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FT-NMR ANALYSIS OF SILANE HYDROGEN, PHENYL, AND VINYL CONTENT OF SEVERAL SILOXANE PRE-POLYMER MATERIALS

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DEVELOPMENT DIVISION

MARCH 1979

Process Development

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FT-NMR ANALYSIS OF SILANE HYDROGEN, PHENYL, AND VINYL CONTENT OF SEVERAL SILOXANE PRE-POLYMER MATERIALS

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ABSTRACT

The vinyl contents of siloxane pre-polymer materials were determined by proton FT-NMR. It was determined that the presence of silane hydrogen in these pre-polymers compromises and in some cases negates vinyl content data reported by use of the iodine monochloride procedure. The active hydrogen species reacts with ICl and produces high iodine numbers, even if no vinyl is present. Siloxane aromatic compounds have also been detected by proton FT-NMR, and they also function as an interfering species and produce high iodine numbers by the ICl procedure.

DISCUSSION

FT-NMR characterization and analysis of the silicone pre-polymer system has previously been concerned with the determination of the silane hydrogen content of these materials. An NMR procedure has shown itself to be a specific, rapid, and acceptably precise method(*1*). This portion of the study is concerned with the potential application of NMR methods to the determination of the vinyl content of these pre-polymer materials.

The initial phase of this segment of the study included the spectral characterization of the materials. Fig. 1 presents the proton (^{1}H) spectrum of a typical vinyl containing siloxane, Dow Corning Dielectric Gel A (31). The material was dissolved in deuterochloroform and run on a Nicolet NT-150 FT-NMR. At 0.1 ppm is seen the resonance peak arising from the methyl protons of the dimethylsiloxane group. At higher gain (spectrum plot offset) the vinyl group proton resonance peaks are seen between 5.75 and 6.40 ppm, present as a group of 12 peaks resulting from three doublets of doublets, as all three vinyl protons are magnetically non-equivalent. Further downfield from the vinyl group are proton resonance peaks arising from aromatic siloxane material(s). The resonance pattern centered at approximately 7.59

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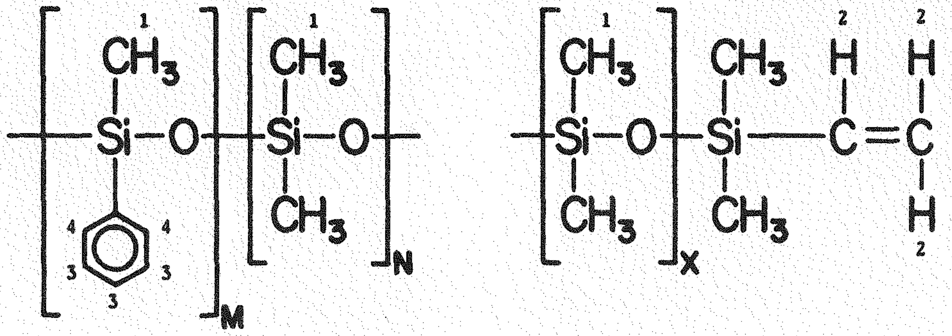
(1) *George L. Clink, FT-NMR Determination of the Silane Hydrogen Content of Siloxane Pre-Polymers, MHSMP-78-45 (October 1978).*



