

Study of Anionic and Nonionic Silicone Lattices by ^{29}Si NMR Spectroscopy

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SYNOPSIS

The curing of silicone lattices has been studied using ^{29}Si NMR spectroscopy. It has been found that cross-linking occurs prior to removal of the water. Stabilizers prevent gelation by slowing down the rate of condensation, particularly of higher functionality cross-linkers.

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INTRODUCTION

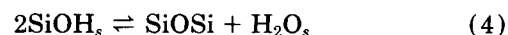
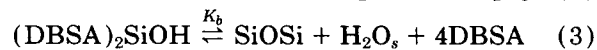
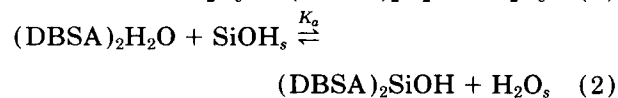
Nonreactive silicone emulsions containing trimethylsiloxy-terminated siloxanes are often used as coating release agents and as antifoams in the cosmetic, paint, and pharmaceutical industries. Reactive emulsions containing either hydroxyl or hydrolyzable end-stopped silicones are used primarily as coatings for fibers and as foams and elastomers. Nonreactive emulsions are prepared by emulsifying preformed methyl-terminated silicone oils with nonionic surfactants. Reactive emulsions can be prepared similarly employing hydroxyl-terminated siloxanes. This method, however, is limited to silicones of relatively low molecular weight. High-molecular weight reactive emulsions are best prepared by an anionic or cationic polymerization method.

Hyde¹ reported the first emulsion polymerization of silicones $\text{R}_n\text{SiO}_{4-n/2}$ where R = alkyl is polymerized in water with strong mineral acids such as hydrochloric acid or strong alkaline catalysts such as sodium hydroxide or ammonium hydroxide. The dispersant can be of the cationic, anionic, or nonionic type. The emulsion is rendered neutral to stop the polymerization. The emulsions are claimed to have extreme stability and small particle size.

In the early 1960s, Weyenberg and Findlay² studied the emulsion polymerization of siloxanes

using surface-active catalysts. Siloxanes of the formula $\text{R}_n\text{SiO}_{4n/2}$ are polymerized in the presence of $\text{RC}_6\text{H}_4\text{SO}_3\text{H}$ where R = alkyl. After polymerization is complete, the siloxane can be recovered by breaking the emulsion or the emulsion can be neutralized to a pH above 7. The surface-active catalyst also functions as the emulsifier.

The condensation polymerization of silanediols in water has been extensively studied by Saam and Huebner.³ The reaction is found to obey second-order kinetics in silanol and to be correlated to the surface area of oil at the oil-water interface. A mechanism similar to that for surface catalysis is proposed as shown below:



A silicone emulsion of pH of 9–11.5 containing a continuous aqueous phase and dispersed anionically stabilized silicone phase, colloidal silica, and an organic tin compound, which provides an elastomer upon removal of the water, was disclosed by Johnson⁴ in 1980. In the absence of the organic cure catalyst, these emulsions do not produce an elastomer after evaporation of the water immediately after compounding, but rather require a storage period such as five months. The addition of the organic

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compounds reduces the storage time between compounding the emulsion and formation of a silicone latex to three days. The preferred amine for pH adjustments is diethylamine.

Several papers have appeared in the literature in which the chemistry of silicone emulsions has been examined.^{5a-d} These authors suggest, based on intrinsic viscosity measurements and electron microscopy of the latex particles, that anionic lattices are crosslinked prior to water removal. The emulsions prepared according to the method of Johnson were found to be elastomeric after 4–6 h drying time, but swelled in water or heptane. The tensile properties of the cured materials showed two regions of distinct behavior. At low strains the material exhibits a high modulus and at higher strains, the profile becomes more rubber-like. The investigators postulate that the initial part of the stress-strain curve results from the response of the filler phase and the final section corresponds to the response of the polymeric phase.^{5a,b}

The critical coagulation concentration of a variety of ionic flocculants was measured and found to agree with the theoretical values predicted by the Schulze-Harvey rule for colloids stabilized through an electric double layer. The stability of the emulsion toward ions greatly increases upon adjustment of the pH to 10.8, addition of catalyst and colloidal silica and aging the resultant emulsion for 48 h. This result suggests that a different stabilization mechanism is operative under these conditions. These workers conclude that the silanols are grafted onto the silica while the system is still in the dispersed state. The organic catalyst interacts with the silicates and transports them into the oil phase where it catalyzes the condensation reaction. Thus, the PDMS cures within the emulsion particles, which then coagulates upon removal of the water.^{5a,b}

A second composition⁶ has been described which contains an anionically stabilized silicenediol, dialkyl tin dicarboxylate, alkylorthosilicate, and inert filler. This composition yields an elastomer upon removal of the water immediately upon mixing the ingredients of the formulation. When 2-amino-2-methyl propanol (AMP) was incorporated into the formulation, the emulsion showed no gelation upon aging.

