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The Effect of Phase-Transfer Catalysts on Polysilane Formation

S. Gauthier and D. J. Worsfold*

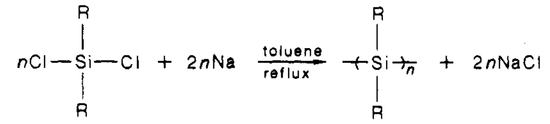
National Research Council of Canada, Ottawa, Ontario, Canada K1A 0R9.

Received August 22, 1988; Revised Manuscript Received November 2, 1988

ABSTRACT: Polysilanes are most often prepared by a Wurtz-type coupling of organodichlorosilanes with sodium metal in refluxing toluene. The addition of a catalytic amount of crown ether to the reaction mixture was found to increase the rate of disappearance of the monomer with increasing crown ether concentration, suggesting that anionic species are involved in the polymerization mechanism. Higher yields of polymer relative to cyclic material were obtained, and the polymer displays a monomodal distribution. Better reproducibility of the yields and molecular weight of the polymers can be achieved. The presence of cryptand was found to have similar effects although some degradation of the polymer upon continued refluxing of the reaction mixture was observed. Degradation experiments on poly(*n*-hexylmethylsilane) with sodium in refluxing toluene showed that the polymer degraded to cyclics in a few minutes with cryptand but not with crown ether.

Introduction

Polysilanes display a range of properties such that their usefulness in a variety of applications such as precursors to silicon carbide, photoresists, or photoconductors, is being investigated.[1,2] The polymers are most often prepared by coupling of organodichlorosilanes with sodium metal in refluxing toluene.[3-5]



$$n\text{Cl}-\underset{\text{R}}{\overset{\text{R}}{\text{Si}}}-\text{Cl} + 2n\text{Na} \xrightarrow[\text{reflux}]{\text{toluene}} \left(\underset{\text{R}}{\overset{\text{R}}{\text{Si}}}\right)_n + 2n\text{NaCl}$$

Unfortunately, the yields in polymer and the reproducibility of the reaction are usually quite poor.[1,2] The mechanism of the polymerization of dichlorides to polysilanes is still uncertain. Indeed, it is even suspected that more than one mechanism may be involved. Although appearing to be a condensation type polymerization, the appearance of high molecular weight material when little dichloride has reacted and in nonstoichiometric reactions argues against this.[6] This type of behavior is usually associated with a chain-growth process, with active radical or ionic chain ends propagating the polymerization. Zeigler has suggested[7,8] that the polymerization of dichlorosilanes with sodium occurs through a radical mechanism. Miller and his co-workers have found that the addition of a small amount of dimethoxyethane or other similar complexing ethers produced an increase in the yield of polymer.[9] Although they had first attributed this effect to the presence of anionic chain propagating species, more recent experiments showed that the addition of small amounts of a nonpolar solvent such as heptane had a similar effect on the polymerization.[1]

It is possible that two different mechanisms are active in these polymerizations and that different reaction conditions promote one mechanism over the other. This could also explain the occurrence of two major peaks in the GPC curves of these polymers. GPC traces for the polymerization of phenylmethyldichlorosilane and *n*-hexylmethyldichlorosilane are shown in Figure 1. The material giving rise to the PI peak has been identified as cyclic pentamers for *n*-hexylmethyldichlorosilane and for phenylmethyldichlorosilane.[6] This cyclic material often represents an appreciable fraction of the products and cannot be transformed into polymer. The curve shows a bimodal distribution (PII and PIII) in the polymeric region. It has been possible to increase the yield in PIII to some extent by conducting the polymerizations at lower stirring speed (lower surface area of sodium metal);[6] nevertheless, the

