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Anions and radicals as intermediates in the reductive coupling of disubstituted dichlorosilanes with sodium

Trapping the intermediate radicals in polymerization of allyl- and hexenyldichlorosilanes

Hwan Kyu Kim and Krzysztof Matyjaszewski

Department of Chemistry, Carnegie Mellon University, 4400 Fifth Avenue, Pittsburgh, PA 15213, USA

SUMMARY

Polymerization of four monomers with alkenyl groups: allylmethyldichlorosilane, allylphenyldichlorosilane, 5-hexenylphenyldichlorosilane and 5-hexenylmethyldichlorosilane was studied by reductive coupling with sodium in the presence of ultrasound at ambient temperatures. Soluble homopolymers and copolymers with phenylmethyldichlorosilane with molecular weights $M_n > 10{,}000$ were obtained for the first three monomers. UV and ^{29}Si NMR studies indicate a high degree of Si-Si catenation for allyl derivatives. Approximately half of the alkenyl groups remain in the polymer after a few hours. This indicates that after the formation of the polysilane backbone alkenyl groups are predominantly trapped intramolecularly in a process resembling cyclopolymerization of diallylsilanes. The main mechanistic conclusion is that in the reductive coupling process radicals are present as short living intermediates which are rapidly reduced to anions at higher polymerization degrees, but which are efficiently trapped at a monomeric or dimeric level. Thus, electron transfer proceeds in two one-electron transfer steps from a chloroterminated chain to a radical, and then to a macromolecular silyl anion. The latter reacts with a monomer via a nucleophilic substitution. Polymerization is an anionic chain growth process.

INTRODUCTION

Rapidly increasing interest in polysilanes originates in the attractive physical and chemical properties of these new organometallic polymers and their potential applications in electronics, ceramics, and integrated optics (1,2,3). The reductive coupling of disubstituted dichlorosilanes with molten sodium in nonpolar solvents (2,3) remains the most successful synthetic method for high molecular weight polysilanes. The products of the synthesis consist of an oligomeric cyclic fraction (mostly cyclopenta- and cyclohexasilanes), a fraction with a relatively low molecular weight ($M_n < 5{,}000$) and a high molecular weight polymer ($M_n > 100{,}000$). The relative proportions of the three products depend on the reaction conditions such as solvent, rate of addition of monomer or sodium, temperature, various additives, etc (4, 5). Synthesis of high molecular weight polysilane with relatively narrow polydispersity is important for some applications and for the structure property relationship. Searching for new synthetic pathways to polysilanes we have recently accomplished the sonochemical synthesis of polysilanes (6) by the reductive coupling of disubstituted dichlorosilanes with sodium at ambient temperatures. This resulted in the exclusive formation of high molecular weight polymer (in addition to cyclics which could be easily separated since they are soluble in isopropanol or in ethanol, contrary to polymer). Some experimental results indicate that polymerization proceeds as a chain growth process. Silyl radicals and silyl anions are the possible active sites (4,5,6). It is important to understand the mechanism of the reductive coupling of dichlorosilanes in order to further improve and optimize the synthetic procedure. Below we report on the attempts of trapping the intermediate radicals in the reductive coupling process by using dichlorosilanes with alkenyl groups. The resulting polymers with unsaturated side groups can be used as materials for further functionalization (7).

EXPERIMENTAL

Dichlorosilanes (Petrarch) were distilled prior to use and dried over CaH_2. Toluene was distilled from CaH_2 and dried over Na/benzophenone. Known amounts of sodium were placed in a flask filled with toluene and purged with dry argon. This flask was placed in the ultrasonic bath (75-1970 Ultramet II Sonic Cleaner, Buehler Ltd.) until a stable dispersion of sodium was formed. In some experiments an immersion-type ultrasonic probe was used (W-140, Heat Systems-Ultrasonics, Inc.). A toluene solution of alkenyldichlorosilane or its mixture with phenylmethyldichlorosilane was added to the reaction flask in a controlled manner under inert gas. The reaction was quenched after the required time by equimolar mixtures of water and ethanol. The organic phase was later added to a large excess of isopropanol leading to the precipitation of the polymer. The polymer was dried under vacuum and the yield determined gravimetrically. Molecular weights were determined by gpc using polystyrene standards, and Waters 100, 500, 1000, 10,000 Å and linear columns. Polydispersities were calculated using Nelson software. The compositions of polymers and oligomers were determined by ^{1}H NMR. Solutions of polymers were characterized by UV-VIS (IBM 9430) and by ^{29}Si NMR (IBM NR/300.) The filtrate remaining after the evaporation of the isopropanol was analyzed by gc/ms, gpc and hplc.