Although previous workers suggested that silicone lattices were cross-linked prior to film deposition,^{5a-d} no spectroscopic studies of the cross-linking reaction have been reported. We, therefore, decided to study silicone latex model systems using ²⁹Si nuclear magnetic resonance (NMR) spectroscopy. In addition

to determining at which point the system is cured (i.e., does the cross-linking reaction occur in the emulsified state or upon removal of the water), we also examined the effect of the cross-linker ligation on condensation rates and studied the effect of 2-amino-2-methylpropanol on gelation. The results of our investigations are described herein.

EXPERIMENTAL

PS 340, a hydroxyl-terminated polydimethylsilicone with a Dp of 7 determined by ²⁹Si NMR and gel permeation chromatography (GPC), was obtained from Hüls America. Tetraethylorthosilicate and methyltrimethoxysilane were obtained from Aldrich and used without further purification. A stock catalyst solution was prepared by emulsifying a mixture of 33% Bu₂Sn (laurate)₂ in water stabilized by polyvinyl alcohol (hereinafter referred to as condensation catalyst emulsion).

A model anionic emulsion was prepared by combining PS 340 and water (50/50) and aminedodecylbenzenesulfonate (1%) in a blender. The pH of the resultant mixture was adjusted to 10.1 with 50% aqueous diethylamine. The emulsion was then combined with the various constituents of the formulation and the reactions were monitored by ²⁹Si NMR spectroscopy. A typical anionic model formulation contained 10 g of PS 340 emulsion, 2 g D₂O, 1 g tetraethylorthosilicate (TEOS), 0.4 g methyltrimethoxysilane (MTMS), 1 g of condensation catalyst emulsion and amines at levels of 0.1–0.2 g. A nonionic model emulsion was prepared by homogenizing a hydroxyl-terminated polydimethylsilicone of Dp 10 obtained from GE Silicones, Waterford, NY and water (50/50) with nonylphenoxypoly(ethyleneoxy) ethanol (Igepal CO850 from GAF Corporation) and trimethylnonylpolyethyleneglycol ether from Union Carbide (Tergitol TMN) (1% of each). A typical nonionic formulation contained 10 g of the above nonionic emulsion adjusted with succinic acid to pH of 3.3, 2 g D₂O, 1 g methyltrimethoxysilane, 0.5 g Nalco 1034A (acidic colloidal silica), and 1 g of condensation catalyst emulsion.

²⁹Si NMR spectra were recorded on a Varian XL300 instrument with ²⁹Si at 59.59 MHz using D₂O as the solvent. Gated decoupling was used with a 30-s pulse delay and a 0.5-s acquisition time, thereby acquiring data over a time period of 65 h. Tetramethylsilane was used as an internal reference. ²⁹Si NMR assignments were determined using authentic

samples of the individual constituents or products and appropriate model compounds and recording their spectrum using D₂O as the solvent.

Spectrum numbers versus time are given below:

Spectrum #	Time (h)	Spectrum	Time (h)
1	0	10	17
2	1	11	21
3	2	12	25
4	3	13	30
5	4	14	35
6	5	15	41
7	7	16	47
8	9	17	53
9	13	18	59

Gel permeation chromatography (GPC) was performed on a Hewlett Packard 1090 Liquid Chromatograph with a 1047A refractive index detector using two mixed bed D columns from Polymer Laboratories. Chloroform at 1 mL/min was used as the eluant. The molecular weights were calibrated using both polystyrene standards and a broad silicone standard.

