4878 Macromolecules 1993, 26, 4878-4887

Evaluation of the Synthesis of Polysilanes by the Reductive-Coupling of Dihaloorganosilanes

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Received October 16, 1992; Revised Manuscript Received May 25, 1993

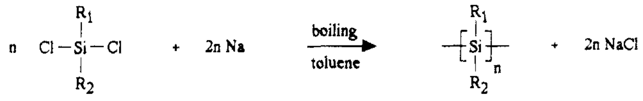
ABSTRACT: The blue color that develops during the alkali metal-mediated reductive-coupling of dihaloorganosilanes to form polysilanes has been shown to arise from colloidal alkali metal particles. The development of the color is demonstrated to mark the end of reaction, and the role that the colloid particles play in determining the proportion of very high molecular weight polymer that develops in these systems is discussed. The overall polymodal molecular weight distributions that result are explained in terms of an anionic mechanism of polymerization and the heterogeneous reaction conditions. Oligomeric materials that are always present in the product mixtures are shown to arise from alkali metal-induced polymer degradation reactions and from otherwise unreacted monomer that is consumed during the polymer isolation procedure. The problems of the reproducibility and control of such preparative methods are assessed in the light of these conclusions.

Introduction

Since the discovery that soluble high molecular weight polysilanes may be prepared by a Wurtz–Fittig type reductive-coupling of dichloroorganosilanes by alkali metals[1,2] shown in Scheme I, there have been a rapidly increasing number of publications reporting their properties.[3-5] In high-resolution microlithography, polysilanes have potential for application as top-layer imaging resists in multilayer processing[6] and as contrast enhancement layers.[7] They have been shown to be successful as preceramic materials for the manufacture of Si–C fibers[8] and other reinforcement materials.[9] They are known photoinitiators of vinyl polymerizations,[10] and recently polysilanes have been utilized as photoconductors[11] and as nonlinear optical materials.[12]

The Wurtz-type preparation of polysilanes often yields only a low fraction of the desirable high molecular weight polymer and a far greater proportion of linear and cyclic oligomers. Although high molecular weight, narrow distribution polymers have been reported[13] to be formed in low yield in nontransfer solvents, molecular weight distributions are otherwise commonly very broad and polymodal and reproducibility is achieved only with the most rigorous attention to detail in the synthetic procedures. Sakurai and co-workers[14,15] have reported an alternative synthesis involving the intermediacy of masked disilylenes that can be applied to the formation of poly(dialkylsilane)s and which offers far greater structural specificity, but to date, reductive-coupling reactions still hold the greatest promise for achieving controllable syntheses on anything like an industrial scale.

Scheme I



$$n\ \mathrm{Cl{-}Si(R_1)(R_2){-}Cl} + 2n\,\mathrm{Na} \xrightarrow[\text{toluene}]{\text{boiling}} \left[\mathrm{Si(R_1)(R_2)}\right]_n + 2n\,\mathrm{NaCl}$$

R_1, R_2 = alkyl or aryl groups

Although preparations of high molecular weight, narrow distribution polysilanes have been reported,[13] most commonly the molecular weight distributions that result prior to any fractionation are trimodal as follows: (i) $M_{r,w} <$ 1500 (the linear and cyclic oligomers); (ii) $M_{r,w} = 1500$ to 10^5 (this fraction is commonly of two overlapping peaks); (iii) $M_{r,w} = 10^5$ to several million. Mechanistic studies of the reaction conducted with a view to achieving tighter control and improving the yield of the high molecular weight fraction have been sparse.[16,17] Such a rapid reaction in a boiling medium containing molten alkali metal does not readily lend itself to detailed mechanistic investigation. Only general, and to an extent contradictory, conclusions have been drawn. The approach has been on two fronts. The first has been directed to gaining an understanding of the solvent effects in the hetergeneous medium, which as well as consisting of metallic and solvent liquid phases also includes solid phases comprising the growing polymer and an increasing amount of an alkali metal halide. Zeigler and co-workers[18,19] have advanced a model that rationalizes the observed effects in terms of the monomer concentration at the alkali metal surface. This is considered to be determined by the rate of diffusion of the monomer from the solvent bulk through a barrier of the polymer and the salt, the permeability of which is considered to vary with the ability of the solvent to extend the polymer away from the metal surface. The second approach has been directed toward determining the nature of the polymerization process itself. Though stoichiometrically it seems to resemble a step growth polymerization reaction, it is more reasonably explained in terms of chain growth. Various intermediates have been considered to be involved in the growth reaction including silylenes, disilenes, silyl radicals, silyl anions, and silyl radical anions, and only the involvement of silyenes has been eliminated through studies in the presence of known silylene traps.[18,20] Zeigler and co-workers[18,19] have presented evidence based upon bulk solvent effects that support the intermediacy of silyl radicals, having observed lower molecular weights resulting from the use of monomers and solvent media that are susceptible to chain transfer reactions through hydrogen atom abstraction; these arguments are lent support by evidence of Si–H infrared absorption bands in the low molecular weight fractions of the product polymers. Furthermore, whereas the formation of poly(*n*-hexylmethylsilane) proceeds to a "normal" yield under Wurtz conditions, in complete contrast dichloro(5-hexenyl)methylsilane was observed to give rise to only a trace of non-polysilane material under the same conditions of reaction. This is interpreted in terms of an intramolecular cyclization in the latter system, inhibiting the polymer-

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ization reaction, and again points to radical involvement in the mechanism by analogy with the known cyclization of corresponding carbon-centered radicals.[13] Notwithstanding this quite considerable evidence for the involvement of radical intermediates, to the best of our knowledge, no defined radical mechanism has ever been communicated. On the other hand, increased yields obtained in studies involving polyether solvents[21] or the addition of cryptand derivatives[22] has been argued to lend weight to the possibility of the intermediacy of silyl anions in a mechanism of polymerization that has been represented.[22] It is commonly thought that the overall polymerization may proceed by competing noninteractive radical and ionic mechanisms, and it is this possibility that is generally advanced to rationalize the polymodal molecular weight distributions. However, there is evidence in some cases, typically in the preparation of poly(methylphenylsilane), that the heterogeneity of the reaction system might also be responsible.[19]

In a recent communication[23] we reported studies of the formation of various polysilanes through the sodium-mediated reductive dechlorination of dichloroorganosilanes in the presence of 15-crown-5 in refluxing diethyl ether. Agitation must be maintained, but reflux conditions have subsequently been shown not to be essential, and although the presence of a cyclic polyether increases yields it is usually at the expense of molecular weight. At these lower temperatures, the reaction is much slower but nonetheless goes to completion. Mechanistic and spectroscopic studies are more readily conducted under these much moderated reaction conditions, and this paper is a report of such studies together with a fuller discussion of their diverse implications with respect to the search for alternative reducing agents for the Wurtz synthesis of polysilanes than we have previously reported.[24]

Experimental Section

Materials. Dichlorodiphenylsilane, dichlorodimethylsilane, dichloromethylphenylsilane, dichlorocyclohexylmethylsilane, dichlorodi-*n*-hexylsilane, trichloromethylsilane, 1,10-dibromodecane, 1,10-dichlorodecane, dichlorophenylsilane, 4-propenylanisole, and chlorobenzene were supplied by Aldrich. Diphenylsilane was supplied by Fluorochem Ltd. Sodium and potassium were supplied by Fisons and stored under paraffin oil prior to use. A solution of a hydrosilation catalyst in $(CH_2{=}CHSiMe_2)_2O$ was used as supplied by the Toshiba Silicone Co. General purpose solvents were also obtained from Fisons, and those for use in monomer preparation, as polymerization solvents, or in polymer isolation procedures were rigorously dried over sodium/potassium alloy. All glassware for use in preparations was oven-based at 150 °C before use.

