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Synthesis and Polymerization of Novel Cationically Polymerizable Monomers

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SYNTHESIS AND POLYMERIZATION OF NOVEL CATIONICALLY POLYMERIZABLE MONOMERS

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ABSTRACT

The use of novel chemo- and regioselective hydrosilation reactions to prepare several series of ambifunctional silicon-containing epoxy monomers and oligomers is described. These monomers can be polymerized using traditional cationic initiators or by employing onium salt photoinitiators.

INTRODUCTION

The addition of silicon hydride groups across a carbon—carbon double or triple bond is known as the hydrosilation reaction. This reaction is depicted schematically in Eq. (1) [1]:

$$R-CH=CH_2 \ + \ R'_3Si-H \ \xrightarrow[\text{or } h\nu]{\text{catalyst}} \ R-CH_2-CH_2 \ + \ R-CH-CH_3$$
$$\underset{R'_3Si}{|} \qquad \underset{R'_3Si}{|}$$

(1)
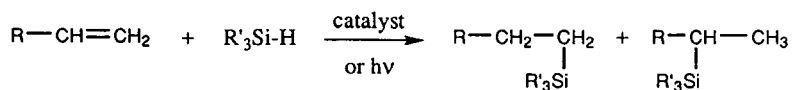
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The hydrosilation reaction has been investigated by a large number of workers and finds considerable industrial application as one of the major routes for the synthesis of compounds bearing silicon—carbon bonds. While the hydrosilation reaction can be catalyzed by UV light and sources of free radicals, the main method by which this reaction is currently carried out is by noble metal catalysis [2]. This field was pioneered by Speier who made the key discovery that chloroplatinic acid is a very excellent catalyst for the hydrosilation reaction [3]. Over the years, a large number of metal complexes have been found to catalyze the hydrosilation reaction including those of platinum, palladium, rhodium, and iridium. Despite the long and widespread use of the noble metal catalyzed hydrosilation reaction, it is a testimony to the complexity of this fundamental reaction that many investigators continue to be engaged in the elucidation of its mechanism. Even now, some aspects remain to be fully understood.

At the present time it is believed that hydrosilation can proceed by two separate mechanistic pathways: one involving homogeneous catalysis and the other taking place by a heterogeneous mechanism. The mechanism proposed by Chalk and Harrod [4] and shown in Scheme 1 for RhCl(Ph$_3$P)$_3$ involves catalysis by the classical homogeneous mechanism which involves repetitive oxidative-addition reductive-elimination steps proceeding through a transition metal center stabilized by coordinating ligands.
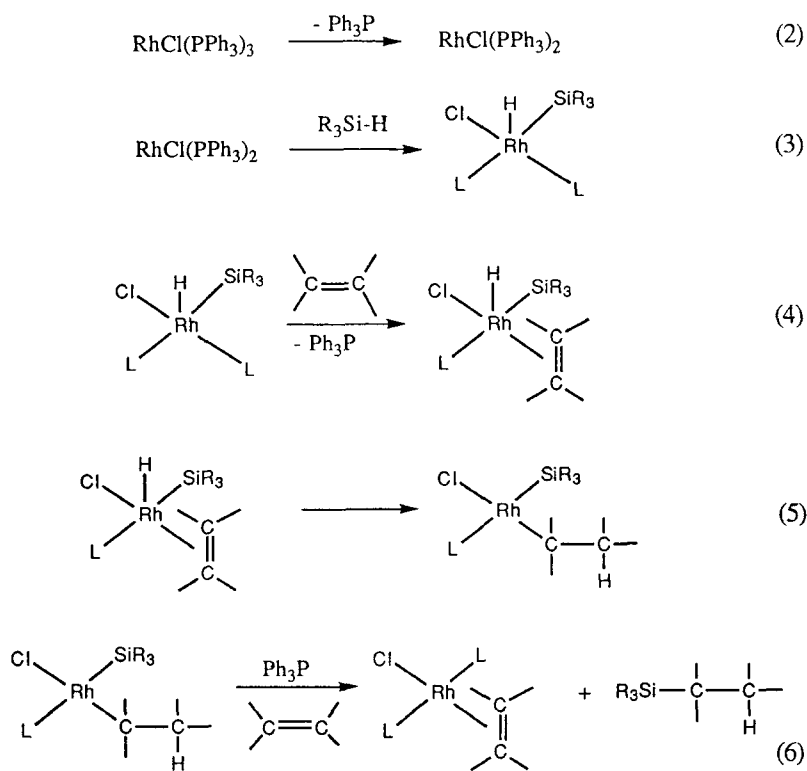
SCHEME 1.

A second mechanism, recently proposed by Lewis [5], invokes catalysis by metal colloids. This heterogeneous mechanism shown in Scheme 2 proceeds heterogeneously at a colloidal platinum metal surface.

The reaction mechanism depicted in Scheme 2 typically involves those metal complexes in which the ligands are readily removed under the reaction conditions. For example, olefin–platinum complexes are readily stripped of their olefinic ligands by hydrosilation. The resulting coordinatively unsaturated metal complexes collapse to form metal aggregates which further combine to give colloidal metal species. The overall reaction thus involves a reduction at the platinum metal center. Such platinum metal surfaces are capable of further interacting with silanes to form complexes in which the Si—H bond becomes activated. In this respect the heterogeneous hydrosilation reaction is directly analogous to metal-catalyzed reductions of olefins by molecular hydrogen [6, 7].
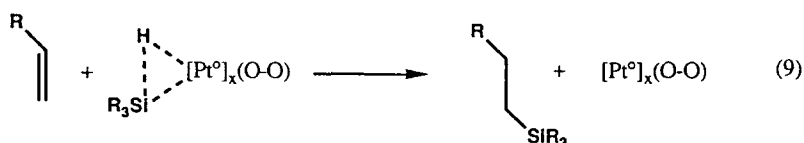
Thus, depending on the specific catalyst type and the ligands about the metal center, either heterogeneous, homogeneous, or a combination of both hydrosilation mechanisms may take place.

RESULTS AND DISCUSSION

Metal-Catalyzed Ring-Opening Polymerizations

The focus of our interest in hydrosilation chemistry was to employ this reaction for the preparation of a series of silicon-containing epoxide monomers. It was believed that depending on their structure, the polymers derived from these monomers might have properties which would markedly differ from the typical hard, brittle characteristics usually associated with epoxy resins. In addition, we wished to examine the ability of these silicon-containing monomers to undergo cationic ring-opening epoxide polymerizations.

Accordingly, the direct platinum-catalyzed hydrosilation of 3-vinyl-7-oxabicyclo[4.1.0]heptane by 1,1,3,3-tetramethyldisiloxane was carried out with the result shown in Eq. (10):

$$Pt^{2a}X_{2a}L_b \xrightarrow[\text{slow}]{\text{xs } R_3SiH, O_2} H_2L \;+\; [Pt^\circ]_x(O\text{-}O) \;+\; 2aXSiR_3 \quad (7)$$

$$[Pt^\circ]_x(O\text{-}O) \xrightarrow{R_3SiH} \underset{R_3Si}{\overset{H}{\cdots}}[Pt^\circ]_x(O\text{-}O) \quad (8)$$

$$\quad (9)$$

SCHEME 2.

$$2 \quad \underset{O}{\triangle}\!\!\!\diagdown\!\!\!\searrow \;+\; H\!-\!\underset{CH_3}{\overset{CH_3}{\underset{|}{\overset{|}{Si}}}}\!-\!O\!-\!\underset{CH_3}{\overset{CH_3}{\underset{|}{\overset{|}{Si}}}}\!-\!H \xrightarrow[\text{catalyst}]{Pt} \left[\cdots \right]$$
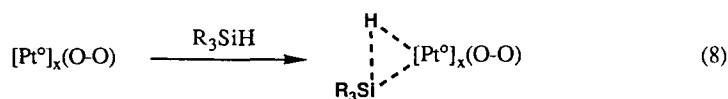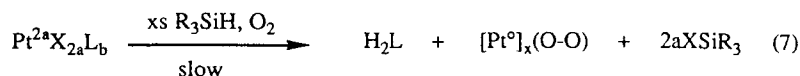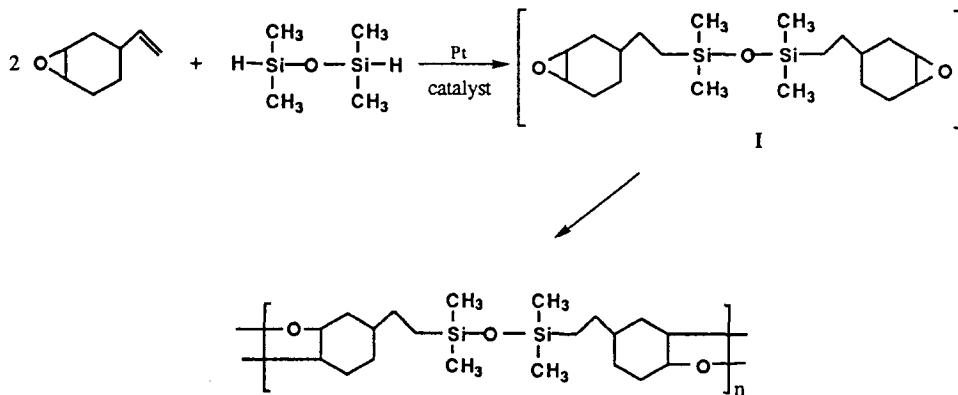
(10)