RESULTS AND DISCUSSION

Table I lists the ²⁹Si NMR chemical shifts for the various constituents of the model systems. We began our studies by examining the condensation of a nonionically stabilized system at both acidic and basic pH regimes. In the first experiment, an acidic emulsion adjusted to pH 3.3 with succinic acid, was combined with methyltrimethoxysilane, Nalco 1034A (acidic colloidal silica) and condensation catalyst emulsion; and the ²⁹Si NMR was recorded immediately after preparation (Fig. 1). Peaks at -21 ppm correspond to dimethylsiloxo groups and at -9.2 ppm to hexamethylcyclotrisiloxane. Partial hydrolysis and condensation of methyltrimethoxysilane is evident as seen by the appearance of resonances at -56 ppm and -67 ppm. Polymer endgroups (silanols) occur at -14 ppm and it is apparent that little condensation of the polymer endgroups has occurred. By the sixth spectrum all of the methyltrimethoxysilane has been consumed and the ratio of silanol endgroups to dimethylsiloxo groups has changed from 2 : 26 initially to 2 : 117. The number of silanol groups continues to decrease over the 65-

h time period and can be attributed to continued silanol-silanol endgroup condensation or grafting of the polymer onto the colloidal silica. Unfortunately, ²⁹Si NMR cannot distinguish between these two possibilities.

Condensation under basic conditions (pH 10.0) is much more rapid (Fig. 2). After the first spectrum, all of the methyltrimethoxysilane has been fully condensed to trisiloxo groups and the ratio of silanol endgroups to dimethylsiloxo units is 2 : 55, nearly twice that found under acidic conditions. By the sixth spectrum, the ratio has become 2 : 1466. At the end of the 65-h period, all of the silanol has been consumed.

Table I Chemical Shifts (ppm) for Various Silicon Functionalities

Silicon Group	Chemical Shift (ppm)
$\begin{array}{c} \text{Me} \\ \\ \sim\text{SiOH} \\ \\ \text{Me} \end{array}$	-14 (in acidic or basic water)
$\begin{array}{c} \text{Me} \\ \\ \text{-(SiO)}_3 \\ \\ \text{Me} \end{array}$	-9.2
$\begin{array}{c} \text{Me} \\ \\ \sim\text{O-Si-O}\sim \\ \\ \text{Me} \end{array}$	-21
$\begin{array}{c} \text{Me} \\ \\ \text{-(Si-O)}_4 \\ \\ \text{Me} \end{array}$	-19
$\begin{array}{c} \text{Me} \\ \\ \text{MeO-Si-OMe} \\ \\ \text{OMe} \end{array}$	-41
$\begin{array}{c} \text{Me} \\ \\ \text{SiO-Si-OSi} \\ \\ \text{OMe} \end{array}$	-56
$\begin{array}{c} \text{Me} \\ \\ \text{SiO-Si-OSi} \\ \\ \text{OSi} \end{array}$	-67
Si-(OR)_4	-81