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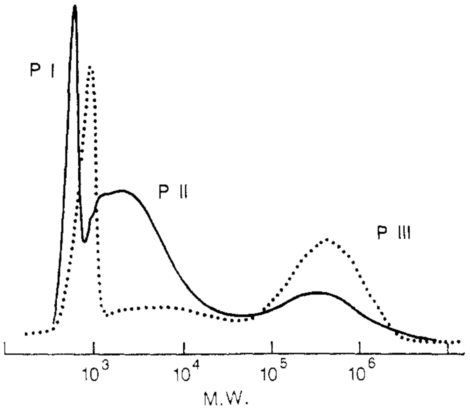
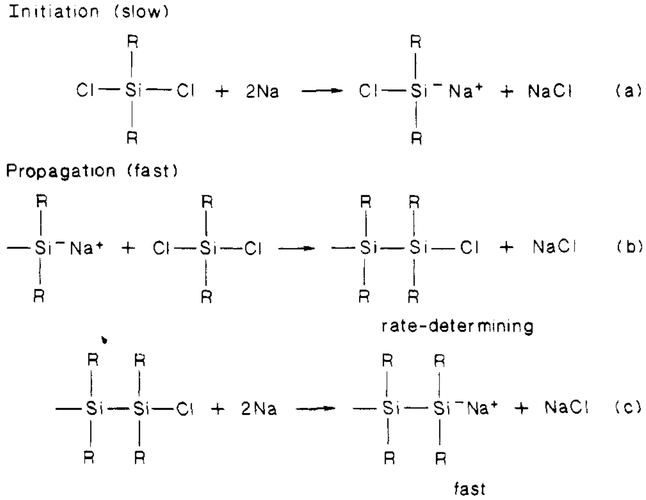


Figure 1. Typical GPC traces of the complete polymerization mixtures: ···, n-HexMeSiCl$_2$; —, PhMeSiCl$_2$.

Scheme I

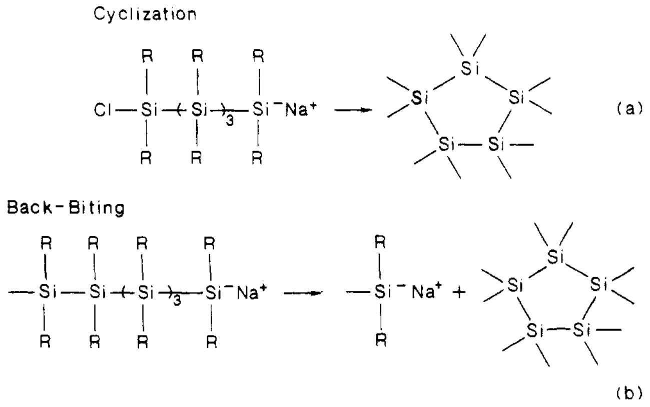


molecular weight distribution and the overall yield in polymer are often difficult to reproduce. It would be advantageous to find reaction conditions that would minimize the production of the cyclic material and increase the reproducibility in the yield of polymer.

A two-stage mechanism was proposed for the propagation step of this polymerization.[10] The initiation was suggested to be a very slow reaction of the dichloride with the Na metal to form a Na-ended chain. In the propagation, the rate-determining step appeared to be the reaction of this end with more dichloride followed by rapid reaction with the Na metal to regenerate the Na-ended chain (Scheme I). Two different mechanisms are possible for the formation of cyclic material[6] (Scheme II). In order to investigate the possibility that anionic species are contributing to the polymerization process and in the hope of increasing the yields in polymer, a catalytic amount of a phase-transfer catalyst was added to the standard polymerization mixture. It was found to have an appreciable effect on the disappearance of the monomer as well as on the molecular weight distribution of the products.

Phase-transfer catalysts are known to promote reactions involving anionic species. There are several types of phase-transfer catalysts, the most frequently used being quaternary ammonium salts, crown ethers, and cryptands. Phase-transfer catalysts have found numerous applications in polymer chemistry.[11-13] Cryptands have been used to dissolve alkali metals in polar and nonpolar solvents to form electrides. These solubilized metals may then initiate the anionic polymerization of vinylic monomers.[14,15] Considerable increases in the polymerization rates and in the molecular weights of the polymers produced were generally observed. The use of cryptands in conjunction with the usual organometallic or radical anion initiators resulted in the same improvements in rates, yields, and molecular weights.[14,15] This publication describes investigations of the influence of the presence of crown ethers and cryptands on the reductive coupling polymerization of n-hexylmethyldichlorosilane. The rate of disappearance of the monomer and the molecular weight distribution of the products were monitored as the concentration and the nature of the phase-transfer catalyst, the stirring speed, and the solvent were varied. Because of its very fast rate of polymerization, only a few experiments were conducted with phenylmethyldichlorosilane.

