

POLYMERIZATION OF OCTAMETHYLCYCLOTETRASILOXANE WITH HEXAMETHYLDISILAZYL-LITHIUM AS INITIATOR*

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Abstract This work focused on the anionic polymerization of octamethylcyclotetrasiloxane (D_4 , $D = Me_2SiO_{22}$) initiated by a new kind of initiator hexamethyldisilazyl-lithium (MM^{NLi}). ^{29}Si -NMR spectroscopy and gas chromatography (GC) were used to characterize the polymerization products. The process was accelerated by adding a small amount of high activity monomer D_3 and by raising the polymerization temperature. At the end of polymerization more than 95% of the monomer was converted to polymer and only a very small amount of D_4 and D_3 remained in the polymers.

Keyword High purity polydimethylsiloxane, Octamethylcyclotetrasiloxane, Hexamethyldisilazyl-lithium, Anionic polymerization

INTRODUCTION

Polysiloxanes have many excellent properties such as resistance to high and low temperature, weatherability, good hydrophobicity, good electrical insulating properties and good biocompatibility. They are extensively used in many harsh environments, e.g. in aviation, aerospace, automobile, medical apparatus and electronic industries, etc. Moreover, the anionically initiated ring-opening polymerization of cyclosiloxane has been the most important method to prepare polysiloxane both in the industry and in the laboratory.

The traditional anionic polymerizations of cyclosiloxane initiated with potassium hydroxide or tetramethylammonium silanolate or tetra-*n*-butylphosphonium silanolate are equilibrium processes, and the polysiloxane obtained often contains about 14% cyclosiloxanes^[1]. Even after the polysiloxane was treated by distillation under vacuum, it still contained about 3%~6% macrocyclic siloxanes and other low molecular weight linear polysiloxane. These low molecular weight substances would volatilize from the rubber matrix and worsen the performance of instruments under super high vacuum if they are used in space flight and in high performance electronic products. Moreover, these low molecular weight substances could be harmful to health if they transuded from the rubber matrix that was used as materials implanted in the human body. It is essential to find new method for preparing high purity polysiloxane to satisfy these rigorous demands.

Since 1970 a number of studies have focused on the anionic non-equilibrium polymerization of cyclosiloxane initiated by organo-lithium, especially the polymerization of hexamethylcyclotrisiloxane (D_3)^[1, 2]. In this kind of non-equilibrium polymerization the lithium silanolate propagation centers have weaker alkalinity compared with potassium or sodium silanolate etc. It only turns the cyclosiloxanes into a linear polymer, but hardly attacks the polymer chains to induce rearrangement. The cyclosiloxane monomer could be converted to high polymer with nearly 100% conversion, and no macrocyclic siloxane and low molecular weight linear polysiloxanes were produced. In this way, new high purity polysiloxane suitable for applications under super high vacuum or in the human body could be expected. However, the difficulty of preparing D_3 hindered its

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practical applications. Octamethylcyclotetrasiloxane (D_4) was the most widely used cyclosiloxane monomer in the organosilicon industry. However, due to the puckered structure of D_4 , its ring strain is lower than that of the planar D_3 ring, and its ring opening is much more difficult than that of D_3 .^[3] To date few studies concerned with anionic non-equilibrium polymerization of D_4 have been reported.

In this paper the polymerization of D_4 with a new kind of anionic initiator MM^{NLi} was studied in order to develop a new route for preparing high purity polydimethylsiloxane.

EXPERIMENTAL

All solvents were A.R. grade and were treated by normal methods^[4]. D_4 was dried with CaH_2 and deaerated and purged with N_2 . D_3 was prepared in our laboratory. D_4 and D_3 monomers were examined by ^{29}Si -NMR and GC, to ensure that no other cyclosiloxanes were present. MM^{NLi} was prepared by the method of E.H. Amonoo-Neizer^[5].

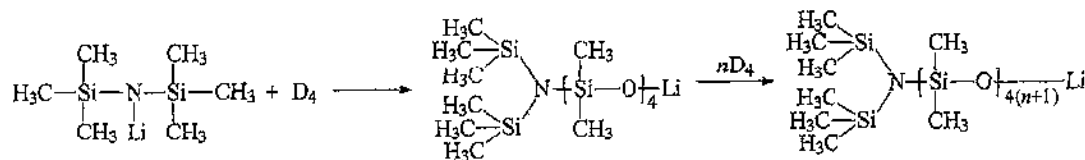
The polymerization of D_4 was performed at 60 and 100°C under N_2 atmosphere with a mechanical agitator. Dimethyl sulfoxide (DMSO) was selected as the promoter. After a certain period of time the temperature was lowered to room temperature to stop the polymerization. The obtained polydimethylsiloxane was dissolved in toluene and precipitated with ethanol. The toluene-ethanol mixture was analyzed with gas chromatography. Intrinsic viscosity, $[\eta]$ was determined with Ubbelohde-type viscometer in toluene at 30°C.