However, the desired difunctional epoxy monomer I was not obtained. Instead, rapid, exothermic crosslinking polymerization leading to insoluble infusible gels was observed in every case [8, 9]. In this reaction, several commercially available platinum-containing complexes were employed. An 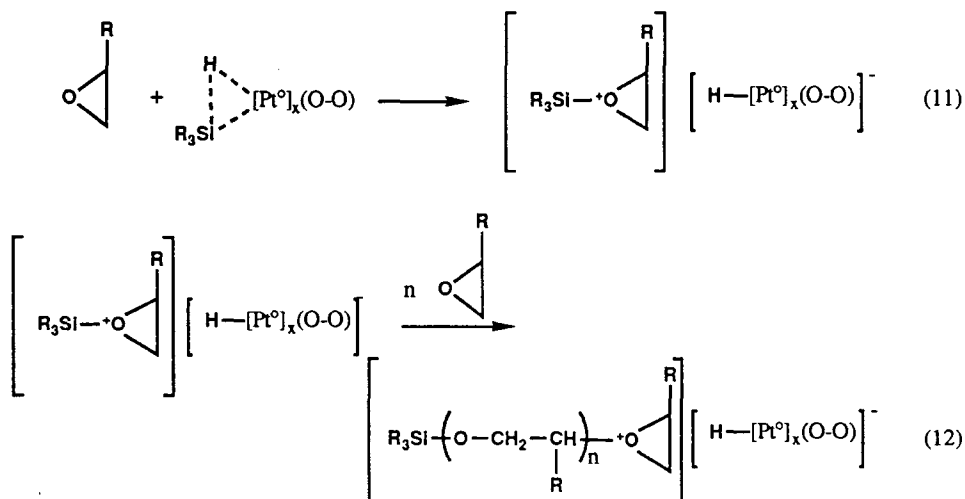analysis of the polymers formed showed that under the reaction conditions, epoxide ring-opening polymerization occurs simultaneously with hydrosilation to give network polymers whose structure is represented in Eq. (10). Further investigations demonstrated that this novel transition-metal-catalyzed polymerization reaction was completely general and could be applied to a wide variety of structurally diverse epoxide monomers. Similarly, a variety of complexes of rhodium, iridium, palladium, and cobalt were active for these novel transition-metal catalyzed ring-opening polymerizations [10, 11]. Based on these observations as well as many others, the mechanism shown in Scheme 3

$$\underset{O}{\triangle}^{R} \;+\; \begin{matrix} H \\ \vdots \\ R_3Si \end{matrix} [Pt^\circ]_x(O\text{-}O) \longrightarrow \left[R_3Si\!-\!{}^+O \underset{}{\triangle}{}^R \right] \left[H\!-\![Pt^\circ]_x(O\text{-}O) \right]^- \quad (11)$$

$$\left[R_3Si\!-\!{}^+O \underset{}{\triangle}{}^R \right] \left[H\!-\![Pt^\circ]_x(O\text{-}O) \right]^- \;\xrightarrow{\; n \; \underset{O}{\triangle}{}^R \;}\; \left[R_3Si\!\!\left(\!O\!-\!CH_2\!-\!\underset{R}{\overset{}{\underset{|}{CH}}}\!\right)_{\!n}\!{}^+O\underset{}{\triangle}{}^R \right] \left[H\!-\![Pt^\circ]_x(O\text{-}O) \right]^- \quad (12)$$

SCHEME 3.

was proposed for the platinum-catalyzed ring-opening polymerization of epoxides [9, 10].

The mechanism shown in Scheme 3 constitutes a new type of transition-metal-catalyzed cationic polymerization reaction which involves the involvement of colloidal metal species in both the initiating and propagating steps. As previously stated, the coordination of silanes with colloidal platinum, rhodium, or iridium affords species which, when coordinated by hydrogen functional silanes, can be regarded as sources of electrophilic silicon. Attack of these species on the oxygen atom of the epoxide leads to the formation of an oxonium intermediate. This species subsequently undergoes propagation by a conventional cationic ring-opening polymerization mechanism. The corresponding counterion consists of a colloidal metal cluster in which the negative charge is stabilized over the entire surface of the colloid. Similarly, these catalysts can induce the polymerization of many other types of cationically polymerizable heterocyclic monomers as well as vinyl ethers. Investigations in this laboratory are currently in progress to explore the scope of these transition-metal-catalyzed cationic polymerizations. However, in the present case this epoxide ring-opening polymerization was considered a complicating side reaction and, consequently, means for reducing or eliminating it completely were considered.

### Chemoselective Hydrosilations

The recognition that transition metal colloids were the active catalytic agents in the undesired ring-opening polymerization shown in Eq. (10) led us to propose a possible means for its elimination. It appeared that one way of avoiding this side reaction altogether was to employ noble metal complexes which specifically undergo only homogeneous hydrosilation. Indeed, it was discovered that this postulate was correct and that a variety of metal complexes could be employed to conduct these hydrosilations provided that the ligands attached to the metal center are carefully chosen so that they are not removed under the reaction conditions. For example, Wilkinson's catalyst, $RhCl(Ph_3P)_3$, is a very active *chemoselective* hydrosilation catalyst; i.e., reaction occurs exclusively at one of two possible chemically different sites, namely, the double bond, and not at the epoxide ring of a vinyl epoxide. This catalyst can be employed for the facile, high yield synthesis of a wide variety of di- and multifunctional silicon-containing epoxy monomers [12, 13]. Under the usual conditions at which this hydrosilation reaction is conducted, no ring-opening polymerization can be observed. Table 1 shows the structures of a few typical examples of di- and multifunctional epoxide monomers prepared using this catalyst.

As may be noted from Table 1, the reaction is general, and monomers containing up to four highly reactive epoxycyclohexyl groups have been prepared in high yields using this chemistry. Although the reaction proceeds best for trisubstituted silanes bearing a single Si—H group, monomers such as **VI** and **VII** have been prepared in which double hydrosilation of a disubstituted silane bearing two hydrogens bound to the same silicon atom has taken place. The reaction is also reasonably tolerant of other functional groups; for example, **X** contains a secondary amine as well as the two epoxycyclohexyl groups.

TABLE 1. Structures of Epoxy-Functional Silanes and Siloxanes

Structure	Notation	Structure	Notation
	I		VI
	II		VII
	III		VIII
	IV		IX
	V		X

Figure 1 shows the differential scanning photocalorimetry curves (DPS) for the photoinitiated cationic polymerization of several typical epoxy–silicone monomers. In this study, 0.5 mol% of the cationic photoinitiator (4-octyloxyphenyl)phenyliodonium hexafluoroantimonate was used. Silicon-containing monomers containing the epoxycyclohexyl group are especially reactive in photo- and electron-beam-
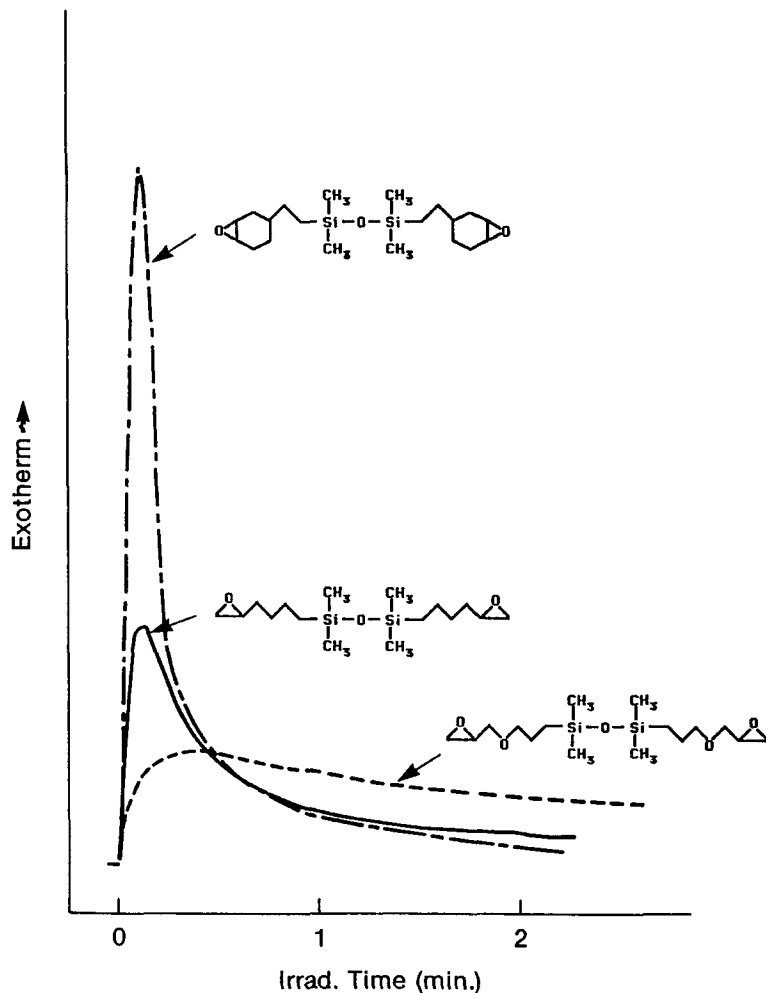

(13)
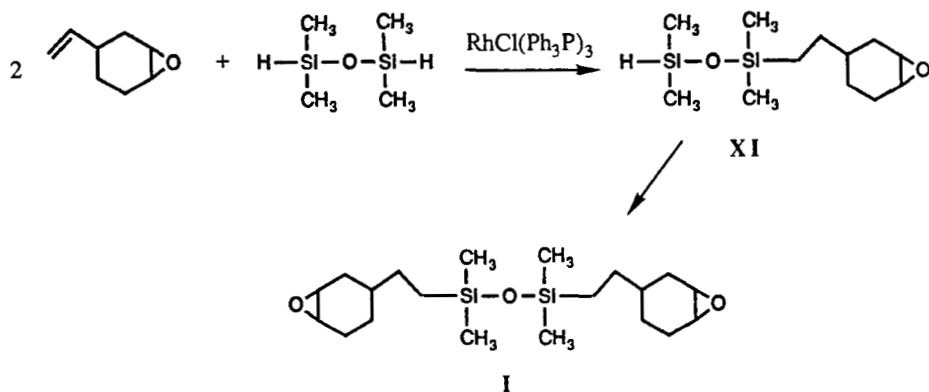
FIG. 1. DSP curves for various epoxy silicone monomers at 30°C using 0.5 mol% (4-octyloxyphenyl)phenyliodonium hexafluoroantimonate.

induced cationic polymerizations and are currently being investigated in this laboratory as potential coatings for spacecraft and for use in oxygen-plasma-resistant aerospace composites. For this reason the bulk of the work reported in this communication focuses on preparing monomers containing the epoxycyclohexyl group.

