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Sonochemical Synthesis of Polysilylenes by Reductive Coupling of Disubstituted Dichlorosilanes with Alkali Metals

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ABSTRACT: Monomodal polysilylenes with relatively narrow molecular weight distributions (M_w/M_n < 1.5) have been prepared by the reductive coupling of methylphenyldichlorosilane and di-*n*-hexyldichlorosilane with alkali metals in toluene in the presence of ultrasound. The optimum conditions for the sonochemical synthesis of well-defined polysilylenes in the presence of an immersion-type probe were studied. Sonochemical synthesis is accompanied by selective degradation which decreases the molecular weight to the limiting value of $M_n \approx 50\,000$ and also reduces polydispersities (M_w/M_n < 1.2). Polymerization depends strongly on the substituents on the silicon atoms, solvents, alkali metals, and temperature. For example, the polymerization of methylphenyldichlorosilane in toluene with potassium, in contrast to that with sodium, does not produce a polysilylene because the reactivity of potassium is too high, leading to side reaction.

I. Introduction

Polysilylenes make up a new class of polymers which consists of a linear Si–Si catenation in the main chain and two organic substituents at each silicon atom.[1] The organic substituents are usually alkyl or aromatic groups. Polysilylenes often behave as thermoplastic materials which are soluble in common organic solvents. The physical and chemical properties of these novel σ-conjugated polymers can lead to several potential applications. Polysilylenes are photosensitive in the UV region and can be used as self-developing high-contrast positive photoresists in microlithography.[2] σ-Electrons in the main chain of polysilylenes are strongly delocalized.[3] This delocalization leads to semiconductivity after doping, excellent photoconductivity, and promising nonlinear optical properties.[4-6] Polysilylenes are used as precursors for Si–C fibers, reinforcing agents for ceramics, and initiators for radical polymerization.[7-9]

Although the reductive coupling of dichlorosilanes with alkali metals is the main synthetic pathway to high polymers,[1] alternative methods provide polymers with better structural control and with functional groups. Dehydrogenative coupling of primary silanes,[10] anionic polymerization of masked disilenes,[11] and ring-opening polymerization of strained cyclosilanes[12] are the most important new preparative methods.

Synthesis of polysilylenes by the reductive coupling of dichlorosilanes with sodium in toluene above 100 °C is poorly reproducible and results in polymodal molecular weight distributions. The products of the reductive coupling with alkali metals usually consist of three fractions: a high molecular weight polymer ($M_n > 10^5$), a low molecular weight polymer ($M_n < 10^4$), and cyclic oligomers (Si_4, Si_5, and Si_6), which are the dominant products.[1,13-17] The polymers can be easily separated from cyclics by precipitation into isopropyl alcohol, but polymer fractionation is usually difficult and tedious. The polymodality of polysilylenes limits some characterization techniques and disables some applications.

Low molecular weight polymers could be formed due to side reactions or by a different mechanism than one by which the high polymer is formed. Various chemical reactions have different activation energies. By changing temperatures, different proportions of high and low molecular weight fractions are expected. A decrease in temperature to ambient temperatures, however, leads to the formation of solid sodium, which does not react with dichlorosilanes. Activation of the sodium surface under these conditions could be achieved by ultrasound.[18] The active surface of sodium dispersion increases under sonication. This originates in the surface erosion of sodium, which is malleable at ambient temperatures. Sonochemistry is based on the implosive collapse of cavities associated with high pressures and high temperatures existing locally for a short time.[19] The sonochemical synthesis of organometallic compounds has recently received considerable attention.[20] Not only have higher yields been reported, but new compounds have been prepared, such as cyclotrisilanes[20] or cyclotristannanes.[21]

We have used a similar method for the preparation of well-defined, high molecular weight polysilylenes.[18,22] Polymers prepared by this method are monomodal and have relatively low polydispersities (M_w/M_n < 1.5). The reproducibility of the synthesis enables more systematic kinetic and mechanistic studies of the reductive coupling of dichlorosilanes.

This paper describes the synthesis of well-defined polysilylenes with controlled molecular weights and low polydispersities and the mechanistic studies of the reductive coupling of dichlorosilanes with alkali metals in the presence of ultrasound. The effects of substituents at the silicon atoms, solvents, alkali metals, and reaction temperature on polymerization are also discussed.

II. Experimental Section

1. Materials. Dichlorosilanes (Petrarch Systems) were distilled and dried over CaH_2 prior to use. Grignard reagents and phenyllithium were obtained from Aldrich and used as received. Toluene and tetrahydrofuran were dried over CaH_2, distilled over CaH_2, and then distilled over a Na–benzophenone system. Diglyme was dried and distilled over $LiAlH_4$ under reduced pressure. Hexane was dried and distilled over CaH_2. α,α′-Dibromo-*p*-xylene (Aldrich), crown ethers (Aldrich), tris[2-(2-methoxyethoxy)ethylamine], and cryptand[2.2.2](4,7,-

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13,16,21,24-hexaoxa-1,10-diazabicyclo[8.8.8]hexacosane; Merck) were used as received. All materials were stored over drying agents or under inert gas prior to use. Liquid Na−K alloy (1:1 mole ratio) was prepared in a 50 mL three-necked, round-bottomed flask under inert argon gas by adding solid potassium to an equimolar amount of molten sodium and used as reductive coupling agent. Alkali metal naphthalenides were prepared by the reactions of alkali metals with an equimolar amount of naphthalene in THF. 1,4-Diiodooctahexyltetrasilane ($I(n\text{-}Hex_2Si)_4I$) was prepared by the reaction of octa-*n*-hexylcyclotetrasilane (0.76 g) with an equivalent of I_2 (0.242 g) in 2 mL of hexane. 1,4-Diiodooctahexyltetrasilane was reacted with 1 equiv of PhMgCl (2 M in THF) to yield 1-iodo-4-phenyloctahexyltetrasilane.

2. Sonochemical Synthesis of Polysilylenes. A 50 mL three-necked, round-bottomed flask was fitted with an immersion-type probe (W-385, Heat Systems-Ultrasonics, Inc.). The flask was fitted with a reflux condenser and a pressure-equalizing addition funnel. In some experiments an ultrasonic bath (75-1970 Ultramet II sonic cleaner, Buehtler Ltd.) was used. All systems were thoroughly flame dried under argon. Known amounts of sodium (0.03 mol) were added to the flask, which was filled with 30 mL of toluene and purged with dry argon. Sodium particles were irradiated by ultrasound until a stable dispersion of sodium was formed. After irradiation for approximately 1 h, a solution of dichlorosilane (0.013 mol) in 8 mL of toluene was added dropwise to the reaction flask in a controlled manner (3 drops/min) under argon. Dichlorosilane was added to the flask within 15 min, and the reaction mixture turned from gray to dark purple. Samples were withdrawn from the reaction mixture at different time intervals, quenched with 10 mL of ethanol, and washed several times with 75 mL of water. The organic phase was later added to a large excess (250 mL) of isopropyl alcohol, leading to the precipitation of the polymer. The polymer was dried and the yield was determined gravimetrically.

Molecular weights and polydispersities were determined by GPC based on polystyrene standards. In some cases, the number-average molecular weight (M_n) was determined by membrane osmometry. The polymers were characterized by IR, UV, ^{1}H NMR, ^{13}C NMR, and ^{29}Si NMR. The copolymer compositions were determined from ^{1}H NMR spectra. The filtrate remaining after the evaporation of solvents was analyzed by GC/MS, GPC, ^{1}H NMR, and ^{29}Si NMR.

The polymerization was carried out with some variations in the reaction conditions including temperatures, mole ratio of monomer to sodium, solvent, reaction times, and the alkali metal. In the case of potassium, a high-quality dispersion was formed with an immersion-type probe in 10 min without a cooling system.

3. Reductive Coupling of Dichlorosilanes with Homogeneous Reducing Agents. The reductive coupling of dichlorosilanes with a homogeneous reducing agent was carried out by either adding sodium naphthalenide to monomer solutions in toluene or THF or adding monomer solutions to sodium naphthalenide. The reaction medium was filtered with a cotton precoated syringe to remove NaCl and precipitated into a large amount of isopropyl alcohol. The final products remaining after all the solvent was evaporated were analyzed by GPC, GC/MS, ^{1}H NMR, and ^{29}Si NMR. In the cases of the trapping experiments of silylene intermediates with triethylsilane and silyl radicals with allylphenyldichlorosilane the final products were analyzed by GC/MS, GPC, and ^{1}H NMR without precipitating.

4. Preliminary Kinetic Studies. Polymerization of methylphenyldichlorosilane containing hexamethyldisilane as a standard in ^{1}H NMR was carried out in toluene and also in a mixture of toluene and 25% diglyme, according to the procedure of sonochemical synthesis of polysilylenes. Samples were withdrawn from the reaction mixture at various reaction times (every 2 min in toluene or every 30 s in the mixture of toluene and 25% diglyme). The rate of methylphenyldichlorosilane disappearance was investigated by comparison of the integration area of methyl groups in the remaining monomer to the area of methyl groups in the standard. The change of monomer concentration versus the reaction time was plotted for toluene and for the mixture of toluene and diglyme (3:1) at 60 °C.

5. Degradation of Polysilylenes. (a) Sonochemical Degradation. A stoppered test tube was thoroughly flame dried and purged with dried argon. Then it was placed in an ultrasonic cleaner (75-1970 Ultramet II sonic cleaner, Buehler Ltd.). A precise amount of alkali metal (10 wt % of polysilylene) and 10 mL of toluene were added to the test tube. The mixture was irradiated by ultrasound until a high-quality sodium dispersion was fomred. A toluene solution of polysilylene at various concentrations was added to the sodium dispersion using a syringe. The polysilylene solution was irradiated by ultrasound. In some experiments toluene solutions of polysilylenes were irradiated by ultrasound in the absence of sodium. The degraded polymers were analyzed at various irradiation times by ^{1}H NMR, UV, and GPC.

(b) Chemical Degradation by Alkali Metals. A flask was sealed with a septum and thoroughly flame dried under argon. Precise amounts of alkali metals or homogeneous chemical reductants in THF (Na or Li naphthalenide) were added to the flask. THF solutions (0.8 wt %) of polysilylenes were added to the flask using a syringe. The mixtures were stirred at room temperature in the dark. The degraded polymers were analyzed at various times by GPC and ^{29}Si NMR.