Dibromodiphenylsilane was synthesized by the direct reaction between diphenylsilane and bromine in bromoethane solution in accordance with the general method outlined by Eaborn.[25] Dichloromethyl-*p*-tolylsilane was prepared by a standard Grignard reaction of *p*-tolylmagnesium bromide and trichloromethylsilane in diethyl ether. Dichloro-[1-(4-methoxyphenyl)-propyl]phenylsilane was prepared by the hydrosilation of 4-propenylanisole with dichlorophenylsilane following the method outlined by Hayase.[26]

Dihaloorganosilanes were freshly distilled before use. Sodium and potassium dispersions were prepared immediately prior to use by melting the freshly cut metal in rapidly stirred mineral oil. Following the dispersion of the alkali metal the oil was removed by twice washing with the deaereated solvent of reaction (diethyl ether, hexane, toluene, or benzene as required). Deaereated solvent and monomer were then added under an inert atmosphere using syringe techniques; this is the so-called *normal addition* mode. Agitation was maintained throughout the polymerization reaction (3–4 h at ambient temperature) during which the mixtures became increasingly cloudy as both polymer and alkali metal halide precipitated in the reaction medium. For those investigations in which the total isolation of the polymeric fraction was of prime importance, the reaction mixtures were initially quenched by the careful addition of water to ensure that any unreacted alkali metal was consumed. This resulted in the full precipitation of the polymeric and oligomeric materials which were subsequently extracted into toluene solution prior to reprecipitation in methanol. Oligomeric materials were extracted from the polymeric products using *n*-hexane. A typical preparation was as follows:

Preparation of Poly(methylphenylsilane) Using Sodium Dispersion in Diethyl Ether in the Presence of 15-Crown-5. To a two-necked round bottom flask (50 mL) equipped with an egg-shaped PTFE (25 × 12 mm) stirring bar, a condenser, and a rubber septum was added freshly cut sodium metal (0.7 g, 0.0304 mol) under an argon atmosphere using Schlenk-line techniques. The sodium was transformed to a fine dispersion as outlined above and carefully washed with diethyl ether to remove mineral oil. To the sodium dispersion were added diethyl ether (30 mL) and 15-crown-5 (0.6 mL, 0.003 mol), and the apparatus was transferred to an oil bath located upon a laboratory stirrer/hot plate. The temperature was then raised until the solvent reached reflux. Over a period of 30 s, undiluted dichloromethylphenylsilane (2.5 mL, 0.0154 mol) was added. The reaction mixture was rapidly stirred throughout the 3-h reaction period, after which the mixture was allowed to cool to room temperature. While rapid stirring was maintained, water (50 mL) was added *cautiously* to remove the unreacted sodium metal and terminate any reactive chain ends. The organic layer was decanted and added to stirred methanol (250 mL) at room temperature (25 °C), after which the precipitated polymer was collected by filtration on a Büchner funnel and air-dried. The polymer was further purified at ambient temperature by reprecipitation from toluene (50 mL) using methanol (250 mL) and dried under high vacuum. Oligomeric materials were extracted from the dried polymer by vigorously stirring the powder with *n*-hexane (50 mL) at room temperature for 4 h, followed by filtration on a Büchner funnel prior to drying *in vacuo*.

As long as material quantities were maintained from preparation to preparation, these procedures were found to lead to molecular weight parameters that were reproducible to within 10%, and essentially constant distributions were observed. Yields were more variable, but on the larger scale (50-g preparations) these were consistently greater than 70% as long as conditions of vigorous agitation were attained.

A well-recognized but little understood characteristic that the alkali metal-mediated polymerization of dichloroorganosilanes have in common with all Wurtz-type coupling reactions is the appearance of a color of bluish (sodium-mediated systems) or purplish (potassium-mediated systems) hue when the consumption of the alkali metal is virtually complete.[27] Taking the appearance of this color to be an end marker (*vide infra*) of our reactions in which the reagents are in close to stoichiometric ratio, reaction mixtures were then filtered under an inert atmosphere. The solid phase was washed with diethyl ether and dried *in vacuo* for subsequent spectroscopic studies and analyses. In the dry state, the color of these materials was found to be maintained, and they were of a powdery texture. The polymer and low molecular weight materials in the liquid phase were precipitated by dropwise addition to methanol prior to analysis.

The following abbreviations for the names of polymers have been adopted: poly(methylphenylsilane), PMPS; poly(methyl-*p*-tolylsilane), PMTS; poly(diphenylsilane), PDPS; poly[{1-(4-methoxyphenyl)propyl}phenylsilane], PMPPPS; poly(cyclohexylmethylsilane), PHMS; poly(di-*n*-hexylsilane), PDHS; polyethylene, PE.

Apparatus and Procedures. ^1H, ^{13}C, and ^{29}Si NMR spectra were recorded at probe temperature using a JEOL GX-270 spectrometer from solutions in $CDCl_3$. Chemical shifts were referenced to residual proton shifts.

Ultraviolet–visible spectra were recorded in the diffuse reflectance mode on a Shimadzu UV-240 spectrometer operating in the range 190-900 nm. Any visible particles of residual alkali metal were removed very quickly using tweezers under a stream of argon prior to the samples being sealed into a reflectance cell.

EPR spectra of the blue/purple powders were recorded in sealed quartz tubes on a JEOL PE-IX spectrometer operating within

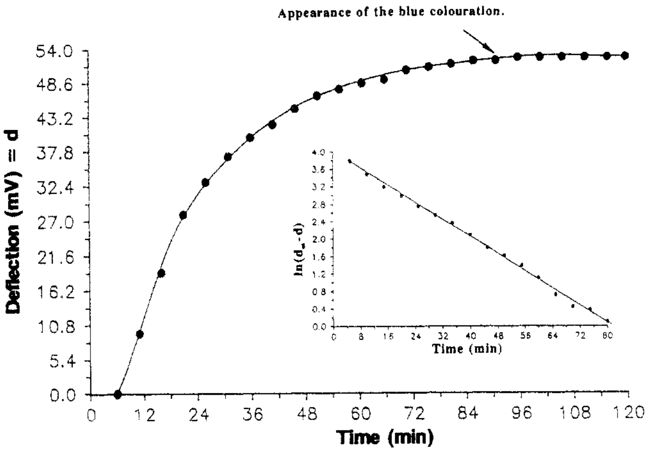


Figure 1. Thermogram for the sodium-mediated polymerization of DCMPS in diethyl ether at ambient temperature.

the temperature range 4–298 K. g values were measured against the diphenylpicrylhydrazyl (DPPH) radical (g = 2.0036). The EPR spectra of reaction mixtures were recorded at probe temperature in an apparatus comprising a small Schlenk tube equipped with a 4-mm EPR tube on a side arm. This apparatus permitted the necessary rapid stirring of the reaction mixtures up to the instant of the desired measurement, at which part of the contents were decanted into the side arm.

Molecular weights of PMPS were measured as linear polystyrene equivalents in tetrahydrofuran solution using size exclusion chromatography equipment supplied by Polymer Laboratories Ltd. A dual column bank of 500 and 10^4-Å 5-μm Plgel columns was used. Calibration was over the molecular weight range 162–1.03 × 10^6. Molecular weights of polysilanes are recognized to be at least twice those of linear polystyrene equivalents.[28]

Calorimetric measurements employed a thermistor immersed in a reaction mixture contained within a stirred adiabatic calorimeter of 50-mL volume. The thermistor output was fed to a chart recorder and the variations of the temperature of the reaction mixture were accordingly monitored.

