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Investigation of the transmission of substituent effects by ^{29}Si NMR

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Long range substituent effects on the ^{29}Si NMR chemical shifts in a series of alkylene- and arylene-bridged triethoxysilanes were observed over as many as 11 bonds. The hydrolysis reaction of an ethoxide caused the resonance of the silicon on the opposing end of the bridging unit to move downfield. The alkylene bridging units ranged from ethylene to octylene while the arylene bridging units included phenyl and biphenyl. Resonance assignments were confirmed by the absence of these shifts for the triethoxysilyl in 1-triphenylsilyl-2-triethoxysilylethane. The magnitude of the downfield shift decreased as the length of the bridging unit between silicon atoms increased. Transmission of the substituent effect along a polymethylene chain was successfully modeled by a through-bond mechanism with an attenuation factor of 1.88 for each methylene unit.

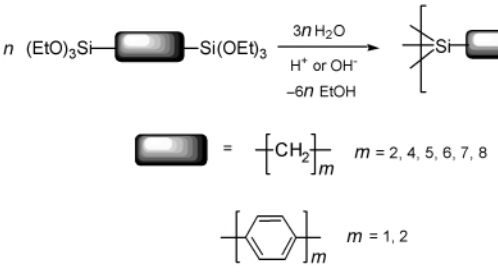
Introduction

The transmission of polar substituent effects within a molecule has been widely used to test our understanding of the relationship between a molecule's structure and properties.[1] Accurate measurements of transmission properties in a variety of environments are necessary in order to provide an incisive test of proposed transmission models. Most of these measurements have been made on purely organic systems using reactivity probes such as equilibria ionization or physical property probes such as ^{13}C and ^{19}F NMR chemical shifts. In this paper we present a new probe, the ^{29}Si NMR chemical shift, to explore the transmission of substituent effects in a series of hybrid organic/inorganic molecules.

Alkoxysilanes and substituted alkoxysilanes are the building blocks used in the sol–gel preparation of network siloxanes such as silica, silasesquioxane, and hybrid organic–siloxane gels.[2] Solution ^{29}Si NMR spectroscopy has been utilized extensively to examine the reaction kinetics of these systems.[3] Because of the sensitivity of the ^{29}Si nuclei to their chemical environment, key details of the early structural evolution of the network polymer can be obtained by examining the populations of the hydrolysis and condensation products and the manner and rate by which they change. Relatively small changes to the substituents attached to the silicon atoms in the monomer are translated into significant changes in the chemical shifts measured in the NMR experiment. Hydrolysis of an ethoxide group to a hydroxide attached to a silicon in sol–gel monomers is accompanied by the appearance of a new resonance shifted downfield from that of the precursor by $\Delta\delta = 2$–3 ppm. When these silanols react with each other or another alkoxysilane to give a siloxane bond (Si–O–Si), an even greater shift upfield of the original monomer by $\Delta\delta = 7$–9 ppm is observed.[4]

As most sol–gel polymerizations involve monomers with three or more alkoxide substituents attached to a single silicon atom, these short-range substituent effects rapidly translate into complex ^{29}Si NMR spectra. The structural and steric effects of substituents on the chemical shifts of silicon have been the subjects of an extensive body of work by Schraml.[5] Recently it has been shown that the chemical shift of a silicon nucleus in sol–gel systems is sensitive to longer range substituent effects such as the nature of the hydrocarbon (Me, Et, Pr, Ph) in the alkoxide and the nature and stereochemistry of substituents on the silicon attached to the nuclei of interest through a siloxane bond. This sensitivity has been employed to examine the molecular level connectivity in sol–gel co-polymers of monomers with different numbers of alkoxide and organic substituents.[6] However, this substituent effect, formally through as many as 4 or 5 bonds, does not compare with the long range F–C, F–H, and C–P substituent effects that have been studied in other organic systems. In this paper, we describe the discovery of a long range ^{29}Si substituent effect in alkylene and arylene-bridged triethoxysilanes that can be observed over as many as 11 bonds.

