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FTNMR ANALYSIS OF SILOXANE POLYMERS AT 200 MHz

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INTRODUCTION

Proton NMR is an accepted method for analyzing silicone cushion material for methyl, phenyl, and vinyl content. Recent interest in the preparation of cushion material with a low vinyl content has required that we reevaluate the NMR method of analysis and this we have done in some detail. The new analytical requirement was that vinyl fragment contents were to be measured at the 0.20 weight percent level with an accuracy of ten percent. We have used a 200 MH$_z$ high resolution Fourier transform NMR spectrometer and optimized those parameters that most directly affect the analysis.

(A) NMR Spectra of Siloxane Polymers

The general features of the proton spectrum of siloxane polymers at 200MHz, are shown in Fig. 1. This spectrum arises from the proton resonances of the methyl, phenyl, and vinyl groups attached to a polysiloxane backbone (Appendix I) and minor trace components. The polymers are dissolved in $CDCl_3$ which contains 0.1% or less of $CHCl_3$ and possibly absorbed H_2O, Fig. 2. The water peak is slightly downfield from the methyl peak and can vary in intensity, width, and position. It normally does not interfere with integration of the methyl peak. The $CHCl_3$ peak is always a part of the phenyl region and leads to an inaccuracy of the phenyl area of ∿1%, as determined from analysis of phenyl free polymers, which is insignificant for our present needs. The phenyl and vinyl fragment resonances are downfield (+ ppm) from the methyl fragment. The identification of the resonances is unambiguous and follows immediately from chemical shift and intensity considerations. In addition, polymers without vinyl groups and standards without phenyl groups substantiate the identifications. Futhermore, a comparison of a theoretical with an actual vinyl spectrum has been made, Fig. 3, and good agreement is found.

Perhaps the most distinguishing feature of the proton spectrum of the siloxane polymers is the large differences in signal size of the methyl, phenyl and vinyl protons. The methyl proton resonance always dominates the spectrum. The vinyl protons are lost in the baseline when the methyl peaks are on scale, Fig. 4. This difference in size of the vinyl and methyl peaks is the major factor in the difficulty of accurate measurements of siloxane polymers by FT-NMR and will be discussed at length.