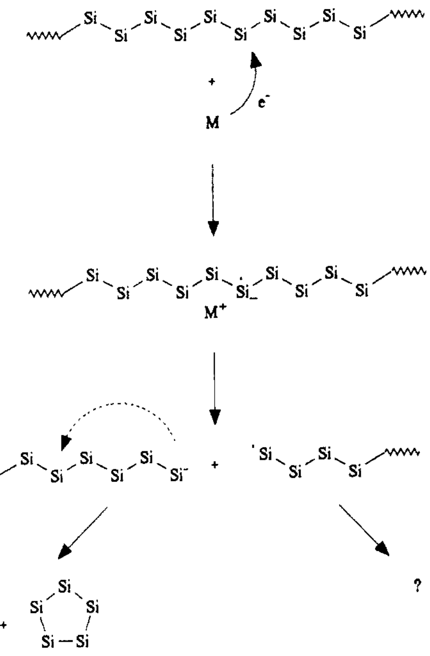
The total sodium content of the powder products was determined using a Perkin-Elmer 1100B atomic absorption spectrophotometer equipped with a flame ionization detector.

Results

Figure 1 shows a typical thermogram for the sodium-mediated polymerization of dichloromethylphenylsilane in diethyl ether at ambient temperature. Following an induction period of about 5 min, the reaction, in which about a 5% stoichiometric excess of sodium was used, apparently obeys a first-order rate law ($t_{1/2}$ = 15 min) for at least 97% of its subsequent course. After about 90 min, over a period of no more than 5 min, the blue coloration appeared in the gelatinous precipitate that was by then evident in the system. From the plot, it is clear that this point can reasonably be taken to mark the end of reaction. It is our observation that the more rapid the polymerization, by virtue of temperature, solvent, or any other influence, the sooner this point is reached and the more abrupt is the appearance of the coloration. It should be noted, however, that this qualification says nothing about the apparent density of the color which, variable though it is, can only be a subjective matter.

The presence of 15-crown-5 in the reaction mixture was observed to have little effect upon the time taken for the appearance of the color marking the end of reaction, but it did serve to maximize the yield of high molecular weight polymer. The overall yield and molecular weight parameters of the products of the sodium-mediated polymerization of dichloromethylphenylsilane at room temperature are very similar to those previously reported[23] for the reaction in refluxing diethyl ether. However, when the reaction was performed under identical conditions using potassium in place of sodium as the reducing agent, the product polymers were found to be of lower molecular weight, and a much greater proportion of oligomeric material was produced. This observation accords with those of studies by Matyjaszewski and co-workers[29] in which preformed PMPS in THF solution was observed to be degraded to oligomeric species by either sodium or, more rapidly, potassium. These observations were rationalized through the reactions depicted in Scheme II. As a further illustration of the polymer degradation by alkali metal, Figure 2 depicts the effect of extending the Wurtz reaction conditions in the presence of an excess of sodium on the yield and molecular weight of a PMPS. For the purposes of demonstrating that these effects are more general in diethyl ether, Figure 3 shows the variation of the size exclusion chromatograms of a PMPPPS when reaction conditions were maintained for a short period after the appearance of the coloration in a refluxing reaction mixture in which the monomer and sodium are in stoichiometric ratio. A shift toward higher molecular weights is evident for a period, but even with this initial condition, degradation to oligomers occurs if reaction conditions are prolonged and is evident in this system after 5 h.

Scheme II



The liquid phases of a range of polysilane reaction mixtures were monitored using EPR spectroscopy. Care was taken during decantation of the liquors to ensure that the alkali metal dispersions were not also transferred into the EPR tube attached to the Schlenk tube. After the EPR spectra were recorded, the liquors were returned to the reaction mixtures. White precipitates were always evident a few minutes after the addition of the dichlorosilane monomers, but the liquid phase and the precipitates were EPR silent throughout the course of the reactions. When the alkali metal dispersions were present in the EPR tube, only signals attributable to bulk alkali metals were evident. A representative signal, that for the dichloromethylphenylsilane–sodium system, is shown in Figure 4. Different signals, typically that shown in Figure 5, were only observed from the precipitates 90 min after the onset of the reaction, on the appearance of the ubiquitous blue color.

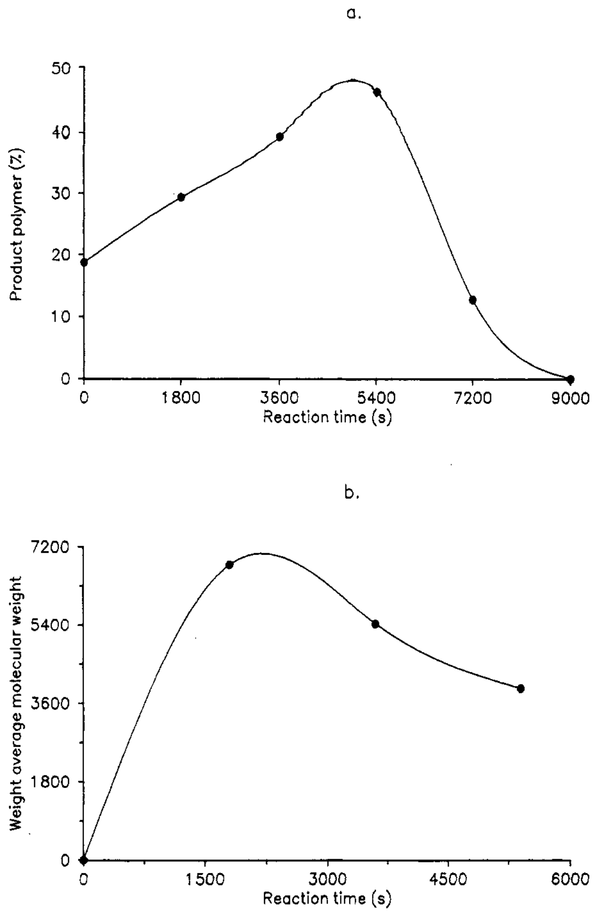


Figure 2. Effect of extending the Wurtz polymerization conditions upon polymer yield (a) and molecular weight, (b) when an excess of sodium is employed.

In the absence of moisture, the dried powders and their colors were found to be remarkably air-stable. The appearance of the PDPS/NaCl system remained unchanged for well over a year and this system would appear to be indefinitely stable. The potassium systems are much less stable but the color of the PDPS/KCl system endured for several days. EPR signals obtained from these powders are the same as those obtained in the solvent-wet state at the end of the polymerizations, as typified by the EPR spectrum of Figure 5. The spectrum for the PDPS/KCl system, which differs significantly from that of the PDPS/NaCl system, is shown in Figure 6. Both the colors and the EPR signals are rapidly discharged by the addition of water, and for those systems in which the polysilanes are tractable, by dry toluene or dry tetrahydrofuran. The reaction with water was always exothermic, and in some cases the rate of discharge of heat was sufficient to discolor the polymer; this is taken to indicate that particles of alkali metals are still present in the powders, even though they are not visible to the eye. Since the further effect of the water is to dissolve the alkali metal halide and that of the organic solvents is to dissolve the polymer, it is concluded that the colors and the EPR signals arise from the same structures and that these are stable only by virtue of the intimate admixture of the salt and the polysilane; i.e., in the case of the organic solvent, it is the destruction of this intimate admixture through the dissolution of the polymer that results in the discharge of the color.