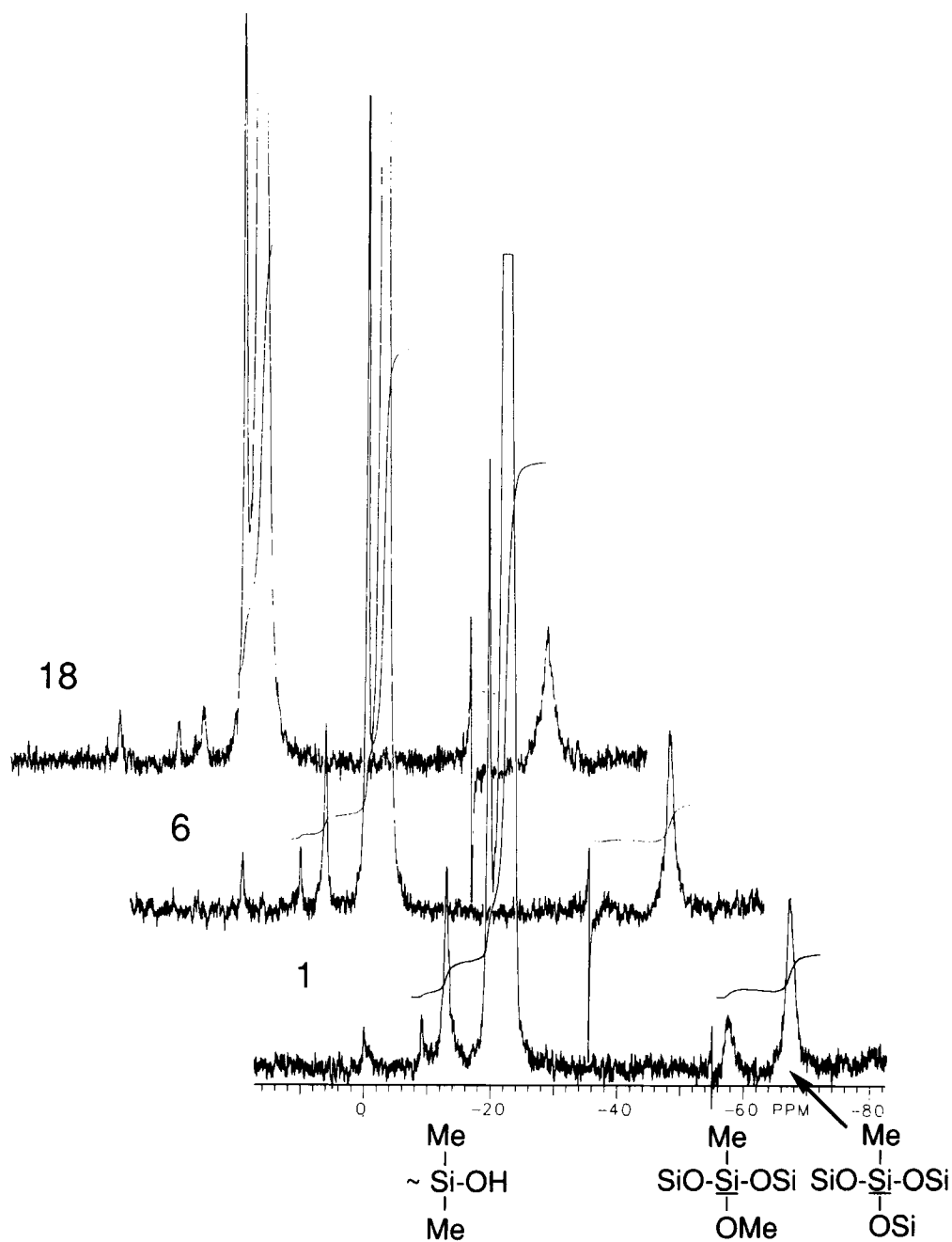


Figure 1 ^{29}Si NMR spectra of model for nonionic emulsion at low pH with colloidal silica, MTMS, and condensation catalyst emulsion (numbers are spectrum numbers).

In order to determine the rate of silanol-silanol condensation, the model emulsion was adjusted to pH 10 with diethylamine, and the condensation catalyst emulsion was added to the emulsion. No colloidal silica or cross-linker was incorporated into the formulation. After 17 h, the emulsion was broken with dichloromethane and the resulting polymer was analyzed by GPC. The molecular weight of the poly-

mer had doubled. The rate at which endgroups were lost as determined by ^{29}Si NMR was comparable to the rate at which the molecular weight increased as determined by GPC. Therefore, in the formulations containing colloidal silica we cannot determine if the disappearance of silanol endgroups is due to grafting or chain growth, or a combination of both processes.

