The Chemically Initiated Solid-State Polymerization
of Hexamethylcyclotrisiloxane

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Synopsis

The HBr-initiated solid-state polymerization of hexamethylcyclotrisiloxane has been investigated. Up to about 70% conversion, the rate of polymerization is found to be constant but the molecular weight of the polymer formed was observed to increase with conversion. Temperature did not have a marked effect on the polymerization rate as an activation energy of only 2.8 kcal/mole was observed, whereas the rate was found to be exponentially related to the HBr vapor pressure. The HBr and the radiation-initiated solid-state polymerization are compared.

INTRODUCTION

While solid-state polymerization reactions can be initiated by chemical catalysts, only a few studies have been made in this area. In the case of crystalline monomers, the chemical initiators are usually deposited onto the solid monomers. The polymerization then starts from the surface and grows either into or along the surface of the monomer crystals. In this manner, trioxane placed under n-hexane has been polymerized in the solid state using $BF_3 \cdot OEt_2$ as a catalyst.[1]

N-Vinyl carbazole has also been polymerized in the solid state using Friedel-Crafts catalysts such as $SnCl_4$, $AlBr_3$, and $FeCl_3$, and more recently gaseous catalysts such as chlorine, HCl, N_2O_4, etc.[2-4]

The present study of the solid-state polymerization of hexamethylcyclotrisiloxane (D_3) by halogen hydrides was undertaken to determine if there was any correspondence between chemical and radiation-initiated polymerizations. D_3 has been polymerized in the solid state by $SnCl_4$, but no conclusions as to the relationship between monomer state and polymerization rate or differences between chemical and radiation induced polymerization were drawn.[5]

EXPERIMENTAL

Materials

The hexamethylcyclotrisiloxane (D_3) used in these experiments was carefully purified in the manner described earlier.[6]

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Anhydrous HCl and HBr were obtained from Matheson of Canada Limited and were used as received.

HI was synthesized in the laboratory and was purified by passage through sulphuric acid.

Polymerization Procedure

The crystalline monomer (mp 64.5°C) was crushed in a mortar and the powder of mesh size 60–200 was used. About 1 g of the D_3 was weighed into a preweighed sample tube, after which the tube was attached to a vacuum manifold. After cooling the sample in liquid nitrogen, the polymerization tube was evacuated to better than 10^{-5} torr pressure. The liquid nitrogen was replaced by a water bath thermostatted at the temperature at which the reaction was to be studied. After about 1 hr, when D_3 had reached the bath temperature, the initiating gas was introduced into the tube at the desired pressure, and the system was closed by turning the stopcock provided in the system.

After the desired reaction time, the stopcock was opened to vacuum and the unreacted HBr gas and D_3 were pumped off. To complete the removal of monomer, the sample tube was heated in an oil bath at 100°C. Depending on the extent of conversion of D_3 to poly(dimethylsiloxane) (PDMS), it took from 1 to 3 min to remove the unreacted D_3. The polymer remaining was then pumped to a constant weight and the yields were determined gravimetrically.

Molecular weights were measured viscosimetrically at 25°C in toluene using the relation[7] $[\eta] = 8.25 \times 10^{-5} \bar{M}_n^{0.72}$.

The molecular weight distribution was determined by gel permeation chromatography (Waters Associate Model 200) using standard polystyrene samples for calibrations. In determining the molecular weights for PDMS, the Q method was used. The parameter Q, defined as the molecular weight per angstrom length of polymer, was calculated from the bond angles and bond lengths in a fully extended chain to be 50.6. The assumption was also made that the length of the PDMS molecule at a given elution volume was equal to that of the polystyrene molecule at the same volume. The calculations were performed according to Harmon's method.[8]

RESULTS AND DISCUSSIONS

The Polymerization Yield–Time Relationships

The chemically induced solid-state polymerizations of D_3, in the initial studies, were carried out at 30°C in the presence of HCl, HBr, and HI gases which were at a partial pressure of 3.4 cm Hg. (At 30°C, D_3 has a vapor pressure[9] of 0.6 cm Hg, and thus the total pressure read on the manometer was 4 cm Hg.) The results from these polymerizations are shown in Table I. It is clear from the results that HBr gives the highest polymerization rate, with HCl causing a considerably slower reaction and HI being