Scheme II



Experimental Section

1. **Polymerizations.** The polymerizations were conducted under nitrogen, in a four-neck flask equipped with a nitrogen inlet, a mechanical stirrer, and a condensor. Samples of the reaction mixture were withdrawn through the arm positioned at the front of the flask.

Dry toluene (40 mL) was transferred with a syringe to the reaction flask and heated to reflux. Freshly cut sodium (3.5 g, a 1.5-fold excess) was added to the refluxing solvent and the stirrer speed adjusted to the desired rate. The phase-transfer catalyst was added and the heating mantle removed. Freshly distilled dichlorosilane monomer (10 mL) was then carefully syringed in; the hexylmethyldichlorosilane monomer could usually be added fairly rapidly (30 s) and without cooling of the reaction mixture. Extreme care had to be exercised, however, with phenylmethyldichlorosilane due to its much greater rate of polymerization. The phenylmethyldichlorosilane monomer was thus added dropwise at a rate sufficient to maintain gentle reflux. The mixture was refluxed for 2 or 3 h. Samples were withdrawn from the reaction mixture at different intervals and analyzed by GC and GPC. The mixture was then cooled in an ice bath and water added carefully to destroy the excess sodium and any active chain ends.

The reaction mixture was washed with water three times and the polymer recovered by precipitation of the toluene solution into isopropanol.

2. **Degradation Experiments.** Poly(n-hexylmethylsilane) (0.5 g) was dissolved in 30 mL of dry toluene, and the mixture set to reflux. Sodium metal (1 g) was added; the mixture was stirred until all of the metal had melted. The phase-transfer catalyst (0.25 mol %) was then added and the progress of the reaction monitored by GPC.

3. **Materials.** Toluene was stirred over portions of concentrated sulfuric acid until the acid remained colorless. It was then washed with water, dried over calcium hydride, degassed, and stored on a high vacuum line. About 50 mL was distilled into a dry flask before each polymerization.

Phenylmethyldichlorosilane (Petrarch) and n-hexylmethyldichlorosilane (Petrarch) were fractionally distilled under reduced pressure (10 mmHg, 78 and 71 °C, respectively) immediately before use.

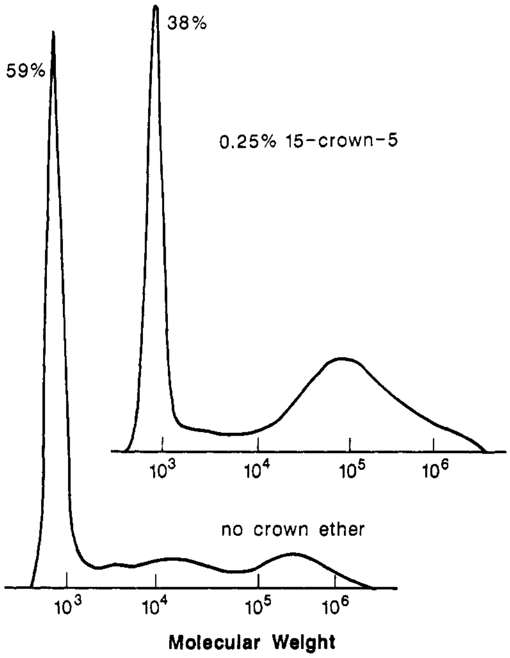


Figure 2. Molecular weight distributions for the polymerization of n-HexMeSiCl$_2$ in the absence and in the presence of crown ether.

The phase-transfer catalysts 15-crown-5 (Aldrich) and Kryptofix 222 (Merck-Schuchardt) were used without further purification.

A 1-lb lump of sodium (Anachemia, packed under nitrogen) was divided into four or five portions and stored in petroleum ether until use. The amount of sodium required for a polymerization was cut from these blocks, exposing fresh surfaces, and added immediately to the refluxing toluene.