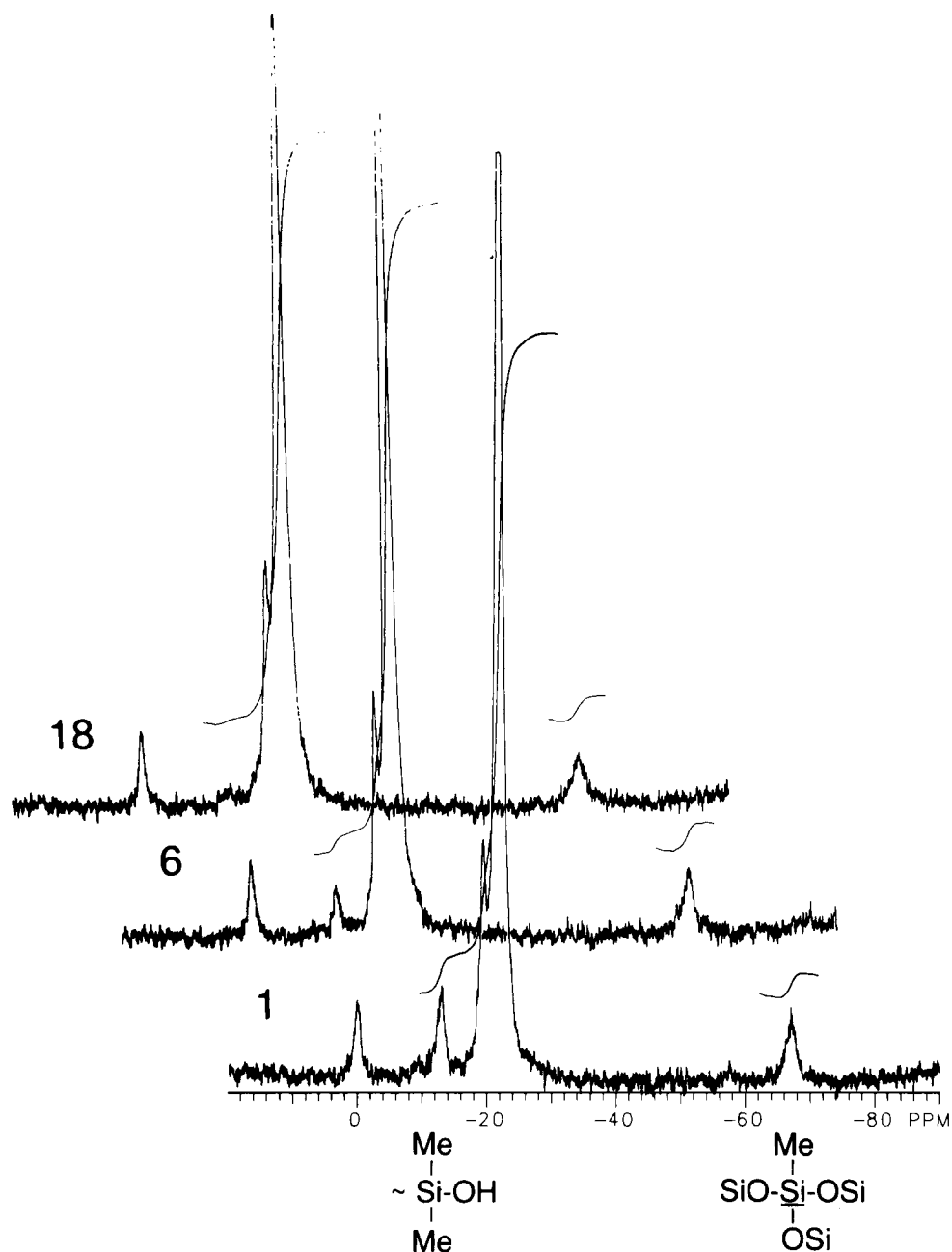


Figure 2 ^{29}Si NMR spectra of model for nonionic emulsion at high pH with colloidal silica, MTMS, and condensation catalyst emulsion.

A model of an anionic silicone emulsion without a stabilizer against premature gelation such as AMP was prepared using 10 g of PS 340 in water (50/50) with aminedodecylbenzenesulfonate as surfactant, diethylamine, tetraethylorthosilicate, methyltrimethoxysilane, and condensation catalyst emulsion. The ^{29}Si NMR spectrum was obtained immediately after preparation of the sample and an additional 17 times over the 65-h time period (Fig. 3). The

initial spectrum in Figure 3 indicates complete consumption of the tetraalkoxysilane by the absence of peaks at -81 ppm and the trialkoxysilane (no peaks at -55 or -67 ppm) as well as partial condensation of the hydroxyl-terminated polymer. The sample gelled in less than 1 h and did not cure to an elastomer upon removal of the water. At the end of 48-h, no diol endgroups are present.