Regioselective Hydrosilation Reactions

A detailed study of the hydrosilation of 3-vinyl-7-oxabicyclo[4.1.0]heptane with 1,1,3,3-tetramethyldisiloxane led to the conclusion that this reaction proceeds in two discrete steps as shown in Eq. (13) [14] on page 1006. Figure 2 shows the results of a gas chromatographic analysis of the above hydrosilation reaction. It is
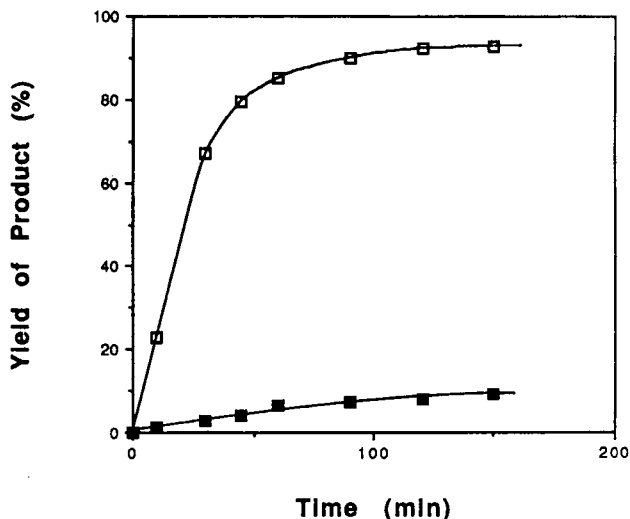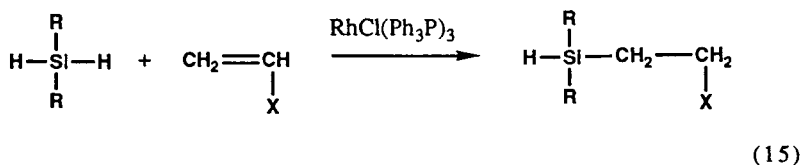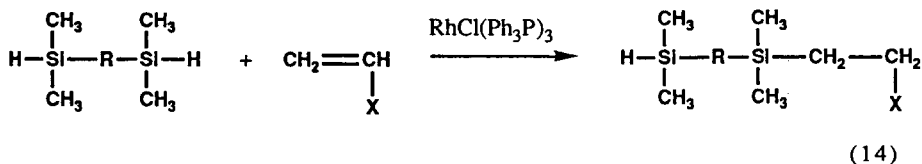
FIG. 2.   Study of the hydrosilation of VCHO with TMDS. 0.01 mol TMDS, 0.02 mol VCHO, and 0.02×10^{-4} mol RhCl(Ph$_3$P)$_3$ in 10 mL toluene at 55°C: ($\square$) monoadduct **XI**; (■) diadduct **I**.

clear that the monoadduct, **XI**, is first generated and then decays as the diadduct, **I**, is formed. The high yield of **XI** indicated in Fig. 2 and its slow decay suggested the possibility that this monoadduct could be isolated.

Astonishingly, **XI** can be isolated in >96% yield through the use of a 1:1 molar ratio of the reactants instead of the 2:1 ratio shown in Eq. (13). This is particularly impressive since the reactivity at both of the Si—H sites in 1,1,3,3-tetramethyldisiloxane toward hydrosilation would be assumed to be very similar. Further investigation of this reaction using a variety of disubstituted Si—H-containing compounds showed that in all cases one can carry out monohydrosilation very selectively. Thus, in addition to being *chemoselective*, the reaction may also be said to be *regioselective* since reaction occurs at only one of two identical Si—H functional groups. Similarly, we now report that this reaction is very general and that many other difunctional Si—H compounds with widely differing structures

$$\underset{\substack{CH_3 \\ | \\ H-Si-R-Si-H \\ | \\ CH_3}}{\overset{\substack{CH_3 \\ | }}{}} \ + \ CH_2\!\!=\!\!\underset{X}{\overset{}{CH}} \quad \xrightarrow{RhCl(Ph_3P)_3} \quad \underset{\substack{CH_3 \\ | \\ H-Si-R-Si-CH_2-CH_2 \\ | \\ CH_3}}{\overset{\substack{CH_3 \\ |}}{}} \underset{X}{\overset{}{}}$$

$$(14)$$

$$\underset{\substack{R \\ | \\ H-Si-H \\ | \\ R}}{} \ + \ CH_2\!\!=\!\!\underset{X}{\overset{}{CH}} \quad \xrightarrow{RhCl(Ph_3P)_3} \quad \underset{\substack{R \\ | \\ H-Si-CH_2-CH_2 \\ | \\ R}}{} \underset{X}{\overset{}{}}$$

$$(15)$$

also undergo regioselective hydrosilation reactions [15]. Further, the regioselective hydrosilation reactions are not limited only to 3-vinyl-7-oxabicyclo[4.1.0]heptane but also may be applied to other carbon—carbon double-bond-containing compounds as well. Equations (14) and (15) (seen on page 1008) are intended to depict the very general nature of this reaction.

In the above equations, X can represent a moiety containing an aliphatic or aromatic group bearing such functional groups as halogens, nitriles, amines, epoxides, or alkoxy silanes. Application of this novel regioselective hydrosilation reaction leads to the direct synthesis of several series of ambifunctional monomers containing two different reactive function groups in the same molecule. The remainder of this article will focus on examples in which this reaction has been exploited to prepare several novel ambifunctional monomer types and on their subsequent cationic photopolymerization.

Synthesis of α-Hydrogen-ω-Epoxy Silanes and Siloxanes

Surprisingly, hydrosilation of the series of α,ω-oligopolysiloxanes in which the Si—H groups are distantly removed from one another also proceeds with high regioselectivity. For example, 1,1,3,3,5,5-hexamethyltrisiloxane (HMTS) and 1,1,3, 3,5,5,7,7-octamethyltetrasiloxane (OMTS) give monoadducts **XII** and **XIII** in 99 and 95% yields, respectively.

$$\text{XII} \quad n = 1$$
$$\text{XIII} \quad n = 2$$
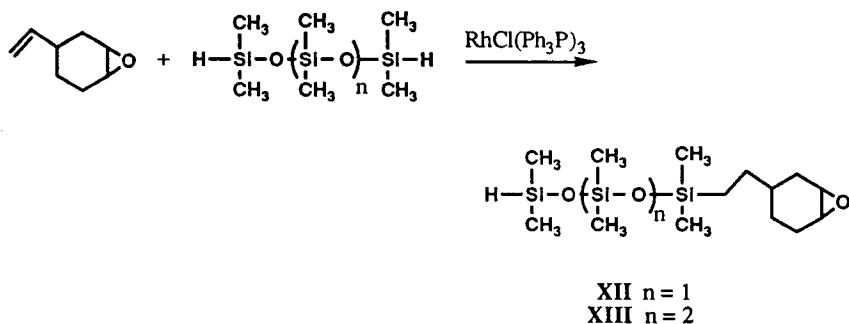
$$(16)$$

Thus, the regioselectivity is preserved even though the two reactive Si—H sites are separated by four and six bond lengths, respectively.

As noted in Table 2, in addition to α,ω-hydrogen functional oligopolydimethylsiloxanes, other α,ω-hydrogen functional silanes and siloxanes can be condensed with a variety of vinyl-containing cycloaliphatic and open-chain epoxides to give the desired monoadducts in good to excellent yields. All of the compounds in Table 2 are new and were thoroughly characterized using ^{1}H, ^{13}C, and ^{29}Si NMR, infrared spectroscopy, and elemental analysis. Typically, the monoadducts exhibit a strong, sharp bands at 2160 cm^{-1} in the infrared and a peak at δ 4.7 ppm in the ^{1}H NMR characteristic of the Si—H chromophore. Figure 3 gives the ^{1}H-NMR spectrum for α-hydrogen-ω-epoxy silane **XI** which is typical for this class of compounds.

Of special interest in Table 2 are compounds **XVII**, **XVIII**, **XIX**, and **XX**. The dialkylsilanes, methylphenylsilane, and diphenylsilane give very high yields (>90%) of the monoadducts, **XVII** and **XVIII** by hydrosilation with 3-vinyl-7-

TABLE 2.   Structures of α-Hydrogen-ω-Epoxy Functional Silanes and Siloxanes

Structure	Nota-tion	Structure	Nota-tion
	XI		XVI
	XII		XVII
	XIII		XVIII
	XIV		XIX
	XV		XX

oxabicyclo[4.1.0]heptane. In contrast to these latter compounds in which the added vinyl epoxy groups become attached to the same silicon as the hydrogen atom are compounds XIX and XX in which the two Si—H groups are on two different silicon atoms separated by a 4,4'-diphenylether group or a benzene ring, respectively.

The cationic ring-opening polymerization of the Si—H functional epoxy silanes and siloxanes takes place readily in the presence of a variety of Lewis and Brønsted acids to give linear polyethers having pendant Si—H groups. The cationic photopolymerization of these compounds using onium salt photoinitiators is especially facile [15]. For example, the polymerization of XI can be readily carried out in bulk or in toluene solution using a diaryliodonium salt photoinitiator, as shown in Eq. (17).
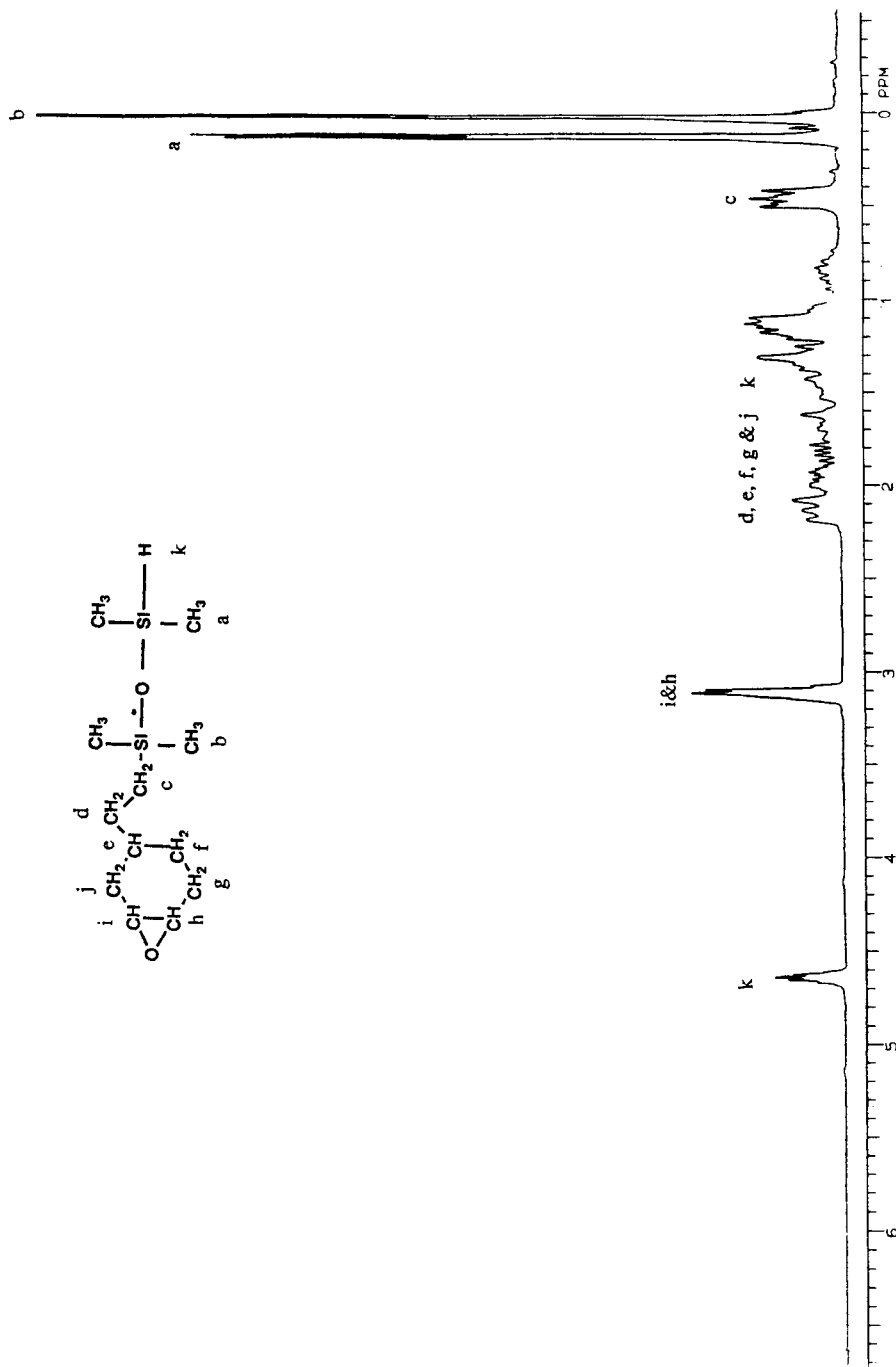

