Preparation of poly(dimethylsiloxane) macromonomers by the 'initiator method': 2. Polymerization mechanism

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Propagation and redistribution reactions were investigated in the non-equilibrium polymerization of hexamethylcyclotrisiloxane (D_3) by the 'initiator method' using partially lithiated alkenylsiloxanol as initiator. The findings in this study are: the condensation reaction of silanol groups takes place when the conversion of D_3 is higher than 80%; the redistribution reaction, which involves an exchange of siloxane units between two terminal silanolate groups, takes place during the course of polymerization; the redistribution reaction causes increases in the M_n and M_w/M_n of the polymers.

(Keywords: poly(dimethylsiloxane); non-equilibrium polymerization; initiator method; redistribution reaction)

INTRODUCTION

The synthesis and applications of poly(dimethylsiloxane) macromonomers (PDMS-M), prepared by non-equilibrium (or minimum equilibrium) polymerization of hexamethylcyclotrisiloxane (D_3) using a lithium catalyst, have previously been investigated[1-3]. Several studies have been concerned with the mechanism of polymerization. For example, Frye and coworkers[4] showed that the reaction of organolithium reagents with D_3 generated lithium n-butyldimethylsilanolate ($BuMe_2SiOLi$) instead of the simple adduct ($Bu-(Me_2SiO)_3Li$). Fessler and Juliano[5] studied the reactivity of solvated $BuMe_2SiOLi$ with D_3 and reported that $Bu-(Me_2SiO)_n-Li$ underwent a redistribution reaction to increase and decrease its number of dimethylsiloxane units (*Scheme 1*). Hölle and Lehnen[2] and Boileau[6] reported the kinetics of ring-opening polymerization.

Scheme 1

$$\text{n-Bu-}(Me_2SiO)_pLi + \text{n-Bu-}(Me_2SiO)_qLi \rightarrow$$

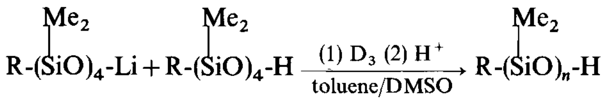
$$\text{n-Bu-}(Me_2SiO)_{p+1}Li + \text{n-Bu-}(Me_2SiO)_{q-1}Li$$

Me: methyl, Bu: butyl

However, little work has been done to understand the relationship between the redistribution reaction and ring-opening polymerization or to define the SiOH–SiOLi exchange in polymerization where partially lithiated silanol is the initiator, although the existence of such exchange was suggested many years ago[1].

In the course of our investigation of the 'initiator method'[7], which utilizes partially lithiated alkenylsiloxanol as an initiator (*Scheme 2*) and gives PDMS-M containing an alkenyl group at one end, several facts regarding what is happening during non-equilibrium polymerization have been found.

Scheme 2



$$\text{R-}(\overset{Me_2}{Si}O)_4\text{-Li} + \text{R-}(\overset{Me_2}{Si}O)_4\text{-H} \xrightarrow[\text{toluene/DMSO}]{(1)\ D_3\ (2)\ H^+} \text{R-}(\overset{Me_2}{Si}O)_n\text{-H}$$

R = vinyl, hexenyl

In this paper we present data on the rate of propagation and on molecular-weight growth, discuss the redistribution reaction catalysed by lithium and try to establish what is happening during non-equilibrium polymerization.

EXPERIMENTAL

Materials

D_3 was distilled under reduced pressure and used as a 50 wt% solution in toluene which had been dried with molecular sieves (activated at 350°C for 3 h). Dimethylvinylchlorosilane was distilled under reduced pressure. n-Butyllithium (n-BuLi) in hexane was used as purchased. Solvents were distilled and dried over activated molecular sieves.

Preparation of $H_2C{=}CH-(Me_2SiO)_3-Si(Me_2)Cl$ (VD_3Cl)

Into a dry flask were placed D_3 (222.5 g, 1 mol), dimethylformamide (7.3 g, 0.1 mol) and CH_3CN (75 g, 1.83 mol). Dimethylvinylchlorosilane (120.7 g, 1 mol) was added with vigorous stirring at room temperature. After the solution had been mixed for 3 h at room temperature, the reaction was stopped by distilling off CH_3CN. VD_3Cl was obtained by distillation *in vacuo* (b.p. 61.5–63°C/1 torr; purity 99.9% by gas–liquid chromatography (g.l.c.); 44% yield).