The *g* values and the EPR spectral line shapes of the polysilane/NaCl systems were observed to be invariant with temperature down to 4 K. Likewise, there was no discernible variation with temperature for the EPR spectra of the polysilane/KCl systems.

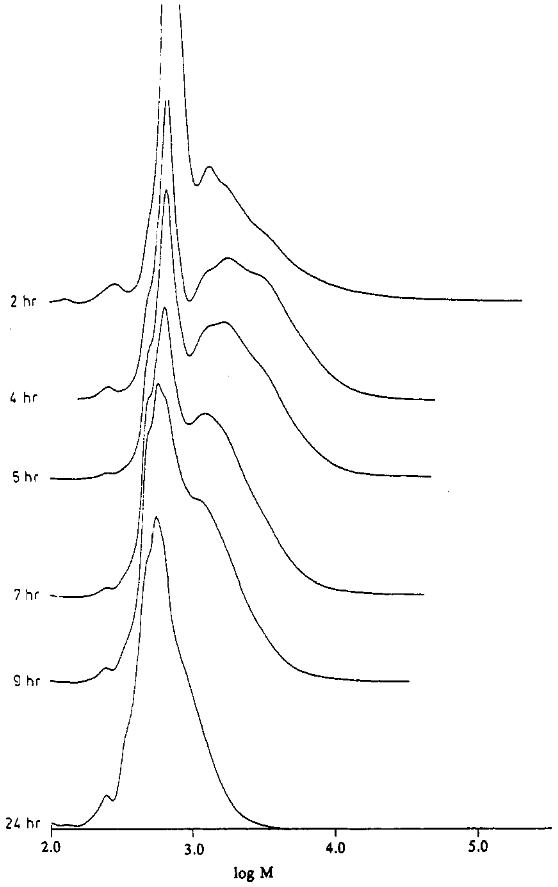


Figure 3. Variation of the size exclusion chromatograms of a PMPPPS synthesis with respect to time. Degradation is evident after 5 h of reaction.

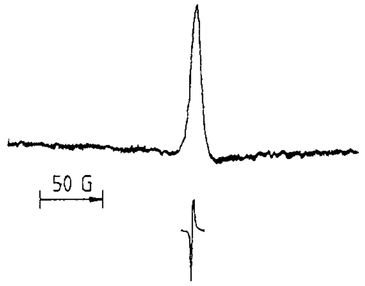


Figure 4. X-band EPR spectrum of bulk sodium showing the highly asymmetric derivative line shape. Microwave power 10 mW, modulation 5 G, gain 3.2 × 10^2; g (corrected for line shape) = 2.0014 ± 0.0002, ΔH_{pp} = 17 ± 1 G.

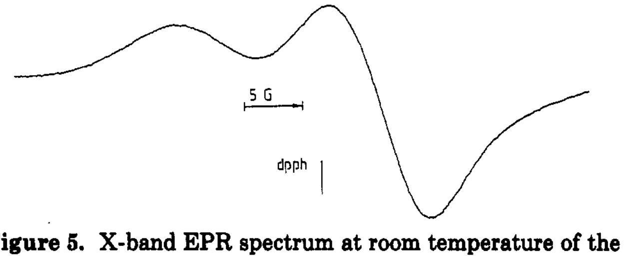


Figure 5. X-band EPR spectrum at room temperature of the dried purple powder isolated from the reaction of dichlorodiphenylsilane with sodium in diethyl ether, recorded in a 10-mm-diameter tube. Microwave power 10 mW, modulation 5 G, gain 1.8 × 10^2; $g_{\parallel}$ = 2.0112 ± 0.0001; $g_{\perp}$ = 2.0005 ± 0.0001, ΔH_{pp} = 8.8 ± 0.2 G.

As typical examples, the UV–visible absorption spectra of the powders isolated for the PMPS/NaCl, PMPS/KCl, and the PDPS/NaBr systems are shown in Figure 7. The electronic transitions characteristic of polysilanes were observed below 400 nm,[28] together with broad transitions centered in the visible region of the spectrum which give rise to the characteristic colors of the materials. The

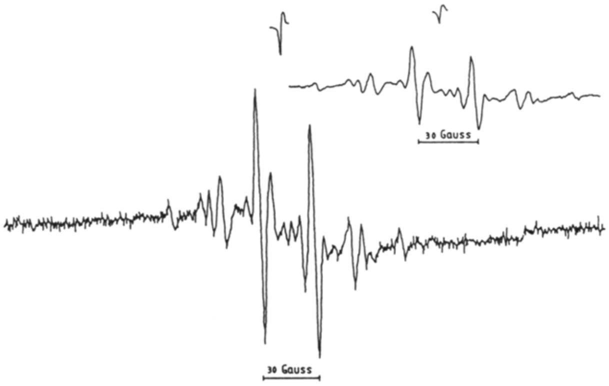


Figure 6. X-band EPR spectrum at ambient temperature of the blue powder isolated from the reaction of dichloromethylphenylsilane with potassium in diethyl ether, recorded in a 10-mm-diameter tube. Insert shows an expansion of the silicon-centered radical. Microwave power 10 mW, modulation 2 G, gain 2.5×10^2; *g* approx. free-spin.

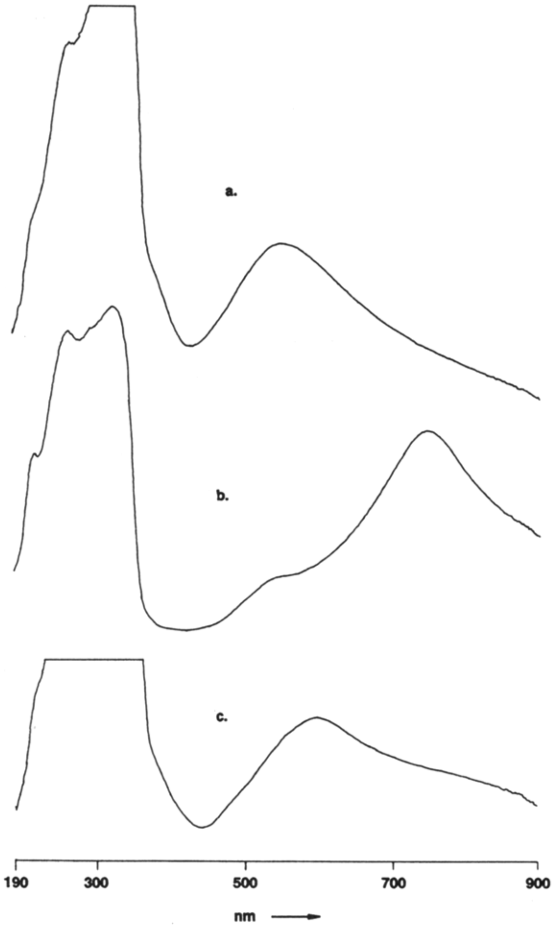


Figure 7. UV–visible diffuse reflectance spectra of the dried powders obtained from the reaction in diethyl ether of dichloromethylphenylsilane with sodium (a), dichloromethylphenylsilane with potassium (b), and dibromodiphenylsilane with sodium (c).

positions of these maxima in the visible region of the spectrum vary with the nature of the alkali metal and with the halogen element but were found to be independent of the polysilane structure. Table I records the wavelengths of the observed maxima in the visible spectra of the powders resulting from a range of reagent combinations including some in which the nonmetallic reagents were dibromodecane or dichlorodecane instead of dihaloorganosilanes; these were chosen for their potential as precursors to carbon-based polymers in order to show that the spectral characteristics are not to be associated with some interaction involving the silicon backbone.