4. Chromatography. Gas chromatographic analyses of the amount of monomer remaining in the reaction mixture were conducted on a Perkin-Elmer 3920 B chromatograph equipped with an OV-17 column. The rate of disappearance of monomer was determined by the change in the monomer/toluene ratio with time.

Gel permeation chromatographic curves were obtained on microstyragel columns using tetrahydrofuran as eluent. Before the analyses, the samples were washed with water three times and the toluene was evaporated under an air flow. A small amount of the resulting mixture was dissolved in THF, filtered, and injected into the chromatograph. The molecular weights given are based on a polystyrene calibration.

Thin-layer chromatography was performed on Baker-flex silica gel sheets; hexanes was used as eluent.

Results and Discussion

The influence of the presence of phase-transfer catalysts on the reductive coupling of organodichlorosilanes was investigated by looking at the rate of disappearance of the monomer and at the molecular weight distribution of the products as the reaction progressed. It had been found previously[10] that quantitative kinetic studies could not be conducted in these systems due to reaction variation in the shape of the sigmoidal curves usually obtained with these systems. These variations were attributed to the heterogeneous nature of the reaction and variations among different batches of dichloride used, despite redistillation. Information, however, may still be obtained from the study of the rate of disappearance of the monomer by qualitative comparison of results obtained under different reaction conditions.

Addition of 0.25 mol % of 15-crown-5, a crown ether specific for sodium ion, to a polymerization mixture under conditions that would normally give a poor yield of polymer, was found to have a profound effect of the molecular weight distribution of the products. The most important change was that the molecular weight distribution became virtually monomodal in the polymeric region (Figure 2). The yield of polymer also becomes less dependent on variables such as stirrer speed and is consistently good in relation to the yield of cyclic material. The variation of the product distribution with reaction time is shown in Figure 3. As was found for polymerizations conducted without phase-transfer catalyst,[6] high polymer is present in the mixture before total consumption of the monomer (40 min), suggesting the occurrence of a chain process. As the last of the monomer is consumed, the proportion of product found at an intermediate molecular weight (PII) decreases and disappears almost entirely. It thus appears that the polymer chains in PIII are formed by a continuous growth mechanism and then terminate. But the polymeric chains found in PII at intermediate conversions can still increase in molecular weight, either by coupling or chain growth. The proportion of cyclic material PI stays virtually unchanged (within experimental error) throughout the reaction. This could be an indication that the cyclic material is formed by a cyclization process, soon after initiation. Figure 3 shows that further refluxing of the polymerization mixture after total consumption of the monomer (40 min) has little effect of the molecular weight or the distribution of the products.

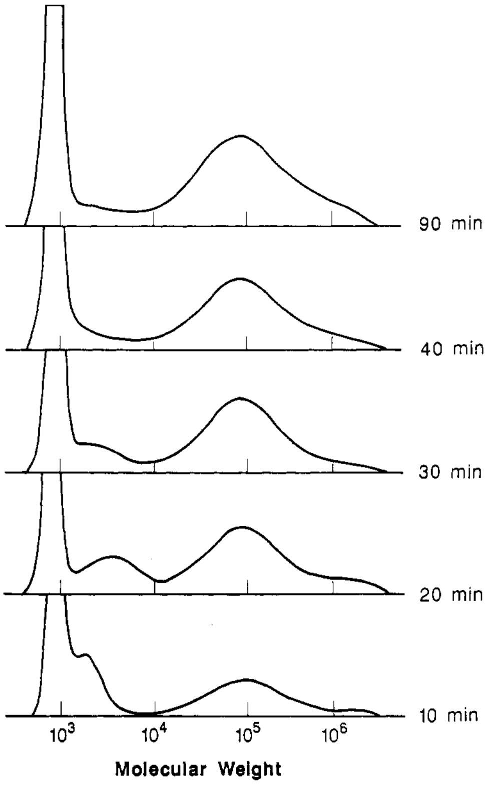


Figure 3. Variation of the molecular weight distribution with reaction time at [crown ether] = 0.25 mol % and [n-HexMeSiCl$_2$] = 0 after 40 min.