RESULTS

Polymerization of four monomers with alkenyl groups: allylmethyldichlorosilane, allylphenyldichlorosilane, 5-hexenylmethyldichlorosilane and 5-hexenylphenyldichlorosilane was studied by reductive coupling with sodium in the presence of ultrasound at ambient temperatures. There are three special features of the sonochemical synthesis: first, ultrasound leads to continous regeneration of the sodium surface and removal of sodium chloride even at temperatures below melting point of sodium; second, the dispersion is prepared in a reproducible way without addition of any stabilizers; third, ultrasound cleaves polymers with molecular weight exceeding $M_n \approx 100{,}000$. Polymerization occurs by a chain growth (not by a step growth process) since high polymer is formed at the very beginning of the reaction and degree of polymerization is independent of the $[Na]_o/[Si\text{-}Cl]_o$ ratio. There is some evidence that anionic intermediates are responsible for the chain growth: dialkyldichlorosilanes cannot homopolymerize at ambient temperatures but can copolymerize with phenylmethyldichlorosilane (6); trichlorosilanes form soluble polymers (8); polymerization is strongly influenced by solvent effects and by additions of crown ethers and cryptands (9). Nevertheless, radicals could be present as short living intermediates, and could be trapped by pendant alkenyl groups.

In Table 1 results of the sonochemical homopolymerization of allylmethyldichlorosilane and its copolymerization with phenylmethyldichlorosilane are shown. Polymers were separated by precipitation from ispropanol. From the NMR studies the degree of unsaturation for polymers and oligomers (about 50%) was determined. Homopolymerization leads to the formation of a small amount of insoluble polymer and oligomers. The time required for homopolymer formation was longer than that for polymerization of phenylmethyldichlorosilane but shorter than for dialkyldichloro-silane. Thus, a β-double bond facilitates the electron transfer. A copolymer enriched in phenylmethylsilylene units was formed by the simultaneous copolymerization with phenylmethyldichlorosilane. Lower yield was observed in the sequential addition of allylmethyl and then phenylmethyldichlorosilane. Approximately half of the alkenyl groups were consumed in the final polymer.

Table1
Sonochemical Copolymerization of Allylmethyldichlorosilane (M1) and Phenylmethyldichlorosilane (M2) with Sodium

M1/M2	1/0	1/1	1/1#	0/1
yield, %	2.7@	8.0	4.0	12.0
m/n$	-	1/3.0	1/1.18	-
Mn_H* x 10^{-4}	insoluble	2.9	-	10.4
Mn_L x 10^{-3}	-	-	-	-
H/L+	-	1/0	1/3	1/0
% = unreacted	-	48	50	-
λ_{max} (nm)	-	334	327	340
ε_{max} x 10^{-3} M^{-1} cm^{-1}	-	5.9	-	9.0
oligomer, %	89	83	80	88
% = unreacted	62	35	30	-

$[M]_0$=0.32 mol/L, $[Na]_0/[Si\text{-}Cl]_0$= 1.1, 1 hr, toluene, 60 °C, immersion-type probe
#: sequential addition of $PhMeSiCl_2$ after addition of $AllylMeSiCl_2$: 70% of insoluble copolymer and partially soluble in organic solvents; other copolymerization by simultaneous addition
@: the resulting polymer after 5 hrs is insoluble in organic solvents; no reaction after 1 hr
$: the ratio of copolymer composition:[AllylMeSi]/[PhMeSi]
*: molecular weights based on polystyrene standards
+: the ratio of high polymer (H) to low polymer (L)