Preparation of $H_2C{=}CH-(Me_2SiO)_4-H$ (VD_3OH)

Into a flask were placed 80 g of ice, 150 g of water, $NaHCO_3$ (11 g, 130 mmol) and 100 ml of diethyl ether (Et_2O), and then they were mixed. The flask was cooled with an ice–NaCl bath. VD_3Cl (30 g, 87 mmol) was added dropwise slowly with vigorous stirring so that the temperature did not exceed 0°C. After the addition was completed, the mixture was allowed to warm to room temperature. The water layer was separated and extracted with Et_2O. The combined ether layer was washed with water and dried over Na_2SO_4. The VD_3OH was obtained by stripping off the Et_2O *in vacuo* at room

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temperature (purity 99.5% by g.l.c.; 97% yield). VD_3OH was stable for about one week when stored in a polyethylene bottle and refrigerated.

Polymerization

All procedures were conducted under dry nitrogen. Into a dry 100 ml vial was charged a specified amount of VD_3OH. A specified amount of n-BuLi was added with stirring. Immediately after the completion of n-BuLi addition, a mixture of D_3/toluene/dimethylsulphoxide (DMSO) was added as quickly as possible. The vial was immersed in a water bath thermostated at 25±0.2°C. Periodically 5 ml aliquots were withdrawn from the solution and quenched with a slight excess of acetic acid to the added n-BuLi. Each aliquot was then analysed by g.l.c. to determine the D_3 conversion, and some were analysed by gel permeation chromatography (g.p.c.) to determine molecular-weight growth.

Redistribution

All procedures were conducted under dry nitrogen. Into a dry 30 ml vial was charged VD_3OH (1 g, 3.08 mmol). n-BuLi (1.64 M) was added with stirring (BuLi/VD_3OH molar ratio: 1.0 and 0.1). Immediately after the completion of the addition of n-BuLi, a mixture of toluene/DMSO (1/0.024 weight ratio) was added. The vial was immersed in a water bath thermostated at 25±0.2°C. Periodically 1 ml aliquots were withdrawn from the solution and quenched with one drop of acetic acid. Each aliquot was then analysed by g.l.c.

Measurements

G.l.c. analysis was done using a Shimadzu GC-7 AG chromatograph equipped with a thermal conductivity detector and a glass spiral column (3 mm x 2.1 m) packed with Chromosorb W coated by SE-30 (1.5%). The carrier gas was helium. Silanol compounds were successfully detected by this instrument without any derivatization. Supercritical fluid chromatography (s.c.f.c.) was used to observe the molecular distribution of the polymers with a resolution of each degree of polymerization (number of repeating units). The instrument was a Lee Scientific 501 SCFC model equipped with a flame-ionization detector and a glass capillary column (50 μm x 20 m) coated with SE-54 (0.25 μm thickness). The mobile phase was CO_2, the density of which was increased from 0.14 to 0.76 g ml^{-1}. G.p.c. analysis was done using a Tosoh HLC-802A model. The eluent was toluene and the columns were TSK G3000H8, 4000H8, 5000H6 and 6000H6. The detector was a refractometer and standard PDMS samples were used for calibration.

RESULTS AND DISCUSSION

Polymerization kinetics

Two sets of polymerizations were done to obtain the reaction order for DMSO, which is the solvating agent for the lithium catalyst, as seen in *Table 1*. In the first set the lithiation ratio was 1.0 and in the second set it was 0.1.

As Hölle and Lehnen reported[2], the polymerization reaction was first-order with respect to D_3. The relative rate constant was obtained from the slope of the plot of $\log([D_3]_0/[D_3]_t)$ as a function of polymerization time, where $[D_3]_0$ is the initial concentration of D_3 and $[D_3]_t$ is the concentration of D_3 at the observation time t. If the conversion of D_3 was smaller than 0.8, all plots gave straight lines. The reaction order for DMSO was calculated from the slope of each line and the molar concentration of DMSO. The average of the reaction orders obtained for DMSO was 2, which means two molecules of DMSO solvate one lithium silanolate.