Miller and his co-workers[1] using close to equimolar concentrations of crown ether obtained lower yields of polymeric material which also had a much lower molecular weight.

Influence of the Concentration of the Crown Ether. The influence of the concentration of crown ether on the polymerization was investigated by adding different amounts of 15-crown-5 to the polymerization mixture under conditions that gave poor yields in its absence. The kinetic results are presented in Figure 4 as a plot of the variation of the monomer present in the mixture with reaction time. As can be seen in this figure, the presence

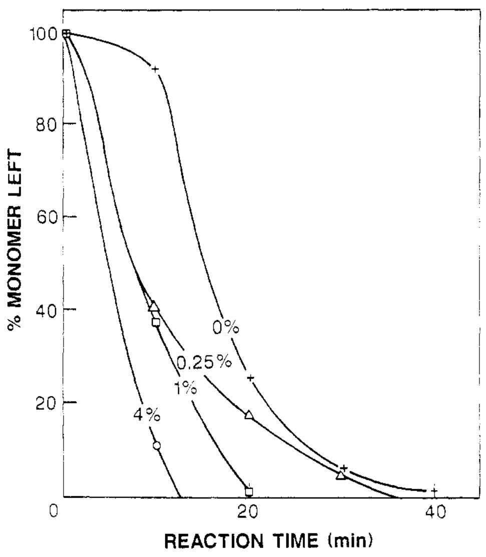


Figure 4. Rate of disappearance of n-HexMeSiCl$_2$ at different crown ether concentrations (concentrations in mol % of monomer).

of crown ether results in the almost total elimination of the induction period, while the actual maximum rate of disappearance of the monomer remains largely unaffected. Indeed, after the induction period, the slopes of the different curves are all parallel, within experimental error, until about 60% of the monomer has been consumed. Beyond this point, however, there is a decrease in the rate of disappearance of monomer, which is more important for lower concentrations of crown ether.

It was suggested in the Introduction (Scheme I), that the reaction of a Cl-ended chain with the sodium surface was fast and not rate-determining. This is confirmed by the apparently small effect of the complexing agent. Thus, even if electrides are formed, this activation of the sodium in the propagation in a non rate-determining step would not modify the overall rate.

Figure 5 shows GPC curves of the products obtained for the difference polymerizations; it can be seen that all of the polymerizations conducted in the presence of crown ether display a virtually monomodal distribution in the polymeric region at 100% conversion. The position of the maximum of this peak is independent of the crown ether concentration and corresponds to a molecular weight of 92000 g/mol; it is centered between the two peaks PII and PIII which are usually obtained in the absence of a phase-transfer catalyst. As the concentration of crown ether is increased, the high molecular weight shoulder (10^6), which probably corresponds to PIII in the polymerizations conducted without crown, disappears. This seems to indicate that the presence of crown ether promotes the mechanism responsible for the original PII at the expense of that producing the original PIII polymer.

The influence of the presence of crown ether on the reaction products does suggest that anionic species are involved in the production of this polymer. A large effect on the kinetics is the marked reduction of the induction period, suggesting that the initiation of chains is facilitated by the crown ether (Scheme Ia). The reduction of the molecular weight (Figure 5) also suggests that more chains are formed. The lack of marked change in the maximum rate of monomer disappearance suggests that the actual propagating species is little affected by the crown ether in its reaction with more dichloride as in Scheme Ib. The reaction in Scheme Ic, which is comparable to Scheme Ia, might well be facilitated, but as it is not rate-determining according to this scheme, it would not affect the kinetics.