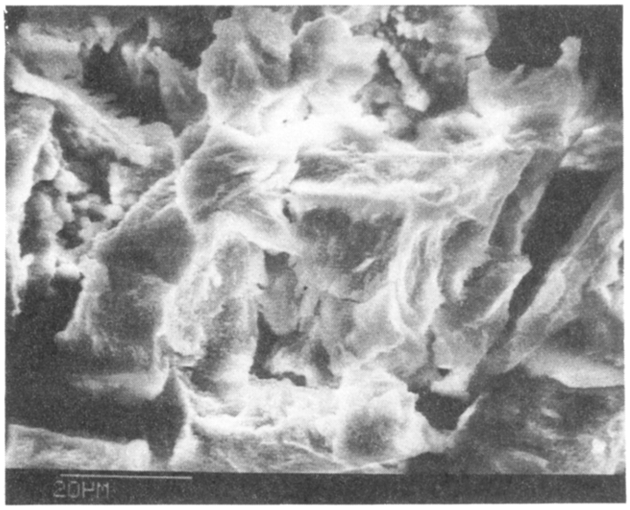


Figure 8. Scanning electron micrograph of the blue powder isolated from a sodium-mediated Wurtz synthesis of poly(methylphenylsilane) in diethyl ether at room temperature.

Table I. UV–Visible Absorption Maxima of the Colored Powders Obtained from a Variety of Reagent Combinations

polymer	metal halide	$\lambda_{max} \pm 5$ (nm)
PDPS	NaCl	560
PDPS	NaBr	600
PDPS	KCl	745
PMPS	NaCl	560
PMPS	KCl	750
PE	NaCl	565
PE	NaBr	600

Stoichiometric analysis of the PMPS/NaCl powder was carried out using a sensitive spectrotitrimetric method[30] as follows: Samples of the blue powder were hydrolyzed with deionized water, and the pH of the resulting solutions was measured through the absorbance at 548 nm of added methyl red indicator. The method was calibrated using standard solutions of sodium hydroxide spanning the relevant range and checked against a sample of pure sodium chloride. On the assumption that the diethyl ether wash of the powder isolation procedure has satisfactorily removed any unreacted monomer, a level of alkalinity that develops can be attributed directly to the presence of unreacted sodium in the solid material, which is readily estimated to be 0.4% of the total sodium content.

Figure 8 shows a scanning electron micrograph of the powder resulting from the PMPS/NaCl system. It is evident that even in the dry state the surface of the material can best be described as open and porous with an appearance akin to that of a microtomed size exclusion chromatographic particle.[31] Attempts to study the material using transmission electron microscopy were unsuccessful as the powders proved to be extremely sensitive to beam damage: polysilanes undergo radiation-induced main chain scission reactions[20] (the very property that facilitates their use as resists), and it is also known that alkali metal halides are damaged by electron irradiation at the required voltage.[32]

Table II represents the modality of the immediate products observed from the wider range of polymerizations that have been included in our investigations. As well as these being conducted at the boiling temperatures of the relevant media, a number of the reactions have been conducted at lower temperatures. Although this has led to variations in the proportion of the various fractions, it has not led to marked shifts in the peak molecular weights.

Table II. Peak Molecular Weights Relative to Polystyrene Standards of Polysilanes, $-(R_1R_2Si)_n-$, Prepared under a Variety of Conditions[a]

polysilane				$10^{-3}M_w < 1.5$	$1.5 < 10^{-3}M_w < 100$		$10^{-3}M_w > 100$
R_1	R_2	solvent	metal	fraction i	fraction ii		fraction iii
Me	Ph	diethyl ether	Na	0.8 (P) 0.5 (P)	4.0 (P)	31 (Sh)	2500 (P) 12400 (Sh)
Me	Ph	diethyl ether	K	0.5 (P)	4.8 (P)	17 (Sh) 37 (Sh)	1570 (P)
Me	Ph	diethyl ether	Na/K	0.6 (P)	3.3 (P)	47 (Sh) 9 (Sh)	
Me	Ph	petroleum ether, 40–60 °C	Na	0.5 (P) 0.8 (P)	2.8 (P) 11 (P)	75 (Sh)	2160 (P)
Me	Ph	di-*n*-butyl ether	Na	0.5 (P)	3.5 (P) 6.4 (P)	27 (Sh) 41 (Sh)	
Me	Ph	toluene	Na	0.5 (P)	3.4 (P)	8.9 (Sh) 31 (Sh)	
Me	Ph	THF	Na/K	0.7 (P) 1.4 (P)	16 (P)		
Me	*p*-Tol	diethyl ether	Na	1.2 (P)	4.7 (P)	11 (Sh)	
Me	*p*-Tol	toluene	Na	0.6 (P) 0.9 (P)	3.2 (P) 6.0 (P)		
Me	*n*-Hex	diethyl ether	Na	0.3 (P) 0.8 (Sh) 1.3 (Sh)	22 (P)	3.4 (Sh) 36 (Sh)	
Me	*n*-Hex	hexane	Na	0.8 (P)	3.7 (P) 65 (P)	39 (Sh)	
n-Hex	*n*-Hex	diethyl ether	Na	1.5 (Sh)	41 (P)	7.3 (Sh) 96 (Sh)	413 (P)
Et	Me	diethyl ether	Na	0.5 (P) 0.9 (P)	2.8 (P)	6.0 (Sh)	
Me	cyclohexyl	diethyl ether	Na	0.4 (P) 0.7 (Sh)	6.7 (P)	1.8 (Sh)	
Me	cyclohexyl	toluene	Na	0.4 (P) 0.7 (Sh)	1.8 (P)	4.4 (Sh)	2381 (P)
Me	cyclohexyl	hexane	Na	0.4 (P) 0.6 (P)	1.6 (P) 7.4 (P)		
Me	cyclohexyl	benzene	Na	0.4 (Sh) 0.6 (Sh) 1.2 (P)	2.7 (P)	3.9 (Sh)	2034 (P) 2772 (Sh)

[a] P and Sh indicate peak and shoulder, respectively.

These have been tabulated in accordance with the fractions indicated in the introductory section.

As a typical example, Figure 9 depicts the size exclusion chromatograms of the polymers isolated separately from the precipitate and filtrate of the product mixtures of a PMPS/NaCl system. The two fractions are of approximately equal amounts of polymer. That from the precipitate is of higher molecular weight and displays a symmetrical major peak centered at $M_{r,w}$ = 24 000 and a minor peak extending well beyond one million. The chromatogram of the polymer from the filtrate is of much lower average molecular weight, displaying a symmetrical peak centered at $M_{r,w} \approx 4000$ and a minor peak at about 500 associated with mixed linear and cyclic oligomers. As indicated in the Introduction, the chromatogram of the total polymer formed in a typical polymerization in diethyl ether would commonly display one or the other of the two major peaks as a prominent shoulder on the side of the other. Accordingly, to illustrate this point, the total chromatogram is included on Figure 9.

The ^{29}Si NMR spectra of the oligomeric fraction of the product mixture of a PMPS/NaCl system that has been quenched in the normal way by the addition of water is shown in Figure 10. For purposes of comparison the ^{29}Si spectrum of the polymeric fraction is also shown. It is evident that the environments of the silicon atoms of the two fractions are quite distinct and that some low molecular weight linear polymer is carried with the oligomeric fraction in the hexane extraction. Carbon and hydrogen analyses of these fractions are shown in Table III. It is clear that experimental and calculated analyses for the polymeric fraction are in close agreement, while the analysis figures for the oligomeric fraction show little resemblance to those of an oligosilane structure.