^{29}Si -NMR spectrum was recorded on a Bruker 300 MHz NMR spectrometer. The samples were dissolved in chloroform- d with tetramethylsilane (TMS) as the external standard and with $Cr(acac)_3$ as a relaxation agent. The whole polymerization process was monitored with ^{29}Si -NMR spectroscopy.

GC analysis was performed on a 103 gas-chromatograph analyzer (Shanghai analytical instrument factory) equipped with a thermal conductivity detector and a stainless steel spiral column (3 mm $\times$ 200 mm) packed with 60~80 mesh Shangshi 102 stationary phase coated with 15% di- n -nonyl phthalate. Column temperature was programmed to 400°C and the carrier gas was N_2 (60 mL/min.).

RESULTS AND DISCUSSION

In 1997 $Si-N^-$ anion derived from silazyl-lithium was first used as polymerization initiator of hexamethylcyclotrisiloxane in the preparation of star polysiloxane containing cyclotrisilazane in the polymer chain by our research group^[6]. In this work the new MM^{NLi} initiator was used to initiate the polymerization of D_4 (see Scheme 1). The peculiar properties of $Si-N$ bond impart several advantages to the new MM^{NLi} initiator. The MM^N end group linked to $Si-N$ bond could be converted into hydroxyl group or alkoxy group or the other groups through hydrolysis or alcoholysis reaction, and the living propagation center could be terminated with the needed end-capping reagent, such as dimethylvinylchlorosilane. Then a kind of polydimethylsiloxane having different functional groups at the two chain ends, i.e. multifunctional polydimethylsiloxane, could be prepared.



As shown in Table 1, D_4 did not polymerize within 26 h at room temperature (25°C). In Boileau's report^[7], the polymerization of D_4 was certain at the same temperature with Me_3SiCH_2Li as initiator, [211] cryptand as promoter and toluene as solvent. However, the polymerization process took very long time, after 100 h the yield of polydimethylsiloxane was only 76%. Thus a higher temperature was necessary to achieve the ring-opening polymerization of D_4 in a short time.

In Fig. 1, the NMR peak at $\delta = 2.6$ is assigned to the chemical shift of the MM^N end group. After polymerization for 30 min, a portion of D_4 ($\delta = -19.1$) was converted to polydimethylsiloxane ($\delta = -21.8$). It

indicates that the initiation of MM^{NLi} was definite when the temperature was raised. About 94.5% of D_4 was converted to polydimethylsiloxanes within 21 h in sample No. 4 (cf. Table 1), and only a small amount of D_4 still remained in the product, NMR peaks for other cyclosiloxanes were not observed as shown in Fig. 2. This characteristic is obviously different from that of the equilibrium polymerization.

Table 1. Polymerization results

Sample	Monomer D_4 (g)	MM^{NLi} (g)	Promoter DMSO (mL)	T ($^{\circ}C$)	t (h)	Conv. (%) ^{29}Si -NMR	$[\eta]$ (mL/g)	M ($\times 10^{-4}$) ^a
1	15.3	0.05	0.5	25	26	Not polymdZ	/	/
2	19.6	0.02	1	60	30	93.9	/	/
3	17.4	0.87	2	100	10	95	9.17	0.87
4	19.6	0.02	0.5	100	21	94.5	82	28.2
5	19.6 (3%mol D_3)	0.02	0.5	100	21	96.8	53.88	14.5

^a $[\eta] = kM^{\alpha}$, $k = 0.03$ mL/g, $\alpha = 0.63$, measured at $30^{\circ}C$ with toluene as the solvent^[8]

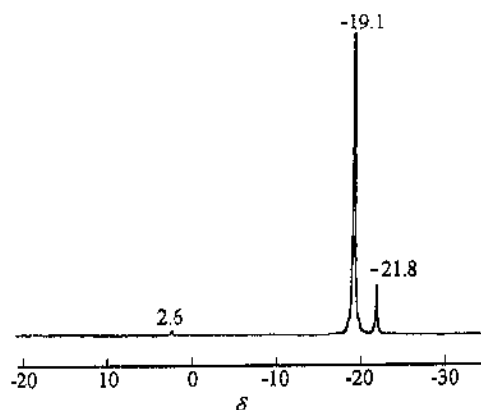


Fig. 1 ^{29}Si -NMR of polydimethylsiloxane obtained by the anionic polymerization of D_4 at $60^{\circ}C$ for 30 min

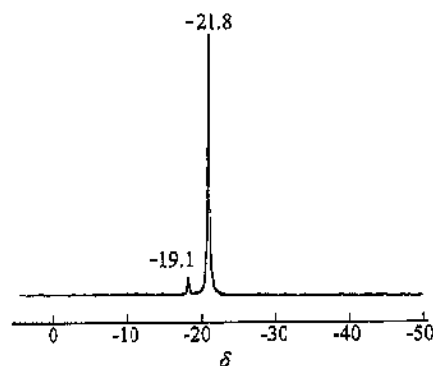


Fig. 2 ^{29}Si -NMR of polydimethylsiloxane obtained by the anionic polymerization of D_4 at $100^{\circ}C$ for 21 h