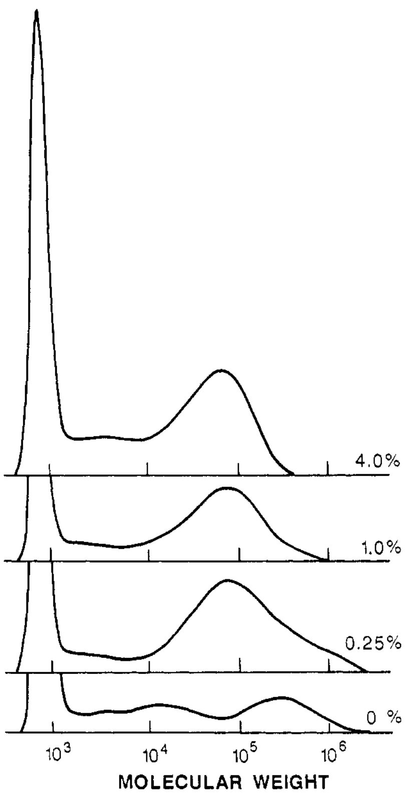


Figure 5. Molecular weight distribution for polymerizations of n-HexMeSiCl$_2$ conducted at different crown ether concentrations (concentrations in mol % of monomer).

Table I
Homopolymerization of *n*-Hexylmethyldichlorosilane: Influence of Concentration of Crown Ether

	GPC peak areas, %		
[crown ether], mol %	PI	PII	PIII
0.0	59	25	16
0.25	38	9	53
1.0	37	9	54
4.0	41	21	38

The relative proportions of the cyclic and polymeric products have been determined from the GPC curves and are listed in Table I. Under the same reaction conditions, cyclics were obtained in 59% yield in the uncatalyzed system but in only 38% yield in the presence of crown ether, while the yield of high polymer was increased in the opposite direction.

Influence of Stirring Speed. It had been observed before[6] that the rate of stirring which, in turn, determines the surface area of the sodium metal had an appreciable influence on the product distribution in these polymerizations. In the presence of crown ether, the size of the high molecular weight shoulder (10^6) increased with increasing stirring speed, suggesting that the mechanism responsible for this high molecular weight polymer found in uncatalyzed reactions is promoted by a larger sodium surface area. The position of the peak maximum in polymerizations conducted in the presence of crown ether (Figure 6) is independent of the stirring speed. The large effect of stirring speed on the product distribution found in uncatalyzed reactions[6] was thus moderated in the presence of crown ether where the yield of high polymer remained consistently good.

In the uncatalyzed systems,[6] polymerizations were found to show little increase in the maximum rate of disappearance of the monomer with an increase in the sodium surface area. This was found to be true also in the presence

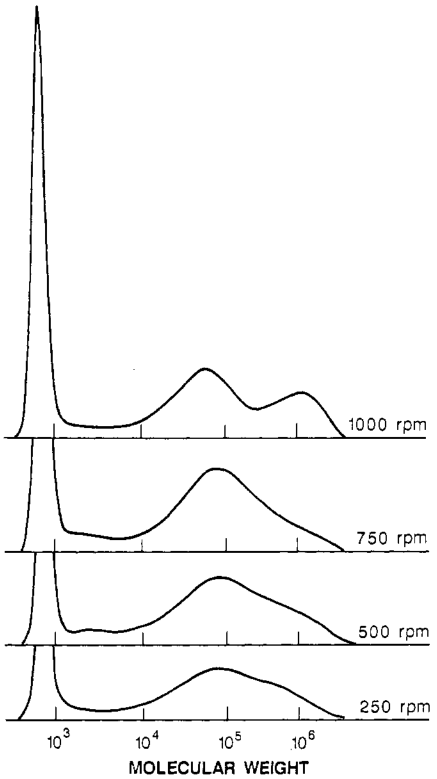


Figure 6. Molecular weight distribution for polymerizations of n-HexMeSiCl$_2$ conducted at different stirring speeds.

Table II
Homopolymerization of *n*-Hexylmethyldichlorosilane: 0.25% Cryptand [2.2.2]

	GPC peak areas, %		
reaction time, min	PI	PII	PIII
20	47	5	48
40	46	8	46
60	46	9	45
90	50	9	41
120	57	8	35
180	61	7	31

of 0.25 mol % of 15-crown-5.