Discussion

Spectroscopic Studies. Since there have been a number of studies directed toward establishing the mechanism of the Wurtz reaction[33] and even greater interest in determining the mechanism in relation to the synthesis of polysilanes, it is surprising that there have been no earlier reports of attempts to determine the nature of the species that gives rise to the color that is the apparent end marker of the reaction.

The EPR and UV–visible absorption studies of the present investigation both present strong evidence for the color arising from colloidal alkali metal particles stabilized in an intimate mixture of the polysilane and the alkali metal halide byproduct. The line width of 8.8 G in the EPR spectrum of the PDPS/NaCl system in Figure 5 is characteristic of colloidal sodium, and the maximum at 560 nm in the visible region of the spectrum of the same material, or of the PMPS/NaCl system shown in Figure 7, is consistent with that of the absorption spectra of colloidal sodium in matrices of sodium chloride.[34–36] Beneath the hyperfine structure of the EPR spectrum of the PDPS/KCl system a reproducible line width of 100 G is discernible, reflecting the stronger spin–orbit coupling within potassium. The absorption maximum at 750 nm for the PDPS/KCl system in Figure 7 is likewise consistent with those observed for potassium colloids in matrices of potassium chloride. From Table I it is evident that the structure of the polymer has no apparent effect on the

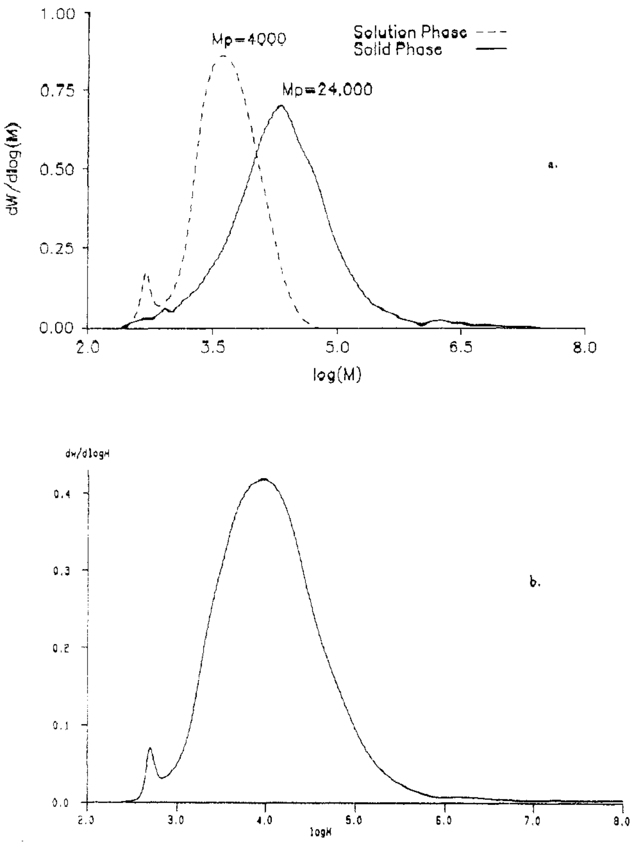


Figure 9. Size exclusion chromatograms of the separately isolated polymer fractions from both the filtrate and precipitate (a) of the PMPS/NaCl system and that of the total isolated polymer (b).

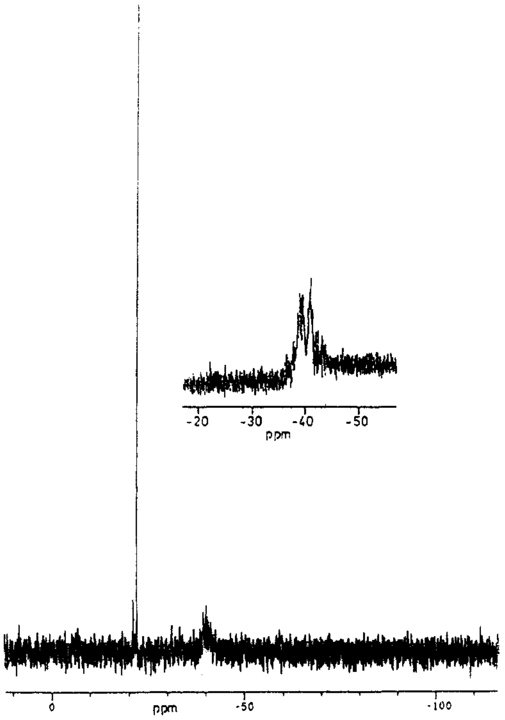


Figure 10. ^{29}Si NMR spectrum of the oligomeric fraction obtained from the hydrolysis of the reaction mixture PMPS/NaCl. The insert shows the ^{29}Si NMR spectrum of the corresponding polymeric fraction.

Table III. C/H Microanalyses of a Polysilane Immediately Following Isolation and of the Same Sample after Extraction with n-Hexane

sample	% C expected	% C found	% H expected	% H found
PMPS as isolated	70.01	67.60	6.67	6.60
PMPS extracted with n-hexane	70.01	69.23	6.67	6.81

color but that the nature of the anion does; accordingly, the visible absorption maxima of the PDPS/NaBr and PE/NaBr systems are similarly rationalized as colloids of sodium in matrices of sodium bromide. For the full details of the supporting arguments for the assignment of the EPR and UV–visible spectra to colloidal alkali metal particles the reader is referred to an earlier publication.[37] Only those features of the spectra together with those of the spectra of associated materials which are of relevance to the mechanism of the polymerization reaction will be examined here.

The additional feature in the EPR spectrum of the PDPS/NaCl system, which is also seen to arise in other sodium-mediated systems, indicates an axially symmetric environment for the sodium colloids. Almost all the published data on the EPR spectra of metal colloids relate to colloids in cubic symmetric environments such as pure alkali metal halide crystals. Clearly, axial symmetric effects do not arise in such systems. Furthermore, they are not observed when low molecular weight products result from the Wurtz coupling reaction, typically from the coupling of 1,10-dichlorodecane, which only produces an oily/waxy product from which a single signal is observed with a g value equal to a third of the Trace of the $\mathbf{g}$ tensor of the axially symmetric spectra. Although the characteristic color is still developed in these systems, they are less stable. These observations imply that in the more stable systems, the colloids are associated with the polymer chain ends rather than just with the cubic symmetric sodium chloride crystals, the aerobic stability of the dried colloids presumably arising from the protection afforded by the hydrophobic polysilane acting as a barrier to the ingress of atmospheric moisture. This is consistent with a picture of a mechanism of polymerization involving polymer chains growing on metal particles which are progressively consumed during the reaction[17,18] with residual colloidal metal particles precipitated within an intimate mixture of solid polymer and metal halide at the end of reaction.