Table 1 Polymerization with varying [DMSO]. The values shown are D_3 conversion by g.l.c. (%)

Time (min)	Lithiation ratio[a]	1.0			0.1		
	[DMSO] (mol l^{-1})	0.23	0.49	0.71	0.39	0.54	0.81
	[VD_3OH]	0.086	0.086	0.086	0.32	0.32	0.32
	[n-BuLi]	0.086	0.086	0.086	0.032	0.032	0.032
	[D_3]	3.89	3.89	3.89	3.89	3.89	3.89
5				29			
10				54			
15		14	42	72			57
30		26	71		26	36	81
60		47			46	62	
90		64			61	79	

[a] [n-BuLi]/[VD_3OH] (molar ratio)

Table 2 Polymerization with varying lithiation ratio. The values shown are D_3 conversion by g.l.c. (%)

Time (min)	Lithiation ratio	1.0	0.1	0.01
	[VD_3OH]	0.086	0.086	0.086
	[n-BuLi]	0.086	0.0086	0.00086
	[D_3]	3.89	3.89	3.89
	[DMSO]	0.23	0.23	0.23
15		14		
30		26		
60		47	29	14
90		64		
120			58	31
180			75	46
240				58

The effect of lithiation ratio ([n-BuLi]/[VD_3OH]) on the propagation rate was investigated and the result is shown in *Table 2*. As expected, the larger the lithiation ratio, the faster the polymerization.

Polymer growth

In this series, each molar concentration was set as follows: [VD_3OH] = 0.32, [D_3] = 3.89, [DMSO] = 0.27, and [n-BuLi] was varied from 0.32 to 0.0016 mol l^{-1} (lithiation ratio = 1.0 to 0.005). The molar ratio of DMSO to lithium silanolate was set at a relatively low value so that the polymerization did not proceed too fast. The propagation rate was not largest when the lithiation ratio was 1.0 as seen in *Figure 1* because of the lack of free DMSO. It was largest with the lithiation ratio 0.2 when each lithium silanolate can take two molecules of DMSO.

The observed M_n values are plotted in *Figure 2* as a function of D_3 conversion. Great deviations from the calculated M_n, based on D_3 conversion, are seen when the conversion is larger than 0.8. The reason for the deviations is assumed to be silanol condensation (*Scheme 3*).

Scheme 3

$$2Vi(Me_2SiO)_nH \xrightarrow{Li} Vi(Me_2SiO)_{2n-1}Si(Me_2)Vi + H_2O$$

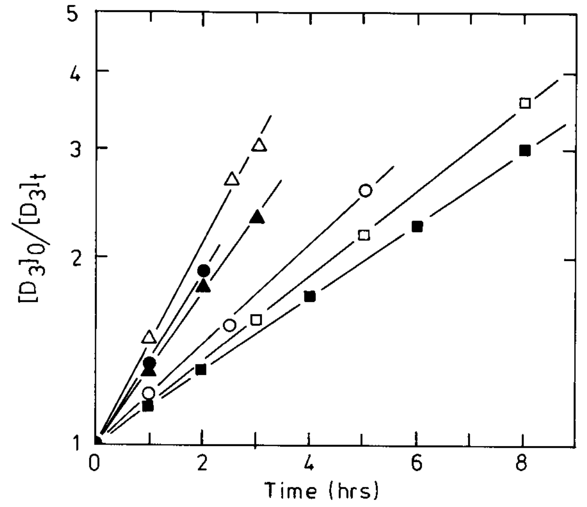


Figure 1 Polymerization of D_3 with various lithiation ratios: (○) 1.0; (●) 0.5; (△) 0.2; (▲) 0.1; (□) 0.01; (■) 0.005. $[D_3]_0$ is the initial concentration of D_3, and $[D_3]_t$ the concentration of D_3 at observation time t

