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Technical Report No. 11

HOMOPOLYMERIZATION AND COPOLYMERIZATION OF ALKENYLDICHLOROSILANES
BY REDUCTIVE COUPLING

by

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Prepared for Publication

in the

American Chemical Society Polymer - Preprints

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March 23, 1989

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REPORT DOCUMENTATION PAGE

Form Approved
OMB No. 0704-0188

1a. REPORT SECURITY CLASSIFICATION Unclassified			1b. RESTRICTIVE MARKINGS		
2a. SECURITY CLASSIFICATION AUTHORITY			3. DISTRIBUTION / AVAILABILITY OF REPORT Approved for Public Release		
2b. DECLASSIFICATION / DOWNGRADING SCHEDULE					
4. PERFORMING ORGANIZATION REPORT NUMBER(S) Report No. 11			5. MONITORING ORGANIZATION REPORT NUMBER(S)		
6a. NAME OF PERFORMING ORGANIZATION Carnegie Mellon University		6b. OFFICE SYMBOL (If applicable)	7a. NAME OF MONITORING ORGANIZATION ONR		
6c. ADDRESS (City, State, and ZIP Code) Department of Chemistry 4400 Fifth Avenue Pittsburgh, PA 15213			7b. ADDRESS (City, State, and ZIP Code) Department of Navy Arlington, VA 22217		
8a. NAME OF FUNDING / SPONSORING ORGANIZATION ONR		8b. OFFICE SYMBOL (If applicable)	9. PROCUREMENT INSTRUMENT IDENTIFICATION NUMBER		
8c. ADDRESS (City, State, and ZIP Code) 800 N. Quincy St. Arlington, VA 22217			10. SOURCE OF FUNDING NUMBERS		
			PROGRAM ELEMENT NO.	PROJECT NO.	TASK NO.
11. TITLE (Include Security Classification) Homopolymerization and Copolymerization of Alkenyldichlorosilanes By Reductive Coupling					
12. PERSONAL AUTHOR(S) H. K. Kim and K. Matyjaszewski					
13a. TYPE OF REPORT Preprints		13b. TIME COVERED FROM _____ TO _____		14. DATE OF REPORT (Year, Month, Day) 3/23/89	
15. PAGE COUNT					
16. SUPPLEMENTARY NOTATION Submitted for publication in "American Chemical Society Polymer Preprints"					
17. COSATI CODES			18. SUBJECT TERMS (Continue on reverse if necessary and identify by block number)		
FIELD	GROUP	SUB-GROUP	→ Polysilanes, Silyl Radical, Silyl Anions, Alkenyl Groups Mechanism.		
19. ABSTRACT (Continue on reverse if necessary and identify by block number) Sonochemical reductive coupling of dichlorosilanes containing allyl and 5-hexenyl group leads to the formation of high molecular weight polymers and oligomeric fractions. Both products contain unreacted alkenyl groups. These results indicate that radicals are short living intermediates in the reductive coupling process, and that radicals are rapidly converting to more stable polymeric silyl anions. Resulting homopolymers of allylmethyldichlorosilane, allylphenyldichlorosilane and 5-hexenylphenyldichlorosilane as well as their copolymers with phenylmethyldichlorosilane absorb above 330 nm which is typical for long chain catenation of silicon atoms.					
20. DISTRIBUTION / AVAILABILITY OF ABSTRACT ☐ UNCLASSIFIED / UNLIMITED ☒ SAME AS RPT ☐ DTIC USERS			21. ABSTRACT SECURITY CLASSIFICATION Unclassified		
22a. NAME OF RESPONSIBLE INDIVIDUAL Dr. K. J. Wynne			22b. TELEPHONE (Include Area Code) (202) 696-4410		22c. OFFICE SYMBOL