UV absorption in the range of $\lambda \approx 330$ nm and extinction coefficients $\varepsilon \approx 6{,}000$ $M^{-1}cm^{-1}$ indicate the catenation of at least 20 silicon atoms in the main chain (10). This can be translated to 20 consecutive reactions of the active chain end with a monomer prior to trapping the radical by the pendant alkenyl group. Copolymerization with phenylmethyldichlorosilane occurs readily, but the ratio of polymer units is m/n=1/3 for the simultaneous copolymerization of the equimolar mixtures of comonomers. This indicates that allylmethylsilylene units are preferentially incorporated into oligomeric species.

Table 2 presents similar data obtained for allylphenyldichlorosilane. Soluble oligomers were analyzed by NMR for the unsaturation and by gc-ms. The volatile fraction consisted of a mixture of dimers and trimers (silanes with higher molecular weights have too low vapor pressure to be analyzed by this method). Allylphenyldichlorosilane can be easily homopolymerized, but the copolymer is enriched (1/1.6) in phenylmethylsilylene units when an equimolar comonomer ratio is used. This does not mean the reactivity of allylphenyldichlorosilane is lower than that of phenylmethyldichlorosilane, but the latter is again preferentially incorporated to a high polymer.

Table2
Sonochemical Copolymerization of Allylphenyldichlorosilane (M3) and Phenylmethyldichlorosilane (M2) with Sodium

M3/M2	1/0	1/1	0/1
yield, %	7.2	13.4	12.0
m/n$^{\$}$	-	1/1.63	-
$Mn_H{}^{*} \times 10^{-4}$	3.5	5.8	10.4
$Mn_L \times 10^{-3}$	9.3	6.8	-
H/L^{+}	1/2	1/1.5	1/0
% = unreacted	43	50	-
λ_{max} (nm)	338	338	340
$\varepsilon_{max} \times 10^{-3}$ $\underline{M}^{-1}$ cm^{-1}	0.65	2.1	9.0
oligomer, %	92	81	88
% = unreacted	48	42	-

conditions identical as in Table 1; *,+,$: cf. Table 1

Approximately 50% of alkenyl groups remained unreacted after a few hours (cf. Figure 1). Polymers initially soluble crosslink even if stored in the dark after a few weeks.

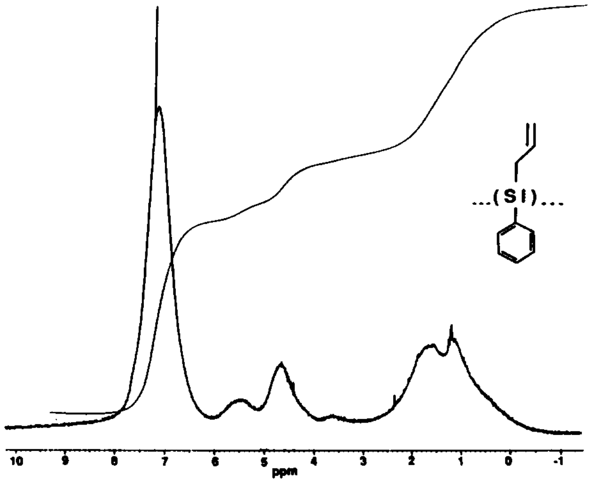

Fig. 1. ^{1}H NMR spectrum of poly(allylphenylsilylene) in $CDCl_3$

Bimodal molecular weights were observed in the case of homo and copolymerization (cf. Figure 2). UV maxima resemble those found for homopoly-(phenylmethylsilylene), but extinction coefficients are much smaller (Figure 3). This could indicate shorter Si-Si catenation. However, ^{29}Si NMR studies of the resulting polymers reveal only one signal at -25 ppm. The possible species ...-C-$\underline{\text{Si}}$-Si-... which should absorb approximately 25 to 30 ppm downfield (11) were not detected.