We have observed the changes in ^{29}Si chemical shifts in the alkylene and arylene bridged silasesquioxanes shown in Scheme 1,[7] where *m* varied from 1 to 8. The spectrum of each monomer exhibits a single resonance for the 2 identical silicons. The substituents were generated *in situ* by the acid-catalyzed hydrolysis of the triethoxysilanes with a limited amount of water. The hydrolysis of one or more ethoxide groups resulted in an observable change in the chemical shift of the silicon on the *opposite end* of the chain. The change could be measured for silicons that were 11 bonds removed from the site of the substitution. The relationship between the transmission factor and chain length were successfully described by a through-bond model with an attenuation factor similar to that reported earlier for purely organic materials.[8]



Scheme 1

Experimental

Solutions were prepared by the acid-catalyzed hydrolysis of silasesquioxane monomer (1 M) in anhydrous ethanol. An

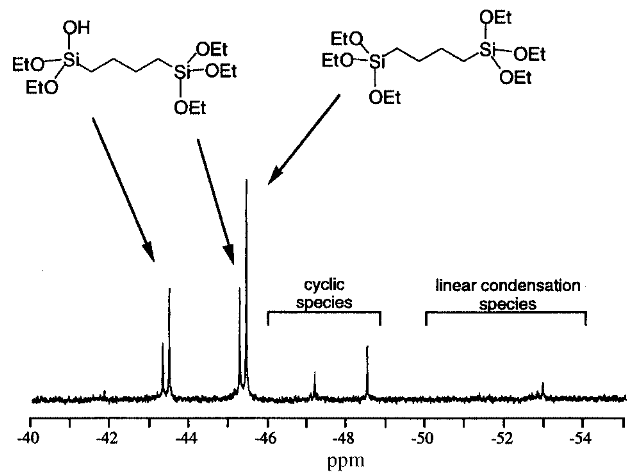


Fig. 1 ^{29}Si NMR spectrum of the butylene-bridged triethoxysilane after reacting for 10 min.

appropriate amount of 1 M HCl and H_2O were added to provide a nominal pH of 1.9 and an H_2O : Si molar ratio (R) of 0.38. The syntheses of the monomers have been reported previously.[9] All solutions were prepared at room temperature unless otherwise indicated.

The ^{29}Si NMR spectra were acquired at 79.5 MHz on a Bruker AMX-400 spectrometer with a 5 mm broadband probe. Chromium acetylacetonate, 5 mM, was added to shorten the spin-lattice relaxation time. All spectra were acquired using single-pulse excitation with inverse-gated decoupling to suppress the NOE. Spectra were acquired beginning 10 min after preparation and thereafter recorded as a function of time. The spectral linewidths were typically 0.5 Hz, equivalent to 0.006 ppm. All chemical shifts were internally referenced to tetramethylsilane.

Results and discussion

The ^{29}Si NMR spectrum of the butylene-bridged silasesquioxane monomer consists of a single resonance at −45.4 ppm. The spectrum of butylene-bridged silasesquioxane acquired 10 min after addition of 1 M aqueous HCl is shown in Fig. 1. There are several features, which must be interpreted. The group of small resonances near −53 ppm appears 7 to 8 ppm upfield from the monomer. This shift is typical of silicon, which has undergone a single condensation reaction.

The silicons on each end of the bridge can condense with each other to form a cyclic structure with strained bond angles. Previous studies have shown that bond angle strain causes the silicon resonance to be shifted downfield. For example, the six membered ring formed by the condensation reactions of tetraethoxysilane is shifted 7 ppm downfield while the eight membered ring is shifted 1 ppm downfield from the corresponding linear condensation products.[10] The resonance at −48.5 ppm which is shifted 4.5 ppm downfield from the acyclic products is assigned to the seven membered cyclic species, which can be isolated and characterized.[11] The resonance at −47.1 ppm is assigned to the first hydrolysis product of the cyclic species.

The first hydrolysis product of a tetraethoxysilane usually exhibits a *single* resonance approximately 2 ppm downfield from the monomer. Fig. 1 shows that the butylene-bridged monomer has a pair of resonances in this region. In addition, we observe a resonance shifted only 0.2 ppm downfield from the resonance of the unreacted monomer. We believe that the splitting of both the monomer resonance and the first hydrolysis product is due to the influence that a substituent has on a silicon on the opposite end of the bridge. The observed monomeric species and their associated chemical shifts are (a), (b) and (c), as shown.