HOMOPOLYMERIZATION AND COPOLYMERIZATION OF ALKENYLDICHLOROSILANES BY REDUCTIVE COUPLING

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Introduction

Polysilanes are novel materials with interesting physical and chemical properties ^{1,2}. Up to now the only successful synthesis of high molecular weight polysilanes is accomplished by the reductive coupling of disubstituted dichlorosilanes with molten sodium in nonpolar solvents ^{1,2}. The products of the synthesis consist of oligomeric cyclic fraction (composed mostly from cyclopenta- and cyclohexasilanes), fraction with relatively low molecular weight ($M_n < 5,000$) and a high 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 ^{3,4}. The separation of high molecular weight polymer from low molecular weight fraction is difficult. Synthesis of the high molecular weight polysilane with relatively narrow polydispersity is important for some applications and for the structure property relationship. We have recently accomplished the sonochemical synthesis of polysilanes ⁵ by the reductive coupling of disubstituted dichlorosilanes with sodium at ambient temperatures which 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 ^{3,4,5}. The presence of the alkenyl groups on long lived silyl radical would prevent the formation of polysilane because of the rapid intramolecular cyclization. Therefore, the reductive coupling of dichlorosilanes containing alkenyl groups will not only provide novel functional polymers but also will contribute to the understanding of the mechanism of the reductive coupling of dichlorosilanes. This is important for the further improvement and optimization of the polymerization procedure.

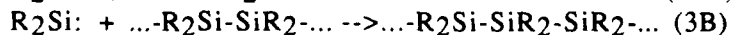
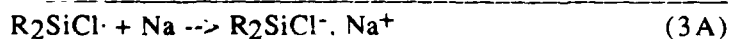
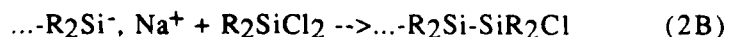
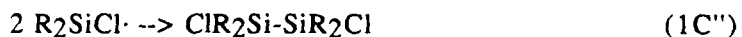
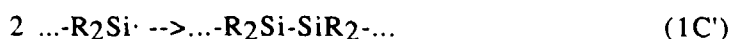
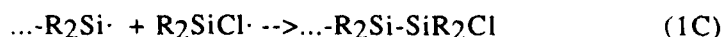
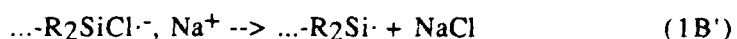
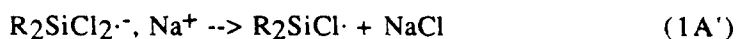
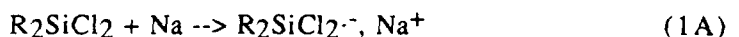
Results and Discussion

The reductive coupling process can proceed via several different intermediates. The first slow step should involve the electron transfer from sodium to monomer to form monomeric radical anion. This species should very rapidly isomerize to the monomeric radical and sodium chloride, insoluble in the reaction

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medium (1A). Identical reaction between sodium and chloroterminated polymer chain will provide polymeric radical anion and eventually polymeric radical (1B). Monomeric and polymeric radicals can recombine in the chain growth process (1C), which will involve radical intermediates exclusively. It is known, however, that silyl radicals which contain phenyl groups can be easily further reduced to silyl anions. The polysilane chain may also facilitate this reaction (2A). The resulting polysilyl anion will react in the nucleophilic substitution reaction (probably S_N2) with a monomer which is a stronger electrophile (contains two electron withdrawing Cl-groups) than a chloroterminated 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); disilenes are however very reactive and they should rapidly polymerize if it is thermodynamically possible. Silylene can also lead to the formation of strained reactive cyclic intermediates which would convert to polysilanes via ring-opening polymerization. However, as we will discuss later mechanism based on silylene is not of primary importance since silylene traps do not affect polymerization ⁴.



It is highly probable that various possible mechanistic pathways have different activation energies and that temperature change would lead to the preferential polymerization by one mechanism. Our experimental results indicate that at ambient temperatures, contrary to boiling toluene, only high polymer ($M_n=100,000$) is formed and low polymer ($M_n=2,000$ to $5,000$) is absent ⁵.

Let us discuss in more detail the available information on the reductive coupling process. It is well established that

polymerization proceed as a chain growth and not a step growth process. High polymer is formed from the very beginning of the reaction and independent of the $[\text{sodium}]_0/[\text{silane}]_0$ ratio. Step growth mechanism would lead to the initial formation of dimers, tetramers, etc. Therefore, polymerization resembles classical chain mechanism with slow initiation, rapid propagation, and termination. Slower initiation than propagation has the origin in the easier electron transfer to the chloroterminated polysilane chain rather than to the monomer.