6. Spectroscopic Measurements. NMR spectra were recorded at room temperature on $CDCl_3$ solutions with an IBM 300 MHz NR-300 instrument. ^{29}Si NMR chemical shifts were determined using external standards (tetramethylsilane (0.0 ppm) or hexamethyldisiloxane (7.22 ppm)) in benzene-d_6 solutions. Electronic spectra were measured over the range 190−820 nm on either a Hewlett-Packard 8452 UV diode array spectrometer or an IBM 9430 UV−vis spectrophotometer in CH_2Cl_2 solutions. Infrared spectra were recorded on a Nicolet 5-DX FTIR instrument. Mass spectra were determined on a Hewlett-Packard 5970 mass selective detector with a 5890A GC. All GPC analyses were carried out using a Waters GPC equipped with three Ultrastyragel columns (linear, 500 and 100 Å) in series, a Model 510 HPLC pump, a Model 410 refractive index detector, and a Model 450 UV detector. The molecular weights and polydispersities reported are based on polystyrene standards.

III. Results and Discussion

Sonochemical Synthesis of Polysilylenes. The sonochemical synthesis of polysilylenes at ambient temperatures leads to the formation of monomodal high molecular weight polysilylenes. Polydispersities (M_w/M_n) of these polymers may be below 1.5. Either an immersion-type probe or an ultrasonic cleaning bath was used. Cavitation depends on the position of the flask in the bath, on the level of liquid in the bath, on the temperature, and on the amount of solvent. The probe is preferred because it enables better temperature control and gives reproducible results.[22]

The sonochemical polymerization of methylphenyldichlorosilane and di-*n*-hexyldichlorosilane with alkali metals has been studied, since these monomers behave differently.[18,22] Typical GPC traces of poly(methylphenylsilylene) prepared by reductive coupling of methylphenyldichlorosilane with sodium in the ultrasonic bath are shown in Figure 1. In contrast to thermal condensation, a monomodal high molecular weight polymer and cyclic oligomers are formed. Cyclic oligomers (mostly cyclic pentamer), usually formed in high yield, can be easily separated from the mixture, since they are soluble in isopropyl alcohol and the polymer is not. The polymers were characterized by IR, UV, ^{1}H NMR, ^{13}C NMR, and ^{29}Si NMR. The oligomers were analyzed by GC/MS, GPC, ^{1}H NMR, and ^{29}Si NMR. The spectroscopic data are summarized in Table 1. Two phenomena may be related to the formation of monomodal polymers. The first is the suppression of some reactions

Table 1. Spectroscopic Data for Poly(methylphenylsilylene) and Cyclic Oligomers Produced by the Sonochemical Synthesis of methylphenyldichlorosilane with Na in Toluene and for Poly(di-*n*-hexylsilylene) and the Corresponding Cyclic Oligomers Produced by Sonochemical Synthesis of Di-*n*-hexyldichlorosilane with K in Toluene

	Poly(methylphenylsilylene)
^{1}H NMR[a]	7.5−6.0 (broad peak, 5H), 0.5 to 1.0 (broad peak, 3H)
^{13}C NMR[a]	135−125 (two broad peaks, 5H), −10 (broad singlet, 3H)
^{29}Si NMR[a]	−39.2, −39.9, −41.2 (three broad peaks)[b]
IR (cm^{-1})	~3030 (ν_{C-H}, aromatic), 2960 and 2870 (ν_{C-H}, CH$_3$); 2000−1660 (δ_{C-H}, aromatic); 1600 and 1530 (phenyl group, overlap); 1430 and 1100 (δ_{Si-Ph}); 1265 (d_{Si-Me}); 830−650 (out-of-plane aromatic); 460 (η_{Si-Si})
	Cyclic Oligomers
^{29}Si NMR[a]	~−30.8[c] (ring size: 5); ~−33.8,[c] (ring size: 6); ~−21 (siloxanes, D$^{PH}_3$ and D$^{Ph}_4$); −27.0 and ~−33.0 (intensity = 2:2)[a]
	Poly(di-*n*-hexylsilylene)
UV	$\lambda_{max} = 318$ nm; $\epsilon_{max} = 9700$
^{1}H NMR[c]	1.7−0.6 (two broad peaks, 26H)
	Cyclic Oligomers
^{29}Si NMR[a]	~−20.4 (ring size: 4); ~−34.4 (ring size: 5); ~−41.0 (ring size: 6(?))

[a] In ppm. [b] Due to atactic, syndiotactic, and isotactic structures, respectively. [c] Several isomers. [d] Oxacyclotetrasilane (−*Si*−O−*Si*−: −27 ppm; −O−Si−*Si*−*Si*−Si−: −33 ppm).

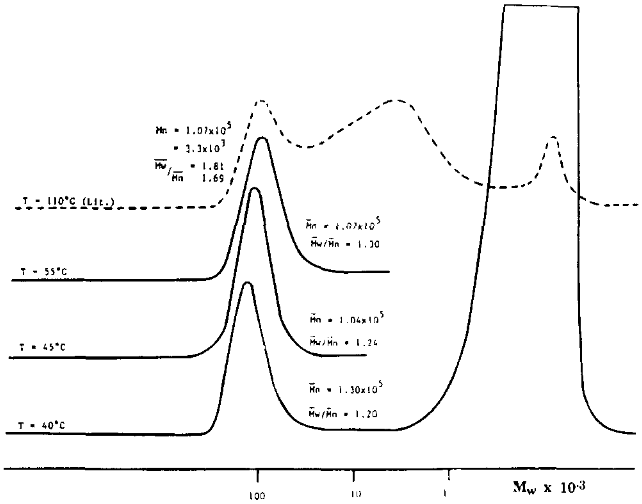


Figure 1. GPC traces of the polymerization of methylphenyldichlorosilane with Na in toluene as a function of temperature in the presence of a cleaning bath.

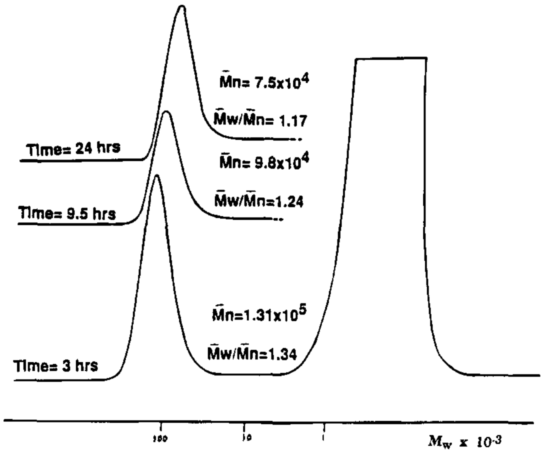
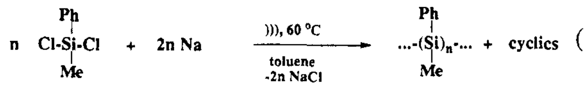


Figure 2. GPC traces of the polymerization of methylphenyldichlorosilane with Na in toluene as a function of time in the presence of a cleaning bath.

or physical processes at ambient temperatures. The second is the formation of a high-quality sodium dispersion which is continuously regenerated during the coupling process.

The reductive coupling reaction of methylphenyldichlorosilane with sodium in the presence of an immersion-type probe is usually rapid and is completed within 25 min after the addition of methylphenyldichlorosilane (eq 1), where))) represents ultrasound. Under ultrasonication, the active surface of the sodium dispersion increases due to cavitational erosion and the removal of NaCl coated on the surface of Na. The ultrasound also ensures a local excess of sodium by the continuous regeneration of the metal surface.[18] Similar effects were reported in sonochemical hydrogenation with Ni catalysts.[23]

 (1)

$$n\ \mathrm{Cl{-}\overset{\overset{\displaystyle Ph}{|}}{\underset{\underset{\displaystyle Me}{|}}{Si}}{-}Cl} + 2n\,\mathrm{Na} \xrightarrow[\text{toluene}\atop -2n\,\mathrm{NaCl}]{))),\ 60\ ^\circ\mathrm{C}} \dots(\overset{\overset{\displaystyle Ph}{|}}{\underset{\underset{\displaystyle Me}{|}}{\mathrm{Si}}})_n\dots + \text{cyclics} \quad (1)$$

We have found that higher molecular weight polysilylenes are degraded in the presence of ultrasound, as shown in Figure 2.[22] The continued sonication of the reaction mixture as well as the sonication of the isolated polymer is accompanied by a decrease in molecular weight to a limiting value of $M_n \approx 50\,000$ and by a strong decrease in polydispersity ($M_w/M_n < 1.2$). Below the limiting value of $M_n = 50\,000$ polymers cannot degrade. A similar effect has been observed previously for polystyrene, poly(methyl methacrylate), dextran, and other polymers.[24]

Effect of Reaction Temperature. 1. Polymerization of Methylphenyldichlorosilane. Polymerization was carried out at reaction temperatures ranging from −18 to +110 °C in the presence of either a cleaning bath or an immersion-type probe. In the latter case, the reaction temperature was easily controlled with various cooling systems, such as a silicone oil bath, a water bath, an ice-water bath, or a dry ice/CCl$_4$ bath (Table 2). The reaction temperatures were measured using a precalibrated thermocouple placed inside the reaction mixture.

The results of the sonochemical reductive coupling of methylphenyldichlorosilane with sodium in toluene are shown in Table 2. At temperatures of 20−60 °C polymerization typically results in a 10−15% yield of high polymer with $M_n \approx 100\,000$ and relatively low polydispersity ($M_w/M_n < 1.5$). Molecular weights and polydispersities are hardly affected by the reaction temperatures within the range.

At −20 °C it was observed that sodium particles aggregated to form chunks of Na. A polymer with a bimodal molecular weight distribution was formed with a 20% yield of high polymer. At 75 °C a bimodal polysilylene was also obtained. This could have resulted from a decrease in the efficiency of the ultrasound with increased temperature. As the reaction temperature reached the boiling point of toluene, only a low molecular weight polymer was formed in high yield with a broad polydispersity, in contrast to the thermal con-

Table 2. Effect of Temperature on Poly(methylphenylsilylene) Synthesis in the Presence of Ultrasound in Toluene[a]

	temp, °C								
	110	100	75	60	20	−18	50	45	40
		outside bath							
		silicone oil	silicone oil	water	ice	dry ice/CCl_4			
% polymer	55	82	23	12	7	5.5	15.4	12.6	11.1
HP/LP	1/3	0/1	1/1	1/0	1/0	1/4	1/0	1/0	1/0
$M_n \times 10^{-3}$ (HP)	107		174	104	113	50	107	104	130
$M_n \times 10^{-3}$ (LP)	3.3	4.0	5.5			1.2			
M_w/M_n (HP)	1.81		2.3	1.5	1.5	1.04	1.30	1.24	1.20
M_w/M_n (LP)	1.70	2.9	1.9			1.13			

[a] $[PhMeSiCl_2]_0$ = 0.32 M and $[Na]_0/[Si-Cl]_0$ = 1.2. [b] Reaction time = 24 h for thermal polymerization. [c] Reaction time = 1 h for polymerization in an immersion-type probe. [d] Reaction time = 6 h for polymerization in a cleaning bath.

