

Gamma Ray-Induced Liquid-State Polymerization of Hexamethylcyclotrisiloxane and Octamethylcyclotetrasiloxane

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Synopsis

The radiation-induced bulk polymerization of liquid hexamethylcyclotrisiloxane has been achieved. Appreciable yields of polymer from octamethylcyclotetrasiloxane liquid have also been obtained. These results were achieved on "ultra-dry" monomers and are interpreted in terms of an ionic polymerization mechanism.

INTRODUCTION

Okamura has pointed out¹ that there are a number of monomers which polymerize in the crystalline state but do not do so in the liquid state. One of the suggested reasons for this behavior is the presence of ionic scavengers in the monomer, usually water, which inhibit the polymerization. It has been observed that trioxane can be made to polymerize in the liquid state if the monomer is rigorously dried with Na-K alloy.² This success, combined with the recent liquid state studies on ultradry monomers such as styrene^{3,4} and α -methylstyrene^{5,6} have shown that the ionic polymerization of a monomer can be completely inhibited by quantities of water at the $10^{-5}M$ concentration level in easily diffusable media. In all of the above-cited monomers, the active species for polymerization were shown to be free cations, and the rates of propagation were very high.³

The radiation-induced liquid-state polymerization of hexamethylcyclotrisiloxane (D_3) has been attempted before, but without success.^{7,8} The present studies on the gamma ray-initiated liquid-state polymerization of D_3 were undertaken, following completion of a solid-state polymerization study, to determine if the reported inability to polymerize was due to some structural factors or was simply due to the presence of ionic impurities.

Another cyclic siloxane which has been of great interest in polymerization studies is octamethylcyclotetrasiloxane (D_4), mp 17.5°C. This compound has also been irradiated in the liquid state, but the only products found in

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appreciable yields were dimers.⁹ Wolf et al.¹⁰ were able to obtain small quantities of larger molecules at a very high dose. Tabata et al.¹¹ have succeeded in polymerizing this compound just below its melting point, but the rates were exceedingly low, with less than 6% conversion obtained at a total dose of 25 Mrads. Indeed, at such a low level of efficiency, it is difficult to apply the term "polymerization."

In the present report, a short study of gamma ray-induced bulk polymerization of liquid D₄ is described in conjunction with the liquid D₃ work.

EXPERIMENTAL

Materials and Their Purification

The D₃ used here was purified and dried in the manner described previously¹² for the solid-state polymerization.

The D₄ was supplied through the courtesy of the Silicone Product Department of the General Electric Company, Waterford, N.Y. It was purified by distillation through a packed column and its purity was shown by means of gas chromatography to be better than 99.98%. The experimental procedure and the apparatus used were the same as those described for D₃.¹²

For the drying of D₄, barium oxide (Fisher Scientific, anhydrous lumps) was used, with the drying procedure being otherwise identical to that used for D₃. Following the drying, the monomers were distilled into dilatometers. All of the manipulations were done under vacuum, and for the transfer of the monomers from one sample tube to another, only break-seal arrangements were used. The type of apparatus used was similar to the one described previously.¹² Following the transfer of D₄ into the dilatometers, they were sealed under vacuum.

Irradiation

The gamma-irradiation facility has been described elsewhere.¹² The irradiations were performed at a dose rate of 3.8×10^5 rads/hr. For temperature control, a small oil bath inside the irradiation chamber was used. The specially designed heater used in the oil bath was such that it dissipated a little more energy in the upper parts than it did in the lower parts (accomplished by having a few extra turns of heating wire in the upper region). This arrangement prevented the distillation of monomer from the bulb to the space above the capillary of the dilatometer. Temperature control was better than $\pm 0.2^\circ\text{C}$.

The level of monomer inside the capillary tubing was read by means of a cathetometer. After every 5 to 10 min of irradiation, the sample was raised from the "irradiating position" for a reading. When the desired number of readings had been taken, the dilatometer was taken out of the source, broken open, and the yield of polymer was determined gravimetrically.