TABLE I
Polymerization of D₄ with Hydrogen Halides

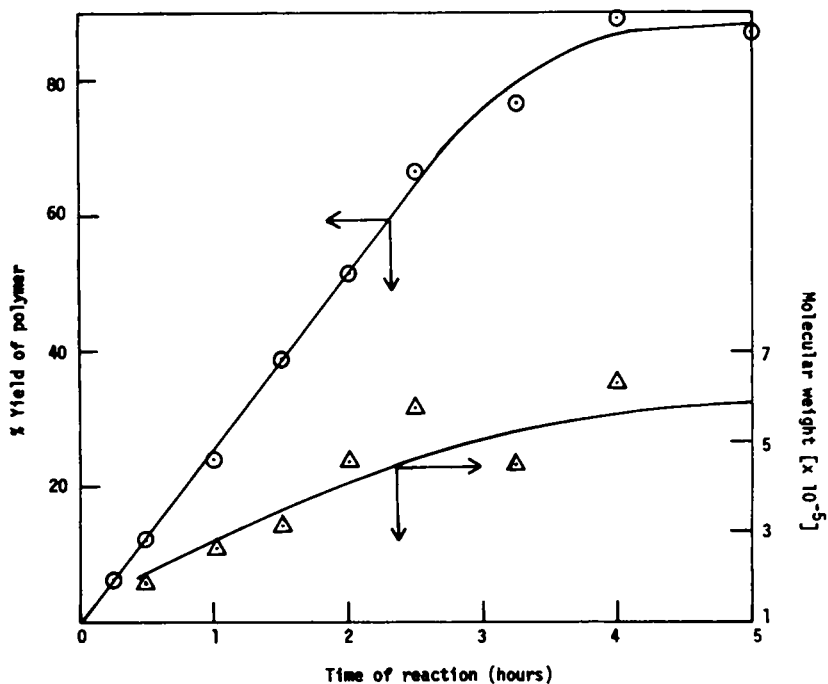| Gas used	Time of reaction	Yield of polymer, %	Yield per hr, %
HCl	2 hr	6.0	3.0
HBr	15 min	6.23	24.9
HI	8 hr	0.00	0.0

Fig. 1. Polymerization of solid D₃ with HBr: partial pressure of HrB = 3.6 cm Hg; temperature of polymerization = 30°C; (○) polymerization rate; (△) molecular weight.

inert. As a result of these observations, only HBr was used in the more detailed studies which follow.

Polymer yields and product number-average molecular weights, $\bar{M}_n$, are shown in Figure 1 for a large number of polymerizations where HBr was the catalyst.

No induction period is in evidence, and the rate of polymerization is linear up to about 70% conversion. The molecular weight of the polymer samples obtained are observed to vary in approximately the same manner as the yield. These results are in close agreement with those of Prut et al.[5] who polymerized D_3 up to 12% conversions, using $SnCl_4$ as a cationic surface initiator.

The behavior shown in Figure 1 demonstrates that the reaction is zero order in monomer concentration up to very large extents of conversion.

TABLE II

Effect of HBr Vapor Pressure on Solid-State Polymerization of D_3[a]

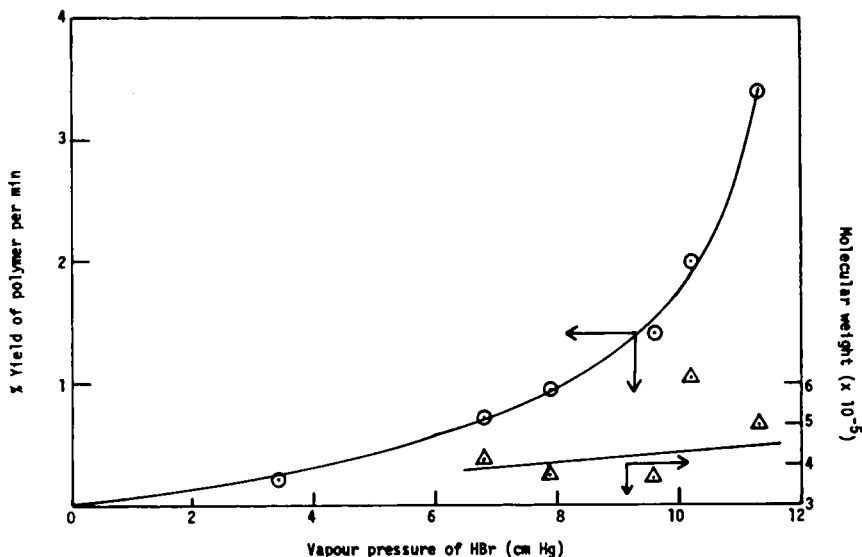| Vapor pressure of HBr, cm Hg	Time of reaction, min	Yield of polymer, %	Yield of polymer per min, %	Molecular weight $\bar{M}_n$ of polymer $\times 10^5$
3.4	30	6.69	0.223	—
6.8	30	21.60	0.720	4.16
7.9	10	9.48	0.948	3.75
9.6	12	16.99	1.414	3.67
10.2	30	60.05	2.002	6.15
11.3	10	34.22	3.422	4.93