Propagation is the reaction most important since it is responsible for the formation of the entire chain (except the end groups). Therefore, the understanding of the mechanism of the propagation step is of primary importance. There is some information in literature, which allows to reject the silylene mechanism ⁴. Thus, the choice remains between radical and anionic mechanism. Observed solvent effects ^{3,5} and high yield of cyclics support anionic intermediates. Cyclic polysilanes can hardly be formed via radical process since this would require simultaneous presence of two radicals at both chain ends, unless extensive transfer operates. The high energy of the Si-Cl bond does not favor the Cl-atom transfer with radical intermediates. 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 had additional evidence which supports anionic mechanism from copolymerization studies ⁵. The sonochemical reductive coupling at ambient temperature is successful for phenyl methyldichlorosilane but not for the dialkyldichlorosilane. However, the dialkyldichlorosilane can be incorporated in 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 dialkyl dichlorosilane into polymer chain.

Rate constant of the Cl-atom transfer from *tert*-butylchloride to triethylsilyl radical is $k=2 \times 10^6 \text{ M}^{-1}\text{s}^{-1}$ and the C-Cl bond cleavage energy is (81 kcal/mol) ⁶. Since the energy of dissociation of the Si-Cl bond (114 kcal/mol) is much higher, the rate constant of the Cl-atom transfer between Si-Cl and Si $\cdot$ should be lower. The rate constant of the reaction of the silyl radical with toluene ($k=1.2 \times 10^6 \text{ M}^{-1}\text{s}^{-1}$) ⁷ should be faster than of the reaction with a monomer. Taking into account low concentration of chlorosilane in the reaction mixture, the formation of the high molecular weight polymer in toluene solution excludes radical intermediates.

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 step from 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 cyclohexene and hexene ⁸ are $k=0.9 \times 10^6 \text{ M}^{-1}\text{s}^{-1}$ and $k=4.6 \times 10^6 \text{ M}^{-1}\text{s}^{-1}$. These rate constants are very close to one for the reaction of the silyl radical with toluene ($k=1.2 \times 10^6 \text{ M}^{-1}\text{s}^{-1}$). The intramolecular reaction with 4-pentenyl substituent has also been studied and the limit of the rate constant set as $10^7 \text{ s}^{-1} < k < 10^9 \text{ s}^{-1}$. Thus, the intramolecular cyclization may compete with the second electron transfer which converts a radical to anion. Anions react with primary alkenes slow.

The cyclization process for carbon-based radicals leads predominantly to exo-product (five-membered rings) for pentenyl derivatives. Contrary, the silyl radicals led in large excess to the endo-product (six-membered rings) ⁸. Five membered rings were observed when disilane with the β -allyl groups was converted to the radical ⁹. This was again the endo-cyclization.

We have used in our studies dichlorosilanes with 5-hexenyl and allyl groups. Dichlorosilanes with pendant alkenyl groups were homopolymerized and copolymerized using sodium as reducing agent at ambient temperatures in toluene in the presence of ultrasound. Reaction products were separated into oligomers soluble in isopropyl alcohol and polymers insoluble in isopropanol. Both products were analyzed by NMR to determine the composition of copolymers and also the amount of the unreacted double bonds. Polymers were additionally characterized by size exclusion chromatography and by UV spectroscopy in order to determine the proportion of the Si-Si linkages.

The results for polymerization of allylmethyldichlorosilane, allylphenyldichlorosilane, and 5-hexenyl-phenyldichlorosilanes are shown in Tables 1.

We have reported earlier that at ambient temperatures in toluene only aryl containing dichlorosilanes react rapidly. Dialkyldichlorosilanes do not react with sodium within 10 hours. Allyl group activate dichlorosilane in the electron transfer process. No polymer was found after 1 hour but after 5 hours 2.7% of polymer was formed. At that time still 8% of monomer was unreacted. Under the same conditions 5-hexenylmethyldichlorosilane did not react within 5 hours, in agreement with our previous studies ⁵. Poly(allylmethylsilylene) was insoluble in any organic solvent. Oligomers (formed in 89% yield) show 62% unreacted double bonds. Copolymerization of equimolar mixture of allylmethyldichlorosilane with phenylmethyldichlorosilane gave 8% of a copolymer with 25% of allylmethylsilane and 75% of phenylmethylsilane units. Molecular weight distribution ($M_w/M_n=2.8$) was much broader than for the homopoly(phenylmethylsilylene) ($M_w/M_n=1.3$). Molecular weights were also considerably lower ($M_n=29,000$ vs $M_n=100,000$). In the copolymer 48% of allyl groups remained intact. The maximum of absorption and extinction coefficient for a copolymer ($\lambda_{\text{max}}=334 \text{ nm}$, $\epsilon=5,900 \text{ M}^{-1} \text{ cm}^{-1}$) were nearly the