Table 3. Effect of Temperature on Poly(di-*n*-hexylsilylene) Synthesis in the Presence of Ultrasound in Toluene[a]

	temp, °C			
	60	80	85	100
% polymer	0.0	12.0	13.0	13.0
reacn time (h)	24	24	6	1
$M_n \times 10^{-3}$		70.0	121	520
M_w/M_n		2.73	2.10	5.61

[a] $[Hex_2SiCl_2]_0$ = 0.32 M, $[Na]_0/[Si-Cl]_0$ = 1.2, immersion-type probe.

Table 4. Effect of Time on Poly(methylphenylsilylene) Synthesis in the Presence of Ultrasound in Toluene[a]

	time, h				
	3.0	6.0	9.5	24	72
% polymer[b]	16.6	16.4	16.7	16.8	
$M_n \times 10^{-3}$	131	107	98.0	75.0	55.0
$M_w \times 10^{-3}$	176	140	120	88.0	62.0
M_w/M_n	1.34	1.30	1.24	1.17	1.11

[a] $[PhMeSiCl_2]_0$ = 0.32 M, $[Na]_0/[Si-Cl]_0$ = 1.2, 55 °C, cleaning bath, addition time of monomer solution = 60 min. [b] The yield of the final polymer was determined gravimetrically after the precipitation of the reaction medium into isopropyl alcohol.

Table 5. Effect of Time on Poly(methylphenylsilylene) Synthesis in the Presence of Ultrasound in Toluene[a]

	during addition of monomer			after addition of monomer			
	5 min	10 min	15 min	30 min	60 min	80 min	120 min
$M_n \times 10^{-3}$	380	224	230	182	148[b]	106	40
$M_w \times 10^{-3}$	1710	668	635	373	267	157	59
M_w/M_n	4.5	2.98	2.71	2.05	1.73	1.48	1.17

[a] $[PhMeSiCl_2]_0$ = 0.32 M, $[Na]_0/[Si-Cl]_0$ = 1.2, 60 °C, immersion−type probe. [b] Number-average molecular weight (M_n): 2.05 × 10^5 by membrane osmometry.

densation, which led to a polymer with a bimodal molecular weight distribution.

2. Polymerization of Di-*n*-hexyldichlorosilane. The effect of temperature on the sonochemical polymerization of di-*n*-hexyldichlorosilane with sodium in toluene is shown in Table 3. Homopolymerization is not possible at temperatures below 60 °C, but it is possible at temperatures above 80 °C. Polymers with higher molecular weights are formed at higher temperatures. This originates in slower degradation by the less efficient action of ultrasound. The vapor pressure of toluene at higher temperatures (>80 °C) is too high to form bubbles and cavities.[18,19] Therefore, the mechanical degradation by shear force is reduced[25] and polydispersities are high (M_w/M_n > 2). At 60 °C dialkyldichlorosilane does not react with the sodium dispersion in 24 h.

Effect of Reaction Time. The effect of reaction time on the sonochemical synthesis of poly(methylphenylsilylene) in a cleaning bath or with an immersion-type probe are shown in Tables 4 and 5, respectively. In a cleaning bath, the high molecular weight polymer was formed with low polydispersity (M_w/M_n < 1.34) after 3 h. The reaction conditions in the bath, however, cannot be easily controlled due to irreproducible cavitation. The higher molecular weight polymers were degraded by ultrasound as observed by a decrease in the molecular weight and the polydispersity. After 72 h, the number-average molecular weight (M_n) was 5.5 × 10^4 and the polydispersity was 1.11. In addition, the yields of polymers did not change with reaction time. These results indicate that cyclics and polymers do not interconvert under these conditions.

With the probe during the addition of monomer (15 min), higher molecular weight polymers were formed. Table 5 shows that these polymers were degraded by the continued sonication. The sonochemical degradation led to a decrease in the number-average molecular weight (M_n) to 5.9 × 10^4 and a decrease of the polydispersity to 1.18 after 2 h.

Effect of Monomer Concentration. As reported previously,[18,22] propagation competes with the intramolecular cyclization at the stage of tetramer to hexamer. Propagation is a bimolecular reaction which is dependent on the monomer concentration. Conversely, the cyclization is a unimolecular reaction which is independent of the monomer concentration. To reduce the probability of the intramolecular cyclization and to enhance the polymer yield, the monomer concentration should be increased.

The results showed that the yield of polymer was weakly increased by the monomer concentration. Unfortunately, the quality of sodium dispersion was very poor at monomer concentrations higher than 0.64 mol/L. This leads to polymers with broad polydispersities. M_w increases with the monomer concentration $[M]_0$. The change of the quality of sodium dispersion with monomer concentration under sonication did not allow quantitative studies of the effect of monomer concentration. With respect to polydispersity, the optimum monomer concentration is approximately 0.32 mol/L in the reductive coupling reaction of methylphenyldichlorosilane with sodium in toluene in the presence of an immersion-type probe for 1 h.

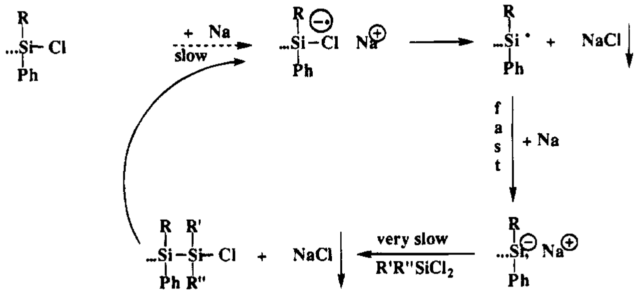
Effect of Mole Ratio of Sodium to Dichlorosilane. It was observed that high molecular weight polysilylene was formed at low conversion (see Table 5). This result indicates that polymerization resembles a chain growth process. Typical step growth polymerizations (e.g., polycondensation) depend on the ratio of reagents.[26] We have investigated the effect of the mole ratio of sodium to dichlorosilane. The yield of polymers and the molecular weights of polymers were hardly affected by the mole ratio. This suggests that polym-

Table 6. Effects of Substituents and Solvents on Sonochemical Synthesis[a]

	monomer/solvent				
	$PhMeSiCl_2$/ toluene	Hex_2SiCl_2/ toluene	(Hex_2SiCl_2 + $PhMeSiCl_2$) (1:1)/toluene	$PhMeSiCl_2$/ (toluene + 25% diglyme)	Hex_2SiCl_2/ (toluene + 25% diglyme[b])
% polymer	12.0	0.0[c]	12[d]	35	24
$M_n \times 10^{-3}$	104		175	4.3	45
M_w/M_n	1.50		1.66	2.26	1.73

[a] $[M]_0$ = 0.32 M, time = 60 min, $[Na]_0/[Si-Cl]_0$ = 1.2, 60 °C, immersion−type probe. [b] +3% 18-crown-6 ($[\text{crown ether}]_0/[Na]_0$ = 0.18): polymer (%) = 63.4, $M_n = 9.2 \times 10^3$, and M_w/M_n = 3.6. [c] No reaction after 24 h. [d] Ratio of [PhMeSi]/[Hex_2Si] in the copolymer was 3/1.

Scheme 1. Sonochemical Copolymerization of Methylphenyldichlorosilane with Di-*n*-hexyldichlorosilane with Na in Toluene



erization takes place as a chain growth process. It must be noted, however, that a reductive coupling process is under heterogeneous conditions and, like for interfacial polymerizations, some of the above reasons may not fully apply. Additional evidence supporting a chain growth process is based on the fact that oligosilanes have higher electron affinity than monomer toward alkali metals.[27,28] The low reactivity of monomer toward alkali metals results in slow initiation. Longer chains can react with alkali metals more easily than the monomer. Therefore, the monomer is consumed slowly at the initiation step and then consumed more rapidly in propagation.

M_w and polydispersity slightly decrease with increasing mole ratio of $[Na]_0/[M]_0$ (≤ 1). This could be based on more efficient sonochemical degradation by the additional mechanical force of the Na particles. Similar results have been observed in the sonochemical degradation of polysilylenes with a different ratio of [Na]/[repeating unit] in isolated polysilylene.[25,29] Since excess sodium leads to the formation of high molecular weight polymer with low polydispersities, the optimum mole ratio is in the range from 1.15 to 1.20.

Effect of Substituents and Solvents. The results of the effects of substituents and solvents are illustrated in Table 6. Polymerization of disubstituted dichlorosilanes by reductive coupling with sodium at ambient temperatures in nonpolar sovlents such as toluene or xylene requires the presence of an aromatic substituent at the silicon atom. Dialkyldichlorosilanes do not react with the sodium dispersion below 80 °C in toluene[16,18] (see Table 3). It has been reported that dichlorosilanes with aryl groups have a less negative reduction potential than dialkyldichlorosilane.[28] It seems that the reduction potential of dialkyldichlorosilanes is too high and the reaction is too slow at ambient temperatures. Methylphenyldichlorosilane reacts with sodium faster than dialkyldichlorosilanes, because the aromatic group facilitates electron transfer and stabilizes the radical anions.

However, dialkyldichlorosilanes can be copolymerized with methylphenyldichlorosilane.[18] Twenty-four hours after addition of dialkyldichlorosilane, methylphenyldichlorosilane was sequentially added to the reaction medium. A copolymer containing 25% dialkylsilylene units, was formed from the equimolar mixture, and the yield of the copolymer was 12%. The molecular weight (M_n) and polydispersity were 1.75×10^5 and 1.66, respectively. The simultaneous addition of comonomers led to the formation of a copolymer which contains 15% dialkylsilylene units.

Copolymerization suggests that polymerization proceeds by polar intermediates. The polymeric silylsodium can react with both dichlorosilanes, although only methylphenyldichlorosilane can react with sodium to initiate polymerization. The presence of a phenyl group in either the α- or the β-position on the chloro-terminated polysilylene allows reductive coupling. Therefore, dialkyl monomers can copolymerize, but they cannot homopolymerize under sonochemical conditions below 80 °C in toluene. This again indicates that activation energy for initiation is much higher than for propagation.

Polymerization via radical intermediates should lead to a homopolymer of methylphenyldichlorosilane and unreacted dialkyldichlorosilane unless an extensive chain transfer process occurs. The large yields of cyclics (≈80%), which are the products of end-biting reactions of silylsodium with Cl-terminated chains, also support polar intermediates.[22] They can react with both monomeric dichlorides in an S_N2-type reaction providing a copolymer (Scheme 1).