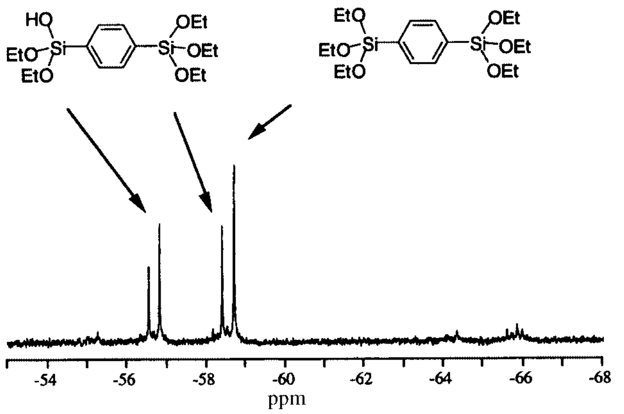
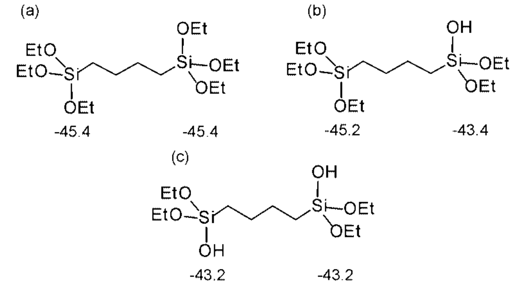


Fig. 2 ^{29}Si NMR spectrum of the phenylene-bridged triethoxysilane after reacting for 10 min.



The shifts observed for product (b) are unique to that molecule and this means that if our interpretation is correct then the intensities of these two resonances should always be equal to each other. This equality relationship is observed throughout the reaction process. The exchange of the carbon atom in an ethoxide group for a hydrogen atom in an alcohol causes a downfield shift of 0.2 ppm in the silicon, which is 7 bonds removed from the substitution site.

Fig. 2 shows the spectrum for the corresponding experiment using the phenyl-bridged monomer. The rigidity of the bridging unit prevents the formation of cyclic species, so only linear condensed species and their first hydrolysis products are observed in the upfield region. Again the spectral regions of both the monomer and the first hydrolysis products consist of two resonances. The intensities of the resonances at −56.8 and −58.4 track each other throughout the reaction and are assigned to the singly hydrolyzed monomer, (b), in the above scheme. The chemical shift of the silicon has reflected changes occurring at a site removed by 7 bonds.

To confirm our interpretation we synthesized a bridged monomer in which only one of the silicons could undergo hydrolysis. In this instance we expect that the spectrum of the silicon being hydrolyzed would exhibit the usual simple hydrolysis pattern, while the silicon on the opposite end of the bridge would only be affected by the long-range substituent. Fig. 3 shows the spectra of 1-triphenylsilyl-2-triethoxysilylethane before and after reaction. Before hydrolysis, the triphenylsilyl and triethoxysilyl resonate at −9.30 and −45.77 ppm, respectively. After hydrolysis, the triethoxysilyl silicon exhibits a simple hydrolysis pattern in which each successive hydrolysis causes a downfield shift of approximately 2 ppm. The triphenylsilyl silicon cannot undergo hydrolysis but is split into components at −9.30, −9.23 and −9.18 ppm, which reflect the effect of substitution of the silicon on the opposite end of the bridge. Although the resonances are overlapped, the intensities of these three peaks correspond qualitatively with the intensities of the triethoxysilyl silicons, which have undergone 0, 1 and 2 hydrolysis reactions.