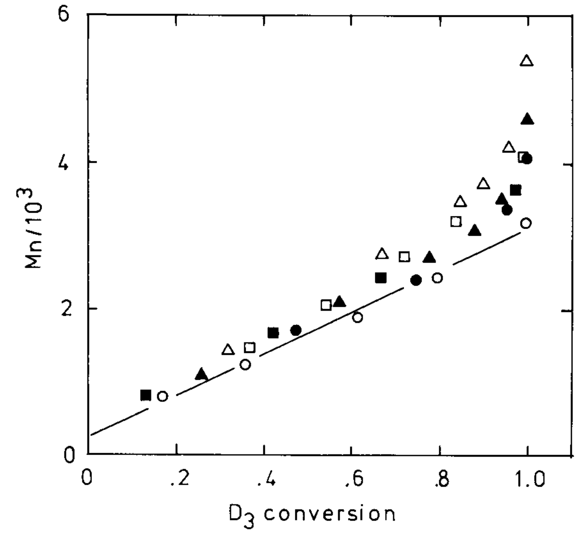


Figure 2 Plots of M_n as a function of D_3 conversion with various lithiation ratios: (○) 1.0; (●) 0.5; (△) 0.2; (▲) 0.1; (□) 0.01; (■) 0.005. The straight line shows calculated M_n

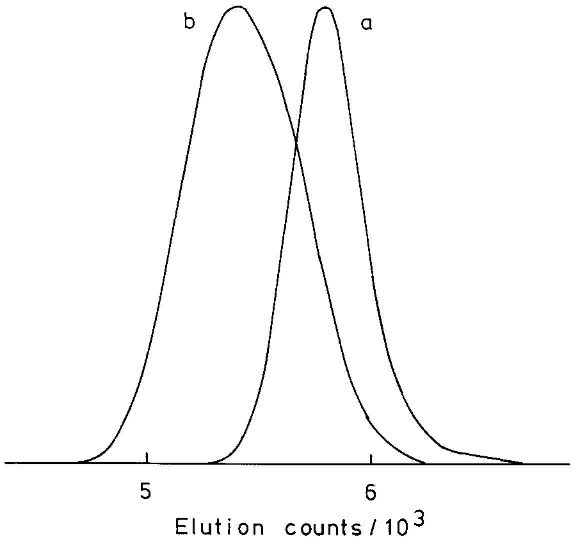


Figure 3 G.p.c. traces of a sample (lithiation ratio = 0.1; D_3 conversion = 1.0) before and after hydrosilylation with $HMe_2SiOSiMe_2H$: trace a, before hydrosilylation (M_n = 4210); trace b, after hydrosilylation (M_n = 12000)

In order to confirm the occurrence of condensation, a sample (lithiation ratio = 0.1 and D_3 conversion = 1.0) was end-capped with a trimethylsilyl group and allowed to react with $HMe_2SiOSiMe_2H$ in the presence of a Pt catalyst. *Figure 3* shows the g.p.c. traces of the sample before and after the hydrosilylation. Condensation was confirmed by the broadening of the molecular-weight distribution upon hydrosilylation, which is in contrast to the absence of such broadening for a sample whose D_3 conversion was 0.75[7].

It is seen in *Figure 2* that the observed M_n values are in good agreement with calculated ones for samples of lithiation ratio 1.0. The major reason for this is, of course, that there are no condensable silanol groups in the reaction mixture. Other samples have slightly higher observed M_n even when conversion is smaller than 0.8. The mechanism for the slight increase of M_n is discussed in the later part of this paper.

Redistribution

As Fessler and Juliano reported[5], lithium organosiloxanolates undergo a redistribution reaction (reshuffling). They proposed that the reshuffling occurs at the terminal silanolate–silicon atoms so that the molecular structure is retained (no bifunctional silanolate oligomer was found).

Figure 4 shows the g.l.c. patterns for a sample of VD_3OH before and 10 min after the addition of n-BuLi. It is seen that various molecules having different molecular weights came out. *Table 3* shows the g.l.c. areas of each peak at various observation times. The assignment of peaks was done by assuming that the difference between each pair of adjacent peaks is the difference of the number of silicon atoms.