Table 3 shows results for the homopolymerization of 5-hexenylphenyldichlorosilane. A very small amount of high polymer was found in addition to oligomers which had 75% alkenyl groups consumed. This result shows that the monomeric radicals can be efficiently trapped by the 5-hexenyl group, but not by allyl group because the resulting four-membered ring would be too strained. Incomplete consumption of the alkenyl groups indicate that monomeric radicals can also react with another monomer and escape intramolecular cyclization. A small amount of the formed polymer should be due to much faster conversion of polymeric radicals to anions which cannot react with alkenyl groups.

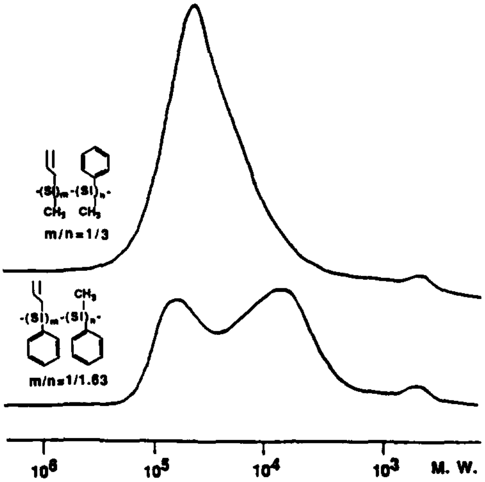

Fig. 2. GPC traces of two copolysilanes

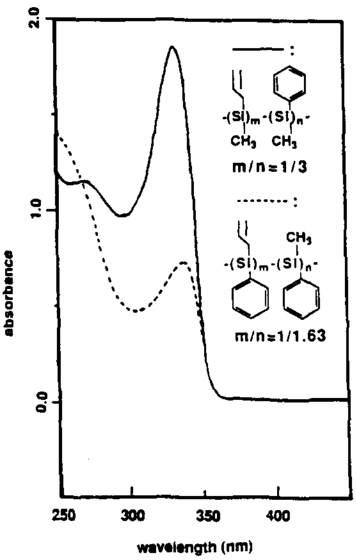

Fig. 3. UV spectra of polysilane solutions in CH_2Cl_2 at 25 °C

Hexenylmethyldichlorosilane could not be homopolymerized sonochemically, resembling other dialkyldichlorosilanes. The olefin group is too far from silicon to facilitate the electron transfer necessary for the first initiation step.

Table 3
Sonochemical Homopolymerization of 5-Hexenylphenyldichlorosilane (M4) and Phenylmethyldichlorosilane (M2) with Sodium

M4/M2	1 / 0	0 / 1
yield, %	<1.0#	2.0
Mn* x 10^{-4}	6.8	10.4
H/L+	1 / 0	1 / 0
% = unreacted	-	-
λ_{max} (nm)	-	340
ε_{max} x 10^{-3} $\underline{M}^{-1}$ cm^{-1}	-	9.0
oligomer, %	96	88
% = unreacted	75	-

conditions identical as in Table 1; *,+, : cf. Table 1
#: no reaction of 5-hexenylmethyldichlorosilane after 5 hrs

DISCUSSION

The presented results can be summarized in the following way:

1. Soluble high molecular weight polymers and copolymers of dichlorosilanes with side alkenyl groups were formed in the sonochemical reductive coupling with sodium.
2. Large extinction coefficients, long wavelength absorption, and the predominant (>95%) formation of silicon atoms connected to two other silicon atoms (^{29}Si NMR) indicate a high degree of catenation of polysilanes in the main chain (≈20 Si-Si bonds without Si-C interruption).
3. Approximately half of the alkenyl groups were consumed in polymers as well as in oligomers.

These observations suggest that the reactive intermediate in the reductive coupling process may involve short living radicals. Nevertheless, the intermediate radicals must be very rapidly reduced further to anions which can participate in the usual nucleophilic displacement with a monomer (S_N2). Otherwise, a high degree of Si-Si catenation could not be realized. Monomeric radicals cannot be converted to stable anions, and therefore they can be trapped efficiently by 5-hexenyl substituents; trapping by allyl substituents, which would lead to a strained cyclosilabutane, is much less probable.