(17)
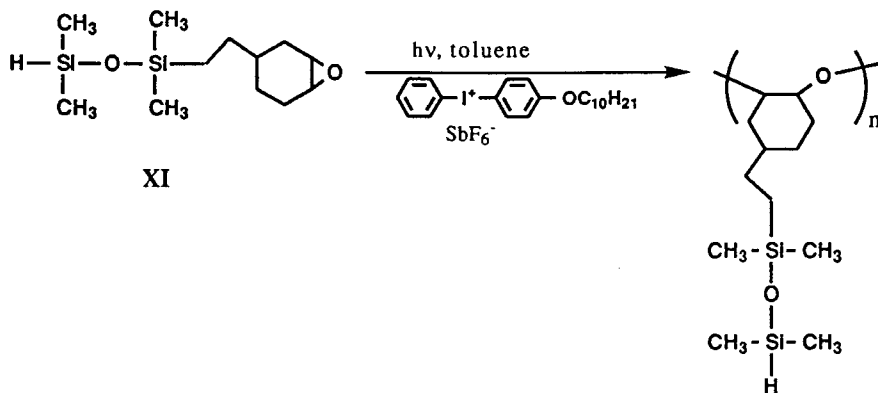
FIG. 3. ^{1}H-NMR spectrum of monoadduct **XI** in CDCl$_3$.

Further reaction of the pendant Si—H groups on this polymer by hydrosilation with olefins in the presence of Wilkinson's or other hydrosilation catalysts gives rise to new series of polyethers containing various pendant groups.

Ambifunctional Epoxy Silanes and Siloxanes

The α-hydrogen-ω-epoxy silanes and siloxanes shown in Table 2 possess active Si—H groups which can be easily further functionalized by hydrosilation chemistry. This makes them very valuable as intermediates for the preparation of still other classes of novel and interesting ambifunctional monomers. One synthetic strategy which was employed and is illustrated in Eq. (18) was to carry out hydrosilation reactions at the remaining Si—H site of an α-hydrogen-ω-epoxy silane or siloxane with an appropriate vinyl functional epoxy compound to produce difunctional monomers containing two different types of epoxy functional groups [16].

(18)
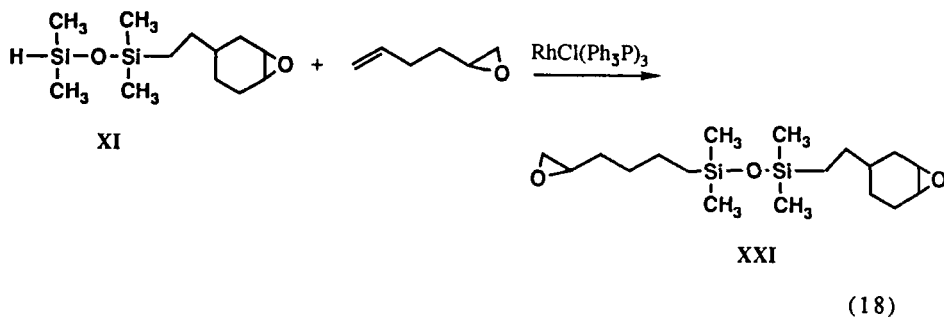
The same monomer may be prepared by reaction of α-hydrogen-ω-epoxy silane, **XIV**, with 3-vinyl-7-oxabicyclo[4.1.0]heptane as depicted in Eq. (19).

(19)
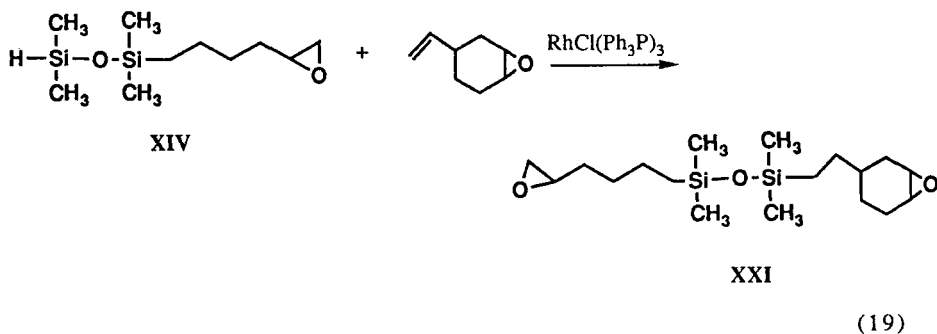
In Fig. 4 is shown the ^{13}C-NMR spectrum of monomer **XXI**.

The above condensation reactions were carried out at 80–85 °C in the absence of a solvent. To avoid the ring-opening polymerization of the epoxycyclohexyl groups, chemoselective rhodium-containing catalysts were employed for the hydrosilation. In an analogous fashion, the synthetic schemes outlined in Eqs. (18) and (19) were used for the generation of a number of additional monomers having two different epoxy functionalities in the same molecule, each with correspondingly different polymerization reactivities. The structures of some of these compounds
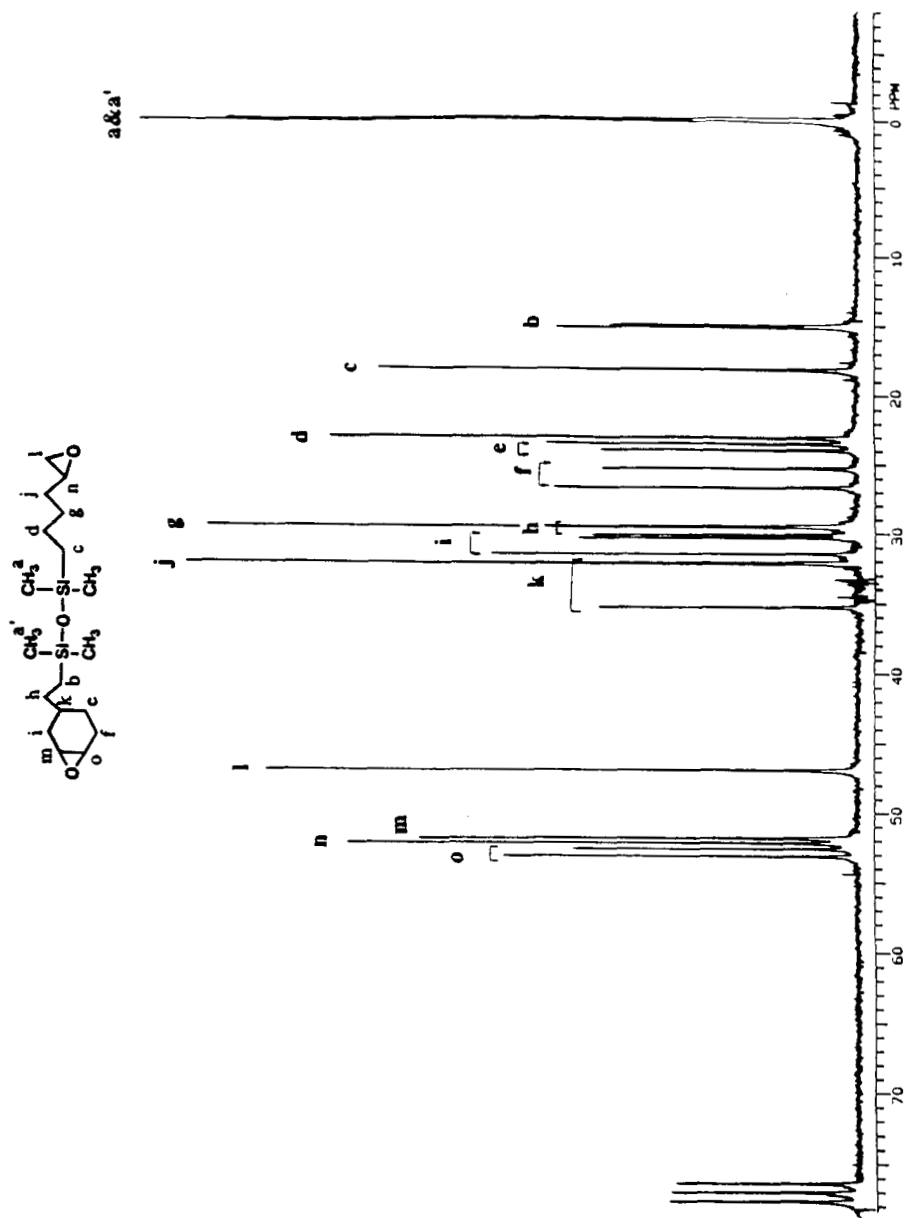
FIG. 4. ^{13}C-NMR spectrum of monomer **XXI** in CDCl$_3$.