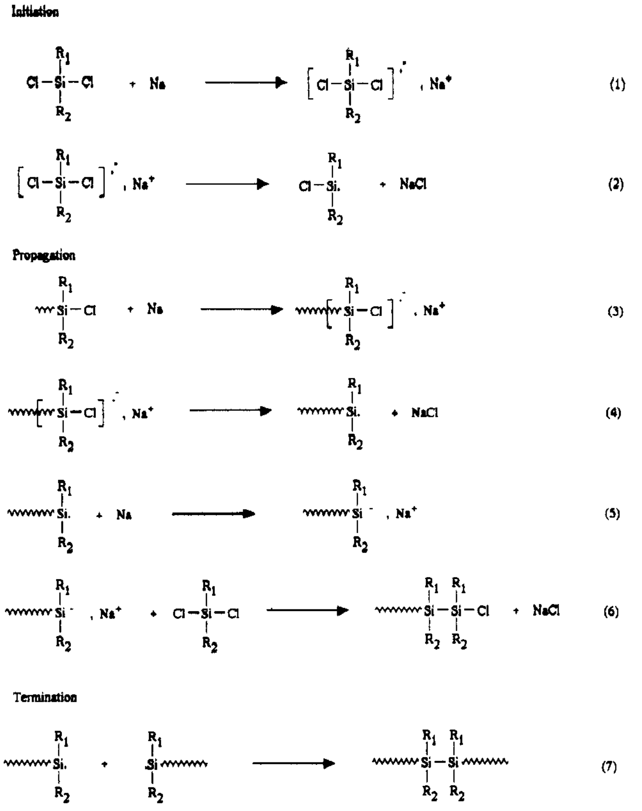
Superimposed above the 100-G signal that is characteristic of the potassium colloid systems at room temperature is another signal displaying a complex hyperfine splitting pattern in which short-range delocalization is evident. Regardless of the monomer used, this type of splitting pattern is always observed for the potassium systems and never for the sodium systems. We are unable to specify explicitly the structure of the radical from which it arises, but we tentatively assign it to a silane radical produced by midchain degradation of the polymer during its synthesis.[38] Since the hyperfine couplings to ^{29}Si and to the protons of the methyl and phenyl substituents differ, a simpler pattern results if the silicon atoms do not bear substituents with α-carbon atoms, e.g., for PDPS systems as opposed to PMPS systems. On the basis of this observation the radical can be postulated to arise from the cleavage of a silicon–phenyl bond.

The EPR signals for large metal colloids become asymmetric with Dysonian line shape as the temperature is lowered to that of liquid helium.[39] The invariance of the line shape of the main component of the EPR signals from the PMPS/NaCl colloid systems demonstrates that the diameter of the colloids is less than the microwave skin length at 4 K. This is consistent with our previous estimate[37] of 2-nm particle diameter which was based on the width of the visible absorption bands. Consistent with the small size of the colloid particles is the low value of 0.4% determined for the free sodium content in the PMPS/NaCl system. For the potassium systems, the temperature dependence of the line shapes could not be determined because of the very strong superimposed signal of the silane radical, so there is no confirmation of the approximately 40-nm diameter previously estimated from the width of the visible absorption band.

Polymerization Studies. The observation that high and low molecular weight polymer fractions are found respectively in the solid and solution phases at the end of the polymerization reaction, as depicted in Figure 9, can be rationalized in terms of the solubility of the polymer in the sustaining solvent. In the Zeigler model of the polymerization the compatibility of the polymer and the solvent determines the extent to which the growing chains extend away from the alkali metal surface and into the bulk solvent. It is reasonable to assume that as the reaction proceeds, under conditions of agitation polymer actually enters solution to the limit of its solubility in the given solvent and at the given temperature. In fact, it must do so, for the number of reaction sites on the alkali metal surface is steadily decreasing as the metal is consumed. Polymer molecules will thus be displaced from their growth sites. In the early stages of reaction, only low molecular weight material will be present in the system, and it is this that would progressively saturate the solution. Although dissolution is an equilibrium process, the increasingly higher molecular weight polymer formed in the later stages of reaction, being less soluble, would not displace the lower molecular weight material from solution. Instead, beyond the solubility limit, the higher molecular weight material would remain in the precipitate of alkali metal halide with its chain ends remaining associated with the alkali metal surface at which they would continue to extend, until in their turn they are displaced from the depleting metal surface, not into solution, but as disengaged precipitate. The two fractions would thus appear to be "noninteractive". Beyond this, there is another significant and quite general point that should be made about the polymer that is "attached" to the metal at the growth sites. Even if the sustaining solvent is a good solvent of the polymer such as toluene, the total amount of polymer found in the solution phase is less than the amount required to saturate the solution, even when there is more than enough total polymer to do so. We had earlier reasoned that this required that the alkali metal halide play an important role in determining the solubility of the polymer. However, the polymer chains extending to a greater or lesser extent from the alkali metal surface in accordance with the Zeigler model,[19] though anchored at one end, will nonetheless be contributing to the saturation of the solution. Thus, the material that is completely dissolved (i.e., in free solution) is at a concentration that is always less than that at the saturation limit.

The EPR studies offer no evidence for the intermediacy of radicals or radical anions. However, it would not be expected that they would and though the anionic chain mechanism proposed by Gauthier and Worsfold[22] was earlier shown[40] to be sufficient to argue an explanation of the observed polymodal molecular weight distribution, the body of mechanistic evidence available to date does point to the involvement of radicals in the overall mechanism. However, it is unnecessary to invoke noninteracting mechanisms in order to explain the molecular weight distribution. A modification of the chain reaction recently proposed by Matyjaszewski[41] is depicted in Scheme III. This involves propagation reactions which sequentially generate silyl radical anions, silyl radicals, silyl anions, and –Si–Cl, the growing chains thus constantly switching from nonpolar structures to polar structures, the lifetimes of which would be determined by the polarity of the medium in the vicinity of the solvent–metal interface. In the polar forms, the chain ends must prefer to remain associated with the medium of the alkali metal and its salt, and effectively remain insoluble. Only when they are in nonpolar structures could polymer chain ends favor entering bulk solution, and in so doing they would cease to participate in growth as has been described above. Radical coupling reactions on or near the metal surface might be a further contributory factor to this effect, but otherwise the mechanism shown does not preclude the possibility of such reactions occurring in the bulk solution prior to its saturation. Beyond the saturation point, however, such radicals as might leave the metal surface would be trapped in the polymer/salt agglomerate. As their concentration built up they would be detectable by ESR studies, and as we have shown, this is not the case in general.

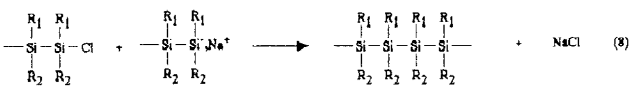
Scheme III



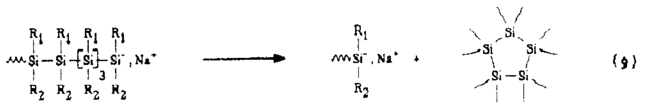
It is stressed that the mechanism as represented in Scheme III is not considered to be definitive. However, with the exception of silylenes it takes account of all the possible intermediates that have been proposed to be involved in Wurtz syntheses of polysilanes and for which there is evidence. It is a simplification of the mechanism represented by Matyjaszewski because the following arguments are not dependent upon or affected in any way by not considering the primary-radical termination reactions and silylene insertion reactions that he included.