The previous experiments were conducted with a limited amount of water so that each silicon underwent a maximum

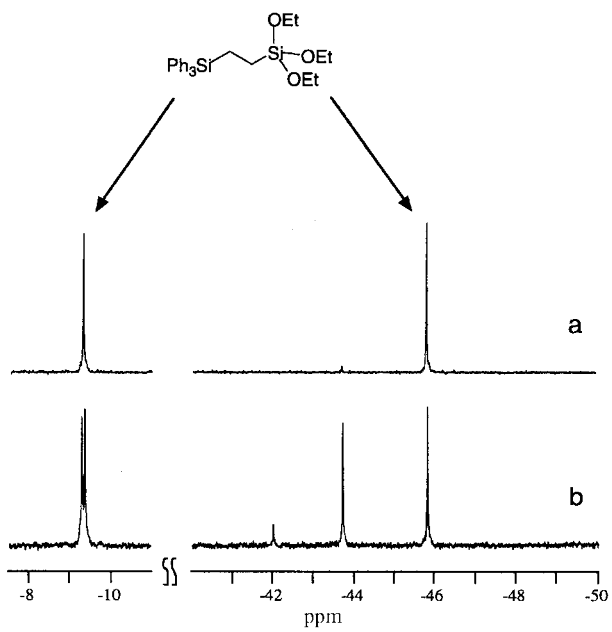


Fig. 3 ^{29}Si NMR spectra of 1-triphenylsilyl-2-triethoxysilylethane after reacting for 10 min.

Si_Y / Si_X	T_0	T_1	T_2	T_3
T_0	**T_0T_0 (m)**	**T_0T_1 (a, b)**	**T_0T_2 (d, e)**	T_0T_3
T_1	**T_1T_0 (b, a)**	**T_1T_1 (c, c)**	**T_1T_2 (f, g)**	T_1T_3
T_2	**T_2T_0 (e, d)**	**T_2T_1 (g, f)**	T_2T_2	T_2T_3
T_3	T_3T_0	T_3T_1	T_3T_2	T_3T_3

Fig. 4 Matricx showing all possible hydrolysis species expected for complete hydrolysis of Si$_X$ and Si$_Y$. The spectral assignments are shown in parentheses. The **m** refers to the unreacted monomer peak.

of 2 hydrolysis steps. Fig. 4 shows all possible monomeric species when the water content is increased and each silicon can undergo the full range, 0, 1, 2, and 3, of hydrolysis reactions. The nomenclature has been previously described by Engelhardt where "T" is used to represent a silicon that is bonded to three oxygens.[11] The subscript refers to the number of directly attached –OH groups. A superscript can be used to denote the number of bonds to other silicons by an oxygen bridge but since we are only considering monomeric species, the superscript is left out for simplicity. The parenthetic expressions refer to the spectral assignment (*vide infra*).

The diagonal species (T_0T_0, T_1T_1, ...) give rise to a single resonance in each hydrolysis region. Off-diagonal species produce two resonances. For example, the T_1T_1 species exhibits a single resonance while T_2T_1 has a resonance in both the T_2 and T_1 regions. These two resonances exhibit equal intensities for all reaction conditions and times. A total of 10 species is possible, resulting in 16 resonances (four in each hydrolysis region). We were only able to observe the 5 species (8 resonances) in bold print, however, for the reaction conditions that we investigated.

Fig. 5 shows the ^{29}Si NMR spectrum of the butylene-bridged triethoxysilane reacted with $R = 0.5$ at 263 K. The water content was increased to produce a larger number of the hydrolysis species depicted in Fig. 4. The reaction was carried out at 263 K in order to slow the hydrolysis rate so that spectra could be accumulated before significant condensation took place. The ^{29}Si NMR spectrum of the butylene-bridged triethoxysilane, acquired approximately 10 min after preparation, shows a single peak for the unreacted monomer and eight peaks due to partially hydrolyzed species. The key to silicons in the various species (**a**, **b**, ...) is given in Fig. 4 and the assignments are illustrated in Fig. 5. Peaks **a** and **b** are due to species in which one of the Si atoms is unhydrolyzed (**a**) and the other one is monosubstituted (**b**). They are connected by a line in Fig. 5 to show that they are components of the same monomeric species. Peak **c** is due to species in which both Si atoms contain a single –OH group, and its intensity is independent of any other peak in the spectrum. Peaks **d** and **e** are due to species with an unhydrolyzed Si atom (**d**) and a disubstituted Si atom (**e**). Finally, peaks **f** and **g** are due to species in which both Si atoms are hydrolyzed. In this case, **f** is monosubstituted and **g** is disubstituted. These assignments are supported by appropriate integral relationships which hold throughout the time that the reaction mixture was observed.