[a] Temperature of polymerization = 30°C.

Fig. 2. Effect of HBr vapor pressure on rates of D_3 polymerization: (○) polymerization rate; (△) molecular weight.

Furthermore, the absence of an induction period indicates that diffusion of catalyst into the monomer was not a prerequisite to reaction. It is therefore concluded that this polymerization, as was the case in the irradiation-induced polymerization,[10] is initiated at the surface. The manner in which the molecular weight increases supports this proposal.

For a surface-initiated reaction, the number of initiating sites should be proportional to the amount of HBr chemisorbed on the D_3 surface. With an increase in vapor pressure, the amount of HBr chemisorbed will increase in a manner determined by the chemisorption isotherm of HBr on the D_3 surface, as will be the rate of polymerization. Therefore, the observed polymerization rate behavior with change in HBr vapor pressure, shown in Figure 2, is postulated to be the external manifestation of the chemisorption behavior of HBr on the D_3 surface. The rate of polymer-
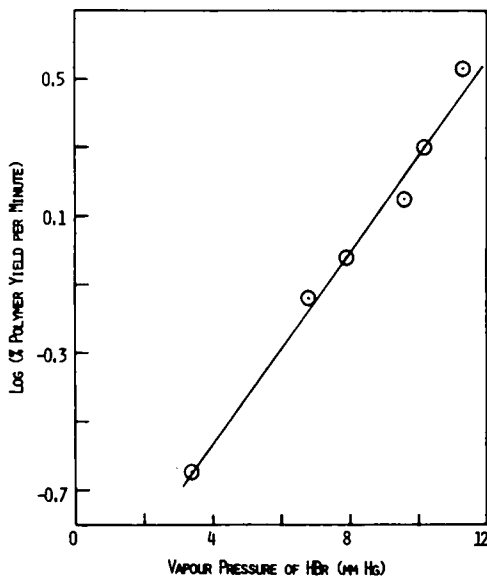
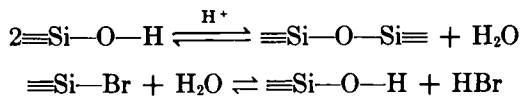Fig. 3. Log of rate of polymerization vs. HBr vapor pressure.

ization increases in an exponential manner as is seen from the linear curve obtained from the plot of the log of the rate of polymerization versus HBr vapor pressure (Table II, Fig. 3).

Reaction Mechanism for D_3 Polymerization

Hurd[11] has proposed the polymerization mechanism of D_4 with anhydrous HCl, HBr, and other acids. The polymerization of D_3 is explained along similar lines. HBr breaks the siloxane linkage in D_3 via an electrophilic attack on an oxygen atom, forming silanol and silicon halide.

$$\equiv\!Si\!-\!O\!-\!Si\!\equiv\ +\ HBr \rightleftharpoons\ \equiv\!Si\!-\!O\!-\!H\ +\ \equiv\!SiBr$$
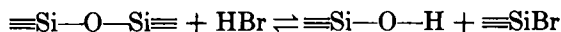
Silanols are unstable in the presence of an acid and condense, eliminating water. Moreover, the silicon bromide may react with water to give silanol and HBr:

$$2\!\equiv\!Si\!-\!O\!-\!H \xrightleftharpoons{\ H^+\ } \equiv\!Si\!-\!O\!-\!Si\!\equiv\ +\ H_2O$$

$$\equiv\!Si\!-\!Br\ +\ H_2O \rightleftharpoons\ \equiv\!Si\!-\!O\!-\!H\ +\ HBr$$

It has been reported[12] that reactivity of low molecular weight silicon compounds toward acids follow the order $D_3 \gg MM > MDM$. As commonly used in the literature, $D\ =\ \text{+O}\!-\!Si(CH_3)_2$ and $M\ =\ \text{+O}\!-\!Si(CH_3)_3$.

