount of monomer present.

It was stated earlier that the polymer-

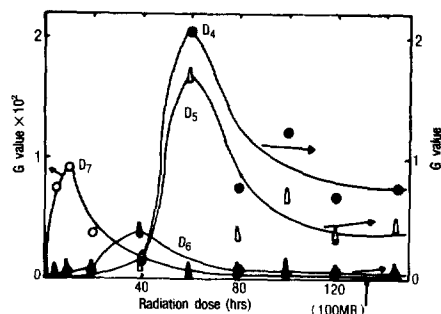


Fig. 4. G(cyclic product) from irradiated D_3 as a function of dose. (dose rate=0.73 MR/hr).
[●: D_4 , ▲: D_6 , △: D_5 , ○: D_7]

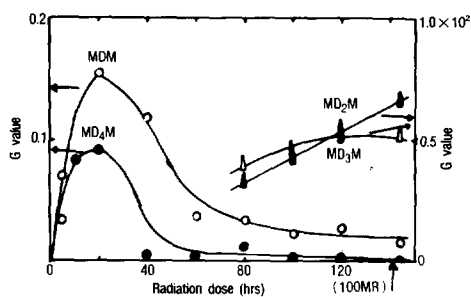
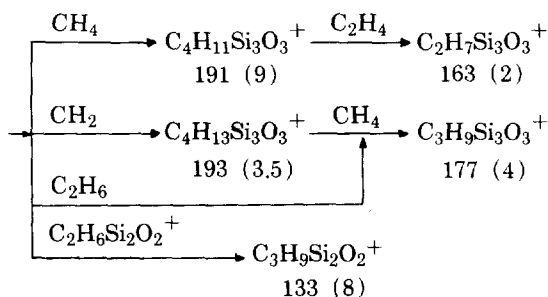
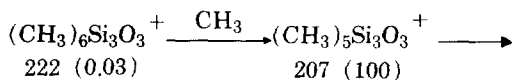


Fig. 5. G(linear product) from irradiated D_3 as a function of dose. (dose rate=0.73 MR/hr).
[▲: MD_2M , △: MD_3M , ○: MDM , ●: MD_4M]

ization is assumed to be ionic. Further support for such a path is gained from the work of Orlov¹⁵ who, in a mass spectrometric study of D_3 , found the following gas phase fragmentation behaviour:



(The numbers appearing below the ions represent the mass numbers with relative abundances, based on mass 207 fragment, given in brackets). This pattern shows that ion-molecule reactions can be expected to play a predominant role and can thus explain the presence of even the very high siloxanes such as D_{21} and D_{22} .

The G value for total gas yield=2.75 from the gamma irradiated D_3 can be related to the crosslinking efficiency of polydimethylsiloxane and is in reasonable agreement with the value of $G(\text{crosslinking})=2.5 \pm 0.3$ determined by Barnes¹⁶ and $G(\text{crosslinking})=3.0$ by Miller.¹⁷

SUMMARY AND CONCLUSIONS

The gamma irradiation of D_3 at doses of the order of 15 to 100 MR yields the gaseous products hydrogen, methane and ethane, Non-polymeric liquid and cyclic siloxanes, not observed in previous work,^{1,2} and crosslinked polymer are also produced in significant amounts. Their presence apparently results from the ion interactions with the highly reactive D_3 . However, the G values for their formation are relatively insignificant relative to the yields of crosslinked polymer but still offer insight into observed changes in G value for polymer formation with increase in dose.

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