TABLE 3.   Structures of Ambifunctional Epoxy-Functional Silanes and Siloxanes

Structure	Nota-tion	Structure	Nota-tion
	XXI		XXVI
	XXII		XXVII
	XXIII		XXVIII
	XXIV		XXIX
	XXV		XXX

are shown in Table 3. Preparation of these compounds by alternative synthetic techniques would be difficult.

An even more straightforward approach to the synthesis of the monomers given in Table 3 is illustrated in Eq. (20) for the preparation of unsymmetrical monomer **XXI**.
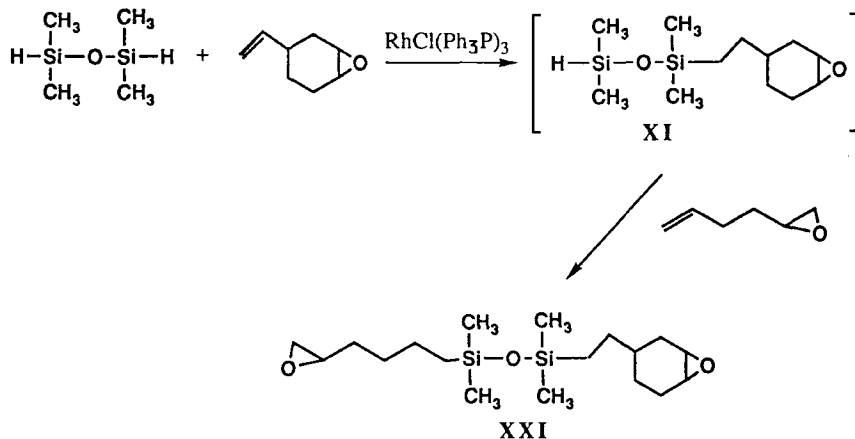
$$\text{(20)}$$

Since it has been shown that the rate of hydrosilation at the first of the two Si—H groups of simple disilanes or disiloxanes is so much faster than at the second Si—H group, an essentially pure monohydrosilated product, **XI**, can be obtained. When this first reaction was complete, a second, different vinyl epoxide could be added in a two-step, one-pot reaction to give the desired ambifunctional monomer, **XXI**, directly.

The ambifunctional monomers shown in Table 3 are very reactive and undergo facile cationic polymerization to give highly crosslinked, insoluble network polymers. To obtain a more detailed profile of the reactivity of these novel monomers, several typical members of this series were subjected to photopolymerization and monitored by differential scanning photocalorimetry (DSP). In Fig. 5 is shown the DSP curves for the cationic photopolymerization of several of these monomers. The curves were obtained in air under isothermal conditions at 30°C. Photoinitiation of the polymerizations was begun 0.5 minutes after the start of the run by the automatic opening of a shutter and exposure of the sample to UV irradiation.

Excellent reactivity as determined by the response and sharpness of the DSP curves was displayed for each of the monomers. The polymerizations are substantially complete 30 seconds after irradiation commences. Differences in the size of the exothermic peak are related to the molecular mass of the monomer, and this is confirmed by calculation of the heats of polymerization which are all similar and range from 120 to 150 kJ/mol. It may be noted that all the DSP traces are monomodal. This suggests that despite the observed dissimilar reactivity of the two different epoxy groups in these molecules in their respective cationic homopolymerizations [12], the two functional groups undergo extensive copolymerization under these conditions. Photoinitiated cationic copolymerizations using model monofunctional epoxide monomers confirm this conclusion.

Synthesis of Epoxy Functional Telomers

The observation that the hydrosilation of multifunctional Si—H-containing compounds proceeds in a stepwise fashion suggested that it might be possible to use this reaction for the preparation of a new class of well-defined telechelic epoxy-functional oligomers. The literature contains only a few examples of such materials [17, 18]. It has been found that such telomers can be prepared directly by a convenient, two-step synthesis according to Scheme 4 [19].

The first step again involves the regioselective addition of the vinyl epoxide at only one of the two Si—H groups of an α,ω-Si—H difunctional disiloxane to give the monoadduct. In the second step of this scheme, the monoadduct is further condensed with diolefins in a subsequent hydrosilation reaction generating the desired diepoxy-terminated oligomer. As shown in Table 4, this general scheme has been applied to three diolefins; 1,5-hexadiene, 1,7-octadiene, and diallyl ether. Figure 6 shows the ^{1}H-NMR spectrum of **XXXI** which is typical of this class of novel difunctional epoxy-terminated oligomers.

A related series of tri- and tetrafunctional epoxy telechelic oligomers was prepared by the reaction of α-hydrogen-ω-epoxyfunctional siloxanes with tetravinyl-silane and the triolefin, 1,2,4-trivinylcyclohexane, according to Eq. (23, seen on page 1017). Table 5 gives the structures of these tri- and tetrafunctional epoxy
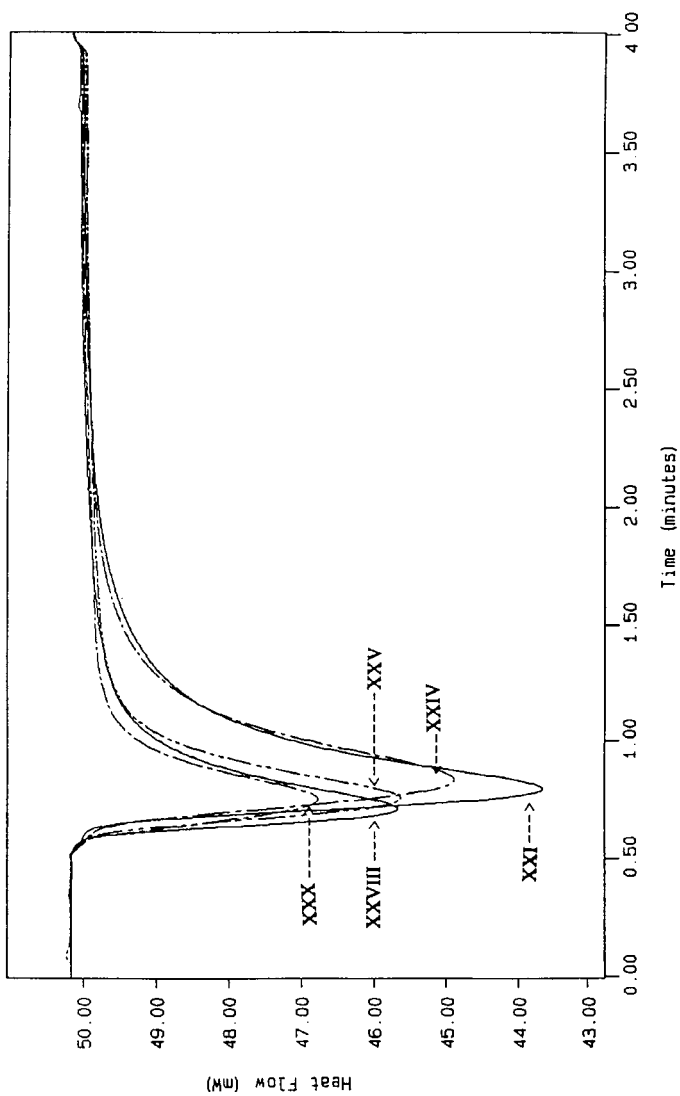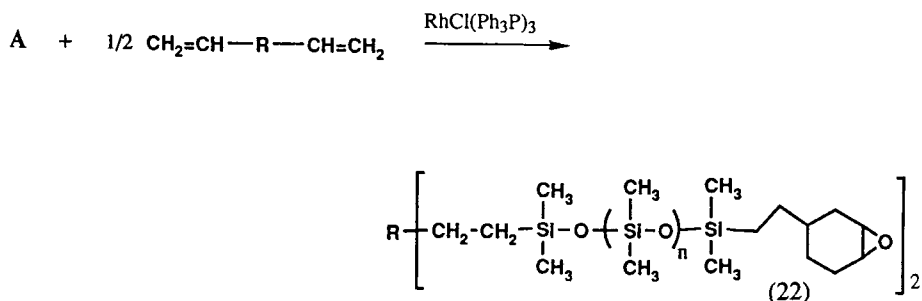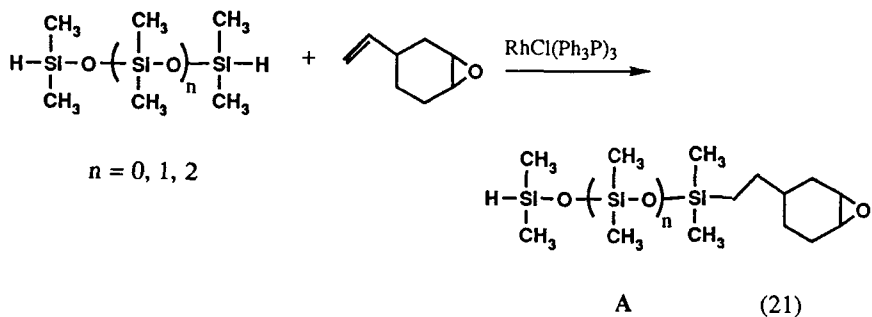
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FIG. 5.   DSP study of the cationic photopolymerization of various ambifunctional epoxy monomers at 30°C using 0.5 mol% (4-octyloxy-phenyl)phenyliodonium hexafluoroantimonate.

$$n = 0, 1, 2$$

A (21)

$$A + 1/2 \ CH_2=CH-R-CH=CH_2 \xrightarrow{RhCl(Ph_3P)_3}$$

(22)

SCHEME 4.