It is unnecessary to specify a reaction mechanism in order to recognize that the polymer chain end that is remote from the active center must bear a halogen atom. However, accepting the mechanism of Scheme III and the previous reasoning, the molecules of the low molecular weight fraction that enter solution in the early stages of reaction would bear halogen atoms at both ends. These will remain

Scheme IV



Scheme V



potential sites for reactions but being of markedly lower mobility than the dihalosilane monomer, and thus with a lesser ability to penetrate the polymer/alkali metal halide barrier which surrounds the active centers in the vicinity of the alkali metal surface, the probability of these chain-end halogen atoms being involved in reaction is small. They will do so, however, in accordance with Scheme IV for just as polymer molecules diffuse into the pores of swollen gel particles in size exclusion chromatography, so these will penetrate the swollen and expanded porous structure of the polymer/salt aggregates (see Figure 8). Such reactions will terminate growth at the given active center, but in so doing, very much higher molecular weight polymer will be produced as it is a polymer–polymer coupling reaction. Furthermore, the resulting molecule will still be available to undergo the same process again. Whatever the propagation step in what is otherwise a chain mechanism, we propose that the reaction has this one feature in common with a step growth polymerization and that this is the most likely route to the formation of the very high molecular weight fraction that is invariably formed in any of the polymerizations in diethyl ether and which is frequently formed in polymerization in other solvents. It is clear that different solvents, conditions of agitation, and other preparative variations, together with different polymer structures will all influence the permeability of the solid agglomerate by preformed polymer chains and therefore the extent to which high molecular weight material will be formed by such coupling reactions involving the lower molecular weight fractions.

The other phenomena that we have observed to be commonplace after the apparent end of a Wurtz polymerization as characterized by the appearance of the blue color in the systems of the present study are also worthy of consideration, i.e., the (i) if reaction conditions are maintained for a period, there is a slow increase in the high molecular weight fraction of the product polymer at the expense of the lower molecular weight fractions even in those systems that do not contain an excess of alkali metal and (ii) if the reaction conditions are maintained for too long, particularly in the presence of excess alkali metal, the polymer will eventually degrade to oligomer. It is thought that the presence of colloidal alkali metal at this stage of reaction is sufficient to explain the first of these effects, for even in the colloidal state it is still acting as a locus maintaining active centers for the chain-extending reactions. The second effect, however, almost certainly arises through the back-biting chain mechanism of Scheme V proposed by Gauthier and Worsfold[22] which is supported by the observation of cyclic degradation products by Zeigler and co-workers.[13] From a simplified kinetic analysis applied to those reactions that are operative at the late stages of the overall reaction, eq 10 can be derived. The rate constants are numbered in accordance with the reactions of Schemes III–V and M, P*, and P respectively represent monomer, polymer with active chain ends (i.e., at the sodium surface), and polymer with chlorine chain ends (i.e., in solution). R_{CYC} is the rate of formation of cyclic oligomer by the back-biting reaction and R_{CE} is the rate of chain extension.

$$\frac{R_{\mathrm{CYC}}}{R_{\mathrm{CE}}} = \frac{k_9[\mathrm{P}^*]}{k_6[\mathrm{P}^*][\mathrm{M}]+k_8[\mathrm{P}^*][\mathrm{P}]} = \frac{k_9}{k_6[\mathrm{M}]+k_8[\mathrm{P}]} \tag{10}$$

Since the concentrations of both monomer and polymer are continually decreasing, eq 10 shows that when $k_6[\mathrm{M}] + k_8[\mathrm{P}] < k_9$, a critical point is reached at which this competitive first-order reaction of active chain ends (back-biting) dominates over the combined effects of the second-order propagation and polymer–polymer reactions. It thus seems that reaction conditions should not be prolonged in the vain hope that chain extension will result. If alkali metal is used in considerable excess over monomer, such a condition will be reached at much lower degrees of polymerization, and the overall effect would be further exacerbated by the electron transfer reaction proposed by Matyjaszewski (Scheme II) which is supported by the EPR results of the present study.

Consideration must also be given to the likelihood of cyclic oligomer being formed during the early stages of the polymerization. This was a component feature of the Gauthier and Worsfold anionic mechanism[22] but an equivalent reaction is not included in the "Matyjasewski" mechanism of Scheme III. Nevertheless, on the basis of ^{29}Si NMR resonances, Matyjaszewski et al.[29] have subsequently identified this product as being a cyclopentasilane, while the oligomeric material formed by polymer degradation is characterized as a cyclohexasilane. The ^{29}Si NMR resonances of the fractionated PMPS materials of Figure 10 are at chemical shifts that are comparable with those recorded by Matyjaszewski, but whereas the microanalysis of the polymeric fraction is satisfactorily consistent with the empirical formula of the polymer, the analysis figures, recorded in Table II, of the immediately isolated material that includes the oligomeric fraction are well removed from those calculated for poly- and cyclosilane structures. Only on the assumption that the oligomeric contains oxygen in molar quantity approaching that of the silicon can the analysis figures be made to tally, thus suggesting a cyclosiloxane rather than cyclosilane structure. Sakurai[43] has observed strong infrared bands in polysilanes produced by the Wurtz reaction that accord with the presence of substantial numbers of silicon–oxygen linkages. The ^{29}Si resonances of a silicon atom in a siloxane[44] is found at approximately the same chemical shift as that thought to be from the cyclopentasilane, i.e., at $\delta \approx -35$. Furthermore, in the early stages of reaction the monomer concentration is high in the bulk solvent and probably also at the alkali metal surface, as there would be little in the way of a barrier layer to resist its ingress; i.e., there would be little or no barrier to propagation. On the other hand, although cyclization to five- and six-membered ring structures are thermodynamically favorable processes, one end of the growing chain is anchored to the metal surface, so there would be a significant steric barrier to cyclization. We therefore propose that reaction cyclization in the early stages of reaction is not important as long as propagation is rapid and that the oligomers in question are siloxanes. The most likely way in which siloxane linkages could arise in these systems is through the reaction of excess monomer with water or with the hydroxyl groups of alcohols during the normal isolation procedure. Since some of the alkali metal must be presumed to be consumed through polymer degradation reactions even in Wurtz polymerizations that endeavor to employ monomer and alkali metal in stoichiometric ratio, the likelihood of there being no unreacted monomer at the apparent end of reaction is slim. If excess alkali metal is used, then polymer degradation will be enhanced. Thus the desired polymer product will always be contaminated to a greater or lesser extent with one or the other oligomer, and it is evident that the difficulties inherent in attempting to reproduce the reaction exactly are virtually insurmountable.

A single heterogeneous polymerization mechanism can thus explain the observed polymodal molecular weight distributions resulting from the alkali metal-mediated reductive-coupling of dihaloorganosilanes. The bulk of the product will commonly be of two intermediate molecular weight fractions, and though a small amount of very high molecular weight material will usually be formed, along with the other fractions this will in due course degrade to a mixture of linear and cyclic oligomers if reaction conditions are maintained. If the reactions are quenched with water or alcohols, cyclic siloxanes will result from any monomer that might still be present. The contribution of either of the oligomers to the overall yield depends critically on the duration of the reaction. Their presence in the product mixture is always at the expense of the polymer and though they are readily removed by extraction into hexane, it is nonetheless a nuisance that this is necessary. To achieve effective control it is essential that a means be found of reducing the rates of the reactions in order that their optimum duration can be realized reapeatedly. This control will be tighter if polymer degradation reactions can be avoided, and only then will consistently high yields be realized. To achieve this, satisfactory altnerative reducing agents to the alkali metals must be identified. We have recently demonstrated that this is a realistic goal.[24]

Acknowledgment. We gratefully acknowledge the Royal Society's support for R.E.B. through the award of a University Research Fellowship and the SERC for a Postdoctoral Research Fellowship for A.C.S. We also thank the Toshiba Silicone Co. for the generous gift of the platinum hydrosilation catalyst, Professor A. E. Beezer for help with the calorimetry, Beatrice Albert of École National Supérieure de Chimie de Montpellier, a visiting student under the Erasmus scheme, for valuable experimental assistance, GEC Marconi Materials Technology (Caswell) Ltd. for permission to publish Figure 8, and Mr. Neil Griffin for the scanning electron microscopy.

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