Influence of the Nature of the Phase-Transfer Catalyst. Cryptand complexes are generally stronger than the corresponding crown ether complexes;[16] greater interionic distances and more reactive anions may thus be expected in these systems. A polymerization was conducted in the presence of 0.25 mol % of a [2.2.2] cryptand, and the kinetics and product distribution examined. Reaction curves are shown in Figure 7 for polymerizations conducted without phase-transfer catalyst, with 0.25 mol % of 15-crown-5 and with 0.25 mol % of cryptand [2.2.2]. This plot shows that these two types of phase-transfer catalysts have similar effects on the kinetics of the polymerization, both reducing the induction period but leaving the maximum rate more or less unaffected.

Degradation Studies. The variation of the product distribution between PI, PII and PIII with reflux time is listed in Table II and shows a decrease in the proportion of PIII with increasing reflux time. This could be explained by the occurrence of degradation of the high polymer upon prolonged reflux. GPC traces showed a decline in the molecular weight of the polymer for reflux times greater than 60 min, from 140 000 to 67 000 g/mol, confirming this hypothesis. This behavior is in contrast to that of systems catalyzed by crown ethers, where no variation was observed in the product distribution or the position of the PIII peak upon refluxing. The data tabulated in Table II indicate that there is very little change in the proportion of low molecular weight polymer PII upon refluxing. The proportion of PIII, however, is seen to decrease markedly while PI increases correspondingly. This could be accounted for by the back-biting degradation mechanism of Scheme IIb.

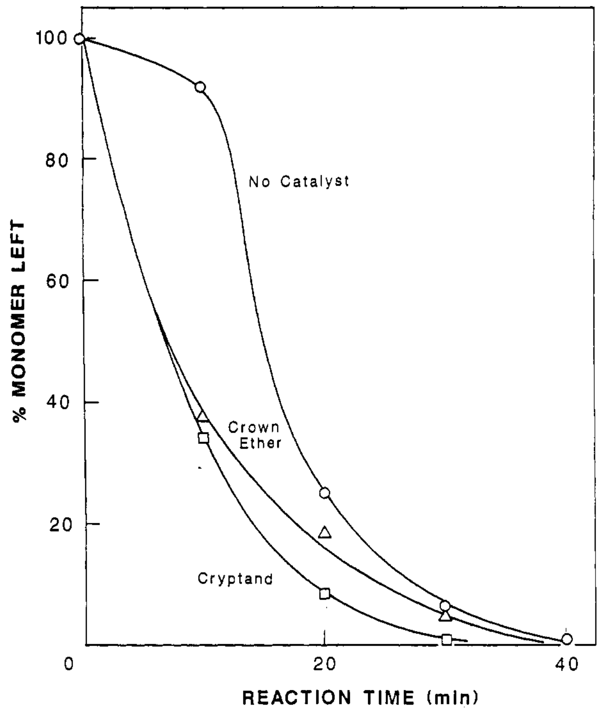


Figure 7. Rate of disappearance of n-HexMeSiCl$_2$ in the absence of catalyst or in the presence of 0.25 mol % of 15-crown-5 or cryptand [2.2.2].

Earlier degradation experiments by alkali metals conducted in this laboratory[6] had shown that when degradation did occur, cyclic material was produced at a very rapid rate from high polymer. Poly(n-hexylmethylsilane) was found to degrade to cyclics in the presence of Na or K metal in tetrahydrofuran but to be resistant to the same metals when refluxed in toluene.

Some degradation experiments were conducted by refluxing poly(n-hexylmethylsilane) with sodium metal in toluene in the presence of 15-crown-5 or cryptand [2.2.2]. While no degradation was observed in the presence of crown ether, complete degradation of the polymer to cyclic material occurred in the cryptand system in less than 5 min. TLC and GPC analyses indicated that the cyclic material formed upon degradation is the same as that formed during the polymerization. The complexes formed between cryptands and alkali-metal cations are stronger than the corresponding crown ether complexes.[14] Charge separation is expected to be greater which should increase the reactivity of anionic chain ends.

These experiments are in agreement with the back-biting degradation mechanism. This would explain the increase in the proportion of PI upon prolonged refluxing in polymerizations conducted in the presence of cryptand. It is known[17,18] that hexaorganodisilanes are cleaved by alkali metals in THF. Evidently, similar cleavage must occur on the polymer in THF or in the presence of the cryptand in toluene to produce anionic chain ends.