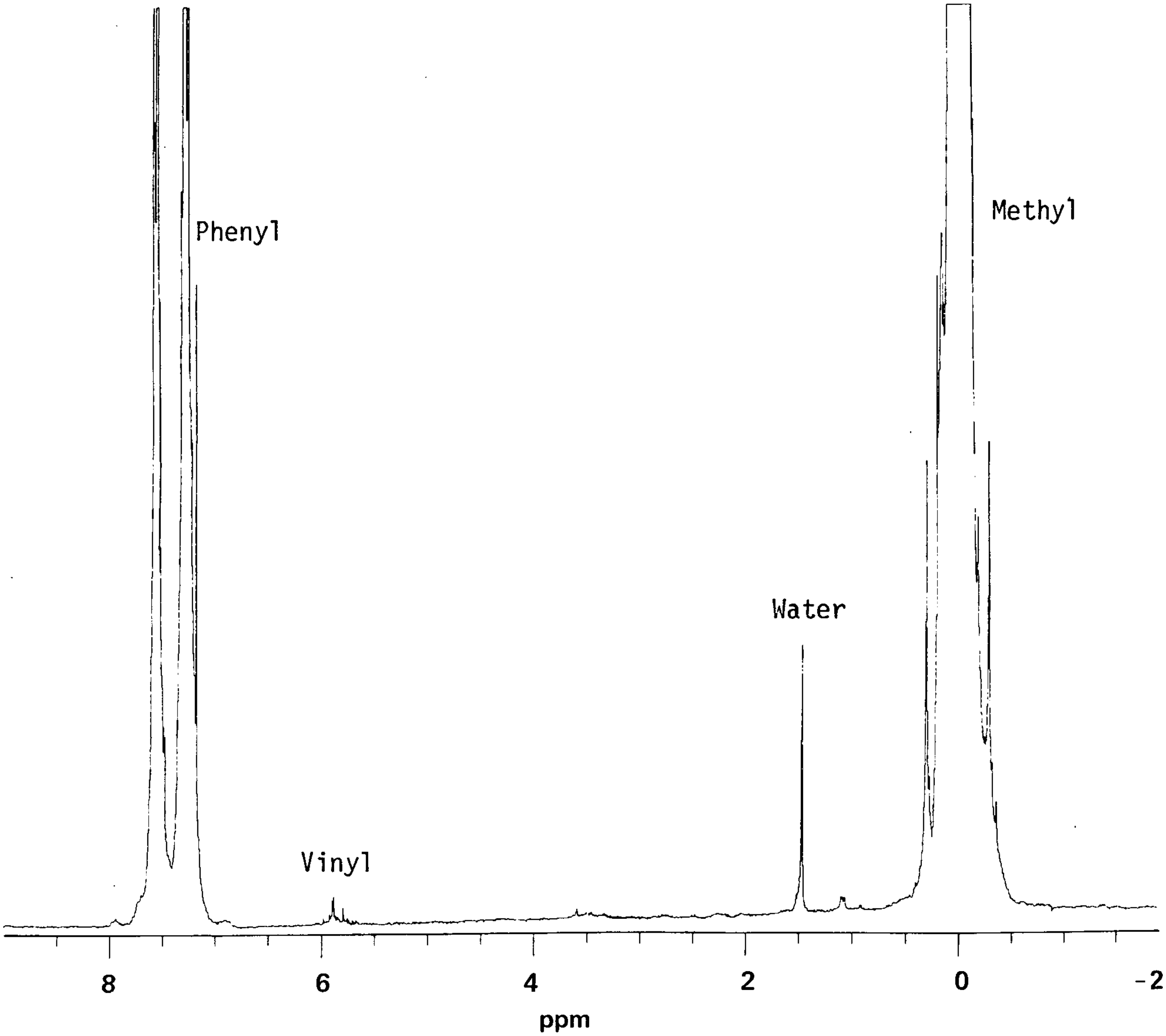


Figure 1

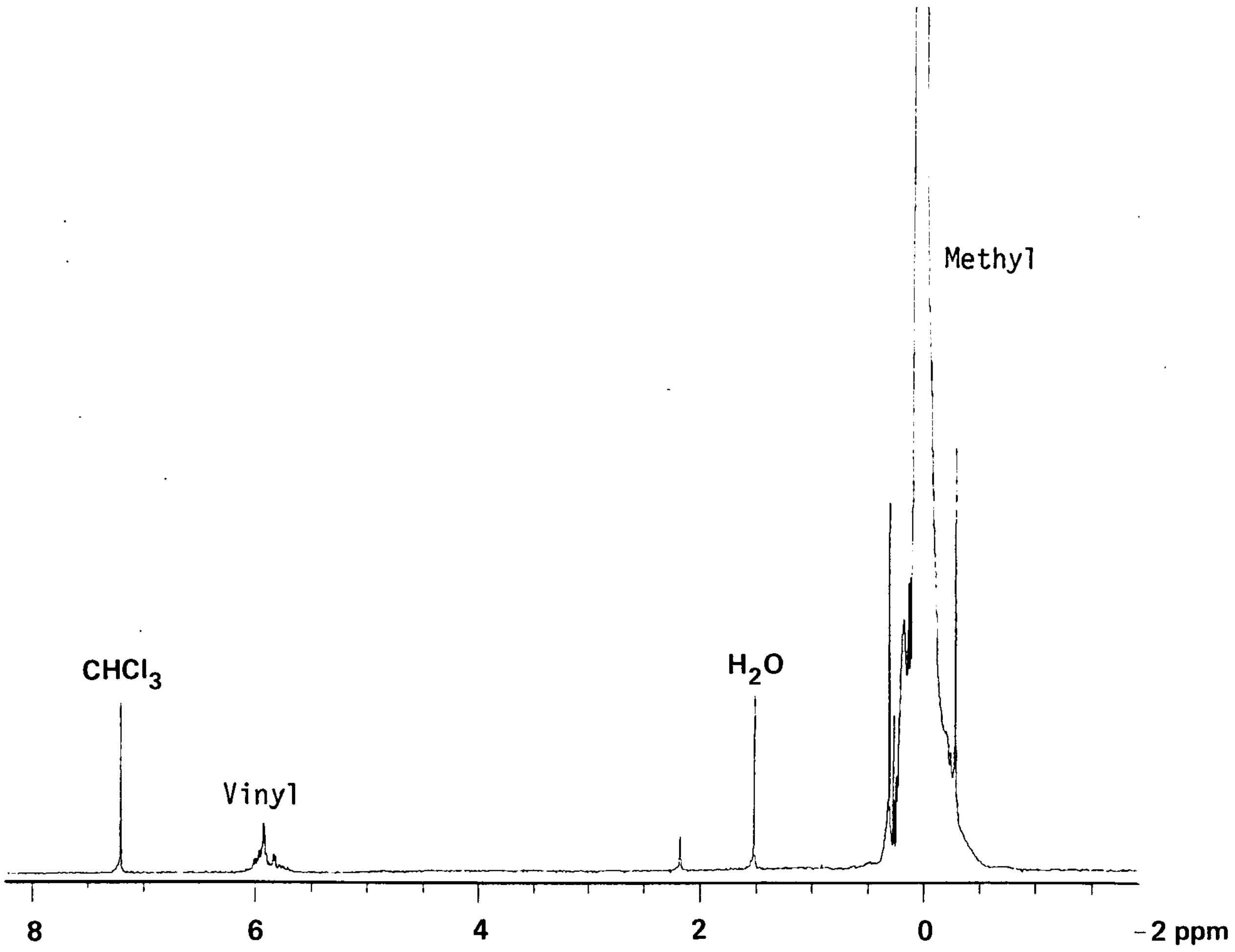


Figure 2

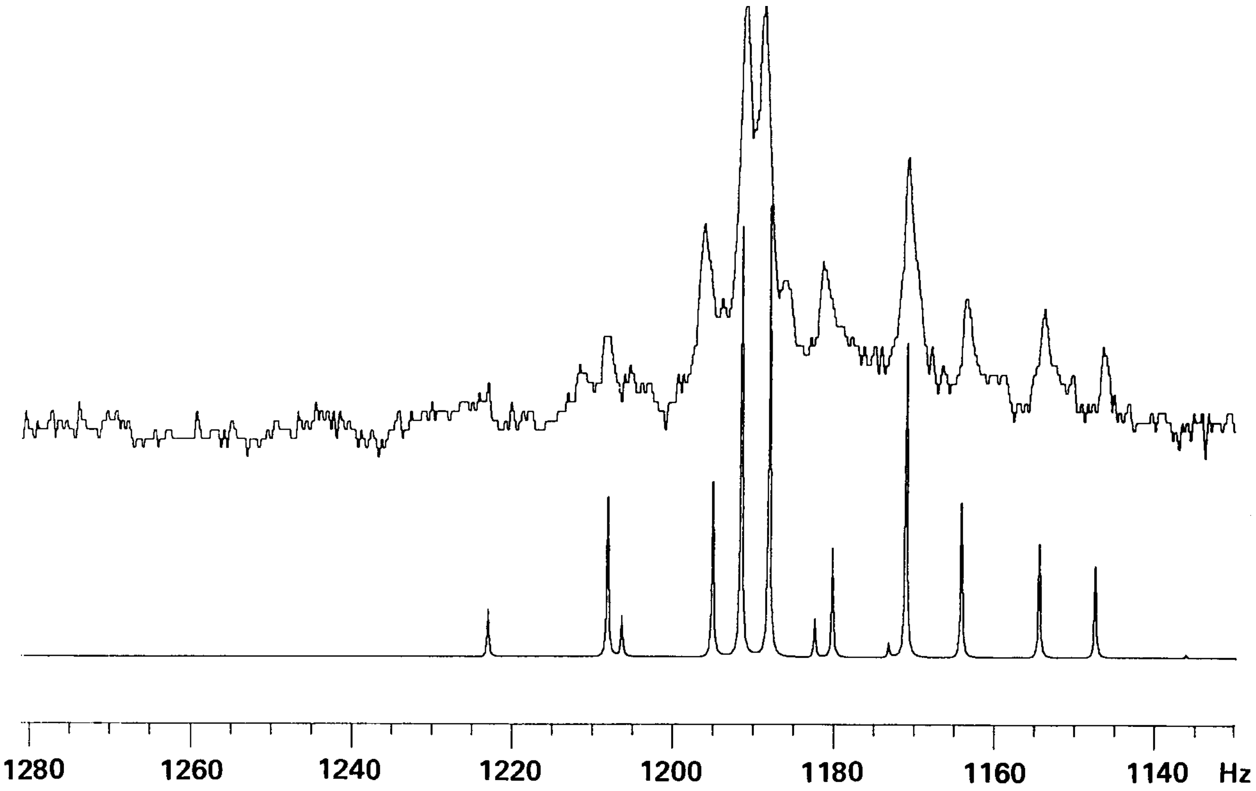


Figure 3

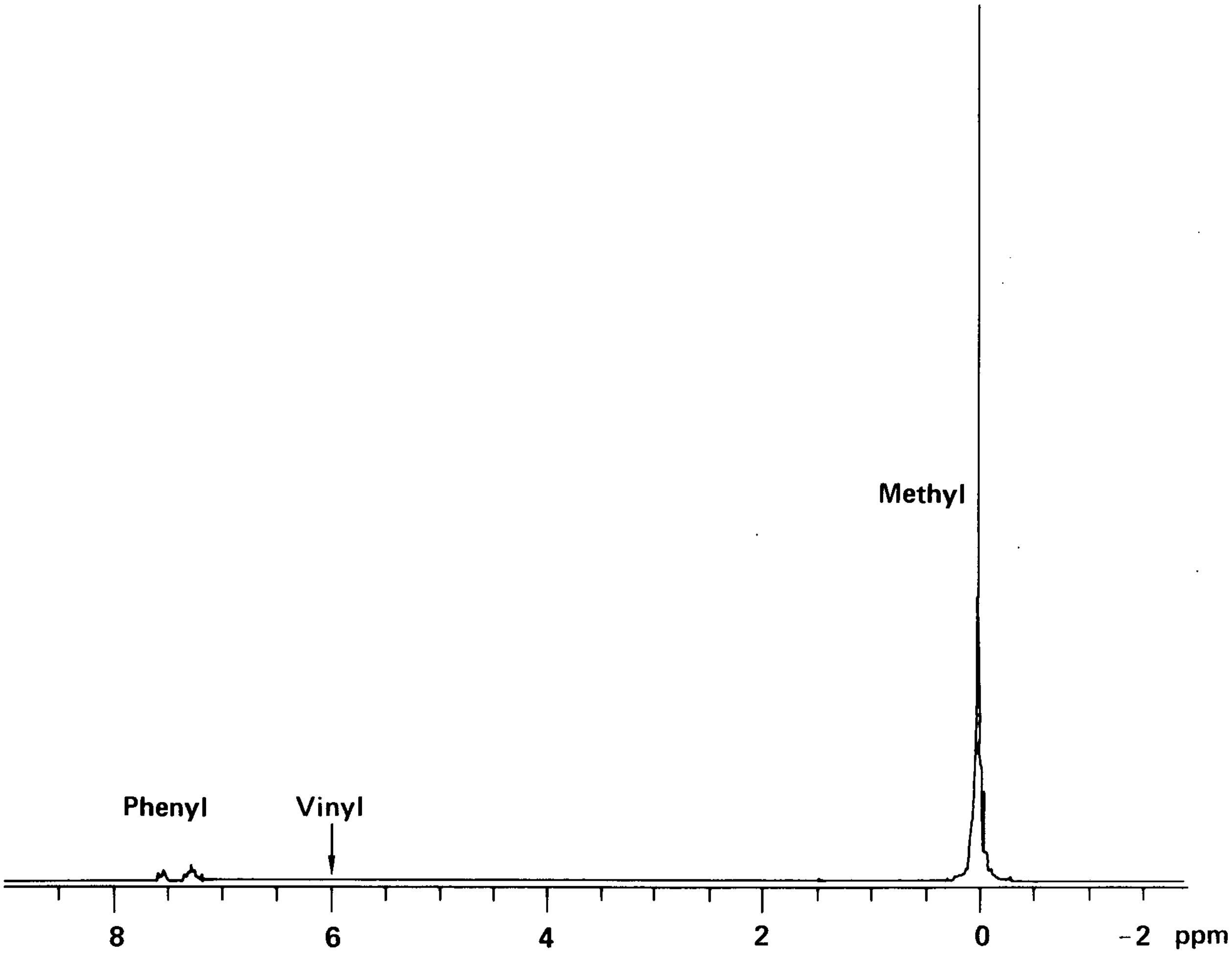


Figure 4

(B) Dynamic Range Considerations

The accurate measurement of a small peak in the presence of a large one by Fourier transform NMR requires consideration of the dynamic range capabilities of the NMR spectrometer. In particular, the size of the analog-to-digital (A/D) converter and computer word length are important. The usual operating procedure is to fill the A/D converter with a free induction decay (FID) signal derived from one rf pulse. The A/D must be able to accurately digitize the smallest as well as the largest signal components i.e., the smallest signal must be larger than the step size of the A/D converter. The larger the small signal is, compared to the A/D step size, the more accurate the signal measurement will be. The usual 12-bit A/D can resolve 1 part in 4096 while a 15-bit A/D can resolve 1 part in 32,768. The methyl to vinyl ratio of the SE-54 type polymers is about 4000. A 12-bit A/D should suffice, especially for higher vinyl concentrations. We have, however, used a 15-bit A/D in our measurements. In fact, we have observed that if the 15-bit A/D is completely filled with signal from one pulse the resulting spectrum exhibits distortions, i.e., broadening of lines, poor line shapes, and base line distortions. We therefore reduced the size of the signal into the A/D until these distortions disappear. The size of the smallest signal component must still be larger than the step size of A/D for faithful reproduction of the signal. This is more easily accomplished with the 15-bit A/D than the 12-bit A/D.

The computer word length, 20-bits for the Nicolet Instrument, is important in determining the total number of scans that can be averaged before the memory is full. The computer word length can be effectively doubled by using double precision as discussed more fully later. The general area of digitization and data processing in Fourier transform NMR is discussed quite throughly in the review by Lindon and Ferrige.[1]

The dynamic range problem associated with the analysis of siloxane polymers is illustrated in figures 4,5 and 6. Figure 4 is the spectrum of a typical siloxane. The methyl group is full scale, the phenyl group is barely detectable, and the vinyl group is completely hidden in the baseline at these gain settings. In Fig. 5 the y-scale has been increased 1000 times to display the vinyl protons. Fig. 6 also illustrates some beats, wiggles, and base line curvature that can appear with increased gain.