telomers. The epoxy functional telomers were all prepared in high yields and were characterized by means of their NMR spectra and their elemental analyses. A study of the cationic polymerization of these epoxy functional telomers showed that they all possessed similar reactivity irrespective of structure and chain length. This is illustrated in Fig. 7 which shows a DSP comparison of the exothermic curves for several difunctional epoxy telomers given in Table 4.
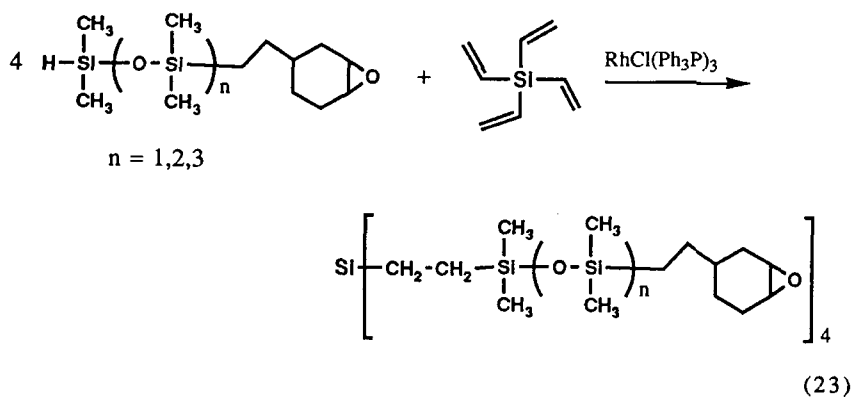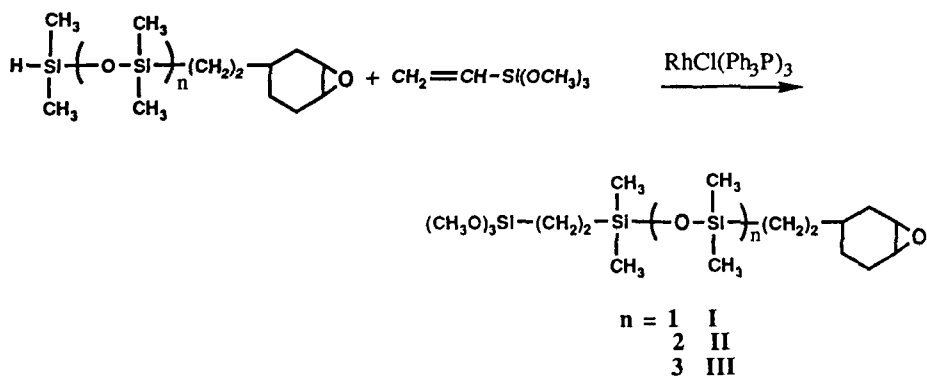

$$n = 1,2,3$$

(23)

TABLE 4. The Preparation of Oligomeric Silicon-Containing Epoxides

Structure	Notation	Yield (%)	Elemental Analysis		
				%C	%H
(CH₂)₆ [—Si(CH₃)—O—Si(CH₃)—CH₂—cyclohexene oxide]₂	XXXI	99.5	calc: fnd:	60.26 60.42	10.45 10.28
(CH₂)₈ [—Si(CH₃)—O—Si(CH₃)—CH₂—cyclohexene oxide]₂	XXXII	97	calc: fnd:	61.34 61.22	10.45 10.41
O [—(CH₂)₃—Si(CH₃)—O—Si(CH₃)—CH₂—cyclohexene oxide]₂	XXXIII	99	calc: fnd:	61.26 60.78	10.63 10.63
(CH₂)₆ [—(Si(CH₃)—O)₂—Si(CH₃)—CH₂—cyclohexene oxide]₂	XXXIV	80	calc: fnd:	54.69 54.29	10.45 10.34
(CH₂)₈ [—(Si(CH₃)—O)₂—Si(CH₃)—CH₂—cyclohexene oxide]₂	XXXV	89	calc: fnd:	60.26 60.57	10.45 10.63
O [—(CH₂)₃—(Si(CH₃)—O)₂—Si(CH₃)—CH₂—cyclohexene oxide]₂	XXXVI	88	calc: fnd:	53.51 53.10	9.78 9.81
(CH₂)₆ [—(Si(CH₃)—O)₃—Si(CH₃)—CH₂—cyclohexene oxide]₂	XXXVII	92	calc: fnd:	51.01 51.47	9.62 9.77
(CH₂)₈ [—(Si(CH₃)—O)₃—Si(CH₃)—CH₂—cyclohexene oxide]₂	XXXVIII	90	calc: fnd:	52.06 52.29	9.76 9.75

$$H-Si(CH_3)_2(O-Si(CH_3)_2)_n(CH_2)_2\text{-cyclohexene oxide} + CH_2=CH-Si(OCH_3)_3 \xrightarrow{RhCl(Ph_3P)_3}$$

$$(CH_3O)_3Si-(CH_2)_2-Si(CH_3)_2(O-Si(CH_3)_2)_n(CH_2)_2\text{-cyclohexene oxide}$$
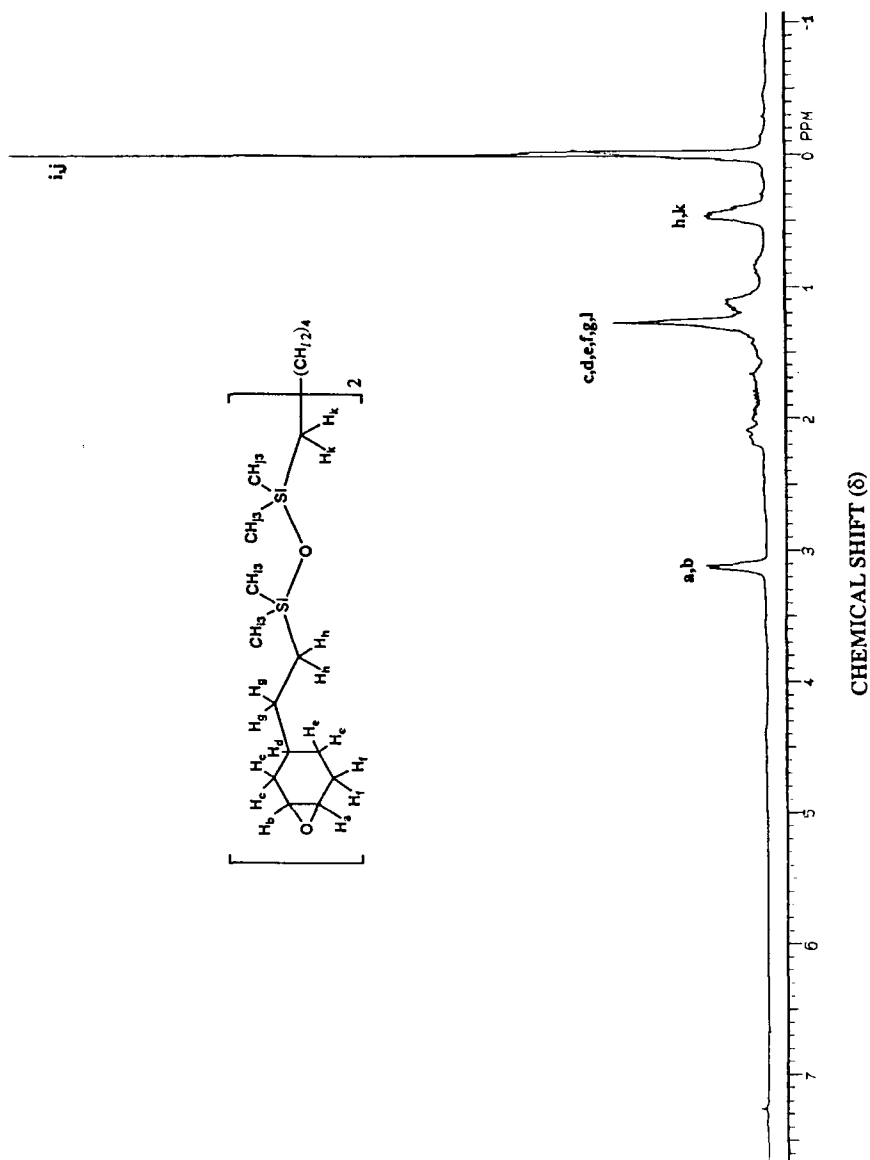
n = 1 I
    2 II
    3 III

(24)

FIG. 6. ^{1}H-NMR spectrum of difunctional epoxy-terminated oligomer **XXXI** in CDCl$_3$.

TABLE 5.   The Preparation of Epoxy Functional Telomers

Structure	Nota-tion	Yield (%)	Elemental Analysis %C	%H
(structure XXXIX)	XXXIX	86	calc: 61.46 fnd: 61.05	10.34 10.49
(structure XXXX)	XXXX	95	calc: 57.47 fnd: 56.92	9.99 9.64
(structure XXXXI)	XXXXI	90	calc: 51.61 fnd: 50.09	9.78 9.47
(structure XXXXII)	XXXXII	92	calc: 48.33 fnd: 47.82	9.50 9.24