Influence of the Nature of the Solvent. To eliminate the possibility that proton reaction from toluene was limiting the molecular weight or chain end concentration, n-octane was substituted as solvent in a polymerization reaction. No significant change in rate or in the product was observed.

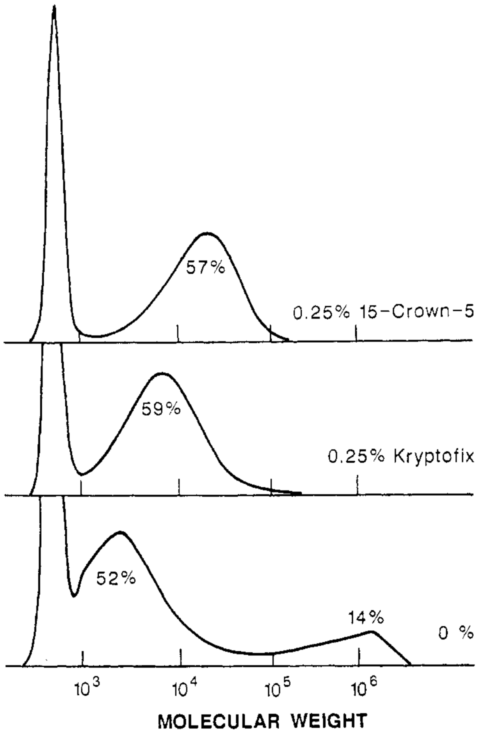


Figure 8. Molecular weight distribution for the polymerization of $PhMeSiCl_2$ in the absence of catalyst and in the presence of 0.25 mol % of 15-crown-5 and cryptand [2.2.2].

Polymerization of Phenylmethyldichlorosilane. The kinetics of the polymerization of phenylmethyldichlorosilane were not determined here because of its very fast rate of polymerization. The influence of the presence of phase-transfer catalysts on the product distribution in polymerizations conducted with 0.25 mol % of 15-crown-5 or of the [2.2.2] cryptand was examined (Figure 8). As was found in the polymerization of the hexyl derivative, the product distribution becomes almost monomodal in the polymeric region with a shift of the original PII peak toward higher molecular weights and the elimination of the original PIII peak. In contrast with the hexyl system, however, the peak molecular weight is seen to be dependent on the nature of the phase-transfer catalyst and the proportion of cyclic material is not affected by the presence of the phase-transfer catalyst. The polymerization conducted in the presence of [2.2.2] cryptand was also accompanied by degradation of the high polymer to cyclic material upon extended refluxing.

Conclusions

The most remarkable effect of the presence of phase-transfer catalysts on the reductive coupling polymerization of *n*-hexylmethyldichlorosilane is the increase in reproducibility of the reactions and the less complex molecular weight distribution of the polymer produced. The independence of the molecular weight of the polymer upon crown ether concentration and of the polymer yield upon stirring speed renders these polymerizations much more manageable.

The effect of the phase-transfer catalysts suggests that anionic species are involved in the polymerization process in their presence. This, however, does not eliminate the possibility of the simultaneous occurrence of two different mechanisms in the uncatalyzed systems. The phase-transfer catalyst could merely by promoting the anionic mechanism over the other in the catalyzed polymerizations. This would explain the molecular weight distribution of the polymer produced in these polymerizations. The presence of a shoulder on the polymer peak at the lowest concentration of crown ether could reflect incomplete elimination of this second mechanism at low catalyst concentrations.

On the basis of the results obtained in this study, a decision could not be made of the most likely mechanism for the production of cyclic pentamers. However, their production was more controlled and often reduced.

Registry No. 15-Crown-5, 33100-27-5; [2.2.2]cryptand, 23978-09-8; poly(hexylmethylsilane) (SRU), 88003-15-0; poly(hexylmethylsilane) (homopolymer), 88002-83-9; poly(phenylmethylsilane) (homopolymer), 31324-77-3; poly(phenylmethylsilane) (SRU), 76188-55-1; hexylmethyldichlorosilane, 14799-94-1.

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