RESULTS AND DISCUSSION

The Liquid-State Polymerization of D_3

At a pressure of 1 atm, D_3 exists in the liquid state over only a small temperature range, mp = 64.5° and bp = 134°C. The polymerization was studied at three different temperatures, 76°, 98°, and 132°C. Before irradiation, it was shown that the compound does not polymerize thermally by heating it at 130°C for 4 hr. All of the samples polymerized were from the same batch, and, in calculating the yield of polymer, it was assumed that the yields varied linearly with change in volume.

The polymerization results are shown in Figure 1. No induction period is in evidence, and the rate of polymerization increases slightly with conversion and more markedly with temperature. The polymers obtained were always crosslinked.

For comparison of the liquid- and solid-state polymerization, the same D_3 was polymerized in the solid state at 30°C using the same dose rate as that used for the liquid state (3.8×10^5 rads/hr). The results are shown in Figure 2.

It is seen from Figures 1 and 2 that the rate of polymerization in the liquid state at 76°C is very nearly the same as that in the solid state at 30°C. Taking the temperature difference into consideration, however, it is obvious that the solid-state reaction is inherently faster than that in the liquid state.

The slight upward curvatures of the conversion curves in Figure 1 are interpreted on the basis of a diminution of inhibitor molecules with time.

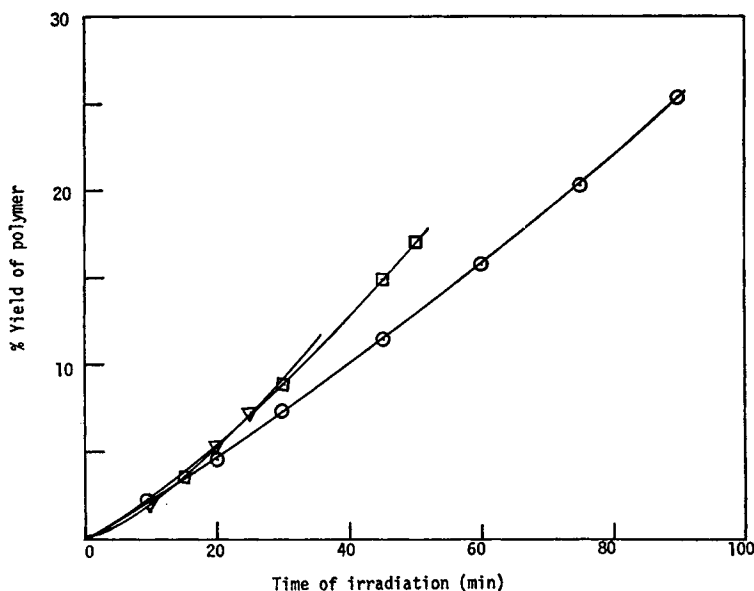


Fig. 1. Polymerization of D_3 in the liquid state at different temperatures: (○) 76°C; (◻) 98°C; (◄) 132°C.

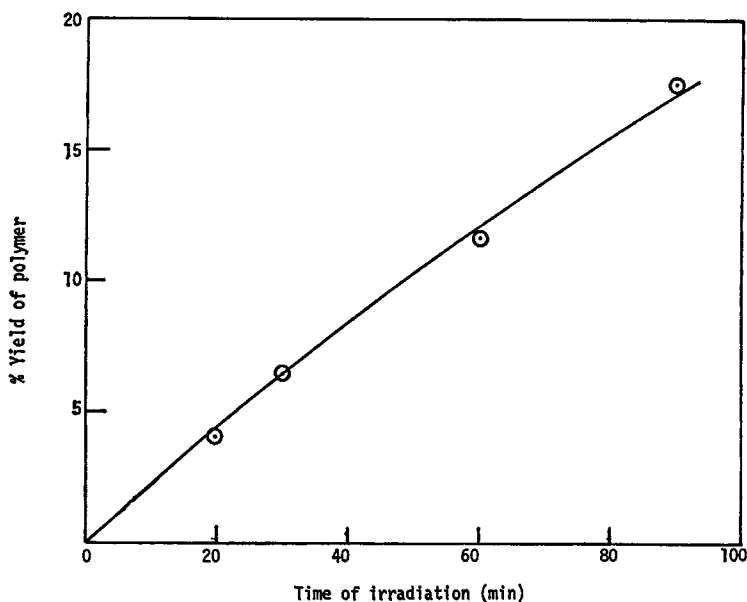


Fig. 2. Polymerization of D_3 in the solid state at 30°C .