Homopolymerization of dialkyldichlorosilanes at ambient temperatures is possible for only in the presence of etheral solvents. For example, poly(di-*n*-hexylsilylene) with molecular weight (M_n) for 75 000 was prepared in toluene/diglyme (3:1) mixtures. The addition of more polar solvents, such as diglyme or 18-crown-6, which are known to effectively interact with sodium and potassium cations, leads to an increase of the polymer yield and a strong decrease of molecular weights. There are two possible explanations for these observed phenomena. Etheral solvents may increase the reactivity of silyl anions which may participate in various side reactions. One possible side reaction is transfer to the solvent or termination by the cleavage of ether and the formation of less reactive alkoxy anions. The other explanation is the relatively higher rates of initiation in more polar solvents. Thus, more chains start at once and a smaller share of monomer per chain is available. Preliminary kinetic results (see Figure 5) indicate slow initiation for the polymerization in toluene (sigmoidal curves) and faster initiation in the presence of etheral solvents.

We observed that even 1% of diglyme decreases the molecular weight significantly and increases the polymer yield. Addition of small amounts of crown ethers also increases polymerization rates and yields.[30-32] More polar solvent facilitates the back-biting process, which will lead to the complete degradation of polysilylene to cyclic oligomers.[25,29] We have found that in nonpolar solvents such as toluene no back-biting occurs at ambient temperatures. Therefore, cyclic products must be formed by an end-biting process (i.e., intramo-

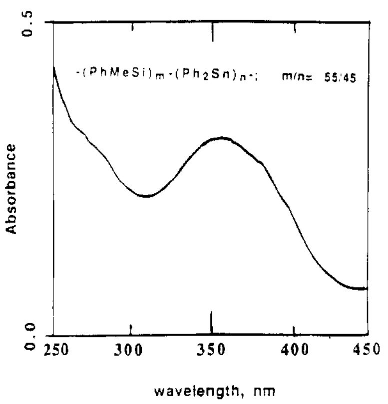


Figure 3. UV spectrum of a poly(methylphenylsilylene)-*co*-poly(diphenystannane) copolymer in CH_2Cl_2 at 25 °C.

lecular cyclization of pentasilane or hexasilane with one chloro-terminated and one anionic end). The anion reacts easily with a more electrophilic monomer, but entropy favors intramolecular cyclization, especially at lower monomer concentrations. The chain growth process has a higher activation energy than the intramolecular process, since fewer cyclics are formed at higher temperature.

The sonochemical synthesis has also been successfully applied to the preparation of polysilylene and polystannane copolymers from the mixture of methylphenyldichlorosilane and diphenyldichlorotin. The copolymer was formed with a yield of 75%, with M_w = 4000 and M_w/M_n = 3.7. It was soluble in common organic solvents. The ^{1}H NMR spectrum of the copolymer showed the presence of 44% of diphenyltin units. The UV spectrum contained an absorption band at 354 nm tailing into the visible region (Figure 3). Some polymer was insoluble due to cross-linking or crystallinity. It is possible that tin atoms will interact intermolecularly by expanding valencies and lead to pseudo-cross-linking.

Effect of Alkali Metals and Solvents on the Sonochemical Synthesis of Polysilylenes. The sonochemical polymerization of disubstituted dichlorosilanes containing aromatic groups at the silicon atom with sodium at ambient temperatures in toluene is successful for the preparation of monomodal polysilylenes. Dialkyldichlorosilanes do not react with the sodium dispersion under these conditions, because the reduction potential of the monomer is higher than the oxidation potential of Na. The oxidation potential can be increased using potassium or Na−K alloy. The effect of alkali metals and solvents on the sonochemical synthesis of polysilylenes was explored. The effect of a homogeneous reducing agent on the polymerization of methylphenyldichlorosilane in THF and in the mixture of toluene and THF (3:1) was also studied.

1. Effect of Alkali Metals on the Polymerization of Hex_2SiCl_2 in the Presence of Ultrasound. The effects of alkali metals and solvents on the preparation of poly(di-*n*-hexylsilylene) are illustrated in Table 7. All reactions, except for the reaction with Na, are run with an excess of monomer in order to eliminate additional degradation of polymers by the alkali metal.

Table 7. Effect of Alkali Metals and Solvents on Sonochemical Synthesis of Poly(di-*n*-hexylsilylene)[a]

	Na					
	tol[b]	tol + 25% diglyme	tol + 3% 18-crown-6	tol + 3% TDA[c]	Na-K tol	K tol
time, h	24	1	1	1	2	1
% polymer	0.0	24	63.4	49	12	13
$M_n \times 10^{-3}$		45	9.2	16	113	150
M_w/M_n		1.73	3.6	3.27	1.72	1.76

[a] $[M]_0$ = 0.32 M; temperature = 60 °C; [Met]/[Si−Cl] = 0.98/1. [b] tol = toluene. [c] TDA = tris[2-(2-methoxyethoxy)ethylamine).

Table 8. Effect of Alkali Metals and Solvents on Sonochemical Synthesis of Poly(methylphenylsilylene)[a]

	Na		Na-K		K	
	tol[b]	+33% THF	tol	+33% THF	tol	+33% THF
time, h	1	1	2	1	6[c]	1
% polymer	12.0	14.0	1.6	16.0	0.0	18.0
$M_n \times 10^{-3}$	104	3.2	7.1	3.5		4.12
M_w/M_n	1.50	1.58	3.84	1.65		2.95

[a] $[M]_0$ = 0.32 M, temperature = 60 °C; $[Met]_0/[Si-Cl]_0$ = 0.98/1. [b] tol = toluene. [c] After 15 h: % polymer, 47.0; $M_n = 3.5 \times 10^3$ and M_w/M_n = 1.48.

The coupling reaction of di-*n*-hexyldichlorosilane with Na−K alloy (1:1) leads to the formation of monomodal, high molecular weight polymers with low polydispersities. These results can be explained in two ways. The oxidation potential of Na−K alloy, which has a value between those of Na and K, is high enough to react with di-*n*-hexyldichlorosilane. The other explanation is as follows: di-*n*-hexyldichlorosilane can react with K to generate longer polymeric chains which then can react with Na because longer chains have higher electron affinities toward alkali metals.[1e] To understand the role of Na−K alloy, the polymerization of di-*n*-hexyldichlorosilane with Na−K alloy or the mixture of Na and K was performed. With Na−K alloy, poly(di-*n*-hexylsilylene) was formed with a yield of 12% after 2 h. For the mixture of Na and K, Na remained unreacted after 2 h. Thus, Na−K alloy and the mixed Na and K behave differently, indicating that the oxidation potential of Na−K alloy is between those of Na and K.

With K, we have found the color change of the reaction medium immediately after addition of the monomer solution. The color changes due to formation of colloidal particles of alkali metals in the salts (KCl or NaCl).[17] After 1 h of reaction time, a high molecular weight polymer ($M_n = 1.5 \times 10^5$) was obtained with M_w/M_n = 1.76 (see Table 7). Therefore, the increased reactivity of K led to the formation of monomodal, high molecular weight poly(di-*n*-hexylsilylene) with relatively low polydispersity, in contrast to no polymerization with sodium. Thus, the oxidation potential increases in the following order: Na < Na−K alloy < K.

2. Effect of Alkali Metals and Solvents on the Sonochemical Synthesis of Poly(methylphenylsilylene). The effects of alkali metals and solvent polarity on the polymerization of methylphenyldichlorosilane are shown in Table 8. All reactions, except for the reaction with Na, are run with an excess of monomer in order to eliminate additional degradation of polymers by alkali metal.

With Na, we have found the formation of monomodal, high molecular weight polymers. The polydispersities (M_w/M_n) of these polysilylenes can be below 1.50. In the case of K in toluene, the color of the polymerization medium changes immediately after the addition of a small amount of monomer solution, but only oligomers were formed after 6 h. After 15 h of polymerization, oligomers shifted to low molecular weight polymers (M_n = 3500) with low polydispersity (M_w/M_n = 1.48), but these polymers were not polysilylenes.[33] They did not have the typical absorption at 340 nm (Figure 4). The IR, ^{1}H NMR, and ^{13}C NMR spectra of the final products were compared with the spectroscopic data of poly(methylphenylsilylene). NMR spectra indicate that

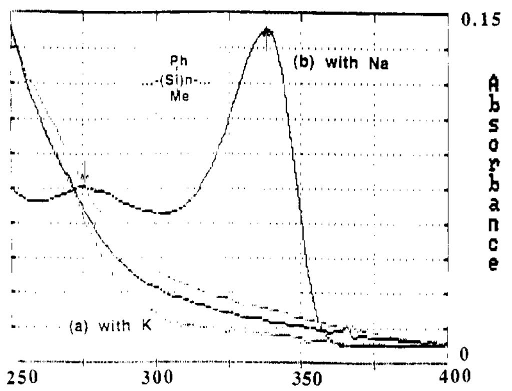
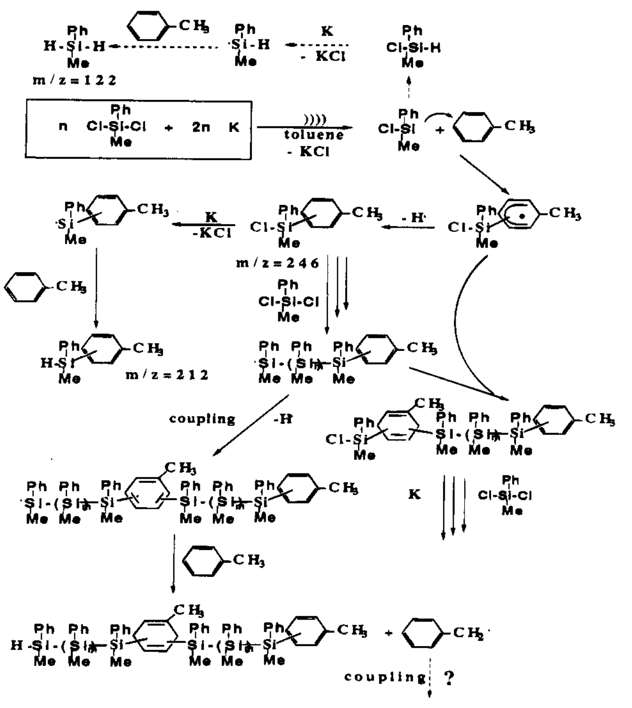


Figure 4. UV spectra of the final products from the sonochemical polymerization of methylphenyldichlorosilane with K (a) and Na (b) in CH_2Cl_2 at 25 °C.