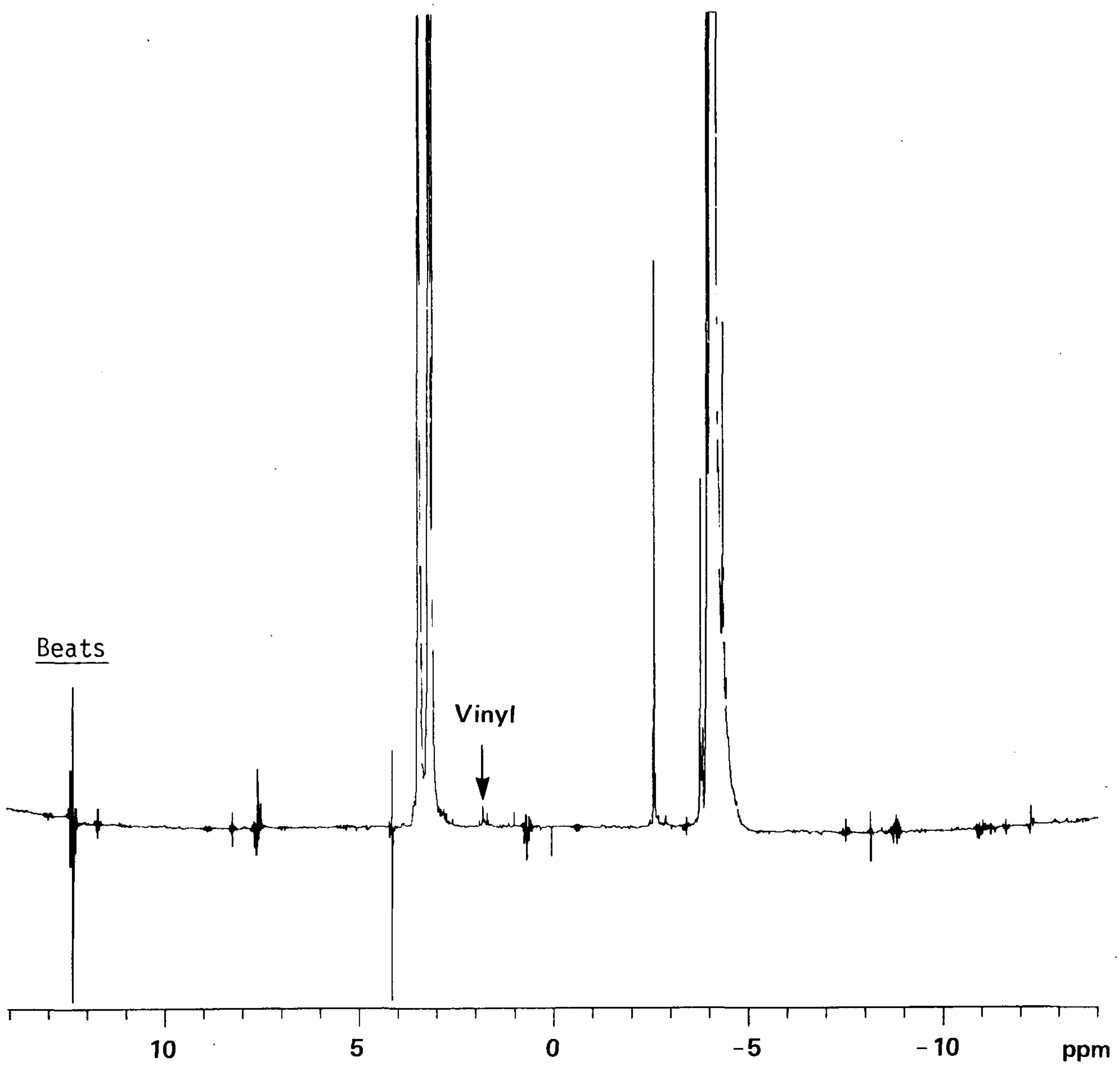


Figure 5

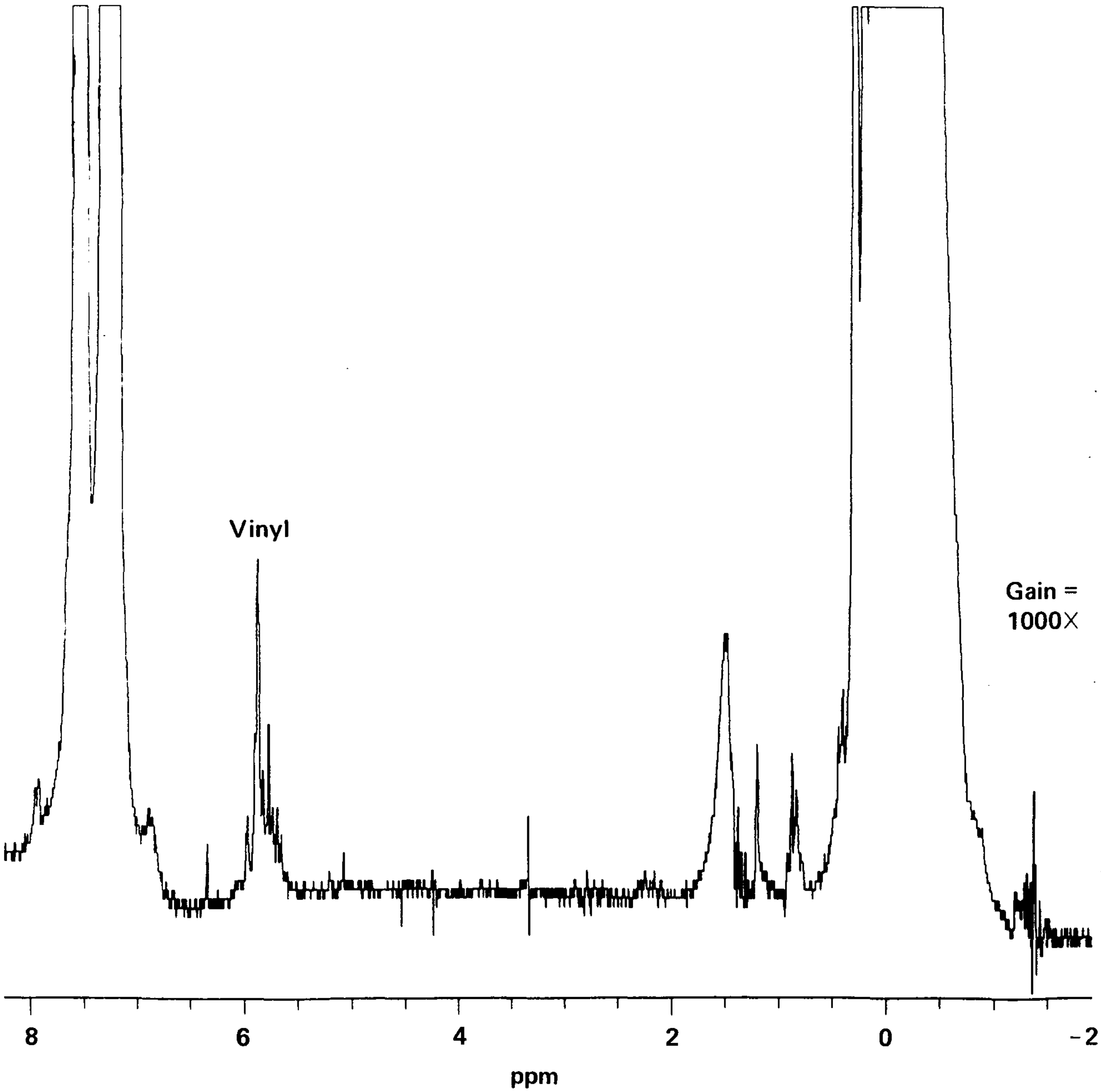


Figure 6

(C) Obtaining Proton NMR Spectra of Siloxane Polymers

In principle the proton NMR spectrum of a siloxane polymer will yield distinct absorption peaks for the methyl, phenyl, and vinyl fragments of the polymer as defined in Appendix I. Under restricted conditions the area of these peaks is directly proportional to the amount of fragment present within the polymer. We determined the conditions required to obtain accurate, repeatable, and moderately fast NMR analysis with the LLNL 200 MHz Fourier Transform Spectrometer.

Samples are prepared as described below and examined in 5mm NMR tubes. The spectrometer is locked internally to the deuterium NMR signal of the $CDCl_3$ solvent. The magnetic field homogeneity is maximized for each siloxane sample. Our unusual procedure is to first adjust the homogeneity, both spin and non-spin shims, on a standard 9% o-dichlorolbenzene solution in dimethylsulfoxide -d_6. For each solution of siloxane polymer, the resolution is then maximized by adjusting the spin only shims. We do this with the Nicolet SU command by maximizing the integrated FID produced by the siloxane polymer. We have observed in our proton probe that due to a physical displacement of the lock coil from the observe coil the best resolution is obtained by maximizing the FID signal and not the lock signal.

Because of the sensitivity and complexity of modern broadband NMR spectrometers, there may be unwanted signals hidden in the "noise" of the baseline. These unwanted signals can be due to instrumental artifacts and/or chemical impurities in the sample, Fig. 6. For example, images from quadrature phase detection of large signals can readily be hidden in the base line noise. When, however, it is important to detect small signals in the presence of large ones, the quadrature phase detected images become apparent under increased gain. Unwanted signals and peak distortions can also appear due to other system nonlinearities in the preamplifier or rf amplifiers. We have attempted to minimize these effects and will note those parameters that have been found to be most important.

Signal Amplitude:

There are a number of parameters that affect signal amplitude: sample size, sample concentration, pulse width, recycle delay, preamplifier setting, rf and audio amplifier settings and possible rf pulse droop. The sample size is fixed by the probe design, 5 mm in our case. The sample concentration can be varied, but too high a concentration of siloxane makes the solution so viscous as to be almost impossible to transfer to an NMR tube. We have settled on a concentration of 0.34 gms siloxane per 2ml $CDCl_3$. We have found, as listed in Appendix II, that with our 15 bit A/D a pulse width of 7μ sec, a delay of 10 sec, a preamp setting of 30 dB, a RF setting of 1, and an audio gain of 8x10 will yield an undistorted spectrum. Perhaps higher gain settings could be used without signal distortion to shorten the