same as for homopoly(phenylmethylsilylene) ($\lambda_{\max}=340$ nm, $\epsilon=7,800 \text{ M}^{-1} \text{ cm}^{-1}$). This indicates that long Si-Si sequences must be present in polysilane chains and that Si-Si catenation is not interrupted by carbon atoms ¹⁰. Thus, the allyl groups can be either consumed at the very early stage of the reaction or after polymer is formed. The proportion of unreacted double bonds in oligomers is lower (35%). This may indicate that the second electron transfer and conversion of the radical to anion is favored for longer polysilane chains. The pendant allyl groups on polysilane chains can react using the polysilane matrix only if the proper tacticity is provided. In such systems seven membered rings can be formed and than can be interrupted by the unreacted allyl groups. It is known that polysilanes form usually atactic materials and therefore the degree of consumption of allyl groups in the template-like manner cannot be high. It has been reported that diallylsilane form soluble polymers ¹². The head-to-tail intramolecular endo-cyclization leads mostly to six membered rings. Seven membered rings are expected for the cyclization based on the polysilane template. The NMR analysis of the polymers confirms this structure.

Allylphenyldichlorosilane reacts readily with sodium at ambient temperatures. Homopolymer formed in 7.2% yield contains 43% of unreacted allyl groups. Polymer has bimodal molecular weight distribution with $M_{\text{peak}}=35,000$ and 9,300. The ratio of high to low polymer equals 1:2. Polymer absorbs in UV at $\lambda_{\max}=338$ nm with $\epsilon=650 \text{ M}^{-1} \text{ cm}^{-1}$. The low extinction coefficient indicate that the catenation degree of Si atoms is lower than in the previous case. 92% of oligomers soluble in isopropanol were isolated. According to NMR they contain 48% of unreacted allyl groups.

Allylphenyldichlorosilane copolymerizes readily with phenylmethyldichlorosilane. Copolymer composition is 38% / 62%. 50% of the allyl group are consumed in the polymer chain. These results are surprising since the presence of the phenyl group on the same silicon atom as allyl group should lead to the shorter life time of the radical and less efficient trapping. Probably post-polymerization of allyl groups is equally possible for allyl methyl and allyl-phenyl segments. The formation of the insoluble homopolymer for the allylmethyl derivative may suggests that in addition to the intramolecular reaction, also bimolecular process operates.

5-Hexenylphenyldichlorosilane gives in 96% oligomers and only in 1% polymer with $M_n=68,000$ and broad molecular weight distribution. Oligomers contain 75% of unreacted double bonds. Apparently the more flexible chain which can cyclize already at the monomeric level gives higher yield of oligomers. Small amount of a polymer indicates that not all radicals are trapped and above certain polymerization degree the second electron transfer must be fast enough to compete with intramolecular cyclization. As pointed out before 5-hexenylmethyldichlorosilane does not react under the present reaction conditions.

The brief summary of the reported results is as follows:

1. High polymers are formed in the reductive coupling sonochemical polymerization from dichlorosilanes with pendant allyl and 5-hexenyl substituents. Reductive coupling proceeds with the short lived radical intermediates which can be trapped during propagation.
2. Depending on the structure of monomers and molecular weight, approximately 30 to 75% of double bonds remain in oligo and polysilanes formed in this process.
3. Homopolysilanes and copolysilanes have long wavelength absorption and relatively large extinction coefficients. Life time of the radicals is very short since high polymers are formed and these polymers contain long Si-Si sequences which are rarely interrupted by carbon atoms from the trapped alkenyl groups.

Acknowledgments: This research has been partially supported by the grant from the Office of Naval Research.

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