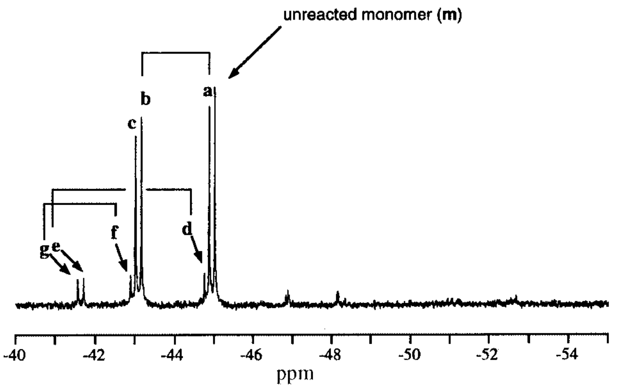


Fig. 5 ^{29}Si NMR spectrum of the butylene-bridged triethoxysilane after reacting for 10 min at 263 K and $R = 0.5$. The intensities of the peaks that are connected track each other throughout the reaction.

A simple statistical analysis can be used to show that the intensities of the resonances are reasonable. The analysis also demonstrates why only 5 out of the 10 possible species are observed. We expect that the probability of a silicon undergoing hydrolysis is independent of the hydrolysis state of the silicon on the opposite end of the butylene bridge. In addition, if we assume that the first, second and third hydrolysis reactions are equally probable, then we can estimate the distribution of species for an arbitrary concentration of silanol groups. Although this last assumption is not strictly true, it is a reasonable approximation for the purposes of this calculation.

Initially, each "T" silicon has 3 ethoxide groups that can undergo hydrolysis. The hydrolysis state of a single silicon is then represented by T_s where s is equal to the number of silanol groups and it is implicitly assumed that the silicon has not undergone a condensation reaction. If the probability of an ethoxide group being hydrolyzed is x, then the relative probabilities of the various T species, $P(T_s)$, can be calculated from the binomial distribution:

$$P(T_0)\text{: } 1(1 - x)^3$$
$$P(T_1)\text{: } 3(1 - x)^2x$$
$$P(T_2)\text{: } 3(1 - x)x^2$$
$$P(T_3)\text{: } 1x^3$$

The probability for a particular pair of silicons attached to a butylene bridge is then just the product of the probabilities for each silicon. For example, the probability for the T_1T_2 species is:

$$P(T_1T_2) = P(T_1)P(T_2) = 9(1 - x)^3x^3$$

Si$_X$ \ Si$_Y$	0	1	2	3
0	29.3 (24.6)	20.0 (21.0)	4.5 (3.1)	0.3 (—)
1	20.0 (22.3)	13.6 (19.2)	3.1 (2.7)	0.2 (—)
2	4.5 (3.6)	3.1 (3.6)	0.7 (—)	0.1 (—)
3	0.3 (—)	0.2 (—)	0.1 (—)	0.0 (—)

Fig. 6 Matrix showing the calculated distribution of hydrolysis species for a solution in which 18.5% of the ethoxide groups have been hydrolyzed. The degree of hydrolysis for each silicon ranges from 0 to 3. The values in parentheses were experimentally determined.

The relative intensities of all of the silicons in the -41 to -46 ppm region of the spectrum in Fig. 5 were measured. The overall probability for an ethoxide group to be hydrolyzed was calculated to be 0.185. The probabilities for each silicon pair were then calculated from the above equations and displayed in matrix form in Fig. 6. The upper numbers are the calculated probabilities, while the lower numbers in parentheses represent experimentally determined probabilities. This exercise supports two observations: first, it is not surprising that only eight resonances are seen for this set of reaction conditions. The predicted concentrations of the 8 least probable species are well under 1% of the total silicon concentration and their resonances would be hidden in the noise. Second, the experimental and calculated values for the observed species are in reasonable agreement. This agreement lends strong support to the argument that the fine structure in each region can be attributed to the state of hydrolysis of the silicon on the opposite end of the butylene bridge.