The reductive coupling process can proceed via several different intermediates (cf. Scheme below). The first slow step should involve electron transfer from sodium to monomer to form a monomeric radical anion. This species should very rapidly isomerize to the monomeric radical and sodium chloride, which is insoluble in the reaction medium (1A). An identical reaction between sodium and the chloro terminated polymer chain will provide a polymeric radical anion and eventually a polymeric radical (1B). Monomeric and polymeric radicals can recombine in a chain growth process (1C), which involves radical intermediates exclusively. It is known, however, that silyl radicals which contain phenyl groups can be easily reduced further to silyl anions. The polysilane chain may also facilitate this reaction (2A). The resulting polysilyl anion will react in a nucleophilic substitution reaction (probably S_N2) with a monomer which is a stronger electrophile (contains two electron withdrawing Cl-groups) than a chloro terminated chain. This is an anionic pathway (2B).

The second electron transfer to monomeric radical will provide silylene (3A) which can easily insert between Si-Si linkages (3B). Silylene can dimerize to form disilene - species which have been recently isolated for compounds with bulky substituents (e.g. mesityl) (12). Disilenes are, however, very reactive and they should rapidly polymerize if thermodynamically possible. Silylene can also lead to the formation of strained reactive cyclic intermediates which would be converted to polysilanes via ring-opening polymerization. However, as we will discuss later, the mechanism based on silylene is not of primary importance, since silylene traps do not affect polymerization (4):

$R_2SiCl_2 + Na \dashrightarrow R_2SiCl_2^{\cdot -}, Na^+$ (1A)
$R_2SiCl_2^{\cdot -}, Na^+ \dashrightarrow R_2SiCl^{\cdot} + NaCl$ (1A')
$...\text{-}R_2SiCl + Na \dashrightarrow ...\text{-}R_2SiCl^{\cdot -}, Na^+$ (1B)
$...\text{-}R_2SiCl^{\cdot -}, Na^+ \dashrightarrow ...\text{-}R_2Si^{\cdot} + NaCl$ (1B')
$...\text{-}R_2Si^{\cdot} + R_2SiCl^{\cdot} \dashrightarrow ...\text{-}R_2Si\text{-}SiR_2Cl$ (1C)
$2\ ...\text{-}R_2Si^{\cdot} \dashrightarrow ...\text{-}R_2Si\text{-}SiR_2\text{-}...$ (1C')
$2\ R_2SiCl^{\cdot} \dashrightarrow ClR_2Si\text{-}SiR_2Cl$ (1C")

$...\text{-}R_2Si^{\cdot} + Na \dashrightarrow ...\text{-}R_2Si^{-}, Na^+$ (2A)
$...\text{-}R_2Si^{-}, Na^+ + R_2SiCl_2 \dashrightarrow ...\text{-}R_2Si\text{-}SiR_2Cl$ (2B)

$R_2SiCl\cdot + Na \dashrightarrow R_2SiCl^-, Na^+$ (3A)

$R_2SiCl^-, Na^+ \dashrightarrow R_2Si: + NaCl$ (3A')

$R_2Si: + ...\text{-}R_2Si\text{-}SiR_2\text{-}... \dashrightarrow ...\text{-}R_2Si\text{-}SiR_2\text{-}SiR_2\text{-}...$ (3B)

There are some literature data which are against the purely radical process. Observed solvent effects, addition of crown ethers and cryptands, and a high yield of cyclics support anionic intermediates. Cyclic polysilanes can hardly be formed via a radical process since this would require the simultaneous presence of two radicals at both chain ends, unless extensive transfer operates (rate constant of the Cl-atom transfer for the *tert*-butylchloride is $k=2x10^6\ \underline{M}^{-1}s^{-1}$ and the C-Cl bond cleavage energy is (81 kcal/mol) (13); since the energy of dissociation of the Si-Cl bond (114 kcal/mol) is much higher, the rate constant of the Cl-atom transfer should be lower). The anionic chain end would, however, very efficiently "end-bite" the chloroterminated chain end because of the high anchimeric assistance in the five and six membered rings.