analysis time, but each case should be examined individually. Our analysis also requires that the Fourier transform of the 90° rf pulse uniformly spans the frequency domain of the proton spectrum of the siloxane polymers. In other words, the signal strength of all protons must be independent of the proton frequency setting. We have determined that our instrument satisfies this requirement by measuring the methyl to phenyl ratio with the radio-frequency set in the methyl region or the phenyl region. These measurements each give the same ratio for sample

BB103: 16.87 and 16.72. Sample BB103 is a particular batch of polymer type SE-54 studied extensively in this paper (Table I).

In principle the signal amplitude should be adjusted to nearly fill the 15-bit digitizer but still provide at least one bit of noise. For our spectrometer, this requires that the signal from one pulse just fill the scope when the vertical gain setting of the 1180 computer is set to 4K. This will allow

$$2^{W-D} = 2^{20-15} = 32$$

scans before memory is full. W is the word length of the computer and D is the size of the A/D converter. We have observed, however, even though the FID appears undistorted under these conditions, the transformed spectrum can be distored, e.g., lines are broadened, extraneous beats and wiggles, etc. appear. We avoided these distortions by reducing the size of the FID by a factor of 8 while maintaining the requirement of adequate noise for digitization. The reduction in signal size allows more scans before the memory is filled. For a typical sample we routinely sum 256 scans.

The signal to noise ratio for the siloxane vinyl peaks is insufficient for accurate integration of the peak areas after only 256 FIDs. The only method of increasing the number of FIDs given the restrictions of the A/D noted above, is to block average groups of 256. This is accomplished in the Nicolet software with the BA command. Blocks of 256 FIDs are averaged in double precision (40-bit data) on the disk. For the SE-54 series, we have found that a minimum of four blocks must be averaged to obtain accurate integrations.

We chose to adjust the spectrometer gain settings, i.e., preamplifier, RF and audio, to minimize spectral distortions. We further chose to set the pulse width, P2, equal to a 90° pulse. This requires the recycle delay plus acquisition time be sufficiently long for all nuclei to relax before the next pulse. This time can be estimated by comparing the area ratios of the phenyl and methyl groups as a function of the recycle delay time, Fig. 7. The rf pulse could be shortened to less than 90° which would in turn allow a shorter recycle time. This change would also decrease the signal size, but allow more scans in a given block. It seemed, however, unwise to shorted the pulse width since signal/noise is sacrificed which can only be required by devoting more time to accumulating FIDs. We have not examined this point in sufficient detail to suggest an alternative set of values to these reported in Appendix II.