A model emulsion was prepared which incorpo-

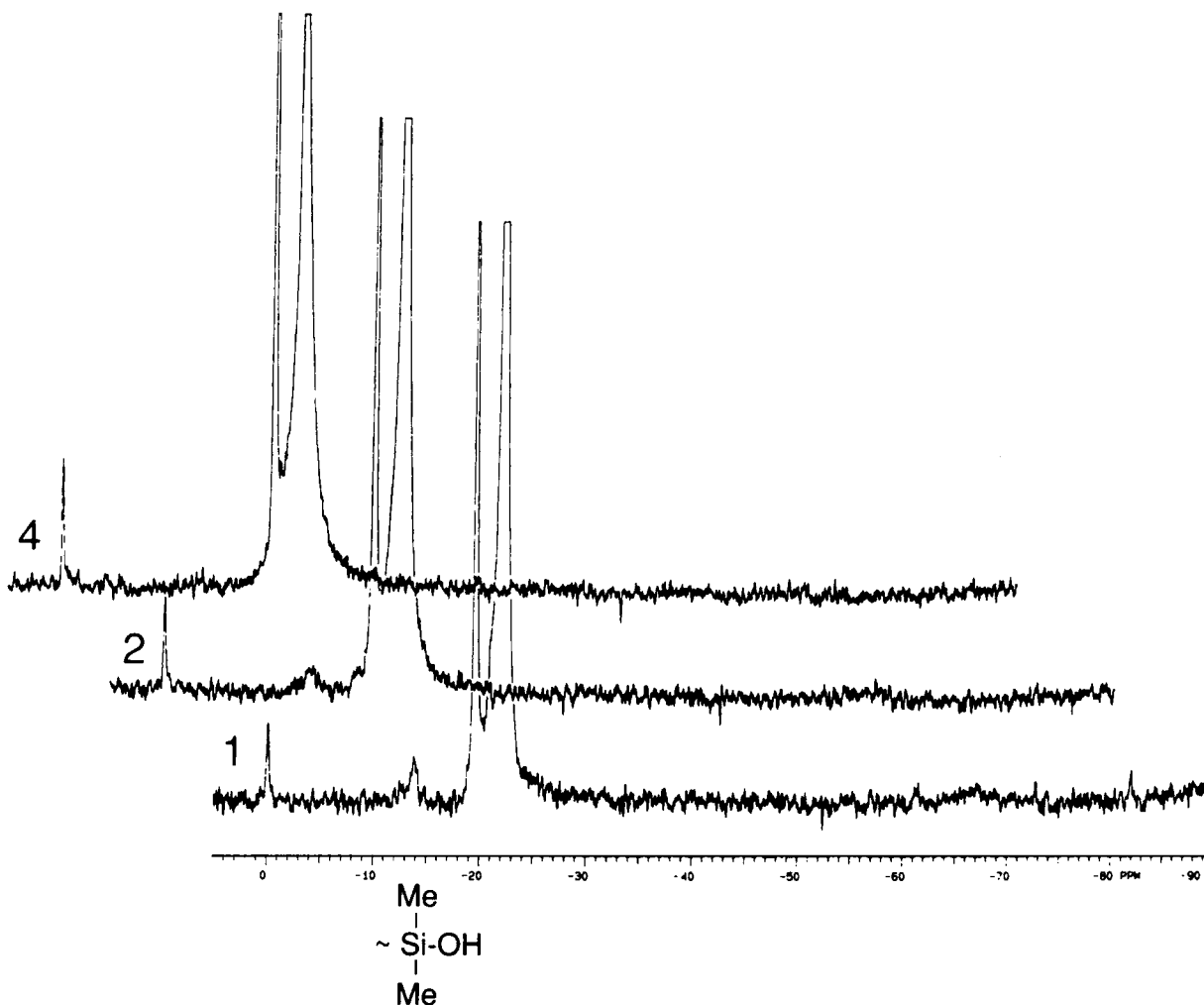


Figure 3 ^{29}Si NMR spectra of unstabilized anionic emulsion with TEOS, MTMS, and condensation catalyst emulsion.

rated 2-amino-2-methylpropanol rather than diethylamine. In the initial spectrum (Fig. 4), peaks assignable to tetraethylorthosilicate (-81 ppm), (trimethylsiloxy) methylsilane groups (-67 ppm), and silanol endgroups (-14 ppm) are evident. The resonance at -9.2 ppm is due to hexamethylcyclotrisiloxane and the peak at -19 ppm to octamethylcyclotetrasiloxane. The overall rate of condensation of this model system is much slower than in the absence of aminomethylpropanol, and the resonances due to the alkylorthosilicate and hydroxyl-capped polymer disappear at nearly equivalent rates. These results indicate that the aminomethylpropanol mediates the reaction by decreasing not only the overall rate of condensation, but the rate of self-condensation of tetraethylorthosilicate as well. Therefore, no gelation due to the rapid self-conden-

sation of the alkylorthosilicate occurs. Cross-linking is complete within 17 h. Thus, cross-linking has occurred completely before water removal unlike room temperature vulcanizing (RTV) compositions. Evaporation of the water leads to destabilization of the emulsion and coagulation of the latex particles to form a continuous film.

In order to unequivocally determine that the systems are crosslinked prior to water removal rather than self-condensation of the alkoxy silane and silanol polymer in two separate phases, the emulsion was broken with methylene chloride after 17 h. If the silanol was undergoing self-condensation reactions, then higher molecular weight polydimethyl silicones should be present in the extract since the initial silanol polymers can only under chain growth processes by silanol-silanol reactions. GPC analysis