We have additional evidence from copolymerization studies which support an anionic mechanism. The sonochemical reductive coupling at ambient temperature is successful for phenylmethyldichlorosilane but not for the dialkyldichlorosilane. On the other hand, the dialkyldichlorosilane can be incorporated from 20 to 40% into polymer chains via simultaneous copolymerization. The radical mechanism would lead only to the homopoly(phenylmethylsilylene). Under the anionic conditions the growing silyl anion can react with both electrophilic monomers and incorporate the dialkyldichlorosilane into a polymer chain.

A polymer with a degree of polymerization $DP\approx 10^3$ is usually formed in less than 100 s at a monomer concentration lower than $[M]_o<0.1$ mol/L in toluene as a solvent ($[Toluene]_o\approx 10$ mol/L). Thus, the ratio of the rate constants of propagation to transfer should be above 10^5. The rate constant of the reaction of triethylsilyl radical with toluene is quite high ($k=1.2x10^6\ \underline{M}^{-1}s^{-1}$) (14). Assuming similar reactivity of the macromolecular radical, one gets a rate constant of propagation well exceeding limits of the diffusion controlled process. Thus, purely radical mechanism of a chain growth cannot operate for the polysilanes formation.

Nevertheless, it has been of interest to establish whether the radicals are formed as short-living intermediates in two one-electron transfer steps from chlorosilanes to anions, or the anions are formed in one two-electron transfer step from macromolecular chlorosilanes. The use of dichlorosilanes with a pendant alkenyl group gives the possibility of testing the presence of radical intermediates. The kinetics and mechanism of intra and intermolecular reactions between silyl radicals and alkenes have been studied for several systems. Bimolecular reaction of triethylsilyl radical with alkenes depends on the electronic and steric effects of the alkene. For example, rate constants as high as $k=1.1x10^9\ \underline{M}^{-1}s^{-1}$ and $k=2.2x10^8\ \underline{M}^{-1}s^{-1}$ were reported for acrylonitrile and styrene, respectively. On the other hand, the rate constant for the reaction with cyclohexene and hexene are $k=0.9x10^6\ \underline{M}^{-1}s^{-1}$ and $k=4.6x10^6\ \underline{M}^{-1}s^{-1}$ (15). The latter rate constants are very close to the reaction of the silyl radical with toluene ($k=1.2x10^6\ \underline{M}^{-1}s^{-1}$). The intramolecular reaction with 4-pentenyl substituent has also been studied and the limits of the rate constant set as $10^7\ s^{-1}<k<10^9\ s^{-1}$. Thus, the intramolecular cyclization may compete with the second electron transfer which converts a radical to anion. Anions react with primary alkenes very slowly.

The cyclization process for carbon-based radicals leads predominantly to exo-product (five-membered rings) for pentenyl derivatives. On the contrary, the silyl radicals led in large excess to the endo-product (six-membered rings). Five membered rings were observed when disilane with β-allyl groups was converted to the radical (16). This was again the endo-cyclization.

The pendant allyl groups on polysilane chains can react using the polysilane matrix in a way similar to the radical cyclopolymerization of diallyl and triallyl silanes which form soluble polymers (17). In our system seven-membered rings can be formed, if allowed by a proper tacticity of substituents. If not, a "ladderlike" polymer is interrupted by the unreacted allyl groups. The intermolecular reaction is usually much slower, but the precipitate of the crosslinked polymer is observed after a few weeks. Probably radicals generated by the Si-Si scission react with remaining, isolated unreacted allyl groups to form an insoluble gel.

The main conclusions from the reported studies are that radicals are present as short-lived intermediates which are rapidly reduced to anions at higher polymerization degrees, but which are efficiently trapped at a monomeric or dimeric level. Thus, the electron transfer proceeds as two one-electron transfer processes. Polymers with a high degree of Si-Si catenation are formed. Some of the alkenyl groups are consumed intramolecularly after polysilane is formed, but at longer reaction times crosslinking is observed.

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