Scheme 2. Reaction Pathway of $PhMeSiCl_2$ with K in Toluene



substantial amount of toluene is incorporated to the polymer. In the ^1H NMR spectrum, the Si−H bonds appeared around 3.5 ppm and the double bonds of 1,4-cyclohexadiene around 5.4 ppm were present. ^{13}C NMR showed the methyl group of toluene at approximately 23 ppm. In addition, the characteristic peaks of Si−H bonds appeared in the IR spectrum around 2165 cm^{-1}. This product might be obtained from the reaction of silylene with toluene or the reaction of radical species with the toluene molecule. The participitation of silylene intermediates was investigated by a trapping experiment with Et_3SiH. Similar results were obtained in the presence and absence of Et_3SiH. This indicates that silylenes do not play an important role in this process. Similar conclusions have been reached in ref 16.

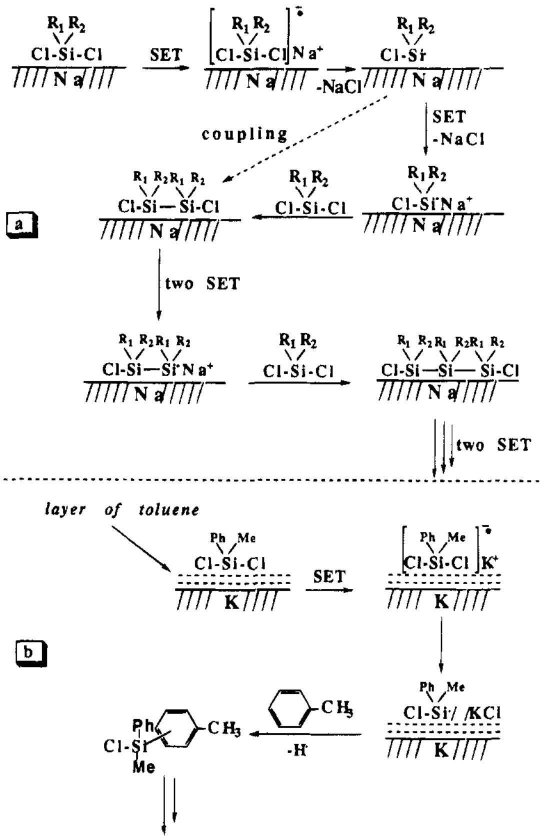
Samples were taken after 0.5, 1.5, and 15 h. After 0.5 h the monomer remained unreacted. After 1.5 h, the monomer was consumed. GC/MS indicated products with molecular ions $m/e = 122$, 212, and 246. The first one was identified as H(PhMeSi)H. The latter two ions corresponded to H(PhMeSi)−toluene and Cl(PhMeSi)−toluene, which are formed by the trapping of a radical intermediate $ClPhMeSi^\bullet$ with toluene (the rate constant of the reaction of the triethylsilyl radical with toluene is 10^6 mol^{-1} s^{-1}).[34] After 15 h, these products disappeared and were converted into a low molecular weight polymer ($M_n = 3.5 \times 10^3$ and $M_w/M_n = 1.48$). NMR spectra and GC/MS data show that the radical intermediates react with toluene. The oligomeric products are not polysilylenes, which indicates that the Si−Si catenations are very often interrupted by a toluene moiety. The schematic reaction of $PhMeSiCl_2$ with K in toluene is illustrated in Scheme 2.

A possible explanation for this unusual result is that the much higher oxidation potential of potassium allows electron transfer from a longer distance to the reactive methylphenyldichlorosilane. This may not happen at close proximity to the potassium surface, but when methylphenyldichlorosilane is separated by a layer of one or two toluene molecules. The intermediate monomeric radical with one chlorine atom may attack toluene or form silylene and participate in some side reactions. On the other hand, less reactive di-*n*-hexyldichlorosilane must be much closer to the potassium surface and can more efficiently couple with other silyl radicals to form dimers, trimers, etc. When the oligomer is sufficiently long, it will then start to propagate. The rate-limiting step in the entire polymerization is the building of the oligosilane of sufficient chain length which will have the required electron affinity. Thus, the higher reactivity of potassium leads to very easy electron transfer for methylphenyldichlorosilane and directs the reaction to side products rather than to oligosilane. Methylphenyldichlorosilane approaches the less reactive sodium much closer, which provides oligosilanes in a clean way as indicated by the faster overall polymerization. A similar situation where distance is important to electron transfer is present in Grignard reactions, which are more selective for chlorides and bromides than iodides.[35] The formation of the radical in solution, and not directly at the surface, leads to side reactions. A possible scheme of the reaction of dichlorosilanes with alkali metals is illustrated in Scheme 3. The reductive coupling with Na can occur at the surface of Na to generate polysilylenes in route a. However, the reductive coupling reaction of dichlorosilanes containing aromatic groups at the silicon atoms with highly reactive K can occur from longer distance. This less selective process is accompanied by side reactions b.

The addition of more polar solvents to the potassium system, such as THF (see Table 8), led to the formation of low molecular weight polysilylene with a yield of 14−18% and $M_n \approx 4000$. The product was a regular poly(methylphenylsilylene). It absorbed at ≈340 nm (see Figure 4) and its ^1H NMR spectrum showed a typical microstructure.[36] This result might suggest that the second electron transfer from alkali metal to radical species occurs faster in the mixture of toluene and THF than in toluene, due to the solvation of counterions with THF. The resulting anions react with monomer in the substitution process to form oligosilanes.

The effect of the alkali metal on polymerization of dichlorosilanes might give some information about the energy diagram of the reaction between alkali metal and dichlorosilanes. The oxidation energy of K is higher than the reduction potential of di-*n*-hexyldichlorosilane. This reaction can occur easily. The oxidation energy of Na is lower than the reduction potential of di-*n*-hexyldichlorosilane. This reaction can occur very slowly with low conversion at ambient temperatures. The oxidation energy of K is much higher than the reduction potential of methylphenyldichlorosilane. The higher

Scheme 3. Possible Reaction Scheme of Reductive Coupling of Dichlorosilanes with Alkali Metals in Toluene: Rout a, Reductive Coupling of $PhMeSiCl_2$ with Na or Hex_2SiCl_2 with Na and K; Route b, Reductive Coupling of $PhMeSiCl_2$ with K



reactivity of K toward methylphenyldichlorosilane can lead to the side reactions.

3. Effect of a Homogeneous Reducing Agent on the Polymerization of Methylphenyldichlorosilane. The reductive coupling of dichlorosilanes with alkali metals in nonpolar solvents led to the formation of high molecular weight polymers. The heterogeneity of reductive coupling impairs good control of polymerization conditions. Therefore, reductive coupling was attempted using a homogeneous reducing agent, such as sodium naphthalenide. The use of sodium naphthalenide with Ph_3SiCl and $PhMe_2SiCl$ has been previously reported to yield disilanes as the major products and a small amount of 1,4-bis(triphenylsilyl)-1,4-dihydronaphthalene.[37] However, in contrast to triphenylchlorosilane, the reaction of trimethylchlorosilane with sodium naphthalenide yields only 1,2-bis(trimethylsilyl)-1,4-dihydronaphthalene.[38] No hexamethyldisilane was obtained. It is not clear whether a radical intermediate or an anionic intermediate is involved. With dichlorosilanes the reaction of other homogeneous reducing agents, such as sodium naphthalenide, was not studied. The reaction of dichlorosilanes with a homogeneous agent was attempted by either adding monomer solution to a homogeneous agent or adding the homogeneous agent to the monomer solution. The results are summarized in Table 9.

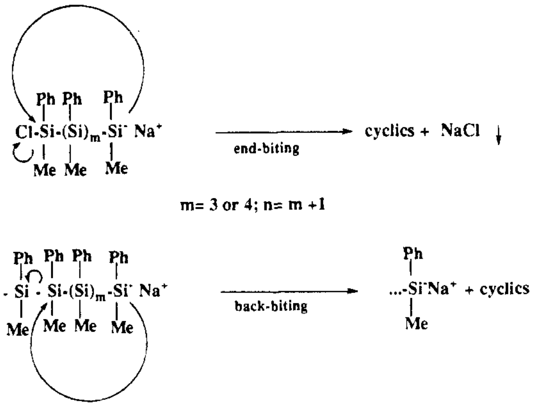
Silyl anions containing dialkyl substituents at the silicon atoms can lose an electron to naphthalene to generate silyl radicals.[39] To eliminate this reaction the polymerization of methylphenyldichlorosilane was performed with homogeneous reducing agents, such as sodium naphthalene/THF (sodium naphthalenide), in THF or in the mixture of toluene and THF (9:1).

Table 9. Results of the Reactions of Chlorosilanes and Dichlorosilanes with Sodium Naphthalenide in Various Solvents

chlorosilane	solvent[a]	mode of addition	products	ref
Ph_3SiCl	DME	A[b]	disilane (83%)[c]	37
Ph_3SiCl	DME	B[b]	disilane (90%)	37
$PhMe_2SiCl$	THF	A	disilane (62%)	37
$PhMe_2SiCl$	THF	B	disilane (91%)	37
$PhMeSiCl_2$	THF	A	five-membered ring	d
$PhMeSiCl_2$	THF	B	five-membered ring	d
$PhMeSiCl_2$	THF:tol (1:9)	A	five-membered ring	d
$PhMeSiCl_2$	THF:tol (1:9)	B	five-membered ring	d

[a] DME = 1,2-dimethoxyethane, THF = tetrahydrofuran, tol = toluene. [b] A: a solution of sodium naphthalenide was added to a chlorosilane solution. B: a chlorosilane solution was added to the solution of sodium naphthalenide. [c] The remaining proportion is the yield of disiloxanes. [d] This work.

Sodium naphthalenide was prepared by the reaction of naphthalene with an equimolar amount of Na in THF. In order to avoid chemical degradation, the homogeneous reductive agent in THF was added to an excess amount of dichlorosilane. The final product was analyzed by GPC and ^{29}Si NMR. The results show that the final product is a five-membered ring (−30.8 ppm versus TMS in ^{29}Si NMR).[36] This may be explained by greater ionic character of Si−Na bonds in solvents which are more polar than toluene.[40] Thus, an end-biting reaction as well as a back-biting process of silyl anions can occur easily to form a five-membered ring (eq 2).[25,29] On the other hand, heterogeneity of the reaction may slow down the end-biting process.