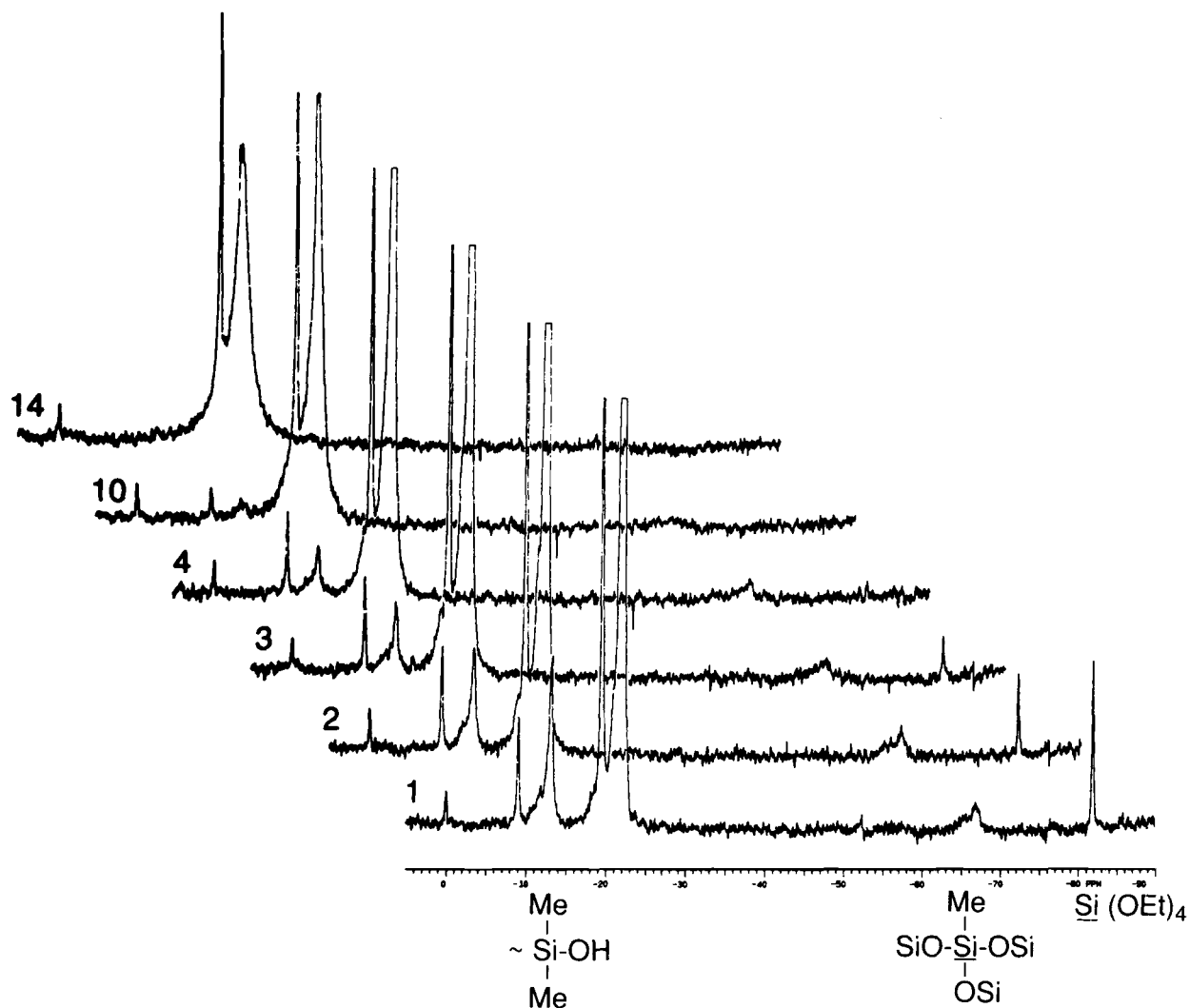


Figure 4 ^{29}Si NMR spectra of anionic emulsion stabilized with AMP with TEOS, MTMS, and condensation catalyst emulsion.

of the resultant extract yielded no high-molecular weight polymers. At the time the emulsion was broken, only 10% of the initial polymer weight was still extractable. ^{29}Si NMR analysis of the extract indicated that only cyclic oligomers were extracted. These results confirm that the systems are cured prior to water removal.

There are two possible mechanisms for stabilization of anionic lattices by aminomethylpropanol which may be operative. First, aminomethylpropanol may function as a surfactant, thereby preventing agglomeration of particles. Second, it may undergo exchange with tetraethylorthosilicate to form a new alkoxy silane which undergoes hydrolysis and condensation at a slower rate. To test the latter hypothesis, we prepared



by metathesis of tetraethylorthosilicate with neopentyl alcohol, which has the same steric properties as 2-methyl-2-aminopropanol. The spectra of a model emulsion which did not contain aminomethylpropanol but did incorporate (1) is shown in Figure 5. In the initial spectrum resonances for silanol (-14 ppm) and tetraalkoxysilane (1) (-81 ppm) are evident. The rate of condensation in this system is much slower than systems without stabilizers and indeed the last part of the system to condense is the alkoxy silane. Thus, it is possible that aminomethylpropanol may in fact exchange with tetraethylorthosilicate, thereby producing a crosslinker which condenses at a much slower rate.