Therefore, the D_3 molecule is consumed preferentially owing to (i) its high reactivity with initiating HBr and (ii) its high concentration. When most of the D_3 has been used up, the reactive species begin attacking the polymer chains, and rearrangement and equilibration among the polymer

TABLE III
GPC Analysis of PDMS Obtained by HBr-Initiated Polymerization of D_3
in Solid State

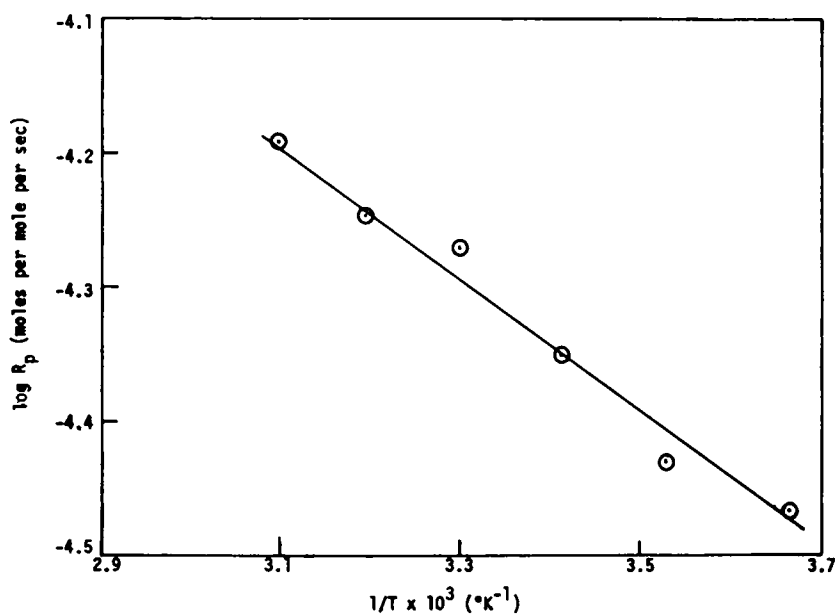| Time of reaction, hr	Conversion, %	$\bar{M}_n \times 10^5$	$\bar{M}_w \times 10^5$	$\bar{M}_w/\bar{M}_n$
0.5	37.0	1.59	2.76	1.731
1.0	68.17	1.51	2.71	1.796
1.5	88.8	2.12	3.75	1.771
2.25	89.0	3.35	5.96	1.688
3.25	89.5	3.38	5.5	1.626
20.0	89.5	1.462	2.95	2.01
20.0	89.5	1.495	3.06	2.052

Fig. 4. Arrhenius plot to determine activation energy of D_3 polymerization.

molecules take place. In this scheme, reformation of D_3 is highly un-
likely as D_3 has a ring strain energy of 3–4 kcal/mole.[13]   This is seen from
the increasing and then leveling of the molecular weights in Figure 1 and
more clearly from the gel permeation chromatograph results shown in
Table III.   At first, the molecular weights increase and molecular weight
distribution is narrower.   At longer exposure times, the $\bar{M}_w/\bar{M}_n$ approaches
2, the most probable value in equilibrated system (Table III).
   From the plot of the rates of polymerization versus inverse of tempera-
ture (Fig. 4), the activation energy E_a for the polymerization at constant
HBr pressure was found to be 2.8 kcal/mole.   This is remarkably close to
the heat of fusion of the monomer,[9] 3.7 ± 0.1 kcal/mole, and since the
polymeric product formed is in the liquid state (mp ≈ −40°C), the ac-

tivation energy appears to be simply the energy of fusion of the monomer. It should be recalled that the E_a values in the cases of the base-catalyzed liquid-state polymerization and the radiation-induced polymerization of solid D_3 were 17.5 and 7.9 kcal/mole, respectively.[13,14]

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