(2)

Effect of Monohalo-Terminated Oligosilanes on the Sonochemical Synthesis of Polysilylenes. Cyclics (four- to six-membered rings) are formed in high yields by end-biting of silylsodium with chloro-terminated oligosilanes. The rate-determining step in the entire polymerization is the building of an oligosilane of sufficient chain length (probably longer than hexamer) which cannot participate effectively in the intramolecular cyclization. To reduce the intramolecular cyclization $Ph(n\text{-}Hex_2Si)_4I$ was used. It can be called a promoter, because longer chains have a higher electron affinity toward sodium than monomer does and they react with sodium more easily than monomer.[1e] This experiment was carried out by adding a mixture of methylphenyldichlorosilane and promoter to the sodium dispersion.

$Ph(n\text{-}Hex_2Si)_4I$ could efficiently eliminate the end-biting of silyl anions with chloro-terminated oligosilanes, since it is blocked at the chain end with an inactive phenyl group. The polymer yield increased from 12 to 19.2% and the polydispersity was $M_w/M_n = 1.66$. From GPC data, the number-average molecular weight (M_n)

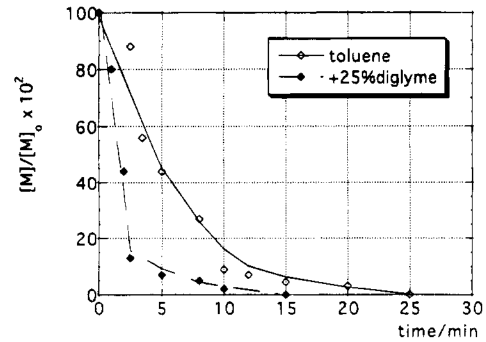


Figure 5. Disappearance rate of $PhMeSiCl_2$ in toluene and in a mixture of toluene and 25% diglyme in the presence of ultrasound as a function of time.

was 6.2×10^4 (a theoretical $M_n = 1.01 \times 10^4$). Cyclics are still formed in high yield (≈80%). The ^1H NMR spectrum shows that the ratio [repeating unit]/[promoter] in a polymer is 92. This ratio is higher than the starting mole ratio by a factor of 1.23, indicating that 15–20% of promoter was incorporated into a polymer.

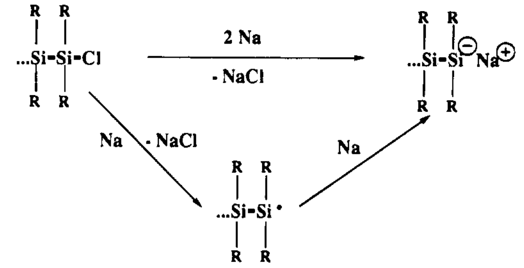
These results may be explained in two ways. The first explanation is based on the coupling reaction between promoter ($Ph(n\text{-}Hex_2Si)_4I$) and oligomeric anions ($Ph(n\text{-}Hex_2Si)_4^-$) which yields dimers ($Ph(n\text{-}Hex_2Si)_8Ph$) soluble in a large amount of isopropyl alcohol. The second is based on the competition reactions of monomer and promoter with sodium. A portion of monomer may react with the promoter while some may react directly with sodium due to easier monomer diffusion to provide polymeric chains. It is possible that the reactivity is more influenced by the presence of a phenyl group in a monomer than by the tetrasilane chain in the dihexyl promoter. It will be interesting to apply a promoter to homogeneous polymerization systems.

Preliminary Kinetic Studies. The rate of disappearance of $PhMeSiCl_2$ in toluene and in the mixture of toluene and 25% diglyme in the presence of ultrasound has been investigated by ^1H NMR studies. These experiments were carried out by comparing the integration ratio of methyl groups in the mixed products to hexamethyldisilane, used as an internal standard in the ^1H NMR spectra. The methyl groups of methylphenyldichlorosilane, hexamethyldisilane, and the mixed products (cyclics and polymer) appeared at 1.05, 0.09, and 0.09 to −0.5 ppm, respectively.

Preliminary kinetic results show slow initiation (sigmoidal curves) for the polymerization in toluene and faster initiation in the presence of etheral solvents, as shown in Figure 5. In toluene monomer disappears slowly at the beginning and faster after some induction period. The addition of diglyme in the polymerization mixture results in the elimination of the induction period, suggesting that the rate of the initiation reaction is accelerated by the addition of polar solvents stronger than propagation. The increase in initiation rate leads to a decrease in molecular weight, since more chains start polymerizing. The influence of polar solvents on polymerization suggests that polymerization proceeds by the anionic mechanism. The macromolecular silyl chloride reacts with sodium in a two-electron-transfer reaction to form a silyl anion. The exact nature of the silylsodium is not known and may also have a covalent character.[40]

Worsfold obtained similar results for thermal polymerization of hexylmethyldichlorosilane.[14] He has also reported the apparent independence of the propagation reaction on the surface area of the sodium, which suggests that the reaction of chloro-terminated macromolecules with sodium could not be the rate-determining step.[14,30] The strong effect of the polar solvents on polymerization can be explained by the more ionic character of silylsodium due to the solvation of counterions. Thus, it seems that the rate-determining reaction is the reaction of polymeric anions with dichlorosilanes (see Scheme 1).

Scheme 4. Formation of Anionic Species by either One Two-Electron-Transfer Step or Two One-Electron-Transfer Steps via Radical Intermediates



Trapping of Radical Intermediates. The results discussed previously indicate that sonochemical reductive coupling of disubstituted dichlorosilanes with alkali metals proceeds by a chain growth process with slow initiation and rapid propagation.[18,30,33] The rate-determining step in the propagation is the reaction between silylsodium and monomer to form silyl chloride end groups. Then silyl chloride is reduced by sodium to silylsodium. The question remains whether this takes place in one step or two single-electron-transfer steps via radical intermediates (see Scheme 4).

In order to solve this ambiguity, the sonochemical homopolymerization of dichlorosilanes with pendant allyl and 5-hexenyl groups and their copolymerization with methylphenyldichlorosilane were studied. The detailed results were reported previously[41] and will be briefly summarized here.

Homopolymers and copolymers were formed with the usual yields of ≈10% and molecular weights in the range of M_n = 30 000–70 000. Homopolymers and copolymers absorbed in the wavelength above 330 nm, which indicates long Si–Si catenation. However, extinction coefficients were smaller than for poly(methylphenylsilylene), which also indicates that the polymer chain was sometimes interrupted by incorporation of the Si–C linkages in the main chain. UV spectroscopy and also ^{29}Si NMR provide an estimation of approximately 10–20 noninterrupted Si–Si sequences.

It has also been determined from ^1H NMR spectra that approximately half of the alkenyl groups have been consumed in the polymers. This suggests a postpolymerization of alkenyl groups on the preformed polysilylene matrix without cross-linking. Radical polymerization of diallyl- and triallylsilanes also provides soluble high molecular weight polymers.[42] Initially soluble polymers slowly cross-link (even in the solid state) to form insoluble materials after a few days.

Thus, polymerization of dichlorosilanes with pendant alkenyl groups is possible; however, alkenyl groups occasionally trap short-lived radical intermediates. A radical either can be trapped by a pendant alkenyl group or can get an electron from sodium to form silyl anion. Anions react with alkenes very slowly.

These results indicate that chlorosilanes are reduced to silylsodium in two one-electron-transfer steps with short-lived radical intermediates, but propagation involves silylsodium and dichlorosilane in the rate-limiting step. The second electron transfer must be very fast.

Silyl radicals react very rapidly with 1-hexene[34] ($k = 5.0 \times 10^6$ mol^{-1} s^{-1} for the triethylsilyl radical at 25 °C) in the intermolecular reaction and even faster in the intramolecular process (10^7 s^{-1} $< k <$ 10^9 s^{-1}).[43] The second electron transfer must be 10–20 times faster than the intramolecular process in order to get the 10–20 Si–Si bond sequence. It should be noted that silyl radicals also react very rapidly with toluene ($k = 1.2 \times 10^6$ mol^{-1} s^{-1} for the triethylsilyl radical at 25 °C).[34] Formation of high polymer (DP > 1000) again indicates that the lifetime of radicals must be very short; otherwise only short oligomers could be formed. Nevertheless, short-lived radicals do exist on the pathway from chloro-terminated chain ends to silylsodium. The polymer chain is built, however, by the reaction of monomer with sodium end groups.

Radical intermediates have been proposed due to solvent effects[44] but they were later assigned to other phenomena.[16]

Structure of End Groups. The structure of end groups has been investigated in two experiments: (1) the sonochemical polymerization of partially deuterated monomer ($C_6D_5MeSiCl_2$) with an excess of sodium in a mixture of toluene and diglyme (3:1) followed by termination with $Ph_2SiMeCl$; (2) the coupling reaction of propagating silyl species with α,α′-dibromo-*p*-xylene.

Integration of NMR signals in deuterated polymer indicates that average 90% of chains contain two ends which reacted with an electrophilic $Ph_2MeSiCl$. The coupling with xylene derivative leads to polymers with an increased molecular weight and with a bimodal MWD. Analysis of the enhancement of molecular weights indicates that average 60% of chains contain two active sites.

There are some difficulties with the interpretation of the obtained results. First is the validity of the GPC calibration based on polystyrene standards. Second is the possible reaction of the α,α′-dibromo-*p*-xylene with silyl anions as well as with the remaining sodium. Third is the possibility of macrocyclization. The last reaction is of lower probability due to the relatively high concentration of the reagents. Nevertheless, the hydrodynamic volume of the cyclic polymer is less than that of the respective linear polymer. No peak at lower molecular weight was found and all signals of the products move to the higher molecular weight region, indicating qualitatively that all chains were active. The bimodality of the molecular weight distribution indicates, however, that either only a small fraction of chains were carrying two anionic species per chain or only a small fraction of chains had sufficient reactivity toward α,α′-dibromo-*p*-xylene in comparison with sodium. In fact, the NMR spectra of the coupled product show two new peaks at 2.2 and 2.8 ppm ascribed to ...–PhMeSi–**CH₂**–Ph–**CH₂**–CH₂–Ph–CH₂–PhMeSi–..., respectively. Thus, some coupling of the α,α′-dibromo-*p*-xylene also occurs. There are two possible reasons for the existence of silyl anions of various reactivities. One possibility is that some silyl anions are strongly attached to the surface of the remaining sodium particles, while others that remain in solution have varying reactivities (free anions, ion pairs, various aggregates). It is possible that only the most reactive species can couple with α,α′-dibromo-*p*-xylene before it reacts with sodium. Otherwise, one gets a discrepancy between the overall increase of the molecular weight observed by GPC in the reaction with α,α′-dibromo-*p*-xylene (60% of anionic species) and quenching with $Ph_2SiMeCl$ (>90% of anionic species).

It has to be remembered that the extrapolation of these results to a typical polymerization in toluene may not be so easy. Diglyme stabilizes the anionic intermediates while less polar toluene does not. It is possible that growing anions may lose an electron to become a polymeric radical which will terminate by a fast reaction with solvent.