Finally, we wish to compare the difference between the chemical shift of the silicons in the starting monomer and the chemical shift of an unreacted silicon, **a**, attached by an alkylene or arylene bridge to a singly hydrolyzed silicon.

The chemical shift difference between the silicons in the starting monomer and silicon, **a,** in the butylene-bridged triethoxysilane is 0.17 ppm, while the difference between the corresponding silicons in the phenylene-bridged triethoxysilane is 0.30 ppm. These differences are a reflection of the effectiveness with which the substituent effect is transmitted for the various molecules.

Two models have been proposed to explain the transmission of polar substituent effects in saturated C–C bonded compounds. The "through bond" inductive model assumes that the polarization of the substituent is attenuated by an equivalent amount by each C–C bond. This model predicts that the logarithm of the chemical shift difference should be linearly dependent on the number of bridging C–C bonds. The "through space" model assumes that the electric dipole of the substituent directly affects the probe. Knowledge of the molecular geometries as well as the effective permittivities are required to test the predictions of this model.

Fig. 7 shows a semilog plot of the chemical shift difference as a function of the number of intervening bonds for both the alkylene- and phenylene-bridged series. Since the phenylene bridge provides multiple interaction pathways, it is not surprising that the shifts of this series are greater than those of the alkylene series for an equivalent number of intervening bonds. The propylene-bridged triethoxysilane undergoes rapid cyclization, so a measurement of its chemical shift difference could not be determined. Since only two phenylene-bridged compounds were available for study, the functional dependence of the chemical shift difference on the number of intervening bonds could not be determined for this bridging unit.

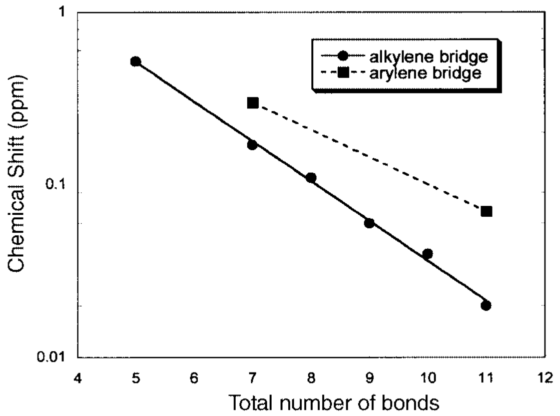


Fig. 7 Semilog plot of the chemical shift difference as a function of the number of bonds between the probe site and the substituent when the substituent undergoes the reaction from Si–O–$C\mathrm{H_2CH_3}$ to Si–O–H. The structures of the alkylene- and arylene-bridged triethoxysilanes are shown in Scheme 1.

The logarithmic behavior of the chemical shift difference for the alkylene-bridged series suggests that each additional methylene unit attenuates the substitutional effect by an equivalent amount. The attenuation factor, defined as the negative slope of the fitted line, is calculated to be 1.88. This result is in excellent agreement with a value of 1.78 obtained by Bianchi *et al.*[8] for the attenuation factor of the ^{13}C chemical shifts of the double-bond carbons in various compounds. The linearity of the logarithm of the chemical shift difference is consistent with the simple "through-bond" mechanism. A test of the "through-space" model requires calculations that are beyond the scope of this study. We anticipate that the range of bridging chemistries, pathlengths and geometries that are available with bridged silicon compounds will stimulate additional research in this area.

Conclusions

We have shown that the chemical shift of silicon is sensitive to the extent of hydrolysis of the silicon at the opposite end of the chain in alkylene- and arylene-bridged triethoxysilanes. Each hydrolysis reaction causes a downfield shift that decreases in magnitude as the length of the bridging unit between the silicon atoms increases. The transmission of the substituent effect between silicons bridged by a polymethylene chain was successfully modeled by a through-bond mechanism with an attenuation factor of 1.88.

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