Positioning of Radio frequency:

Following the suggestions of Lindon and Ferrige,[1] we positioned the radio frequency on top of the most intense peak in the sample, i.e., the methyl group. This has definitely improved the quality of our spectra, i.e., removed extraneous peaks and wiggles.

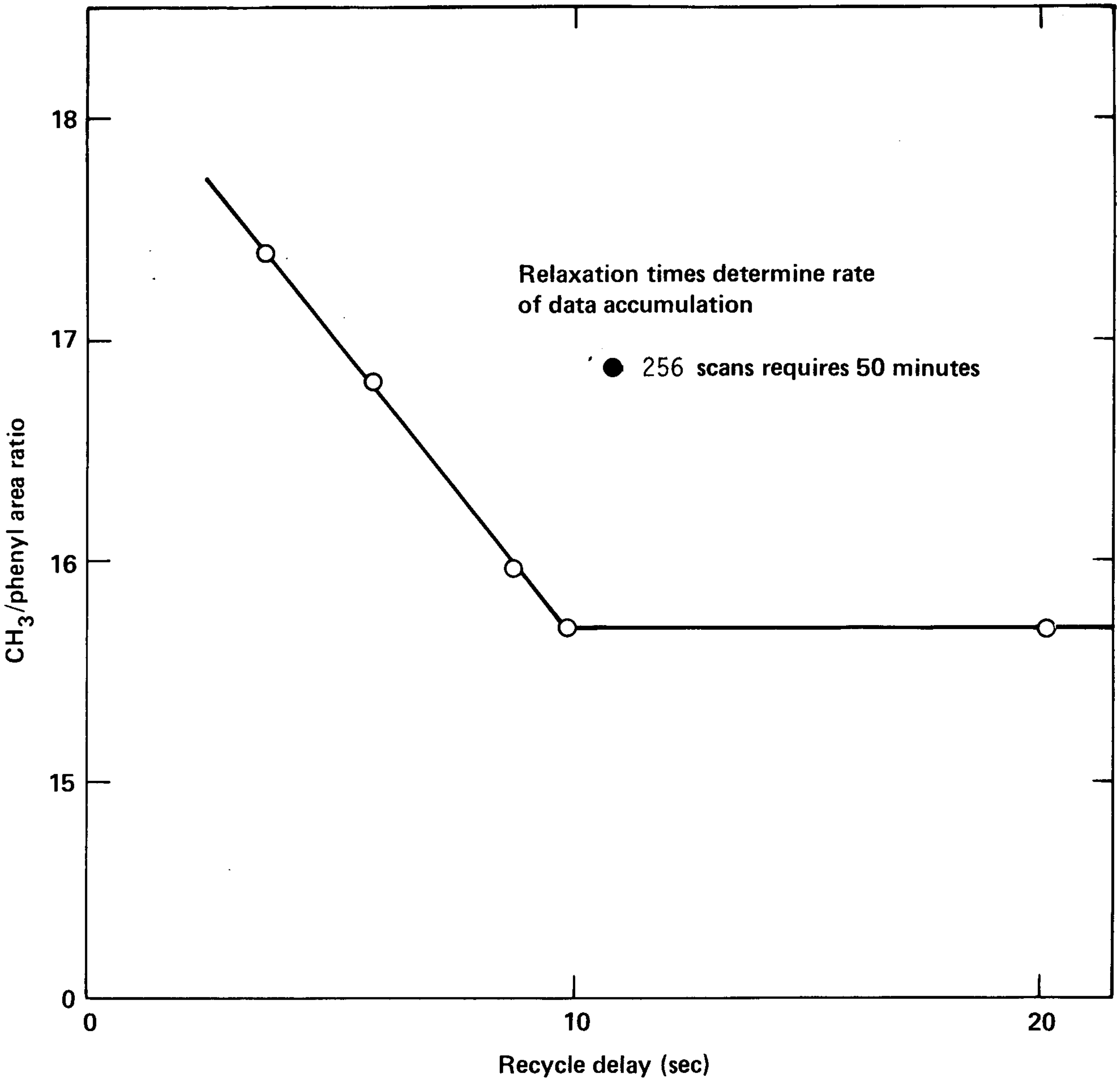

18
17
16
15
0
CH3/phenyl area ratio
0
10
20
Recycle delay (sec)
Relaxation times determine rate of data accumulation
● 256 scans requires 50 minutes

Figure 7

(D) Treatment of Data

Once a block averaged FID of sufficient signal to noise has been obtained, the FID must be transformed to the frequency domain and the peaks integrated. We have found the Nicolet software adequate for our integration purposes.

The block averaged FID, stored in double precision on the disk, is recalled to the computer. The base line is corrected to remove DC offsets, smoothed by exponential multiplication, Fourier transformed, and phased, all in double precision format.

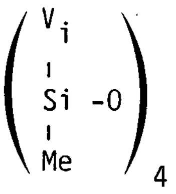
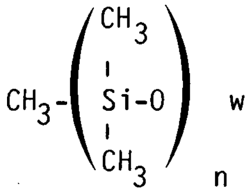
Manipulation of double precision data is more time consuming than manipulation of single precision data. It is possible to convert the block averaged double precision FID to single precision prior to Fourier transformation with truncation of word size. Although we have not made an extensive study of this approach, we have treated the data from SE-54 samples both ways, and there appears to be little difference.

Integration of Data.

After the FID is Fourier transformed and phased properly, the data is converted to single precision for integration purposes. The water resonance, due to moisture contamination of the $CDCl_3$ or unreactive SiOH groups, is near but downfield of the methyl groups. The presence of this water peak can make adjustment of the initial slope of the integration curve difficult. Since the initial slope is important in obtaining good integrals it is helpful to shift the water peak to the "high field" side of the methyl group with the SR (Spectrum Reverse) command. The methyl group of the siloxane is integrated first and the area assigned a fixed value. The phenyl and vinyl groups are then integrated and compared to the methyl integral.

We have often found base-line curvature of the frequency domain spectrum to be a nuisance in obtaining good integrals. At best the base line should be flat throughout the spectrum. The high gain required for the low level vinyl protons signal magnifies any base-line curvature. The sweep width we use causes the methyl, phenyl, and vinyl peaks to appear in regions where the base line is changing smoothly. The zoom command is used to pick out the regions of interest and if need be there are subcommands which can be used to mathematically straighten the base-line.