Degradation of Polysilylenes. Polysilylenes are known to decompose in the presence of light.[2] The degradation of polysilylenes upon irradiation with UV light leads to the formation of silyl radicals and silylenes. On the other hand, much less is known about the chemical and mechanical stability of polysilylenes. Si–Si bonds can be easily cleaved by various nucleophiles and electrophiles. Si–Si bonds can also be cleaved homolytically at elevated temperatures and by shear forces. Here, sonochemical degradation and chemical degradation are discussed.

1. Sonochemical Degradation. Sonochemical polymerization in toluene at ambient temperatures leads to monomodal polysilylenes with relatively high molecular weights ($M_n \approx 100\,000$) and no low molecular weight fraction ($M_n \approx 5000$) is observed.[18,29] We have explained the monomodality by the suppression of side reactions responsible for the formation of the low molecular weight fraction. Low polydispersity of the high polymer ($M_w/M_n < 1.5$, as low as $M_w/M_n = 1.2$) is due to sonochemical degradation.[29] Decrease of the molecular weight to a limiting value of $M_n \approx 50\,000$ has been observed with prolonged sonication in toluene. This decrease in molecular weight can be attributed to selective homolytic cleavage of Si–Si bonds in both poly(methylphenylsilylene) and poly(di-*n*-hexylsilylene) by shear forces. The decrease in polydispersity might be based on the preferential cleavage of Si–Si bonds in the middle of the chain. Similar action of ultrasound has previously been described for other organic polymers.[24] Polysilylenes degrade more easily than organic polymers due to the relative weakness of the Si–Si bond in comparison with the C–C bond.

The homolytic cleavage of Si–Si bonds leads to the formation of radicals. The fate of these radicals is not known. It might be expected that silyl radicals could react with toluene to produce a final product containing toluene. In order to test the possibility of the reaction of silyl radicals with toluene, high molecular weight poly(methylphenylsilylene) ($M_n = 2.0 \times 10^5$) was used, in which Si–Si bonds could be cleaved four times to a reduced molecular weight ($M_n \approx 4 \times 10^4$). The final product was analyzed by ^{1}H NMR. The ^{1}H NMR spectrum of the degraded product shows a small peak corresponding to the methyl groups of the toluene moiety at 2.32 ppm. The integration area ratio of the methyl groups in the toluene moiety to that of the methyl groups in poly(methylphenylsilylene) is 0.46%, which agrees with the proportion of end groups in the final product based on molecular weight. This reaction can be potentially used for the end functionalization of some polysilylenes.

Examples of the decrease in molecular weights are presented in Figure 6. Degradation of poly(methylphenylsilylene) in the presence of sodium dispersion proceeds slightly faster. However, no cyclopolysilanes have been detected during this degradation, in contrast to chemical degradation discussed in the next section. This may indicate that in nonpolar solvents the efficiency of the electron transfer is very low and radicals and/or anions are very rapidly trapped by traces of moisture and other impurities in the degradation systems. Thus, the unusual molecular weight distribution observed in

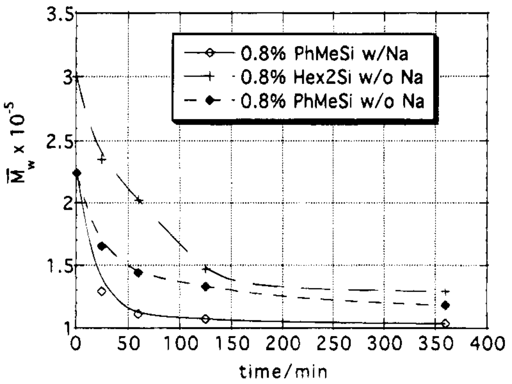


Figure 6. Plots of M_w versus time in the sonochemical degradation of polysilylenes with sodium.

Table 10. Summary of Chemical Degradation of Polysilylenes with Alkali Metals[a]

solvent	alkali metal	$(PhMeSi)_n$	$(n\text{-}HexSi)_n$
THF	K	<10 min	>2 h
THF	Na	>2 h	no
THF	Li	no	no
THF	Na^+, $Naphth^-$	<10 min	>10 h
THF	Li^+, $Naphth^-$	<10 min	>10 h
toluene	K	no	no
toluene	Na	no	no
toluene	Na[b]	>2 h	>10 h

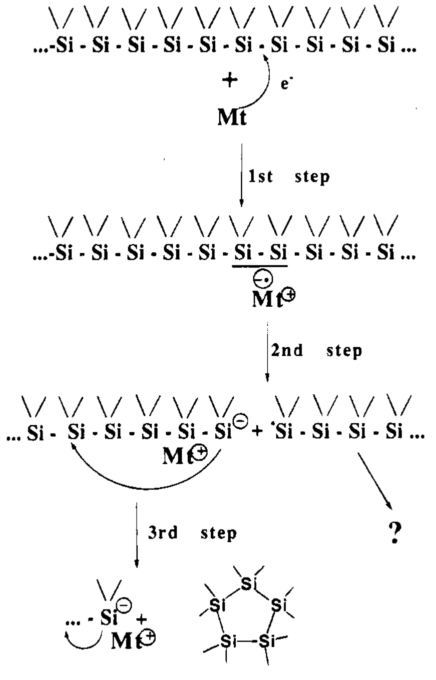
[a] Li^+ or Na^+: metal naphthalenide in THF. [b] Addition of cryptand[2.2.2] or THF after polymerization.

sonochemical synthesis stems from two reasons: mechanical degradation of the very high molecular weight fraction and suppression of side reactions that leads to low molecular weight polymer. Low molecular weight polymer cannot be degraded by ultrasound since the lower limit for the sonochemical degradation at the frequency of 20 kHz is $M_n \approx 50\,000$. No cyclic oligomers are formed by sonochemical degradation at ambient temperature in toluene.

2. Anionic Degradation of Polysilylenes by Alkali Metals. Polysilylenes are usually prepared by the reductive coupling of disubstituted dichlorosilanes with alkali metals in nonpolar solvents such as toluene, benzene, or octane.[1,16,17,44,45] No substantial degradation of the polymer is observed in the presence of an excess of alkali metal under these conditions. In THF or diglyme polysilylenes can be degraded by an excess of alkali metal. The degradation products are essentially cyclic oligomers. The rate of degradation depends on the substituents at the silicon atom, solvent, alkali metal, and temperature. Qualitative degradation results are shown in Table 10.

Chemical degradation of polysilylenes with alkali metals is much faster in THF than in toluene due to a difference in solvation of counterions. For example, poly(methylphenylsilylene) was degraded with K in THF within 10 min, but no degradation with alkali metals in toluene was observed. Addition of cryptand[2.2.2] or THF to toluene increases the degradation rate. The solvation of alkali metal cations with more polar solvents facilitates chemical degradation due to stabilization of ionic intermediates. The rate of degradation strongly increases with the reactivity of the alkali metal. Poly(methylphenylsilylene) degrades in THF with K faster than with Na but does not degrade with Li even in the presence of ultrasound. Poly(di-*n*-hexylsilylene) degrades with K but does not degrade with Na or Li. These results indicate that the reactivity of alkali metals is in the order K > Na > Li. This reactivity order is consistent with the results obtained from the reductive coupling of dichlorosilanes with alkali metals. The effect of the counterion seems to be less important, since degradation, initiated by sodium and lithium naphthalenides proceeds nearly as fast as with potassium.

Scheme 5. Chemical Degradation of Polysilylenes with Alkali Metals in Three Steps



Degradation is much faster for poly(methylphenylsilylene) than for poly(di-*n*-hexylsilylene). This agrees with the general trend of the stability of the silyl anions discussed in the previous section. Aryl groups on the silicon atom stabilize anionic intermediates.

Cyclics are the main product of chemical degradation. They are the true thermodynamic products of the reductive coupling. Molecular weight of the degraded polymers remains high till the very end of the degradation, indicating that degradation is a chain process. The mechanism of the degradation is shown in Scheme 5.

The first step, in which a polymeric radical anion is formed, may be rate limiting. It is facilitated in polar solvents because of the energy gain by the solvation of alkali metal cations. The intermediate radical anion is cleaved to form a radical and an anion. The fate of the radical is not known. It may react with solvent, it may take a second electron to form a silyl anion, or the radicals may recombine (although the radical concentration is usually very low). The silyl anions now start cleaving Si−Si bonds. Because of entropic effects, the rate of intramolecular reaction must be faster than the rate of the intermolecular process. Anchimeric assistance (or the neighboring group participation) is highest for a five-membered ring, which has the lowest strain. Chemical degradation leads to the formation of cyclopentasilanes and cyclohexasilanes. The back-biting process for larger or smaller rings is retarded for enthalphic reasons.

The back-biting process has to be distinguished from the end-biting process which may occur during the synthesis of polysilylenes. Polymerization proceeds by the reaction of silyl anions (which may have some covalent bond character) with dichlorosilane (a monomer) via a chain growth process. At the level of tetra-, penta-, or hexasilane, the anionic center present at one end may react with its chloro-terminated end instead of reacting with monomer. This end-biting process will also lead to the formation of cyclics.

The present results indicate that the back-biting (or degradation) is not important in toluene without additives, nor is it very important for poly(di-*n*-hexylsilylene) in THF. However, polymerization of methylphenyldichlorosilane with any alkali metal in THF will result in cyclics rather than poly(methylphenylsilylene). Polymerization in diethyl ether also led to reduction of yields and molecular weights.[14] Evidence for a different mechanism of end-biting and back-biting processes is provided by the structure of cyclic oligomers which are formed during the synthesis of poly(di-*n*-hexylsilylene). More than 80% of octa-*n*-hexylcyclotetrasilane ($\delta = -20.3$ ppm in ^{29}Si NMR) is formed in the reductive coupling process in the mixture of toluene and isooctane while degradation leads to the formation of deca-*n*-hexylcyclopentasilane ($\delta = -34.6$ ppm in ^{29}Si NMR).

IV. Summary of Mechanistic Studies of Polysilylene Synthesis

Let us summarize the information on the sonochemical reductive coupling reported here and compare these results with others reported previously for the thermal process in order to create a unified view on the synthesis of polysilylenes from disubstituted dichlorosilanes and alkali metals.

Polymodal Molecular Weight Distribution and Polydispersity. Polysilylenes are the only products of the reductive coupling if the reaction is carried out in inert solvents, under appropriate conditions and with exclusion of moisture and oxygen. The intensity of the Si−O and Si−H bonds in the IR spectrum is very low, and UV spectra indicate a long noninterrupted sequence of Si−Si bonds.