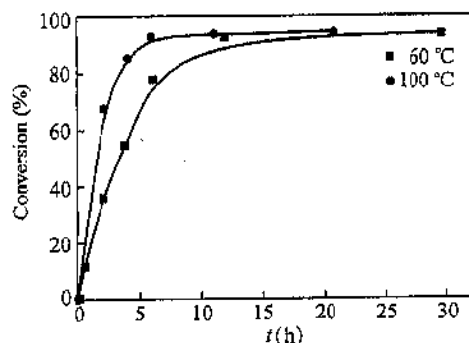


Fig. 3 Conversion of D_4 to polydimethylsiloxane at different polymerization time and at $60^{\circ}C$ and $100^{\circ}C$

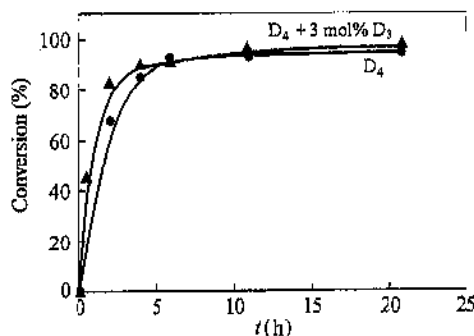


Fig. 4 Conversion of D_4 to polydimethylsiloxane at different polymerization time for sample 5 and 4 at $100^{\circ}C$

Temperature is the most important factor that affects the polymerization rate, as shown in Fig. 3. The conversion or the polymerization rate of D_4 to polymer is higher at the beginning and then flattens out with the

advance of time. The reason for this is that during polymerization the concentration of monomer is decreasing and the living centers are enclosed by polymer chains in bulk polymerization. In Fig. 4 it shows that the polymerization rate of D_4 (sample 4) was accelerated by adding a small amount of D_3 (sample 5). Within 4 h. the conversion of monomer D_4 rose to 80%, because D_3 was more easily be initiated by MM^{NLi} than D_4 , and the MM^{NLi} initiator was converted into lithium silanolate living centers more completely in sample 5 than that in sample 4. A difference in the number of living centers results in a different molecular weight of the polymer products.

The polymeric products were characterized by gas chromatography. It was found that only a very small amount of D_5 remains in the mixture of toluene and ethanol in addition to D_4 . The amount of D_5 in toluene-ethanol was too small to be detected in ^{29}Si -NMR spectrum, but it could be detected by GC analysis (Fig. 5). DMSO and this small amount of D_4 and D_5 can be easily removed by vacuum distillation. This procedure provides a very practical route for preparing high purity polysiloxane. The D_5 generated in the polymerization could only be attributed to chain rearrangement, but this "rearrangement" is very different from the typical equilibrium process. In a typical equilibrium polymerization (Fig. 6), a large amount of D_2 and a small amount of D_3 , D_5 and D_6 exist in the product. The other macrocyclic siloxanes produced in the polymerization could not be vaporized and detected by GC, but their existence was definite^[1].

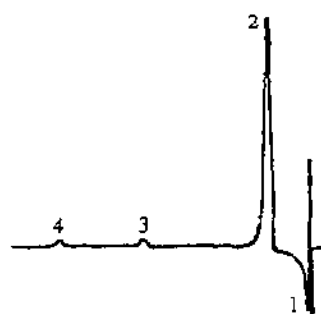


Fig. 5 GC chromatogram of the extractives from the polydimethylsiloxane (with MM^{NLi} as initiator) using ethanol-toluene as the extractants
Eluting peaks: (1) ethanol, (2) toluene, (3) D_4 and (4) D_5



Fig. 6 GC chromatogram of the products obtained from the equilibrium polymerization of D_4
Eluting peaks: (1) ethanol, (2) toluene, (3) D_3 , (4) D_4 , (5) D_5 and (6) D_6

An ideal non-equilibrium polymerization process should have all the characteristics of living polymerization. Certainly, in a non-equilibrium polymerization of D_3 with lithium silanolate living species at room temperature, the attack of living centers on the chain was more difficult than that in the polymerization of D_4 with lithium silanolate living species at higher temperature (60°C or 100°C). The effect of temperature must be the key reason for the occurrence of rearrangement. So the polymerization of D_4 initiated by MM^{NLi} at a higher temperature can not be considered as a strictly ideal non-equilibrium polymerization. However, it was markedly different from the typical equilibrium polymerization. More dependable judgement can only be obtained from subsequent research. Even so, high purity polydimethylsiloxane could still be prepared through this polymerization of D_4 after simple treatment.

CONCLUSION

Polymerization of D_4 could be achieved at a suitable temperature by using the new initiator MM^{NLi} . At a higher temperature and by the addition of a small amount of high activity monomer D_3 , the polymerization could be accelerated. But a weak rearrangement was brought about on polymerization at higher temperature. Through this process, it is feasible to prepare high purity polydimethylsiloxane.

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