Accuracy and Precision of Data:

The accuracy of vinyl analysis is illustrated in Table 1. Mixtures of  $\left(\begin{array}{c} V_i \\ | \\ Si-O \\ | \\ Me \end{array}\right)_4$ and  $CH_3-\left(\begin{array}{c} CH_3 \\ | \\ Si-O \\ | \\ CH_3 \end{array}\right)_n$ with known (0.1 to 1.0 wt %) vinyl content were prepared by weighing and analyzed by NMR. The data, Fig. 8, has been fitted by a least squares procedure and the equation $y=0.985X-0.005$ obtained. The correlation coefficient is 0.9995.

The precision of the data appears in Table 1 where the results of analyzing SE-54 type samples is given. Each sample was analyzed three times. It is apparent from the data that we have met our requirement of being able to analyze vinyl containing polymers in the range of 0.20 wt % vinyl to ± 10%.

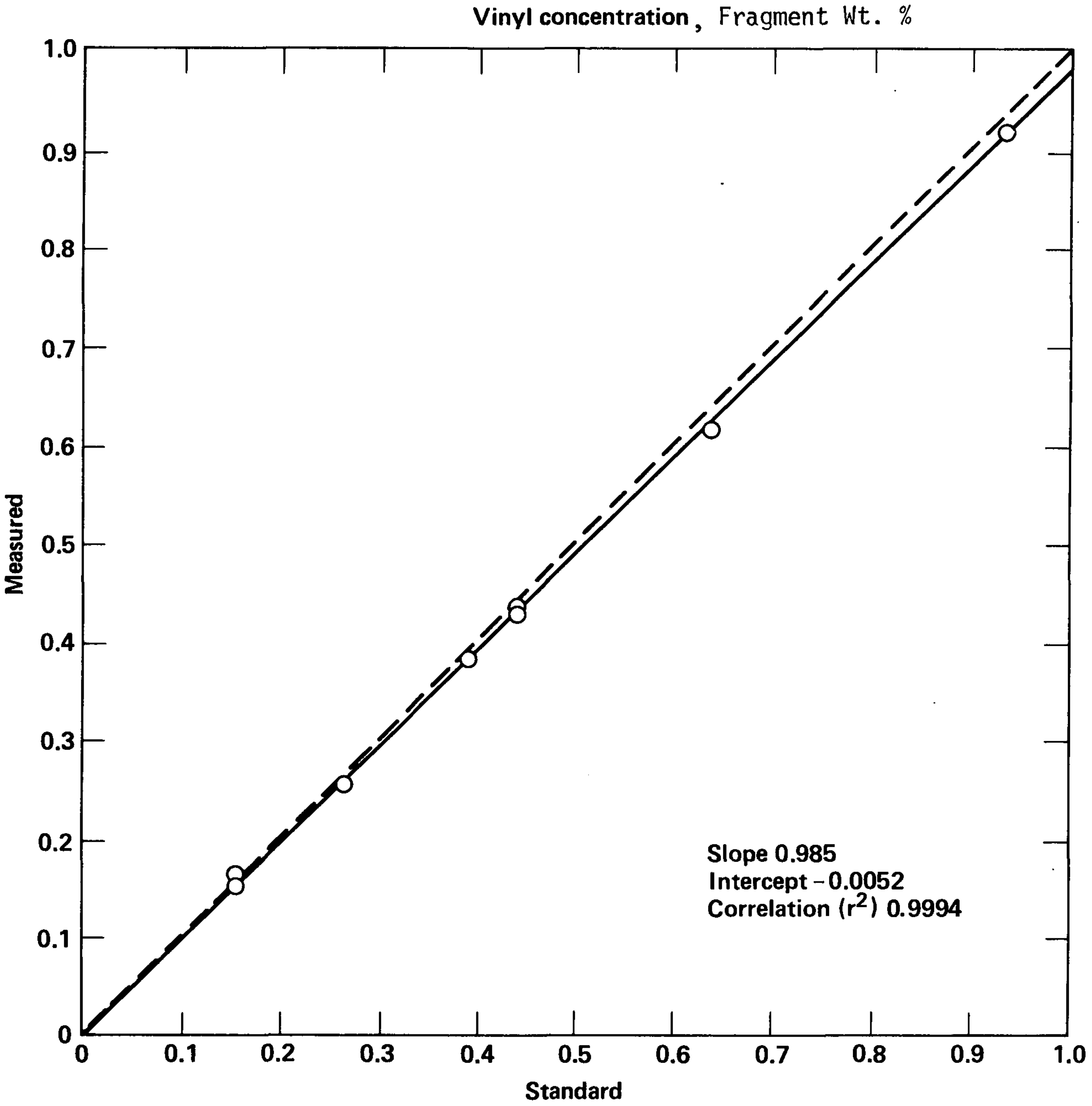
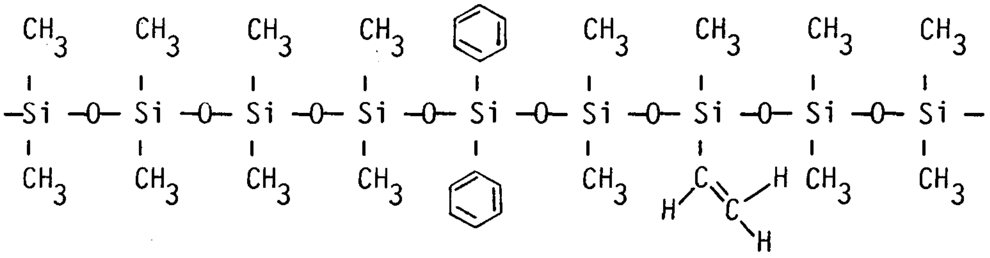

Vinyl concentration, Fragment Wt. %
Measured
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1.0
Standard
Slope 0.985
Intercept -0.0052
Correlation (r^2) 0.9994

Figure 8

Appendix I Model Used For Analysis

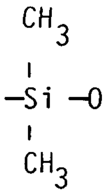
The weight percentages of methyl, phenyl, and vinyl fragments are calculated from the NMR data by using the following model.