Assignment	Shift (ppm)
1	0.1
2	5.75-6.40
3	7.35
4	7.59

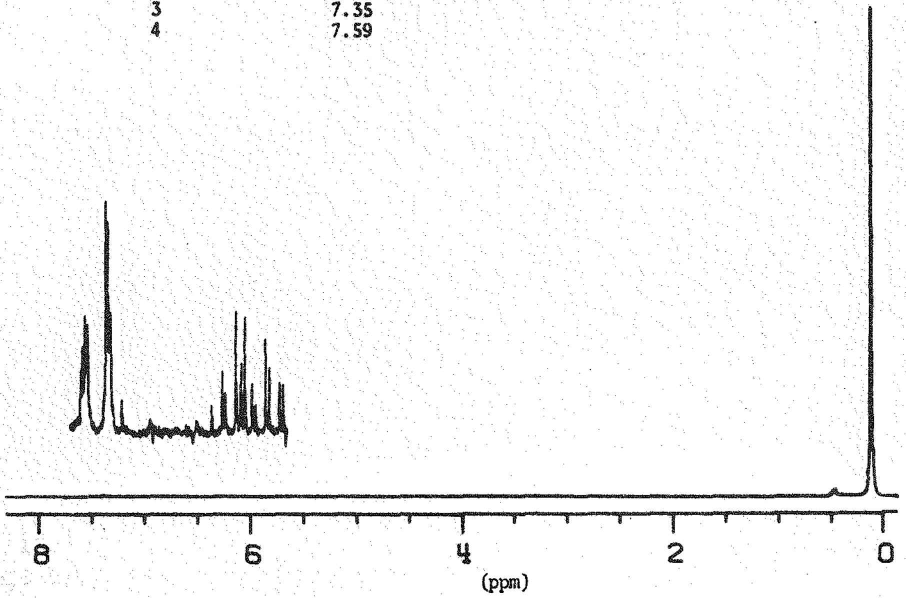


Fig. 1. Proton NMR Spectrum of Dow Corning Dielectric Gel (A) in $CDCl_3$

ppm results from the deshielded ortho protons, as silicon is an electron withdrawing group when bonded to an aromatic ring. The group centered at approximately 7.35 ppm results from the meta and para protons. Aromatic siloxane material(s) were detected in all of the siloxane components studied, with the exception of Dow Corning DC 1107-69 (Table I). Proprietary addition of phenyl substituted dimethyl siloxanes to pre-polymer materials is not uncommon. The percentage formulation will vary, depending on the particular polymeric characteristics desired, which include increased lubricity, oxidation resistance, thermal stability, hydrolytic resistance and shear resistance. The phenyl group introduced into methyl positions in the polymer will also increase rigidity in the silicone chain. Results presented in Table I were obtained by analyzing a deuterochloroform solution containing known weights of pre-polymer material and spectro quality dimethylformamide. The formyl proton of dimethylformamide was used as the internal quantitative standard (8.04 ppm, not shown).

Table I. Aromatic Content of Several Silicone Pre-Polymer Materials

(Wt %, As C_6H_5-)

Material	1	2	3	Average	σ
Sylgard 184A (31)	0.42	0.48	0.47	0.46	0.03
Sylgard 184B (31)	0.48	0.48	0.54	0.50	0.03
Sylgard 184A (36)	0.39	0.41	0.47	0.42	0.04
Sylgard 184B (36)	0.22	0.26	0.21	0.23	0.03
Sylgard 186A (47)	0.38	0.39	0.35	0.37	0.02
Sylgard 186B (47)	0.47	0.49	0.43	0.46	0.03
Sylgard 186A (64)	0.42	0.48	0.46	0.45	0.03
Sylgard 186B (64)	0.44	0.49	0.46	0.46	0.03
Dielectric Gel A (31)	1.80	1.73	1.77	1.77	0.04
Dielectric Gel B (31)	1.77	1.74	1.78	1.76	0.02
Dow Corning DC 1107-69	-	-	-	-	-
Accelerator (99)	1.17	1.23	1.20	1.20	0.03

The silane hydrogen content of the several materials studied was determined by the NMR method previously reported(*1*). The weighed amounts of material and spectrograde p-dioxane were dissolved in deuterochloroform and subsequently run on the NMR. As seen in Table II, the results obtained by NMR and by the manometric measurement of evolved hydrogen (Pantex Quality Laboratory procedure) are effectively identical. Fig. 2 presents the proton spectrum of a typical silane hydrogen—containing dimethylsiloxane prepolymer, Dow Corning DC-1107-69. The Si-H resonance is seen at 4.64 ppm.