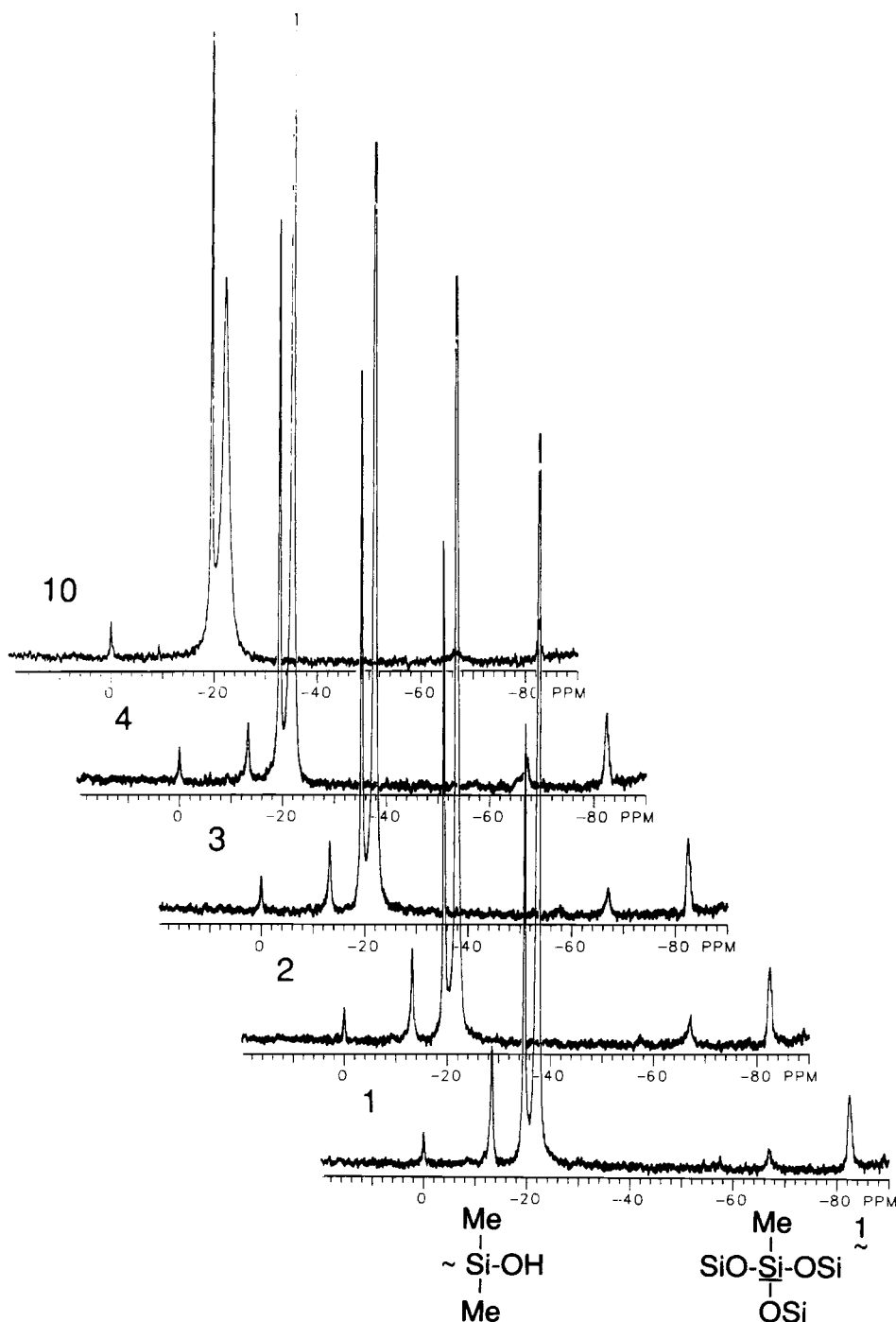


Figure 5 ^{29}Si NMR spectra of anionic emulsion with MTMS, condensation catalyst emulsion, and (1).

CONCLUSION

We have shown that both nonionically and anionically stabilized lattices are cured before water removal. Additionally, aminomethylpropanol slows down the condensation rate of the formulations

which then prevents gelation. Studies are continuing to further define the chemistry of water-based silicone elastomers.

We extend our thanks to a referee who suggested that we provide evidence that self-condensation is not occurring.

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