α-Epoxy-ω-trialkoxysilanes and Siloxanes

Regioselective hydrosilation can be used to introduce two very chemically dissimilar groups into the same molecule. For example, we have employed three different methods for the synthesis of α-epoxy-ω-trimethoxysilanes. The first method used and illustrated by Eq. (24) (see page 1018) involves the hydrosilation of α-hydrogen-ω-epoxysiloxanes with vinyltrialkoxysilanes. Starting with an α-hydrogen-ω-epoxysilane or siloxane prepared by the regioselective monohydrosilation of a di-Si—H-functional siloxane with a vinyl epoxide, the remaining Si—H group was condensed with vinyl trimethoxysilane. The reaction proceeds rapidly at temperatures above 80°C to give very good yields of the desired pure α-epoxy-ω-trimethoxysilanes. Employing a variety of different α-hydrogen-ω-epoxysilanes and siloxanes, a number of structurally diverse representative examples of these novel
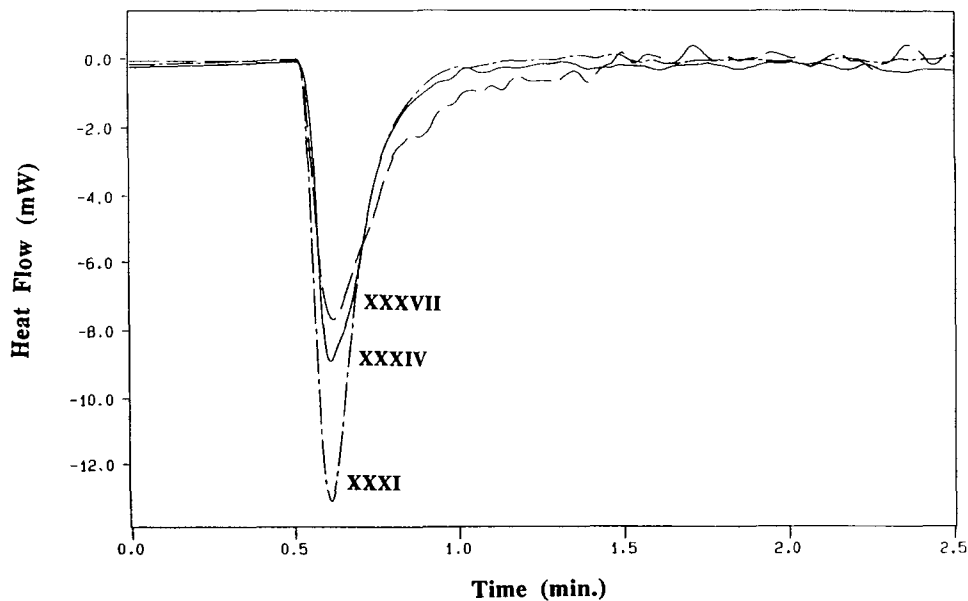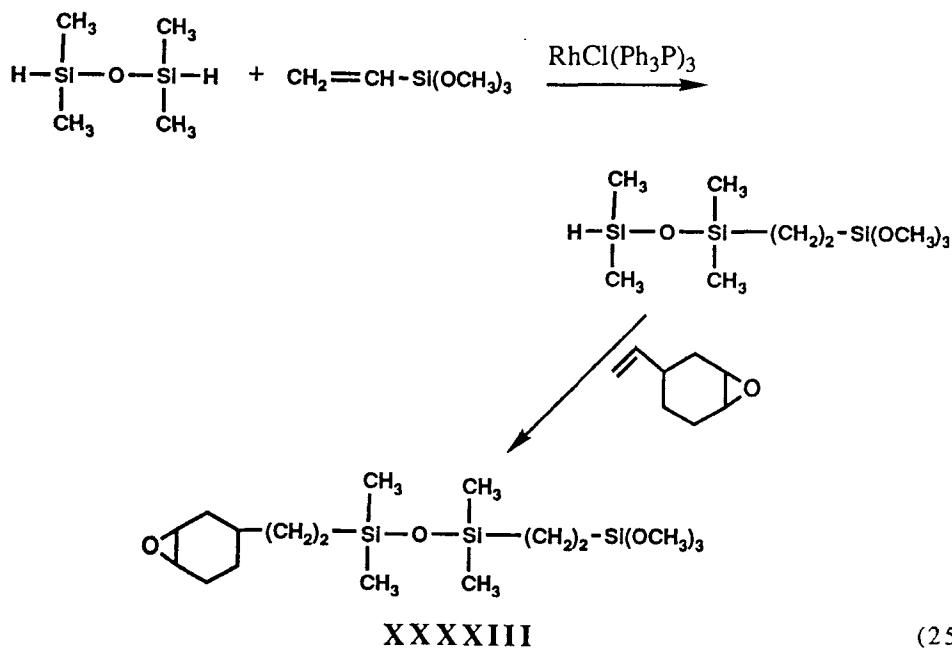
FIG. 7.   DSP study of the cationic photopolymerization of oligomers **XXXIV** (− −), **XXXVII** (− ·), and **XXXI** (− -) at 30°C using 0.5 mol% (4-octyloxyphenyl)phenyliodonium hexafluoroantimonate.

XXXXIII   (25)

compounds were prepared using this same synthetic approach and are shown in Table 6. Both α- and β-hydrosilation take place at the double bond of vinyltrimethoxysilanes. For the sake of simplicity, only the majority β-isomers are shown in Table 6.

In addition to the above synthetic method, the preparation of α-hydrogen-ω-epoxy siloxanes by the inverted route shown in Eq. (25) (see page 1021) has also been explored.

Vinyltrimethoxysilane and 1,1,3,3-tetramethyldisiloxane readily undergo regioselective hydrosilation to give the monoadduct 1-(trimethoxysilyl-2-ethyl)-1,1,3,3-tetramethyldisiloxane in 86% yield. The corresponding diadduct was isolated in approximately 10% yield. Further hydrosilation of the monoadduct with 3-vinyl-7-oxabicyclo[4.1.0]heptane gave **XXXXIII** (only the β-isomer is shown) in excellent yield. (See also Fig. 8).

When mixtures of the α-epoxy-ω-trimethoxysiloxanes (shown in Table 6) were combined with 0.5 mol% of (4-octyloxyphenyl)phenyliodonium hexafluoroantimonate and then exposed as 1 mil films to a 200-W medium pressure mercury arc lamp, they underwent rapid photoinduced polymerization to give hard, transparent, colorless, crosslinked polymers. The polymerized monomers showed no solubility and little tendency to swell in the presence of any common solvents. Accordingly, the simultaneous acid-catalyzed ring-opening polymerization of the epoxycyclo-

TABLE 6. α-Epoxy-ω-Trimethoxysiloxanes

| Structure	Notation	Yield (%)	Elemental Analysis	
			%C	%H
$(CH_3O)_3Si$—...—Si—O—Si—...—epoxycyclohexyl	XXXXIII	82	calc: 50.25 fnd: 50.28	9.36 9.37
$(CH_3O)_3Si$—...—Si—(O—Si)$_2$—...—epoxycyclohexyl	XXXXIV	92	calc: 47.50 fnd: 47.90	9.17 9.05
$(CH_3O)_3Si$—...—Si—(O—Si)$_3$—...—epoxycyclohexyl	XXXXV	98	calc: 45.49 fnd: 45.57	9.04 8.90
$(CH_3O)_3Si$—...—Si—O—Si—...—epoxycyclohexyl	XXXXVI	80	calc: 47.37 fnd: 47.57	9.47 9.39
$(CH_3O)_3Si$—...—Si—O—Si—...—epoxide	XXXXVII	89	calc: 50.00 fnd: 49.90	9.80 9.71
$(CH_3O)_3Si$—...—Si—O—Si—...—diepoxide	XXXXVIII	84	calc: 45.45 fnd: 45.17	9.00 9.11
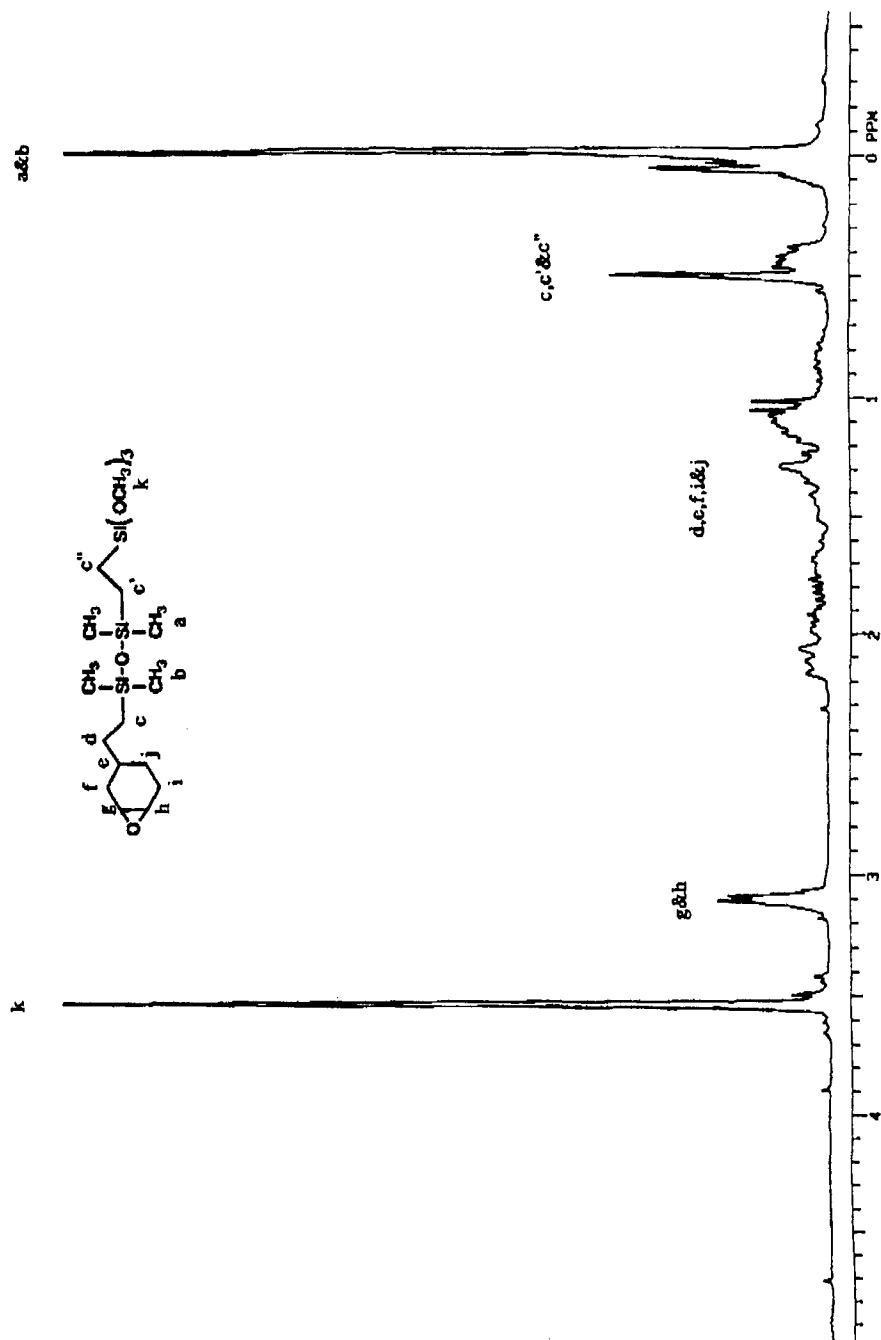
FIG. 8. ^{1}H-NMR spectrum of Compound **XXXXIII** in CDCl$_3$.

hexyl groups as well as condensation polymerization of the alkoxysilane groups are proposed as depicted in Eq. (26).