A random, very long, polymer chain of average molecular weight and of the form



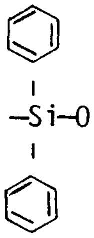
I

is assumed. Methyl, phenyl and vinyl <u>fragments are defined</u> by the structures

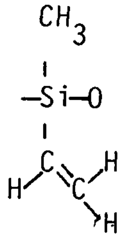


$$-\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{Si}}-O$$

,



, and



II III IV

The formula weights of II, III, and IV are 74.154, 198.286, and 86.164 respectively. The ratios of methyl and vinyl groups to phenyl groups are calculated using the appropriate NMR areas and the following expressions, where Vi stands for vinyl

$$\text{Ratio } \frac{CH_3 \text{ groups}}{\text{Phenyl groups}} = \frac{(\text{NMR Area } CH_3) \times 5}{(\text{NMR Area } C_6H_5) \times 3} = R_{CH_3}$$

$$\text{Ratio } \frac{\text{Vi groups}}{\text{Phenyl groups}} = \frac{(\text{NMR Area } C_2H_3) \times 5}{(\text{NMR Area } C_6H_5) \times 3} = R_{Vi}$$

Phenyl groups = 1, by definition

where 5/3 is a normalization factor which counts the number of protons in each group.

The fragment percentages are then calculated using the following expressions,

$$\frac{(R_{CH_3} - R_{Vi})}{2} \times 74.154 = \text{Wt Methyl fragment}$$

The contribution of the CH_3 on the vinyl fragment is subtracted from the total CH_3 to phenyl ratio to yield a pure methyl fragment to phenyl fragment ratio.

$$\frac{(R_{phenyl} = 1)}{2} \times 198.286 = \text{Wt Phenyl fragments}$$

$$(R_{Vi}) \times 86.164 = \text{Wt Vinyl fragments}$$

Total Wt of fragments = Wt Methyl + Wt Phenyl + Wt Vinyl

$$\text{Wt\% Fragments} = \frac{\text{Wt}}{\text{Total Wt}} \times 100$$

that is

$$\text{Wt\% Vinyl Fragment} = \frac{\text{Wt Vinyl}}{\text{Total Wt}} \times 100$$

The Fragment Wt% can be converted to % groups by multiplying by the appropriate molecular weight ratio. For example, for vinyl the ratio would be 27.044/86.16, and for phenyl it would be 154.20/198.286.

Appendix II

Summary of Experimental Conditions for Analysis of Siloxane Polymers by FTNMR at 200 MHz using a Nicolet spectrometer.

- Sample dissolved in $CDCl_3$, 0.34 gms/2ml
- NMR instrument locked internally to $CDCl_3$
- Homogeneity maximized on sample FID signal
- Start Frequency placed in center of methyl region
- Sweep width chosen to encompass entire spectrum and minimize base-line curvature.
- Recycle delay sufficiently long to allow NMR relaxation; 10 sec or longer.
- Gain setting adjusted to avoid peak distortions
- Block averaging of scans to obtain sufficient signal-to-noise for integration of peaks. With the conditions listed above, 256 scans requires $\sim$ 50 min. Thus 1024 scans will take 200 min or 3.3 hrs. We have found the following data accumulation times are required for analysis of the vinyl fraction contents of siloxane polymer.
    1. If the vinyl fraction content is $\sim$ 0.45% or larger then a single measurement of 1024 scans is required. The results is good to better than ± 0.005.
    2. For vinyl fraction concentrations of 0.2% the minimum number of scans for a determination is 1024. Three determinations should be averaged to insure a precision of ± 10%.

- Experimental Parameters: One-Pulse Sequence

P2 = 7.00 USEC   Preamp 30dB
D5 = 10.00 SEC   AF Gain 8x10
RF Gain 1

NS = 216   DG= 4
SIZE = 16384
AT = 1.67 SEC
ABC ON   OPD ON = 1
ADC = 15 BITS   AI = 10
SW = +/- 2450.98   DW= 204
F2 = 46.739281
OF = .41
SF = 200.069958
EM = .20
PA = 47.1
PB = 62.8

SCALE: 245.09 HZ/CM
= 1.2250 PPM/CM

Table I. Analysis of SE 54 type polymers in fragment weight percent

	Vinyl	Phenyl
KG 461	0.216 ± 0.023	13.719 ± 0.030
BB 103	0.213 ± 0.012	13.656 ± 0.016
AN 727	0.205 ± 0.003	14.522 ± 0.001
BA 195	0.196 ± 0.006	14.209 ± 0.022

Reference

1. J. C. Lindon and A. G. Ferrige, "Digitization and Data Processing in Fourier Transform NMR," Progress in NMR Spectroscopy 14, 27-66 (1980).

Figure Captions

Figure 1. Proton NMR spectrum at 200 MHz of a siloxane polymer. Vertical scale has been expanded to show all peaks. The peaks are phenyl (7.5 ppm), vinyl (5.7 ppm), water (1.5 ppm) and methyl protons (0 ppm).

Figure 2. Proton NMR spectrum of a siloxane polymer lacking phenyl groups. This spectrum shows the $CHCl_3$ resonance which overlaps the phenyl resonance.

Figure 3. Observed (top) and calculated (bottom) spectrum of vinyl group. The vinyl group was simulated as an ABC type spectrum with J_{AB}=14.85 Hz (cis), J_{AC}=19.43 Hz (trans), and $J_{B,C}$=4.00 Hz (gem) as coupling constants. The chemical sifts for spins A and C were 5.0 Hz and 60.5 Hz upfield from the B-spin, respectively.

Figure 4. "On-Scale" proton spectrum of siloxane polymer. This spectrum illustrates the large differences in the size of the largest peak, the methyl group, and the smallest peak, the vinyl group.

Figure 5. Proton spectrum of siloxane with the gain increased 1000x over that used in fig. 4. Note the "digitization noise" displayed on the base line.

Figure 6. This proton spectrum of a siloxane polymer illustrates the beats and wiggles that appear when the radiofrequency is positioned not on top of the methyl group but in between the methyl and phenyl regions. This spectrum also illustrates base line curvature that can effect the integration of peaks.

Figure 7. The Methyl to Phenyl area ratio as a function of the recycle delay time in sec. A constant value of this ratio shows that the proton NMR system has returned sufficiently close to equilibrium for accurate area measurements.

Figure 8. A plot of the measured vinyl weight percent vs a known or standard concentration as described in the text. The dotted line pertains to a theoretical slope of 1.00.