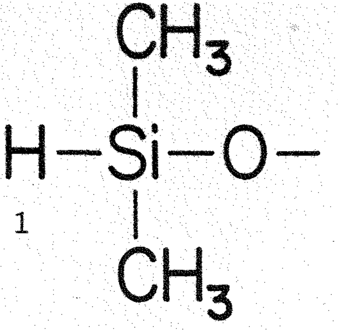
The siloxane vinyl content was determined by using the formyl proton of spectrograde dimethylformamide as the internal quantitative standard. Because the vinyl resonances consist of twelve peaks and cover a range of 0.65 ppm (98 Hz), integration over this range would not be expected to produce highly accurate percentages, but analysis of samples made from high purity vinyl siloxane standards (Penninsular Chemical Co.) produced results of 92 to 96% of actual value. The results of the vinyl content analysis run on the various prepolymer materials are presented in Table III. Results obtained by the iodine monochloride method are included for comparison. Examination of the data in Tables III and IV shows that when analyzing the "A" components (those with no silane hydrogen) the results from the NMR and ICl methods are within a reasonable range of one another, but with materials containing the active hydrogen species (B components), the ICl procedure produces vinyl content percentages excessively higher than those found by NMR methods. The most prominent example occurs with the analysis of Dow Corning DC 1107-69. Examination of the ^1H spectrum

Table II. Active (Silane) Hydrogen Content of Several Silicone Pre-Polymer Materials

(Wt %)

Material	Manometric Method	NMR				
		1	2	3	Average	σ
Sylgard 184B (31)	0.456	0.46	0.44	0.44	0.45	0.01
Sylgard 184B (36)	0.442	0.43	0.44	0.44	0.44	0.01
Sylgard 186B (47)	0.088	0.11	0.10	0.08	0.10	0.02
Sylgard 186B (64)	0.097	0.12	0.10	0.10	0.11	0.01
Dielectric Gel B (31)	0.180	0.21	0.16	0.20	0.19	0.03
Dow Corning DC 1107-69	1.575	1.58	1.61	1.60	1.60	0.15

Assignment	Shift (ppm)
1	4.63



$$\mathrm{H{-}\overset{CH_3}{\underset{CH_3}{Si}}{-}O{-}}$$

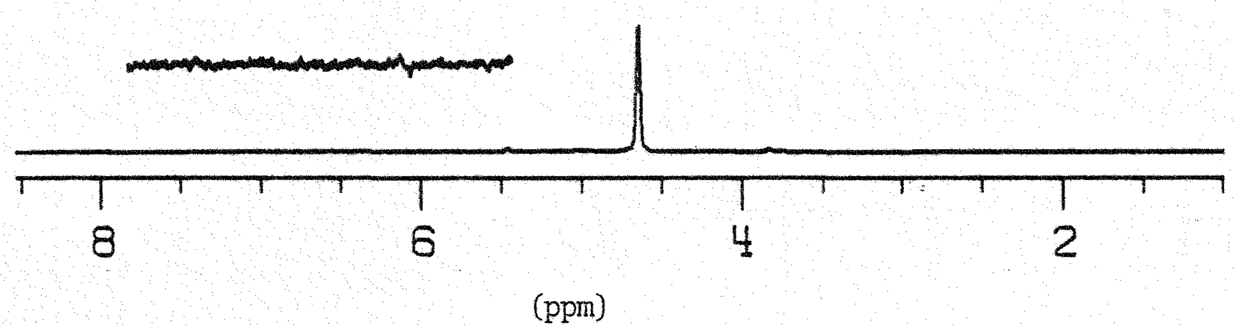


Fig. 2. Proton NMR Spectrum of Dow Corning DC 1107-69, in $CDCl_3$

Table III. Vinyl Content of Several Silicone Pre-Polymer Materials

(Wt %, As CH_2=CH-)