$$+\quad 3\ CH_3OH \tag{26}$$
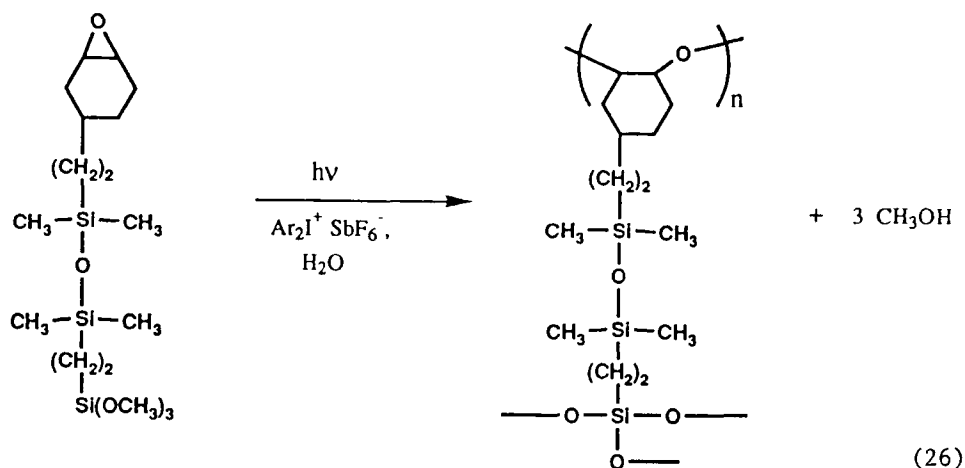
Of course, the reaction depicted in Eq. (26) is idealized, and it is recognized that the condensation of the trimethoxysilyl groups may not proceed to completion under these conditions. However, the thin films of the monomers do undergo sufficiently rapid equilibration with atmospheric moisture under the irradiation conditions used so that crosslinked films insoluble in all organic solvents are obtained. Furthermore, infrared spectra of the monomers taken before and after UV irradiation show that the infrared bands at $1340\ cm^{-1}$ (methoxy methyl groups attached to silicon) and $700\text{–}850\ cm^{-1}$ (Si—O—C) decrease. In addition, new bands at 3000 and $1220\ cm^{-1}$ assigned respectively to the Si—OH and Si—O—Si groups are formed after irradiation. These results provide further evidence for the proposed photoassisted acid-catalyzed hydrolysis and condensation of the trialkoxysilane groups in these monomers. An in-depth study of the structure–polymerization reactivity relationships of the compounds shown in Table 6 will be reported in a subsequent publication [20].

Mechanistic Studies

By employing a considerable, though incomplete, understanding of the mechanisms of hydrosilation and ring-opening polymerization, it has been possible to develop chemoselective transition metal catalysts. These homogeneous catalysts permit the exclusive hydrosilation of vinyl-containing epoxy compounds without inducing the cationic ring-opening polymerization of the epoxy groups. In contrast, the exact nature of the mechanism of the regioselective hydrosilation is only poorly understood at this time. Fortunately, this has not impeded the use of these versatile reactions which have resulted in the synthesis of several novel series of ambifunctional monomers and oligomers as has been described in this communication.

While this work was in progress, a similar report of the monohydrosilation of a difunction Si—H compound appeared in the literature. Itoh and coworkers [21]

reported that 1,2-bis(dimethylsilyl)ethane, shown in Eq. (27), undergoes anomalously rapid, RhCl(Ph₃P)₃-catalyzed hydrosilation with ketones, olefins, and acetylenes to form monoaddition products regioselectively.

(27)
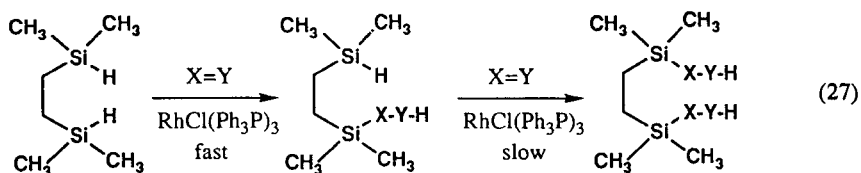
Where X=Y is a ketone, olefin or acetylene

Further reaction to generate the difunctional adducts proceeds at a much slower rate. The selectivity which these authors observed was ascribed to an enhanced reactivity of the first of the two Si—H groups due to the ability of 1,2-bis(dimethylsilyl)ethane to act as a bidentate ligand to a rhodium(V) metal center. In support of this argument, they reported a strong correlation of the regioselectivity with the number of methylene groups inserted between the two Si—H groups. When four methylene groups were present, the reactivity of both Si—H groups was identical and similar to that of monofunctional Si—H compounds, such as EtMe₂SiH, and no regioselectivity was observed.

The excellent selectivity for monosubstitution which we observed for the series of α,ω-Si—H functional substrates [1,1,3,3-tetramethyldisiloxane (TMDS), 1,1,3,3,5,5-hexamethyltrisiloxane (HMTS), and 1,1,3,3,5,5,7,7-octamethyltetrasiloxane (OMTS)] are not well explained by simply invoking a cooperative interaction of the two Si—H functional groups through bidentate ligation to the same rhodium metal center. This would require rhodium complexes containing ligands with four-, six-, and eight-membered rings, respectively. In this series the ring strain should be greatest with the four-membered ring and decrease as the ring size increases. On this basis it is difficult to rationalize the observation that a high level of regioselectivity should result for each of the cyclic rhodium complexes independent of the ring size of the ligand. Further, this proposed mechanism cannot explain the highly regioselective hydrosilation of either 1,4-bis(dimethylsilyl)benzene or 4,4′-bis-(dimethylsilyl)diphenyl ether since neither compound would appear capable of bidentate coordination to the same rhodium metal center.

It would appear that another mechanism must be invoked to explain our observations. We considered the possibility that some electronic interaction may exist between the first and last silicon atoms in the siloxane chain even over a considerable number of silicon—oxygen bonds. This interaction could lead to a considerable difference in the reactivity of the second Si—H group once the first

one has undergone hydrosilation. To investigate the possibility of this interaction we have employed ^{29}Si-NMR spectroscopy. Very large ^{29}Si chemical shifts in the NMR are normally observed in response to rather small changes in the electronic environment about silicon atoms. Thus, ^{29}Si NMR can serve as a sensitive probe in our attempt to understand the effects of one silicon atom on another in a siloxane chain. Table 7 gives the results of such a study in which three α-hydrogen-ω-epoxy functional siloxane compounds are compared with themselves and with their α,ω-dihydrogen functional siloxane precursors. It is particularly interesting to note the chemical shift (δ) values for the silicon atoms bearing the Si—H groups (Si$_1$ atoms) in this series of compounds. As expected, the Si$_1$ chemical shift for tetramethyldisiloxane ($\delta = -4.05$) is different than for all the other chemical shifts for the other compounds in this series since the Si$_1$ silicon atoms are bound to each other through an oxygen atom rather than through a chain of dimethylsiloxy groups. However, the δ values for the Si$_1$ silicon in the other compounds shown in Table 7 are very

TABLE 7. ^{29}Si NMR Spectral Assignments for Various Silicon-Hydrogen Functional Compounds

Compound	^{29}Si δ (ppm, CDCl$_3$)			
	Si$_1$	Si$_2$	Si$_3$	Si$_4$
	-4.05			
	-6.41	10.49		
	-6.38	-17.64		
	-6.73	-19.27	8.28	
	-6.45	-19.47		
	-6.56	-19.79	-21.14	8.19

nearly the same ($\delta = -6.4$ to -6.7 ppm), indicating that their electronic environments are also nearly identical. The values are remarkably similar for both the α,ω-dihydrogen functional siloxanes as well as for the α-hydrogen-ω-epoxy functional siloxanes irrespective of the chain length. Based on these results, one must rule out the possibility of electronic interactions between the first and last silicon atoms in a siloxane chain to account for the differences in reactivity of the two Si—H groups. Likewise, it is difficult to invoke steric considerations to explain the results obtained since in the cases of TMDS, HMTS, and OMTS the steric requirements for reaction at both sites should be identical. The possibility of a heterogeneous reaction at a solid catalytic surface was also considered. However, as mentioned previously, it is generally believed that the hydrosilation reactions involving RhCl(Ph$_3$P)$_3$ proceed by homogeneous catalysis rather than by colloidal rhodium species observed in other transition-metal-catalyzed hydrosilation reactions [4].

Clearly, the ability to isolate and characterize the monoadducts is due to the demonstrated large difference in the rates of reaction resulting from a corresponding difference between the activation energies of the hydrosilation of the first Si—H bond and the second. Using the rate data extracted from the slopes of the time versus conversion curves at various temperatures, such as is shown in Fig. 2, the activation energies for the hydrosilation at the two sites in TMDS can be estimated. For the reaction at the first Si—H group, an activation energy, E_a(I), of approximately 26 kcal/mol was calculated, while the corresponding activation energy for hydrosilation at the second Si—H site, E_a(II), was found to be approximately 58 kcal/mol. A more than twofold difference in the activation energy between the reactivities of the first and second Si—H groups explains our observation that monoadducts such as **XI** are readily isolable in high yields provided that the temperature is kept low and the reaction times relatively short.

A study of the comparison of the rates of monohydrosilation of various vinyl epoxide substrates using 1,1,3,3-tetramethyldisiloxane showed that there is little difference in their rates irrespective of the type of olefin employed. This implies that the difference in the rates of mono- versus dihydrosilation which lead to the observed regioselectivity is controlled primarily by an interaction of the disilane and the rhodium complex. At the same time, the rate of regioselective monohydrosilation of 3-viny-7-oxabicyclo[4.1.0]heptane is fastest for OMTS and slower and nearly the same for both HMTS and TMDS.

At present, a detailed understanding of the mechanism of the regioselective hydrosilation is not in hand. Further investigations in this laboratory continue with the object of shedding more light on this subject.

CONCLUSIONS

The discovery that the hydrosilation of di- and multifunctional Si—H compounds with olefins takes place in a discrete, stepwise fashion has led to the development of novel synthetic methods for the preparation of ambifunctional monomers bearing differentiated functionality at both ends of the molecule. A key factor in this discovery was the observation that the catalyst, RhCl(Ph$_3$P)$_3$, effectively suppresses the competing epoxide ring-opening polymerization while permitting the formation of a high proportion of monohydrosilation to dihydrosilation. This has

led to the preparation of α-hydrogen-ω-functional silane and siloxane compounds in high yield which cannot only serve as interesting monomers in their own right but also as intermediates for the introduction of other functional groups by subsequent hydrosilation reactions. Application of this chemistry has resulted in the preparation of interesting and novel classes of well-characterized ambifunctional monomers and oligomers. Further studies directed toward the preparation of still other new classes of novel silicon-containing monomers and oligomers are in progress.

ACKNOWLEDGMENTS

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