In *Table 4* computer simulation results of reshuffling are listed. The assumption for the simulation is that each molecule gains or loses only one Me_2SiO unit in one reshuffling step, and these processes occur at similar rates (15% for each in the case of *Table 4*). The good agreement

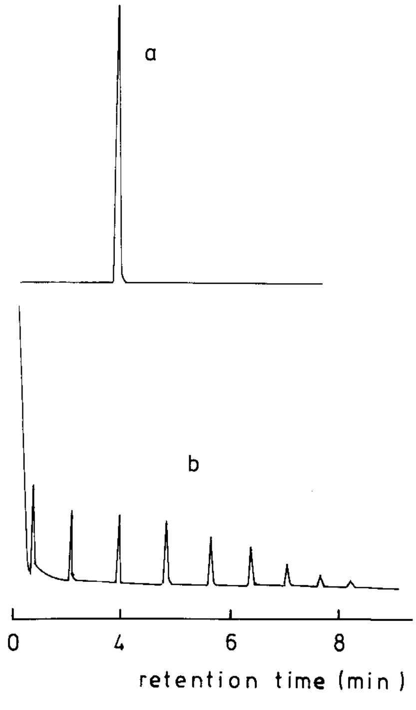


Figure 4 G.l.c. patterns of redistributed Vi–$(Me_2SiO)_4$–H: trace a, before the addition of n-BuLi; trace b, 10 min after the addition of n-BuLi, followed by quenching with acetic acid

Table 3 Reshuffling of VD_3OH. Values shown are g.l.c. areas of peaks

Time (min)	Number of Si atoms 1	2	3	4	5	6	7	8	9	10	11	12	13
Lithiation ratio 1.0													
1	–[a]	0	17	72	10	0.5							
3	–	0	23	59	16	2.2							
10	–	9	28	37	20	5.7	1.0						
60	–	18	23	21	16	11	6.2	3.5	1.4				
Lithiation ratio 0.1													
0.2	–	0	13	69	16	1.9							
3	–	16	17	23	21	13	6.3	2.4	0.6				
10	–	22	14	16	15	13	9.4	6.2	3.3	1.3			
60	–	22	15	14	12	10	8.3	6.8	4.9	3.5	2.5	1.5	0.6

[a] $H_2C{=}CH{-}Si(Me_2)OH$ could not be detected because of interference of solvent peak

Table 4 Computer-simulated reshuffling

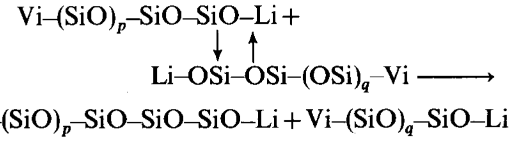
No. of reshuffling (times)	Number of Si atoms 1	2	3	4	5	6	7	8	9	10	11	12	13
1	0	0	15	70	15								
2	0	2.3	21	54	21	2.3							
4	0.9	6.9	23	38	23	6.9	0.9						
10	5.1	13	20	23	20	12	5.1	1.6	0.4	0.1			
26	8.0	16	16	14	11	8.1	5.1	2.9	1.4	0.6	0.2		
45	7.8	15	15	14	12	10	8.3	6.3	4.4	2.9	1.8	1.0	0.5

between the data in *Tables 3* and *4* indicates that the mechanism proposed by Fessler and Juliano (*Scheme 2*) is applicable to this study.

It is seen from *Tables 3* and *4* that the reshuffling is very fast especially at lithiation ratio = 0.1. The experimental result for 3 min corresponds to 10 reshuffling steps in the simulation, whereas it corresponds to the distribution with only two reshuffling steps for lithiation ratio = 1.0. This means that silanol–silanolate exchange is extremely fast and the reshuffling is accelerated by the decrease of lithium (relative increase of DMSO).

Fessler and Juliano[5] concluded that the redistribution reaction might be unimportant in non-equilibrium polymerization because the concentration of active ends is small. However, the s.c.f.c. pattern of a polymer prepared by the 'initiator method' shows a wide molecular-weight distribution, as shown in *Figure 5*. This wideness and the fact that every third peak is not larger than the other two are proof of reshuffling during the polymerization. (If there were no reshuffling, the degree of polymerization of each molecule would be $3n+4$). Since it was confirmed in previous reports[7,8] that the molecular structure was very well retained (only and exactly one terminal vinyl group per chain), the reshuffling during the polymerization is assumed to occur only at the terminal silanolate–silicon atoms (*Scheme 4*), as is the case of the absence of D_3.