Material	Iodine Monochloride Results	NMR				
		1	2	3	Average	σ
Sylgard 184A (31)	0.60	0.48	0.53	0.52	0.51	0.03
Sylgard 184B (31)	2.32	0.68	0.72	0.70	0.70	0.02
Sylgard 184A (36)	0.60	0.51	0.49	0.53	0.51	0.02
Sylgard 184B (36)	2.14	0.37	0.41	0.40	0.39	0.02
Sylgard 186A (47)	0.25	0.29	0.25	0.28	0.27	0.02
Sylgard 186B (47)	1.91	0.29	0.34	0.31	0.31	0.03
Sylgard 186A (64)	0.54	0.43	0.45	0.43	0.44	0.01
Sylgard 186B (64)	1.93	0.35	0.35	0.32	0.34	0.02
Dielectric Gel A (31)	0.79	0.63	0.66	0.61	0.63	0.03
Dielectric Gel B (31)	1.21	0.57	0.61	0.57	0.58	0.02
Dow Corning DC 1107-69	3.87	-	-	-	-	-

Table IV. Comparison of Vinyl Content Results of Silane Hydrogen Containing Silicones by ICl and NMR Methods

Material	Active Hydrogen (Wt %)		Vinyl Content (Wt %)	
	Manometric	NMR	ICl	NMR
Sylgard 184B (31)	0.46	0.45	2.32	0.70
Sylgard 184B (36)	0.44	0.44	2.14	0.39
Sylgard 186B (47)	0.09	0.10	1.91	0.31
Sylgard 186B (64)	0.10	0.11	1.93	0.34
Dow Corning DC 1107-69	1.58	1.60	3.87	-

of Dow Corning Dielectric Gel A (Fig. 1) produces the quite obvious and characteristic twelve peak multiplet found in vinyl containing siloxanes (5.7 - 6.4 ppm) and this material contains reported vinyl percentages of 0.63 (NMR) and 0.79 (ICl). The ^1H spectrum of DC 1107-69 on the other hand, displays no spectral evidence of siloxane vinyl (Fig 2, plot offset), but has the highest vinyl content reported of any of the materials studied, 3.87% by ICl method. Coincidently, DC 1107-69 contains the highest silane hydrogen content reported for any of the materials analyzed in this study (1.6%). Silane hydrogen is a fairly good reducing agent, and the probability of substantial iodine consumption through interaction with silane hydrogen is strongly indicated, and can account for excessively high iodine numbers and subsequent high vinyl content percentages reported. Indeed, Siggia(2) has identified both aromatic ring compounds and active hydrogen among the causes of high iodine numbers when using the iodine monohalides to determine olefinic unsaturation. Table IV presents comparative reported percentages of silane hydrogen (manometric and NMR) and siloxane vinyl (ICl and NMR), the differences in vinyl content by method being quite appreciable.

Four high purity silane hydrogen samples were subjected to the iodine monochloride method to determine if any vinyl content would be reported based upon iodine number. All samples were initially run on NMR to determine their purity and particularly the absence of vinyl. The materials were obtained from Silar Laboratories, Inc. Following is a list of these materials, accompanied by the reported vinyl content percentages:

Diphenyl Silane	2.71% Vinyl
Diphenylmethyl Silane	3.72
Triethyl Silane	2.95
2,4,6,8-Tetramethylcyclotetrasiloxane	2.69

An attempt to correlate vinyl content reported with silane hydrogen actually present would not produce stoichiometric results. Whether this is due to reaction temperature, digestion time, limiting equilibrium, or some other cause is only speculative at this time.

COMMENTS

The use of the iodine monochloride method for determination of olefinic unsaturation is an acceptable procedure where interfering groups are not present. Unfortunately, most if not all of the siloxane pre-polymer materials employed in the present siloxane

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(2) *S. Siggia, Quantitative Organic Analysis via Functional Groups, John Wiley & Sons, p 296 (1963).*

polymer formulations do contain such species. Even in the Sylgard A series, which do not contain silane hydrogen, some amounts of aromatic ring compounds do exist and can cause high iodine numbers, although the variance in content reported between NMR and ICl method results is not substantial. However, in systems containing silane hydrogen, the ICl method is obviously not usable.

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