There are generally three fractions of polysilylenes which can be easily detected by size exclusion chromatography. The lowest molecular weight products are cyclopolysilanes with the ring size depending on the structure of the substituent. Preferred ring size decreases with bulkiness of substituents: cyclohexasilane for dimethyl, cyclopentasilane for methylphenyl,[46] cyclotetrasilane for di-*n*-hexyl and diphenyl,[47] and cyclotrisilane for dimesityl systems.[48] Cyclic silanes are usually quite soluble in organic solvents and cannot be precipitated with isopropyl alcohol, in contrast to higher molecular weight products. These usually appear as a mixture of lower (<10 000) and higher (>100 000) molecular weight polymers. This trimodality is observed in most cases although under some conditions cyclics are accompanied only by either low or high polymer.

The polymodality must result from the fact that once a macromolecule (or oligomer) reaches a certain size, it proceeds in one of two directions from which there is no return. It is easy to imagine this event for the tetra-, penta-, or hexasilane containing electrophilic SiCl and SiNa structures at the ends. This oligomer may either cyclize intramolecularly to form a cyclopolysilane (end-biting) or may add a monomer molecule to grow to a size at which it will no longer be possible due to enthalpic reasons. Therefore, the proportion of cyclics should increase at lower monomer concentration. Cyclics may also be formed by back-biting when the active site attacks its own chain (see eq 2). This process is found in the degradation of polysilylenes by strong nucleophiles in polar solvents, leading to the total destruction of linear chains into more thermodynamically stable cyclics.

The fate of polymers in the range of degree of polymerization approximately 50 is more difficult to explain. One of the simplest explanations is macrocyclization as observed for polysiloxanes. However, the molecular weight distribution of this fraction and the presence of end groups reject this pathway. It is possible that the higher stiffness of polysilylenes[49] decreases the probability of this process.

The simultaneous formation of high and low molecular weight polymers was previously explained by diffusion processes[13,44] and was related to the macroscopic properties of the solvent mixture. Some results of the present and previous studies[1,16,18,30,33] indicate that molecular weights and polydispersities are extremely sensitive to a small amount of additives and solvents which interact strongly with alkali metal cations such as crown ethers, cryptands, and glymes. This is related more to the specific solvation of the active site rather than to the bulk solvent property.

In addition, there is very interesting information on the scrambling process in the formation of the periodic polymer ($-$Me$_2$Si$-$Hex$_2$Si$-$Me$_2$Si$-$) from the corresponding 1,3-dibromo trimer.[50] Cyclohexasilane and low molecular weight polymer have clean periodic structures, but high molecular weight polymer is scrambled with a random distribution of the repeating units. This result indicates that high molecular weight polymer participates in the process of trans-silylation which does not occur for low polymer. It also indicates that cyclics are formed by an end-biting process, not back-biting (otherwise they should also be random). Trans-silylation cannot occur via typical cleavage of a polysilylene chain by silylsodium intermediates since this process would favor a unimolecular back-biting reaction. Thus, the most likely explanation is that high molecular weight chains collapse on the surface of sodium particles and participate in some kind of the metathesis process which leads to the scrambled structures. We tried to simulate this process by adding poly(di-*n*-hexylsilylene) and poly(di-*n*-butylsilylene) to sodium dispersion but found no scrambling. It is possible that chains must be anchored to the surface by the formation of silyl sodium intermediates which keep them in the close proximity to the surface. Therefore, the polydispersity is affected by bulk solvent effects and, to an even greater extent, by solvation and the state of silylsodium intermediates.

Thus, polysilylene chains after growth to the polymerization degree of ≈50 either depart to solution or stick to the sodium surface and grow by reaction with monomer (or with another Si−Cl end groups). Chains may also participate in the scrambling by an undefined metathesis process. The limit of DP ≈ 50 and proportion of low molecular weight fraction may strongly depend on solvent and temperature. This will be discussed later during analysis of the structure of the reactive intermediates, but it suffices to say that in more polar solvents ...−SiNa end groups will be better solvated and can depart easier to solution than in less polar solvents. Silylsodium will react very rapidly with monomer in solution to form silyl chloride. The macromolecular silyl chloride will have difficulties returning to the sodium surface (although decrease of this fraction with reaction time is sometimes observed)[30] and they may be terminated by the reaction with solvent at the stage of radical. Lower molecular weights in more polar solvents can also be due to relatively faster initiation.

The proportion of high molecular weight polymer decreases with temperature and with polarity of the reaction medium. Higher temperature will favor the departure of chains from the sodium surface and will increase the probability of the reaction with solvent and termination of the growing chains. In that case, polydispersity might be also affected by the particular structure of solvent molecules (e.g., H transfer ability, e.g., toluene vs benzene).

Polymer of sufficiently high molecular weight will "stick" to the surface due to various interactions: bulk solvent effects, reversible formation of polymeric radical anions by segments located in the middle of chain, and eventually formation of silylsodium growing species. In the last case the presence of active sites at both ends is very important, since chains will be always anchored to the surface by one end. Polarity of the solvents and additives solvating alkali metal ions and ion pairs will help the departure of chains from the surface.

It seems that the heterogeneous nature of the reductive coupling may play an important role in the generation of linear polymers. Homogeneous reducing agents (sodium naphthalenide, electric current) will degrade any preformed polymer in media of sufficient polarity (unfortunately they are usually used under such conditions). In addition, the proportion of cyclics may be lower if the silylsodium is sterically more hindered. This can happen in the case of a heterogeneous reaction as well as in the presence of some crown ethers in nonpolar media and for dialkyl-substituted monomers.

Thus, the best conditions for the generation of high molecular weight polymer will be low temperature, nonpolar solvent, and relatively high monomer concentration. The sonochemical process requires a low concentration of sodium dispersion (unless inverse addition is applied) and allows decrease of the reaction temperature due to the cavitational erosion of the surface of the metal.

Nature of Active Sites. The nature of the active sites has been probably the most controversial topic in the mechanism of polysilylene formation. The active sites could have either an anionic or a radical nature. As shown in this paper both views are partially correct, but silylsodium intermediates are definitely involved in propagation. These data as well as some previous results indicate chain growth nature with slow initiation and fast propagation. The precise mechanism of the initiation process is not known. It probably includes generation of the oligosilanes with reactivity sufficient for fast propagation. Initiation may also involve some impurities (oligosilanes) present in minute amounts and may also involve some strain rings, radicals, or silylenes. The unusually slow reductive coupling of methylphenyldichlorosilane with potassium in toluene provides very good evidence that not only reduction potential but successful generation of oligosilanes is necessary for the subsequent propagation.[33]

Initiation may proceed by the surface coupling of monomeric radicals and subsequent surface reactions (involving anions?) to form chloro-terminated oligosilanes of a length sufficient to have reductive coupling potential similar to chloro-terminated polymer chains.

The sequence of the elementary reactions involved in propagation was shown in Scheme 1. A chloro-terminated chain rapidly takes one electron to form a radical anion and eventually a silyl radical. The silyl radical takes the subsequent electron from a sodium particle to form polymeric silylsodium. The nature of this bond is not known. Is it truly anionic in nonpolar solvent? It may have a large proportion of covalent character.[40] Nevertheless, it has sufficient reactivity to consume dichlorosilane in the growth process. Thus, the chain extension and probably the rate-limiting step in propagation involve a reaction between monomer and polar (anionic?) polymeric silylsodium. The generated polymeric silyl chloride is in close proximity to the sodium particle and is rapidly reduced in two one-electron-transfer steps. Trapping the radical intermediates provided evidence that this is not a single two-electron-transfer process.[41]

Nevertheless, there are plenty of results which are in disagreement with purely radical propagation: solvent and additive effects, high proportion of cyclic oligomers and copolymerization of nonhomopolymerizable monomers.[16,18,30,33]

Silylsodium reacts preferentially with a monomer possessing two electron-withdrawing chloride atoms rather than with a chloro-terminated chain end. Only in the case of penta- and hexasilanes does high neighboring group participation enhance the end-biting process resulting in cyclopolysilanes. The chance for a similar reaction with long chains may be much smaller due to their lower concentration and lower reactivity as well as their short lifetime. It is, however, possible that a few Si−Si bonds in linear chains are formed by the reaction between chain ends. Nevertheless, the vast majority of Si−Si bonds are created by the reaction of silylsodium with monomer.

What Is Special about the Sonochemical Method? High local temperatures and pressures found during sonication have little if any effect on the reductive coupling process. Reaction of dialkyldichlorosilane in toluene with sodium requires temperatures of at least 80 °C in both thermal and sonochemical synthesis. Arylalkyldichlorosilanes can be polymerized sonochemically at lower temperatures due to their higher reactivity. Sonochemistry simply allows the reduction of reaction temperature and assures a continuous supply of the fresh sodium surface by cavitational erosion. Apparently, it does not remove polysilylene chains anchored to the surface because they can reach high molecular weight at the early stages. Similar effects can be ascribed to some additives, such as ethyl acetate,[16] which also enables low-temperature synthesis. However, ultrasound has only a physical action on the process, whereas the additives may also moderate the electron-transfer process or be part of the solvation sphere.

Sonochemistry has the additional effect on the degradation of the preformed polymers. This selective degradation leads to polymers with low polydispersity. Degradation occurs by the homolytic cleavage of chains by mechanical forces.

V. Conclusion

Sonochemical polymerization of methylphenyldichlorosilane and di-*n*-hexyldichlorosilane with alkali metals in toluene leads to the formation of monomodal polysilylenes with relatively narrow molecular weight distributions ($M_w/M_n < 1.5$). The optimum conditions for the sonochemical synthesis of well-defined polysilylenes in the presence of an immersion-type probe are as follows: $[M]_0 \approx 0.30$ M, reaction temperature ≈ 60 °C, polymerization solvent = toluene, $[Mt]_0/[Si{-}Cl]_0 \approx 1.15$, alkali metal = Na for poly(methylphenylsilylene) and K for poly(di-*n*-hexylsilane). Sonochemical degradation controls molecular weight and polydispersity.

Polymerization proceeds by a chain growth process. A strong solvent effect and copolymerization studies support the existence of polar intermediates as active centers. Anionic growing species are formed via radical intermediates which are produced by the first electron transfer from alkali metals to chloro-terminated polymeric chains. Trapping experiments show that radical species are present as short-lived species that are converted into anionic species by the rapid second electron transfer from alkali metals.

Polymerization is strongly dependent on substituents at the silicon atoms, solvents, alkali metals, and reaction temperature. Dichlorosilanes containing an aromatic group are more reactive than dialkyldichlorosilane because the aromatic group facilitates an electron transfer.

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