It is assumed that they are in effect scavenged in the course of terminating a growing chain. We further assume, on the basis of our previous work with crystalline monomer, that the polymerization proceeds by a cationic mechanism¹² in both cases.

The liquid-state polymerization of D_3 , which has been achieved here for the first time, has been possible only by the exercise of extreme care in purifying, drying, and handling of monomer. The present studies further support the conviction that water acts as an ionic scavenger for radiation-induced polymerization reactions and that its removal is critical.

Polymerization of Liquid D_4

Before irradiation it was ascertained, by keeping one sample at 165°C for 5 hr, that D_4 does not polymerize thermally under these conditions. The results of polymerization studies at 69° , 102° , 135° , and 168°C are shown in Figure 3. It appears that, in this case, there is an induction period the length of which depends on the temperature of polymerization. This behavior, with an accelerating rate, is once again rationalized on the basis of the scavenging of inhibitor molecules by the polymerizing species. As in the case of D_3 , the polymer obtained was crosslinked.

From this study a $G(\text{monomer})$ of 460 at 69°C , at a total dose of 0.63 Mrads, was calculated. In the previous attempt at gamma-ray polymerization of liquid D_4 , a $G(\text{monomer})$ value of about 130 at 70°C at a total dose of 2.8 Mrads, using a dose rate of 1.3 Mrads/hr, was reported.⁹ This lower yield can possibly be explained on the basis of a dose rate effect¹³ but is

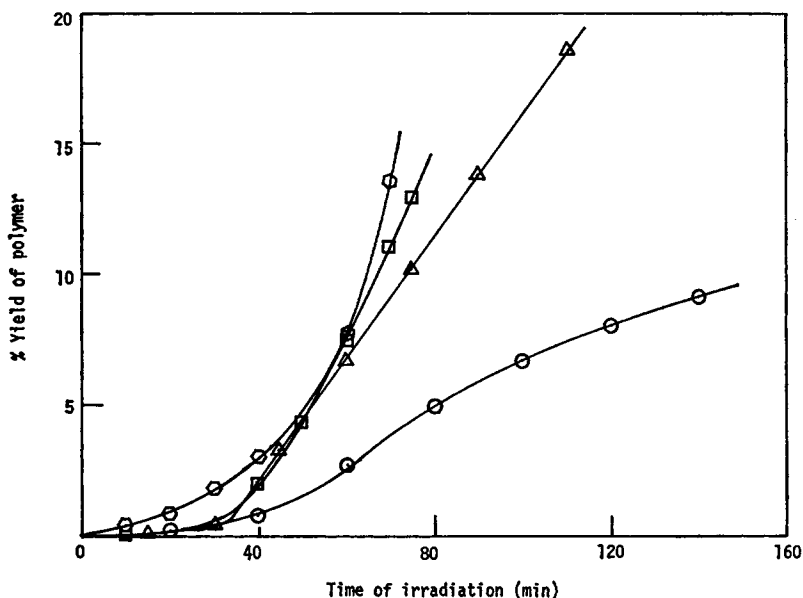


Fig. 3. Polymerization of the liquid D_4 at different temperatures: (○) 69°C; (△) 102°C; (◻) 135°C; (◊) 168°C.

thought to be at least partially due to the presence of larger quantities of ion scavengers in the monomer used.

These results suggest that, by following the techniques of Okamura et al.,¹ a large number of liquid-state polymerizations heretofore attempted without success may indeed be possible.

The assistance of the National Research Council of Canada in supporting this work is gratefully acknowledged.

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Received February 14, 1972