Scheme 4



$$\begin{array}{c} Vi{-}(SiO)_p{-}SiO{-}SiO{-}Li + \\ \downarrow\ \uparrow \\ Li{-}OSi{-}OSi{-}(OSi)_q{-}Vi \longrightarrow \\ Vi{-}(SiO)_p{-}SiO{-}SiO{-}SiO{-}Li + Vi{-}(SiO)_q{-}SiO{-}Li \end{array}$$

Computer simulation was applied to the combination of reshuffling and propagation. *Figure 6* shows the results of two simulations. The following assumptions were made based on a rough comparison of the propagation rate and reshuffling speed.

(1) In total 800 chances of reshuffling or propagation.

(2) The probability of reshuffling is 0.2 for one set and 0.02 for the other.

(3) The probability of propagation is 0.01. So, eight molecules of D_3 should be incorporated on average.

The shape of the molecular distribution is very similar to the s.c.f.c. pattern (*Figure 5*). It is also seen that the observed M_n (2330) is slightly larger than the calculated M_n (2105) when the probability of reshuffling is 0.2. When it is 0.02, the observed M_n (2160) is closer to the calculated value. It has become clear that the reshuffling causes the increase of M_n and broadening of the molecular-weight distribution. In *Figure 2*, M_n of the sample for lithiation ratio = 1.0 was very close to the calculated M_n, because the reshuffling was less frequent than for other samples.

CONCLUSIONS

In the non-equilibrium polymerization of D_3 by the 'initiator method', the following has been made clear in this study.

(1) The reaction order for DMSO in the polymerization is 2.

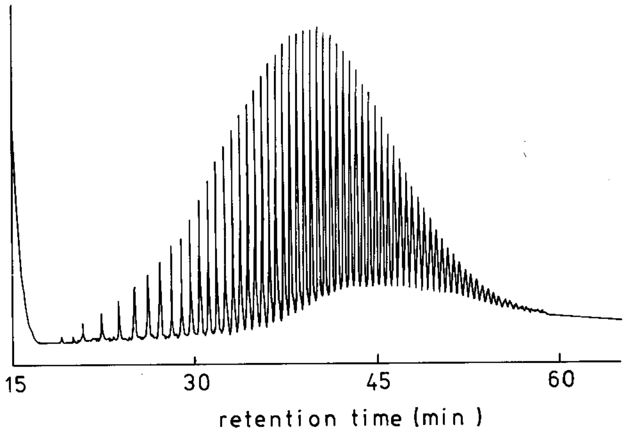


Figure 5 Supercritical fluid chromatogram of a polymer prepared by the 'initiator method'. Intended structure: $H_2C{=}CH{-}(Me_2SiO)_{29}{-}H$

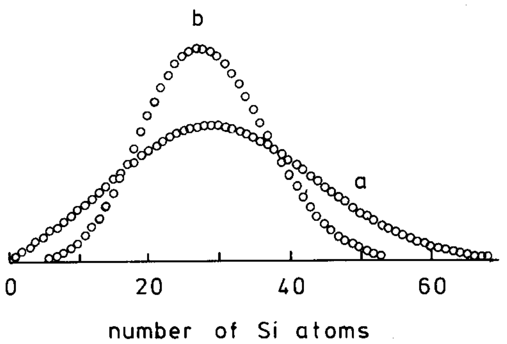


Figure 6 Patterns of molecular distribution obtained by the computer simulation: curve a, probability of reshuffling 0.2, propagation 0.01 ($M_n = 2330$, $M_w/M_n = 1.18$); curve B, probability of reshuffling 0.02, propagation 0.01 ($M_n = 2160$, $M_w/M_n = 1.09$)

(2) The condensation reaction of silanol groups takes place when the conversion of D_3 is higher than 80%.

(3) The redistribution reaction, which involves the terminal silanolate–silicon atoms that withdraw one siloxane unit from one molecule and add it to the other, takes place during the course of polymerization.

(4) The redistribution reaction is accelerated when the lithiation ratio is 0.1 and causes the increase of M_n and M_w/M_n.

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